

GRAPHENE AND TRIPTYCENE BASED POROUS MATERIALS FOR ADSORPTION APPLICATIONS

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ABSTRACT

of thesis to be submitted to **The University of Manchester** by **Aleksandra Gonciaruk** for the degree of **Doctor of Philosophy** and entitled **Graphene and triptycene based porous materials for adsorption applications** in the year **2015**.

There were three main driving forces behind this thesis: global concern over climate change mainly due to uncontrolled carbon dioxide (CO_2) emissions, the excitement over the discovery of graphene and its versatile potential, and the potential to design three-dimensional (3D) or two-dimensional (2D) structures, in our case using unique triptycene molecule. We examined two polymeric materials for CO_2 adsorption and suggested simple design of disordered carbons suitable for gas adsorption studies. The approach in each task was to examine structural and adsorption properties of materials using detailed atomistic modelling employing Monte Carlo and Molecular Dynamics techniques and where possible provide experimental measurements to validate the simulations.

The thesis is presented as a collection of papers and the work can be divided into three independent projects. The aim of the first project is to utilize graphene as an additive in polymer composites in order to increase separation between the polymer chains increasing available surface area. The matrix used is a polymer of intrinsic microporosity (PIM-1), which possess large surface area and narrow nano-sized ($>2\text{nm}$) pore distribution attractive for gas separation membrane applications. Adding a filler can reduce aging of the polymer, and enhance permeability across the membrane, often to the expense of losing selectivity. Therefore, we investigated the packing of PIM-1 chains in presence of discrete 2D graphene platelets and 3D graphene-derived structures and its effect on composite structure and adsorption properties. We found that additives do not alter structural polymer properties at the molecular level preserving the same adsorption capacity and affinity. Potential permeability increase would benefit from the retention of selectivity in the material.

Building on design philosophy of materials with intrinsic microporosity we continued further investigation of 3D graphene-derived structures. The idea is that highly concave molecules or polymer chains pack inefficiently creating microporous materials with sufficient surface area for gas adsorption. 3D propeller-like structures were derived from graphene arms connected through the rigid triptycene and other types of cores. The resulting structures created a large amount of micropores and showed similar CO_2/CH_4 selectivity to activated carbons reported in the literature. It was shown that rigid triptycene core leads to more open structures. The model was also applied to model commercially available activated carbon to predict n-perfluorohexane adsorption. The fitting to experimental structural information proved to be challenging due to trial and error nature of the approach. Nevertheless, the simple packing procedure and diverse structure design have a great potential to serve as a virtual model for porous carbons that possess pore complexity and does not require any previous experimental data to be build on.

The last project concerns CO_2 adsorption and selectivity over CH_4 and N_2 in recently reported triptycene-based polymer. The triptycene shape polymer can form a porous 2D network that can be exfoliated into free-standing sheets and potentially used as a membrane. Sheets stack in the bulk material forming anisotropic channel pores. Additionally it contains fluoro-functional groups, which are known to have a high CO_2 affinity. We explored pore structure and chemistry of stacked material for gas adsorption and predicted comparable capacity and CO_2 selectivity to other microporous covalent materials such as activated carbons and PIMs. The CH_4/N_2 selectivity was similar to currently most selective material belonging to MOF family. We showed that fluoro-group have a positive effect on CO_2 affinity, however predictions are sensitive to the charges of fluorine atoms assigned by different methods.

DECLARATION

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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I did not even consider on taking this journey more than three years ago, back in 2012. I silently submitted my Master's dissertation and started a desperate hunt for job. I was young and inexperienced. My then supervisor had other plans for me. She offered an opportunity to stay for little longer in academia (6 month internship) while searching for a place in industry. We made a deal – if I do not find a job I like during this internship period I stay for PhD under her supervision. I thought “why not? This is a guaranteed job for 3 years”. This turned out to be more than a job. I learned a new discipline, I collaborated with scientists and became OK with presenting to public, I wrote papers, I travelled. I became much more confident in myself. I appreciated how science works. I became smarter at looking into the world. I tasted academia and it has grown me as a person.

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1 INTRODUCTION

Understanding the properties of materials used in separation processes is important for the development of more efficient separations. Small molecule capture and mixture separation are important processes for many applications. One of the applications that is currently on the spotlight is carbon dioxide removal from transport sources and power plant streams. Carbon dioxide is the main cause of scientifically recognised global warming due to uncontrollable emissions; CO₂ increases ocean acidity while increased temperature causes the rise of global water level due to ocean expansion and reduced land ice [1, 2]. This consequently has potential secondary effects such as heat related illnesses and infectious diseases, changes in animal population or habitats and change of weather patterns [1-4]. CO₂ capture is also a key process in obtaining high quality natural gas. Besides moving to alternative CO₂-free energy sources and processes, CO₂ can be captured and stored before it escapes to the atmosphere.

There is a growing interest in separating CO₂ using membranes or adsorption by solid adsorbents. Solid removal process promises to be potentially as selective as established methods, can be operated at wider range of temperatures, less energy demanding for regeneration or environmentally friendly for safe disposal, cheaper to install and operate, especially in remote locations. There are few instances of adsorbent or membrane technology used in CO₂ removal such as UOP LLC's cellulose acetate membrane systems [5] and pressure swing adsorption typically using zeolites and activated carbons. However, currently most materials are not suitable for large scale and high purity CO₂ removal due to low selectivity or small capacity and other problems such as stability [6].

Therefore there is a great interest in designing efficient adsorbents and membranes from scientific community. This work contributes to the adsorption field by studying novel materials with properties of interest for adsorption or membrane separations. All of the materials are purely covalent microporous systems that incorporate either graphene and/or triptycene molecule, namely composites of novel type polymer, polymer of intrinsic microporosity (PIM), mixed with additives derived from graphene and triptycene, network two-dimensional triptycene-based polymer and three-dimensional macromolecules consisting

of graphene and triptycene. Most of these materials, i.e. PIM composites and 3D graphenes are discrete molecules that form amorphous structures, thus we are primarily interested in their packing behaviour from molecular level point of view and how it affects material's structural properties. Therefore combination of computational techniques and experiments are employed. The virtual model of material's framework will provide atomistic level insight onto molecular structure, packing behaviour and favourable adsorption sites, while experimental measurements of adsorption will not only help understand the behaviour of non-idealised material but also complement the model and serve as a validation basis.

Outline

The work is presented as a collection of four publications, which three of them are already published in peer reviewed journals, and fourth will be submitted as soon as peers from our research group collect additional results. Main chapters presenting the work will adopt, with some modifications, the title and content from the publications as they were submitted (or intended to be submitted) to the peer-reviewed journal.

A brief overview of CO₂ separation technologies are provided in this chapter given the importance of developing new porous materials for this application. Materials studied in this work are introduced and put in the context among related sorbents. The following chapter presents the experimental methodology, molecular simulation and characterisation techniques used in this work as well as theory behind adsorption phenomena.

The first publication presented in Chapter 3 discusses the use of graphene as a nanofiller in novel type microporous polymer adsorbent (PIM-1) to increase the porosity and surface area for greater adsorption performance. Chapter 4 presents further effort of disrupting bulk polymer packing by incorporating graphenes that are held in three-dimensional (3D) space by mainly triptycene unit. The interesting 3D shape of these new type of nanographenes raised a question of the properties of the bulk material. The virtual system turned out to be a free-standing microporous framework with geometrical pore complexity potentially suitable for adsorption studies in activated carbons. The details are provided in Chapter 5. The virtual model was also tested for perfluorohexane adsorption prediction in commercially available activated carbon. The work was submitted as an entry for the 8th Industrial Fluid Properties Simulation Challenge and is presented in Chapter 6. Chapter 7 describes prediction study of

gas adsorption in polymer that is chemically and structurally similar to PIMs. However, the combination of polycyclic aromatic ladder-like fragments and triptycene core allows the formation of a multilayer network polymer that possesses well-defined monodisperse pores. Additionally the experimentally obtainable material contains fluoro-functional groups that became the focus for the study due to promising adsorption affinity of fluorinated compounds towards CO₂.

The last chapter summarises the results, where appropriate conclusions are made as well as brief suggestions of future research to improve and/or compliment the results obtained in this study.

1.1 CO₂ Separation

CO₂ is produced in substantial amounts in steam reforming (hydrogen production) and power generation by combustion of coal, natural gas and other sources like biomass. There are three main processes suggested for capturing CO₂ from power plants:

- oxy-combustion
- pre-combustion
- post-combustion capture.

Oxy-combustion technology (Figure 1.1) is the improvement of a current power generation that provides more efficient CO₂ capture. Fuel is burned in almost pure oxygen rather than air. Thus produced stream predominantly consists of CO₂ and water. The method is attractive as the later CO₂ removal from flue gas is easier due to high CO₂ concentration and also eliminates post-combustion NO_x separation. However it requires prior separation of O₂ from N₂, which is energy intensive due to currently used cryogenic distillation for oxygen production.

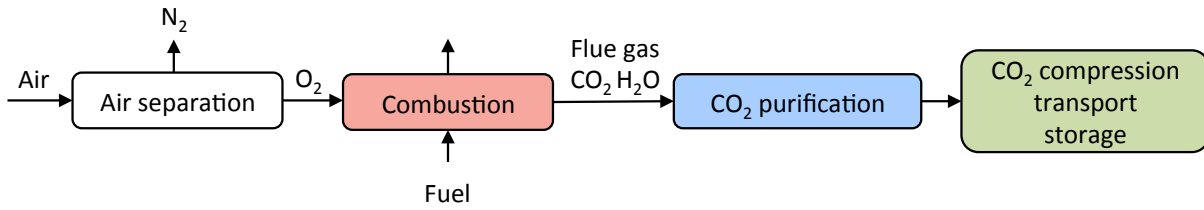


Figure 1.1. Simple flow diagram of oxy-combustion process.

Pre-combustion technology (Figure 1.2) concentrates on separating CO₂ from syngas stream before combustion. Fuel is converted into high pressure and temperature syngas stream containing about 15% of CO₂ besides hydrogen (H₂), carbon monoxide (CO), water and other impurities. CO is further converted to CO₂ in shift reaction with water increasing CO₂ concentration up to 50% in the stream. The CO₂/H₂ has to be separated in order to further use generated hydrogen. Although the technology has very attractive conditions, it is mainly considered only for new integrated coal gasification combined cycle (IGCC) plants, limiting its integration [7].

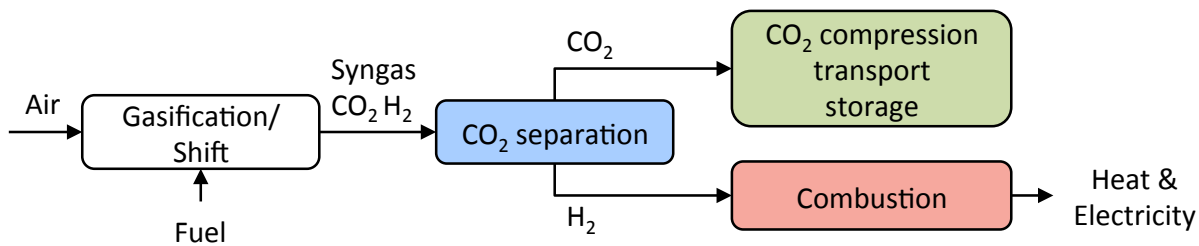


Figure 1.2. Simple flow diagram of pre-combustion process.

Post-combustion (Figure 1.3) design involves CO₂ separation from exhaust flue gas, which has relatively low CO₂ content (5-15%). Flue gas mostly contains N₂ where coal is burned in air, thus CO₂/N₂ separation is the main focus for post-combustion CO₂ capture. The stream is at atmospheric pressure and exit temperature is 30 – 150°C (depending on fuel type [8, 9]), has low CO₂ content and many other gaseous species are present besides moisture [10]. The process is challenging due to its conditions thus requires high performance materials and very efficient processes. Nevertheless the technology is widely considered as it can more easily be adapted to retrofit existing power plants [11].

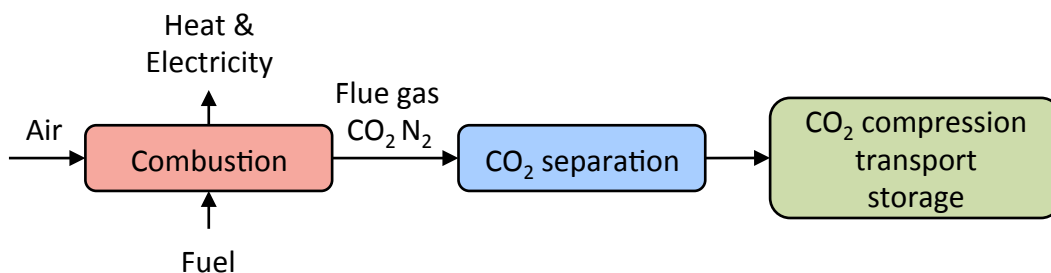


Figure 1.3. Simple flow diagram of post-combustion process.

Despite the importance of investigating materials for CO₂ capture from power plant generation, separation of CO₂/CH₄ and CH₄/N₂ has also attracted the attention of researchers because CO₂ and N₂ have to be separated from natural gas in order to meet the pipe-line quality as a consumer fuel. Some sources may contain large amounts of CO₂ and N₂ thus reducing combustions efficiency of a fuel, wasting equipment capacity and, in case of CO₂, being corrosive for pipelines and equipment when mixed with water. Variation in composition depending on source is large; CO₂ concentration varies from 1 to 40% and nitrogen is typically 5%. CO₂ and N₂ concentrations must be reduced to <8% and <4%, respectively [12]. The CO₂/CH₄ is also a target pair for separation in biogas upgrading, oil recovery, CH₄ extraction from unmineable coal seams.

Oxy-, pre- and post-combustion concepts can also be used in non-energy related industry [13]. Oxygen enriched streams can also be used in iron, steel and ammonia manufacture plants to produce CO₂ rich streams. The pre-combustion approach can be applied where streams has some energetic value, e.g. streams rich in CO that exit blast furnace in iron and steel industry and H₂ rich tail gas in ammonia production. The post-combustion can also be adapted whenever combustion process is involved and CO₂ streams of no energetic value are produced, i.e. in cement manufacture, second largest CO₂ source in this category [13].

Different technologies have been developed to remove CO₂ in the process streams mentioned above. The main technologies are chemical and physical absorption, solid adsorption, membrane separation and phase separation by cryogenic distillation. The benchmark CO₂ removal process is chemical absorption by amine-based solvents, conventional being monoethanolamine (MEA). The typical process consists of two columns, one where the gas is

adsorbed and another where the gas is regenerated (Figure 1.4). This is the most widely used and well-established CO₂ separation technology in many chemical and petrochemical industries with high CO₂ emission as solvents can recover CO₂ streams of high purity. However, the method demands high energy consumption due to the low CO₂ capacity, which then requires heating and cooling large volumes of liquid, high rate of solvent consumption, involves corrosion problems and complex control of the process [11, 14]. Investigation of new solvents and blends, e.g. involving ionic liquids [15] or carbonate-based solutions [7], to improve absorption capacity and reduce energy demand for regeneration is on-going.

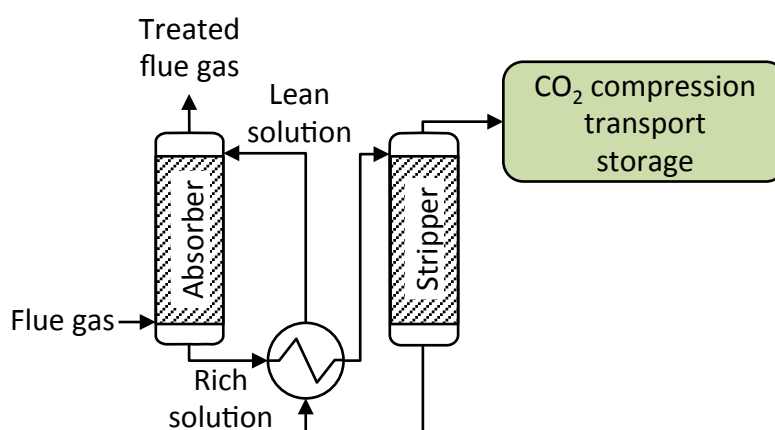


Figure 1.4. Simplified flow diagram of chemical absorption process for post-combustion process.

Another technology is cryogenic liquefaction where CO₂ liquefies at higher temperatures than the remaining components. The process is used where streams already contain high concentration of CO₂; it produces very pure liquid CO₂ which, conveniently, can be directly stored or transported. Cryogenic separation is very energy demanding due to required refrigeration, especially treating dilute streams, thus it is economically feasible only in large fields or where lower limit of CO₂ concentration is 50 % [13], although nitrogen is mainly removed from natural gas using this method [12] even though its concentration is relatively low.

There are few plants that remove CO₂ using solid adsorption [13, 16]. Separation is performed by pressure swing adsorption, temperature swing adsorption or hybrid method in layered beds filled with traditional adsorbents such as activated carbon (AC), aluminosilicate and titanosilicate molecular sieves, alumina, silica gels. Adsorption process is often multicolumn systems, where the scheduling for switching between adsorption, compression,

decompression and regeneration of the column plays an important role in the process optimisation. A typical adsorption process is shown in Figure 1.5. Adsorption operates well at high CO_2 pressures and low temperature, thus it is better suited for pre-combustion CO_2 capture [17, 18]. Adsorption is used in hydrogen purification, CO_2 drying and odour removing from ethanol production plant, and is considered as future technology for natural gas treatment and pre-/post-combustion CO_2 capture [19, 20]. Nevertheless, the commercialisation of adsorption-based process is slow due to semicontinuous operation mode, not sufficient CO_2 capacity and selectivity of some adsorbents at high temperature demanding large scales and low flow rates, rapid performance decline in presence of water and other impurities, and high regeneration temperatures needed [17]. Conventional adsorbents such as zeolites and activated carbons are remaining to be used, while new materials with high surface area and tuned heats of adsorption (e.g. modified carbons and porous organic networks [21-24] of which one of the most famous is MOF family [25]) are designed and studied for adsorption as well as technological processes (e.g. pressure swing adsorption) are further improved to increase efficiency [8, 13].

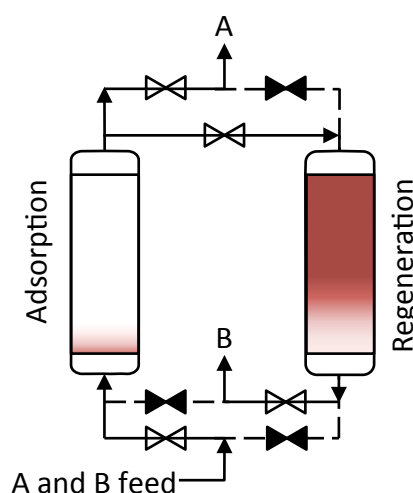


Figure 1.5. Simple 2-column adsorption of gas A and B.

Membrane separations are considered as one of the most energy- and economically-efficient processes that have minimum environmental impact compared to conventional technologies. Membranes are easier to maintain and less expensive due to less complex design as it does not require regeneration unlike adsorption and absorption processes. Primary source of energy consumption is the need for feed compression or depressurisation on the permeate side to

drive the separation process. The first membrane in natural gas treatment separating CO_2/CH_4 was acetate cellulose, which remains to be widely used, however other industrial membranes are largely based on glassy polymers such as polyimides, polysulfones and polycarbonates as they retain relatively high selectivity at industrial conditions [26]. Membranes are limited for streams with high CO_2 concentration and small-scale operations such as natural gas purification. There are different configurations of membrane, e.g. flat sheet packed in spiral-wound modules or hollow fiber, that allows exposing large surface area of a material while keeping units compact (Figure 1.6). Despite some applications, membrane technology is not yet employed at its full capacity; for example, CO_2 removal from natural gas streams by membrane technology takes less than 5% of the market as of 2008 [12].

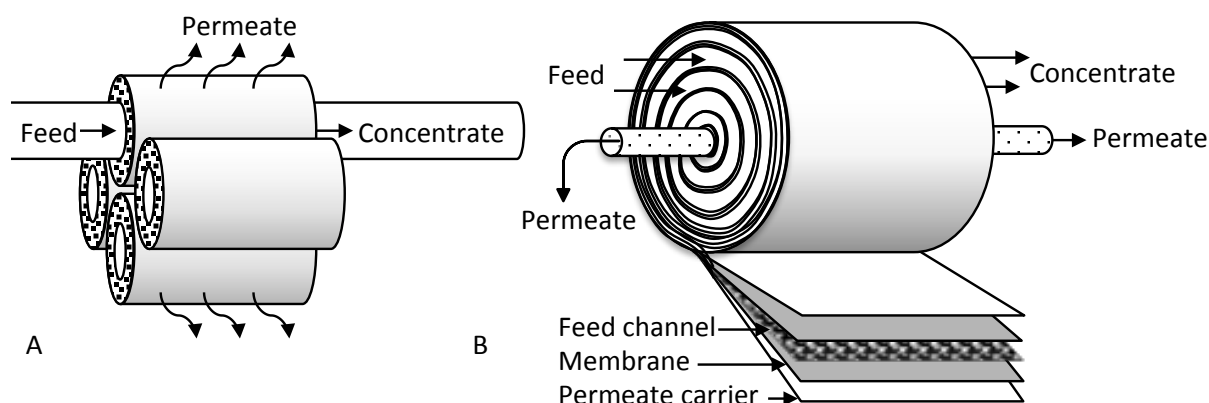


Figure 1.6. Simple depiction of industrial membrane configuration: (A) hollow fiber and (B) spiral-wound module.

Different technologies have their own advantages and shortcomings; furthermore different stream compositions and conditions require unique treatment approaches depending on the available separation materials, investment and maintenance costs, required purity, etc. Although it seems that absorption will continue to be used as it is well-developed technology suitable for retrofit, solid adsorption and membrane separations are more energy efficient and environmentally-friendly alternatives worth exploring.

1.2 Materials for Adsorption and Membrane Separation

This section presents several classes of physical separation materials, both solid adsorbents and membranes. All materials need to meet certain criteria:

- they must be cheap to manufacture to reduce capital and maintenance cost.
- they need to be robust in range of conditions: at different pressures and temperatures, in presence of humidity and other chemicals. Materials also have to withstand regeneration cycles.
- materials, especially solid adsorbents, must have large working capacity, governed by structural properties, surface area and pore volume, and surface chemistry. Large capacity translates in smaller equipment and lower capital cost. Large surface area is also important in membranes as it provides large amount of sites for adsorption increasing rate of adsorption, affecting diffusion of gas molecules and resulting in certain selectivity.
- Kinetics must be optimised for fast separation and to avoid high feed pressurisation using membranes. Lower pressure or temperature swing will be required if capacity of solid adsorbent is reached quickly reducing operating energy consumption and cost. However there is a trade-off in both membrane and adsorption technologies; fast kinetics in membranes often come at the cost of lower selectivity, while in adsorption case, this means that interactions between gas and adsorbent is strong resulting in more energy-intensive regeneration.
- they have to have high selectivity to ensure effective separation and production of high purity product. If process is less selective, additional pretreatment and/or several cycles or stages are required resulting in larger energy penalty, increased capital and operating costs.

The hypothetical ideal materials described above will naturally exhibit trade-off between these properties. Although the fundamentals for all gas separations are similar, different materials are needed to reflect the specific operating conditions of each system.

1.2.1 Adsorbents

Adsorbents can be classified into chemical and physical. Chemical adsorbents yield product of higher purity due to selective CO₂ fixing at very high temperatures, which eliminates stream-cooling step. However the chemical process is slower than physical adsorption, consumes much more energy for regeneration and some adsorbents have lower capacity due to only monolayer formation [27, 28]. Here are considered several promising and/or widely studied adsorbents that separate based on physical bond formation and qualify as low-temperature materials that operate well below 200°C, including carbons, which are closely related to carbon structures studied here.

1.2.1.1 Zeolites

Zeolites are the most popular materials extensively studied in terms of separation processes. Zeolites are made of porous crystalline silicate with some silicon (Si) atoms replaced by aluminium (Al), which creates negative charge and attracts alkali and alkaline earth metal atoms. The ordered structure exhibits uniform distribution of pores in micro-region; it is possible to tune the size of the pore and also interactions strength by changing cations and adjusting Si/Al ratio. Zeolites act as sieves resulting in size based separation, however due to presence of metals it also strongly adsorbs molecules with dipole or quadrupole moment. Therefore zeolites have high selectivity towards CO₂; CO₂/N₂ selectivity ranges from 20 to 70 and can reach over 800 at ambient conditions, showing essentially sieving-based separation [29-32], while CO₂/CH₄ selectivity is form 9 [29] to intrinsic 395 [33]. Typical CO₂ capacity is moderate, about 2 mmol g⁻¹ [34], while 13X, frontrunner among zeolites, is able to accommodate about 5 mmol g⁻¹ of CO₂ at ambient conditions [35-37]. Zeolites show high heat of adsorption (about 30 – 50 kJ mol⁻¹ [30, 36]), resulting in more energy intensive regeneration due to required high temperature. On the other hand, strong affinity leads to fast kinetics, i.e. almost full capacity is reached in first several seconds in many cases [34], allowing more frequent adsorption/regeneration cycles. Performance of zeolites substantially declines in humid conditions as polar water molecules preferentially adsorb on zeolite

reducing adsorption sites for CO₂ [38, 39] and at higher pressures capacities are very sensitive to higher temperatures [29].

1.2.1.2 Metal Organic Frameworks

Metal organic frameworks (MOFs) also belong to the class of porous crystalline materials. MOFs are hybrid networks formed by multidentate organic ligands linked with metals having multiple coordination sites. Changing combinations of organic linkers and metals can create huge variety of MOFs providing options to control structural properties such as surface area and pore size as well as chemical characteristics tuning adsorption affinity. MOFs were found to have CO₂/CH₄ selectivity as low as 2 and as high as 100 [40-42] and 4 – 400 for CO₂/N₂ [42].

Very large surface area can be achieved in MOFs, exceeding 3000 m²g⁻¹ and reaching 10,000 m²g⁻¹, which leads to large capacities. However it is not uncommon for MOFs to have sigmoidal CO₂ isotherm shapes or even a step, i.e. at low pressures loading changes gradually, but after some pressure point adsorption increases significantly with small pressure change and again resumes previous gradual change. Thus such MOFs are better suited for high pressure CO₂ capture and storage. Furukawa *et al.* reported synthesis of MOF-210 that provides exceptionally large surface area of 6240 m²g⁻¹ and saturation CO₂ capacity reaching 54.5 mmol g⁻¹ at high pressure of 50 bar and 25°C temperature, although at atmospheric pressure the uptake was about 1 mmol g⁻¹ [43]. The MOF that possesses good capacity at atmospheric conditions, more suitable for post-combustion CO₂ capture, is Ni/DOBDC (6.5 mmol g⁻¹, which is larger than in zeolites) [44]; few other MOFs with large low pressure loadings were reported over the recent years [45]. Although adsorbed water decreased CO₂ loading in Ni/DOBDC, the degree was not as great as in benchmark zeolites.

Because of the weaker strength between organic linker and metal, many MOFs suffer from low hydrothermal stability, i.e. MOFs structure degrades in presence of water and after many regeneration cycles. However increasing number of MOFs are synthesised that can withstand high temperatures and large amounts of water [46].

Most MOFs have heats of adsorption similar to zeolites or lower, and it is claimed that MOFs' regeneration is less energy intensive compared to zeolites, although some MOFs (amine-modified) were found to have very large heats of adsorption (50 – 90 kJ mol⁻¹ [35, 47]).

1.2.1.3 Carbons

Activated carbons (ACs) are widely used adsorbents and well-established in adsorption technology. ACs are cheap to produce from readily available sources, e.g. coal, biomass such as wood and coconut shells or other organic materials such as polymers and petroleum. Carbonisation (by pyrolysis) and exposure to oxidizing atmosphere at high temperatures achieves activation, or creation of open pores. ACs have large variety of structural and surface chemistry properties depending on their precursor and preparation conditions. Surface area typically ranges from 400 to 1000 m²g⁻¹. Surface chemistry, microporosity and large surface area provide good adsorption conditions. However typical CO₂ capacity at low pressures and ambient temperature is moderate (about 2.5 mmol g⁻¹ [34, 35]) and almost twice lower than that in zeolites at similar conditions [48]. Also, some ACs can adsorb substantial amounts of CO₂ (from ~ 10 to 23 mmol g⁻¹ in commercially available MAXSORB) at high pressures exceeding capacities found in zeolites at similar conditions [49-52]. Thus typical ACs would be better suited for pre-combustion CO₂ capture, where streams are at high pressure. However it is worth to note that CO₂ loadings expressed per surface area rather than mass of adsorbent are nevertheless greater in zeolites showing lower AC affinity for CO₂ compared to zeolites [50]. ACs exhibit isosteric heat of adsorption for CO₂ of about 16-25 kJ mol⁻¹ which results in sufficient affinity and at the same time allows easy regeneration and consequently excellent reproducibility [50, 52]. Moreover, AC performance is not sensitive to moisture content due to carbon inertness and would not be expected for any unmodified carbon-based adsorbent. On the other hand, ACs quite often contain oxygenated groups which attract water molecules thus reducing CO₂ capacity, although the effect is much smaller than in zeolites [53, 54].

Optimised control over precursor and conditions allows creating a special class of activated carbons, carbon molecular sieves (CMSs), that exhibit versatile adsorption properties in broad pressure range due to abundant nanopores (≥1 nm) and large surface area, i.e. CO₂ uptake at

low pressure and ambient temperature is about 4.6 - 4.8 mmol g⁻¹, comparable to zeolites, while capacity is up to 36 mmol g⁻¹ at high pressure (20 bar) and 25°C, which is superior to any activated carbon, even some amine-modified as well as some promising MOFs under same conditions [55-57]. The CMSs showed broad range of CO₂/N₂ selectivity (2 – 14); CO₂/CH₄ selectivity was about 7, although certain CMS, reported by Wahby *et al.* [55], was able completely exclude CH₄ molecules reaching 100% selectivity.

Other carbon-based morphologies and surface modifications are investigated to increase capacity and selectivity, although all modifications inevitably lead to increased production costs. Activated carbons chemically treated with nitrogen containing chemicals were shown to possess higher separation factors compared to unmodified carbons, due to increased basic properties, and larger capacity at some extent [34, 58] although there were cases when functionalization drastically reduced available surface area and consequently lowered capacity [59, 60]. Other carbonaceous forms such as carbon nanotubes (CNT), ordered porous carbons, prepared using templates [61, 62], carbon aerogels [63] and graphene have an advantage of having defined and controllable structure, well developed microporosity and large surface area. CNT tube diameter can potentially be created to commensurate with molecular size of specific gas. Cinke *et al.* demonstrated that CNT can achieve twice larger capacity than activated carbons [64]. Lu *et al.* also showed CNT potential in CO₂ adsorption as modified CNTs were better performers among zeolites and ACs with same modifications [65].

1.2.1.3.1 Graphene

Graphite is a well-known allotrope of carbon and an abundant mineral. Graphite consists of a big honeycomb-like layers stacked together. One of the most known applications of graphite is pencil. In fact, the name of the graphite originates from Greek word *γράφω* [grafō], which means *to draw/write*. In a drawing process, layers of graphite from the pencil are separated leaving thin traces. Looking to the drawing under microscope, among thick pieces of graphite that contains many layers, one could find a transparent monolayer. This one layer of graphite has brought a Nobel Prize in 2010 to researches Andre Geim and Kostya Novoselov from the University of Manchester. They have separated the layer in free form and measured its

properties. This groundbreaking achievement has led to an enormous attention from academia and industry.

Graphite monolayer was named as *graphene* and first referred in 1987 by S. Mouras [66], although up to 10 layers are still considered as graphene [67]. Graphene is a one atom thick and planar polycyclic aromatic hydrocarbon molecule (Figure 1.7) ranging to sizes from few fused benzene rings to sheet of area as big as $0.23 \times 100 \text{ m}^2$ [68]. The perfect graphene consist only of six membered carbon rings bonded through partial double bonds. However graphene can also have defects such as penta- or heptagon rings, vacancies, adsorbed or covalently bonded impurities. The single sheet of graphene is transparent, flexible and extremely strong. Due to honeycomb structure two edges of graphene form *zig-zag* and *armchair* structures that were shown to exhibit distinct electrical properties in narrow graphene strips [69].

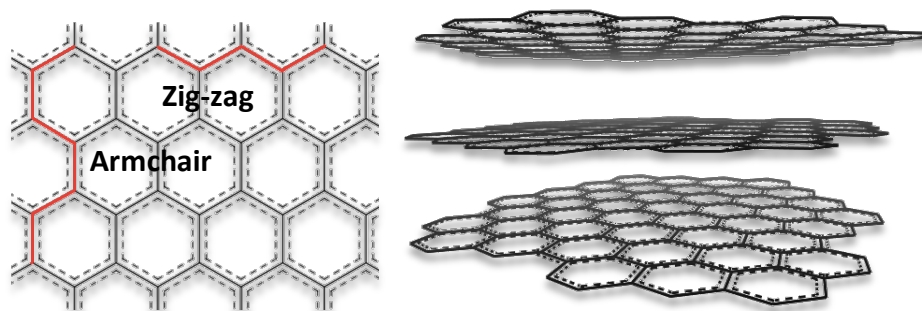


Figure 1.7. Graphene molecular structure and stacking of graphene layers.

Before the isolation of free-standing graphene, perfect 2D crystals were considered as unstable according to theory and experiments unless they were small enough or had defects [70-72]. Unsupported single sheets of polycyclic carbon molecules were known only as wrapped up into fullerenes or rolled to carbon nanotubes, while stable flat sheets were presumed not to exist. Indeed, the study of Meyer *et al.* [70] revealed that graphene sheets are not perfectly planar when exist in a free form and has ripples of about 1 nm high. This might be the reason for the thermodynamic stability of even large and defect-free graphene sheet.

There are several synthetic routes to produce graphene sheets such as oxidation of graphite followed by exfoliation and thermal or chemical reduction of oxygenated groups [73] and graphene growing on a substrate by chemical vapour deposition [74]. The reduction method allows preparing graphene in high concentrations that is particularly attractive for large-scale

application; however it may generate defects in graphene sheets during oxidation as well as leave some residual oxygenated groups unreduced. The bottom-up approach is tedious due to variety of controlling factors, however is more often used for electrical optical devices where contiguous films of specific size are essential. Another method to obtain large essentially defect-free, however less uniform graphene molecules, is graphite exfoliation in a solution with surfactants that facilitates dispersion of graphene sheets [75]. The more out-of-the-box thinking led to another bottom-up synthesis approach that can solve two problems at once; a recent review by Najafabadi [76] summarized various ways of producing graphene from CO₂.

In applications related to adsorption and separation, graphene was exploited for use in various membranes as an additive and on its own [77-79]. Since aromatic rings of graphene are impermeable for common gas molecules even for He atoms due to high electron density [80, 81] the separation through all-graphene membranes can take place only in the gaps between graphene flakes, through defected areas or artificially designed holes in graphene sheet. Jiang *et al.* [77] reported computational study on graphene sheets with “punched” subnanometer holes that exhibited extremely high selectivity for H₂ over CH₄, on the order of 10²³. It was demonstrated that selectivity can be controlled by functionalizing pore and changing its size. Such robust one-atom-thick membranes were also explored in H₂/N₂ [78], CO₂/N₂ [82] separation, water filtration [79] and are anticipated to be useful for many other applications.

There is an emerging interest to use graphene in CO₂ capture. Although exfoliated graphenes show relatively low CO₂ capacity of up to 2 mmol per gram of adsorbent at ambient conditions [83, 84], however it seems the CO₂ affinity might be larger than in typical ACs. Most reported exfoliated graphenes have surface area of about 180 – 500 m²g⁻¹ [83, 84], which is twice smaller than what can be achieved in many ACs, however exfoliated graphenes possess large amount of nanopores of less than 1 nm that is recognised to be essential for good CO₂ adsorption performance. Moreover graphene nanoplatelet, reported by Meng *et al.* [83], with about 20% of oxygenated groups reached remarkably large (56 mmol g⁻¹) CO₂ capacity at high pressure of 30 bar at 25°C exceeding those in zeolite 13X and commercial activated carbon, although the adsorbent’s surface area was at least twice smaller than that of compared materials. The significant loading was attributed to large mesopore volume. The reported ideal CO₂/N₂ selectivity at ambient conditions and 15% CO₂ concentration was 112, which is significantly higher than in any carbon-based material.

Pores formed by edges of graphene platelets are potentially more attractive for CO₂ because of larger partial charges on end carbons; similarly less inert carbons could be found at defect sites and on ripples of sufficiently large sheets [85]. Graphene nanoribbons with possibly bare end carbon atoms irreversibly adsorbed CO₂ and H₂O, except N₂, in experiments reported by Asai *et al.* [86]; molecular simulations of Ohba and Kanoh [87] also showed that dominant columbic interactions attract CO₂ to hydrogen-passivated carbon atoms discriminating basal ones, where instead N₂ and CH₄ preferentially adsorbs resulting in large selectivity exceeding 30 at subatmospheric pressures.

One way to employ attractive properties of graphene is to combine graphene sheets with other materials creating composites with enhanced and unique qualities. Non-exfoliated graphene oxide sheets (GO) were found to be completely tight for investigated gases (He, N₂, H₂, Ar) and liquids (ethanol, hexane, acetone, decane and propanol), but was able to permeate water [81]. Thus graphene found its application in gas barrier materials because of its transparency, light weight and ease of chemical modification [88-90]. Graphene sheets were shown to reduce significantly solubility of gases such as O₂ and N₂ decreasing overall permeability due to created super-tortured path that hindered molecule diffusion accounting for high aspect ratio of graphene and its orientation perpendicularly to gas entering direction. The decrease in water permeability in polypropylene was also accounted for presence of graphene due to its hydrophobicity [88].

On the other hand, ultrathin GO membrane, supported on microporous polyethersulfone, was able to permeate CO₂, H₂ and N₂ by applying sufficient transmembrane pressure (1 bar feed pressure) [91]. The water transport in this membrane was also unrestricted and even resulted in better selectivity for CO₂ as relative humidity increased. The largest CO₂/N₂ selectivity was ~60 exceeding those in polymers of intrinsic microporosity, CMSs, inorganic membranes of zeolite or silica. The largest CO₂/CH₄ selectivity was about 30, while selectivity in unsupported GO was predicted to be even larger (~45) surpassing upper separation performance limit of polymeric membranes [92, 93]. Excellent performance was attributed to the presence of close-packed interlayer slit pores and the interactions between CO₂ and carboxylic acid groups that cover tortured pore channels formed between GO edges. However highly porous and robust substrates are essential in order to retain intrinsic GO membrane selectivities.

Graphene sheets were also deposited on PTMPS membrane, benchmark polymer with very high gas permeability [91]. Unexpectedly, selectivity for O_2/N_2 increased from 1 to 6, which is much closer to some CMS membranes, while high permeability was preserved. GO was also beneficial in other membranes matrixes. Functionalised GO dispersed in commercial low-cost Pebax (polyether block amide) increased CO_2/N_2 and CO_2/CH_4 selectivity about 2.4 times as well as made composite membrane 2.6 times more permeable for CO_2 , although the affect of unfunctionalised GO was not as significant while permeability was even worsened [94]. Both permeability and selectivity were increased in Matrimid (another commercial imide-based membrane) with the addition of equal amounts of GO and CNT [95].

1.2.1.3.2 3D Nanographene Molecules

Polycyclic hydrocarbons with dense π system, namely nanographenes, attracted attention due to their potential use in nanoelectronic [96], fluorescence [97-99] applications and as a platform for drug delivery [100]. Nanographenes self-assemble or assemble at an interface because of the planar structure. Simpson *et al.* aimed at growing planar nanographenes via bottom-up approach at a scale suitable not only for fundamental studies but also for practical applications, but accidentally synthesised three-dimensional (3D) propeller-like macromolecules [101] with the proposed structure shown in Figure 1.8. Although there have been efforts of creating concave polycyclic aromatics inspired by fullerenes [102], the size scale of the propeller molecules is much larger. This is also why these compounds are insoluble. On the other hand, Zhang *et al.* intentionally incorporated triptycene core between the three graphene planes [98, 99] to reduce interplanar interactions and subsequently improve the solubility in common organic solvents. The resulting 3D structure was used as a stable metal-free fluorescent agent with low cytotoxicity and for recognition of nitroaromatic explosives.

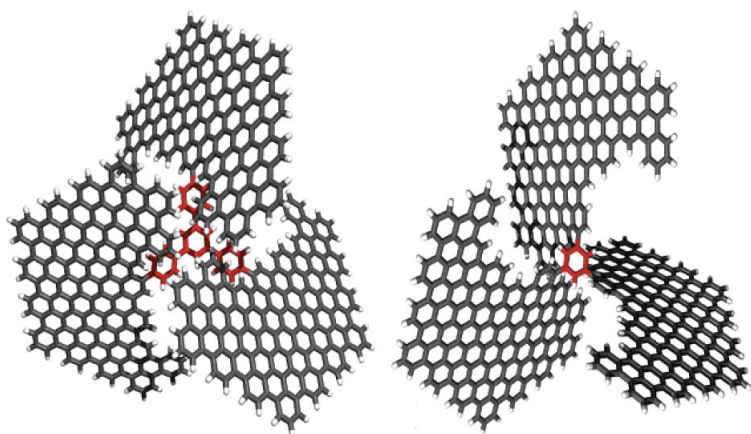


Figure 1.8. 3D nanographenes synthesised by Simpson *et al.* (adapted from [101]).

Despite few applications 3D nanographenes remain unexplored materials and although the main interest is in more efficient utilization of graphene properties, here we are mainly attracted by the 3D shape that could be potentially used as an efficient spacer in polymer increasing composites surface area, retaining large surface area of planar graphene without potentially blocking free volume for gases. We are also interested in exploring the packing of individual 3D nanographenes and possible applications in gas adsorption. It is assumed that such a complex macromolecules will affect the bulk structure of a material, which will be formed by the randomly packed domains of stacked arms.

1.2.1.4 Summary

Zeolites and MOFs are better alternatives in terms of larger CO₂ capacities at low and high pressures, respectively, as well as larger selectivities compared to ACs. Unlike zeolites, MOFs offer possibility to create greater variety of structures and functionalities and can be regenerated with smaller energy penalty. On the other hand, MOFs are often poor performers at low pressures, more expensive and difficult to produce in large scale. Besides MOFs are at the infancy stage and adsorption measurements in real conditions, i.e. in mixtures and in adsorption bed configurations, need to be performed. All of the materials provide possibilities for surface and structure modification to tune in optimum properties. Although there are adsorbents with superior adsorption properties, carbon-based materials are continued to be used and studied due to its low cost, hydrophobicity, thermal stability and reproducibility as

well as potential to create different morphologies and modify its surface. Graphene is an appealing material due to its mechanical and thermal strength, ambient surface for adsorption and potential modification; it can be used on its own and as a building block or filler in composites.

1.2.2 Membranes

Polymers offer an advantage of preparing flexible, thin and light, solution-processable membranes that are easy to scale-up; furthermore their chemistry can be easily manipulated to achieve desired performance. The combination of microporosity and ability to generate film-forming material offers unique benefits in membrane technology. However, conventional polymers do not have sufficient free volume and permeability is too low, which reduces flow rates and requires large areas to permeate the gas, higher feed compression and/or depressurisation on the permeate side. Polymeric materials as gas separation membranes suffer from well-known trade-off between permeability and selectivity; those with high selectivity possess poor permeability properties and vice versa. Robeson's plot [92] for common gas pairs compared empirical relationship between selectivity and permeability of many membranes establishing upper performance bound (for example of CO₂/N₂ see Figure 1.9). The common aim is to design membranes that would overcome this benchmark limit. Generally there are two ways to surpass the trade-off: one is to modify the polymer itself, another – to incorporate additives into polymer framework.

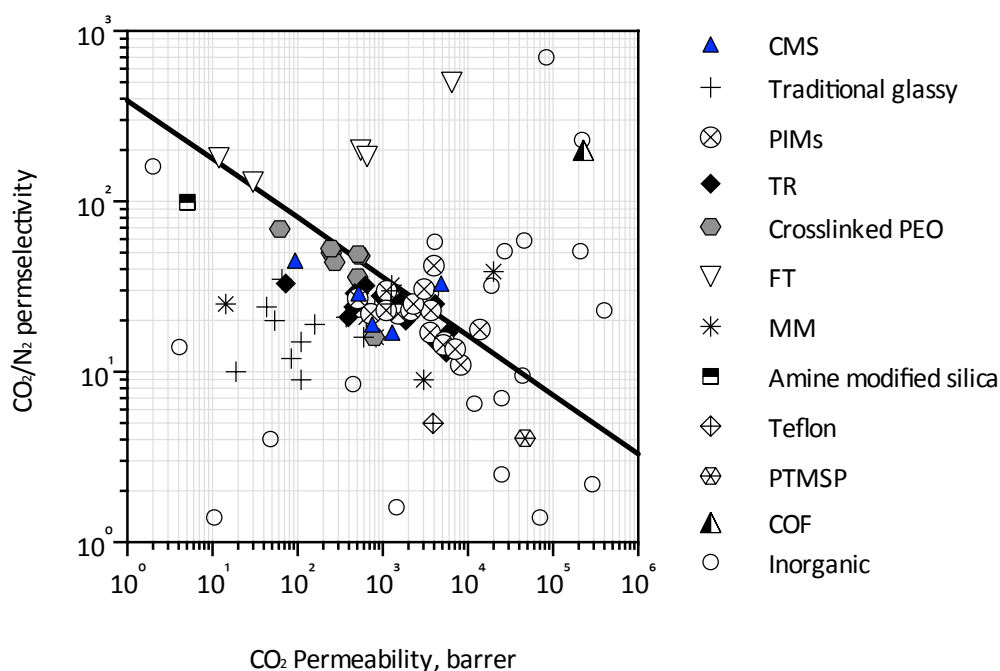


Figure 1.9. CO₂/N₂ selectivity versus CO₂ permeability of different membrane classes. Traditional glassy [103], TR-polymers: thermally rearranged [103], crosslinked PEO: polyethylene oxide [103], inorganic [19, 42, 104-107], CMS, MM: mixed matrix [104, 108-111], PIMs: polymers of intrinsic microporosity [103, 112], FT: facilitated transport [113, 114], COF: covalent organic framework [115], Amine modified silica [116], Teflon [117], PTMSP [117], 1 barrer = 10⁻¹⁰(cm³CO₂) cm cm⁻²s⁻¹cmHg⁻¹.

In the few decades, there were significant improvements in development of polymeric membranes with high permeability. In 1983 T. Masuda *et al.* [118] introduced polymer based on polyacetylene (PTMSP) that had highest O₂ permeability among all polymers known at that time and even now newly synthesised high-free volume polymers are compared to PTMSP. The reason for extremely high permeability is its rigid and bulky structure that, when packed, leaves a lot of free space. The space shows bimodal pore size distribution of PTMSP with big pores being more concentrated and connected. Unfortunately high permeability comes to an expense of selectivity that is one of the lowest among polymer membranes for some gas pairs such as CO₂/CH₄ and CO₂/N₂. Since then many more high free volume highly permeable polymers were developed based on chain rigidity and interchain separation observed in PTMSP, such as perfluoropolymers (i.e. commercially available fluoropolymer Teflon AF2400 [117]), substituted polyacetylenes related to PTMSP such as PMP [119] and indan-based polyacetylenes [120], polymers of intrinsic microporosity (PIMs) [121-124], thermally rearranged polymers [125] and hypercrosslinked polymers (HCPs) [126]. However many high free volume polymers exhibit decrease in permeability over time due to aging.

Chain cross-linking and addition of nanoparticles into polymer framework were shown to be useful for preventing physical aging [127, 128]. Although not conventional polymers and often considered for adsorption and storage rather than membrane separation, it is worth to mention various strains of porous organic networks that have more stable structure with permanent porosity and can potentially reach or already possess record high surface areas and high porosities; those include already mentioned MOFs, structurally related covalent organic frameworks (COFs) [22], porous aromatic frameworks (PAFs) [23, 24].

One of the major drawbacks of some glassy polymer membranes is plasticisation by CO₂, heavy hydrocarbon and other impurities present in industrial streams leading to significantly reduced selectivity and fast material degradation [12, 13, 129]. Robust inorganic (e.g. silicas, zeolites, carbon molecular sieves, metal carbonates, MOFs and dense metal-based) membranes promise higher chemical and thermal stability and well-defined porous structure compared to polymers reducing operating and maintenance costs [7, 19, 130, 131]. Some membranes show modest selectivity and permeability that overcome revised Robeson's upper bound, although some cases can reach impressively large CO₂/N₂ and CO₂/CH₄ selectivities of 10² – 10³ [19, 42, 107]. Such CO₂/N₂ selectivity is similar to what is agreed (20 – >200) as necessary for membranes to achieve satisfactory CO₂ removal from flue gas and to become viable replacement of amine-based absorption [8]. The inorganic membranes are usually more morphologically complex than just pure polymers as a layer of performance material is deposited on mechanically strong substrate such as porous alumina or stainless steel. Arguably, this is one of the shortcomings along with often complex synthesis, difficult scalability, large membrane thickness due to low mechanical stability and significantly larger cost than that of polymeric membranes [132].

The research in synthesis of new material can be a cost- and time-consuming task, while blending existing materials is an attractive alternative as it may combine advantages of its components leading to new materials with enhanced properties. The currently trending membranes are mixed matrix composites (MMM) that combine inorganic materials with polymers to combine advantages of both classes. Traditionally silica, zeolite or carbon-based (e.g. carbon nanotubes and activated carbons) sorbents are dispersed within polymeric matrix, however new materials are emerging involving “sandwiched” membranes with polymer support [19, 133, 134], facilitated transport (FT) membranes containing carriers with special affinity towards gas of interest [114, 135, 136] and blends with state-of-the-art materials such as MOFs [134, 137]. Some mixed matrix membranes were shown to be more selective and/or

permeable or at least more mechanically strong than pure polymeric membranes, while remarkably large CO₂/N₂ and CO₂/CH₄ selectivity values (100-500 [114] and 1000 [136], respectively) were obtained in FT membranes significantly exceeding Robeson upper limit.

Nevertheless there are still technical barriers due to infancy stage of MMMs' development such as still difficult and expensive production, poor compatibility, agglomeration, pore penetration, hydrostability. Therefore there is a continuing interest in designing robust and efficient polymeric membranes (pure or hybrid) that could treat high gas volumes; smaller membrane areas could be used reducing the total cost of equipment, or smaller pressure gradients reducing the operating costs.

1.2.2.1 Polymers of Intrinsic Microporosity

Many new materials were synthesised over past 20 years targeting the separation and storage of gases. One of the new class of materials that are currently of great interest is polymers of intrinsic microporosity (PIMs). PIMs may combine advantages of both zeolites and activated carbons. The polymers may be designed to possess sorption selectivity similar to zeolites and amorphous structure as of activated carbons but, unlikely to the carbons, have chemically well-defined structures [138]. Due to intrinsic structure of PIMs they possess large accessible area and microporosity, which makes them attractive for gas separation. The advantage of and interest in polymer-based porous materials arises from their simpler and versatile processability while maintaining its intrinsic microporosity and synthetic reproducibility. Moreover, properties of PIMs can be manipulated by introducing suitable monomer and/or functional group into polymer chain, thereby enhancing performance of the sorbent (e.g. selectivity, capacity or solubility).

PIMs belong to a family of amorphous glassy polymers that form microporous solids simply because they possess highly rigid and contorted structures, which prevent them from filling the space efficiently. In order to obtain *intrinsically* microporous polymer, rotational freedom in each bond in the polymer skeleton has to be highly restricted and chain has to contain at least one unit with so called *site of contortion* that ensures interchain separation. There are a variety of molecules [139] that could be used to synthesise PIMs due to their contorted structure imposed by either spiro-centre (Figure 1.10, A and B) or steric crowding around the covalent

bond (Figure 1.10, C). Thus necessary properties of PIMs can be tailored by introducing suitable comonomer and/or functional group into polymer chain enhancing performance of the sorbent. Such macromolecular structure makes PIMs inherently microporous; that is, microporosity is achieved due to its specific structure, which is fixed during synthesis and is typically independent from presence of template or solvent from which they were prepared. This gives advantage in terms of less complex preparation, permanent microporosity and moderate stability.

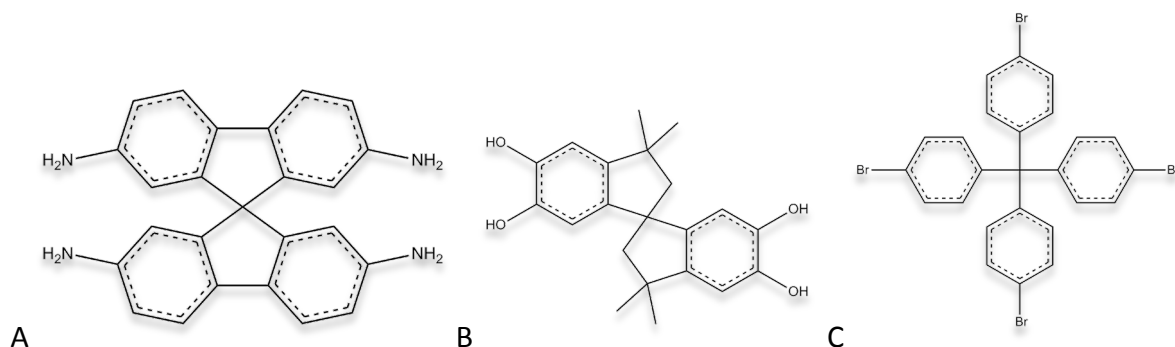


Figure 1.10. An example of possible comonomers for PIM formation: (A) spirobifluorene, (B) spirobisindane and (C) tetrakis(p-bromophenyl)methane.

PIMs possess relatively large accessible surface area ranging from 300 to highest reported 1760 m²/g for triptycene derived PIM [121] and contain large concentration of micropores due to their intrinsic structure, which makes them attractive for gas separation. Free volume in some PIMs is not fixed because PIMs are prone to swelling in presence of some gases such as CO₂. Some of the PIMs exhibit linear increase in adsorbed gas concentration with increase of pressure never reaching saturation capacity. At higher pressures the interactions between adsorbate molecules increases, which can result in a multilayer formation. The adsorbate phase condenses and polymer starts to swell. At such conditions, the polymer changes in size and volume. The volume of the material starts to depend not only on pressure and temperature but also on the amount of gases already adsorbed. The deformations in polymer structure may open pores that were inaccessible before the adsorption, which allows greater loadings. Subsequently broader range of pore sizes affects the selectivity. This effect was observed in PIM-1 during adsorption of CO₂ and CH₄; as the pressure increased PIM-1 became more permeable for CH₄ due to the plasticizing effect of CO₂ [140]. The computational work of Hölck [141] showed that swelling in PIM-1 occurred at sites of wider pores at the expense of smaller pores, which facilitates permeability of larger molecules. Swelling may be an

uncontrollable property that may lead to unpredictable adsorption capacity, selectivity and faster aging of a polymer.

One could assume that PIM chains are entirely rigid due to lack of rotational freedom and contorted structure. However the best known PIM-1 possess excellent film forming properties and its membrane is surprisingly flexible. Indeed, atomistic simulation study of Heuchel *et al.* [142] revealed that PIM-1 angles (Figure 1.11) that govern stiffness of polymer chain are not fixed and oscillate about some average value. This indicates a possible reason for good film forming ability of PIM-1.

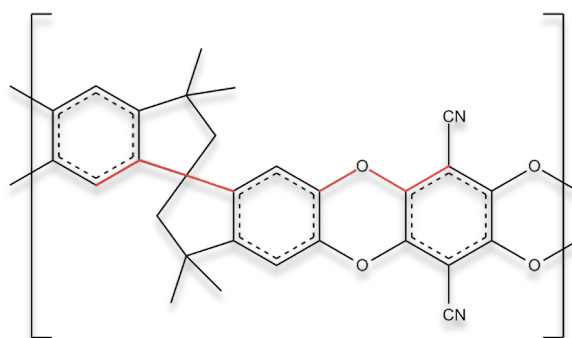


Figure 1.11. PIM-1 chemical structure and torsional angles (red lines) that define chain conformation.

PIMs are among the best performers in gas separation membranes. PIM membranes were first investigated in pervaporative separation of phenols from aqueous solutions showing results comparable to those obtained with conventionally used rubbery polymers [143]. Later applications for gas separation membranes were also successful showing that PIM-1 possess high permeability exceeded only by highly permeable polymers such as PTMSP and Teflon AF2400, whilst selectivity was significantly higher [124]. Due to such results PIMs crossed Robeson's 1991 upper bound [144] for several important gas pairs such as O_2/N_2 and CO_2/CH_4 and contributed to its revision in 2008 [92].

Several studies were performed on improving PIM-1 membrane permeability, selectivity or swelling even further by incorporating various inorganic fillers such as carbon nanotubes [145], silica [146] and organic molecules such polyethyleneimine [147] and porous organic cage molecules [148]. One of the examples involves commercially available Matrimid, which possess high selectivity and low permeability properties for CO_2/CH_4 and O_2/N_2 gas pairs [149]. PIM-1 on the other hand has opposite tendency: selectivity is lower than that of Matrimid, however permeability is much higher. Thus synergetic effect was expected from

PIM-1 and Matrimid blend. The composite with Matrimid content not exceeding 5-10 wt% possessed only slightly higher ideal selectivity for both O_2/N_2 and CO_2/CH_4 pairs than that of pristine PIM-1 while permeability reduced by 13-45%. Due to similar chemistry, good interactions were observed between two polymers and homogeneous distribution was achieved for Matrimid content of 10% or lower. Although results were satisfactorily enough, it has not solved the trade-off problem. Ideally it is desired to incorporate such filler that would prohibit polymer chain packing increasing free volume without sacrificing its selectivity and mechanical properties.

There were number of studies on glassy polymer – carbon nanotube (CNT, Figure 1.12) mixed membranes that showed enhancement of permeability while selectivity was not affected or even increased [150-152]. M. M. Khan *et al.* [145] reported on the first use of multi-walled CNT (MWCT) in PIM-1 for gas separations. Addition of 1% functionalized MWCNT (f-MWCNT) to PIM-1 increased its permeability for O_2 , N_2 , CO_2 and CH_4 gases compared to pristine PIM-1. However measured permeabilities were higher in case of pristine MWCNT than that of f-MWCNT (except for CO_2) accounting for smaller amount of voids at the interface between f-MWCNT and polymer due to better adhesion to polymer matrix. The addition of f-MWCNT to PIM-1 has also increased selectivity for CO_2/N_2 gas pair while it was almost unaffected for O_2/N_2 and even decreased for CO_2/CH_4 gas pairs. The functional group, poly(ethylene glycol), was thought to be the reason for increased selectivity towards polar CO_2 over nonpolar N_2 . Unfunctionalized MWCNT resulted in decreased selectivity in all cases and tended to agglomerate. MWCNT was also shown to enhance mechanical properties of the composite membrane, when filler was dispersed homogeneously [153].

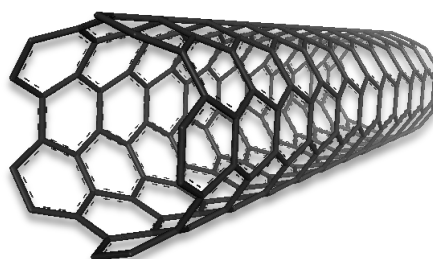


Figure 1.12. Single wall carbon nanotube.

Based on this work, it can be concluded that rigid additives does hinder chain packing creating more free space, however good polymer-additive interaction is crucial to achieve homogeneous material and unaffected selectivity. Additionally one could think about

functionalizing the additive to improve not only polymer matrix compatibility with the additive and prevent re-bundling but also create additional adsorption sites.

1.2.2.2 Triptycene and Ultrathin Membranes

Triptycene is a molecule with three arene rings separated by 120° angle due to connection to [2.2.2]bicyclic bridge (Figure 1.13). Such a rigid and three fold configuration as well as advantage of having aromatic rings was employed in versatile material chemistry applications: as an active cavity site for host-guest complexes [154, 155], as a spacer in complex interlocked molecules (also known as motors [156] and gyroscopes [157]), compounds that create cages such as COFs [158] and metal organic frameworks (MOFs) [159], and as a structure director of other organometallic materials [160, 161]. Additional interest in triptycene-derived molecules was drawn due to properties such as enhanced thermal and mechanical stability, improved solubility due to disrupted molecule packing and other interesting properties such as improved fluorescence and low refractive indices [155, 162-164].

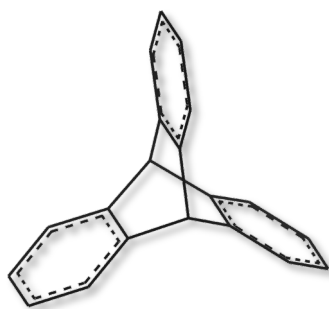


Figure 1.13. Triptycene structure.

In adsorption, triptycene was utilised with the aim of introducing or enhancing free volume and microporosity within the polymer or materials consisting of discrete molecules [121, 165-167]. Increased surface area and improved microporosity was associated with the triptycene unit as its rigid three-blade paddlewheel geometry provides required kink and holds polymer chains or remaining arms apart reducing molecule packing. This in turn provides larger amount of adsorption sites and potentially improves selectivity as well as permeability. Triptycene resulted in obtaining largest surface area PIM [121] as well as cage compound

with largest surface area among materials consisting of purely organic discrete molecules [167]. Triptycene based PIMs have very narrow pore size distribution profile with great amount of subnanometer pores, which was considered to be the reason for highest hydrogen gas capacity among PIMs and comparable to other class materials with similar or even larger surface area [121, 168]. The rigid triptycene unit was also associated with reduced polymer swelling [169].

Membranes permeability is inversely proportional to its thickness. Therefore 2D or few layer materials with controllable and dense pore distribution are the ultimate membranes for ultra-productive and ultra-efficient separation. Graphene (see 1.2.1.3.1 Graphene) sparked the greater interest in two-dimensional (2D) materials. Such materials have large lateral size compared to their thickness, and ultimately are one atom thick, as graphene. Although there exist range of layered materials and each layer can be considered as a 2D structure, however scientific community tend to consider 2D material as the one that can be separated from its counterparts and that preferably can be handled without substrate. Therefore they are perfect for fundamental studies discovering distinct properties and practical manufacture of assembled nanolayered devices, ultrathin membranes with high fluxes and other nanostructures [170, 171]. Many of such materials are inorganic non-covalent crystals such as known lubricant molybdenum disulphide, some metal oxides, other chalcogenides and layered double hydroxides. However organic materials provide unlimited opportunities in diverse architecture. Besides MOFs it is also possible to obtain materials with predictable 2D long-range order network formed exclusively by covalent bonds. There exist variety of organic networks that form lamellar bulk materials [172-174]. Organic materials have an advantage of being lightweight and low-density. Bulk materials can be exfoliated into monolayers due to nonreversible nature of intralayer bonds and weaker interlayer interactions. They can be synthesised from variety of building units as well as later functionalised providing tailored chemistry and structure for specific applications.

Triptycene has been used as a monomer in building 2D covalent materials [158, 175]. Triptycene not only provides overall rigidity, internal free volume and possibility to grow the polymer from its three arms in long range 2D integrity, it has also been shown to reduce the stacking interactions between the layers, which facilitates bulk crystal exfoliation. Aromatic rings of triptycene face perpendicular to 2D sheet, thus layers stack edge-to-edge rendering functional group accessible inside the pore rather than enclosing it between interlayers.

Recently Kissel *et al.* reported on bottom-up synthesis method of layered polymers that supposedly can produce greater quantities of bulk material [176, 177]. Unlike usual synthesis of COFs, the method relies on preorganization of monomers in a crystal before bond formation [178]. In general, the assembly is governed by specific monomer design, which has fixed shape and contains functional groups that are located at separate directions, attract each other and can react forming covalently bonded network. The triptycene core is the perfect example of such monomer, which was used by Kissel *et al.* [177] and studied in this work; it additionally consists of fused aromatic rings (anthracene fragment) connected to triptycene core. Aromatic rings of molecules' arms stack face to face and each molecule's core serves as the corner of a honeycomb structure. Stacked molecule arms chemically react upon UV light exposure within two dimensions forming a layered crystal that can be completely exfoliated into single layers. As generalised in Sakamoto *et al.* review [172] and proven by Murray *et al.* [179], freestanding 2D monosheets using shape-persistent monomer design can be synthesised by bottom-up method at the gas/liquid interface. An advantage over solid substrate approach is in principle easier removal of the sheet from the surface and transfer; while bottom-up synthesis at the interface produce larger sheets (on the order of cm^2) than those obtained from bulk crystal exfoliation [179].

The ordered structure of such polymer makes it distinct from irregular cross-linked network polymers [176] as it has well defined porous structure. The large and consistent surface area and void volume can be potentially useful for post-functionalization, separation, filtration, catalysis, sensing and etc. [173]. The interlayer of stacked unswelled bulk material should be impermeable to guest molecules; as in 2D COFs [174], when layered the voids generate 1D channel pores resulting in anisotropic permeability that could be employed in advanced separation applications. Using triptycene with different functional groups can lead to different pore channel shapes and sizes [180]. Different layer stacking modes can also create different channels and hence affect molecules transport as was demonstrated in Tong *et al.* work [115], where CO_2/N_2 selectivity was changed from 7 to 190 as interlayer passage was narrowed by shifting COF layers.

1.2.2.3 Summary

Polymeric membranes can efficiently separate industrially important gases. PIMs are among the best performers due to high free volume, narrow microporosity and large surface area. However there is a need for improvement in terms of selectivity and permeability in order to surpass Robeson plot even further and reach the region of performance that would allow polymeric membranes compete with well-established technologies such as chemical absorption. Mixed matrix membranes were shown to be viable solution to improve materials performance. Other alternative is to investigate materials with controllable and stable structure such as triptycene that was shown to be the reason for increased gas uptake capacities. Triptycene was also used to create 2D materials; this class of membranes promises high permeability due to being ultrathin and high selectivity because of proper-sized pores and possible targeted functionalization.

1.3 References

1. Doney, S.C., et al., *Ocean Acidification: The Other CO₂ Problem*. Annual Review of Marine Science, 2009. **1**(1): p. 169-192.
2. Oppenheimer, M. and R.B. Alley, *The West Antarctic Ice Sheet and Long Term Climate Policy*. Climatic Change, 2004. **64**(1-2): p. 1-10.
3. Patz, J.A. and S.H. Olson, *Climate change and health: global to local influences on disease risk*. Annals of Tropical Medicine & Parasitology, 2006. **100**(5-6): p. 535-549.
4. Parmesan, C., *Ecological and Evolutionary Responses to Recent Climate Change*. Annual Review of Ecology, Evolution, and Systematics, 2006. **37**: p. 637-669.
5. Cnop, T., D. Dortmund, and M. Schott, *Continued Development of Gas Separation Membranes for Highly Sour Services*. 2007, UOP LLC. <http://www.uop.com/>.
6. Li, J.-L. and B.-H. Chen, *Review of CO₂ absorption using chemical solvents in hollow fiber membrane contactors*. Separation and Purification Technology, 2005. **41**(2): p. 109-122.
7. Figueroa, J.D., et al., *Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program*. International Journal of Greenhouse Gas Control, 2008. **2**(1): p. 9-20.
8. Wilcox, J., et al., *Advancing Adsorption and Membrane Separation Processes for the Gigaton Carbon Capture Challenge*. Annual Review of Chemical and Biomolecular Engineering, 2014. **5**(1): p. 479-505.
9. Bhatta, L.K.G., et al., *Progress in hydrotalcite like compounds and metal-based oxides for CO₂ capture: a review*. Journal of Cleaner Production, 2015. **103**: p. 171-196.

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10. Lu, X.J. and H.N. Xiao, *A REVIEW ON CO₂ SORBENTS*. Reviews on Advanced Materials Science, 2015. **42**(1): p. 50-57.
 11. Haszeldine, R.S., *Carbon Capture and Storage: How Green Can Black Be?* Science, 2009. **325**(5948): p. 1647-1652.
 12. Baker, R.W. and K. Lokhandwala, *Natural Gas Processing with Membranes: An Overview*. Industrial & Engineering Chemistry Research, 2008. **47**(7): p. 2109-2121.
 13. Ritter, J.A. and A.D. Ebner, *Carbon Dioxide Separation Technology: R&D Needs For the Chemical and Petrochemical Industries*. 2007, Chemical Industry Vision2020 Technology Partnership.
 14. Resnik, K.P., J.T. Yeh, and H.W. Pennline, *Aqua ammonia process for simultaneous removal of CO₂, SO₂ and NO_x*. International Journal of Environmental Technology and Management, 2004. **4**(1-2): p. 89-104.
 15. Zhang, X., et al., *Carbon capture with ionic liquids: overview and progress*. Energy & Environmental Science, 2012. **5**(5): p. 6668-6681.
 16. Wills, J., M. Shemaria, and M.J. Mitariten, *Production of Pipeline Quality Natural Gas with the Molecular Gate; CO₂ Removal Process*. 2003, Society of Petroleum Engineers.
 17. Yu, C.-H., C.-H. Huang, and C.-S. Tan, *A Review of CO₂ Capture by Absorption and Adsorption*. Aerosol and Air Quality Research, 2012. **12**: p. 745-769.
 18. Drage, T.C., et al., *Developing activated carbon adsorbents for pre-combustion CO₂ capture*. Energy Procedia, 2009. **1**(1): p. 599-605.
 19. Pera-Titus, M., *Porous Inorganic Membranes for CO₂ Capture: Present and Prospects*. Chemical Reviews, 2014. **114**(2): p. 1413-1492.
 20. Mitariten, M., *Economic N₂ Removal*. Hydrocarbon Engineering, 2004.
 21. Dawson, R., D.J. Adams, and A.I. Cooper, *Chemical tuning of CO₂ sorption in robust nanoporous organic polymers*. Chemical Science, 2011. **2**(6): p. 1173-1177.
 22. Furukawa, H. and O.M. Yaghi, *Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications*. Journal of the American Chemical Society, 2009. **131**(25): p. 8875-8883.
 23. Ben, T. and S. Qiu, *Porous aromatic frameworks: Synthesis, structure and functions*. CrystEngComm, 2013. **15**(1): p. 17-26.
 24. Ben, T., et al., *Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area*. Angewandte Chemie International Edition, 2009. **48**(50): p. 9457-9460.
 25. Li, J.-R., R.J. Kuppler, and H.-C. Zhou, *Selective gas adsorption and separation in metal-organic frameworks*. Chemical Society Reviews, 2009. **38**(5): p. 1477-1504.
 26. Yampolskii, Y., *Polymeric Gas Separation Membranes*. Macromolecules, 2012. **45**(8): p. 3298-3311.
 27. Lee, S.-Y. and S.-J. Park, *A review on solid adsorbents for carbon dioxide capture*. Journal of Industrial and Engineering Chemistry, 2015. **23**: p. 1-11.
 28. Keller, J.U. and R. Staudt, *GAS ADSORPTION EQUILIBRIA: Experimental Methods and Adsorptive Isotherms*. 2005: Springer.
 29. Cavenati, S., C.A. Grande, and A.E. Rodrigues, *Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures*. Journal of Chemical & Engineering Data, 2004. **49**(4): p. 1095-1101.
 30. Hudson, M.R., et al., *Unconventional, Highly Selective CO₂ Adsorption in Zeolite SSZ-13*. Journal of the American Chemical Society, 2012. **134**(4): p. 1970-1973.
 31. Cheung, O., et al., *K⁺ Exchanged Zeolite ZK-4 as a Highly Selective Sorbent for CO₂*. Langmuir, 2014. **30**(32): p. 9682-9690.

32. Akhtar, F., et al., *Strong and binder free structured zeolite sorbents with very high CO₂-over-N₂ selectivities and high capacities to adsorb CO₂ rapidly*. Energy & Environmental Science, 2012. **5**(6): p. 7664-7673.
33. Bao, Z., et al., *Adsorption of CO₂ and CH₄ on a magnesium-based metal organic framework*. Journal of Colloid and Interface Science, 2011. **353**(2): p. 549-556.
34. Choi, S., J.H. Drese, and C.W. Jones, *Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources*. ChemSusChem, 2009. **2**(9): p. 796-854.
35. Samanta, A., et al., *Post-Combustion CO₂ Capture Using Solid Sorbents: A Review*. Industrial & Engineering Chemistry Research, 2012. **51**(4): p. 1438-1463.
36. Harlick, P.J.E. and F.H. Tezel, *An experimental adsorbent screening study for CO₂ removal from N₂*. Microporous and Mesoporous Materials, 2004. **76**(1-3): p. 71-79.
37. Yu, L., et al., *Synthesis of binderless zeolite X microspheres and their CO₂ adsorption properties*. Separation and Purification Technology, 2013. **118**: p. 188-195.
38. Brandani, F. and D.M. Ruthven, *The Effect of Water on the Adsorption of CO₂ and C₃H₈ on Type X Zeolites*. Industrial & Engineering Chemistry Research, 2004. **43**(26): p. 8339-8344.
39. Li, G., et al., *Capture of CO₂ from high humidity flue gas by vacuum swing adsorption with zeolite 13X*. Adsorption, 2008. **14**(2): p. 415-422.
40. Babarao, R., et al., *Storage and Separation of CO₂ and CH₄ in Silicalite, C168 Schwarzite, and IRMOF-1: A Comparative Study from Monte Carlo Simulation*. Langmuir, 2007. **23**(2): p. 659-666.
41. Bae, Y.-S., et al., *Separation of CO₂ from CH₄ Using Mixed-Ligand Metal–Organic Frameworks*. Langmuir, 2008. **24**(16): p. 8592-8598.
42. Krishna, R. and J.M. van Baten, *In silico screening of metal-organic frameworks in separation applications*. Physical Chemistry Chemical Physics, 2011. **13**(22): p. 10593-10616.
43. Furukawa, H., et al., *Ultrahigh Porosity in Metal-Organic Frameworks*. Science, 2010. **329**(5990): p. 424-428.
44. Liu, J., et al., *CO₂/H₂O Adsorption Equilibrium and Rates on Metal–Organic Frameworks: HKUST-1 and Ni/DOBDC*. Langmuir, 2010. **26**(17): p. 14301-14307.
45. Andirova, D., et al., *Effect of the structural constituents of metal organic frameworks on carbon dioxide capture*. Microporous and Mesoporous Materials, 2016. **219**: p. 276-305.
46. Low, J.J., et al., *Virtual High Throughput Screening Confirmed Experimentally: Porous Coordination Polymer Hydration*. Journal of the American Chemical Society, 2009. **131**(43): p. 15834-15842.
47. Demessence, A., et al., *Strong CO₂ Binding in a Water-Stable, Triazolate-Bridged Metal–Organic Framework Functionalized with Ethylenediamine*. Journal of the American Chemical Society, 2009. **131**(25): p. 8784-8786.
48. Chue, K.T., et al., *Comparison of Activated Carbon and Zeolite 13X for CO₂ Recovery from Flue Gas by Pressure Swing Adsorption*. Industrial & Engineering Chemistry Research, 1995. **34**(2): p. 591-598.
49. Sircar, S., T.C. Golden, and M.B. Rao, *Activated carbon for gas separation and storage*. Carbon, 1996. **34**(1): p. 1-12.
50. Siriwardane, R.V., et al., *Adsorption of CO₂ on Molecular Sieves and Activated Carbon*. Energy & Fuels, 2001. **15**(2): p. 279-284.
51. Zhijuan, Z., et al., *Adsorption of CO₂ on Zeolite 13X and Activated Carbon with Higher Surface Area*. Separation Science and Technology, 2010. **45**(5): p. 710-719.

52. Himeno, S., T. Komatsu, and S. Fujita, *High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons*. Journal of Chemical & Engineering Data, 2005. **50**(2): p. 369-376.
53. Shen, W., et al., *Yeast-Based Microporous Carbon Materials for Carbon Dioxide Capture*. ChemSusChem, 2012. **5**(7): p. 1274-1279.
54. Xu, D., et al., *Effects of water vapour on CO₂ capture with vacuum swing adsorption using activated carbon*. Chemical Engineering Journal, 2013. **230**: p. 64-72.
55. Wahby, A., et al., *High-Surface-Area Carbon Molecular Sieves for Selective CO₂ Adsorption*. ChemSusChem, 2010. **3**(8): p. 974-981.
56. Silvestre-Albero, J., et al., *Ultrahigh CO₂ adsorption capacity on carbon molecular sieves at room temperature*. Chemical Communications, 2011. **47**(24): p. 6840-6842.
57. Sevilla, M. and A.B. Fuertes, *Sustainable porous carbons with a superior performance for CO₂ capture*. Energy & Environmental Science, 2011. **4**(5): p. 1765-1771.
58. Sun, N., et al., *Surface-modified spherical activated carbon materials for pre-combustion carbon dioxide capture*. RSC Advances, 2015. **5**(42): p. 33681-33690.
59. Plaza, M.G., et al., *CO₂ capture by adsorption with nitrogen enriched carbons*. Fuel, 2007. **86**(14): p. 2204-2212.
60. Arenillas, A., et al., *CO₂ removal potential of carbons prepared by co-pyrolysis of sugar and nitrogen containing compounds*. Journal of Analytical and Applied Pyrolysis, 2005. **74**(1-2): p. 298-306.
61. Sevilla, M. and A.B. Fuertes, *CO₂ adsorption by activated templated carbons*. Journal of Colloid and Interface Science, 2012. **366**(1): p. 147-154.
62. Wei, J., et al., *A Controllable Synthesis of Rich Nitrogen-Doped Ordered Mesoporous Carbon for CO₂ Capture and Supercapacitors*. Advanced Functional Materials, 2013. **23**(18): p. 2322-2328.
63. Robertson, C. and R. Mokaya, *Microporous activated carbon aerogels via a simple subcritical drying route for CO₂ capture and hydrogen storage*. Microporous and Mesoporous Materials, 2013. **179**: p. 151-156.
64. Cinke, M., et al., *CO₂ adsorption in single-walled carbon nanotubes*. Chemical Physics Letters, 2003. **376**(5-6): p. 761-766.
65. Lu, C., et al., *Comparative Study of CO₂ Capture by Carbon Nanotubes, Activated Carbons, and Zeolites*. Energy & Fuels, 2008. **22**(5): p. 3050-3056.
66. Mouras, S., et al., *Synthesis of first stage graphite intercalation compounds with fluorides*. Revue de chimie minérale 1987. **24**: p. 572-582.
67. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nat Mater, 2007. **6**(3): p. 183-191.
68. Kobayashi, T., et al., *Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process*. Applied Physical Letters, 2013. **102**: p. 023112.
69. Nakada, K., et al., *Edge state in graphene ribbons: Nanometer size effect and edge shape dependence*. Physical Review B, 1996. **54**(24): p. 17954-17961.
70. Meyer, J.C., et al., *The structure of suspended graphene sheets*. Nature, 2007. **446**.
71. Landau, L.D. and E.M. Lifshitz, *Statistical Physics. Part I*. 1980, Oxford: Pergamon.
72. Novoselov, K.S., et al., *Two-dimensional atomic crystals*. Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(30): p. 10451-10453.
73. Park, S. and R.S. Ruoff, *Chemical methods for the production of graphenes*. Nat Nano, 2009. **4**(4): p. 217-224.

74. Kim, K.S., et al., *Large-scale pattern growth of graphene films for stretchable transparent electrodes*. Nature, 2009. **457**(7230): p. 706-710.
75. Khan, U., et al., *High-Concentration Solvent Exfoliation of Graphene*. Small, 2010. **6**(7): p. 864-871.
76. Taheri Najafabadi, A., *Emerging applications of graphene and its derivatives in carbon capture and conversion: Current status and future prospects*. Renewable and Sustainable Energy Reviews, 2015. **41**: p. 1515-1545.
77. Jiang, D.-e., V.R. Cooper, and S. Dai, *Porous Graphene as the Ultimate Membrane for Gas Separation*. Nano Letters, 2009. **9**(12): p. 4019-4024.
78. Du, H., et al., *Separation of Hydrogen and Nitrogen Gases with Porous Graphene Membrane*. The Journal of Physical Chemistry C, 2011. **115**(47): p. 23261-23266.
79. Suk, M.E. and N.R. Aluru, *Water Transport through Ultrathin Graphene*. The Journal of Physical Chemistry Letters, 2010. **1**(10): p. 1590-1594.
80. Bunch, J.S., et al., *Impermeable Atomic Membranes from Graphene Sheets*. Nano Letters, 2008. **8**(8): p. 2458-2462.
81. Nair, R.R., et al., *Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes*. Science, 2012. **335**: p. 442-444.
82. Wu, T., et al., *Fluorine-Modified Porous Graphene as Membrane for CO₂/N₂ Separation: Molecular Dynamic and First-Principles Simulations*. The Journal of Physical Chemistry C, 2014. **118**(14): p. 7369-7376.
83. Meng, L.-Y. and S.-J. Park, *Effect of exfoliation temperature on carbon dioxide capture of graphene nanoplates*. Journal of Colloid and Interface Science, 2012. **386**(1): p. 285-290.
84. Chowdhury, S. and R. Balasubramanian, *Highly efficient, rapid and selective CO₂ capture by thermally treated graphene nanosheets*. Journal of CO₂ Utilization, 2016. **13**: p. 50-60.
85. Dumitrică, T., C.M. Landis, and B.I. Yakobson, *Curvature-induced polarization in carbon nanoshells*. Chemical Physics Letters, 2002. **360**(1-2): p. 182-188.
86. Asai, M., et al., *Marked Adsorption Irreversibility of Graphitic Nanoribbons for CO₂ and H₂O*. Journal of the American Chemical Society, 2011. **133**(38): p. 14880-14883.
87. Ohba, T. and H. Kanoh, *Intensive Edge Effects of Nanographenes in Molecular Adsorptions*. The Journal of Physical Chemistry Letters, 2012. **3**(4): p. 511-516.
88. Song, P.A., et al., *Permeability, Viscoelasticity, and Flammability Performances and Their Relationship to Polymer Nanocomposites*. Industrial & Engineering Chemistry Research, 2012. **51**(21): p. 7255-7263.
89. Compton, O.C., et al., *Crumpled Graphene Nanosheets as Highly Effective Barrier Property Enhancers*. Advanced Materials, 2010. **22**(42): p. 4759-4763.
90. Potts, J.R., et al., *Graphene-based polymer nanocomposites*. Polymer, 2011. **52**(1): p. 5-25.
91. Kim, H.W., et al., *Selective Gas Transport Through Few-Layered Graphene and Graphene Oxide Membranes*. Science, 2013. **342**(6154): p. 91-95.
92. Robeson, L.M., *The upper bound revisited*. Journal of Membrane Science, 2008. **320**(1-2): p. 390-400.
93. Kim, H.W., et al., *High-performance CO₂-philic graphene oxide membranes under wet-conditions*. Chemical Communications, 2014. **50**(88): p. 13563-13566.
94. Li, X., et al., *Efficient CO₂ Capture by Functionalized Graphene Oxide Nanosheets as Fillers To Fabricate Multi-Permselective Mixed Matrix Membranes*. ACS Applied Materials & Interfaces, 2015. **7**(9): p. 5528-5537.

-
95. Li, X., et al., *Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO₂ separation*. Journal of Membrane Science, 2015. **479**: p. 1-10.
96. Müllen, K. and J.P. Rabe, *Nanographenes as Active Components of Single-Molecule Electronics and How a Scanning Tunneling Microscope Puts Them To Work*. Accounts of Chemical Research, 2008. **41**(4): p. 511-520.
97. Yin, M., et al., *Functionalization of Self-Assembled Hexa-peri-hexabenzocoronene Fibers with Peptides for Bioprobng*. Journal of the American Chemical Society, 2009. **131**(41): p. 14618-14619.
98. Zhu, P.-C., et al., *Three-dimensional nanographene based on triptycene for detection of nitroaromatic explosives*. Tetrahedron Letters, 2014. **55**(45): p. 6277-6280.
99. Zhang, C., et al., *Three-Dimensional Nanographene Based on Triptycene: Synthesis and Its Application in Fluorescence Imaging*. Organic Letters, 2012. **14**(23): p. 5912-5915.
100. Liu, Z., et al., *PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs*. Journal of the American Chemical Society, 2008. **130**(33): p. 10876-10877.
101. Simpson, C.D., et al., *Nanosized Molecular Propellers by Cyclodehydrogenation of Polyphenylene Dendrimers*. Journal of the American Chemical Society, 2004. **126**(10): p. 3139-3147.
102. Barnett, L., et al., *The Structure of Hexabenzotriphenylene and the Problem of Overcrowded "D_{3h}" Polycyclic Aromatic Compounds*. Journal of the American Chemical Society, 1999. **121**(4): p. 727-733.
103. Low, B.T., et al., *A parametric study of the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas*. Journal of Membrane Science, 2013. **431**: p. 139-155.
104. Thornton, A.W., et al., *Feasibility of zeolitic imidazolate framework membranes for clean energy applications*. Energy & Environmental Science, 2012. **5**(6): p. 7637-7646.
105. Ozturk, T.N. and S. Keskin, *Computational Screening of Porous Coordination Networks for Adsorption and Membrane-Based Gas Separations*. The Journal of Physical Chemistry C, 2014. **118**(25): p. 13988-13997.
106. Li, S. and C.Q. Fan, *High-Flux SAPO-34 Membrane for CO₂/N₂ Separation*. Industrial & Engineering Chemistry Research, 2010. **49**(9): p. 4399-4404.
107. Krishna, R. and J.M. van Baten, *In silico screening of zeolite membranes for CO₂ capture*. Journal of Membrane Science, 2010. **360**(1-2): p. 323-333.
108. Nafisi, V. and M.-B. Hägg, *Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO₂ capture*. Journal of Membrane Science, 2014. **459**: p. 244-255.
109. Car, A., C. Stropnik, and K.-V. Peinemann, *Hybrid membrane materials with different metal-organic frameworks (MOFs) for gas separation*. Desalination, 2006. **200**(1-3): p. 424-426.
110. Basu, S., A. Cano-Odena, and I.F.J. Vankelecom, *MOF-containing mixed-matrix membranes for CO₂/CH₄ and CO₂/N₂ binary gas mixture separations*. Separation and Purification Technology, 2011. **81**(1): p. 31-40.
111. Meng, L., et al., *Self-Supported Fibrous Porous Aromatic Membranes for Efficient CO₂/N₂ Separations*. ACS Applied Materials & Interfaces, 2015. **7**(28): p. 15561-15569.
112. Song, Q., et al., *Controlled thermal oxidative crosslinking of polymers of intrinsic microporosity towards tunable molecular sieve membranes*. Nat Commun, 2014. **5**.

113. Deng, L., T.-J. Kim, and M.-B. Hägg, *Facilitated transport of CO₂ in novel PVAm/PVA blend membrane*. Journal of Membrane Science, 2009. **340**(1–2): p. 154–163.
114. Huang, J., J. Zou, and W.S.W. Ho, *Carbon Dioxide Capture Using a CO₂-Selective Facilitated Transport Membrane*. Industrial & Engineering Chemistry Research, 2008. **47**(4): p. 1261–1267.
115. Tong, M., et al., *Few-layered ultrathin covalent organic framework membranes for gas separation: a computational study*. Journal of Materials Chemistry A, 2016. **4**(1): p. 124–131.
116. Xomeritakis, G., C.-Y. Tsai, and C.J. Brinker, *Microporous sol–gel derived aminosilicate membrane for enhanced carbon dioxide separation*. Separation and Purification Technology, 2005. **42**(3): p. 249–257.
117. Pinnau, I. and L.G. Toy, *Gas and vapor transport properties of amorphous perfluorinated copolymer membranes based on 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole/tetrafluoroethylene*. Journal of Membrane Science, 1996. **109**(1): p. 125–133.
118. Masuda, T., et al., *Poly[1-(trimethylsilyl)-1-propyne]: a new high polymer synthesized with transition-metal catalysts and characterized by extremely high gas permeability*. Journal of the American Chemical Society, 1983. **105**(25): p. 7473–7474.
119. Morisato, A. and I. Pinnau, *Synthesis and gas permeation properties of poly(4-methyl-2-pentyne)*. Journal of Membrane Science, 1996. **121**(2): p. 243–250.
120. Hu, Y., et al., *Synthesis and Properties of Indan-Based Polyacetylenes That Feature the Highest Gas Permeability among All the Existing Polymers*. Macromolecules, 2008. **41**(22): p. 8525–8532.
121. Ghanem, B.S., et al., *Triptycene-Based Polymers of Intrinsic Microporosity: Organic Materials That Can Be Tailored for Gas Adsorption*. Macromolecules, 2010. **43**(12): p. 5287–5294.
122. Fang, W., L. Zhang, and J. Jiang, *Polymers of intrinsic microporosity for gas permeation: a molecular simulation study*. Molecular Simulation, 2010. **36**(12): p. 992–1003.
123. Budd, P.M., et al., *Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials*. Chem. Commun, 2004: p. 230–231.
124. Budd, P.M., et al., *Gas separation membranes from polymers of intrinsic microporosity*. Journal of Membrane Science, 2005. **251**(1–2): p. 263–269.
125. Park, H.B., et al., *Thermally rearranged (TR) polymer membranes for CO₂ separation*. Journal of Membrane Science, 2010. **359**(1–2): p. 11–24.
126. Tsyurupa, M.P. and V.A. Davankov, *Hypercrosslinked polymers: basic principle of preparing the new class of polymeric materials*. Reactive and Functional Polymers, 2002. **53**(2–3): p. 193–203.
127. Kelman, S.D., et al., *Crosslinking poly[1-(trimethylsilyl)-1-propyne] and its effect on physical stability*. Journal of Membrane Science, 2008. **320**(1–2): p. 123–134.
128. Bernardo, P., E. Drioli, and G. Golemme, *Membrane Gas Separation: A Review/State of the Art*. Industrial & Engineering Chemistry Research, 2009. **48**(10): p. 4638–4663.
129. Staudt-Bickel, C. and W. J. Koros, *Improvement of CO₂/CH₄ separation characteristics of polyimides by chemical crosslinking*. Journal of Membrane Science, 1999. **155**(1): p. 145–154.
130. Zhang, L., et al., *Fast electrochemical CO₂ transport through a dense metal-carbonate membrane: A new mechanistic insight*. Journal of Membrane Science, 2014. **468**: p. 373–379.

-
131. Abanades, J.C., et al., *Emerging CO₂ capture systems*. International Journal of Greenhouse Gas Control, 2015. **40**: p. 126-166.
 132. Mushtaq, A., et al., *A Review: Development of Polymeric Blend Membrane For Removal of CO₂ From Natural Gas*. International Journal of Engineering & Technology, 2013. **13**(2): p. 53-60.
 133. Chunga, T.-S., et al., *Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation*. Prog. Polym. Sci., 2007. **32**: p. 483-507.
 134. Kim, J., et al., *Matrix effect of mixed-matrix membrane containing CO₂-selective MOFs*. Journal of Applied Polymer Science, 2016. **133**(1): p. n/a-n/a.
 135. Dai, Z., et al., *Combination of ionic liquids with membrane technology: A new approach for CO₂ separation*. Journal of Membrane Science, 2016. **497**: p. 1-20.
 136. Kim, T.J., B.A. Li, and M.B. Hagg, *Novel fixed-site-carrier polyvinylamine membrane for carbon dioxide capture*. Journal of Polymer Science Part B-Polymer Physics, 2004. **42**(23): p. 4326-4336.
 137. Tanh Jeazet, H.B., C. Staudt, and C. Janiak, *Metal-organic frameworks in mixed-matrix membranes for gas separation*. Dalton Transactions, 2012. **41**(46): p. 14003-14027.
 138. McKeown, N.B. and P.M. Budd, *Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage*. Chemical Society Reviews, 2006. **35**: p. 675-683.
 139. McKeown, N.B. and P.M. Budd, *Exploitation of Intrinsic Microporosity in Polymer-Based Materials*. Macromolecules, 2010. **43**(12): p. 5163-5176.
 140. Bos, A., et al., *CO₂-induced plasticization phenomena in glassy polymers*. Journal of Membrane Science, 1999. **155**(1): p. 67-78.
 141. Hölck, O., *Gas Sorption and Swelling in Glassy Polymers. Combining Experiment, Phenomenological Models and Detailed Atomistic Molecular Modeling*. 2008.
 142. Heuchela, M., et al., *Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1)*. Journal of Membrane Science, 2008. **318**(1-2): p. 84-99.
 143. Budd, P.M., et al., *Solution-Processed, Organophilic Membrane Derived from a Polymer of Intrinsic Microporosity*. Advanced Materials, 2004. **16**(5): p. 456-459.
 144. Robeson, L.M., *Correlation of separation factor versus permeability for polymeric membranes*. Journal of Membrane Science, 1991. **62**(2): p. 165-185.
 145. Khan, M.M., et al., *Functionalized carbon nanotubes mixed matrix membranes of polymers of intrinsic microporosity for gas separation*. Nanoscale Research Letters, 2012. **7**: p. 504.
 146. Ahn, J., et al., *Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1)*. Journal of Membrane Science, 2010. **346**(2): p. 280-287.
 147. Fritsch, D., et al., *High performance organic solvent nanofiltration membranes: Development and thorough testing of thin film composite membranes made of polymers of intrinsic microporosity (PIMs)*. Journal of Membrane Science, 2012. **401-402**(0): p. 222-231.
 148. Bushell, A.F., et al., *Nanoporous Organic Polymer/Cage Composite Membranes*. Angewandte Chemie International Edition, 2013. **52**(4): p. 1253-1256.
 149. Yong, W.F., et al., *Molecular engineering of PIM-1/Matrimid blend membranes for gas separation*. Journal of Membrane Science, 2012. **407**: p. 47-57.
 150. Kim, S., T.W. Pechar, and E. Marand, *Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation*. Desalination, 2006. **192**: p. 330-339.

151. Cong, H.L., et al., *Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4-phenylene oxide) for gas separation*. J. Membr. Sci., 2007. **294**: p. 178-185.
152. Weng, T.H., H.H. Tseng, and M.Y. Wey, *Preparation and characterization of multiwalled carbon nanotube/PBNPI nanocomposite membrane for H₂/CH₄ separation*. Int. J. Hydrogen Energy, 2009. **34**: p. 8707-8715.
153. Khan, M.M., et al., *Enhanced gas permeability by fabricating mixed matrix membranes of functionalized multiwalled carbon nanotubes and polymers of intrinsic microporosity (PIM)*. Journal of Membrane Science, 2013. **436**: p. 109-120.
154. Guo, J.-B., et al., *Formation of 1:2 Host-Guest Complexes Based on Triptycene-Derived Macrotricyclic and Paraquat Derivatives: Anion- π Interactions between PF₆ and Bipyridinium Rings in the Solid State*. Organic Letters, 2011. **13**(20): p. 5688-5691.
155. Mondal, S., et al., *Synthesis of Triptycene-Based Organosoluble, Thermally Stable, and Fluorescent Polymers: Efficient Host-Guest Complexation with Fullerene*. Macromolecules, 2013. **46**: p. 6824-6831.
156. Zhu, X.-Z. and C.-F. Chen, *A Highly Efficient Approach to [4]Pseudocatenanes by Threefold Metathesis Reactions of a Triptycene-Based Tris[2]pseudorotaxane*. Journal of the American Chemical Society, 2005. **127**(38): p. 13158-13159.
157. Godinez, C.E., et al., *Molecular Crystals with Moving Parts: Synthesis, Characterization, and Crystal Packing of Molecular Gyroscopes with Methyl-Substituted Triptycyl Frames*. Journal of Organic Chemistry, 2004. **69**: p. 1652-1662.
158. Kahveci, Z., et al., *Targeted synthesis of a mesoporous triptycene-derived covalent organic framework*. CrystEngComm, 2013. **15**(8): p. 1524-1527.
159. Vagin, S., et al., *Metal-Organic Frameworks (MOFs) Composed of (Triptycenedicarboxylato)zinc*. Eur. J. Inorg. Chem., 2008: p. 2601-2609.
160. Roy, X., et al., *Molecular Scaffolding of Prussian Blue Analogues Using a Phenanthroline-Extended Triptycene Ligand*. Cryst. Growth Des., 2011. **11**: p. 4551-4558.
161. Munakata, M., et al., *Silver(I) Complex Assemblies with Nonplanar Aromatic Compounds*. Inorganic Chemistry, 1999. **38**: p. 5674-5680.
162. Sydlik, S.A., Z. Chen, and T.M. Swager, *Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices*. Macromolecules, 2011. **44**(4): p. 976-980.
163. Long, T.M. and T.M. Swager, *Molecular Design of Free Volume as a Route to Low- κ Dielectric Materials*. Journal of the American Chemical Society, 2003. **125**(46): p. 14113-14119.
164. Zhu, Z. and T.M. Swager, *Conjugated Polymers Containing 2,3-Dialkoxybenzene and Iptycene Building Blocks*. Organic Letters, 2001. **3**(22): p. 3471-3474.
165. Abbott, L.J., et al., *Characterizing the Structure of Organic Molecules of Intrinsic Microporosity by Molecular Simulations and X-ray Scattering*. The Journal of Physical Chemistry B, 2012. **117**(1): p. 355-364.
166. Rabbani, M.G., et al., *High CO₂ uptake and selectivity by triptycene-derived benzimidazole-linked polymers*. Chemical Communications, 2012. **48**(8): p. 1141-1143.
167. Mastalerz, M., et al., *A Salicylbisimine Cage Compound with High Surface Area and Selective CO₂/CH₄ Adsorption*. Angewandte Chemie International Edition, 2011. **50**(5): p. 1046-1051.

-
168. Ghanem, B.S., et al., *A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption*. Chemical Communications, 2007(1): p. 67-69.
169. Hashem, M., et al., *Enhancing the rigidity of a network polymer of intrinsic microporosity by the combined use of phthalocyanine and triptycene components*. Polymer Chemistry, 2011. **2**(10): p. 2190-2192.
170. Ma, R. and T. Sasaki, *Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites*. Advanced Materials, 2010. **22**(45): p. 5082-5104.
171. Mas-Balleste, R., et al., *2D materials: to graphene and beyond*. Nanoscale, 2011. **3**(1): p. 20-30.
172. Sakamoto, J., et al., *Two-Dimensional Polymers: Just a Dream of Synthetic Chemists?* Angewandte Chemie International Edition, 2009. **48**(6): p. 1030-1069.
173. Colson, J.W. and W.R. Dichtel, *Rationally synthesized two-dimensional polymers*. Nat Chem, 2013. **5**(6): p. 453-465.
174. Feng, X., X. Ding, and D. Jiang, *Covalent organic frameworks*. Chemical Society Reviews, 2012. **41**(18): p. 6010-6022.
175. Zhou, T.-Y., et al., *Single-Step Solution-Phase Synthesis of Free-Standing Two-Dimensional Polymers and Their Evolution into Hollow Spheres*. Macromolecules, 2013. **46**(19): p. 7745-7752.
176. Kissel, P., et al., *A two-dimensional polymer prepared by organic synthesis*. Nat Chem, 2012. **4**(4): p. 287-291.
177. Kissel, P., et al., *A nanoporous two-dimensional polymer by single-crystal-to-single-crystal photopolymerization*. Nat Chem, 2014. **6**(9): p. 774-778.
178. Bhola, R., et al., *A Two-Dimensional Polymer from the Anthracene Dimer and Triptycene Motifs*. Journal of the American Chemical Society, 2013. **135**(38): p. 14134-14141.
179. Murray, D.J., et al., *Large Area Synthesis of a Nanoporous Two-Dimensional Polymer at the Air/Water Interface*. Journal of the American Chemical Society, 2015. **137**(10): p. 3450-3453.
180. Li, P.-F. and C.-F. Chen, *Synthesis, Structures, and Solid State Self-Assemblies of Formyl and Acetyl Substituted Triptycenes and Their Derivatives*. The Journal of Organic Chemistry, 2012. **77**(20): p. 9250-9259.

2 METHODOLOGY

2.1 Adsorption Phenomenon and Experimental Method

Adsorption is a process of sorbate accumulation on the surface of an adsorbent. Reduction in surface energy between sorbate and adsorbent phases is a driving force for the adsorption. Adsorption is classified into two general processes: physisorption and chemisorption. The latter one occurs due to strong covalent bonding, which results in frequently irreversible adsorption; adsorbed molecules form a monolayer on adsorbent surface. Physisorption occurs due to weaker interactions such as van der Waals, hydrogen bond and polar interactions. Therefore the sorbate can be readily desorbed. The interactions between sorbate and adsorbent as well as adsorption mechanism may be quite complex depending on pore size, structure and surface properties of sorbate and adsorbent. Adsorption is a crucial factor for membrane design as it not only shows certain affinity towards sorbate of interest but also indicates its possibly inhibited or promoted motion within membranes matrix.

Volumetric and gravimetric methods are the most commonly used to measure adsorption of gases at laboratory conditions. Using these methods it is also possible to determine surface area, free void volume and density of the adsorbent as well as its pore size distribution (see 2.2.6 Structure Characterization). Measurements are based on physical adsorption of noble gases and nitrogen, thus measured quantity is not direct observable but needs to be linked to property of interest using mathematical models and assumptions.

2.1.1 Isotherms

Experimental adsorption data is typically represented graphically as adsorption isotherm, which shows equilibrium amount of sorbate adsorbed as a function of pressure at constant temperature. The amount is commonly normalised for mass of adsorbent material allowing for comparison between different adsorbents. Adsorption isotherms are normally measured experimentally, although in some cases molecular simulations can provide accurate predictions. Nevertheless, experimental equilibrium data is necessary, particularly for newly developed sorbents. Not only adsorbed amount may be determined from the isotherm, typical pattern of isotherm may also indicate pore size (micro-, meso-, macro- or non-porous), strength of interactions between sorbate-adsorbent and sorbate-sorbate, multilayer adsorption and pore condensation, etc. [1-3]. In some cases, isotherm exhibits hysteresis loop, which occurs when amount of gas absorbed is different from the desorbed amount. In many cases, it is an evidence of capillary condensation, which occurs in mesopores, but it could also be a result of either changes in polymer morphology due to increased gas pressure, plasticization of a polymer or it can be attributed to blocking of narrow openings as well as combination of all these mechanisms [1-5].

Collected data is commonly fitted to mathematical isotherm model to allow for data processing, extrapolation and comparison between different adsorbents. Combining isotherms at two different temperatures it is possible to calculate heat of adsorption and, subsequently, predict loadings at other temperatures of interest (further details in section 2.1.2). Some of the models that are derived from physical assumptions may also provide an insight into adsorption mechanism. There are many adsorption isotherm models, which all have to be applied in consideration of sorbate-adsorbent system and adsorption pattern.

The Henry's law is the simplest interpretation of adsorption process in liquid or rubbery polymers, but can also be relatively accurate at sufficiently high temperatures and low pressures in other materials [6]. The law is described as a concentration linearly dependent on pressure:

$$n = k_H P \quad (2.1)$$

where n is the amount of adsorbed gases, k_H is Henry's constant (or solubility coefficient) and P is pressure. The model is depicted in the Figure 2.1 by a dotted line. However, more often

the dependence of adsorbed gas amount on pressure deviates from linear pattern, and, as a result, a number of isotherm models were derived to account for this deviation.

Here is presented only dual-mode (DM) model that is commonly used for isotherms obtained from glassy polymers [7, 8], which are some of the materials studied in this work. The model has a fundamental basis, which postulates that one population of gas is dissolved in a fraction of the solid according to the Henry's law and another population behaves as in Langmuir model, i.e. at lower pressures sorbate molecules fill free volume of the adsorbent, adsorption rate gradually decreases with pressure until saturation adsorption capacity is reached. The classical expression takes the following form:

$$n = n_1 + n_2 = k_1 P + \frac{mk_2 P}{1 + k_2 P} \quad (2.2)$$

where n_1 and n_2 is the adsorbed amount based on Henry's law and Langmuir model, respectively, k_1 is Henry's law solubility constant, m is Langmuir saturation capacity constant and k_2 is Langmuir hole affinity constant. The k_2 increases with increase in gas-solid interaction energy and decrease with temperature. Figure 2.1 shows graphic representation of DM model and contribution of Langmuir and Henry's law models.

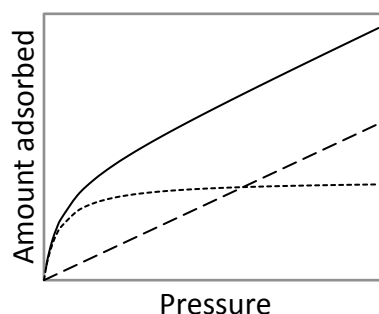


Figure 2.1. DM model (—) and contribution of Langmuir (- - -) and Henry's (- . -) isotherm models.

2.1.2 Heat of Adsorption

Another important quantity that was used in this study is heat of adsorption. It is an indication of how strong the interactions are between the gas molecules and adsorbent, i.e. the higher the value is the stronger interactions are. On the other hand, it is not desirable to have too strong

adsorption because otherwise too much time or energy would be spent for separation processes and material regeneration. The heat of adsorption may also reveal some structural properties of the adsorbent, e.g. existence of smaller pores will translate into higher heat of adsorption. It also indicates adsorbent temperature change during adsorption process; the released heat affects equilibrium and kinetics of the process and suggests operating conditions for optimum adsorbent performance. Heat of adsorption is a useful quantity and commonly used for different material comparison. It can be calculated from isotherms measured at two different temperatures via Clausius-Clapeyron relation:

$$\ln \frac{P_1}{P_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.3)$$

where ΔH is isosteric heat of adsorption, R is the gas constant of ideal gas and T is temperature. The two pressures from two different isotherms at two different temperatures need to correspond to the same loading. One can study the isotherms and interpolate to the same loading data points but it is more elegant to fit each isotherm to mathematical model from which pressure can be calculated by defining the loading.

2.1.3 Selectivity

Henry's constant is a useful quantity that describes adsorbent's affinity towards sorbate particles. Taking ratio of Henry's constants for different sorbates it is possible to obtain numerical value to describe ideal zero coverage selectivity. Selectivity indicates the performance of material and is useful for comparison between different sorbate pairs or different materials. The Henry's constant is defined as sorbate loading divided by its fugacity at the limit of zero pressure. The apparent Henry's constant or solubility at infinite dilution can be calculated from DM model as follows:

$$S_0 = \lim_{P \rightarrow 0} \left(\frac{n}{P} \right) = \lim_{P \rightarrow 0} \left(k_1 P + \frac{mk_2 P}{1 + k_2 P} \right) \cong k_1 + mk_2 \quad (2.4)$$

Adsorption of gas mixtures can be predicted from pure component adsorption isotherms using Ideal Adsorbed Solution Theory (IAST) [9]. The method requires solving a set of equations:

$$Py_1 = P_1^0 x_1 \quad (2.5)$$

$$P(1 - y_1) = P_2^0(1 - x_1) \quad (2.6)$$

$$\int_0^{P_1^0} \frac{n_1^*(P)}{P} dP = \int_0^{P_2^0} \frac{n_2^*(P)}{P} dP \quad (2.7)$$

For binary mixture at equilibrium, equations (2.5) and (2.6) hold if gas phase and adsorbed phase chemical potentials are equal, the mixing is ideal and both phases are at the same temperature. Here, y_i is the mole fraction of a component in gas phase and x_i is its mole fraction in adsorbed phase, n_i^* is the adsorbed amount calculated from pure component isotherms, P_i^0 is the pure component vapour pressure at spreading pressure and temperature as of mixture. The spreading pressure is the measure of adsorbed phase to spread along adsorbent, which is analogous to liquid wetting the container wall. If the spreading pressure is the same for both components and the same surface area is accessible to both components, then equality in equation (2.7) is true. The selectivity is calculated as:

$$S = \frac{x_1/y_1}{x_2/y_2} = \frac{P_2^0}{P_1^0} \quad (2.8)$$

The total amount of mixture adsorbed can be calculated from:

$$\frac{1}{n} = \frac{x_1}{n_1^*(P_1^0)} + \frac{x_2}{n_2^*(P_2^0)} \quad (2.9)$$

2.1.4 Equipment and Gravimetric Method

Adsorption of gases in this work was studied by gravimetric technique, which measures weight change of the sample after gas introduction. The equipment is essentially a complex balance, which has sample on one balance arm and calibrated counterweight on the other arm; additionally it controls pressure and temperature for equilibrium adsorption determination. The gravimetric method is more commonly used for high-pressure and above-room temperature adsorption measurements and condensable vapour studies since the condensate on the walls does not affect the measurement.

The equipment used in this work is Hiden Isochema's (UK) intelligent gravimetric analyser (IGA-001). The IGA is a precise computer-controlled equipment capable to carry out the most accurate measurements of weight change, pressure and temperature. It can simultaneously evaluate kinetic parameters and magnitude of sorption. Temperature and pressure controller and pressure vessel allows measurements under diverse operating conditions from vacuum to 20 bar, from cryogenic to 1000°C, although control of the temperature at sub-zero temperature is challenging due to equipment design where sample has no physical contact with heat or cold source. In this work, the main interest is in determining the adsorption capacity close to room temperature (20°C and 60°C). Mounted microbalances are highly sensitive and capable to measure changes in weight with resolution up to 0.1 µg. Schematic diagram of the IGA is shown in the Figure 2.2, where water bath is only demonstrated as a mean of heating; however, furnace or liquid nitrogen dewar may also be attached.

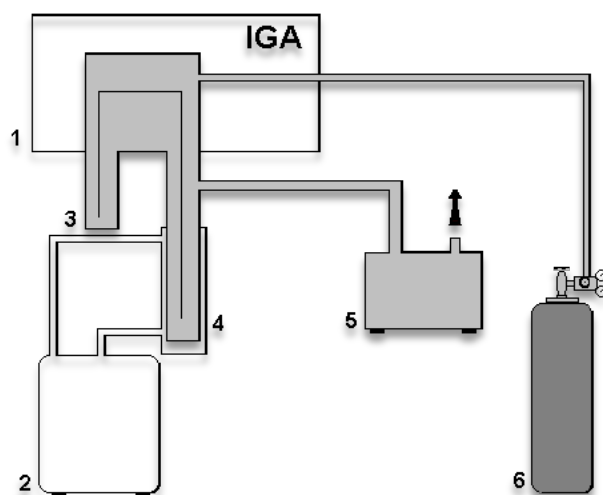


Figure 2.2. Schematic diagram of IGA equipment: 1 – main cabinet, 2 – water bath, 3 – thermostated counterweight, 4 – sample reactor with water jacket, 5 – exhaust pump, 6 – gas cylinder.

Some other advantages of using gravimetric measurements with IGA:

- Small amount (~100 mg) of sample required. This is a real advantage for newly synthesised sorbents as they are produced in tiny amounts.
- Adsorption (or condensation) of pure gases on tubes or vessel walls does not affect measurement accuracy since mass balance of the gas is unnecessary. However, special

treatment of the walls is required if mixture of gases is being analysed as some of components may interact with adsorbent stronger than others.

- Since mass is independent from gas pressure, the experiment may be carried out at extreme pressures without posing any serious problem to measurements. However, it is still recommended always to calibrate empty equipment without adsorbent but filled with sorbate since at low pressures gas adsorption at vessel and/or other part of the balance may occur.
- Weight measurement may be taken every tenth of a second; thus sample activation and even very slow approach to adsorption equilibrium may be recorded.

One of the main disadvantages of the gravimetric method is the need to account for buoyancy effect, which occurs whenever gas is introduced. In the sample chamber, changes in pressure result in changes in the fluid density surrounding the sample. In order to calculate the mass adsorbed, all the forces acting on the sample need to be accounted, which include the upward buoyancy force that tends to lift the sample container. In order to accurately calculate the weight and, consequently, the mass of adsorbed gas the density of the sample has to be known. It is measured prior to experiment by measuring isotherm of an inert gas. The recorded mass plotted with respect to gas pressure must be a straight line indicating that there are no measurable interactions between the sample and He while any change in its slope is due to buoyancy:

$$\Phi_s - \Phi_u + \Phi_i - \Phi_j - m'_s = -V_s \rho_{gs'} + \Phi_z \quad (2.10)$$

where Φ_s , Φ_u , Φ_i , Φ_j are force readings of the balance due to gas interacting with sample, initial unloaded sample container, objects on the sample side and objects on the counterweight side, respectively, and Φ_z is an arbitrary force introduced to correct errors in m'_s , which is estimated sample mass, $\rho_{gs'}$ is the gas density around the sample and V_s is the volume of the sample and gradient of the straight line. The new sample mass is:

$$m_s = \Phi_D - \Phi_u + \Phi_i - \Phi_j + V_s \rho_{gs} \quad (2.11)$$

where Φ_D is the force due to sample and container. Dividing mass by the volume gives sample density, which is then used in all subsequent experiments. The determined density is assumed to be constant throughout the experiment, which is not true with materials that tend to swell or change its confirmation in presence of certain gases.

2.1.5 Experimental Procedure

First, an outgas process is performed in order to release any sorbate that can be adsorbed on the sample. The chamber, containing the sample, is de-pressurised to a vacuum and the temperature is increased using furnace. The temperature is raised in two stages. First, temperature is increased until 100°C and maintained for 3 h to ensure that any water-based sorbates are evaporated from the sample. At the second stage the temperature is increased until 200°C and maintained for 8 h in order to desorb any other contaminants. The heating rate is set to 1°C/min.

The IGA uses conventional *discontinuous gravimetric procedure*, i.e. sorbate is introduced up to desired pressure and measurements for sorption isotherms are taken when equilibrium is reached. The steps are:

- The sample chamber is evacuated to vacuum and sample is brought to temperature of interest.
- Sorbate is introduced until desired pressure is reached and time is allowed to equilibrate. Equilibrium pressure, temperature and mass are registered.
- Step 2 is repeated number of times at different pressures up to maximum of 20 bar to draw a complete isotherm.
- The sorbate is desorbed from adsorbent at pre-determined pressure and temperature. Equilibrium pressure, temperature and mass are registered.
- Step 4 is repeated until desorption line “returns” to 0 bar point.

Since sample density is unknown before the experiment, He isotherm is measured first following the above-listed steps. Once the outgas process and He isotherm were completed actual adsorption experiments are performed. The isotherms are typically measured increasing the pressure from 0 to 20 bar at 1 bar increments and constant temperature (either 20°C or 60°C). Initial pressure intervals are set smaller: 0, 0.1, 0.25, 0.5 and 0.75 bar, to allow having a better insight in the behaviour of adsorbent at pressures below ambient. A pressure ramp rate was set either 100 or 200 mlbar/min depending on the size of adsorbent particle. If the particles are very tiny the faster gas flow may blow out the adsorbent from the container.

At each pressure point the data is collected until gas uptake has reached equilibration and minimum 35 min are set for data collection before the next isothermal point could be initiated. Even if the equilibrium was not acquired, after maximum of 3 hours the system would advance to the next isotherm point to avoid prohibitively long times. The specified criterion for equilibrium is set as a fraction of difference between initial reading at the current pressure increment and predicted asymptote at the next pressure point. The fraction is expressed as percentage and is set to 99%. The asymptotic uptake ($u_0 + \Delta u$) is predicted using the Linear Driving Force model:

$$u(t) = u_0 + \Delta u[1 - \exp(-(t - t_0)/k)] \quad (2.12)$$

where u_0 is the uptake at time origin t_0 , k is the exponential time constant and Δu is the change in uptake.

2.2 Molecular Modelling and Computer Simulations

Procedures used to construct materials studied in this work are presented and the most important aspects of molecular modelling and simulations are described in the following chapters. Molecular modelling and simulations were performed using Accelrys Materials Studio[®] V5.5.3 Software Inc. (San Diego) and MCCCSTowhee v7.0.6 [10]. For structure characterization, Poreblazer v3.0 software developed by Sarkisov and Harrison [11] was additionally employed. The chapter is sourced from 2nd edition book of Leach [12], book of Allen and Tildesley [13], Materials Studio manual and Towhee web manual [14] as well as other references that are cited separately within the text.

Simulation methods allow characterizing bulk thermodynamic and structural properties of macroscopic systems and predicting their behaviour in conditions of interest by studying microscopic replicas of these systems. Two most popular methods are Monte Carlo (MC) and Molecular Dynamics (MD). The major difference between these approaches is that there is no connectivity between two successive iterations in MC method, while MD generates a trajectory of system as the time evolves.

The thermodynamic properties of a system such as temperature, pressure, volume and energy are of interest if one would want to obtain compatibility with experiment. To obtain bulk properties of a real material it would appear to be necessary to process extensive data on configurations and interactions of all atoms the number of which in real systems gain the order of 10^{23} . Due to time and computational capacity limitations, this is not feasible to achieve during simulation. Statistical mechanics makes the link between experimentally measured properties and those calculated in a simulation. The system is replaced by many identical systems but of varying random arrangement. The macroscopic properties are recovered when the averages are carried out over an infinite number of configurations or an infinitely long time. The calculated property is therefore referred to as *ensemble average* or *time averages* depending on the type of simulation carried out. The relatively quick convergence of these averages allows calculating the properties of interest using a finite number of configurations or a finite trajectory.

Simulated microscopic systems have to be sampled in conditions that can also be controlled during experiments in order to represent macroscopic systems and to find compatibility with experimental data. One of the most common approaches is to maintain constant number of particles, volume and temperature (NVT or *canonical ensemble*) in a system. Such conditions permit energy of the system to fluctuate and share with external heat sources. Other important environmental constraints involve:

- *Grand canonical ensemble* (μVT). In addition to energy change, composition of a system is also allowed to change, however chemical potential has to be constant;
- *Microcanonical ensemble* (NVE). The system is considered as thermally isolated;
- *Isothermal-isobaric* (NPT). Here, number of particles, pressure and temperature are kept constant.

Throughout this work, ensembles with fixed temperature were used, such as grand canonical (μVT), canonical (NVT) and isothermal-isobaric (NPT) ensembles.

2.2.1 Monte Carlo Simulation

The statistical properties of a system in equilibrium are described by a partition function (Q). Many useful thermodynamic properties can be related to partition function using the bridge relationship: $F = -k_B T \ln Q$; once the thermodynamic free energy F is known other quantities such as entropy, system volume, chemical potential, etc. can be calculated through fundamental thermodynamic relations. There are several partition functions each derived concerning its conditions, such as constant pressure or volume and constant temperature (further details in Chapter 2.2.1.1). The partition function Q is the sum of all possible states of a system at given conditions. In a real system, the particles move continuously and so the positions r and momenta p change continuously, therefore Q for a system of N particles of mass m at constant temperature T and volume V can be expressed as an integral:

$$\begin{aligned} Q_{NVT} &= \frac{1}{N!} \frac{1}{h^{3N}} \int \int \exp\left(-\frac{\mathcal{H}(r^N, p^N)}{k_B T}\right) dr^N dp^N \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \int \exp\left(-\frac{|p|^2}{2mk_B T}\right) dp^N \int \exp\left(-\frac{E(r^N)}{k_B T}\right) dr^N \end{aligned} \quad (2.13)$$

if the potential energy E is not dependent on particle velocities. In equation (2.11), $\mathcal{H}$ is Hamiltonian that is a total energy of a system (kinetic plus potential), k_B is Boltzmann constant and h is Planck's constant. The first integral is over the momenta p and the second is over the positions r representing kinetic and potential energies, respectively. The analytical solution for the first integral is:

$$\int \exp\left(-\frac{|p|^2}{2mk_B T}\right) dp^N = (2\pi mk_B T)^{3N/2} \quad (2.14)$$

However it is not possible to solve the second configurational integral analytically (except probably of the trivial case of non interacting particles, $E(r) = 0$, or ideal gas). Of course, the integral can potentially be solved numerically and the simplest way would be the trapezium rule. In such case, the number of trapeziums and so the number of functions that need to be solved would be huge if one wants to obtain accurate results. Another way is to carry out a random sampling of the system that generates a collection of configurations, record their energy and Boltzmann factor, i.e. their weight or "importance", and then sum all weighted states obtaining total property of interest. In this case, large number of states needs to be

generated of which large number is not as important since its Boltzmann factor is small. To generate configurations or states that are the most common, i.e. contributes to the sum the most, Metropolis Monte Carlo (MC) method [15] was proposed. The core MC algorithm is as follows (Figure 2.3):

- Three directions (x, y and z) of a particle are randomly displaced.
- Potential energy $E(r^N)$ of a configuration is calculated.
- The new configuration is tested for acceptance based on the potential energy difference (ΔE) between the current and previous states. If the energy is lower than the energy of previous configuration, the new configuration is accepted.
- If it is higher, then the Boltzmann factor is calculated:

$$\exp\left(-\frac{\Delta E(r^N)}{k_B T}\right) \quad (2.15)$$

- The factor is compared to a randomly generated number from 0 to 1. If energy of both states is similar, the Boltzmann factor will be large, closer to 1; if it is larger than the random number, the new configuration will be accepted and become the “current” configuration for the subsequent move. Alternatively, if the factor is lower than the random number, the configuration is rejected and a new attempt to create new configuration is performed.

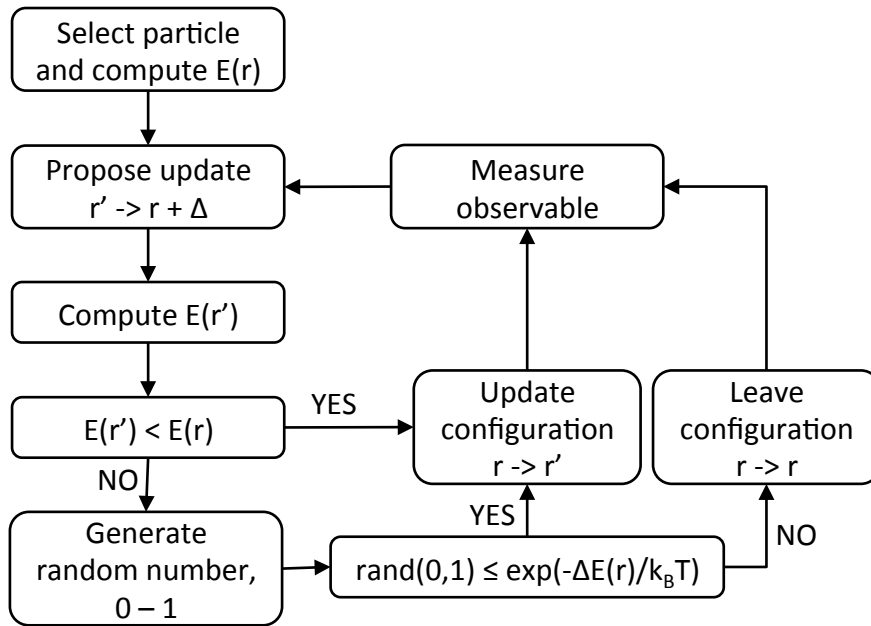


Figure 2.3. Basic Monte Carlo loop.

This approach is not merely an energy minimisation, but allows exploring new configurations with higher energy than the current configuration, which is the way the temperature is introduced in the MC simulations. Therefore, at high temperatures, the system will be able to explore configurations with higher energy than at low temperatures. The results from accepted configurations are accumulated and a distribution function (ensemble average) is derived. The function defines the probability of certain configuration at given conditions.

2.2.1.1 Adsorption Simulation

In this section, the main calculations and theories are presented related to adsorption simulations performed in this work. The classical ensemble in MC simulations is the canonical (NVT), however it is possible to sample from different ensembles such as isothermal-isobaric (NPT) or grand canonical (μ VT), the latter being very useful for adsorption studies.

In the grand canonical ensemble, the system is regarded as open to external reservoir, which contains infinite number of sorbate molecules, while temperature and fugacity of a system are fixed. The partition function describing the system in this ensemble can be expressed using equation (2.13) as:

$$Q_{\mu VT} = \sum_N \exp\left(\frac{\mu N}{k_B T}\right) Q_{NVT} \quad (2.16)$$

There are three main moves in the simulation: particle creation, deletion and displacement (translation or rotation). In Materials Studio, the moves are accepted or rejected according to Metropolis Monte Carlo approach [15]. If the number of molecules does not change between attempts, equation (2.15) defines the acceptance/rejection criterion. If number of particles changes, the creation (p^+) and destruction (p^-) criteria are:

$$p^+ = \exp\left(-\frac{\Delta E(r^N) - \mu_{intra}}{k_B T}\right) \frac{fV}{k_B T N} \quad (2.17a)$$

$$p^- = \exp\left(-\frac{\Delta E(r^N) + \mu_{intra}}{k_B T}\right) \frac{k_B T N}{fV} \quad (2.17b)$$

where f is fugacity, μ is intramolecular chemical potential, and N is the number of particles before an attempt.

During adsorption, system is regarded as frozen in selected positions. New configurations of sorbate molecules are created without requirement to move into directions of lowest energy. It is assumed that sorbate molecules behave as ideal gas and fugacity is equal to actual system pressure.

Henry's constant simulation is also performed in grand canonical ensemble using Metropolis MC in Materials Studio. The approach is equivalent to Widom insertion method [16], the usual approach for determining chemical potential. Only insertion move is performed with acceptance probability equal to 1. All configurations are possible; however overlapping particles will have zero Henry constant. Henry constant is calculated by specific *Henry constant* task implemented in Materials Studio:

$$H = \frac{V}{k_B T} \exp\left(\frac{\mu_{intra}}{k_B T}\right) \left\langle \exp\left(-\frac{E(r^N)}{k_B T}\right) \right\rangle \quad (2.18)$$

where V is the framework volume and E is the total energy of a configuration, μ_{intra} is the intramolecular chemical potential. The μ_{intra} is given as:

$$\exp\left(-\frac{\mu_{intra}}{k_B T}\right) = \left\langle \exp\left(-\frac{E_{intra}}{k_B T}\right) \right\rangle \quad (2.19)$$

where E_{intra} is the intramolecular energy. If sorbate is modelled as a rigid molecule and has only translational and rotational moves associated with it, μ_{intra} simply equals to E_{intra} .

In Towhee, adsorption was simulated using configurational-bias Monte Carlo Method developed by Martin and Frischknecht [17]. Configurational-bias MC method was developed for chain molecules to overcome the problems with correct chemical potential calculation, large molecule insertion into already dense systems due to high-energy configurations resulting from overlaps, and wrong generation of angle distribution of branched molecules [17]. Instead of generating one trial configuration and performing a procedure of its acceptance or rejection, the possible insertion positions (or configurations) for an atom are sampled first from some probability distribution, which is a combination of bond length, angle and non-bonded interaction distributions. Each trial is assigned a Rosenbluth weight; if the trial results in unfavourable energy its weight is very low or zero, thus most likely it will

not be selected or abandoned straight away. The molecule is grown atom by atom at each step sampling positions for new atoms and selecting the move based on its weight, i.e. it is more probable to select the trial with larger weight. Acceptance procedure is again performed once the entire molecule has been grown.

In Towhee, chemical potential is an input variable for grand canonical MC simulations of adsorption, which is calculated in isobaric-isothermal (NPT) ensemble. The corresponding partition function that describes system statistics at constant number of particles, pressure and temperature is:

$$Q_{NPT} = \sum_V \exp\left(-\frac{PV}{k_B T}\right) Q_{NVT} \quad (2.20)$$

Together with random particle displacements, the configurational part now allows for changes in volume:

$$\int \exp\left(-\frac{E(r^N)}{k_B T}\right) dr^N \int \exp\left(-\frac{PV}{k_B T}\right) dV \quad (2.21)$$

Towhee uses volume change algorithm proposed by McDonald [18] to maintain constant pressure in NPT ensemble. Pressure is calculated using virial theorem as described previously by equation (2.32).

Towhee calculates chemical potential as:

$$\mu = -k_B T \ln \left[\left\langle \frac{WV}{(N+1)\Lambda^3} \right\rangle \right] \quad (2.22)$$

where W is the Rosenbluth weight, V is the volume of simulation box and Λ is the thermal de Broglie wavelength ($\sqrt{h^2/2\pi m k_B T}$). The Rosenbluth weight is the probability that a molecule would be inserted in a given position and is calculated according to configurational-bias principles implemented in Towhee.

In this section, it is appropriate to describe how isosteric heat of adsorption is calculated from simulations. Conveniently, Materials Studio calculates heat of adsorption (Q_{ads}) simultaneously during *Henry* task in μ VT ensemble as:

$$Q_{ads} = RT - \langle E \rangle + \mu_{intra} \langle N \rangle \quad (2.23)$$

where R is the gas constant, N is the sorbate loading, $(\langle E \rangle - \mu_{intra} \langle N \rangle)$ is *grand potential* and is a difference between mean total system energy (framework intramolecular energy is not included as it is fixed during simulation) and sorbate intramolecular energy, in other words it is the sorbate-framework and sorbate-sorbate interaction energy.

Isosteric heat of adsorption can also be derived from average energy and particle fluctuations during adsorption simulation as [19]:

$$Q_{ads} = RT - \frac{\langle EN \rangle - \langle E \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (2.24)$$

where E is the potential energy of adsorbed phase. The equation (2.24) is applied to non-zero loading and it is assumed that the sorbate is ideal. The method also requires longer simulations to obtain good statistics especially at low loadings.

2.2.2 Molecular Dynamics

Molecular Dynamics are capable to obtain time average properties. MD approach is based on predictions of new states of a system from its current state. A basic program is as follows:

- Initialise the system by reading particle positions and selecting initial velocities at a specified temperature.
- Calculate forces on all particles:

$$F = -\nabla E(r^N) \quad (2.25)$$

- Solve Newton's second law of motion to determine next configuration:

$$\frac{d^2 r}{dt^2} = \frac{F}{m} \quad (2.26)$$

where r is the position of a particle of mass m on which a force F acts. Newton's law of motion is integrated by dividing calculations into time steps (1 – 10 fs) where force on each particle is assumed to be constant. The last two steps are repeated until evolution of a system (*trajectory*) is generated over the desired time.

- The properties of the system are collected as time averages.

In Materials Studio, velocity Verlet integrator is used, which assumes that positions, velocities and acceleration can be predicted by Taylor expansion until the fourth term. The new positions $r(t+\Delta t)$ at time $t+\Delta t$ are calculated from the current positions $r(t)$, velocities $v(t)$ and acceleration $a(t)$:

$$r(t + \Delta t) = r(t) + \Delta t v(t) + \frac{1}{2} \Delta t^2 a(t) \quad (2.27)$$

New forces $F(t+\Delta t)$ are calculated from new positions, which give new acceleration:

$$a(t + \Delta t) = \frac{F(t + \Delta t)}{m} \quad (2.28)$$

And finally the new velocity is calculated as:

$$v(t + \Delta t) = v(t) + \frac{1}{2} \Delta t [a(t) + a(t + \Delta t)] \quad (2.29)$$

The important factor for efficient MD simulations is the time step (Δt). Too small time step will lead to prolonged simulation times; too large time step may result in particle overlapping violating energy conservation. The time step should be small enough to provide smooth collision and large enough for efficient space coverage. The rule of thumb is to use time step that is one tenth of a shortest period of motion in a flexible molecule system. In atomistic simulations, bonds with hydrogen atoms vibrate the fastest, approximately 10fs, thus 1fs time step is sufficient for most applications, which was set for all simulations in this work.

2.2.2.1 Temperature and Pressure Control in MD

In MD simulations, where packing of a system is concerned, NVT and NPT ensembles were applied to compress the system by applying sequence of varying pressures and heating and cooling sequence to allow the system exploring its conformational space.

To reach and maintain desired temperature, velocities of particles are adjusted appropriately. Temperature can be related to the kinetic energy ($\mathcal{K}$) through the equipartition principle as:

$$\sum_{i=1}^N \frac{p_i^2}{2m} = \mathcal{K} = N_f \frac{k_B T}{2}, \quad \text{thus } T = \sum_{i=1}^N \frac{mv^2}{N_f k_B} \quad (2.30)$$

which states that each degree of freedom (in this case, $p^2/2m$) has the energy equal of $k_B T/2$ associated with it. In the above equation (2.30), p is the momenta of a particle of mass m and N_f is the number of degrees of freedom, which equal to $3N-3$ for unconstrained periodic system since each particle has 3 degrees of freedom (three velocity components, v_x , v_y and v_z) and 3 degrees of freedom are subtracted due to translation of a cell. Additional constrains such as fixed bonds or angles will further reduce the number of degrees of freedom.

The temperature control method used in this work is by Berendsen *et al.* [20], which mechanism can be explained as the system coupled to the external heat bath of fixed desired temperature. Each velocity is scaled uniformly by a factor λ to gradually decay the temperature towards the desired value:

$$\lambda = \sqrt{1 - \frac{\Delta t}{\tau} \frac{T - T_0}{T}} \quad (2.31)$$

where T_0 is the desired temperature, Δt is the time step and τ is the parameter that describes how tightly system is coupled to the bath. When τ is infinitely large, there is no temperature control and MD will sample from its default microcanonical (NVE) ensemble, if it is equal to Δt or less the coupling is too tight and no temperature fluctuations will be allowed, which is not realistic. In all the calculations, coupling parameter was kept 0.1 ps, which is the usual value for condensed phase systems [21]. Even though the Berendsen thermostat does not reproduce a true Canonical trajectory, it was considered as appropriate to generate model structures as it is faster than the Nose-Hoover thermostat.

The pressure is calculated via virial theorem, which says that virial ($\mathcal{W}$) is equal to the product of particle coordinate (r) and intermolecular force (F) acting on it. Pressure is related to the virial as:

$$PV = Nk_B T + \frac{2}{3} \mathcal{W} = Nk_B T + \frac{2}{3} \left(\frac{1}{2} \sum_{i=1}^N r_i F_i \right) \quad (2.32)$$

where first term is due to ideal gas and the second term is the real gas part. The pressure can be expressed as superposition of kinetic energy and virial, since $T=2\mathcal{K}/3Nk_B$:

$$P = \frac{2}{3V}(\mathcal{K} + \mathcal{W}) = \frac{1}{3V} \left[\sum_{i=1}^N m_i v_i^2 + \sum_{i=1}^N r_i F_i \right] \quad (2.33)$$

Due to pairwise interactions and periodic boundary conditions, it is more convenient to express virial as:

$$\mathcal{W} = \frac{1}{2} \sum_{i=1}^N \sum_{j>i}^N r_{ij} F_{ij} \quad (2.34)$$

where $r_{ij} = r_i - r_j$.

In MD, forces between particles are calculated as part of the simulations, so pressure is calculated simultaneously without effort. Changing volume of a system changes the pressure, as is the usual case at the experimental conditions. In simulations for this work, volume change is also achieved by scaling particle coordinates and simulation cell vectors by a factor as proposed by Berendsen *et al.* [20]:

$$\lambda = \sqrt[3]{1 + \frac{\Delta t}{\tau} (P - P_0)} \quad (2.35)$$

where P_0 is the desired pressure and τ is the decay constant that describes how tightly system is coupled to the external pressure bath. In all simulations for this work, τ is set to 0.1.

2.2.3 Boundary Conditions

Realistic representations of a macroscopic system are very important to obtain accurate bulk properties from simulations. However the size of the simulated system is limited by the accessible computing power and time available to researcher. One could attempt to create a small isolated box to increase calculation efficiency. However such molecular system would be subject to significant boundary effects and unlikely to represent bulk properties of a macroscopic matter. Therefore periodic boundary conditions are widely utilised in molecular

simulations for a finite number of particles, in which particles are replicated in all directions forming an infinite lattice. In such way, particles located at the cell boundaries interact with neighbouring particles that can be in the same cell and in the neighbouring one mimicking bulk system. A two-dimensional example model representing periodic boundary conditions is given in Figure 2.4.

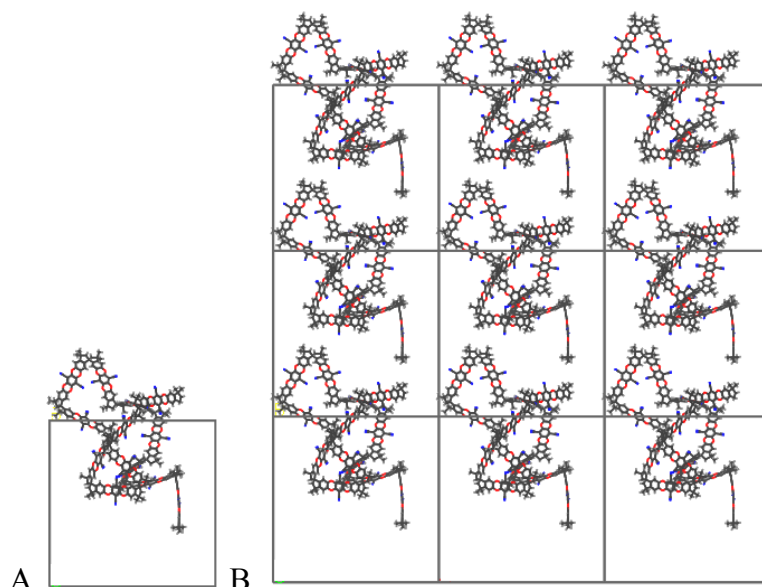


Figure 2.4. Two-dimensional projection of a single polymer chain in a unit cell (A) and fragment of system with periodic boundary conditions (B).

Molecules can drift into neighbouring cells and atoms that belong to one molecule may lie in different cells. When particle leaves the cell through one side its replica is introduced from the opposite side. Thus number of particles in the cell remains constant. During a simulation all replica particles move in the same manner (same velocity vectors, etc.) as the parent particle.

In this work, three different cell shapes were used to study the system, cubic, rectangular and orthorhombic. The cell shape is selected to mimic the shape of the system so that system fills entire cell while maintaining the simplicity of the program. Size should be selected based on the length range of interactions present in the system such as Lennard-Jones or electrostatic interactions; for adsorption studies it is also important to provide enough space to adsorb sufficient number of particles to obtain good statistics. Empirical methods are used to find the right cell shape and size; usually several different cells are created and compared for the effect on obtained results. In our case, most systems were amorphous, so the simplest cubic box was selected, while some amorphous systems were created in rectangular cells keeping in mind the possible future studies of thermal conductivity in order to capture phonon mean free path.

The size of the cell was selected based on the successful studies of either same or similar materials reported in the literature. Another system was crystalline and its cell dimensions and angles were solved from experimental crystallographic data [22].

2.2.4 Force Field

Ideally molecular system should be treated using quantum mechanics theories in order to obtain the most accurate physical representation of the behaviour of a real material. Quantum mechanics deal with both electrons and nuclei of an atom. Unfortunately quantum mechanics calculations are extremely time consuming and, fortunately, are often not needed to obtain realistic representation of the system if no electron transfer or electron excitement processes are involved. Instead molecular mechanics, or force field methods, are often used in molecular simulations. The methods assume that electrons instantly adjust to atom dynamics and provide a mathematical description of molecular interactions as accurate as even highest level quantum mechanical calculations [12].

The general functional form of force field includes both intramolecular forces related to atoms bonded to each other through covalent bonds and intermolecular forces describing electrostatic and van der Waals (vdW) interactions. The set of equations and their constants are designed and parameterised according to a specific purpose, e.g. structure prediction or phase equilibria simulation. There is a large number of specialised force fields developed to predict structures and dynamics of different systems as well as force fields that use generalised approach to describe different types of atoms, bonds, etc that allow studying systems that have not been studied experimentally or where experimental data is limited.

One of such generic force fields, used throughout this work is DREIDING force field developed by Mayo *et al.* [23]. DREIDING is a good robust all-purpose force field developed for modelling structures and dynamics of organic, biological and main group inorganic molecules. Force constants and geometry parameters for DREIDING are derived from general hybridization rules and stored vdW radii and do not depend on specific combinations of atoms. Therefore it is particularly valuable for structures with novel combinations of atoms or

those having no or little experimental data. The function of potential energy encapsulates bonded and non-bonded interactions in the form:

$$E = E_{bonded} + E_{nonbonded} \quad (2.36)$$

The model of bonded interactions (E_{bonded}) is based on processes such as bond stretching (E_S), bending of an angle between bonds (E_A), rotation about single bonds (torsion) (E_T) and molecule inversion (E_I):

$$E_{bonded} = E_S + E_A + E_T + E_I \quad (2.37)$$

Energy of inversion term describes how difficult (or favourable) it is to keep all three atoms bonded to one and the same atom in the same plane. Bond stretch, angle bend, torsion and inversion terms are calculated by equations derived from harmonic oscillator. All four processes are schematically represented in Figure 2.5.

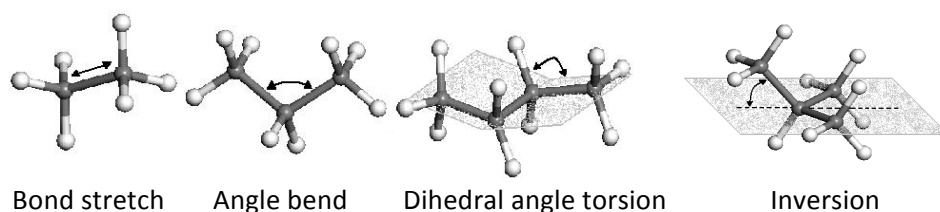


Figure 2.5. Schematic representation of contributors to bonded interactions between carbon atoms in alkane molecules.

Non-bonded interactions are expressed as superposition of vdW (E_W) and electrostatic (E_e) interactions:

$$E_{nonbonded} = E_W + E_e \quad (2.38)$$

The vdW interactions are described using Lenard-Jones 12-6 type (L-J) potential:

$$E_W = D \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right] \quad (2.39a)$$

The better-known form is:

$$E_W = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (2.39b)$$

where D and ε is well depth and defines interaction strength between two particles, R_0 is the distance at which potential has a minima, σ is the distance at which energy is zero, R is the

distance between particles (graphical representation is in Figure 2.6). The L-J potential is computationally simple and time efficient as only two parameters are involved, therefore it is the most widely used in molecular simulation.

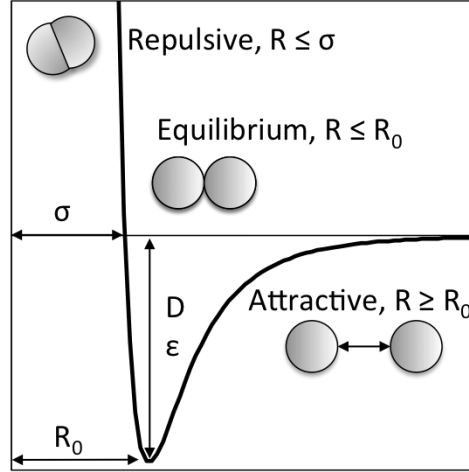


Figure 2.6. Potential energy curve with respect to separation distance R .

Lorentz-Berthelot mixing rules are used to calculate interactions between unlike atoms:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \text{ or } D_{ij} = \frac{D_{ii} + D_{jj}}{2} \quad (2.40)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \text{ or } R_{0ij} = \sqrt{R_{0ii}R_{0jj}} \quad (2.41)$$

Calculating interactions in a many atoms system may be a time consuming task and often not practical for tracking interactions between the atoms that are long distance apart where these interactions are negligible. Instead, a cut-off distance can be applied to reduce computational time. It is possible to calculate interaction energy up to a cut-off distance beyond which all interactions are ignored, and instead a long-range correction is included. Such direct method is computationally effective but may lead to discontinuity of the potential energy and cause errors in MD simulations, especially if cut-off distance is very short. To avoid these errors, a switching function is used to approximate non-bonded interactions such that it reaches zero smoothly and continuously at the cut-off radius. The method is based on a function of distance, which equals to unity at short distances and rapidly reduces as separation between interacting particles increases and becomes zero at a specified cut-off distance (Figure 2.7). The interactions beyond the cut-off are not counted in total energy calculations. The

convention is to use cut-off distance equal or smaller than half of the length of shortest box side.

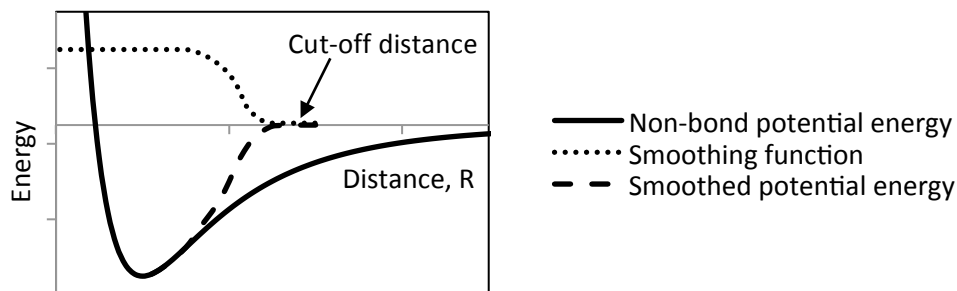


Figure 2.7. Decay of L-J potential as a function of intermolecular separation.

The electrostatic energy is expressed in terms of partial charges using classical Coulomb's law:

$$E_e = 322.0637 \frac{q_i q_j}{\epsilon R_{ij}} \quad (2.42)$$

where q_i and q_j are partial charges of two points (atoms), which are separated by the distance R_{ij} , ϵ is dielectric constant and constant 322.0637 is used to convert units to kcal/mol. Electrostatic interactions are non zero for much larger distances than vdW interactions, therefore the Ewald summation method [24] is used to properly treat long-range interactions.

There are other generic force fields reported in the literature, such as the universal force field (UFF) [25], the optimised potentials for liquid simulations-all atom (OPLS-AA) [26], the consistent-valence force field CVFF [27] and the transferable potential for phase equilibria (TraPPE) [28]. UFF, DREIDING and OPLS-AA force fields were compared for accuracy in describing methane adsorption in metal organic frameworks (MOFs) that are structurally and chemically close to some materials studied in this work [29]. It was shown that adsorption isotherms are not sensitive to the choice of force field, however all simulated isotherms tended to overestimate experimental methane adsorption. The outcome is rather expected, as these force fields were developed to model covalent rather than non-bonded interaction [30]. On the other hand, DREIDING was also used for some materials studied in this work and remarkably similar experimental and simulated adsorption solubility values were showed [7]. Therefore DREIDING force field was used in almost all simulations performed in this work as it was implemented in Materials Studio.

Other force fields used in this work were applied to better represent sorbate molecules and all of the force fields are implemented in Towhee:

- Elementary Physical Models (EPM) force field was used to describe CO₂ molecule [31] as it can accurately reproduce experimental vapour-liquid coexistence curve and critical temperature. Bond between C and O atoms is rigid of 1.149 Å length, but the angle is flexible and its potential is described by harmonic oscillation. It uses standard Lennard-Jones (12-6) potential and assigns stored point charges to an atom to represent electrostatic interactions.
- CH₄ molecule was described as a single particle using DREIDING force field with the modified L-J (12-6) potential parameters taken from [32]. The single particle L-J model was shown to correctly predict vapour pressure curve.
- TraPPE-EH force field [33] (official name in Towhee) with L-J (12-6) potential model was used to describe N₂. Towhee implemented three-site model for the molecule, where the third site is a dummy atom with positive charge in between two negatively charged nitrogen atoms. The force field assigns predefined point charges to the atoms to reproduce quadrupole moment of N₂ molecule. The bond is rigid and its length is 1.10 Å, which is an experimental value. The force field can predict accurate vapour-liquid coexistence curve for pure N₂ and binary mixture with alkanes.

2.2.5 Charge Calculation

Partial atomic charges are an important quantity for describing non-bonded electrostatic interactions. Ideally charges are calculated from precise *ab initio* calculations of electron density, which are based on fundamental laws. However quantum mechanics calculations require extensive computational recourses and different partitioning methods used to assign charges onto atoms may still yield broad range of values [34]. Instead, approximate atomic charges could be specified in seconds without losing accuracy in results by charge equilibration methods [34-37]. The QEq method [35], which is implemented in Materials Studio, was mostly used in this work. The energy of the atom is differentiated with respect to charge and an optimum value of charge is found when derivatives of all atoms are equal. QEq method use experimental data, namely atomic ionization potential, electron affinity, atomic

radii, and needs atomic positions and atomic number as an input. The QEq method do not require calculation of wavefunctions and electron density that makes it very efficient charge calculations method especially suitable for materials screening [38]. Charges can be re-equilibrated during/after simulation using this method.

The developers of this method A. K. Rappe and W. A. Goddard showed transferability of QEq method to any kind of polymer, biological systems and semiconductors with excellent agreement with values obtained from *ab initio* calculations [35]. C.E. Wilmer *et al.* [39] successfully applied slightly modified QEq method for charge equilibration in MOF molecules. Modification was made due to larger disagreement between partial charges on metals calculated with QEq method and *ab initio* method. They have found that there were no systematic over- or under predictions of partial charges comparing QEq method with *ab initio* method leading to an accurate prediction of CO₂ adsorption at low pressure. Materials studied in this work contain only light elements and mainly carbon, therefore QEq method was chosen as a feasible approach for assigning partial charges.

Another semi-empirical charge equilibration method applied in this work is Gasteiger (also implemented in Materials Studio) [40]. The method exploits the electronegativity notion of bonded atoms. Electrons flow from less electronegative atom to more electronegative one resulting in positive charge on less electronegative atom and negative charge on more electronegative one. Gasteiger assumes polynomial dependence between electronegativity of valence orbital and transferred charge, which leads to lower electronegativity as charge density increases. The method uses iterative procedure to minimise the transferred charge to equalise electronegativity of orbitals participating in bond formation.

Another set of charges are derived by fitting electrostatic potential (ESP) on a surface around the molecule [41] with Gaussian 09 [42] at the B3LYP/6-31G* level of theory. ESP charges were commonly used in the subsequent force field based adsorption simulations [43-45]. The set of charges is fitted to electrostatic potential calculated at different points from wavefunction with the constrain that the sum of charges is equal to zero or net charge. In this work, the grid points surrounding the molecule were selected using Merz-Singh-Kollman scheme [41, 46]. This charge derivation method is computationally expensive and is not feasible for large systems. The large systems are broken into smaller fragments of suitable size, e.g. polymer into dimer that still retain its immediate environment, for which the method

is applied, and then the rest of the atoms are assigned the same charge as of symmetrically equivalent atoms.

2.2.6 Structure Characterization

One of the main factors governing adsorption and diffusion of molecules is the structural properties of an adsorbent. Therefore it is important to know the size of molecules that can fit in the accessible free space (surface area and free volume) as well as how this space is connected (topology of pores). The adsorption capacity is proportionally related to free accessible volume, while pore connectivity affects diffusivity of adsorptive molecules and permeation of a membrane. Poreblazer v3.0 developed by L. Sarkisov was used to explore created structures in addition to properties calculated in Materials Studio. Poreblazer is a computational tool designed to calculate accessible surface area, pore size distribution and pore connectivity of porous media. Poreblazer has been widely used for structure characterization of materials with complex morphology such as PIMs [7], MOFs [11], amorphous discrete molecules [47] and perforated graphene [48].

The differences between structural properties obtained from different projects (either simulation or experimental) ought to be compared with care. They may arise due to difference in simulation details such as force fields or size of probe used as well as differences in constructed models in cases of amorphous materials. Deviations between simulated values and those measured experimentally may be delivered by presence of defects, residual solvent or impurities in experimental samples and/or inadequate virtual model as well as differences between methods used to calculate a property in simulations and to measure it in experiments.

2.2.6.1 Density

The density of a virtual model is simply defined as the mass of a system divided by cell volume. It was pointed out that such density definition gives underestimated values for porous materials with large free pore and interparticle volume when compared to experimental values

[49, 50]. Experimentally, gas can enter this volume, thus it is not included in the density calculation. Therefore skeletal density definition was introduced for better comparison with experimental values:

$$\rho_{skel} = \left(\frac{1}{\rho_{sim}} - \frac{V_{pore}}{m} \right)^{-1} \quad (2.43)$$

where ρ_{sim} and ρ_{skel} are simulated and skeletal density, respectively, V_{pore} is pore volume and m is the mass of a solid. The pore volume is taken as volume outside of the solvent surface area accessible to helium atom (see the following section 2.2.6.2 Surface).

Helium is selected as probe in order to obtain comparable densities to those measured experimentally: either by the common method helium pycnometry or via the gravimetric method used in this work. Both methods are based on gas displacement; gravimetric method is based on weight loss observed when sample is immersed in a gas (see 2.1.4 Equipment and Gravimetric Method) while pycnometry determines sample volume from volume change. Commonly used gas expansion pycnometer consists of two connected chambers, one of which is a reference and the second holds a sample. Volume of both chambers is known. Both chamber are evacuated and then one of the chambers is pressurised by introducing gas. Once the two chambers are connected, pressure decreases in one of them and increases in the other. Sample volume is calculated from the volume-pressure relationship derived using Boyle's law ($P_1V_1 = P_2V_2$).

Experimental density is the ratio of sample mass to the volume inaccessible to helium, thus it is an apparent density and can be regarded as skeletal only if there is no gas adsorption during measurement and there are no closed pores [51].

2.2.6.2 Surface

The total solvent surface area is defined by a line that the centre of a probe draws while rolling along the vdW surface of adsorbent. A schematic representation is provided in Figure 2.8. The accessible surface area of an adsorbent is defined in the same way, however regions that cannot be accessed externally are excluded. For calculations of accessible surface area, a

nitrogen molecule (kinetic diameter 3.68 Å) is chosen because it is usual probe used in experiments used to calculate surface area and, therefore, will allow comparison with other materials and validation of a model.

The most widely employed experimental method is based on BET theory, outlined by Brunauer, Emmett and Teller [52]. Surface area is determined by the amount of nitrogen adsorbed at low pressures and 77 K assuming nitrogen forms closed-packed monolayer. Of course, one can calculate surface area from simulated isotherms to be consistent with the experiment but it is a time consuming task. Furthermore, BET method may not necessarily produce correct absolute surface area values for microporous materials [53, 54] due to assumptions such as adsorption due to layer formation, no interactions between layers, monolayer formation in P/P_0 region between 0.05 and 0.3 and surface area being homogenous. Nevertheless, it has been shown that BET and geometric surface areas can be remarkably similar even for microporous heterogeneous surface of MOFs and zeolites [55-57].

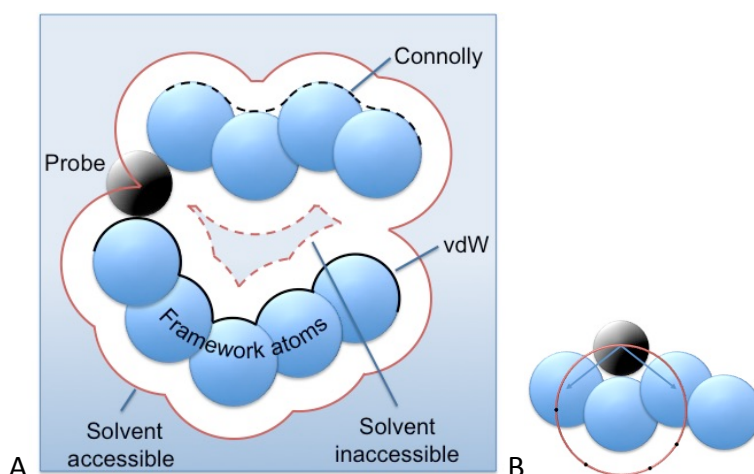


Figure 2.8. (A) Schematic representation of surface area and (B) two-dimensional visual representation of algorithm used to calculate surface area.

Another definition of surface used in this work is a Connolly surface. It is a line created by points where the edge of a probe touches the vdW surface of an adsorbent. The Connolly surface follows vdW surface except hollows where probe is too large to fit. The Connolly surface area obtained with probe radius equal to zero is just vdW surface area.

The probe is actually not rolled over adsorbent in Poreblazer calculations. Instead, a Monte Carlo integration technique is used. A sphere with radius (r_i) equal to the sum of probe's and solid atom's radii is created at the centre of preselected atom of a solid system (see Figure 2.8

a). A point is randomly generated on the surface of the sphere. Then the centre of the probe is placed over the point and tested for overlaps with all other atoms. The summed non-overlapping points form a line “drawn” by the probe that defines surface area. The surface area of the solid is calculated from accessible surface area of all its atoms as:

$$SA_{solid} = \sum_{i=1}^N \frac{\text{number of nonoverlapping points}}{\text{points created}} \pi r_i^2 \quad (2.44)$$

Unoccupied volume is determined taking into account the simulation cell and is considered as a region outside the defined surface. The solvent surface definition is used for calculations of the accessible solvent volume. For the comparison with experiments, helium (kinetic diameter 2.6 Å) is selected as a probe as it is used in experimental pycnometry measurements.

2.2.6.3 Pore Size Distribution

Pore size distribution (PSD) is an important characteristic of a porous material as it may significantly affect selectivity and permeability of a membrane. Poreblazer employs Monte Carlo procedure proposed by Gelb and Gubbins [58]. A point is placed in a simulation cell and tested for overlaps. If no overlaps occur, the largest possible sphere that can be placed at that point without overlapping with other particles is recorded as the pore size (Figure 2.9). Cumulative pore volume function $V(d)$ is generated representing the volume that can be occupied by a probe of diameter d or smaller. PSD function $dV(d)/dd$ can be obtained differentiating $V(d)$. Poreblazer uses Connolly surface definition for the volume calculation.

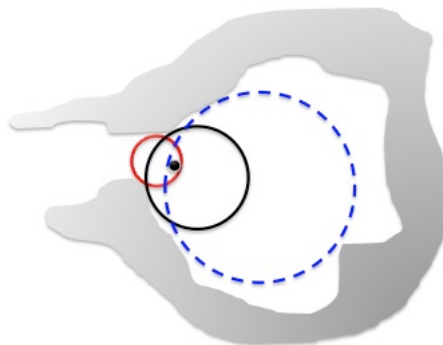


Figure 2.9. Representation of the geometric pore. Three different size circles all belonging to the same point can be placed into the pore, but only the dashed circle is recorded as the largest.

Molecular simulations provide the most accurate and fastest calculation of PSD in a real material as long as its virtual structure is well described. For crystalline materials, such as MOFs and zeolites, the approach is straightforward and any deviations will point to the non-ideality of a real material, i.e. impurities and defects, or inappropriate force field. However for disordered materials, additional model validation is required before molecular simulation can replace experimental measurements.

The most widely used experimental method for calculating material's PSD is also based on gas adsorption isotherm at low temperature (usually N₂ at 77 K). Isotherm data is fitted to models such as conventional Horvath-Kawazoe (HK) [59] and Barrett-Joyner-Halenda (BJH) [60] that can be applied for micro- and meso-porous materials, respectively, assuming simple geometry pores (slit-shaped or cylindrical). Non Local Density Functional Theory is now acknowledged as the most accurate PSD calculation method for even ultramicroporous materials as it is based on theoretical molecular description of known adsorbate-adsorbent systems [61-63], although it also assumes simple pore geometries. Adsorption method is known to have other limitations besides the dependence on models and assumptions, i.e. nitrogen adsorption at cryogenic temperature is slow and may not reach equilibrium thus not all pore regions are accessed distorting real PSD "image". Probing with carbon dioxide at higher temperature (273 K) is used to complement nitrogen isotherms because molecules can reach narrower parts due to its higher kinetic energy. Nevertheless, not all ultramicropores may be accessible to the probe in principle due to size restriction or pressure limit of an instrument, therefore HK method produces inflated first peak as all pores below resolution limit are grouped to the smallest pores that are accessible [49].

Positron annihilation lifetime spectroscopy (PALS) [64] is another independent techniques commonly used to determine PSD in microporous region. When the source emits positron it can react with electron creating positronium (Ps) which annihilates after certain lifetime creating gamma rays which are detected. Positron in Ps can pick up molecularly-bound electron and quickly annihilate reducing Ps lifetime. In electron deficient volume, i.e. larger pores, the time between positron emission and detection of rays will be longer. The relation between pore size and positronium lifetime is described by empirical Tao-Eldrup model [65, 66], assuming simple pore geometry. The advantage over isothermal method is that the particle can access very small and even closed pores without any threat to change structure of a sample. However, PALS cannot distinguish between smooth channels and interconnected

small and larger pores due to Ps diffusion, resulting in either averaged broad or bimodal distribution [4, 67].

All of these techniques: simulation, N₂ or CO₂ adsorption method and PALS, produce different PSDs for disordered microporous materials with large free volume such as PIM-1 and PTMSP [4, 49, 68] (Figure 2.10). Simulated PSD shows large concentration of pores of about 4 Å and has pronounced shoulder towards large pores. Such characteristics reflect well PIM separation behaviour: larger pores allow unrestricted passage resulting in high permeability, while smaller pores or bottlenecks promote large selectivity. PSD calculated from adsorption isotherm follows simulated PSD, however due to low resolution is not able to capture pores narrower than 4 Å, although CO₂ molecule explores slightly smaller microporous region. Similar agreement was found between simulated and BJH PSDs of amorphous mesoporous materials [58]. Although PALS indicates an existence of ultramicropores and large pores, PSD has well pronounced bimodal shape different from shapes produced by other methods; this is considered to be due to incorrect mathematical data treatment [68]. The work shows difficulty of comparing not only experimental and simulated PSD, but also experimental data derived using different methods.

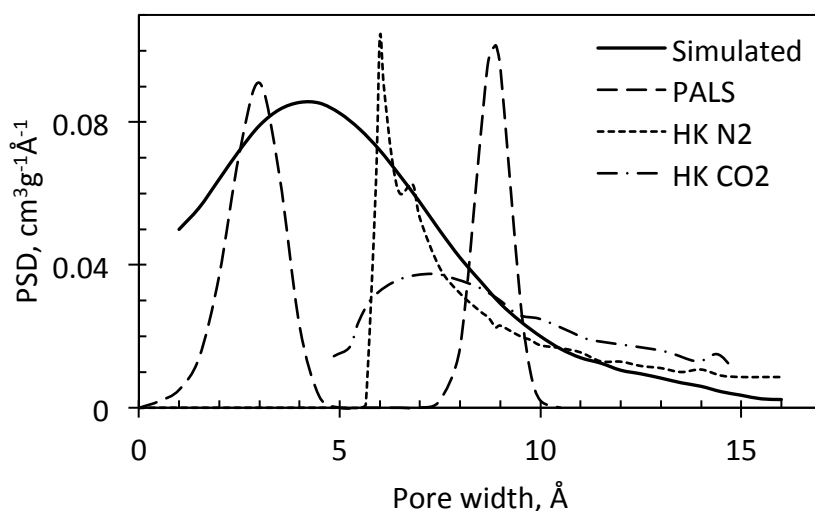


Figure 2.10. Pore size distribution of PIM-1 derived from different methods. Data is taken from ref. [4] and [49].

2.3 References

1. Keller, J.U. and R. Staudt, *GAS ADSORPTION EQUILIBRIA: Experimental Methods and Adsorptive Isotherms*. 2005: Springer.
2. Sing, K.S.W., *Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (IUPAC Recommendations 1984)*. Pure and Applied Chemistry, 1985. **57**(4): p. 603-619.
3. Thommes, M., et al., *Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)*, in *Pure and Applied Chemistry*. 2015. p. 1051.
4. McKeown, N.B. and P.M. Budd, *Exploitation of Intrinsic Microporosity in Polymer-Based Materials*. Macromolecules, 2010. **43**(12): p. 5163-5176.
5. Ghanem, B.S., et al., *Triptycene-Based Polymers of Intrinsic Microporosity: Organic Materials That Can Be Tailored for Gas Adsorption*. Macromolecules, 2010. **43**(12): p. 5287-5294.
6. Rouquerol, J., F. Rouquerol, and K. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*. 1 ed. 1999: Academic Press.
7. Del Regno, A., et al., *Polymers of Intrinsic Microporosity Containing Troger Base for CO₂ Capture*. Industrial & Engineering Chemistry Research, 2013. **52**(47): p. 16939-16950.
8. Hölk, O., et al., *Gas sorption isotherms in swelling glassy polymers—Detailed atomistic simulations*. Journal of Membrane Science, 2013. **428**: p. 523–532.
9. Myers, A.L. and J.M. Prausnitz, *Thermodynamics of mixed-gas adsorption*. AIChE Journal, 1965. **11**(1): p. 121-127.
10. Martin, M.G., *MCCCS Towhee: a tool for Monte Carlo molecular simulation*. Molecular Simulation, 2013. **39**(14-15): p. 1212-1222.
11. Sarkisov, L. and A. Harrison, *Computational structure characterisation tools in application to ordered and disordered porous materials*. Molecular Simulation, 2011. **37**(15): p. 1248-1257.
12. Leach, A.R., *Molecular Modelling. Principles and Applications*. 2 ed. 2001: Pearsin Education Limited.
13. Allen, M.P. and D.J. Tildesley, *Computer simulation of liquids*. 1987-many reprints, New York, US: Oxford University Press.
14. Martin, M.G. *MCCCS Towhee Web Manual*. [cited 2014-2015; Available from: <http://towhee.sourceforge.net>].
15. Metropolis, N., et al., *Equation of State Calculations by Fast Computing Machines*. J. Chem. Phys., 1953. **21**: p. 1087.
16. Widom, B., *Some Topics in the Theory of Fluids*. The Journal of Chemical Physics, 1963. **39**(11): p. 2808-2812.
17. Martin, M.G. and A.L. Frischknecht, *Using arbitrary trial distributions to improve intramolecular sampling in configurational-bias Monte Carlo*. Molecular Physics, 2006. **104**(15): p. 2439-2456.
18. McDonald, I.R., *NpT-ensemble Monte Carlo calculations for binary liquid mixtures*. Molecular Physics, 1972. **23**(1): p. 41-58.
19. Karavias, F. and A.L. Myers, *Isosteric heats of multicomponent adsorption: thermodynamics and computer simulations*. Langmuir, 1991. **7**(12): p. 3118-3126.

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20. Berendsen, H.J.C., et al., *Molecular dynamics with coupling to an external bath*. J. Chem. Phys., 1984. **81**: p. 3684-3690.
 21. Hunenberger, P.H., *Thermostat algorithms for molecular dynamics simulations*. Adv. Polymer. Sci., 2005. **173**: p. 105-149.
 22. Kissel, P., et al., *A nanoporous two-dimensional polymer by single-crystal-to-single-crystal photopolymerization*. Nat Chem, 2014. **6**(9): p. 774-778.
 23. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
 24. Karasawa, N. and W.A. Goddard, *Acceleration of convergence for lattice sums*. The Journal of Physical Chemistry, 1989. **93**(21): p. 7320-7327.
 25. Rappe, A.K., et al., *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations*. Journal of the American Chemical Society, 1992. **114**(25): p. 10024-10035.
 26. Jorgensen, W.L., D.S. Maxwell, and J. Tirado-Rives, *Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids*. Journal of the American Chemical Society, 1996. **118**(45): p. 11225-11236.
 27. Dauber-Osguthorpe, P., et al., *Structure and energetics of ligand binding to proteins: Escherichia coli dihydrofolate reductase-trimethoprim, a drug-receptor system*. Proteins: Structure, Function, and Bioinformatics, 1988. **4**(1): p. 31-47.
 28. Rai, N. and J.I. Siepmann, *Transferable Potentials for Phase Equilibria. 9. Explicit Hydrogen Description of Benzene and Five-Membered and Six-Membered Heterocyclic Aromatic Compounds*. The Journal of Physical Chemistry B, 2007. **111**(36): p. 10790-10799.
 29. Fairen-Jimenez, D., P. Lozano-Casal, and T. Duren, *Characterisation of Porous Solids VIII: Proceedings of the 8th International Symposium on the Characterisation of Porous Solids*. 2009, Cambridge: RSC Publisher.
 30. Amrouche, H., *In Silico Design of Metal Organic Frameworks for Greenhouse Gas Capture*, in *Chemical Engineering*. 2011, The University of Manchester: Manchester.
 31. Harris, J.G. and K.H. Yung, *Carbon Dioxide's Liquid-Vapor Coexistence Curve And Critical Properties as Predicted by a Simple Molecular Model*. The Journal of Physical Chemistry, 1995. **99**(31): p. 12021-12024.
 32. Fischer, J., et al., *Influence of intermolecular potential parameters on orthobaric properties of fluids consisting of spherical and linear molecules*. Molecular Physics, 1984. **52**(2): p. 485-497.
 33. Potoff, J.J. and J.I. Siepmann, *Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen*. AIChE Journal, 2001. **47**(7): p. 1676-1682.
 34. Heinz, H. and U.W. Suter, *Atomic charges for classical simulations of polar systems*. J. Phys. Chem. B, 2004. **108**: p. 18341-18352.
 35. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358-3363.
 36. Meister, J. and W.H.E. Schwarz, *Principal components of ionicity*. J. Phys. Chem., 1994. **98**: p. 8245-8252.
 37. Xiong, R., et al., *Effect of charge distribution on RDX adsorption in IRMOF-10*. Langmuir, 2010. **26**: p. 5942-5950.
 38. Hamad, S., et al., *Atomic charges for modeling metal-organic frameworks: Why and how*. Journal of Solid State Chemistry, 2015. **223**(0): p. 144-151.
 39. Wilmer, C.E. and R.Q. Snurr, *Towards rapid computational screening of metal-organic frameworks for carbondioxide capture: Calculation of framework charges via charge equilibration*. Chemical Engineering Journal, 2011. **171**: p. 775- 781.

40. Gasteiger, J. and M. Marsili, *Iterative partial equalization of orbital electronegativity—a rapid access to atomic charges*. Tetrahedron, 1980. **36**(22): p. 3219-3228.
41. Singh, U.C. and P.A. Kollman, *An approach to computing electrostatic charges for molecules*. Journal of Computational Chemistry, 1984. **5**(2): p. 129-145.
42. M. J. Frisch, G.W.T., H. B. Schlegel, G. E. Scuseria, , et al., *Gaussian 09*. 2010, Gaussian, Inc.: Wallingford CT.
43. Pérez-Pellitero, J., et al., *Adsorption of CO₂, CH₄, and N₂ on Zeolitic Imidazolate Frameworks: Experiments and Simulations*. Chemistry – A European Journal, 2010. **16**(5): p. 1560-1571.
44. Ramsahye, N.A., et al., *Charge distribution in metal organic framework materials: transferability to a preliminary molecular simulation study of the CO₂ adsorption in the MIL-53 (Al) system*. Physical Chemistry Chemical Physics, 2007. **9**(9): p. 1059-1063.
45. Mellot, C.F. and A.K. Cheetham, *Energetics and Structures of Fluoro- and Chlorofluorocarbons in Zeolites: Force Field Development and Monte Carlo Simulations*. The Journal of Physical Chemistry B, 1999. **103**(19): p. 3864-3868.
46. Besler, B.H., K.M. Merz, and P.A. Kollman, *Atomic charges derived from semiempirical methods*. Journal of Computational Chemistry, 1990. **11**(4): p. 431-439.
47. Regno, A.D. and F.R. Siperstein, *Comparison of generic force fields for packing of concave molecules*. Molecular Physics, 2014. **112**(17): p. 2241-2248.
48. Baburin, I.A., et al., *Hydrogen adsorption by perforated graphene*. International Journal of Hydrogen Energy, 2015. **40**(20): p. 6594-6599.
49. Larsen, G.S., et al., *Methane adsorption in PIM-1*. Adsorption, 2011. **17**: p. 21–26.
50. Larsen, G.S., et al., *Molecular Simulations of PIM-1-like Polymers of Intrinsic Microporosity*. Macromolecules, 2011. **44**(17): p. 6944-6951.
51. Rouquerol, J., et al., *Recommendations for the characterization of porous solids (Technical Report)*, in *Pure and Applied Chemistry*. 1994. p. 1739.
52. Brunauer, S., P.H. Emmett, and E. Teller, *Adsorption of Gases in Multimolecular Layers*. J. Am. Chem. Soc., 1938. **60**(2): p. 309-319.
53. Hart, K.E., L.J. Abbott, and C.M. Colina, *Analysis of force fields and BET theory for polymers of intrinsic microporosity*. Molecular Simulation, 2013. **39**(5): p. 397-404.
54. Walton, K.S. and R.Q. Snurr, *Applicability of the BET Method for Determining Surface Areas of Microporous Metal–Organic Frameworks*. Journal of the American Chemical Society, 2007. **129**(27): p. 8552-8556.
55. Duren, T., Y.-S. Bae, and R.Q. Snurr, *Using molecular simulation to characterise metal-organic frameworks for adsorption applications*. Chemical Society Reviews, 2009. **38**(5): p. 1237-1247.
56. Bae, Y.-S., A.Ö. Yazaydın, and R.Q. Snurr, *Evaluation of the BET Method for Determining Surface Areas of MOFs and Zeolites that Contain Ultra-Micropores*. Langmuir, 2010. **26**(8): p. 5475-5483.
57. Dören, T., et al., *Calculating Geometric Surface Areas as a Characterization Tool for Metal–Organic Frameworks*. The Journal of Physical Chemistry C, 2007. **111**(42): p. 15350-15356.
58. Gelb, L.D. and K.E. Gubbins, *Pore Size Distributions in Porous Glasses: A Computer Simulation Study*. Langmuir, 1999. **15**: p. 305-308.
59. Horv, et al., *METHOD FOR THE CALCULATION OF EFFECTIVE PORE SIZE DISTRIBUTION IN MOLECULAR SIEVE CARBON*. Journal of Chemical Engineering of Japan, 1983. **16**(6): p. 470-475.

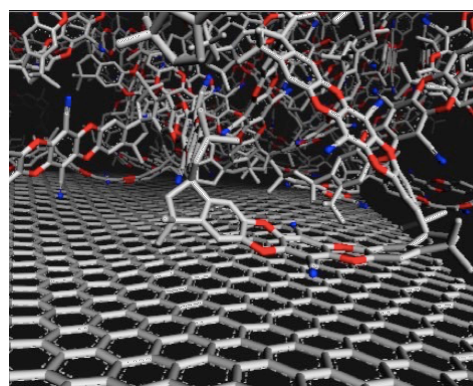
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60. Barrett, E.P., L.G. Joyner, and P.P. Halenda, *The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms*. Journal of the American Chemical Society, 1951. **73**(1): p. 373-380.
 61. Lastoskie, C., K.E. Gubbins, and N. Quirke, *Pore size distribution analysis of microporous carbons: a density functional theory approach*. The Journal of Physical Chemistry, 1993. **97**(18): p. 4786-4796.
 62. Jagiello, J. and J.P. Olivier, *Carbon slit pore model incorporating surface energetical heterogeneity and geometrical corrugation*. Adsorption, 2013. **19**(2): p. 777-783.
 63. Ravikovitch, P.I. and A.V. Neimark, *Density Functional Theory of Adsorption in Spherical Cavities and Pore Size Characterization of Templated Nanoporous Silicas with Cubic and Three-Dimensional Hexagonal Structures*. Langmuir, 2002. **18**(5): p. 1550-1560.
 64. Pethrick, R.A., *Positron annihilation—A probe for nanoscale voids and free volume?* Progress in Polymer Science, 1997. **22**(1): p. 1-47.
 65. Tao, S.J., *Positronium Annihilation in Molecular Substances*. The Journal of Chemical Physics, 1972. **56**(11): p. 5499-5510.
 66. Eldrup, M., D. Lightbody, and J.N. Sherwood, *The temperature dependence of positron lifetimes in solid pivalic acid*. Chemical Physics, 1981. **63**(1-2): p. 51-58.
 67. Staiger, C.L., et al., *Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer*. Chem. Mater., 2008. **20**(8): p. 2606-2608.
 68. Shantarovich, V.P., et al., *Structural heterogeneity in glassy polymeric materials revealed by positron annihilation and other supplementary techniques*. physica status solidi (c), 2007. **4**(10): p. 3776-3779.

3 PIM-1-GRAPHENE COMPOSITE: A COMBINED EXPERIMENTAL AND MOLECULAR SIMULATION STUDY

This chapter is adapted from the manuscript published in *Microporous and Mesoporous Materials*¹. Authors: Aleksandra Gonciaruk², Khalid Althumayri³, Wayne J. Harrison³, Peter M. Budd³, Flor R. Siperstein². Author contribution: the work was carried out and the manuscript was drafted by A. Gonciaruk through discussions with F. R. Siperstein, K. Althumayri with support from W. J. Harrison synthesised and prepared the samples under P. Budd supervision.

Abstract

This work presents a combined molecular simulation and experimental study to understand the effect of graphene on the packing and gas adsorption performance of a new class of polymers, known as polymers of intrinsic microporosity (PIMs). PIMs can be processed to membranes or other useful forms and their chemistry can be tailored for specific applications.



Their rigid and contorted macromolecular structures give rise to a large amount of microvoids attractive for small molecule adsorption. We show that the presence of graphene in the composite affects the structure of the membrane as evidenced by the change in colour and SEM micrographs, but it does not reduce significantly the adsorption capacity of the material.

¹ Adapted from “PIM-1-Graphene composite: a combined experimental and molecular simulation study”, A. Gonciaruk, Khalid Althumayri, Wayne J. Harrison, Peter M. Budd, F. R. Siperstein. *Microporous and Mesoporous Materials*, 2014. doi:10.1016/j.micromeso.2014.07.007.

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3.1 Introduction

The new class of materials that are currently of great interest, polymers of intrinsic microporosity (PIMs), could be promising sorbents for efficient gas separations. PIMs belong to a family of amorphous glassy polymers that form microporous solids simply because they possess highly rigid and contorted structures, which prevent them from filling the space efficiently. There are a variety of molecules [1] that can form PIMs thus necessary properties of PIMs can be potentially tailored by introducing a suitable co-monomer and/or functional group into the polymer chain, enhancing performance of the sorbent such as selectivity, capacity, solubility and stability.

The combination of microporosity and ability to generate solution-processable film-forming material offers unique benefits in membrane technology. PIM membranes were investigated in pervaporative separation of phenols from aqueous solutions, showing selectivity and total fluxes comparable to those obtained with conventionally used rubbery polymers [2]. Later applications for gas separation membranes were successful as well, showing that PIM-1 possesses high permeability exceeded only by highly permeable polymers such as PTMSP and Teflon AF2400, whilst its selectivity was significantly higher [3]. PIMs crossed Robeson's 1991 upper bound [4] for several important gas-pairs such as O_2/N_2 and CO_2/CH_4 , which contributed to its revision in 2008 [5]. The bound shows the trend of selectivity against permeability towards common gas pairs for many membrane materials. Polymeric materials as gas separation membranes suffer from a well-known trade-off between permeability and selectivity; those with high selectivity possess poor permeability properties and vice versa.

Incorporation of an additional component to already existing polymer offers a fast and cost-effective alternative for production of new high-performance materials. *Mixed matrix membranes* (MMM) are currently recognised as a competitive approach [6]. Several studies were performed on improving PIM-1 membrane performance in terms of permeability, selectivity or swelling by incorporating various inorganic fillers such as carbon nanotubes [7], silica [8], zeolite [9] and organic molecules such polyethyleneimine [10], Matrimid (polyimide class) [11] and porous organic cage molecules [12]. In most cases filler increased permeability of pristine PIM-1, while the selectivity was affected positively or negatively depending on the filler, gas pairs studied and other membrane properties, however in many cases significant performance enhancement was not achieved.

Ideally it is desired to incorporate such filler that would prohibit polymer chain packing increasing available free volume and surface area. Besides separation properties, the polymer should retain its mechanical properties by ensuring homogeneous mixing. One could also think about functionalizing the additive to improve not only polymer matrix compatibility with the additive and prevent agglomeration but also create additional adsorption sites [7].

The aim of this work is to investigate PIM packing behaviour in the presence of graphene slabs, and understand how it affects PIM structural properties and subsequently adsorption of gas molecules. Permeability in membrane polymers is mainly governed by free volume and its connectivity, while selectivity depends on size of the pores and gas-solid interactions. Typically in high free volume polymers diffusion driven separation is fast, thus has less contribution to selectivity, while selectivity due to solubility becomes much more important. Therefore PIM-1 exhibit reverse selectivity, i.e. condensable gas CO₂ is more permeable than H₂ [3], even though H₂ is smaller molecule. Incorporation of graphene molecule is expected to prevent PIM-1 chain packing further increasing its accessible surface area. Consequently, enhanced solubility driven separation properties can be achieved.

It is anticipated that presence of big and rigid graphene would not only hinder PIM-1 chains from further packing but also create additional well-defined pores. PIM-1 backbone contains polycyclic aromatic 6-membered structure that can be echoed in graphene molecule (Figure 3.1). Due to π - π interactions fairly good adhesion between PIM-1 and graphene can be expected. Taking into consideration that PIM-1 monomers turn by about 90° angle at each spiro centre the arrangement of PIM-1 chain close to graphene surface may create well-defined pores or pathways to graphene sheet. Additional void volume will be created at the interface between graphene and PIM-1 chains. Schematic representation can be seen in Figure 3.2. In such a way permeability and selectivity properties of microporous polymer could be tailored by controlling free volume and its shape.

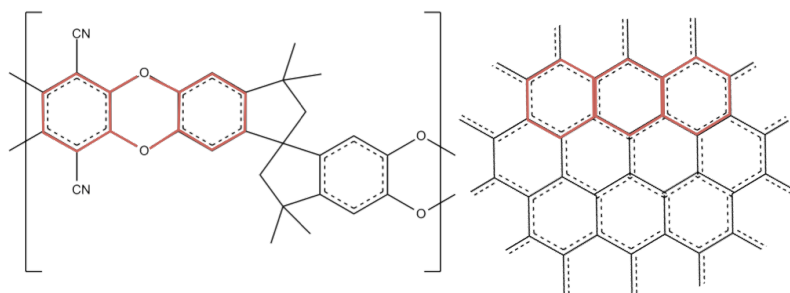


Figure 3.1. Highlighted (red) aromatic fused ring structure that is similar in both PIM-1 and graphene.

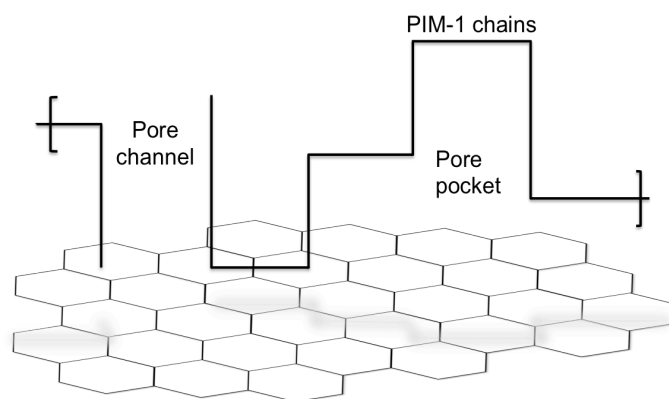


Figure 3.2. Schematic representation of possible arrangement of PIM-1 chains close to graphene sheet.

Graphene offers range of other attractive properties such as:

- One-atom thickness that enables creating thin membranes, which are more efficient due to less energy required to drive high gas flow rates through the membrane.
- Graphene is composed only from carbon that allows developing lightweight composites.
- Graphene has high surface area. For example, single 216-ring sheet of graphene with hydrogen-passivated edges that was used in this work has geometric surface area of about $3000 \text{ m}^2/\text{g}$ that offers increased potential sites for adsorption.
- The major disadvantage of polymer blends is miscibility of the additive in polymer matrix. Often it is limited to several weight percents [11]. Incorporating higher amount of additives may result in non-homogeneous and anisotropic properties of the blend. This may affect not only material's adsorption performance but also worsen mechanical properties. However, graphene surface can be functionalised if needed improving interfacial interactions with polymer matrix as well as tailoring selectivity of the membrane.
- PIM-1 similarly to other high free volume polymers such as PTMSP [13] is known for ageing. Free volume and thus permeability decreases over time [14]. Incorporation of MWCNT improved long-term stability of PIM-1 as permeability reduction for O_2 and N_2 were significantly slowed down [7]. Thus similar effect may be expected with the addition of graphene.

We initially focus on adsorption of carbon dioxide (CO_2) as changes in affinity and capacity may indicate possible structural differences caused by graphene presence. However it is expected that the permeability of the composite material may also be different to that of PIM-

1 and will need attention in future studies. We are mainly interested in understanding the effect on affinity, because based on the information available in the literature, variations in resulting selectivity can be hard to predict by intuition. For this purpose, we employed a combination of virtual molecular models of the composite followed by gas adsorption simulations, as well as experimental characterisation of the composites. The model of the composite system provides an atomistic level insight into molecular structure, while the experimental study on adsorption will complement the model and serve as a validation basis.

3.2 Experimental Method

Adsorption of CO₂ in the sample was studied by the static gravimetric technique using Hiden Isochema's (UK) intelligent gravimetric analyser (IGA-001). The sample was pre-treated in order to release any contaminants. Pretreatment involved thermal depressurising to a vacuum using a turbomolecular pump. The sample was maintained at 373 K for 3 hours and 8 hours at 473 K using an electric furnace. The temperature was increased at a rate of 2 K/min. Helium adsorption was measured prior to collecting the CO₂ isotherm in order to account for the buoyancy effect and to calculate sample density. CO₂ isotherms were measured gradually increasing the pressure from 0 to 20 bar at constant temperature, either 293K or 333K. The system was allowed to equilibrate at each pressure point for a maximum of 3 hours.

Collected adsorption data was fitted to the dual-mode (DM) model using equation (2.2) (see Chapter 2) to allow for data processing and comparison between different materials. The data obtained are valuable in understanding how graphene affects the adsorption performance of PIM-1. The low pressure region will provide insight into the composite's affinity for CO₂, while the high pressure region will indicate how graphene affects free volume and mobility of PIM-1 chains, i.e. swelling. Heat of adsorption was calculated using equation 2.3 described in Chapter 2 once the experimental isotherms were fitted to the DM model combining isotherms at different temperatures.

3.2.1 Samples

Gas. Carbon dioxide and helium of purity 99,995 (4.5 grade) and 99.999 % (5.0 grade), respectively, were used as received from the manufacturer, BOC Gases. Helium was used for buoyancy correction as discussed.

Composite. Materials were prepared as described in reference [15]. The material tested contained a 1 weight% loading of graphene. PIM-1-graphene composite forms a dark green membrane (Figure 3.3), which is evidently different from the bright yellow PIM-1 membranes. Gravimetrically measured density for the composite was $0.999 \pm 0.021 \text{ g/cm}^3$.



Figure 3.3. Pure PIM-1 (left) and PIM-1-graphene (right) membrane containing approximately 1 wt% graphene.

Figure 3.4 and Figure 3.5 show SEM images of the cross section of a pure PIM-1 membrane suggesting it is a fairly uniform material. Figure 3.6 and Figure 3.7 show SEM images of the cross section of a PIM-1-graphene membrane, which is clearly different from the pure PIM-1 membrane. The membrane cross section appears to split into two sections, with the lower section showing a more raised and jagged structure. The membrane structure could have been compromised during the preparation, although different preparation methods (including cutting with scissors and snapping the membrane) showed similar features. It is possible that snapping the membrane does not produce as clean a break as would be desired but that does not prevent us from concluding that there are apparent structural differences between the two

materials. It is immediately obvious, in comparison to pure PIM-1, that the composite membrane has a much rougher texture. There is also a much larger number of visible macropores in the internal structure. These features, suggest that the graphene may have influenced the packing of the PIM-1 macromolecules. The larger pore range and seemingly surface area indicates that the material would exhibit higher levels of permeability and faster adsorption but could also be less selective with certain gas separations.

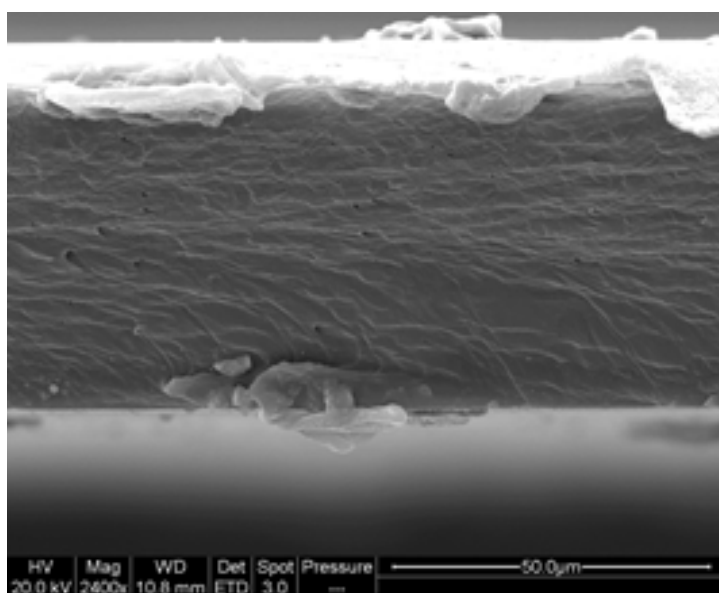


Figure 3.4. Cross section of a 50 μm thick PIM-1 membrane at 2400x magnification.

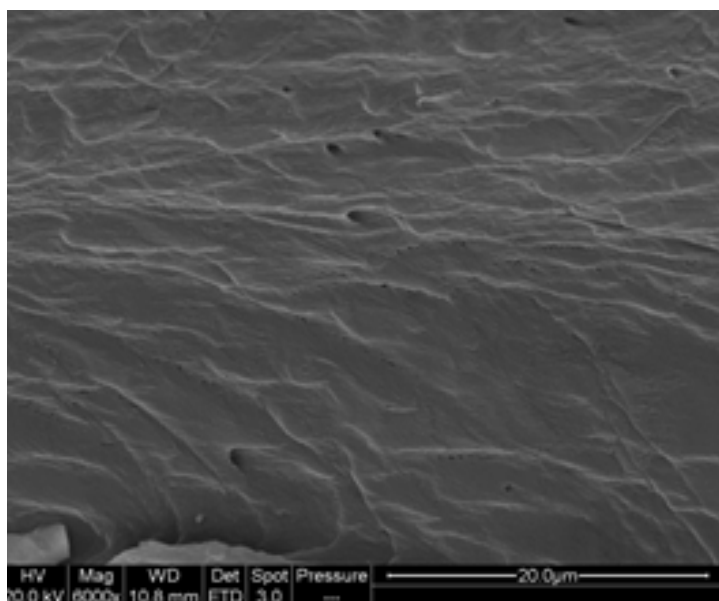


Figure 3.5. Cross section of a 50 μm thick PIM-1 membrane at 6000x magnification.

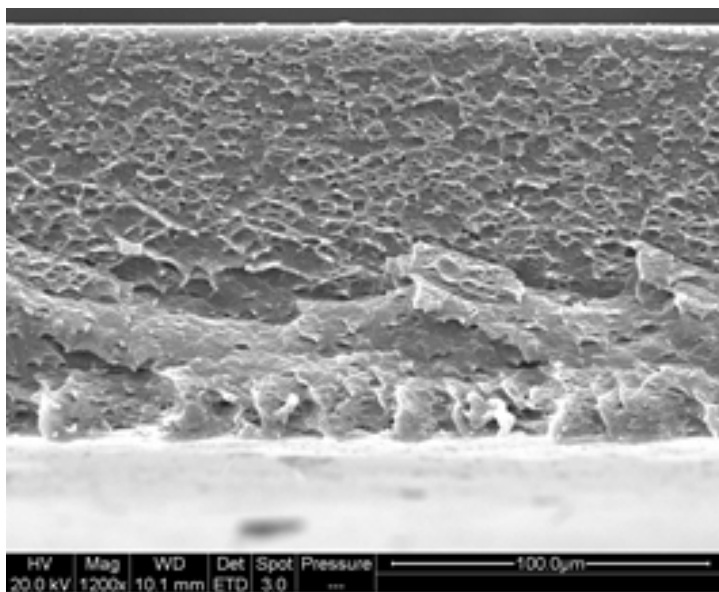


Figure 3.6. Cross section of a 120 μm thick PIM-1-graphene membrane at 1200 x magnification.

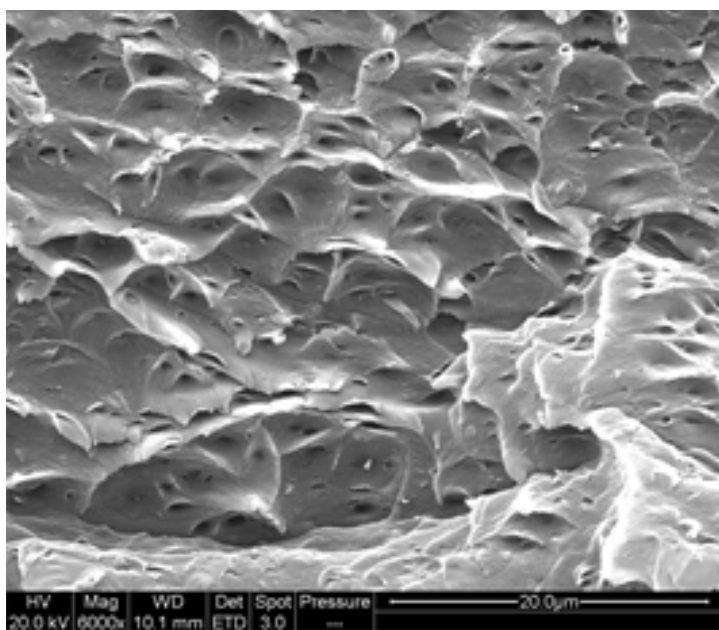


Figure 3.7. Cross section of a 120 μm thick PIM-1-graphene membrane at 6000x magnification.

3.3 Computational Method

Models were constructed and computational results were obtained using software programs from Materials Studio, Accelrys Software Inc. (San Diego, CA). Interactions between atoms were described using the DREIDING force field [16]. The Lennard-Jones 12-6 potential was used to model van der Waals interactions, while electrostatic interactions were calculated using Coulomb's law. Approximate partial atomic charges were specified by the charge equilibration QEq method [17] as implemented in the software. A three-site model was used for the CO₂ molecule where two oxygen and carbon atoms are explicitly modelled. All atom electrostatic charges and Lennard-Jones parameters for PIM-1, graphene and CO₂ molecules are available in the 3.6 Supplementary Information.

The models were characterised and compared in terms of density, skeletal density, accessible nitrogen surface area, and pore size distribution (PSD). The parameters are explained in more detail in Chapter 2.

3.3.1 Structure Generation

The polymer builder module implemented in the software is not capable of constructing ladder polymers such as PIM-1. Therefore, based on Heuchel *et al.*'s procedure [18] the problem was tackled by breaking one of two 5-membered rings in order to create a single-bonded polymer backbone. Hydrogen atoms numbered 1 and 2 were defined as head and tail atoms, respectively. Two monomers were selected to represent possible configurations of the polymer chain due to different orientations of methyl functional groups (Figure 3.8), bonded to 5-membered ring. The group can be oriented either in the same or opposite (referred to as *cis* and *trans*, respectively) direction taking the fused ring system as a reference. Repeat units were selected randomly and connected through carbons 3 and 4, removing head and tail hydrogens during the construction process. Ten random 11 – 15 monomer long chains were created. Examples of polymer chains are provided in Figure 3.9.

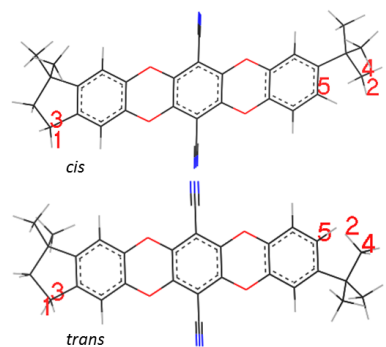


Figure 3.8. PIM-1 repeat units. Colour code: black – carbon, grey – hydrogen, red – oxygen, and blue – nitrogen. Numeration: 1 and 2 – head and tail atoms, 3, 4 and 5 – carbon atoms to be connected during chain construction.

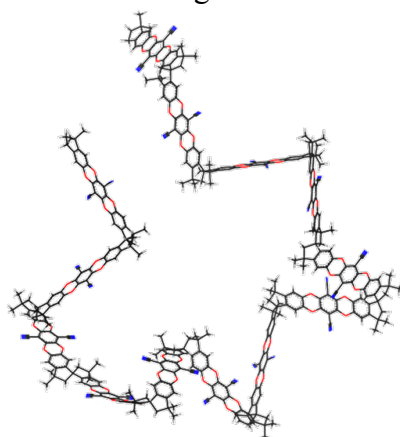


Figure 3.9. Example of a PIM-1 chain generated with the simulation procedure described in this paper.

Graphene sheets were created in planar form by connecting six-membered carbon rings (Figure 3.10). The edge carbon atoms of the graphene were saturated by adding hydrogen atoms. The structures were randomly packed in an amorphous three-dimensional periodic box at low density in Monte Carlo fashion. The initial system contained 10 PIM-1 chains of various lengths and one graphene sheet (Figure 3.10, left) yielding a total of 7752 atoms in the model system. Such composition corresponds to a weight ratio 1:10 (graphene : PIM-1). Three independent models were created to obtain average properties.

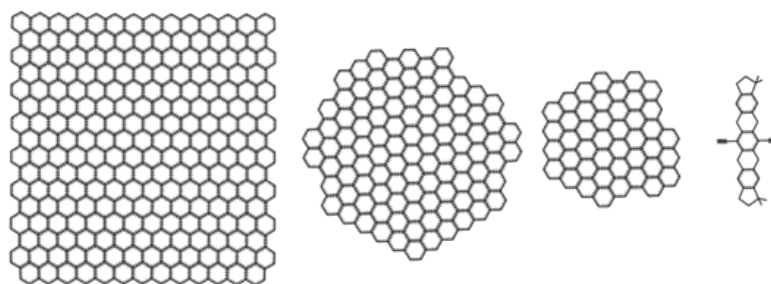


Figure 3.10. Graphene sheets used to create different model systems containing (left) 494, (middle) 236 and (right) 111 carbon atoms compared with the fragment of PIM-1 (far right)

Selection of low initial density is dictated by the stiffness of the polymers. Unlike flexible polymers, PIM-1 has a limited number of conformations and therefore cannot be packed directly to final density. Instead molecules are placed in a low density box and final configuration is reached during a series of molecular dynamic simulations. Larsen *et al.* [19] developed a new generic scheme based on that of Karayannis *et al.* [20], where the PIM model is consistently compressed and relaxed to experimental density. The slow decompression scheme is stated to be reliable in terms of obtaining realistic density without the need to compare with experimental data. This approach has also been successfully used to model other materials in, which their contorted structure prevents them from packing efficiently [21, 22]. Simulation conditions are outlined in 3.6 Supplementary Information.

The initial large graphene slab was split into two and four parts to determine the graphene sheet size effect on the composite properties (Figure 3.10, middle and right, respectively). The two additional systems were created containing the same polymer/graphene overall composition, which resulted in either two intermediate or four small sheets of graphene and the same number of PIM-1 chains as in the system with one large graphene. The diameter of the smallest graphene sheet (Figure 3.10, right) is similar to the size of PIM-1 monomer. It is expected that smaller sheets will occupy pores more efficiently and, consequently, reduce adsorption capacity and gas diffusivity. Small sheets may also travel in the polymer framework more easily and stack to each other, affecting mechanical properties. Large graphene sheets may serve as a barrier blocking pathways to pores during the adsorption process, especially in membrane separations. This will worsen molecule diffusivity and transport through the membrane as well as reduce accessible free volume. Large sheets also possess higher surface area, which may significantly worsen mechanical contact between graphene and polymer. Phase separation may occur due to agglomeration of large sheets, which in turn may make the composite more brittle than pristine polymer. Therefore it is expected to find an intermediate graphene sheet that ensures good mechanical properties and is sufficiently large not to block the material's pores. The resulting composites are labelled Composite L, Composite M and Composite S; the last letter in the name defines the size of the sheets used, i.e. L – large, M – medium and S – small.

3.3.2 Simulation Details of CO₂ Adsorption

Adsorption isotherms were generated using grand canonical Monte Carlo simulations (GCMC) as implemented in Materials Studio. Adsorption of molecules was allowed only in the accessible volume defined with the CO₂ molecule (kinetic diameter 3.3 Å), which is equivalent to experimental conditions. A combination of translation, rotation, insertion, and deletion steps were performed for a total of 5.5×10^6 equilibration and production steps. Interactions between atoms were again described using the DREIDING force field; however Lenard-Jones parameters were adjusted to match experimental and simulated isotherms at low pressures. Gas adsorption was simulated at 293 K over a pressure range from 0 to 20 bar.

3.4 Results and Discussion

3.4.1 Structural Properties

Simulated and experimental structural properties of PIM-1-graphene composite and pure PIM-1 are provided in Table 3.1. Properties of PIM-1 simulated in this work compare well with experimental and simulated data available in the literature. This indicates that the generic DREIDING force field is capable to predict correct structures of PIM-1. Some deviations between simulated values and those measured experimentally are observed. They may be due to the presence of defects, residual solvent, impurities and/or kinetically inaccessible regions in experimental samples that are not captured in the ideal simulated sample, or to uncertainties in the force field parameters used, which were not derived for this specific case.

3 PIM-1-GRAPHENE COMPOSITE: A COMBINED EXPERIMENTAL AND MOLECULAR SIMULATION STUDY

Table 3.1. Structural properties of PIM-1-graphene composite and PIM-1.

	Density, g cm^{-3}	Skeletal density, g cm^{-3}	Accessible nitrogen surface area, $\text{m}^2 \text{g}^{-1}$
Composite L	0.863 ± 0.026	1.007 ± 0.008	853 ± 136
Composite M	0.828 ± 0.037	0.998 ± 0.007	983 ± 151
Composite S	0.872 ± 0.017	1.006 ± 0.002	791 ± 108
Composite experimental	-	0.999 ± 0.021	-
PIM-1 simulated, this work	0.833 ± 0.046	0.977 ± 0.013	901 ± 207
PIM-1 experimental, this work	-	0.948 ± 0.008	-
PIM-1 simulated [ref]	0.98 [19]	0.94 – 1.40 [18, 19, 23-26]	435 [18] 448 [19], 830 [27], 940 [26]
PIM-1 experimental [ref]	-	0.94 – 1.4 [26, 28, 29]	760 – 875 [2, 28, 30]

The predicted structures of composites loaded with large and small platelets were slightly denser than simulated PIM-1 and had smaller accessible surface area. However the system with intermediate graphene sheets had higher surface area compared to other composite systems and pure PIM-1. This suggests that it is indeed possible to change the structural properties of the polymer matrix by carefully controlling graphene size.

Visualization of simulated systems revealed that PIM-1 fragments arranged themselves parallel to the graphene sheet (Figure 3.11). The separation between PIM-1 fragments and graphene sheet was about 3.5 – 4 Å, similar to the distances between stacked layers in graphite. Some of the PIM-1 fragments stacked onto the graphene sheet as in hexagonal phase graphite or by repeating a hexagonal ring pattern. However most of PIM-1 chain fragments were constrained by an arrangement of the whole chain and therefore tended to align rather randomly on the graphene sheet. No additional voids were created in the interface between polymer matrix and graphene sheets. Nevertheless, such stacking indicates good interface adhesion between the graphene sheet and polymer, which probably facilitates graphene dispersion within the polymer matrix and strengthens the resulting composite material. The mobility of PIM-1 may also be affected due to the contact between some chain fragments and the graphene sheet, which potentially can help controlling the polymer aging.

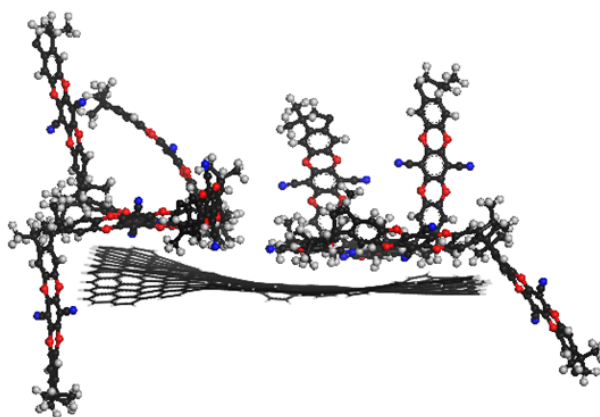


Figure 3.11. Representative arrangement of PIM-1 chain fragments on graphene sheet.

Average pore size distributions of the composite and PIM-1 simulated in this work are provided in Figure 3.12. PSD calculated for simulated PIM-1 by G. S. Larsen *et al.* from two references, [19] and [26], are also included for comparison. Although both of these PSD are generated for PIM-1 using the same method, the two PSDs are slightly different due to one of them being shifted towards higher pore width. This indicates that many possible arrangements occur while packing quirky structures such as PIM-1 into amorphous systems. Therefore the differences between PSD of such structures should not be over interpreted.

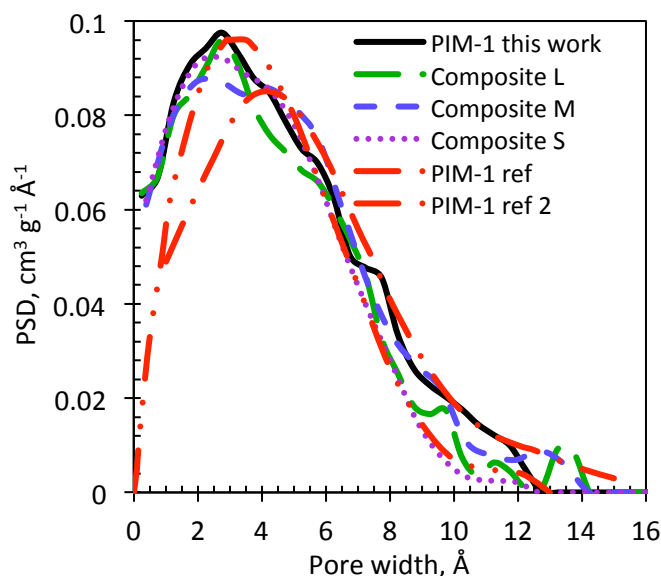


Figure 3.12. Pore size distribution comparison between composite model with varying graphene sheet size and pure PIM-1. Simulated PSD of pure PIM-1 are reprinted from ref [19] and ref 2 [26].

There might be seen some insignificant differences between PSD of different structures. Most pore sizes are scattered around an average value of 3 Å, although PSDs generated in this work are slightly shifted to narrower pore widths compared to the reference PSDs of PIM-1. Nevertheless, all PSDs tended to follow a similar trend: peaks arose at similar pore width values and all PSDs produced shoulders towards higher pore sizes.

3.4.2 The CO₂ Adsorption

The effect of graphene presence in PIM-1 was also tested for carbon dioxide adsorption. Adsorption of CO₂ was simulated only in the system with the large graphene sheet (Composite L) and in pure PIM-1. The simulated isotherms compared with those obtained in experimental samples are provided in Figure 3.13. As expected, the simulated isotherm follows Langmuirian behaviour, i.e. CO₂ adsorption increases significantly at low pressures, whereas at higher pressures a saturation capacity is reached. Experimental isotherms on the other hand tended to have a linear relationship at high pressures between adsorbed CO₂ loading and pressure and did not level off even at 20 bar pressure. This indicates possible polymer swelling and increased dominance of gas-gas interactions. The difference between the shape of simulated and experimental isotherms is also expected as the framework of the system is considered to be rigid, i.e. adsorption takes place only in fixed free volume regions. In real conditions, on the other hand, polymer chains can re-orientate, adjusting to pressure and loading changes. This may affect free volume change leading to greater loadings, especially at higher pressure. This behaviour is observed in both composite and pristine PIM-1. This effect has already been captured by Hölck *et al.* in their work [25] where they showed the same discrepancies between experimental and simulated isotherms for pure PIM-1 and other swelling glassy polymers. In order to match isotherm points at higher pressures it was required to create an additional “swollen” model of the material by introducing gas molecules into the system and allowing material to rearrange its configuration.

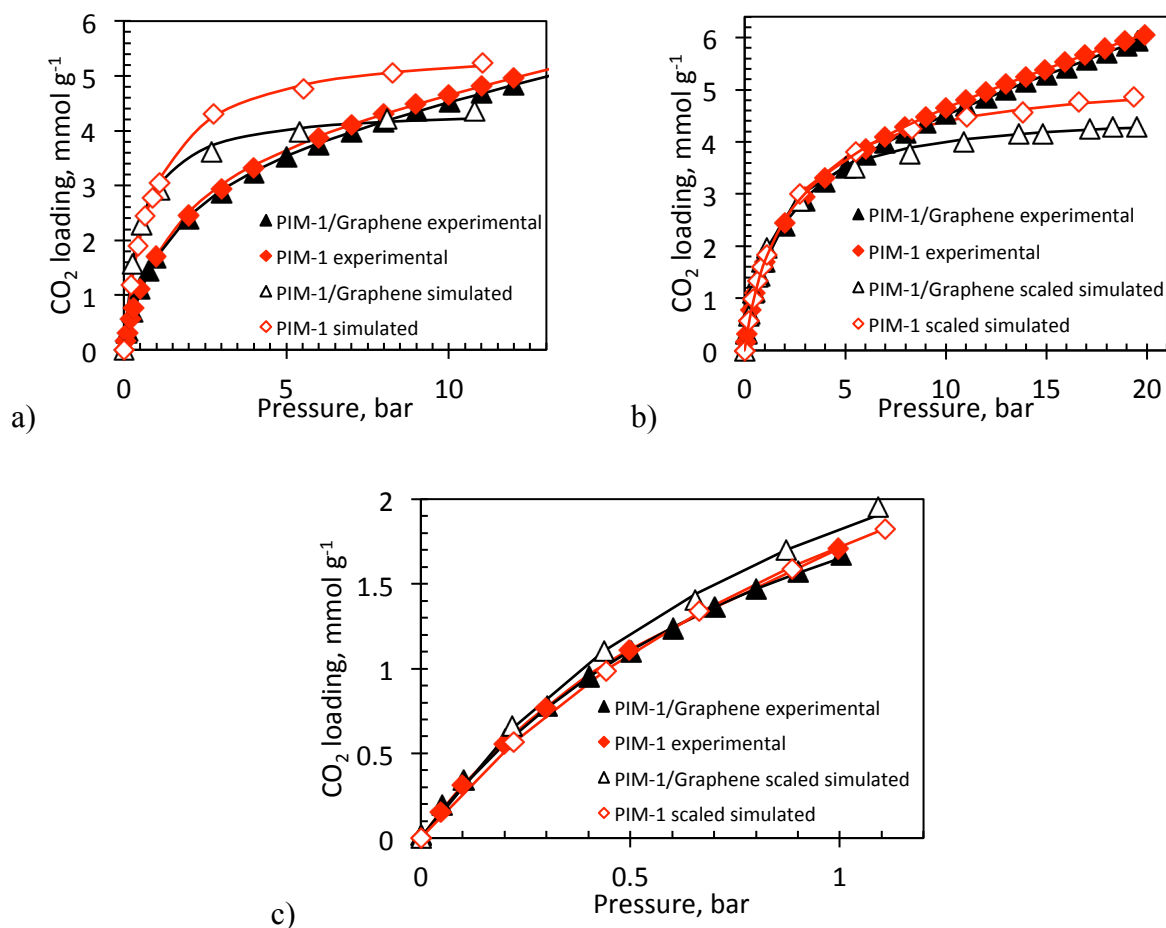


Figure 3.13. Experimental and simulated CO₂ isotherms at 293 K. Simulated isotherm calculated using (a) original L-J parameters and (b-c) reduced L-J interaction strength, ϵ , by 24%. Data in (b) and (c) is the same, except (c) shows the details of the low pressure region. Lines represent the fitting obtained from the DM model. Experimental isotherm of pure PIM-1 is taken from [31].

From the experimental isotherms, it is obvious that addition of graphene has not affected adsorption performance of PIM-1, as the isotherm shape and adsorption capacity is almost the same in both materials. This is also reflected in the DM constants (Table 3.2) where m , k_1 and k_2 values, denoting adsorption capacity, swelling and affinity between CO₂ and adsorbent, respectively, are almost the same between the composite and PIM-1. Moreover, calculated heats of adsorption are also similar for both samples.

Table 3.2. Experimental dual-mode constants at 293K and heat of adsorption.

	Composite	PIM-1
k_1 , mmol g ⁻¹ bar ⁻¹	0.15	0.13
k_2 , bar ⁻¹	0.86	0.67
m , mmol g ⁻¹	3.12	3.77
ΔH , kJ mol ⁻¹	26	24

Simulations show a slightly different CO₂ adsorption in composite and PIM-1 at pressures higher than 1 bar, which is attributed to different surface areas of the two systems. In simulations, both pure PIM-1 and the composite reach the same CO₂ loadings up to approximately 1 bar. In this pressure region, gas-adsorbent interactions are the most important and no swelling is expected to occur. Comparing adsorption at low pressures will indicate, which of the systems possess higher affinity towards adsorbed gas. The fact that both materials adsorb the same amount of CO₂ at low pressure indicates that PIM-1 chains possibly stack closely to graphene, limiting access towards its surface for CO₂ molecules, or attraction between CO₂ and graphene is simply very similar to the attraction between CO₂ and polymer. This encouraging finding suggests that selectivity towards CO₂ should not be worsened in such composite membranes. There have been several attempts reported in the literature to enhance PIM-1 adsorption performance by incorporating nanoparticles such as functionalised carbon nanotubes [7], fumed silica [8] and zeolitic imidazolate framework ZIF-8 [32]. In all of the cases, permeabilities were increased whereas selectivities for CO₂/CH₄ and CO₂/N₂ gas pairs were worsened or increased insignificantly.

The adsorption isotherms calculated using default L-J parameters stored within the DREIDING force field overestimated CO₂ adsorption (Figure 3.13, a). By optimizing the DREIDING force field we were able to match experimental and simulated isotherms. It was achieved by scaling down the strength of the interaction (ϵ), which describes van der Waals interactions between non-bonded atoms. The scaling factor was determined by empirically fitting the calculated adsorption isotherm of CO₂ to experimental data measured at 293 K. The main focus was to reproduce the adsorption isotherm at the low pressure region where van der Waals interactions are dominant and it is assumed that no swelling occurs. The obtained scaling factor is 0.76, which reduces the strength of attraction insignificantly considering that only one parameter and only for CO₂ molecule atoms is scaled down. This scaling is similar to that required to model accurately CO₂ adsorption in other microporous materials [33].

3.4.3 Graphene Size Effect

The size of graphene sheets may affect adsorption performance of an adsorbent. We observed that in all boxes of Composite S phase separation occurred, as stacking of two or three

graphene sheets was observed (Figure 3.14, b). The agglomeration occurred at early stages before compression when system density was low (0.169 g cm^{-3}). In a real PIM-1-graphene composite, the agglomeration may occur during the preparation procedure, before a dense polymer membrane is formed, which would be a similar case to the simulations.

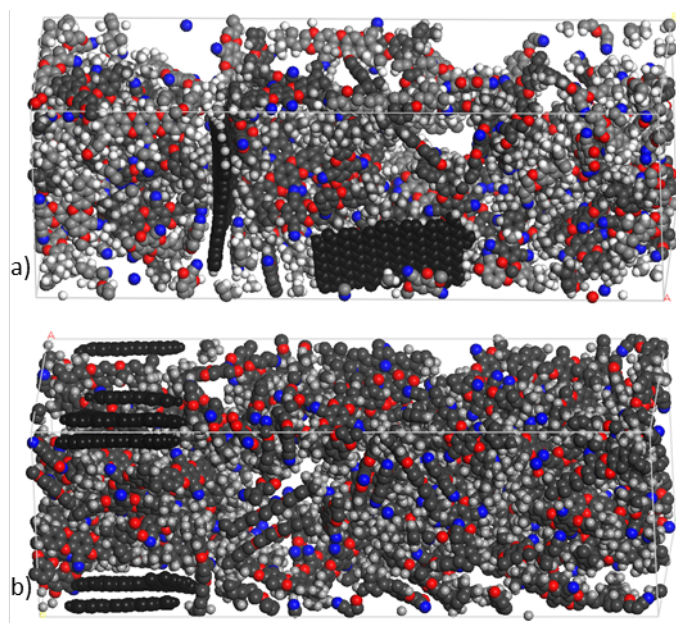


Figure 3.14. Representative snapshots of final configuration boxes of Composite M (a) and Composite S (b). Atoms of graphene sheets are coloured in black, all other carbon atoms are dark grey, hydrogens are light grey, nitrogens are blue and oxygen atoms are red.

Graphene size effect is reflected in the structural properties provided in Table 3.1. Density of the system with the medium graphene sheets is slightly lower than the density of the other composite systems, while surface area is larger and exceeds the surface area of pure PIM-1. No agglomeration of graphene molecules was observed in all three boxes of this system (Figure 3.14, a). This suggests that the hypothesis mentioned earlier that there is an optimum size of graphene sheets that can enhance the material's properties is confirmed: the medium graphene sheet size increases accessible surface area rather than blocking or occupying the pores of the material. However the small difference between properties of the systems studied, including their PSDs, suggests that all systems are quite similar in their structure configurations. Therefore it seems that graphene sheet size, over the size range investigated, does not have a major effect on the bulk structural properties of PIM-1. Further research is recommended to identify the size range of graphene sheets, which should probably be larger than the ones presented in this work, that would affect the structure of the polymer and the adsorption properties.

3.5 Conclusions

The objective of this study was to create a model of PIM-1 loaded with graphene, to understand how graphene affects polymer packing and how it is reflected in structural properties and subsequently adsorption of carbon dioxide compared to pristine PIM-1 adsorbent. It is evident that graphene has some effect on the bulk structure of pure PIM-1, i.e. the membrane changes its colour and gains a ruptured surface compared to a smoother PIM-1 surface. The rougher structure of the composite's surface leads to expect a possible increase in permeability and faster adsorption. However the molecular model of the composite demonstrates that the polymer's structural properties such as density, surface area and PSD in micropore region are preserved in the composite. Moreover, similar adsorption isotherms of pristine PIM-1 and PIM-1-graphene composite suggest that there is no significant effect on affinity towards CO₂ caused by the presence of graphene. This allows expecting that graphene may increase PIM-1 membrane permeability without affecting its selectivity; however further adsorption of other gases (e.g. N₂, CH₄) and permeability studies are necessary to prove this hypothesis.

3.6 Supplementary Information

All atom electrostatic partial charges and Lenard-Jones parameters for PIM-1, graphene and CO₂ molecules are listed in Table 3.3 and Table 3.4. Figure 3.15 shows the fragment of PIM-1 chain with numbered atoms; these numbers are used in Table 3.4 for clear presentation. Simulations steps for slow compression of systems are outlined in Table 3.5. Charge distribution on graphene atoms (Composite L) is depicted in Figure 3.16 where only quarter of the sheet is seen. However it is sufficient to represent how QEq method distributes the charges, i.e. the charges decrease gradually from the edges to the centre of the sheet.

Table 3.3. Nonbonded interaction parameters for simulations.

Element type	D_0 , kcal/mol	R_0 , Å
C	0.0951	3.8983
H	0.0152	3.1950
N	0.0774	3.6621
O	0.0957	3.4046

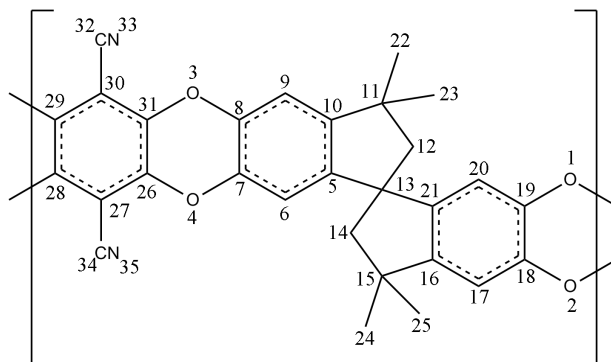


Figure 3.15. Fragment of PIM-1 chemical structure.

Table 3.4. Average partial charges.

Atom type	Number*	Partial charge
PIM-1		
C(aro)-O-C(aro)	1, 2, 3, 4	-0.5824
C(aro)-H	6, 9, 17, 20	-0.1314
O-C(aro)-C(aro)	7, 8, 18, 19	0.2956
	26, 28, 29, 31	0.2188
C(aro)-R	10, 16	0.0140
	5, 21	-0.0247
C(aro)-C(nitrile)	27, 30	-0.0252
C(nitrile)	32, 34	0.3114
	13	0.0138
C	11, 15	0.0217
CH ₂	12, 14	-0.2068
CH ₃	22, 23, 24, 25	-0.3903
N(nitrile)	33, 35	-0.2589
H(aro)	6, 9, 17, 20 **	0.1437
H-CH ₂	22, 23, 24, 25 **	0.1361
H-CH	12, 14**	0.1207
Carbon dioxide		
C		0.8958
O		-0.4479

* numbers correspond to chemical structure presented in Figure 3.15.

** numbers of carbons that have bonds with H

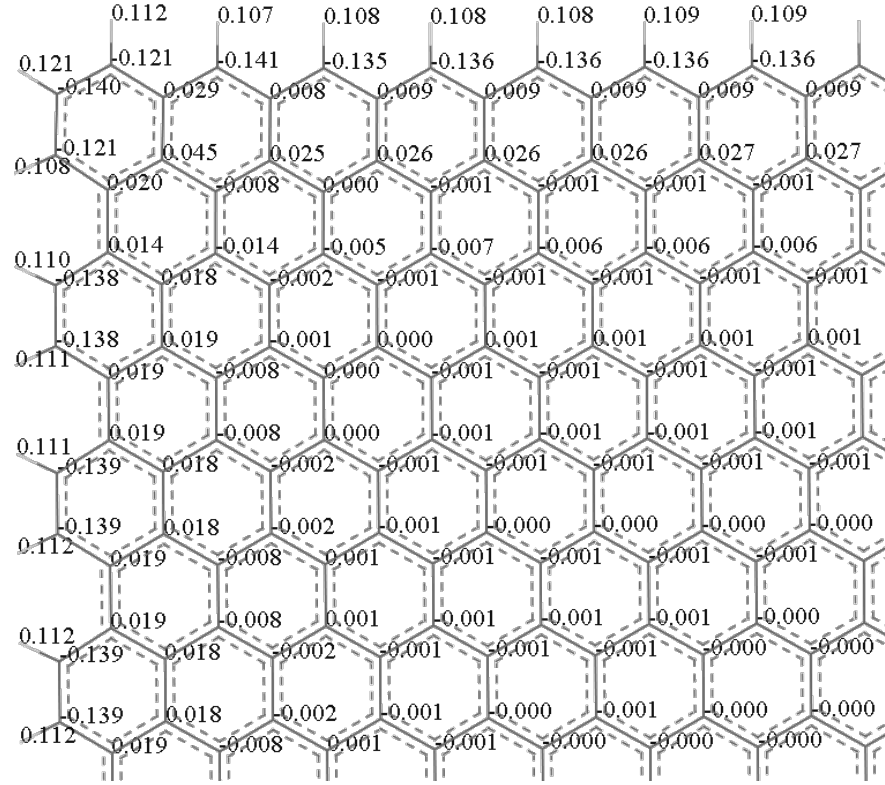


Figure 3.16. Charge distribution on graphene atoms as predicted by QEq method.

Table 3.5. 21-step MD compression-decompression schemes.

Step	Conditions	Duration, ps	Step	Conditions	Duration, ps
1	NVT 600K	50	12	NPT 25,000bar, 300K	5
2	NVT 300K	50	13	NVT 600K	5
3	NPT 1,000bar, 300K	50	14	NVT 300K	10
4	NVT 600K	50	15	NPT 5,000bar, 300K	5
5	NVT 300K	100	16	NVT 600K	5
6	NPT 30,000bar, 300K	50	17	NVT 300K	10
7	NVT 600K	50	18	NPT 500bar, 300K	5
8	NVT 300K	100	19	NVT 600K	5
9	NPT 50,000bar, 300K	50	20	NVT 300K	10
10	NVT 600K	50	21	NPT 1bar, 300K	800
11	NVT 300K	100			

3.7 References

1. McKeown, N.B. and P.M. Budd, *Exploitation of Intrinsic Microporosity in Polymer-Based Materials*. Macromolecules, 2010. **43**(12): p. 5163-5176.
2. Budd, P.M., et al., *Solution-Processed, Organophilic Membrane Derived from a Polymer of Intrinsic Microporosity*. Advanced Materials, 2004. **16**(5): p. 456-459.
3. Budd, P.M., et al., *Gas separation membranes from polymers of intrinsic microporosity*. Journal of Membrane Science, 2005. **251**(1-2): p. 263-269.
4. Robeson, L.M., *Correlation of separation factor versus permeability for polymeric membranes*. Journal of Membrane Science, 1991. **62**(2): p. 165-185.
5. Robeson, L.M., *The upper bound revisited*. Journal of Membrane Science, 2008. **320**(1-2): p. 390-400.
6. Chunga, T.-S., et al., *Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation*. Prog. Polym. Sci., 2007. **32**: p. 483-507.
7. Khan, M.M., et al., *Functionalized carbon nanotubes mixed matrix membranes of polymers of intrinsic microporosity for gas separation*. Nanoscale Research Letters, 2012. **7**: p. 504.
8. Ahn, J., et al., *Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1)*. Journal of Membrane Science, 2010. **346**(2): p. 280-287.
9. Kulprathipanja, S., C. Liu, and S.T. Wilson, *High flux mixed matrix membranes for separations*. 2007, Google Patents.
10. Fritsch, D., et al., *High performance organic solvent nanofiltration membranes: Development and thorough testing of thin film composite membranes made of polymers of intrinsic microporosity (PIMs)*. Journal of Membrane Science, 2012. **401-402**(0): p. 222-231.
11. Yong, W.F., et al., *Molecular engineering of PIM-1/Matrimid blend membranes for gas separation*. Journal of Membrane Science, 2012. **407**: p. 47-57.
12. Bushell, A.F., et al., *Nanoporous Organic Polymer/Cage Composite Membranes*. Angewandte Chemie International Edition, 2013. **52**(4): p. 1253-1256.
13. Nagai, K., B.D. Freeman, and A.J. Hill, *Effect of physical aging of poly(1-trimethylsilyl-1-propyne) films synthesized with TaCl₅ and NbCl₅ on gas permeability, fractional free volume, and positron annihilation lifetime spectroscopy parameters*. Journal of Polymer Science Part B: Polymer Physics, 2000. **38**(9): p. 1222-1239.
14. Staiger, C.L., et al., *Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer*. Chem. Mater., 2008. **20**(8): p. 2606-2608.
15. Althumayri, K., et al., *The influence of few-layer graphene on the gas permeability of the high-free-volume polymer PIM-1*. Philos Transact A Math Phys Eng Sci, 2015.
16. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
17. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358-3363.
18. Heuchela, M., et al., *Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1)*. Journal of Membrane Science, 2008. **318**(1-2): p. 84-99.

19. Larsen, G.S., et al., *Molecular Simulations of PIM-1-like Polymers of Intrinsic Microporosity*. *Macromolecules*, 2011. **44**(17): p. 6944-6951.
20. Karayiannis, N.C., V.G. Mavrantzas, and D.N. Theodorou, *Detailed Atomistic Simulation of the Segmental Dynamics and Barrier Properties of Amorphous Poly(ethylene terephthalate) and Poly(ethylene isophthalate)*. *Macromolecules*, 2004. **37**(8): p. 2978-2995.
21. Del Regno, A., et al., *Polymers of Intrinsic Microporosity Containing Troger Base for CO₂ Capture*. *Industrial & Engineering Chemistry Research*, 2013. **52**(47): p. 16939-16950.
22. Del Regno, A. and F.R. Siperstein, *Organic molecules of intrinsic microporosity: Characterization of novel microporous materials*. *Microporous and Mesoporous Materials*, 2013. **176**(0): p. 55-63.
23. Fang, W., L. Zhang, and J. Jiang, *Polymers of intrinsic microporosity for gas permeation: a molecular simulation study*. *Molecular Simulation*, 2010. **36**(12): p. 992-1003.
24. Larsen, G.S., *Simulations and experiments on gas adsorption in novel microporous polymers*. 2011, The Pennsylvania State University.
25. Hölk, O., et al., *Gas sorption isotherms in swelling glassy polymers—Detailed atomistic simulations*. *Journal of Membrane Science*, 2013. **428**: p. 523-532.
26. Larsen, G.S., et al., *Methane adsorption in PIM-1*. *Adsorption*, 2011. **17**: p. 21-26.
27. Hart, K.E., L.J. Abbott, and C.M. Colina, *Analysis of force fields and BET theory for polymers of intrinsic microporosity*. *Molecular Simulation*, 2013. **39**(5): p. 397-404.
28. McKeown, N.B., et al., *Towards Polymer-Based Hydrogen Storage Materials: Engineering Ultramicroporous Cavities within Polymers of Intrinsic Microporosity*. *Angewandte Chemie International Edition*, 2006. **45**(11): p. 1804-1807.
29. Budd, P.M., N.B. McKeown, and D. Fritsch, *Polymers of Intrinsic Microporosity (PIMs): High Free Volume Polymers for Membrane Applications*. *Macromolecular Symposia*, 2006. **245-246**(1): p. 403-405.
30. Budd, P.M., et al., *Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials*. *Chem. Commun*, 2004: p. 230-231.
31. Larsen, G.S., K.E. Hart, and C.M. Colina, *Predictive simulations of the structural and adsorptive properties for PIM-1 variations*. *Molecular Simulation*, 2014. **40**(7-9): p. 599-609.
32. Bushell, A.F., et al., *Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8*. *Journal of Membrane Science*, 2013. **427**(0): p. 48-62.
33. Pérez-Pellitero, J., et al., *Adsorption of CO₂, CH₄, and N₂ on Zeolitic Imidazolate Frameworks: Experiments and Simulations*. *Chemistry – A European Journal*, 2010. **16**(5): p. 1560-1571.

4 PIM-1 COMPOSITES CONTAINING MODEL CARBON ADDITIVES

This chapter is a complimentary material to the Chapter 3 and will not be submitted as a manuscript.

4.1 Introduction

PIM-1/graphene composites showed practically the same adsorption capacity as pristine graphene [1]. The analysis showed that graphene was not able to increase the accessible surface area by ensuring sufficient separation between polymer chains. Therefore, it was decided to investigate more complex additives that will still retain properties of graphene. The main difference between graphene and complex additives presented in this chapter is that they occupy three-dimensional (3D) space due to graphene arms being connected through rigid cores. Threefold propeller-like structures form free-standing microporous amorphous material despite the fact that the blades are essentially graphene platelets which tend to form stacks. It is expected that the combinations of awkward shapes of both polymer and additives will complicate the packing and result in increased surface area. Although these structures are hypothetical, the study may provide insight into “behaviour” of polymer chains and suggest the optimum shape and size of additive required to affect structural polymer properties. Moreover, the structure of 3D additives are inspired by the real molecules. Simpson *et al.* synthesized polycyclic aromatic hydrocarbon with the proposed 3D propeller-like structure [2] and Xiong *et al.* recently reported the structure of 3D graphene nanoparticle with triptycene core [3], which non-functionalized structure is used as additive in this work. The ability to synthesise such a complex structures that can be soluble provides non-hypothetical possibility to obtain real composite materials.

4.2 Methodology

Figure 4.1 shows different model carbon structures with different graphene arm sizes and Figure 4.2 shows centres studied in this work. Four main graphene (small, medium and larger disk-shaped and medium ribbon) arms were connected through three different cores (*trip*, *CTC* and *octa*). The *trip* and *octa* cores provide the stiffest support for arms, while *CTC* core is the most flexible and is expected to allow forming stacks. The *octa* core connects six arms making it difficult for polymer chains to penetrate closer to the core and wrap around the arms. Thus it is expected that *octa* containing model carbons will provide the largest increase in surface area and additional small pockets for gas adsorption. Model carbons were inserted into simulation box together with PIM-1 chains at the weight ratio of about 1:10 (additive:polymer) (Table 4.1) and packed following 21 step compression method [4] in order to compare with pure PIM-1 and PIM-1-graphene composite properties reported in reference [1]. The systems were described using DREIDING force field [5] and charges were generated using QEq charge equilibration method [6]. The materials were characterized by surface area and pore size distribution (PSD). The parameters are explained in more detail in Chapter 2.

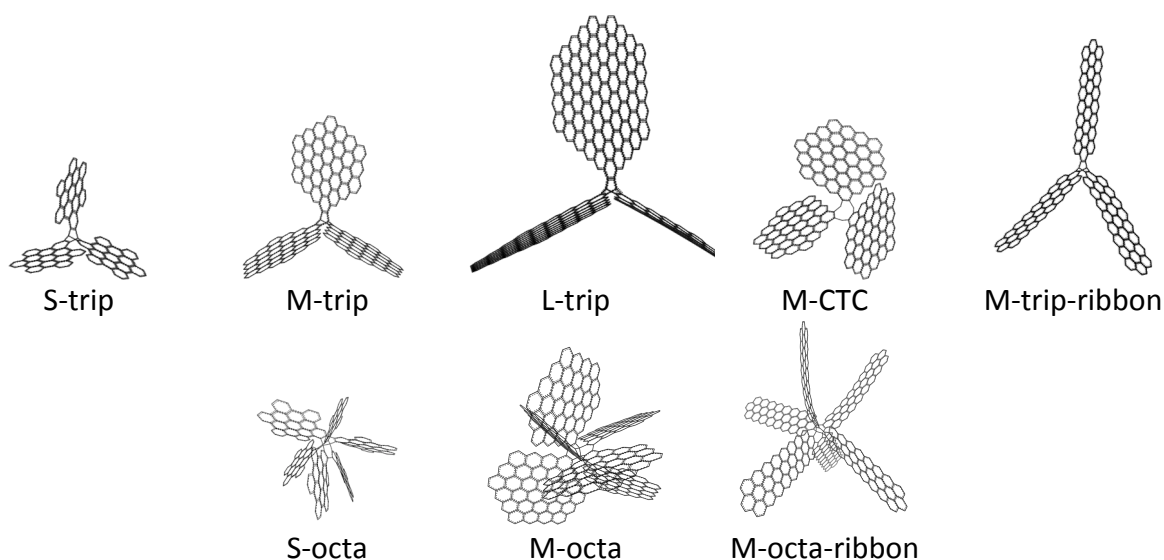


Figure 4.1. Chemical structures of models carbons used as additives to PIM-1. Letters *S*, *M* and *L* denote size of the graphene arm.

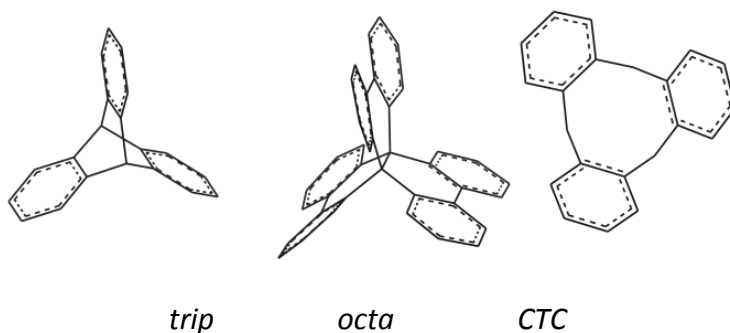


Figure 4.2. Structures of molecule's centres connecting graphene arms.

Table 4.1. Composition of composites.

System	No. of atoms $\times$ No. of molecules in a simulation cell
S-trip	178×4
M-trip	302×2
L-trip	568×1
M-trip-ribbon	286×2
M-CTC	309×2
S-octa	350×2
M-octa	602×1
M-octa-ribbon	566×1

4.3 Results

Figure 4.3 shows that there is only a marginal difference between the surface area of PIM-1 and that of composite materials. Some of the 3D additives increase surface area only by about 7 – 15 %. The model carbons that provided an increase or unaffected surface area are L-trip, M-trip-ribbon and S-octa. Interestingly, medium-sized (M) disk-shaped arms regardless of the core structure decrease surface area similarly to graphene platelets.

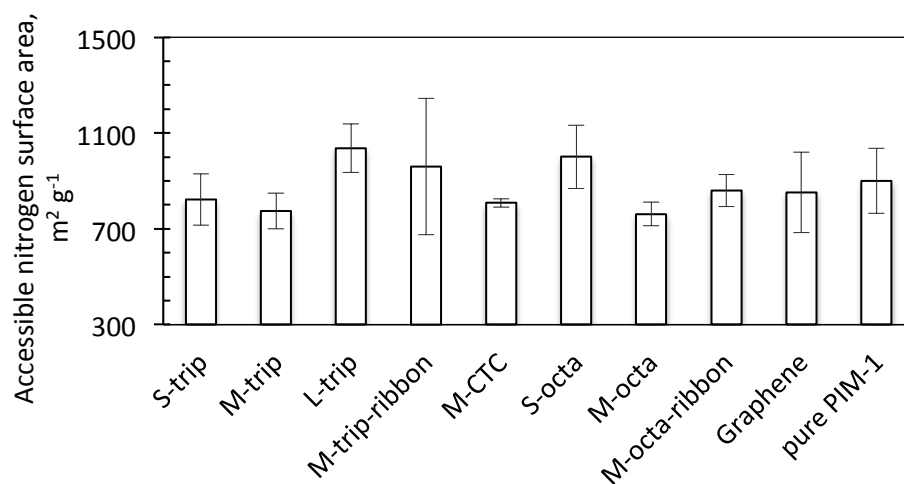


Figure 4.3. PIM-1 and model carbon composite's accessible nitrogen surface area.

The visualised PIM-1 chain arrangements close to model carbon reveal that chains tend to align face-to-face on graphene covering its surface (Figure 4.4). PIM-1 can easily wrap around the medium or small size graphene arms or replicate V-fold structure of trip containing additives due to the similarity between the PIM-1 monomer length and the size of the disk. This arrangement reduces the surface area and blocks the space potentially accessible for a gas molecule.

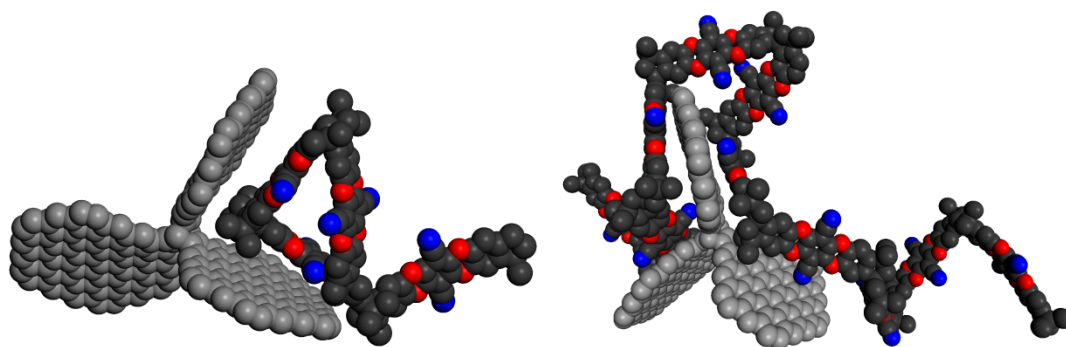


Figure 4.4. Representative arrangements of PIM-1 chain fragments close to M-trip model carbon.

Ribbon and large (L) disk-shaped arms are not commensurate with the monomer size resulting in weaker interactions between the polymer and the graphene arms due to conformational chain rigidity. Model carbons formed by ribbons despite its core slightly increase surface area. An increase in surface area due to presence of L-trip is more complicated; due to large size contribution of the core becomes less important and the affect is similar to the one obtained by mixing polymer with unconnected graphene platelets. Again, due to restricted motion polymer chains cannot pack as efficiently on larger graphene platelets resulting in composites with different structural properties as seen from wide error bar for L-trip in Figure 4.3

The increase in surface area due to presence of S-octa can be explained by its small arms that are tightly crowded on *octa* centre, thus PIM-1 chain cannot come into close contact with the arm.

The variation in surface area between the simulation boxes is large due to awkward polymer chain structure and any differences are within error bars. The presence of 3D carbon additives does not affect significantly the pore size distribution (Figure 4.5). There is slight variation, but PSD follow the same trend: the most pores are about 3 Å wide and the biggest pores are up to 10 – 15 Å wide. In the figure, PSD of only those model carbons that increased surface area are highlighted, while others are greyed out. Those PSD show slightly larger concentration of smaller pores and pores of width ranging from 5 to 15 Å, however the concentration of most common pores (~3 Å) is almost the same as in PIM-1.

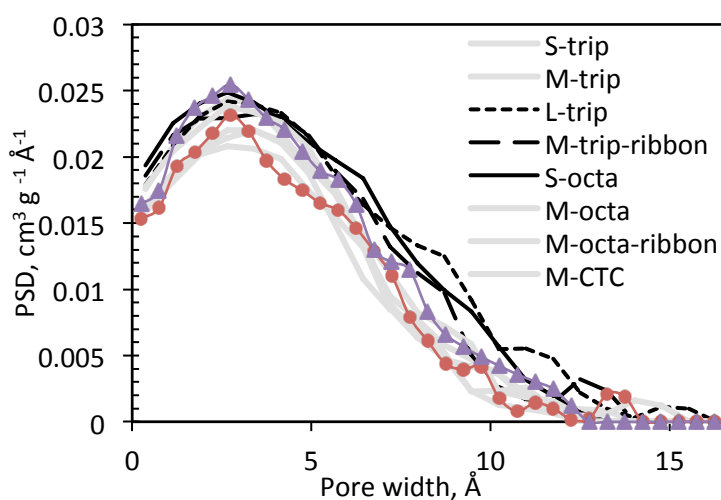


Figure 4.5. Pore size distribution of PIM-1 composites with various additives compared to pure PIM-1.

4.4 Conclusions

Triptycene unit as well as other rigid cores are essential building units to hold fragments in 3D space preventing them from packing efficiently. Nevertheless, the effect is minor when individual 3D molecules are dispersed into a polymer. Results suggest that an increase in surface area can be observed when the arm size of the 3D additives is not commensurate with the monomer length. Small or narrow arms do not promote chain-graphene stacking while larger arms disrupt chain packing on graphene surface due to awkward chain shape. Nevertheless, the increase in surface area is not significant and the results were not encouraging enough to pursue further study.

4.5 References

1. Gonciaruk, A., et al., *PIM-1/graphene composite: A combined experimental and molecular simulation study*. Microporous and Mesoporous Materials, 2014.
2. Simpson, C.D., et al., *Nanosized Molecular Propellers by Cyclodehydrogenation of Polyphenylene Dendrimers*. Journal of the American Chemical Society, 2004. **126**(10): p. 3139-3147.
3. Zhang, C., et al., *Three-Dimensional Nanographene Based on Triptycene: Synthesis and Its Application in Fluorescence Imaging*. Organic Letters, 2012. **14**(23): p. 5912-5915.
4. Larsen, G.S., et al., *Molecular Simulations of PIM-1-like Polymers of Intrinsic Microporosity*. Macromolecules, 2011. **44**(17): p. 6944-6951.
5. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
6. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358–3363.

5 IN SILICO DESIGNED MICROPOROUS CARBONS

This chapter is adapted from the manuscript published in Carbon¹. Authors: Aleksandra Gonciaruk², Flor R. Siperstein²

Abstract

This work presents a computational study on the packing of three-dimensional carbon nanostructures and their effect on gas adsorption properties. We show that it is possible to obtain intrinsically microporous materials without specifying structural properties such as surface area or pore size distribution by packing individual graphene platelets connected at a contortion site. The resulting structures can potential represent disordered carbons and provide understanding of relationship between pore structure and adsorption performance. The calculated CO₂/CH₄ selectivity of these materials at the zero coverage selectivity can be as high as 25, while at low finite pressures (0.05 bar) is between 6 and 10, which is comparable with what is expected for most carbons. We compare the results to the ones obtained from a simple slit pore model and highlight the importance of pore morphological complexity to adsorption of industrially important gases.

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5.1 Introduction

Activated carbons have been used for thousands of years but an accurate microscopic description of their structure is still a mystery. Controlling their properties is a balance between art and science. Much research has been done in understanding the roles of the precursors and activating procedures, and the use of molecular simulation and reconstruction techniques has provided some insight into the fundamental properties of these materials.

The use of predesigned carbonaceous structures in the synthesis of these materials has been proposed by Simpson *et al.* using an aromatic ring at the centre of the molecule or a tetrahedral carbon with graphene-like arms [1]. The materials proposed by Müllen have a flexible core, which is expected to lead to non-porous structures. An alternative is to use a rigid core, similar to the one used in Organic Molecules of Intrinsic Microporosity [2] or Polymers of Intrinsic Microporosity [3] to create an inherently microporous structure. In this work, we aim to predict the properties of in-silico designed porous carbons using a systematic approach. The carbons are constructed using a well-established methodology to pack molecules that form amorphous materials [4]. The carbonaceous molecules contain a central unit that will be named core, and graphene-like arms that will provide the environment for adsorption. The molecules are designed to allow us assessing the role of core centre as well as the size and shape of the arms. Although these materials have not been synthesised to the best of our knowledge, the virtual structures obtained are expected to serve as a starting point to understand the connectivity between twisted and defective carbon sheets, the effect of edges, and packing abilities based on the precursors.

Molecular models of carbons have been studied since the pioneering work of Steele, and the derivation of the 10-4-3 potential for slit pores [5]. The slit pore model has served to characterise porous carbons by inversion of the adsorption isotherms to obtain the pore size distribution. Currently Density Functional Theory (DFT) models to obtain pore size distribution are common practice in most laboratories [6, 7]. Nevertheless, the slit pore model cannot capture all the properties of activated carbon, which possesses great structural and chemical complexity. Significant efforts have been made to construct realistic models of porous carbons. The most physically sound approach is mimetic method that imitates experimental synthesis process. This is achieved using quench molecular dynamic [8, 9] where gas or liquid carbon atoms are rapidly cooled simultaneously forming bonds resulting

in connected amorphous structures or using canonical ensemble Monte Carlo simulation, which evolves amorphous polymer to a disordered sp^2 hybridised carbon by reforming bonds [10]. Another computationally expensive approach is reverse Monte Carlo (RMC) techniques that also reconstructs realistic disordered porous carbons structures by fitting experimental diffraction data of real materials [8, 11-16]. Although these methods provide reasonable model structures for a specific material, it is difficult to generalise the information obtained from the simulations to a broader class of materials. Using well-defined building blocks or periodic structures as part of the model material complements the knowledge gained from very specific models. The amorphous structure of nanoporous carbons can also be represented by fullerenes, bundles of carbon nanotubes or a foam-like hypothetical C_{168} Schwarzite for surface morphology, for adsorption and diffusion studies [17-19]. An alternative approach that has gained significant attention consists in packing of idealised structures: structureless platelets [20, 21], atomistically described platelets [22], the construction of virtual porous carbons [23]. Carbon models formed by unconnected building blocks lack some of the features that make an amorphous carbon self-standing material thus the method requires density, surface area and/or pore size distribution input data. We are particularly interested in exploring the latter approach of individual fragment packing but we introduce connectivity between them to obtain free standing material without the need of structural data.

This work follows on the idea of packing individual molecules to describe a carbonaceous material, but we do not explicitly specify the porosity (surface area or density of the material), which is necessary when using simple molecules like coronene [22]. The equilibrium structure of coronene would not be a porous carbon, but stacks of molecules packed together. We are able to obtain porous structures without imposing a predefined surface area as a result of having rigid contortion sites as part of the designed molecules. Although real carbon materials may not be equilibrium structures as prepared, aging of the materials is expected to move them towards an equilibrium structure, therefore understanding the differences between materials with connected and unconnected graphene platelets can help understanding aging of these materials.

This paper assess properties of carbonaceous materials obtained from packing pre-designed three-dimensional (3D) molecules and compares them with the carbon model proposed by Di Biase and Sarkisov [22]. We test the validity of using a simple slit pore model with the calculated pore size distribution on the model material to predict the CO_2 and CH_4 adsorption

at low pressures, which highlights the importance of platelet edges and various pore shapes observed in different materials.

5.2 Methodology

5.2.1 Preparation of Carbon Materials

Models were constructed and graphical displays generated using Materials Studio, Accelrys Software Inc. (San Diego, CA). Interactions between atoms are described using the DREIDING forcefield [24]. This forcefield has been used previously to model structurally and chemically similar materials known as Organic Molecules of Intrinsic Microporosity [25] and porous aromatic frameworks [26].

Graphene arms were created in planar form by connecting six-membered carbon rings. The edge carbon atoms of the graphene were saturated by connecting hydrogen atoms. Four different arms were constructed (Figure 5.1): small (S), medium (M), large (L) arms of disk shape and medium size ribbon-like arm (M-ribbon). The arms were then connected through two different centres inspired by triptycene ([2.2.2]propellane, hereinafter *trip*) and cyclotricatechylene (hereinafter *CTC*) (Figure 5.2). The spherical structure of *trip* possesses rigid threefold symmetry that keeps graphene arms separated in 3 dimensions, while *CTC* centre is very flexible, thus allows for greater freedom for intramolecular graphene arms to form a single stack. Five different materials were obtained by connecting arms and cores: S-*trip*, M-*trip*, L-*trip*, M-*CTC* and M-*trip*-ribbon.

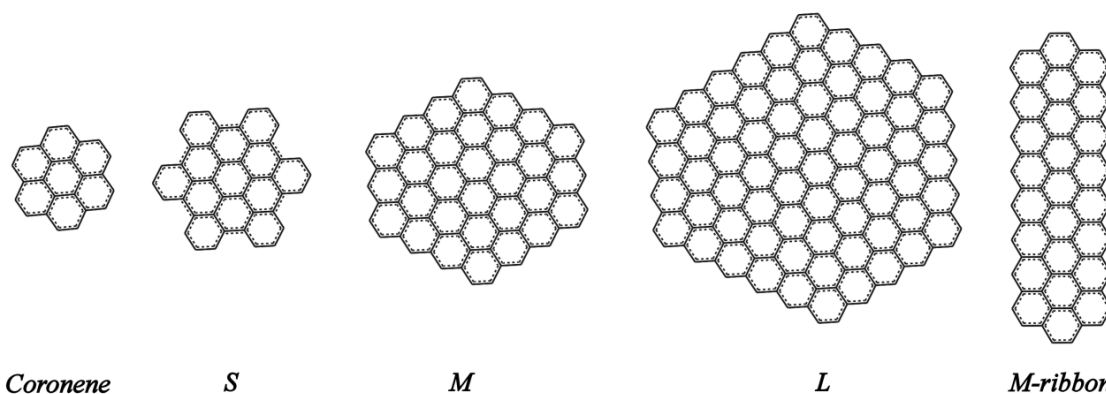


Figure 5.1. Disk shape arms of S – small, M – medium and L – large sizes and ribbon-like arm of M- medium size, and coronene molecule.

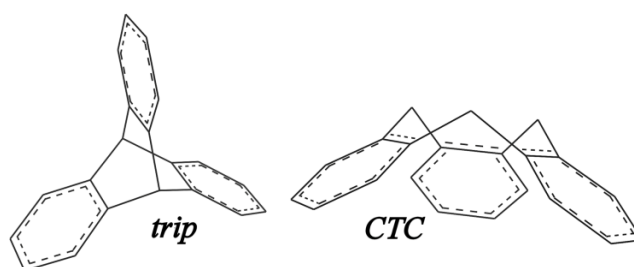


Figure 5.2. Centres of model carbons.

5.2.2 Compression Methodologies

The structures were packed in a low density box of 60 nm^3 with periodic boundary conditions. The number of molecules varied between the systems to achieve a target density 0.49 g cm^{-3} . Three simulation boxes were constructed for each of five model carbon structures obtain averaged results. The systems were then compressed using different packing procedures. The first packing method is based on the 21 step compression and decompression scheme described in Larsen *et al.* work [4]. We used slightly modified procedure to speed up the packing process, where all the NVT steps at 300 K were half as long as what was proposed initially [4]. Another method involves more rapid and less drastic compression pressure. The scheme is provided in Table 5.1. Molecules have more freedom to move at the first stage, where temperature is kept at 600K and initial large volume is constrained. After this extended step system is cooled down and compressed to maximum of 1000 bar pressure following decompression to 1 bar.

In order to assess importance of the core, graphene arms were also packed into boxes without connecting them through the core. In this way, it is expected to obtain denser systems, since movement of unconnected arms are not constrained by the core.

Table 5.1. Molecular dynamic compression schemes.

Scheme 1			Scheme 2		
Step	Conditions	Duration (ps)	Step	Conditions	Duration (ps)
1, 2	NVT 600K, 300K	50, 50	1	NVT 600K	200
3	NPT 1,000 bar, 300K	50	2	NVT 300K	50
4, 5	NVT 600K, 300K	50, 50	3	NPT 1 bar, 300K	50
6	NPT 30,000 bar, 300K	50	4	NVT 600 K	50
7, 8	NVT 600K, 300K	50, 50	5	NVT 300 K	50
9	NPT 50,000 bar, 300K	50	6	NPT1000 bar, 300K	50
10, 11	NVT 600K, 300K	50, 50	7	NVT 600K	50
12	NPT 25,000 bar, 300K	5	8	NVT 300K	50
13, 14	NVT 600K, 300K	5, 5	9	NPT 1 bar, 300K	100
15	NPT 5,000 bar, 300K	5			
16, 17	NVT 600K, 300K	5, 5			
18	NPT 500 bar, 300K	5			
19, 20	NVT 600K, 300K	5, 5			
21	NPT 1 bar, 300K	800			

5.2.3 Slit Pore

We created a slit pore model (Figure 5.3) to test if the simpler model can predict the same CO₂ and CH₄ adsorption as in the system of model carbons. In the slit pore model adsorption occurs on the basal plane of graphene eliminating possibility of adsorption at the edges. Crystal structure of graphite was imported from pre-existing file stored in Material Studio database. The structure is a stack of two infinite graphene sheets (Figure 5.3) confined in the periodic boundary box. The size of the superlattice was expanded parallel to graphene sheets to obtain sheets of 306 rings. The separation between two stacks was varied from 0.4 Å to

20.1 Å to represent the range of pores observed in the model carbons. The DREIDING force field was also used to describe interactions between the atoms.

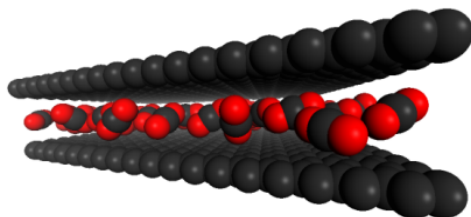


Figure 5.3. Slit pore simulation box with pore size of 0.34 nm. Carbon atoms are shown in black. A single layer of adsorbed CO₂ is also shown.

Additionally, a material where the pores are formed by the edges in the model carbons was constructed. We denote this material as an “edge pore”. The edge pore was modelled as a two stacks of 6 infinite graphene sheet separated by a distance of 3.4 Å, the edges of the carbon sheets were capped by hydrogen atoms (Figure 5.4).

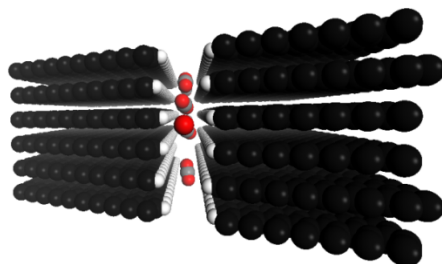


Figure 5.4. Edge pore simulation box. Pore carbon atoms are shown in black and hydrogen atoms are shown in white. Adsorbed CO₂ molecules with carbon (grey) and oxygen (red) atoms are also shown.

5.2.4 Structure Characterisation

The models were characterised and compared in terms of density, accessible nitrogen surface area, helium pore volume and pore size distribution (PSD). The parameters are explained in more detail in Chapter 2. The helium pore volume is provided in 5.5 Supplementary Information along with surface area accessible to CO₂ and CH₄.

Radial distribution functions (RDFs) were calculated for carbon atoms of the developed structures (C-C RDF). An RDF is the measure of probability finding two atoms at a given

spherical distance. The function is commonly given the $g(r)$ symbol. Both experimental and calculated RDFs for carbon atoms are available in the literature and the comparison will shed light onto realism of the obtained structures.

A graphical method was used to understand the shape of the pores around adsorbed molecules. In a given structure, atoms were selected within radial distance of 11 Å from a CO₂ molecule. The range from 4 to 11 Å was divided into 8 bins. The colour to each bin was selected from rainbow spectrum. Atoms that fall within each bin were assigned specific colour: the closest atoms were coloured warmest colour (red) and atoms that are at a 10-11 Å distance were coloured coolest colour (dark blue).

5.2.5 Adsorption of Gases

The computational results were obtained using the aforementioned Material Studio software. The Henry constant simulation was performed using Metropolis grand canonical Monte Carlo (GCMC) method [27] at 298 K. Adsorption of CO₂ and CH₄ were calculated at 298 K and 0.05 bar after 1×10^6 equilibration and 9×10^6 production steps, which include exchange, rotation, translation and regrowth types. The heat of adsorption was obtained from GCMC simulations at fixed 0.05 bar pressure (see 5.5 Supplementary Information). The CO₂/CH₄ selectivity was calculated assuming equimolar mixture composition. A three-site model was used for the CO₂ molecule where two oxygen and carbon atoms are explicitly modelled, and a five-site model was used for CH₄, where all atoms are modelled explicitly. The Lennard Jones parameters and charges for each atom are available in 5.5 Supplementary Information (Table 5.2).

Adsorption of CO₂ and CH₄ in the model carbons as predicted by the slit pore model was calculated on the basis of the model carbon pore size distribution determined using Poreblazer and CO₂ and CH₄ adsorption at 0.05 bar and 298 K in slit pores. The amount of gas adsorbed N at temperature T and pressure P is obtained using the adsorption equation:

$$N(P, T) = \sum_{i=0}^n \rho(w_i, P, T) f(w_i) (w_i - w_{i-1}) \quad (5.1)$$

where ρ is the gas loading in slit pore model of width w , f is pore size distribution as determined by Poreblazer.

RDF were also calculated between CO₂ molecules and aromatic carbon atoms and hydrogen atoms positioned at arm edges in order to investigate the composition of the pore surface and understand how this affects adsorption of gas molecules.

5.3 Results

5.3.1 Structural Properties

Packed model carbons retain microporosity. The rigid 3D structures prevent molecules from packing efficiently leaving free interconnected voids. Model carbons have varying nitrogen surface area ranging from 175 to 500 m² g⁻¹ (Figure 5.5). Although these values are small compared to typical activated carbon, one should keep in mind that the porosity in the materials modelled in this work is a result of the inability to pack efficiently the selected building units. No experimental information, such as the material's density, porosity or XRD was used. The S-trip having smallest arms have the lowest surface area while the rest model carbons have very similar surface area. M-CTC system have slightly smaller surface area most likely due to less rigid core, which allows two of the three arms to overlay in some cases. This is consistent with the work of Abbot *et al.* [28] where they determined direct relationship between core rigidity and surface area in discrete molecules (OMIMs). Nevertheless, the difference between the surface area of M-CTC and M-trip is small. This suggests that packing of the model carbons is governed by the size of the arm rather than its core structure. However a rigid core keeps arms apart preventing structures from packing efficiently. In all of the cases, model carbons have significantly higher surface area comparing to that of coronene and larger platelets, which are not connected through the core. In this case, smaller arms create denser structures as the surface area increases with the increase of the arm. Although it was shown in previous studies that bulkier groups lead to increased porosity [28, 29], in our case, the trend is not clear. S-trip, which has smallest arms also has lowest surface area but M-trip and L-trip create very similar surface area. Presumably, due to planar

shape larger arms sense stronger attraction and layering of the arms is more evident. Shape of the arm does not influence differences as ribbon-like and disk arms have very similar surface area. Differences between the packing schemes are shown in 5.5 Supplementary Information (Figure 5.18).

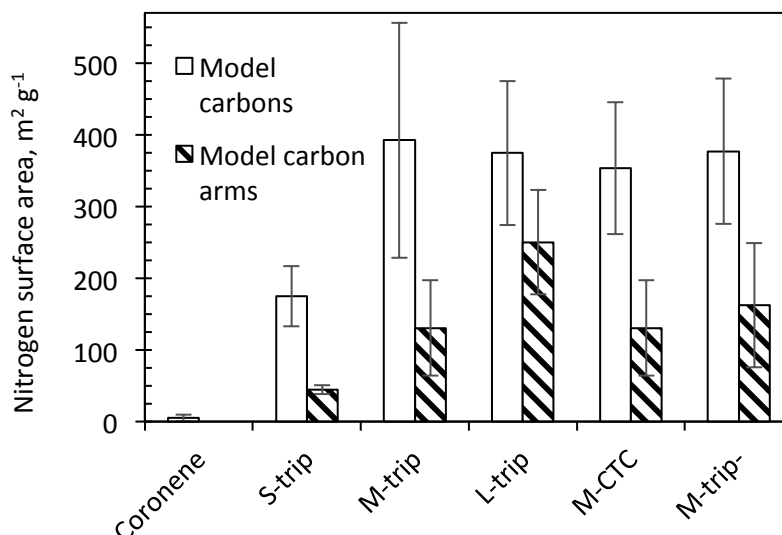


Figure 5.5. Nitrogen surface area of packed model carbons (filled bars) and unconnected graphene platelets (stripped bars).

Coronene form up to 12 molecule stacks in a unit cell leaving a negligible amount of space between the stack edges as small coronene move more freely and interact with other molecules. The stacks do not seem to align in any particular direction over the time of simulation. A slower equilibration and lower temperatures could favour the crystallisation of coronene. Boxes containing only graphene arms of different size and shapes as the ones shown in Figure 5.1 also form stacks. The stacks formed are significantly smaller than those observed with coronene. The materials formed exclusively by graphene arms can reach significant surface areas, but always smaller than the model carbon with same arm size connected to a rigid core.

Figure 5.6 shows RDF between carbon atoms in model carbons. All model carbons produced almost identical functions with the distinctive peaks at 1.45 and 2.45 Å corresponding to first and second carbon-carbon neighbours in graphene lattice. The two peaks in the range from 3.75 to 4.25 Å correspond to interlayer distance between two graphene arms and/or distance between two further carbon atoms within the same graphene sheet. The local ordering

decreased rapidly with no prominent features at distances larger than 8 Å. The function is in good agreement with those calculated for structures generated using computational methods [8-10] and those obtained for real disordered carbon materials [8, 9, 12, 30-32] maintaining all the distinctive features, which indicates disordered nature of the model carbons. However RDF peaks of model carbons obtained in this work are better resolved than RDFs obtained for highly disordered carbon materials. In our work, almost all carbon atoms are locally ordered forming fragments of graphene sheets compared to real disorder carbons where defective five and seven membered rings are observed, generating a significant disorder at short distances. Therefore, it is not surprising that our structure resembles carbon of lesser degree of activation (which is less disordered), where the third peak at about 3 Å is well resolved [31, 32]. It is worth noting that the RDF is not an absolute measure of structure's realism. As discussed in Palmer and Gubbins work [8] two structurally distinctive materials can produce identical RDFs. They further explain that the validity of a structure cannot be determined by an RDF, as materials with an “unphysical morphology” can lead to the same RDF as realistic materials. Therefore the analysis of a model structure RDF should always be accompanied by complementary information.

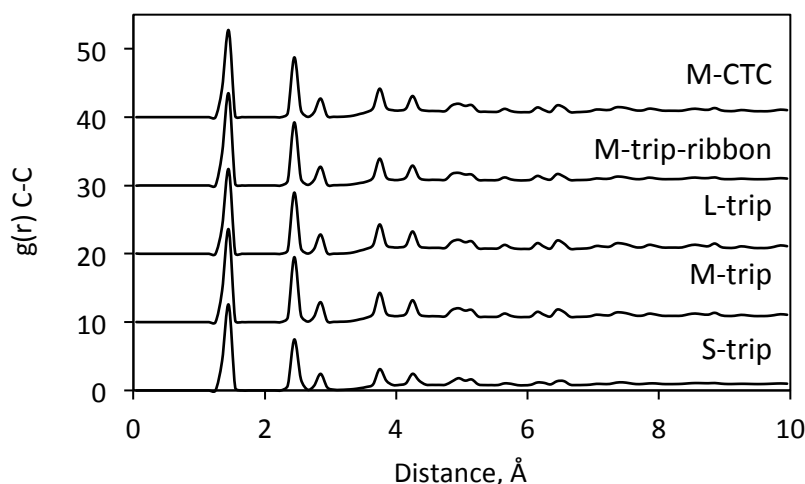


Figure 5.6. Averaged RDF between carbon atoms in model carbons (the values are offset by 10 for clarity).

The pore size distribution (PSD) of all compressed model carbons is very similar (Figure 5.7). All PSDs have similar shape with a significant fraction of the pores smaller than 2 Å; the volume of pores decreases rapidly between sizes of about 2 and 10 Å. All PSDs exhibit tailing towards wider pores. All model carbons possess a high concentration of large pores (>10 Å)

except S-trip. In the case of disordered materials, one must be careful when interpreting the features observed at the largest scale that the simulation box can accommodate, as finite size effects can play an important role.

Average pore sizes for these materials can be obtained from the pore size distribution. Average pore size increases with the increase of arm size ranging from 0.31 nm for S-trip to 0.61 nm for L-trip with M-trip having the middle 0.56 nm average pore size. M-trip-ribbon also have intermediate pore size of 0.54. M-CTC has slightly smaller average pore of 0.49 nm, and coronene have the smallest 0.19 nm pores.

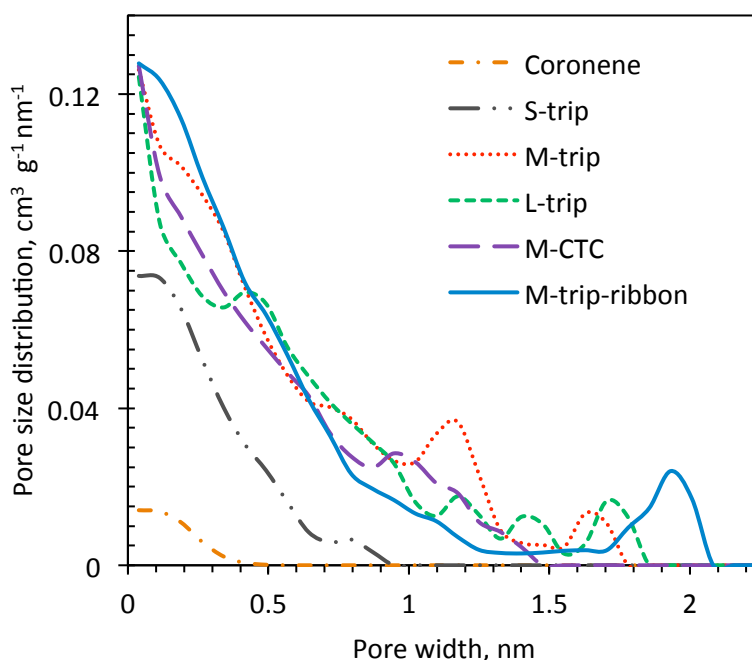


Figure 5.7. Pore size distribution in packed model carbons and coronene.

PSD obtained for model carbons studied in this work has a slightly different shape compared to PSD of experimental carbon materials as well as those generated computationally [8, 22, 30, 33]. PSD peaks of model carbons are shifted to smaller pore sizes and does not capture mesoporous region that is often present in disordered carbons. This can be attributed to smaller pore volume created by these structures in general (see 5.5 Supplementary Information Table 5.4 and Figure 5.21). The high concentration of pores smaller than 0.5 nm can be the result of tiny pores created between the layers of graphene arms. Larger volume can be created by manipulating the packing procedure or extracting the snapshot of desired structure from the range of frameworks created during packing. Great diversity of model

carbons might be created by selecting different core structures that could connect not three but four or more graphene arms of different shapes and sizes thus creating variety of structures tailored to reproduce experimental materials if needed. Furthermore, introduction of graphene sheet imperfections, such as missing carbon atoms, 5-membered carbon rings or carboxylic groups, may produce greater disorder of the structure by increasing interlayer distance.

5.3.2 Adsorption Selectivity and Capacity

Model carbons have higher selectivity towards CO_2 over CH_4 and it can reach up to 23 (Figure 5.8). The selectivity does not appear to depend on the structure of the molecule used to create the carbon structure. S-trip has the highest selectivity of all carbon materials modelled, then the selectivity decreases with the increase of arm size. M-trip-ribbon has very similar selectivity to that of other model carbons connected through *trip* core. The selectivity is lower for coronene, M-CTC and L-trip. This trend is expected as the work of Tan and Gubbins [34] showed that a maximum in selectivity is expected at a specific pore size in slit pores. Nevertheless, the small selectivity showed in M-CTC is not explained by the trend observed in simple systems, suggesting that caution should be taken when extrapolating properties between families of materials with different cores. Coronene seems to be as selective as some model carbons, however this result should be considered with care. Coronene have a very confined space, which is less geometrically restricted for smaller linear CO_2 molecule comparing to larger CH_4 . However the inner free volume of the real material most likely would not be accessible.

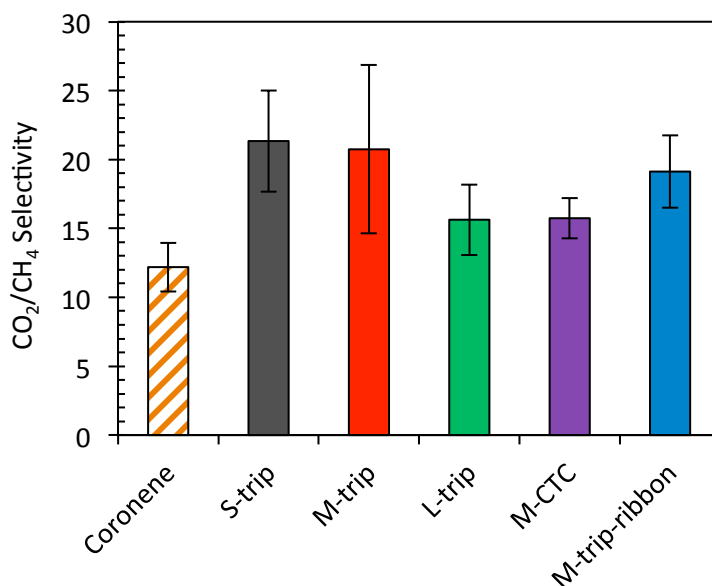


Figure 5.8. The CO₂/CH₄ selectivity in packed model carbons and coronene as calculated from Henry constant simulation at 298 K.

The two methods used to determine the selectivity led to slightly different results. Selectivity calculated from constant 0.05 bar pressure adsorption simulation is more than twice smaller than that obtained from Henry constant simulation (Figure 5.9), except for coronene, which selectivity is almost the same regardless of the method used. When compared to selectivity calculated from Henry constant simulation, the trend itself does not change among model carbons. Even when a pressure of 0.05 bar was considered sufficiently low to be in the Henry's law regime, the differences obtained suggest that the Henry's law is not observed at this pressure. It is possible that a small amount of high-energy sites exist in these materials, which would be completely fully occupied even at low pressures. The CO₂/CH₄ selectivity predicted at 0.05 is on the same order of magnitude as reported for various activated carbons [35-38], however is still higher. This can be explained by the narrow pore size distribution that is distinctly shifted to small pore sizes as compared to real activated carbons; larger pores, more readily accessible for both molecules, are expected to produce lower selectivity.

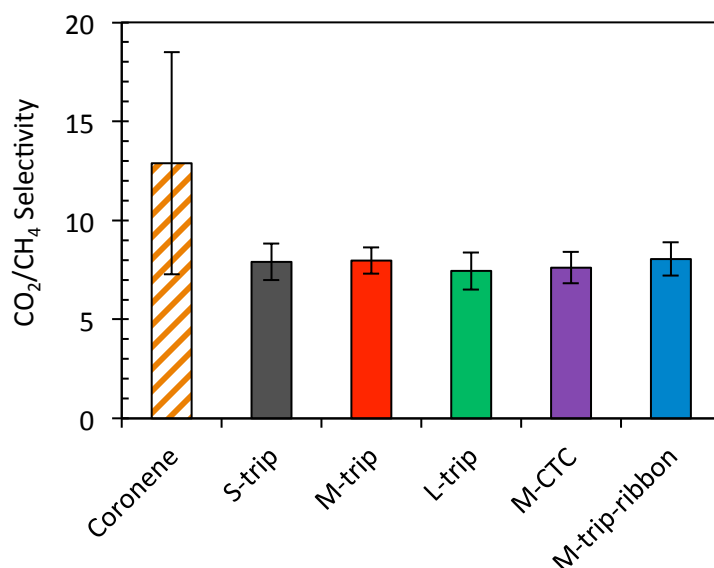


Figure 5.9. The CO₂/CH₄ selectivity in packed model carbons and coronene as calculated from loading at 0.05 bar fixed pressure and 298 K temperature.

Although there is always the temptation to use simple models to predict the behaviour of complex materials, the use of the slit pore model may not be appropriate for all the materials shown in this work. We calculated the adsorption of CO₂ and CH₄ in a collection of slit pores, and used the geometric pore size distribution to determine the total amount adsorbed in a material composed exclusively of slit pores that has the same PSD as the model carbons generated with complex molecules. Figure 5.10 shows that the amount adsorbed of both CO₂ and CH₄ cannot be predicted by simple slit pore model. Even with wide error bars, the agreement is beyond them in some of the cases. Almost all of the model carbons except M-CTC adsorb more CO₂ than the simple slit pore. Even when for some materials, such as M-trip, L-trip and M-CTC there is good agreement, in other cases the discrepancies go beyond the error bars. Carbons with a trip centre adsorb more CO₂ than what the slit pore model predicts, suggesting the existence of more favourable adsorption sites than a simple slit geometry, which can be highly confined spaces created by three or more platelets (Figure 5.11 A). M-CTC shows lowest gas loadings than those predicted by the slit pore model. This suggests that there are weaker interactions between M-CTC and gas molecules than in slit geometry. This is most likely due to a sufficient amount of pores created by the edges of arms or combination of edges and arm surface (Figure 5.11 B-D). Nevertheless, M-trip, L-trip and M-CTC materials could be represented by the slit pore model. This suggest that in materials where the platelets are sufficiently large, the slit pore model is still a good approximation, as

most of the pore volume will be formed by slits, and the contribution of edges or other pore shapes will be negligible (or compensate one with the other).

Adsorption of CH_4 in model carbons versus its loading in slit pore have a different trend to what was observed for CO_2 ; most of the points are below the straight line except for S-trip, which retains more favourable adsorption compared to the slit pore.

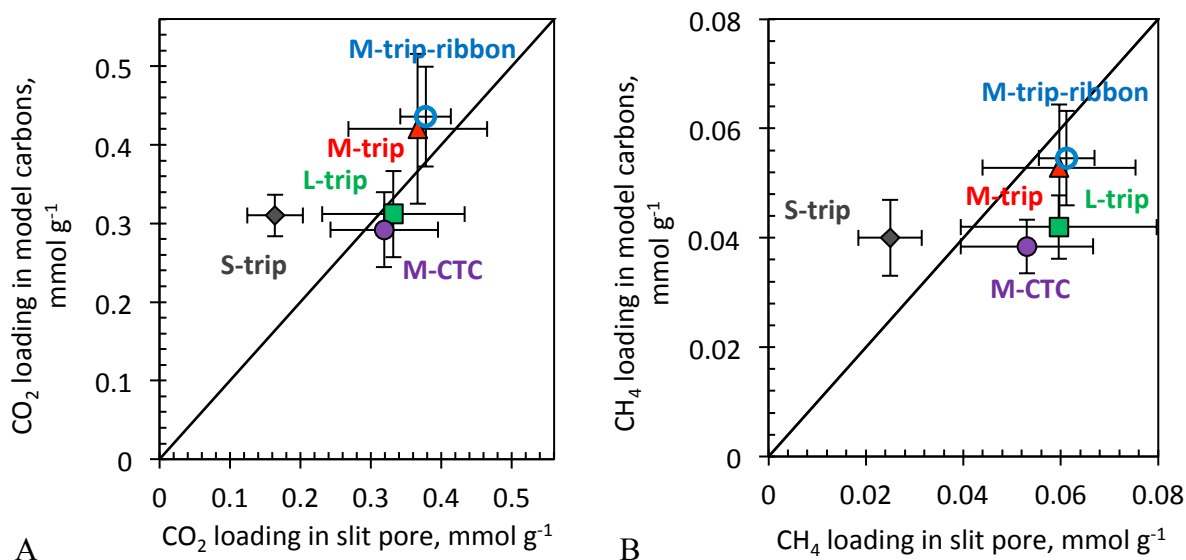


Figure 5.10. CO_2 (A) and CH_4 (B) loading calculated directly in model carbons versus loading predicted by slit pore model at 0.05 bar pressure (diamond – S-trip, triangle – M-trip, square – L-trip, closed circle – M-CTC and open circle – M-trip-ribbon).

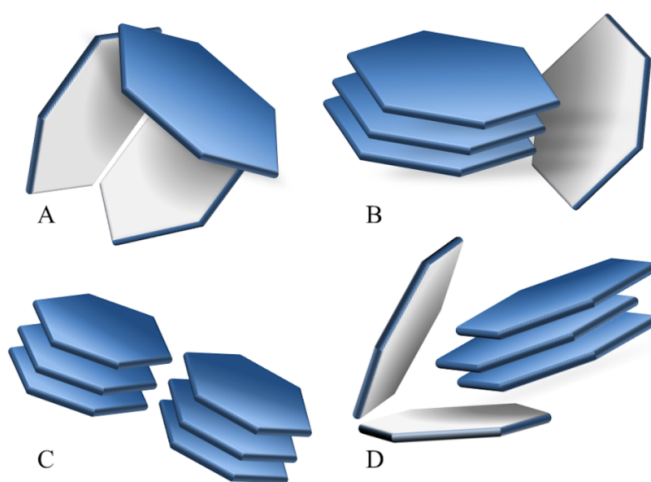


Figure 5.11. Schematic representation of possible arm positions.

The results shown in Figure 5.10 are expanded in Figure 5.12 where each point represents one simulation box, so there are 6 points (three boxes per packing scheme) for every model carbon structure. It is clear that systems with measureable different properties are obtained even if the same packing method is used (Figure 5.13). In general, the 21-step method produces boxes that have a higher density than the method where compression is capped to 1000 bar. Nevertheless, the translation of higher density to higher or lower amount adsorbed is not evident, as the pore structure plays an important role. Interestingly, systems where the predicted amount adsorbed is smaller than the calculated from GCMC simulations have a helium accessible pore volume below $0.075 \text{ cm}^3 \text{ g}^{-1}$ (see 5.5 Supplementary Information Table 5.4 and Figure 5.21). The selectivity is not sensitive to the compression method used, but in all cases the selectivity calculated for model carbons is higher than the predicted one from the slit pore model (5.5 Supplementary Information, Figure 5.20).

The points above the straight line indicate that model carbons have more complex pore morphology and stronger energetics than the slit pore model. The importance of including pores of other geometries such as triangular and rectangular is discussed in the literature [39–41]. Such diversity of structures is important to describe accurately the material's PSD and high heats of adsorption observed experimentally. The materials obtained in this work spontaneously create a variety of pore shapes by simply specifying the structure of the building units.

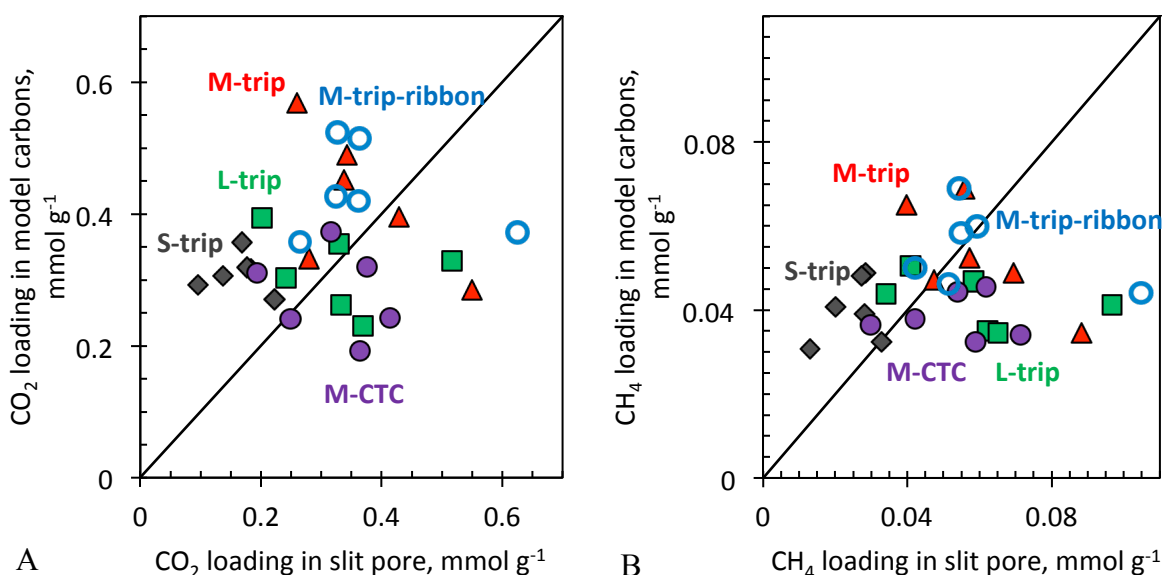


Figure 5.12. CO_2 (A) and CH_4 (B) loading calculated in model carbons versus predicted loading by the slit pore model at 0.05 bar pressure.

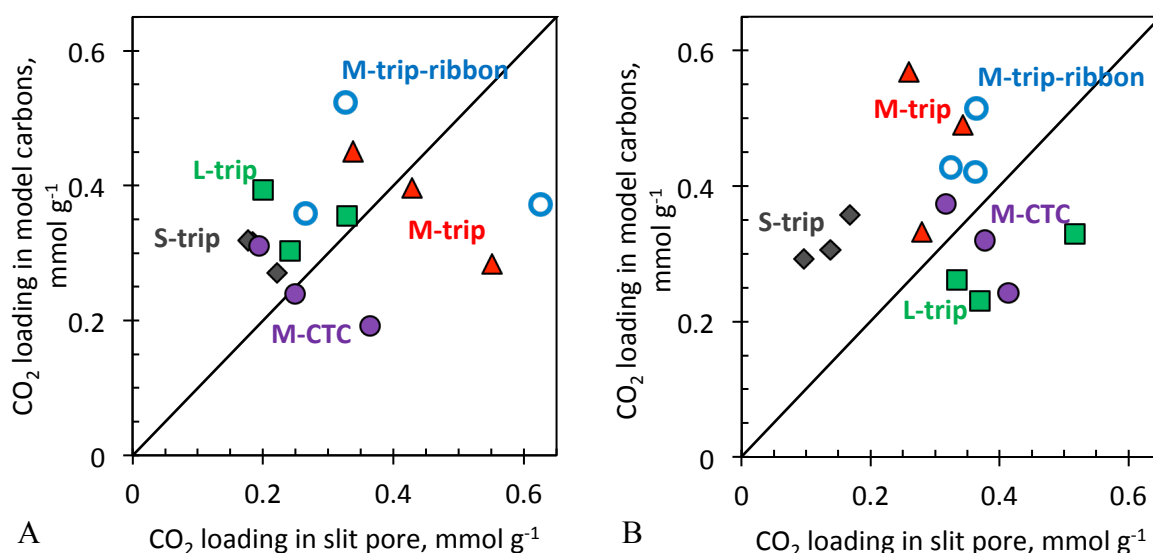


Figure 5.13. CO₂ loading in model carbons generated using scheme 1 (A) and scheme 2 (B) versus predicted loadings in slit pore model at 0.05 bar pressure.

Figure 5.14 and Figure 5.15 shows two RDFs between CO₂ and aromatic carbons (C) or edge hydrogens (H) of the model carbons. In all of the cases, peaks of hydrogen are more intense than peaks of aromatic carbons in the range between 3.75 – 6.25 Å. This is explained by the fact that there are less hydrogen atoms than aromatic carbons in systems thus the normalization factor enhances the value of the CO₂-H RDF first peak. To qualitatively assess the amount of pores formed by edges we compared the ratio of the first peak in the CO₂-H RDF to the first peak in the CO₂-C RDF (Figure 5.16). This comparison shows that L-trip and M-CTC materials form pores where arm edges play an important role in comparison to other materials. In all cases, the contribution of the edges is small compared to the contribution of the slits, given the dramatic difference between the values calculate for disordered model materials and pore formed exclusively by edges. Nevertheless, the difference in structures explains the variation in the applicability of the slit pore model.

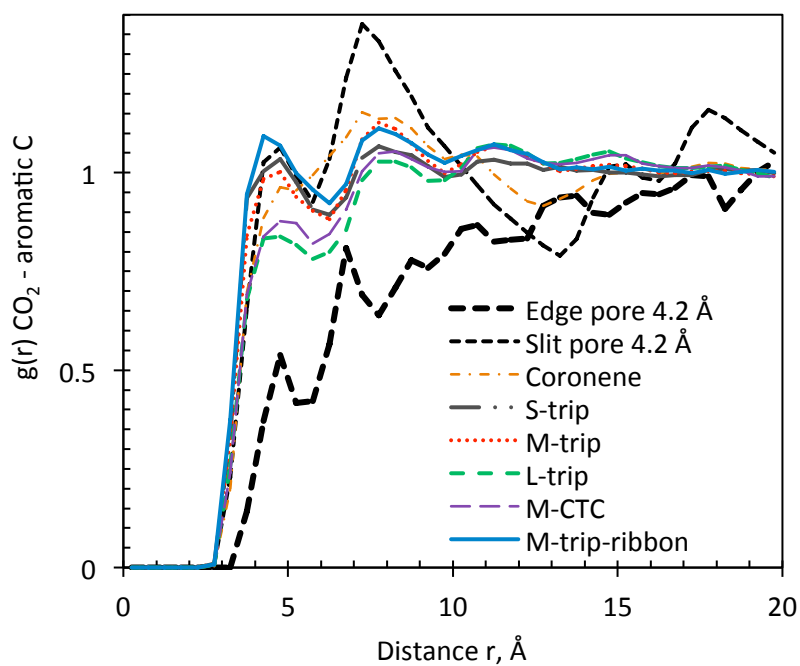


Figure 5.14. RDFs between CO₂ and aromatic carbons.

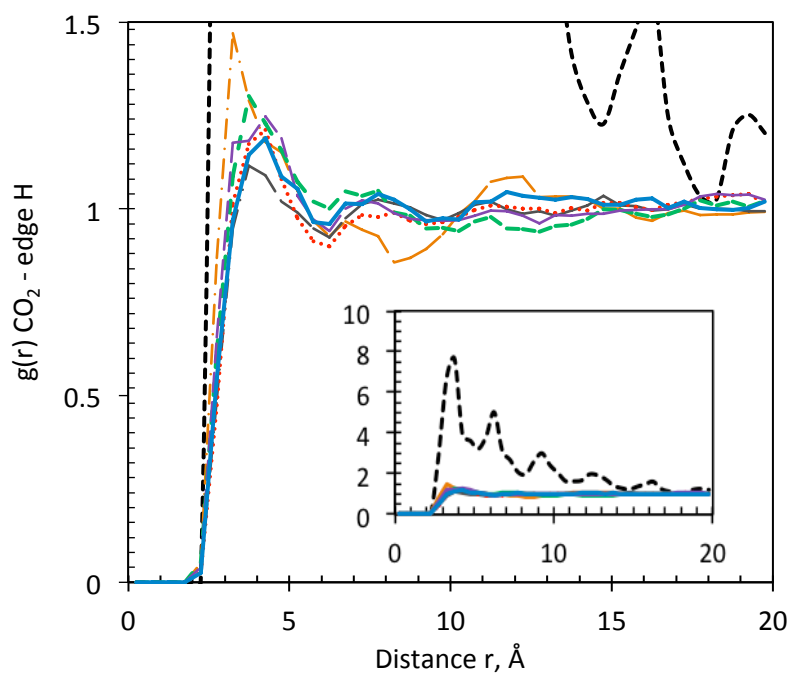


Figure 5.15. RDFs between CO₂ and edge hydrogens (Legend is shown in Figure 5.14).

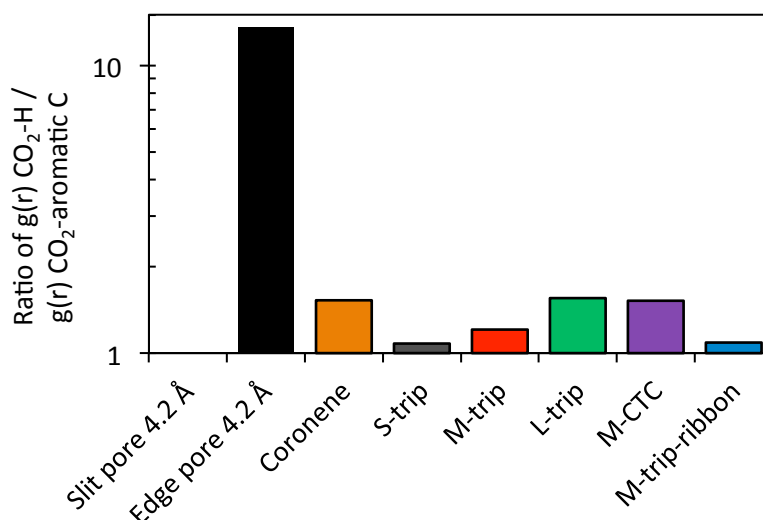


Figure 5.16. Ratio between maximum peak values of $\text{CO}_2\text{-H}$ RDF and $\text{CO}_2\text{-aromatic C}$ RDF within 3.25 – 6.25 Å radial distance.

We propose that a measure of the edge contribution to the pore structure is a ratio of the H/C peak in a model carbon to the H/C peak in an edge pore. This ratio is zero for an infinite slit and 1 for an edge pore. Using this criterion, the amount of pores formed by edges of platelets will range from 8 to 11.5 % in the studied model carbons.

Quantifying the contribution of more energetically favourable pore shapes compared to a perfect slit is difficult, given the diversity in pore structures and the difficulty in systematically identifying them. Representative examples of different kind of pores created in model carbons are shown in Figure 5.17.

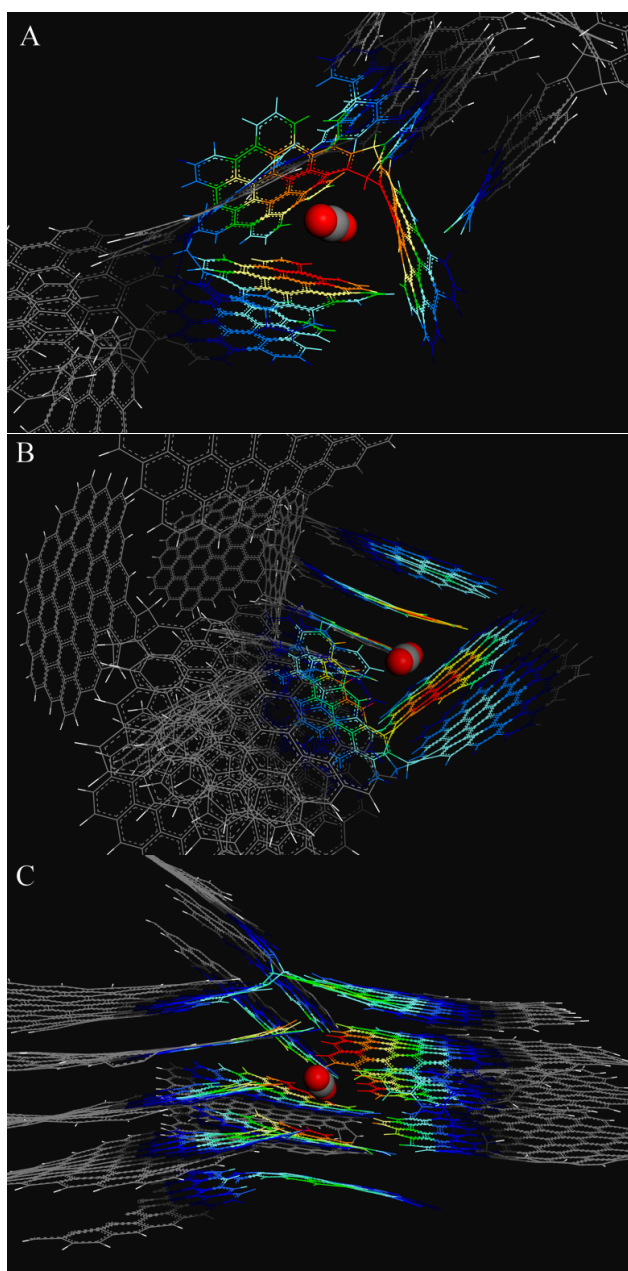


Figure 5.17. Examples of pores created in model carbons: (A) pore of type *A* created by L-trip, (B) pore of type *D* created in S-trip and (C) pore of type *C* created in M-CTC. For pore types see Figure 5.11.

5.4 Conclusions

In this work, we presented the simple approach for representing carbonaceous materials with complex pore geometry. It is possible to pack individual molecules that do not rely on input of structural properties such as porosity, surface area or density, which is otherwise necessary when using simple molecules like coronene. By connecting flat graphene-like platelets through rigid contortion sites we were able to obtain porous structures without imposing restrictions to structural properties of the resulting material. Packed 3-dimensional structures created moderate sizes of free volume and showed CO₂/CH₄ selectivity of the same order of magnitude as selectivity of many carbons. The pore volumes obtained are significantly smaller than most activated carbons, but we expect that constructing building blocks that pack inefficiently one can create more open structures where small stacks of graphene layers are still observed but with pore volumes comparable to typical activated carbons. Alternatively, it is possible to mix different building blocks, which will extend the diversity of materials obtained.

We also found that rigid cores, such as triptycene, lead to materials with a more open structure than flexible cores that allow the arms to form stacks. The choice of the molecule's arms size allows tuning material's properties such as surface area. Some similarities can be found when using building blocks to create organic molecules of intrinsic microporosity [28].

The porous structured created with the methods used contains pores of different sizes and shapes, some formed by the building unit's platelets, while others by edges. We showed that when the contribution of pores formed by edges of the platelets is small, predictions using a simple slit pore model are expected to be accurate, but one must be careful in using a simple slit pore model if the edge effects are significant. We propose a simple method for quantifying the contribution of edge effects using the information obtained from a RDF.

It is well known that amorphous carbons are complex structures and the shapes of the building blocks used in this work represent some of the possible structures that can be found in a real material, nevertheless, it is far from comprehensive. Using the tools presented in this work, further analysis can be carried out to assess the effect of defects and functional groups in amorphous carbon materials.

5.5 Supplementary Information

5.5.1 Methodology

Table 5.2. Non-bonded interaction parameters for the simulation of gas molecules taken from DREIDING force field [24] and charges as calculated by QEq method [42].

Element type	D ₀ , kcal/mol	R ₀ , Å	Charge
C (CO ₂)	0.0951	3.8983	0.8958
C (CH ₄)	0.0951	3.8983	−0.588
H (CH ₄)	0.0152	3.1950	0.147
O (CO ₂)	0.0957	3.4046	−0.4479

5.5.2 Results

The figures below present the structural data of model carbons and coronene. Nitrogen surface area of system generated using two different packing schemes (Scheme 1 and Scheme 2) is given in Figure 5.18 (A) and packing procedures are explained in the paper. It is clear that Scheme 2 creates less dense systems compared to systems generated using Scheme 1. The result is expected since systems are compressed only once, at relatively low pressure, in Scheme 2 whereas in Scheme 1 molecules are compressed gradually increasing pressure up to non-physically high 50,000 bar pressure. Nevertheless, the difference does not affect the CO₂/CH₄ selectivity where it is almost the same within deviation regardless of packing method used (Figure 5.18 B).

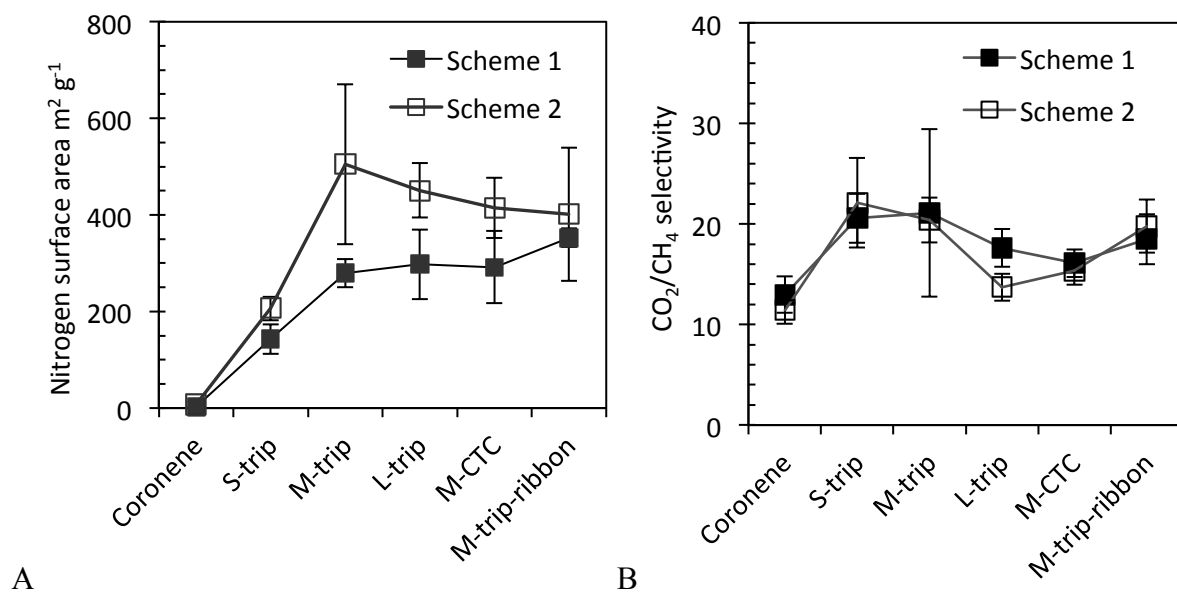


Figure 5.18. (A) Nitrogen surface area of systems generated using two packing schemes and (B) CO_2/CH_4 selectivity in systems generated using two packing schemes.

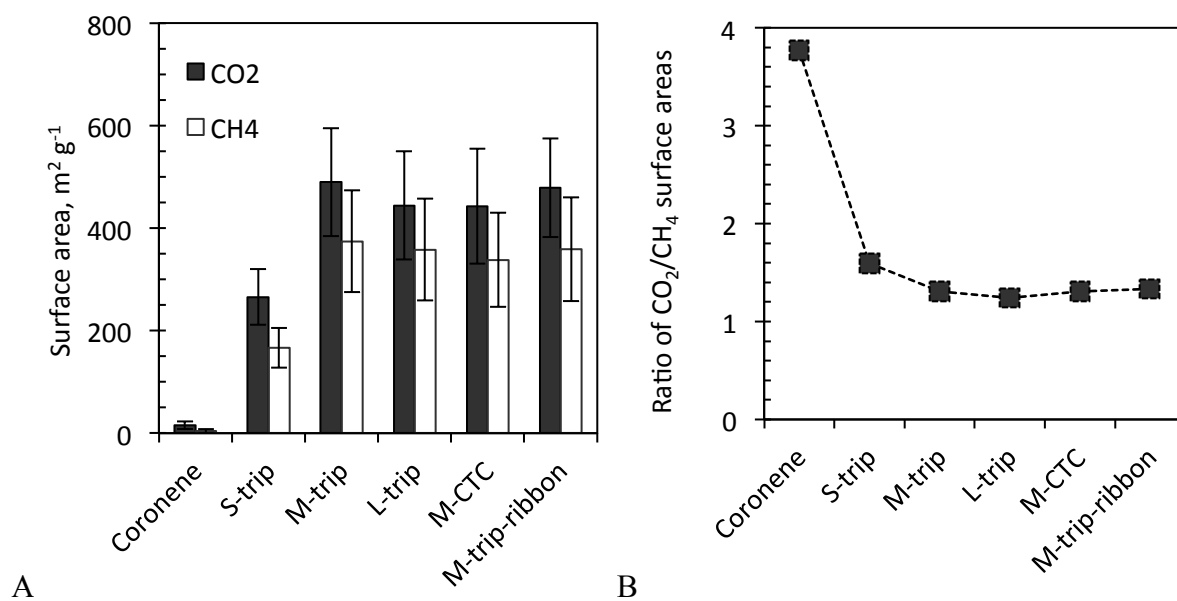


Figure 5.19. (A) Surface area accessible to CO_2 ($d = 3.3 \text{ \AA}$) and CH_4 ($d = 3.775 \text{ \AA}$) and (B) ratio between surface area accessible to CO_2 and CH_4 .

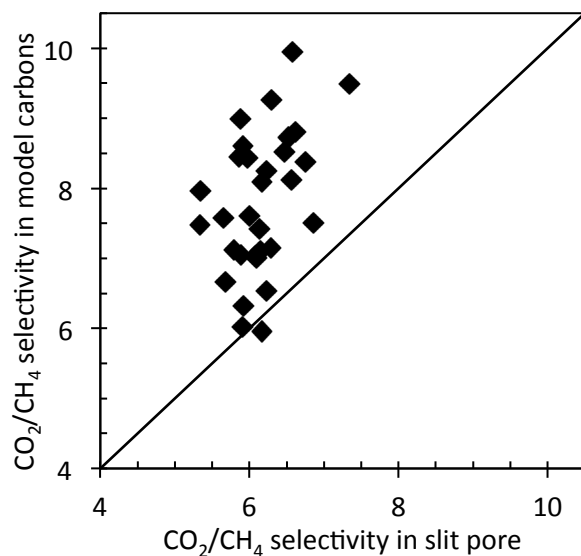


Figure 5.20. CO₂/CH₄ selectivity calculated for model carbons versus selectivity predicted by the slit pore at 0.05 bar.

Table 5.3. Heats of adsorption in kJ mol⁻¹ in all model carbon systems.

	$\Delta H(\text{CO}_2)$	$\Delta H(\text{CH}_4)$
Coronene	30.2 ± 5.7	22.4 ± 6.2
S-trip	34.1 ± 5.9	25.8 ± 2.2
M-trip	32.4 ± 5.9	24.2 ± 5.2
L-trip	32.4 ± 5.7	23.3 ± 5.9
M-CTC	32.5 ± 1.9	23.4 ± 2.0
M-trip-ribbon	34.0 ± 3.9	24.4 ± 4.9

Table 5.4. Accessible helium volume (cm³ g⁻¹) in all model carbon systems.

S-trip	0.038	M-trip	0.059	L-trip	0.075	M-CTC	0.089	M-trip-ribbon	0.066
S-trip	0.033	M-trip	0.189	L-trip	0.131	M-CTC	0.049	M-trip-ribbon	0.073
S-trip	0.045	M-trip	0.089	L-trip	0.091	M-CTC	0.039	M-trip-ribbon	0.063
S-trip	0.021	M-trip	0.049	L-trip	0.049	M-CTC	0.101	M-trip-ribbon	0.053
S-trip	0.030	M-trip	0.048	L-trip	0.038	M-CTC	0.092	M-trip-ribbon	0.167
S-trip	0.031	M-trip	0.070	L-trip	0.071	M-CTC	0.064	M-trip-ribbon	0.059

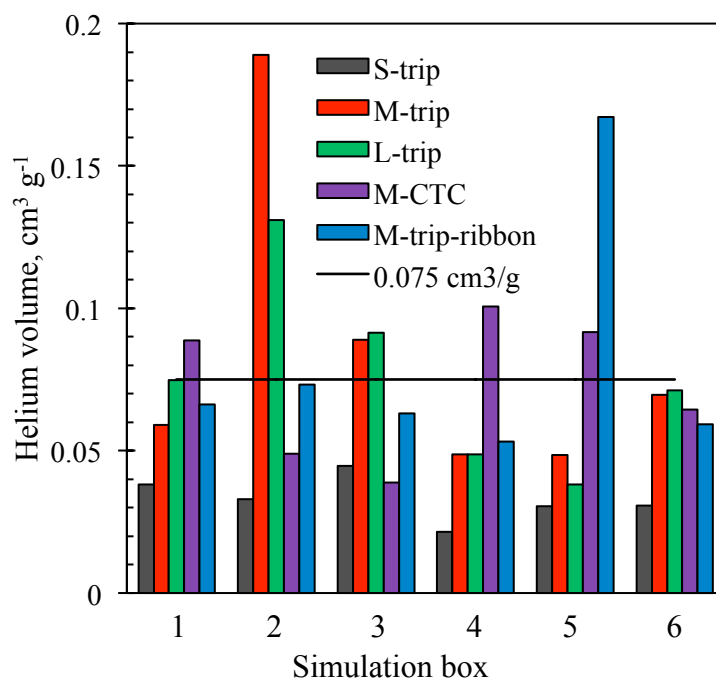


Figure 5.21. Accessible helium volume.

5.6 References

1. Simpson, C.D., et al., *Nanosized Molecular Propellers by Cyclodehydrogenation of Polyphenylene Dendrimers*. Journal of the American Chemical Society, 2004. **126**(10): p. 3139-3147.
2. Abbott, L.J., et al., *Characterizing the Structure of Organic Molecules of Intrinsic Microporosity by Molecular Simulations and X-ray Scattering*. The Journal of Physical Chemistry B, 2012. **117**(1): p. 355-364.
3. McKeown, N.B. and P.M. Budd, *Exploitation of Intrinsic Microporosity in Polymer-Based Materials*. Macromolecules, 2010. **43**(12): p. 5163-5176.
4. Larsen, G.S., et al., *Molecular Simulations of PIM-1-like Polymers of Intrinsic Microporosity*. Macromolecules, 2011. **44**(17): p. 6944-6951.
5. Steele, W.A., *The physical interaction of gases with crystalline solids: I. Gas-solid energies and properties of isolated adsorbed atoms*. Surface Science, 1973. **36**(1): p. 317-352.
6. El-Merraoui, M., M. Aoshima, and K. Kaneko, *Micropore Size Distribution of Activated Carbon Fiber Using the Density Functional Theory and Other Methods*. Langmuir, 2000. **16**(9): p. 4300-4304.
7. Landers, J., G.Y. Gor, and A.V. Neimark, *Density functional theory methods for characterization of porous materials*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. **437**(0): p. 3-32.

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8. Palmer, J.C. and K.E. Gubbins, *Atomistic models for disordered nanoporous carbons using reactive force fields*. Microporous and Mesoporous Materials, 2012. **154**(0): p. 24-37.
 9. Shi, Y., *A mimetic porous carbon model by quench molecular dynamics simulation*. The Journal of Chemical Physics, 2008. **128**(23).
 10. Kumar, A., R.F. Lobo, and N.J. Wagner, *Porous amorphous carbon models from periodic Gaussian chains of amorphous polymers*. Carbon, 2005. **43**(15): p. 3099-3111.
 11. Bock, H., K.E. Gubbins, and J. Pikunic, *Chapter Five - Models of Porous Carbons*, in *Adsorption by Carbons*, E.J. Bottani and J.M.D. Tascón, Editors. 2008, Elsevier: Amsterdam. p. 103-132.
 12. O'Malley, B., I. Snook, and D. McCulloch, *Reverse Monte Carlo analysis of the structure of glassy carbon using electron-microscopy data*. Physical Review B, 1998. **57**(22): p. 14148-14157.
 13. Opletal, G., et al., *Hybrid approach for generating realistic amorphous carbon structure using metropolis and reverse Monte Carlo*. Molecular Simulation, 2002. **28**(10-11): p. 927-938.
 14. Farmahini, A.H., G. Opletal, and S.K. Bhatia, *Structural Modelling of Silicon Carbide-Derived Nanoporous Carbon by Hybrid Reverse Monte Carlo Simulation*. The Journal of Physical Chemistry C, 2013. **117**(27): p. 14081-14094.
 15. Thomson, K.T. and K.E. Gubbins, *Modeling Structural Morphology of Microporous Carbons by Reverse Monte Carlo*. Langmuir, 2000. **16**(13): p. 5761-5773.
 16. Pikunic, J., et al., *Improved Molecular Models for Porous Carbons*, in *Studies in Surface Science and Catalysis*, N.O. Yasuhiro Iwasawa and K. Hironobu, Editors. 2001, Elsevier. p. 647-652.
 17. Arora, G. and S.I. Sandler, *Nanoporous carbon membranes for separation of nitrogen and oxygen: Insight from molecular simulations*. Fluid Phase Equilibria, 2007. **259**(1): p. 3-8.
 18. Klauda, J.B., J. Jiang, and S.I. Sandler, *An ab Initio Study on the Effect of Carbon Surface Curvature and Ring Structure on N₂(O₂)–Carbon Intermolecular Potentials*. The Journal of Physical Chemistry B, 2004. **108**(28): p. 9842-9851.
 19. Kumar, K.V., E.A. Müller, and F. Rodríguez-Reinoso, *Effect of Pore Morphology on the Adsorption of Methane/Hydrogen Mixtures on Carbon Micropores*. The Journal of Physical Chemistry C, 2012. **116**(21): p. 11820-11829.
 20. Segarra, E.I. and E.D. Glandt, *Model microporous carbons: microstructure, surface polarity and gas adsorption*. Chemical Engineering Science, 1994. **49**(17): p. 2953-2965.
 21. Liu, J.C. and P.A. Monson, *Monte Carlo Simulation Study of Water Adsorption in Activated Carbon*. Industrial & Engineering Chemistry Research, 2006. **45**(16): p. 5649-5656.
 22. Di Biase, E. and L. Sarkisov, *Systematic development of predictive molecular models of high surface area activated carbons for adsorption applications*. Carbon, 2013. **64**(0): p. 262-280.
 23. Biggs, M.J. and A. Buts, *Virtual porous carbons: what they are and what they can be used for*. Molecular Simulation, 2006. **32**(7): p. 579-593.
 24. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
 25. Regno, A.D. and F.R. Siperstein, *Comparison of generic force fields for packing of concave molecules*. Molecular Physics, 2014. **112**(17): p. 2241-2248.

26. Fraccarollo, A., et al., *Monte Carlo Modeling of Carbon Dioxide Adsorption in Porous Aromatic Frameworks*. Langmuir, 2014. **30**(14): p. 4147-4156.
27. Metropolis, N., et al., *Equation of State Calculations by Fast Computing Machines*. J. Chem. Phys., 1953. **21**: p. 1087.
28. Abbott, L.J., N.B. McKeown, and C.M. Colina, *Design principles for microporous organic solids from predictive computational screening*. Journal of Materials Chemistry A, 2013. **1**(38): p. 11950-11960.
29. Tozawa, T., et al., *Porous organic cages*. Nat Mater, 2009. **8**(12): p. 973-978.
30. Palmer, J.C., et al., *Detailed structural models for activated carbons from molecular simulation*. Carbon, 2009. **47**(12): p. 2904-2913.
31. Hawelek, L., et al., *Fullerene-like structure of activated carbons*. Diamond and Related Materials, 2008. **17**(7-10): p. 1633-1638.
32. Burian, A., A. Ratuszna, and J.C. Dore, *Radial distribution function analysis of the structure of activated carbons*. Carbon, 1998. **36**(11): p. 1613-1621.
33. IFPSC. *Benchmark data for "Industrial Fluid Properties Simulation Collective. 8th Challenge*. 2014 [cited 2014 15 September]; Available from: <http://fluidproperties.org/8th-benchmarks>.
34. Tan, Z. and K.E. Gubbins, *Selective adsorption of simple mixtures in slit pores: a model of methane-ethane mixtures in carbon*. The Journal of Physical Chemistry, 1992. **96**(2): p. 845-854.
35. Di Biase, E. and L. Sarkisov, *Molecular simulation of multi-component adsorption processes related to carbon capture in a high surface area, disordered activated carbon*. Carbon, 2015. **94**: p. 27-40.
36. Heuchel, M., et al., *Adsorption of Carbon Dioxide and Methane and Their Mixtures on an Activated Carbon: Simulation and Experiment*. Langmuir, 1999. **15**(25): p. 8695-8705.
37. Peng, X., et al., *Adsorption separation of CH₄/CO₂ on mesocarbon microbeads: Experiment and modeling*. AIChE Journal, 2006. **52**(3): p. 994-1003.
38. Palmer, J.C., et al., *Adsorptive behavior of CO₂, CH₄ and their mixtures in carbon nanospace: a molecular simulation study*. Phys. Chem. Chem. Phys., 2011. **13**(9): p. 3985-3996.
39. Soares Maia, D., et al., *Characterization of the PSD of activated carbons from peach stones for separation of combustion gas mixtures*. Adsorption, 2011. **17**(5): p. 853-861.
40. Kaskel, S., et al., *Mixed Geometry Characterization of Activated Carbons PSD*, in *Characterisation of Porous Solids VIII: Proceedings of the 8th International Symposium on the Characterisation of Porous Solids*. 2009, The Royal Society of Chemistry. p. 211-217.
41. Azevedo, D.C.S., et al., *Characterization of PSD of activated carbons by using slit and triangular pore geometries*. Applied Surface Science, 2010. **256**(17): p. 5191-5197.
42. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358-3363.

6 N-PERFLUOROHEXANE ADSORPTION PREDICTION ON ACTIVATED CARBON BAM-109 BY MOLECULAR SIMULATION

This chapter is adapted from the manuscript published in Special section: 8th IFPSC of Adsorption Science & Technology¹. Authors: Aleksandra Gonciaruk², Louis Runcieman³, Carlos Avendano², Flor R. Siperstein². Author contribution: the major work was carried out and the manuscript was drafted by A. Gonciaruk through discussions with F. R. Siperstein and C. Avendano, L. Runcieman obtained Gordon potential parameters for perfluorohexane and C. Avendano calculated saturation pressure of perfluorohexane.

Abstract

We propose a simple approach of packing individual three-dimensional rigid structures to represent microporous region of commercially available BAM-109 activated carbon. Mesopores are represented by planar walls interacting via the standard Steele 10-4-3 potential assuming experimental pore size distribution. The models are used to predict n-perfluorohexane (PFH) adsorption at 273 K temperature. We used uncharged united atom model for PFH molecule. The non-bonded interactions were described by the Gordon potential model with parameters adjusted to reproduce the Mie force field potential, which was designed to accurately represent vapour pressure of alkanes and perfluoroalkanes. Adsorption isotherm was calculated using grand canonical Monte Carlo method implemented in MCCCSTowhee. We show that predicted PFH loading at relative pressures of interest are significantly lower than the experimental ones. The underprediction is attributed to the low aromatic carbon interaction strength and sensitive calculations of chemical potential. Adjusted interaction parameter of aromatic carbon and chemical potential led to PFH adsorption that agreed well with the reported experimental values.

¹ Adapted from “n-Perfluorohexane adsorption prediction on activated carbon BAM-109 by molecular simulation”, A. Gonciaruk, L. Runcieman, C. Avendano, F. R. Siperstein. Submitted to Special section: 8th IFPSC of Adsorption Science & Technology, 2015.

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6.1 Introduction

This work is an entry for 8th Industrial Fluid Properties Simulation Challenge [1]. American Institute of Chemical Engineers, the American Chemical Society, Army Research Lab, Boeing, National Institute of Standards and Technology, The Dow Chemical Company, 3M, and United Technologies Research Center organise the competition annually since 2001 in order to “drive improvements in the practice of molecular modelling, formalise methods for the evaluation and validation of simulation results with experimental data, and ensure relevance of simulation activities to industrial requirements” [1]. The aim of the current challenge is to use state-of-the-art molecular simulation methods and force fields to predict adsorption in relevant and complex porous systems, specifically adsorption of n-perfluorohexane (PFH) on activated carbon BAM-109. The organisers provide experimental structural data such as pore size distribution, surface area and pore volume of the material and argon and carbon dioxide adsorption isotherms in order for the competitors to validate their models and produce most precise predictions.

Activated carbon is one of the most usable materials in modern industry spanning its applications from storage and purification to catalysis. Activated carbons are relatively inexpensive, have high adsorption capacity, and their properties can be tailored for specific applications. The demand for these materials is increasing and the ability to predict and tune its performance using virtual techniques would be essential for cost and time effective product development.

PFH is a hexane derivative where all hydrogen atoms are substituted with fluorine atoms. PFH is used in many industrial and medical applications due to its unique properties such as chemical and thermal stability, biological inertness and ability to dissolve gases from air, just to name a few examples. Until the previous 7th Industrial Fluid Properties Simulation Challenge [2] there were no studies on PFH adsorption in porous media. However PFH is considered to be moderately challenging molecule to model and recognised as potentially one of the strong global warming compounds [2]. Therefore it is important to assess currently available computational techniques and force fields for accurate predictions of PFH adsorption.

The challenge provides important opportunity to test virtual carbon system previously created by us [3] (Chapter 5) in the context of experimental application. The simple approach represents activated carbons as a packed system of individual molecules. These molecules consist of graphene-like flat arms connected through rigid core. The core prevents molecules from efficient packing leading to porous material. By controlling graphene arm size it is possible to adjust the structural properties of the material, such as accessible surface area and pore-size distribution. We have also used idealised slit pores where interactions are represented by the Steele potential to represent mesoporous region. The main differences between the two approaches are discussed in the following section as well as the reasoning behind the selection of molecular simulation method and force field utilised to produce PFH isotherm is explained.

6.2 Simulation Details

6.2.1 Perfluorohexane

The PFH molecules were represented using a united atom approximation with no explicit charges. In a PFH molecule, fluorine atoms are combined with the neighbouring carbon atom to form a single interaction site. The non-bonded and bonded interactions parameters were based on the force field developed by Potoff and Bernard-Brunel, which was reported to accurately describe perfluoroalkanes, alkanes, alkenes and their mixtures [4, 5]. In this force field, site-site interactions are described via the Mie potential (a generalised form of Lennard-Jones 12-6 potential) given by:

$$U(r) = C(n)\varepsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6.1)$$

where ε is the potential well-depth, r is the separation between the pair of interaction sites, σ is the collision diameter, n is the impulsive exponent controlling the softness/hardness of the potential, and $C(n)$ is a normalization that sets the minimum of the potential $-\varepsilon$ for all n , i.e.:

$$C(n) = \left(\frac{n}{n-6}\right) \left(\frac{n}{6}\right)^{6/n-6} \quad (6.2)$$

In this work, simulations are carried out using the MCCCSTowhee v7.0.6, which is a powerful all-purpose Monte Carlo simulation software [6]. Unfortunately the Mie potential is not available in Towhee v.7.0.6. therefore, we have approximated the Mie force field functional form by using the so-called Gordon n-6 potential [7], which is implemented in Towhee, and is given by:

$$U(r) = 4\epsilon C(n) \left[\left(\frac{\sigma}{r - a(n)} \right)^n - \left(\frac{\sigma}{r - a(n)} \right)^6 \right] \quad (6.3)$$

where $C(n)$ and $a(n)$ are constants related to the location of the minimum in the potential energy r_m , and the collision diameter σ through:

$$C(n) = -\frac{1}{4} \left[\left(\frac{\sigma}{r_m - a(n)} \right)^n - \left(\frac{\sigma}{r_m - a(n)} \right)^6 \right]^{-1} \quad (6.4)$$

$$a(n) = \left(2^{1/6} - \left(\frac{n}{6} \right)^{1/(n-6)} \right) \sigma \quad (6.5)$$

$$r_m = 2^{1/6} \sigma \quad (6.6)$$

The Gordon potential represents well the properties of n-paraffins over a significant range of temperatures and pressures. Both Mie and Gordon potential reduce to the standard Lennard-Jones potential when $n=12$. Both potentials described in equations (6.1) and (6.3) benefit from a variable exponent in the repulsion contribution, which can be adjusted to describe the hardness/softness of the molecules of interest. Although clear differences can be found between the Mie potential and the one proposed by Gordon, it is possible to find sets of parameters that will lead to very similar potential curves using the different functional forms of the potential. Considering that the steep repulsion contribution in the non-bonded potential proposed by Potoff and Bernard-Brunel leads to an accurate description of the vapour pressures, we maintained the exponent and the energy well-depth reported by Potoff and Bernard-Brunel, and obtained a collision diameter that can be used in (6.3) and at the same time gives the correct potential curve described by (6.1) with the parameters reported by Potoff and Bernard-Brunel [5]. The agreement between the two models described in (6.1) and (6.3) using the parameters in Table 6.1 can be seen in Figure 6.1.

Following the work of Potoff and Bernard-Brunel, CF_x units were separated by a fixed bond length of 1.54 Å. The bond angle was described by standard harmonic oscillation and OPLS Fluorocarbon Four Term potential was used to describe torsional conformations [5].

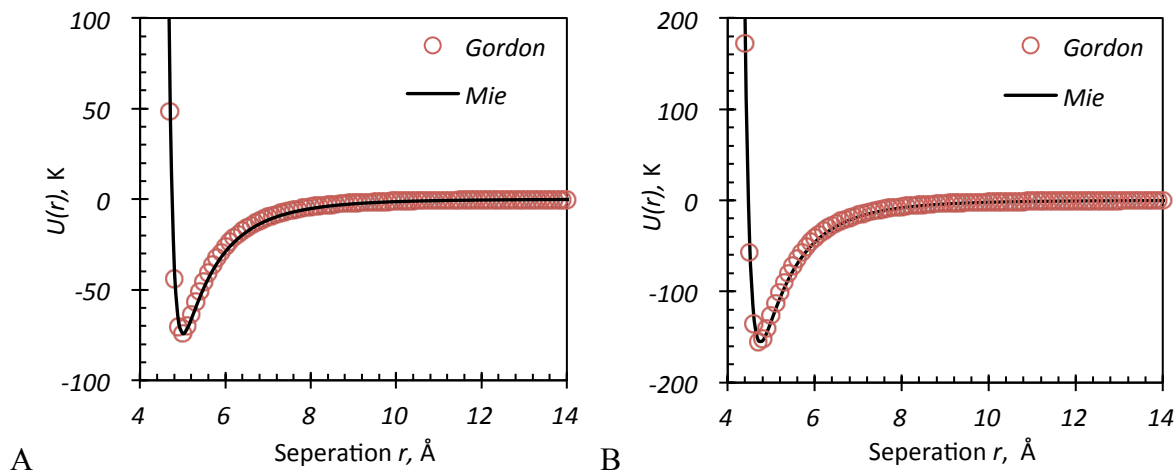


Figure 6.1. Mie and Gordon potential curves for (A) CF_2 and (B) CF_3 units.

Table 6.1. Gordon and Mie potential parameters for perfluorohexane units.

	$\varepsilon/k_B, K$	$\sigma, \text{\AA}$	n	m	$C(n)$	$a(n)$	r_{min}
CF_2							
Mie	74.2	4.750	44	6	1.586	N/A	5.01
Gordon	74.2	4.434	44	6	0.396	0.304	4.98
CF_3							
Mie	155.75	4.475	36	6	1.717	N/A	4.75
Gordon	155.75	4.208	36	6	0.429	0.256	4.72

6.2.2 Microporous Carbon

Model carbons were constructed using Materials Studio, Accelrys Software Inc. (San Diego, CA) [8]. Graphene arms were created in planar form by connecting six-membered carbon rings. The edge carbon atoms of the graphene were saturated with hydrogen atoms. Three different arms were constructed small and large arms of disk shape and a small size ribbon-like arm (Figure 6.2). The arms were then connected through two different centres inspired by the structures of [2.2.2]-propellane (*trip*) and octahedral propellane (*octa*) (Figure 6.3). The *trip* and *octa* structures possess a rigid three-fold symmetry that keeps graphene arms separated in 3D space. The carbon model is described fully atomistically. Although it has

been reported that BAM-P109 contains trace amounts of sulphur, sodium and oxygen as well as some other elements [1] they were not included into the model, but it would be useful to understand the effect of functional group presence to the overall PFH adsorption in the future. For packing procedure interactions between atoms are described using the DREIDING force field [9]. Partial charges are calculated using charge equilibration method QEq implemented in Material Studio [10]. The Lennard-Jones 12-6 potential was used to model the van der Waals interactions, while long-range electrostatic interactions were calculated using the Ewald method.

The system composition is summarised in Table 6.2. Molecules were first packed into a low density box with periodic boundary conditions in the three directions and quickly compressed to a pressure of 1000 bar at a temperature of 273 K. The system with the satisfactory structural properties was selected and its geometry and energy was optimised using the Smart algorithm. The model carbons were characterised and compared in terms of density, surface area, pore volume and pore size distribution (PSD). Parameters are explained in more detail in Chapter 2.

Table 6.2. Composition of the carbon model system.

Number of molecules	Arms	Centre	Total atoms
9	Large disk	Trip	832
3	Ribbon	Trip	286
3	Small disk	Octa	350
2	Ribbon	-	96

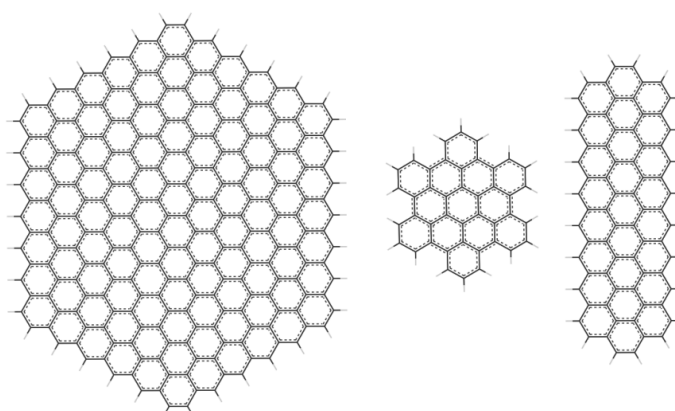


Figure 6.2. Representation of the graphene arms used to model the carbon adsorbent materials. (Left) large and (middle) small disk-like arms, and (right) ribbon-like arm.

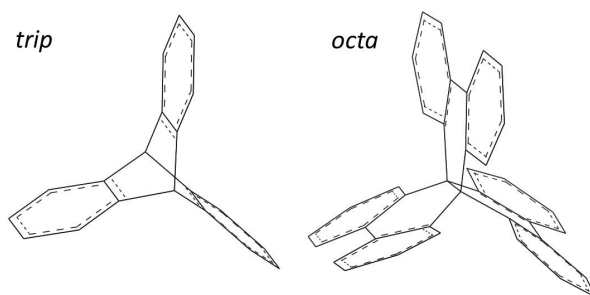


Figure 6.3. Cores of model carbons.

The final snapshot of model carbon structure was converted from a Material studio structure file to a Towhee input file. Adsorption was simulated using GCMC simulations using the Gordon potential with the adjusted parameters as described earlier. The interactions with carbon atoms were calculated using Lorentz-Berthelot mixing rules and the parameters reported in Table 6.3. The framework atoms were frozen in space during the GCMC simulations; therefore all system atoms were unconnected in the input file.

Table 6.3. Gordon potential parameters for carbon model.

	C	H
$\epsilon/k_B, K$	30.137	0
$\sigma, \text{\AA}$	3.416	1
n	12	12

Two carbon structures were created: one that reproduces correct surface area accessible to Ar atom and another that has a free volume and PSD similar to the one measured experimentally (Table 6.4) The PSD in the micropore region is shown in Figure 6.4. It is obvious that our models are not capturing the region of very small pores. This may results in slightly lower Ar loadings at low pressures. However, considering the size of PFH molecule, adsorption of PFH can be expected to occur only in the pores wider than about 0.7 nm from where calculated PSD follows very similar trend to experimental PSD. Nevertheless, we expect that it is possible to obtain desired models, which would represent all experimental structural properties by changing the size of the arms and combination of structures with different arm sizes or shapes. Packed model carbons with similar arm size possess similar structural properties (PSD, surface area and free volume) regardless of arm shape. A slight trend was observed with respect to disk-shaped arms' size: larger arms tend stack better than smaller arms, reducing the surface area, while smaller arms can move more freely penetrating "internal molecular free volume" created between two arms due to three-fold structure of

tritycene. Therefore the large graphene arms were introduced to create the overall network and small arm structures were included to reduce graphene stacking, while ribbons were supposed to penetrate the larger free pores and increase microporosity.

Table 6.4. Structural properties of carbon models.

	Reported	Model 1	Model 2
Density, g cm ⁻³	2.18	1.054 ± 0.018	1.140
Surface area, m ² g ⁻¹	1383	1917 ± 111	1341
Free volume, cm ³ g ⁻¹	0.5163	0.456 ± 0.042	0.244

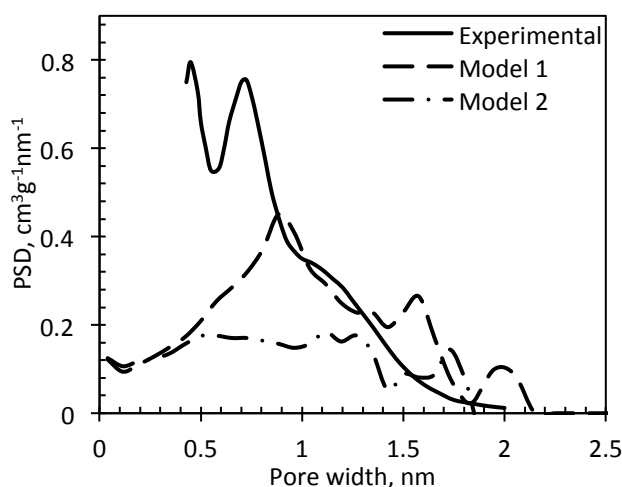


Figure 6.4. Pore size distribution for the two different carbon models compared with the experimental data taken from Ref. [1].

6.2.3 Slit Pore Model

Adsorption of PFH was also modelled using a simple slit pore model. A collection of slit pores with separations narrower than 2 nm was used to represent microporous region of activated carbon. To account for mesoporosity, adsorption was calculated in a slit pores of 13, 16 and 20 nm wide, which are around the local maxima for mesoporous region of PSD as can be seen in the experimental data provided in Ref. [1].

Adsorption on an idealised slit pore model was calculated using the Steele potential [11]. The Steele potential is commonly used to describe adsorption in carbon slits, where the interactions between a fluid particle and a single structureless solid wall are given by:

$$U_{sf}(z) = 2\pi\rho_s\Delta\sigma_{sf}^2\epsilon_{sf}\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z + 0.61\Delta)}\right] \quad (6.7)$$

where z is the distance between the site and the carbon surface wall, Δ is the distance between carbon layers in each slab, ρ_s is the graphitic density, σ_{sf} and ϵ_{sf} are the Lennard-Jones interaction parameters for the fluid-solid interactions, which were obtained using Lorentz-Berthelot mixing rules and the parameters to describe carbon atoms reported in Table 6.3. The parameters used for the simulations are summarised in Table 6.5.

Table 6.5. Solid-fluid interaction parameters for equation (6.3).

Parameter	Units	Value
Δ	$\text{\AA}$	3.35
ρ_s	$\text{\AA}^{-3}$	0.114
$\sigma_{C,CF2}$	$\text{\AA}$	3.925
$\sigma_{C,CF3}$	$\text{\AA}$	3.812
$\epsilon_{C,CF2}/k_B$	K	47.29
$\epsilon_{C,CF3}/k_B$	K	68.51

6.2.4 Vapour Pressure Calculation

The vapour pressure for PFH at high temperatures was obtained using the direct coexistence method [12] using Lammmps [13]. A rectangular box with dimensions $L_x = L_y = 4.786$ nm and $L_z = 23.8$ nm with total of 604 PFH molecules was used and periodic boundary conditions in all directions were considered. The equations of motion were with a time step of 2fs and a Nose-Hoover thermostat was used to control temperature. The system was equilibrated for 2 ns and averages were obtained over 10ns. A typical 2-phase coexistence simulation is shown in Figure 6.5. The coexistence densities were obtained using the density profiles along the larger dimension used (z). The vapour pressure was calculated by using an independent simulation at the vapour density calculated during the direct coexistence simulations. Results from the simulations are shown in Figure 6.6. Simulations were carried out at high temperatures, and the saturation pressure at 273 K was obtained by extrapolation using the

Clausius-Clapeyron equation. It was estimated that at 273 K, the saturation pressure for PFH is 0.144 bar, which is slightly higher than the values reported by National Institute of Standards and Technology (NIST) [14, 15].

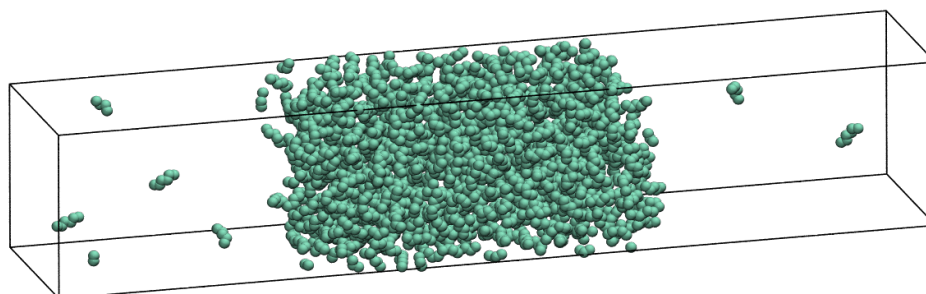


Figure 6.5. Representative configuration of vapour-liquid equilibrium at 300 K obtained using the direct-coexistence method.

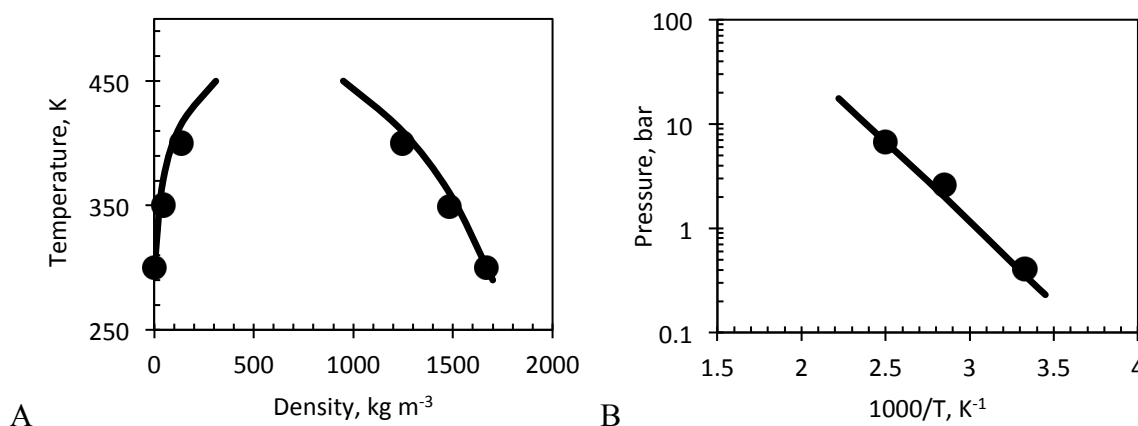


Figure 6.6. Molecular dynamics results for (A) vapour-liquid coexistence and (B) saturation pressure for PFH. Symbols are values calculated in this work and solid curves are data taken from Ref. [5].

6.2.5 Adsorption of Argon

All adsorption simulations were performed using MCCCSTowhee v7.0.6 [6] in the grand canonical ensemble. Adsorption of Ar was simulated using Universal force field [16]. Interaction parameters between unlike atoms were calculated using Lorentz-Berthelot rule. In the simulation, a combination of adsorbate insertion, deletion and translation steps were used.

Each simulation was typically carried out for minimum of 10×10^6 Monte Carlo moves including equilibration and production steps. Framework atoms were frozen in space during adsorption simulation. Ar adsorption was simulated in both carbon models (Model 1 and Model 2). The thermodynamic inputs were temperature of 87.45 K, simulation unit cell volume and chemical potentials corresponding to target relative pressures between 0.2 and 0.7. The relative pressure is defined as the relative to the bulk saturation pressure for 87.45 K temperature and was calculated using Antoine equation with parameters taken from NIST [15, 17]. Units of adsorption data are provided in number of molecules per unit cell, which is then converted to volume per mass of adsorbent in order to compare calculated and experimental results. For the conversion, molar volume (22.4 L mol^{-1}) of an ideal gas at standard temperature and pressure (STP) was used.

Monte Carlo simulations in the NPT ensemble for a system containing only Ar molecules were used to establish correlation between chemical potential and pressure of interest.

6.2.6 Adsorption of Perfluorohexane

Adsorption PFH was simulated using Gordon force field [7] with the adjusted parameters as described in sections 6.2.1 and 6.2.2. A combination of adsorbate insertion, deletion and motion (translation, rotation and conformation change using configurational-bias) steps were allowed. Typically a minimum total of 6×10^6 Monte Carlo moves were used for equilibration and production steps in the model disordered carbon. Shorter simulations were run for the slit pore systems. Adsorption was carried out at the fixed simulation cell volume at temperature of 273 K temperature and constant chemical potentials corresponding to target relative pressures of 0.1, 0.3 and 0.6, taking reported saturation pressure value of 0.0855 bar. As described earlier, units of PFH loading in carbon models are also converted using 22.4 L mol^{-1} ideal gas molar volume as a requirement for the challenge. Prior to adsorption simulation chemical potential – pressure relationship was established using box filled with only PFH molecules.

Total amount of PFH adsorbed $n(P)$ in the slit pores of sizes between 0.5 and 2.2 nm was calculated assuming that the slit pore have the same experimental PSD as carbon model:

$$n(P) = \sum \left[\frac{\int_{H_i}^{H_{i+1}} f(H) dH}{\int_0^{\infty} f(H) dH} N(H, P) \right] \quad (6.8)$$

where $n(P)$ is the amount of PFH adsorbed in microporous slit pores, $N(H, P)$ is the amount of adsorbed PFH at a given pressure P and width H between the carbon walls and $f(H)$ is the PSD of carbon model. The amount of PFH adsorbed in the mesopore of 13, 16 and 20 nm width was calculated assuming that all the mesopore region of the PSD can be represented by a single slit pore.

6.3 Results

6.3.1 Argon Adsorption

Calculated Ar adsorption at 87.45 K is presented in Figure 6.7 along with experimental benchmark isotherm. The Ar adsorption in Model 1 is overestimated, however the disagreement can be attributed to higher surface area of the system comparing to experimental one. The ratio of surface areas is the same as the ratio between adsorbed Ar volumes in simulated system and experimental sample. Therefore we created the system with the satisfactory surface area (Model 2), which is very close to the experimental surface area. In this case, we were able to obtain the same Ar loading in the system as in the experimental sample. Increased slope of experimental isotherm at relative pressure above 0.9 is attributed to multilayer formation in the large pores. However, mesoporosity of the sample is not considered for Ar adsorption calculations. Therefore carbon model does not exhibit increased Ar adsorption at pressures close to Ar saturation pressure. Slightly lower PFH loading at 0.9 relative pressure is due to the short simulation runs used.

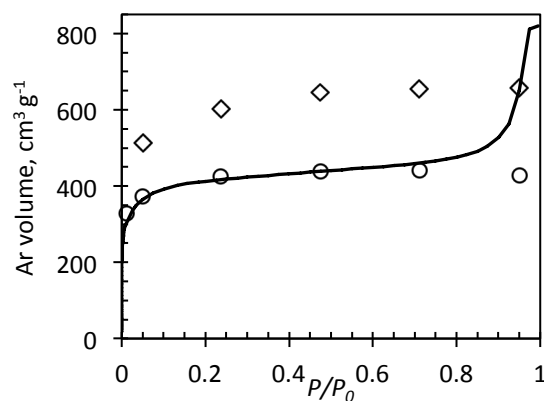


Figure 6.7. Argon adsorption in experimental sample (solid line), in carbon model with correct surface area (open circles) and carbon model with similar free argon volume and pore size distribution (open diamonds).

6.3.2 Perfluorohexane Adsorption

Predicted adsorption of PFH in carbon Model 1 at 273 K is given in Figure 6.8. Loadings in mmol g^{-1} units are given in Table 6.6. Standard deviation was computed directly in Towhee over the five blocks that divide the simulation. From the isotherm figure it is seen that PFH loading increase is insignificant between 0.06 and 0.1 relative pressures. Between 0.1 and 0.6 relative pressures, the model steadily adsorbs PFH and saturation is not expected. A snapshot of PFH molecules adsorbed in carbon model can be seen in Figure 6.9. It shows that PFH molecules tend to align parallel on the surface of graphene arms.

Table 6.6. Adsorbed amount of PFH in carbon model at 273 K.

P/P_0	$n(p)$, mmol g^{-1}	$n(p)$, STP $\text{cm}^3 \text{g}^{-1}$
0.06	0.17 ± 0.05	3.8 ± 1.0
0.10	0.18 ± 0.04	4.1 ± 0.6
0.30	0.35 ± 0.06	7.7 ± 1.3
0.60	0.53 ± 0.06	11.8 ± 1.3

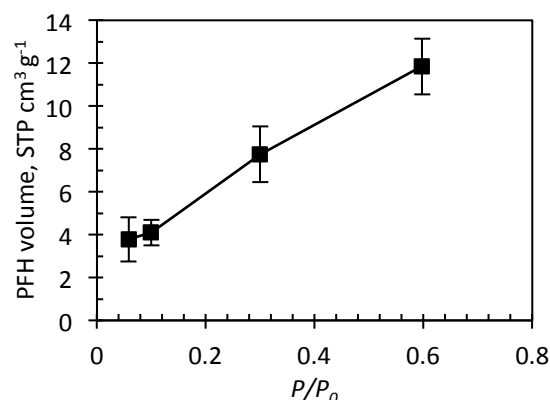


Figure 6.8. Total amount of perfluorohexane adsorbed in carbon model (Model 1) at 273 K.

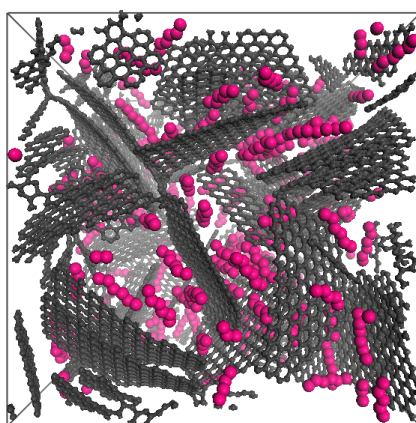


Figure 6.9. Representative in-cell image of perfluorohexane in carbon model (Model 1). Colour code: carbon atoms of carbon model are dark grey and units of perfluorohexane are pink.

Adsorption in slit pores shows clear layering formation as shown in Figure 6.10. All adsorbed molecules preferably adsorb parallel to the pore walls and do not extend perpendicular between two surfaces. No adsorption was observed for pores smaller than 0.7 nm (taking the pore size as the distance between the smooth solid walls).

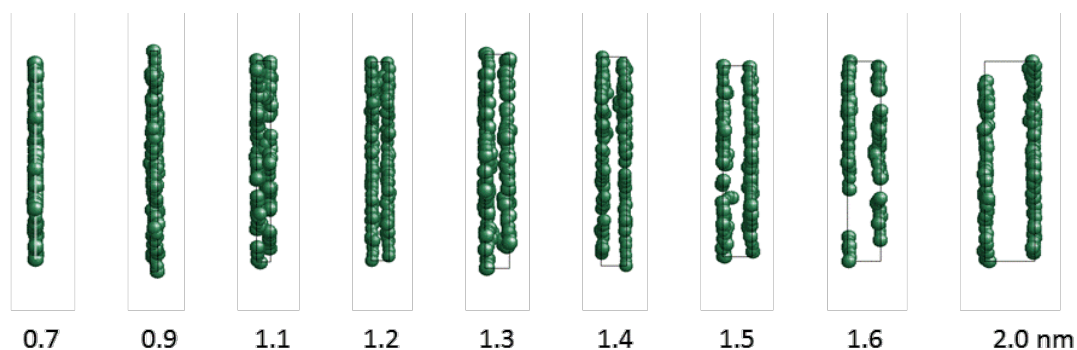


Figure 6.10. Representative configurations showing the adsorption of PFH in microporous slit pores at $P/P_0=0.1$ and 273 K.

Although no significant difference was observed for the amount adsorbed in the 16 nm slit pore at the pressures of interest, at a pressure of $P/P_0=0.8$ condensation in the whole pore was observed. Therefore, the contribution to the amount adsorbed of the mesopore region for the range of pressures of interest is negligible, but an increase in about 1.8 mmol g^{-1} (or $40 \text{ STP cm}^3 \text{ g}^{-1}$) can be expected at high pressures.

Amount of PFH adsorbed in the microporous slit pore model is 0.74 mmol g^{-1} ($16.5 \text{ STP cm}^3 \text{ g}^{-1}$) at 0.1 relative pressure, which overestimates the adsorption compared to PFH loading in carbon model. It is obvious that at even very low relative pressure PFH molecules start to align parallel to each other forming an ordered arrangement, as shown in Figure 6.11 (a). In the carbon models with irregular complex pore structure, it is more difficult for PFH molecules to form ordered structures; therefore less PFH is adsorbed. However, it is possible that both models can reach the same PFH loading at higher pressures. It is interesting to note that in the slit pores of the sizes that commensurate with the length of PFH molecule, some of the molecules form bridges between the walls (Figure 6.11, b). This suggests that packing of the molecules can be significantly higher than what would be expected from the formation of parallel layers to the surface.



Figure 6.11. Alignment of perfluorohexane molecules in the slit pore of (A) 0.9 nm and (B) 1.5 nm width at $P/P_0=0.6$ and 273 K.

Comparing the results with the experimental data it is obvious that our calculations significantly underpredict PFH adsorption, although the slope of the isotherms is very similar (Figure 6.12). We revised our work and believe that the proposed carbon model is still valid and would be beneficial for further adsorption studies as it is simple to construct and maintains the geometrical complexity of the pores. It is evident from visualization of the simulation cell that contains adsorbed PFH that there is still space for additional molecules (Figure 6.9). Also, at higher chemical potential (pressure) the system was able to

accommodate greater amount of PFH suggesting that the selected interaction parameters or incorrect chemical potential cause such a weak adsorption. By careful examination of the implemented approach, we found several points that could affect the underprediction:

- Solid-fluid interaction parameters. The value of epsilon (ϵ) used for aromatic carbon was different for the Ar and PFH simulations. The PFH adsorption simulations used the ϵ for aromatic carbons in the Steele wall. However for Ar adsorption, the UFF force field was used where ϵ is 52.84 K for aromatic carbon. The ϵ from the Steele potential is 1.75 times smaller than UFF value (Table 6.3). Since the calculated Ar adsorption match the experimental isotherm well, it is reasonable to assume that larger value assigned by UFF force field describe aromatic carbon-adsorbate interactions better.
- Charges are not used in the calculations. Knowing that fluorine atoms are highly electronegative, electrostatic interaction might be significant, but whether this would lead to higher adsorption is questionable since the negative “cloud” created by fluorine atoms on each molecule may results in stronger repulsion between the adsorbate molecules. However, long range interactions as well as their magnitude are already incorporated in the parameters reported by Potoff and Bernard-Brunel. On the other hand, interactions between electron rich atom and electron deficient aromatic ring have been recognised in many biomolecules [18]. Consideration of lone pair – π interactions may help to better understand and represent adsorption of fluorinated compounds on activated carbons.
- The default *Martin and Frischknecht 2006* algorithm in Towhee [19] was used for the chemical potential calculation. The Widom insertion method [20, 21] is recommended to ensure correct chemical potential calculation as it performs only one trial for any non-bonded interaction selection step and not ten trials. Unfortunately, due to limited time, we did not establish an accurate pressure-chemical potential correlation.

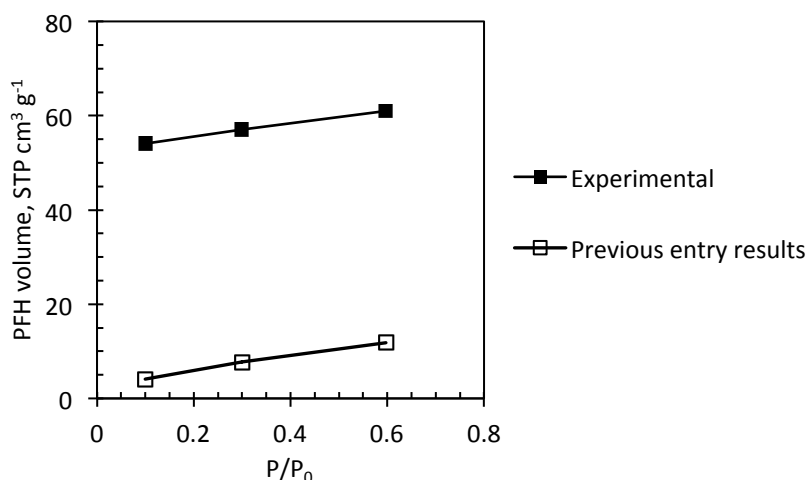


Figure 6.12. Experimental and previous entry results for 8th Fluid Challenge of perfluorohexane adsorption isotherms at 273 K.

We performed additional PFH adsorption simulations at larger chemical potentials and using the same ε as the one used for the Ar adsorption isotherms. The results are summarised in Figure 6.13. The increase in ε resulted in a larger amount adsorbed of PFH in proposed model carbons. Nevertheless, adsorbed PFH adsorbed volume is too low compared to experimental values. Simulations at higher chemical potential showed larger PFH adsorption that are closer to the experimental values suggesting that initially calculated chemical potential does not correspond to pressures of interest. Adsorption in mesoporous region calculated in slit pore model at the same increased chemical potential can additionally contribute about 10 to 11 STP cm³ g⁻¹ of adsorbed PFH.

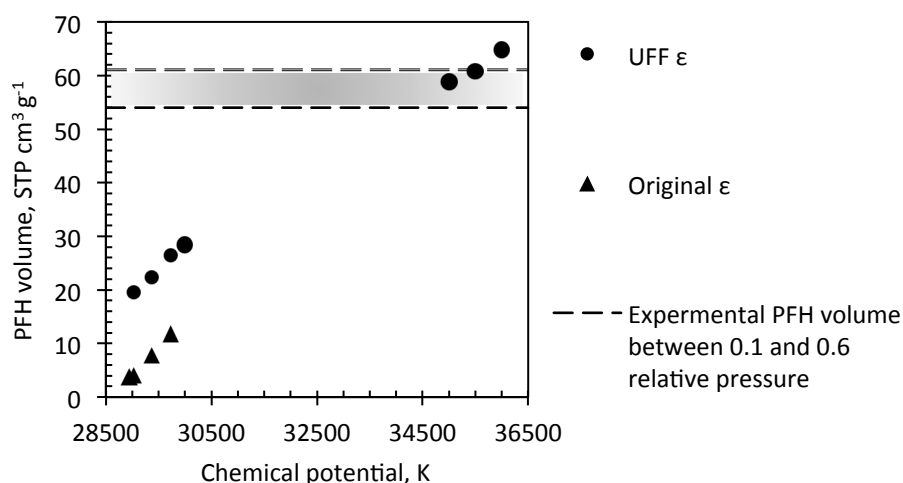


Figure 6.13. Perfluorohexane adsorption in model carbon as a function of chemical potential.

6.4 Conclusions

Perfluorohexane adsorption was predicted in commercially available BAM-109 activated carbon at 273 K and relative pressures of 0.1, 0.3 and 0.6. To represent microporous region, activated carbon model was constructed as a collection of randomly packed individual molecules, which possess 3-dimensional rigid structures. Prior to PFH adsorption, the model system was validated by calculating Ar isotherm and comparing the results with the experimental benchmark data. The model was able to accommodate the same volume of Ar as in experiment up to 0.9 relative pressures. PFH adsorption in carbon model was modelled using Gordon force field and non-bonded interactions were described using modified Gordon n-6 potential with the parameters adapted from the work of Potoff and Bernard-Brunel [5]. We found that the virtual model of activated carbon can adsorb $4.1 \pm 0.6 - 11.8 \pm 1.3 \text{ cm}^3 \text{ g}^{-1}$ of PFH in the range of relative pressures between 0.1 and 0.6, and at higher pressures when the mesoporous region is filled, the amount adsorbed can reach over $40 \text{ cm}^3 \text{ g}^{-1}$. The calculated amounts of PFH loadings in model carbons are significantly underpredicted. Errors in the estimation of the chemical potential are considered to be the main problem in the estimation of the experimental adsorption isotherm.

6.5 References

1. IFPSC. *Benchmark data for "Industrial Fluid Properties Simulation Collective. 8th Challenge*. 2014 [cited 2014 15 September]; Available from: <http://fluidproperties.org/8th-benchmarks>.
2. Ross, R.B., et al., *The seventh industrial fluid properties simulation challenge*. Fluid Phase Equilibria, 2014. **366**(0): p. 136-140.
3. Gonciaruk, A. and F.R. Siperstein, *In silico designed microporous carbons*. Carbon, 2015. **88**(0): p. 185-195.
4. Potoff, J.J. and G. Kamath, *Mie Potentials for Phase Equilibria: Application to Alkenes*. Journal of Chemical & Engineering Data, 2014. **59**(10): p. 3144-3150.
5. Potoff, J.J. and D.A. Bernard-Brunel, *Mie Potentials for Phase Equilibria Calculations: Application to Alkanes and Perfluoroalkanes*. The Journal of Physical Chemistry B, 2009. **113**(44): p. 14725-14731.
6. Martin, M.G., *MCCCS Towhee: a tool for Monte Carlo molecular simulation*. Molecular Simulation, 2013. **39**(14-15): p. 1212-1222.

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7. Gordon, P.A., *Development of intermolecular potentials for predicting transport properties of hydrocarbons*. The Journal of Chemical Physics, 2006. **125**(1): p. 014504.
 8. Accelrys Software Inc., *Material Studio Online help*. 2010.
 9. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
 10. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358–3363.
 11. Steele, W.A., *The physical interaction of gases with crystalline solids: I. Gas-solid energies and properties of isolated adsorbed atoms*. Surface Science, 1973. **36**(1): p. 317-352.
 12. Chapela, G.A., et al., *Computer simulation of a gas-liquid surface. Part I*. Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 1977. **73**(7): p. 1133-1144.
 13. Plimpton, S., *Fast Parallel Algorithms for Short-Range Molecular Dynamics*. Journal of Computational Physics, 1995. **117**(1): p. 1-19.
 14. Crowder, G.A., et al., *Vapor pressures and triple point temperatures for several pure fluorocarbons*. Journal of Chemical & Engineering Data, 1967. **12**(4): p. 481-485.
 15. Lemmon, E.W., M.O. McLinden, and D.G. Friend. *Thermophysical Properties of Fluid Systems*. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 [cited 2014 15 September]; Available from: <http://webbook.nist.gov>.
 16. Rappe, A.K., et al., *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations*. Journal of the American Chemical Society, 1992. **114**(25): p. 10024-10035.
 17. Drii, L.I. and V.A. Rabinovich, *Dependence of Vapor Pressure of Argon*. Zhurnal Fizicheskoi Khimii, 1966. **40**: p. 709-711.
 18. Mooibroek, T.J., P. Gamez, and J. Reedijk, *Lone pair-[small pi] interactions: a new supramolecular bond?* CrystEngComm, 2008. **10**(11): p. 1501-1515.
 19. Martin, M.G. and A.L. Frischknecht, *Using arbitrary trial distributions to improve intramolecular sampling in configurational-bias Monte Carlo*. Molecular Physics, 2006. **104**(15): p. 2439-2456.
 20. Widom, B., *Some Topics in the Theory of Fluids*. The Journal of Chemical Physics, 1963. **39**(11): p. 2808-2812.
 21. Widom, B., *Potential-distribution theory and the statistical mechanics of fluids*. The Journal of Physical Chemistry, 1982. **86**(6): p. 869-872.

7 COMPUTATIONAL STUDY OF GAS ADSORPTION IN 2-DIMENSIONAL POLYMER

This chapter was prepared as a manuscript for the submission to a peer reviewed journal.

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Abstract

A single layer two-dimensional crystalline polymer with uniformly dispersed nanopores and fluoro-functional groups has been recently reported. Its structural and chemical properties make it attractive candidate for membrane separations. As a starting point to explore this material we use computational methods to predict and study adsorption of industrially important gases (carbon dioxide, methane and nitrogen) and binary mixture selectivity. Initial predictions show that the fluorinated polymer is significantly selective for carbon dioxide over methane and nitrogen. However different atomic partial charge calculation methods produce considerably different results primarily due to differences between charges assigned to electronegative fluorine atoms, which affects fluorine-carbon dioxide interactions and gas packing inside the pore. Binary gas mixtures are expected to behave according to ideal adsorbed solution theory. Validation of simulation results with experimental data would be important to select appropriate charge calculation method for further membrane permeation studies.

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7.1 Introduction

Poly(fantrip) is a two dimensional porous polymeric crystalline material that has potential applications in membrane separations. The material has monodisperse pores of nanometre size, low density due to lightweight elements, well defined and rigid architecture that is synthetically reproducible and can be potentially tailored and adjusted for specific applications such as gas separation and storage. Poly(fantrip) can be prepared from the bulk layered crystal of monomers and does not require solid support like some covalent (COFs) and metal organic frameworks (MOFs) [1, 2]. Moreover, poly(fantrip) contains large density of fluoro-functional groups, which were associated with increase in thermal and chemical stability [3] leading to robust materials suitable for industrial environments.

There were also reported a number of microporous organic network polymers that also form laminar crystals and some of them contain fluorine functional groups [4-6]. However all of these materials create stacks as in graphite where layers align face-to-face. Poly(fantrip) and its analogues studied in this work, have an advantage of creating stacks edge-to-edge, so that all functionality (in this case, fluoro-groups and aromatic π electron cloud) is concentrated inside the pore.

It is well known that presence of lone pair or electrophilic electrons facilitates CO₂ adsorption (e.g. amine groups are the usual choice in industry). Fluorine, a halogen element, is electron rich and highly electronegative. Materials containing fluoro-functional groups were found to be among the best performers in terms of CO₂/CH₄ and CO₂/N₂ selectivity especially compared to nonfluorinated analogous [7-9]. Fluorine atoms being bulkier will occupy more space than the analogous materials reducing free volume, this may decrease permeability [10] or permeability may be unaffected due to simultaneous increase in gas solubility as was the case with fluoro-aromatic polymers [8]. Affinity is expected to decrease towards hydrocarbons and other low polarity compounds [10].

We also draw significant attention to the separation of CH₄ from N₂, which are particularly challenging due to their similar molecular size. Current separation method is energetically demanding cryogenic distillation. Separation based on selective adsorption in solid materials is an attractive alternative due to promising energy-efficiency and ability to separate highly contaminated and/or low-flow-rate streams [11, 12]. Poly(fantrip) having high surface area

with uniform monodisperse pore size distribution and polarizable fluorine atoms have a great potential.

Poly(fantrip) synthesis relies on the organization of monomers in 2D sheets, which can also form single crystals. The adsorption properties of poly(fantrip), its nonfluorinated analogous poly(antrip) and antrip crystal are assessed in this work using grand canonical Monte Carlo (GCMC) simulations.

7.2 Methodology

7.2.1 Structures

Poly(fantrip) monomer is three tetrafluoroanthraceno arms connected through a [2.2.2] bicyclic bridgehead core. Triptycene based monomers have been used for synthesis of polymer and carbon materials due to its ability to hold three-dimensional rigid shapes creating free void space between the arms [13-16]. Some of the materials using triptycene core as a contortion site for creating porosity are amorphous but have a relatively narrow pore size distribution [13-16], while in some cases ordered structures can be obtained [2, 17, 18]. Poly(fantrip) (Figure 7.1 left) is an ordered material that is not fragile or brittle, is tough, can be exfoliated into free standing plate-like sheets and does not adsorb moisture even after one month of handling in the open air; however depolymerisation of the materials starts at 160°C slightly limiting its range of applicability [1].

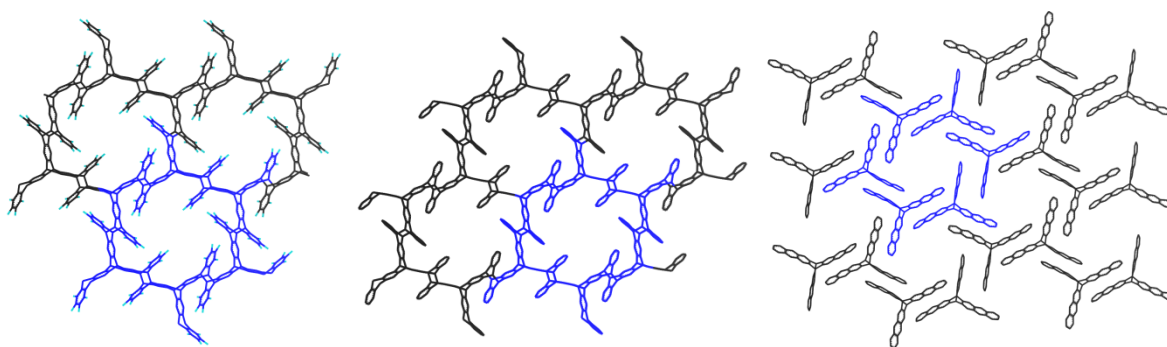


Figure 7.1. Structures of monolayers of (left) poly(fantrip), (middle) poly(antrip) and (right) antrip. Highlighted in blue is a fragment that creates pore. Colour code: carbon atoms are black, fluorine atoms are cyan and hydrogen atoms are omitted for clarity.

Poly(antrip) (Figure 7.1 middle) has similar chemical composition as poly(fantrip) except it lacks fluoro-groups, which are substituted by hydrogens. Poly(antrip) is less thermally stable than its fluorinated analogue [1, 2].

Fantrip (and antrip (Figure 7.1 right)) monomers were shown to possess crystalline lamellar sheets. Monolayers make a hexagonal packing motif as the polycyclic aromatic arms connect face-to-face through non-bonded forces at a 35.3° tilt. Antrip monomer crystals are fragile and disintegrate upon drying suggesting its metastable crystalline state.

7.2.2 Structure Generation and Simulation Details

Models of the solid framework were constructed using Materials Studio, Accelrys Software Inc. (San Diego, CA). Crystal structure data of poly(fantrip) and antrip was obtained in CIF format from references [1] and [2]. The supercell was constructed by replicating given crystal unit cell four times resulting in simulation cells, which parameters are given in Table 7.1. Poly(antrip) was created by replacing fluorine atoms with hydrogens. The geometry was then refined by running the Geometry Optimization task as implemented in Materials Studio. The task uses an algorithm, which is a cascade of the steepest descent, adjusted basis set Newton-Raphson, and quasi-Newton methods. A cell optimization was performed simultaneously with fixed lattice angles to account for possible changes in interlayer distances due to change of functional group bulkiness. Selected images of created structures are presented in Figure 7.2, which shows layering of polymers and monomers as well as resulting cylinder-like pore volume of polymers. The structures were described using the DREIDING force field [19]. The DREIDING force field is commonly used to simulate bonded and non-bonded interactions in structurally and chemically similar crystalline network (MOFs, COFs) and polymeric materials (PIMs, porous aromatic frameworks) [15, 20, 21]. In geometry optimization part, partial charges were calculated using QEq method [22].

Table 7.1. Unit cell dimensions and angles.

Structure	Number of atoms	Dimensions (A, B, C)	Angles (α , β , γ)
Poly(fantrip)	8960	36.056, 58.308, 62.604	94.340, 93.101, 96.984
Poly(antrip)	8960	36.671, 59.074, 62.306	94.340, 93.101, 96.984
Antrip	8400	51.662, 31.847, 66.868	90.000, 95.410, 90.000

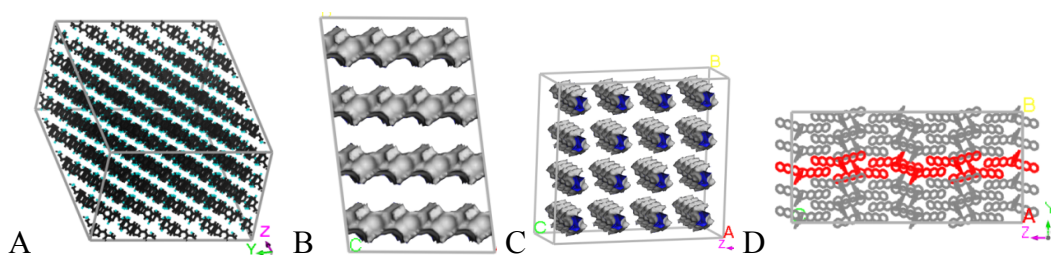


Figure 7.2. (A) Unit cell of poly(fantrip), (B) and (C) unit cell of poly(antrip) showing free volume accessible to helium atom and (D) unit cell of antrip with one layer highlighted in red.

CO₂ was modelled using EPM2 [23] as a three-site model. Nitrogen model was described by TraPPE-EH [24], where nitrogen is a three-site model with two sites located on nitrogen atoms and third site is on the molecule's centre of mass. Charges on atoms of CO₂ and N₂ were assigned by their force field. Methane was modelled as a single-site particle without charges using DREIDING force field with modified ϵ and σ parameters taken from [25]. Interaction parameters between unlike atoms were calculated using Lorentz-Berthelot mixing rule.

7.2.3 Partial Charges

Partial charges on framework atoms were calculated using two semi-empirical charge equilibration methods: QEq [22] and Gasteiger [26], and quantum mechanical density functional theory (DFT) (Table 7.2). The set of charges was considered as static during adsorption simulations.

Both empirical charge equilibration methods exploit electronegativity notion of bonded atoms. In Gasteiger case, electrons flow from less electronegative atom to more electronegative one resulting in positive charge on less electronegative atoms and negative charge on more electronegative one. Gasteiger assumes polynomial dependence between electronegativity of valence orbital and transferred charge, which leads to lower electronegativity as charge density increases. The method uses iterative procedure to minimise the transferred charge to equalise electronegativity of orbitals participating in bond formation. QEq method exploits atomic electrostatic potential. The energy of the atom is differentiated with respect to charge and an optimum value of charge is found when

derivatives of all atoms are equal. QEq method use experimental data, namely atomic ionization potential, electron affinity, atomic radii, and needs atomic positions and atomic number as an input. Both Gasteiger and QEq do not require calculation of wavefunctions and electron density that makes them very efficient charge calculations method especially suitable for materials screening [27].

Another set of charges are derived by fitting electrostatic potential (ESP) on a surface around the molecule [28] with Gaussian 09 [29] at the B3LYP/6-31G* level of theory. ESP charges are commonly used in the subsequent force field based adsorption simulations [30-32]. A representative segment of the poly(fantrip) framework was selected to calculate the charges. Several different fragments (see 7.5 Supplementary Information) were selected in order to understand the effect of environment on the charges on blades. We observed overall good agreement between the different fragments thus just one (Figure 7.3) was adopted for materials and subsequent adsorption study. The calculated charges (see Figure 7.4, Table 7.2 and Table 7.3) were then populated in the periodic structure assuming that symmetric atoms have the same charge and the overall charge of the framework was set to zero by adjusting each charge by a constant.

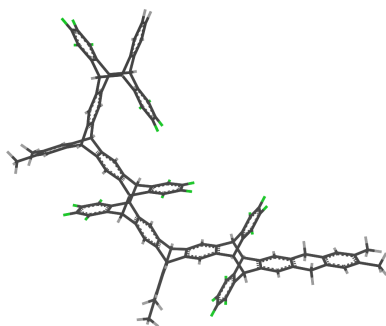


Figure 7.3. Poly(fantrip) fragment chosen for DFT charge calculations. Colour code: black – carbon, green – fluorine, grey - hydrogen.

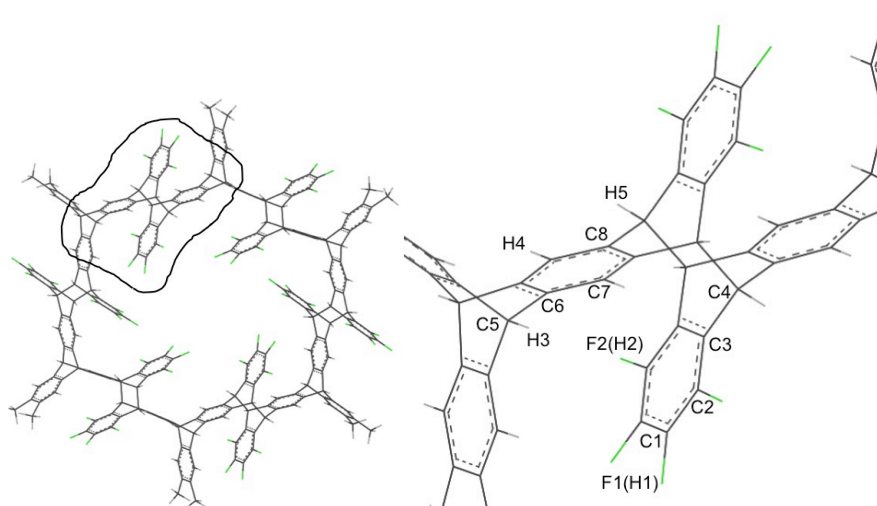


Figure 7.4. Fragment of poly(fantrip). Atom names in brackets correspond to nonfluorinated material.

Table 7.2. Average charges on atoms of the fragment shown in Figure 7.4 used to model poly(fantrip).

Atom	QEq	Gasteiger	ESP
F1	-0.4798	-0.2146	-0.1195
F2	-0.5336	-0.2356	-0.1455
C1	0.4397	0.2291	0.0805
C2	0.3690	0.1962	0.2975
C3	-0.0666	0.0349	-0.1565
C4	-0.0841	-0.0198	0.0743
C5	-0.1149	-0.0201	0.2255
C6	0.0268	-0.0084	-0.0460
C7	-0.0969	-0.0232	-0.3180
C8	0.0293	-0.0086	0.0965
H3	0.1234	0.0322	0.0685
H4	0.1458	0.0319	0.1645
H5	0.1902	0.0320	0.0885

Table 7.3. Average charges on atoms of the fragment shown in Figure 7.4, where fluorine atoms are replaced by hydrogen atoms for modelling poly(antrip).

Atom	QEq	Gasteiger	ESP
H1	0.1011	0.0312	0.0966
H2	0.0789	0.0315	0.0743
C1	-0.1015	-0.0309	-0.1055
C2	-0.1103	-0.0272	-0.1261
C3	0.0536	-0.0090	0.0871
C4	-0.1190	-0.0232	-0.2344
C5	-0.1249	-0.0201	-0.1208
C6	0.0356	-0.0084	0.1268
C7	-0.1445	-0.0232	-0.2181
C8	0.0377	-0.0087	0.0860
H3	0.0882	0.0321	0.1526
H4	0.0952	0.0318	0.1303
H5	0.0855	0.0318	0.1529

7.2.4 Characterization

The virtual materials were characterised in terms of bulk density (ρ), accessible nitrogen surface area (S_A), free void volume (V) and pore size distribution (PSD). Parameters are explained in more detail in Chapter 2.

Radial distribution functions (RDFs) were calculated between oxygen atoms of CO₂ molecule and hydrogen atoms bonded to the core carbon atoms (H3 and H5 in the right image of Figure 7.4) and also between carbon atoms of CO₂ and fluorine atoms. An RDF is the measure of probability finding two atoms at a given spherical distance.

An order parameter was calculated for CO₂ molecules adsorbed at a pressure of 10 bar. Order parameter P is calculated for an angle θ between CO₂ molecule (i.e vector parallel to linear CO₂) and i axis (x, y or z):

$$P_i = \frac{1}{2} (3 \cos^2 \theta - 1) \quad (7.1)$$

If CO₂ molecules align parallel to a given axis, the angle between them is zero or 180° resulting in P being equal to 1, when is it perpendicular P is -0.5 and if the alignment is random P will be 0.

7.2.5 Adsorption

Adsorption of CO₂, CH₄ and N₂ were carried out in MCCCSTowhee v7.0.6 [33]. Framework atoms were frozen in space, therefore all system atoms were unconnected for simpler conversion to input file. Adsorption isotherms were calculated at 298 K after at least 6×10⁶ equilibration and production steps, which include exchange, rotation, translation and regrowth types. Adsorption isotherms were calculated in grand canonical ensemble by providing chemical potential for adsorptive molecule. The chemical potential was calculated in the NPT ensemble MC simulation using box filled only with gas molecules. The simulation was typically carried out for minimum of 2×10⁶ MC moves including equilibration and production steps.

Adsorption isotherms were fitted to Langmuir isotherm model:

$$n = \frac{k m P}{1 + k P} \quad (7.2)$$

where n and P are the amount of gas adsorbed and pressure, respectively, k and m are constants that can be associated with affinity and saturation capacity of the adsorbent, respectively. In cases where the Langmuir isotherm was not a good representation of the experimental data, modified Langmuir isotherm model with additional constant c was used to account for very steep adsorption at low pressure:

$$n = \frac{k m P}{1 + k P} + cP \quad (7.3)$$

The solubility of a gas S_0 at infinite dilution can be obtained by dividing the (7.2) and (7.3) by pressure and taking the limit at zero pressure. The ideal selectivity S_{ij} was obtained by taking the ratio of these parameters calculated from pure gas adsorption isotherms for each gas component i and j :

$$S_0 = \lim_{P \rightarrow 0} \left(\frac{k m}{1 + k P} \right) = k m \quad (7.4)$$

$$S_0 = \lim_{P \rightarrow 0} \left(\frac{k m}{1 + k P} + c \right) = k m + c \quad (7.5)$$

$$S_{ij} = \frac{S_{o,i}}{S_{o,j}} \quad (7.6)$$

Mixture adsorption was carried out similarly to pure gas adsorption using chemical potentials calculated from simulations of a gas mixture at desired composition, temperature and pressure. An additional two-molecule centre of mass switch move was allowed. Adsorption of gas mixtures can also be predicted from pure gas adsorption isotherms using Ideal Adsorbed Solution Theory (IAST) [34] once constants of (7.2) and (7.3) are known. It is a useful measure indicating whether the additional investigations of mixture adsorption are necessary as it was shown that IAST is perfectly applicable for predictions of CO₂, CH₄ and N₂ binary mixtures adsorption in MOFs and zeolites [35, 36]. Mixture adsorption isotherms were fitted to either of the following models:

$$n = \frac{k_i m_i P_i}{1 + k_i P_i + k_j P_j} \quad (7.7)$$

$$n = \frac{k_i m_i P_i}{1 + k_i P_i + k_j P_j} + c_i P_i \quad (7.8)$$

where i and j are two gas components and P is partial pressure. The selectivity was calculated using equation (7.6).

Isosteric heat of adsorption for pure components was calculated from grand canonical ensemble average fluctuations using equation 2.33.

7.2.6 Permeability

Permeability in glassy polymer membranes can be calculated using solution diffusion model:

$$p = D \times S \quad (7.9)$$

where D is the gas diffusivity (cm^2s^{-1}) and S is the gas solubility in a polymer ($\text{cm}^3(\text{STP})\text{cm}^{-3}\text{cmHg}^{-1}$). We estimated permeability at atmospheric pressure (1 bar) and 293K. Permselectivity is then calculated as p_i/p_j .

Solubility is calculated as pressure normalised amount of adsorbed gas:

$$S = n/P \quad (7.10)$$

Volume occupied by polymer required for unit conversion for solubility is calculated from skeletal density [37]:

$$\rho_{skel} = \left(\frac{1}{\rho_{sim}} - \frac{V_{pore}}{m} \right)^{-1} \quad (7.11)$$

where ρ_{sim} and ρ_{skel} are simulated and predicted experimental (or skeletal density), respectively, V_{pore} is helium pore volume and m is the mass of a solid.

Thornton *et al.* [38] showed empirical correlation between diffusivity and polymers' free fractional volume:

$$D = a \exp(\beta f) \quad (7.12)$$

where f is fractional free volume, α and β are empirical constant fitted to experimental permeability data of wide range of polymers with fractional free volume ranging from 10% to 35%. The parameters are listed in Table 7.4. Fractional free volume is calculated as ratio between helium void volume and reciprocal bulk density.

Table 7.4. Parameters used in equation (7.12) to estimate diffusivity of different gases [38].

Gases	α ($10^{-4} \text{ cm}^2 \text{ s}^{-1}$)	β (dimensionless)
CO ₂	42.89	38.42
CH ₄	1.14	48.31
N ₂	11.25	42.01

As no direct simulation of permeability is performed, the method has some limitations [38, 39]. The model does not capture dynamic interactions between material and gas, so there is no information regarding polymer swelling or plasticization effect caused by gases. Diffusivity and permeability dependency on temperature and pressure is also not known for these materials. The method does not include permeability relation to polymer thickness, which is known to be lower in thicker membranes. Finally, the method is derived for amorphous polymers and may not necessarily work for materials with defined anisotropic pores. On the other hand, it is claimed that model can predict permeability in variety of materials including those with very high fractional free volume which were shown to possess interconnected pores that provide free pathways for fast gas diffusion [38, 40]. Continuous connecting pore types can be assumed to be equivalent to the channels formed by our bulk polymer. We would like to note that the permeability calculations made in this work are for predictive screening purposes only and the more detailed simulations are planned in the future in our laboratory.

7.3 Results

7.3.1 Structural Properties

As expected, poly(fantrip) have considerably smaller nitrogen surface area and free void volume accessible to helium atom than that of poly(antrip) and antrip due to bulkier fluorine atoms (Table 7.5). The surface area (SA) is comparable to some amorphous polymers, carbons and crystalline materials; their properties are also shown in Table 7.5 for comparison. Pore size distribution of poly(fantrip), poly(trip) and antrip are given in Figure 7.5. All three materials have monodisperse PSD in microporous region with pores smaller than 10 Å. Polymeric materials have the largest concentration of pores of approximately 5 Å while the crystalline monomer has larger pores of approximately 7-8 Å.

Table 7.5. Structural properties of materials studied in this work and some porous materials reported in the literature.

	ρ , g cm ⁻³	SA, m ² g ⁻¹	V, cm ³ g ⁻¹
Poly(fantrip)	1.26	544	0.073* (0.382)**
Poly(antrip)	0.88	830	0.135* (0.576)**
Antrip	1.01	763	0.149* (0.468)**
Activated carbons	1.14 [41], 1.90-2.20 [42]	600-1100 [43], 635 and 1850 [44], 892 [41], 1160 and 3100 [45], >3551 [42]	0.3-0.45 [43], >1.11 [42], ~ 0.4-2.7 [45]
Zeolite: NaX	1.31 [46]	478 [47], 534 and 542 [48], 573 [49], 598 [50]	0.159 [49], 0.19 [47] [48], 0.22 [48]
PIMs containing triptycene unit:			
Trip(R)-PIM	0.917 [15], 1.27-1.67 [13], 1.4 [16]	618-1760 [13], 1065 [16]	-
Trip-TB-network [15]	0.937	1035	0.015
Trip-TB-ladder [15]	0.903	899	0.021
Derived from discrete organic molecules containing triptycene unit:			
Crystalline TTBI [51]	0.775	2796	1.02
OMIMs [52]	0.704-1.085	155-2053	0.158-0.24
Ni-salphen [53]		Null - 500	

*Volume defined by solvent (helium) surface

**Volume defined by vdW surface

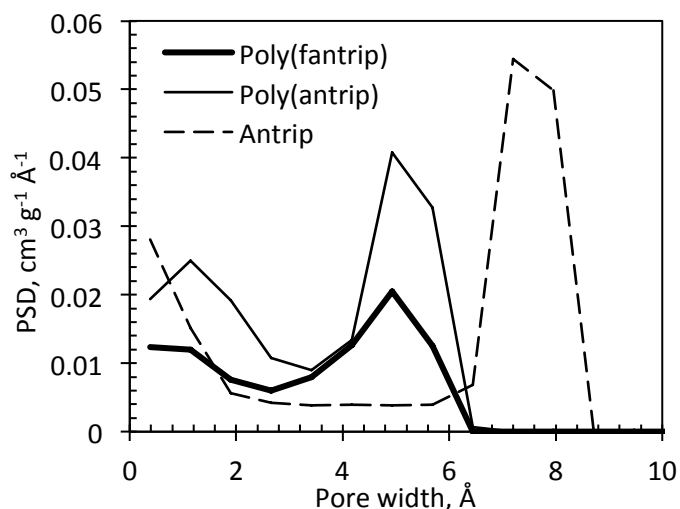


Figure 7.5. Pore size distribution.

7.3.2 Gas Adsorption and Charge Effect

Adsorption isotherms of three gases (Figure 7.6) and gas pair (CO_2/CH_4 , CO_2/N_2 and CH_4/N_2) selectivity at the limit of 0 pressure and 298 K were calculated for poly(fantrip), poly(antrip) and antrip materials (Table 7.6). Poly(fantrip) shows high selectivity towards CO_2 over CH_4 and N_2 compared to nonfluorinated materials, although the value of selectivity strongly depends on the assigned charges, which is discussed in the following paragraphs. Both poly(antrip) and antrip are less selective; the values are closer to the ones observed in activated carbons [44, 54-56].

As expected CH_4 adsorption is not affected by the charges in the framework since the molecule is modelled as a united atom bead with zero charge. N_2 adsorption is less affected than CO_2 due to smaller quadrupole moment and most charge calculation methods with the exception of QEq predict almost the same N_2 adsorption isotherms. Charge calculation method does not have profound effect on CO_2 adsorption in poly(antrip) (Figure 7.6), thus it is expected to be irrelevant for N_2 and especially CH_4 adsorption. Therefore all presented results for poly(antrip) and antrip are with QEq charges only.

Table 7.6. Selectivity at infinite dilution of poly(fantrip), poly(antrip) and antrip with different charges.

	CO ₂ /CH ₄	CO ₂ /N ₂	CH ₄ /N ₂
Poly(fantrip)			
QEq	52	185	3.6
Gasteiger	6.6	32	4.9
ESP	4.8	25	5.2
No charge	3.3	18	5.6
Poly(antrip)			
QEq	3.7	18	4.7
Antrip			
QEq	3.4	16	4.6

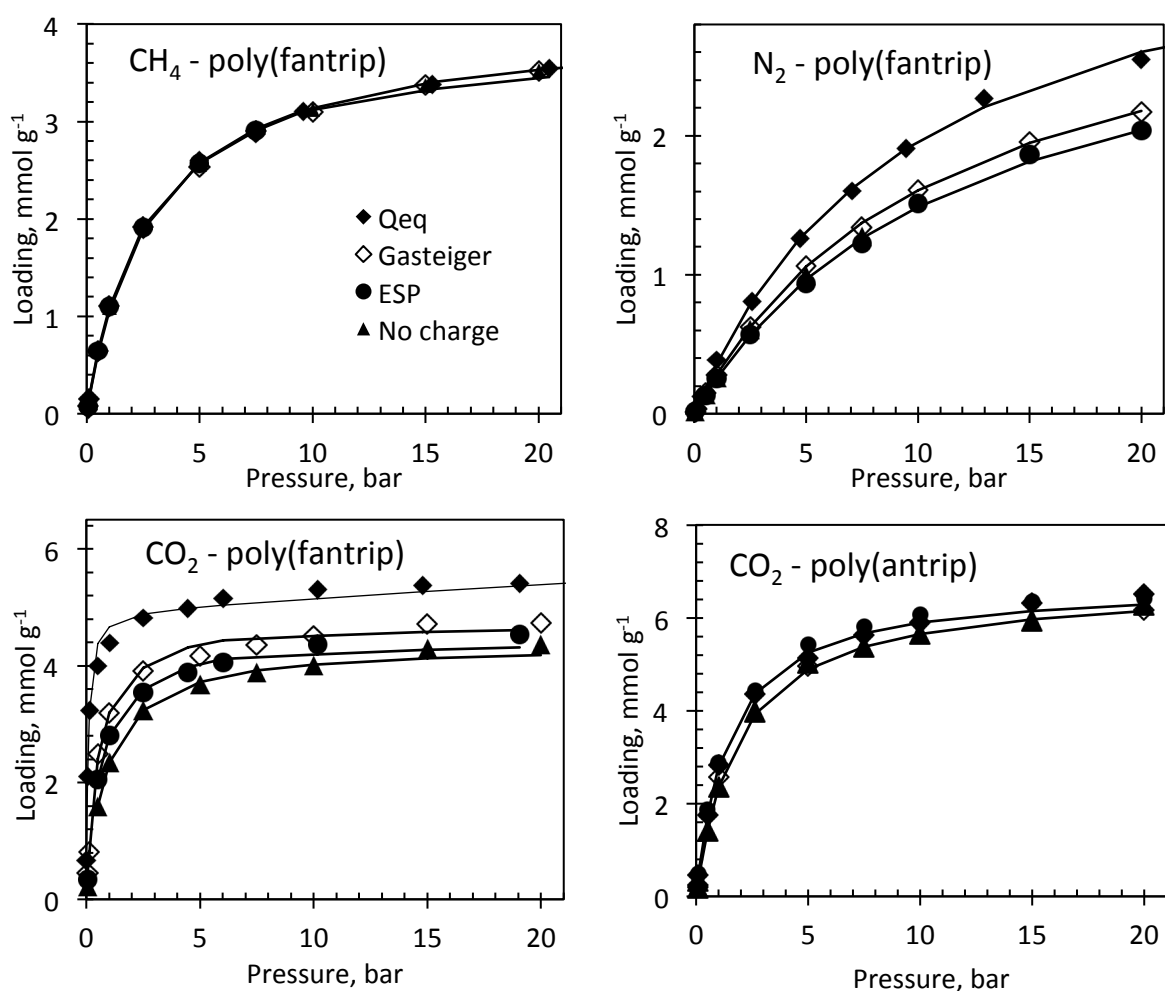


Figure 7.6. Adsorption isotherms of CH₄, N₂ and CO₂ in poly(fantrip) and poly(antrip) showing the differences caused by the selection of charge calculation method. Note that in “N₂ – poly(fantrip)” plot, “ESP” and “No charge” points are indistinguishable.

The presence of fluorine atoms did not affect significantly the CH₄/N₂ selectivity. However CH₄/N₂ selectivity is similar to the one reported for currently most CH₄ selective metal coordinated framework [57, 58]. This is an encouraging finding for unconventional natural gas upgrading industry where considerable amount of nitrogen is present in streams (more than required minimum of 4% [59]). Separation of nitrogen from methane is particularly difficult due to their similar molecular sizes. Materials studied in this work have a cylinder like pores of irregular surface (Figure 7.2 C) that can fit both molecules, thus the separation would be based on interaction strength difference rather than their size. Nevertheless, previous studies showed that pore geometry plays crucial role in CH₄/N₂ separation. It was found that cylinder-like pores of carbon nanotube bundles promotes CH₄ adsorption compared to carbon slit, random or foam pores as there is a greater amount of atoms in the tube perimeter that contributes to solid-CH₄ interactions [60, 61]. Considering methane storage rather than separation, the saturation capacity (115 cm³/cm³ at 35 bar and 298 K) of these materials would not be sufficient as the target set by U.S. Department of Energy in 2012 is 263 cm³/cm³ at 298 K [62].

The charge calculation method has a significant effect on adsorption of CO₂, which is expressed in the change of affinity and saturation capacity of adsorbent. QEq method predicts the largest quantity of CO₂ adsorbed and very steep adsorption at sub-atmospheric pressures, which suggests great affinity towards CO₂. The very large CO₂/CH₄ and CO₂/N₂ selectivity is close to some selective materials such as zeolites and MOFs [6, 36, 63-67]. Gasteiger and ESP charged frameworks reach lower capacity at about 20 bar by about 0.6 mmol g⁻¹ and lower slopes at low pressures. The change in slope is echoed in significant differences in selectivity. QEq predicts very strong affinity towards CO₂ over the other two gases; however selectivity reduces by almost an order of magnitude when Gasteiger or ESP charges are used. Nevertheless, poly(fantrip) exhibit preferential adsorption of CO₂ as CO₂/CH₄ and CO₂/N₂ selectivity is 1.5 – 2 times higher compared to nonfluorinated poly(antrip). The CO₂/N₂ selectivity in poly(fantrip) with charges calculated using methods other than QEq is comparable to selectivity reported for some structurally and chemically similar microporous organic materials, CO₂ uptake at 1 bar is also comparable or even greater compared to many cases summarised by Dawson et.al [68]. Adsorption isotherms for all gases in poly(fantrip) with zero charges and in poly(antrip) are very similar, suggesting that the source of the CO₂ selectivity is the highly electronegative fluorine atoms.

It has been previously reported that adsorption simulation in number of MOFs with QEq charges predicted higher adsorption loadings of CO₂ compared to results obtained with other methods [69, 70]. On the other hand, loadings of CO₂ were also underpredicted in similar number of cases. The discrepancies between results using charge equilibration and quantum chemistry derived charges arose from the notably different charges calculated on heavy metals or electronegative atoms (N or O); however no systematic over- or under-prediction was observed. Therefore it is important to choose the “correct” charges for highly electronegative fluorine atoms that are present in our system and experimental data is needed to validate the choice of method.

Nonetheless, according to the results for the CO₂ adsorption capacity at 1 bar and 298 K (Table 7.7), an increase of about 0.5 – 2 mmol g⁻¹ (depending on the method used for calculating charges) is observed for the fluorinated polymer in comparison with the nonfluorinated one due to possibly specific interactions between fluorine atoms and CO₂. The result is consistent with the adsorption capacity difference of 2 mmol g⁻¹ reported for fluorinated and nonfluorinated versions of MOFs [3] and about 0.5 mmol g⁻¹ for porous organic polymers (POPs) [5, 6]. Stronger poly(fantrip) interaction strength with CO₂ is also reflected in higher isosteric heat of adsorption (-31 – -24 kJ mol⁻¹ depending on charge calculation method) compared to that of poly(antrip) (-19.5 kJ mol⁻¹). The values are again very similar to those reported for microporous organic polymers [6] and are closer when QEq method is used for charge calculation.

Table 7.7. CO₂ capacity at 298K in mmol g⁻¹.

	1 bar	20 bar
poly(fantrip)-QEq	4.38	5.56
poly(fantrip)-Gasteiger	3.18	4.73
poly(fantrip)-ESP	2.80	4.61
poly(fantrip)-No charge	2.34	4.37
poly(antrip)	2.64	6.27
antrip	2.40	5.93

The difference between saturation capacities at higher pressures can be attributed to differences in surface area (Figure 7.7). Fluorinated material has lower capacity compared to nonfluorinated analogous. Similar finding was reported for fluorinated MOF, which possessed significantly lower free volume and surface area [71]. Poly(antrip) having the greatest surface area adsorbs largest quantity of CO₂ and CH₄. The trend in nitrogen adsorptions is slightly

different as poly(fantrip)-QEq have highest capacity for N_2 in spite of having lowest surface area; however capacity is lower than that of poly(antrip) when other charges are used.

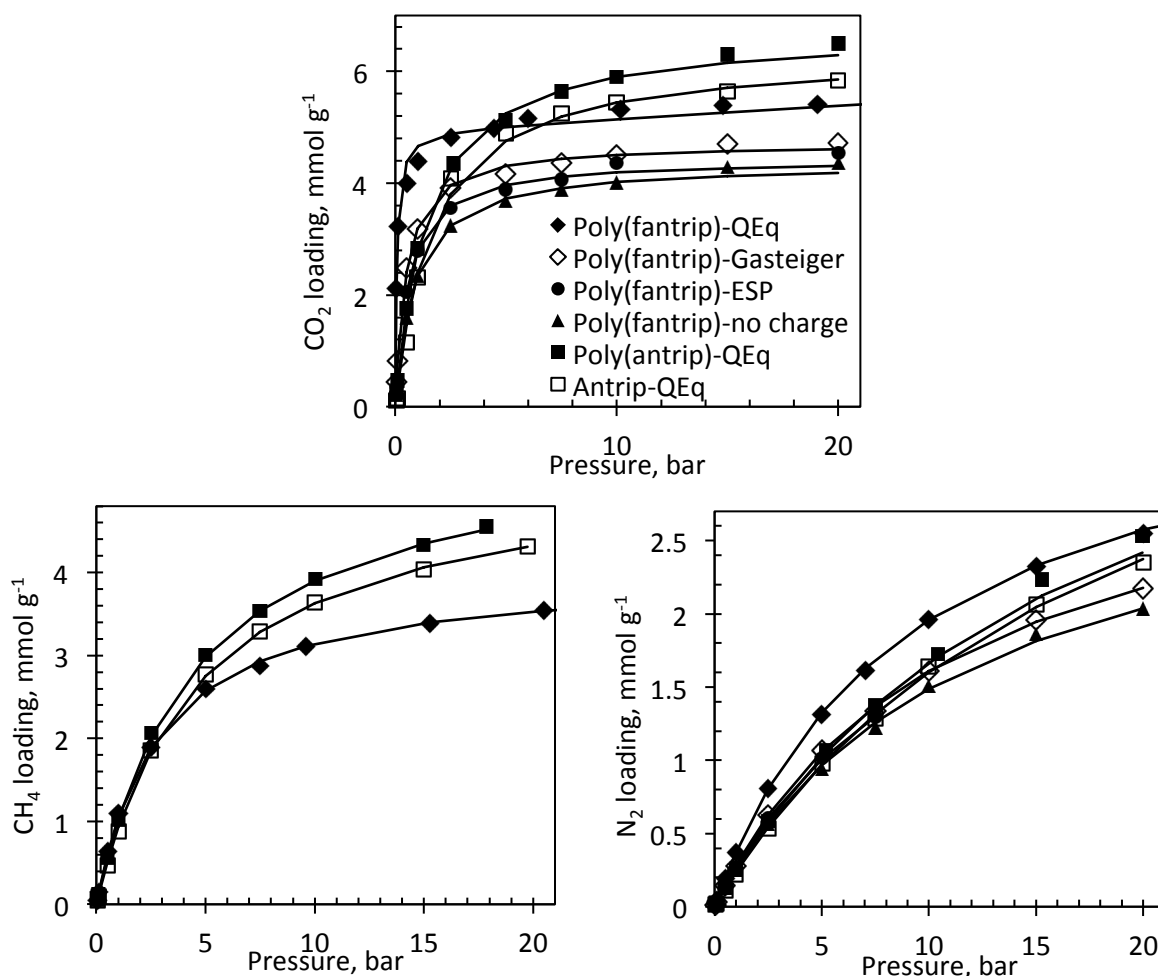


Figure 7.7. Gas uptake at 298K in poly(fantrip), poly(antrip) and antrip.

It is interesting to note that experimental and computational studies to the best of our knowledge were not able to find any specific interactions between fluorine atoms and CO_2 . A number of studies speculated about quadruple-dipole interactions [5, 7, 72]. Raveendran and Wallen suggested that fluorine atoms serve as Lewis basis donating electrons to the carbon atom, while positively charged aromatic ring acts as Lewis acid interacting with negative oxygen atoms in CO_2 [73]. Baradie *et al.* [74] reported very similar results where hydrogen atoms served as stabilising binding sites for oxygen due to more acidic nature in presence of the neighbouring fluorine. Therefore it was noted that there should be an optimal fluorination degree in order to leave partially unsubstituted hydrogen in a molecule's backbone [73, 74].

Based on these findings, enhanced adsorption in poly(fantrip)-QEq can be explained by the fact that the method assigns highly negative charges to fluorine atoms, this induces larger positive charge on core hydrogen atoms (see H1 and H3 from Table 7.2 and Figure 7.4) thus creating geometrically favourable adsorption sites. This is somewhat contradictory to the work reported by Torrisi *et al.* [75] where they concluded that fluorinated benzene lose its CO₂ adsorption energy with comparison to unsubstituted benzene. Diep *et al.* as well reported decreased affinity for CO₂ compared to nonfluorinated analogues [76]. However in both of latter studies considered fluorinated compounds are significantly smaller molecules compared to our polymers and MOFs suggesting that the environment of the fluorinated groups as well as confined pore is important.

In order to clarify the hypothesis regarding Lewis basis-acid interactions between CO₂ and framework, RDF between certain sets of atoms, spatial orientation function was calculated and visual illustration was obtained. Figure 7.8 shows representative image of the gas molecule adsorption positions in poly(fantrip)-QEq at the limit of zero pressure. CO₂ molecules are shifted towards the layer's edge where they are stabilised by triptycene core (hydrogen atom) located on the neighbouring layer. RDF between oxygen atoms of CO₂ molecules and hydrogen atoms show that CO₂ molecules are adsorbed slightly closer when polymer is charged using QEq method (Figure 7.9). The result is not clear as even if one oxygen atom of the CO₂ molecule is close to hydrogen, another will “feel” different environment interfering the RDF results. However, a significant difference between the distributions of CO₂ molecules in different frameworks is observed when analysing the C(CO₂)-F RDF where the first peak is significantly broader when using QEq, and starts at smaller separations than when using other methods. This shows a consistent positioning of CO₂ molecules in a pore.

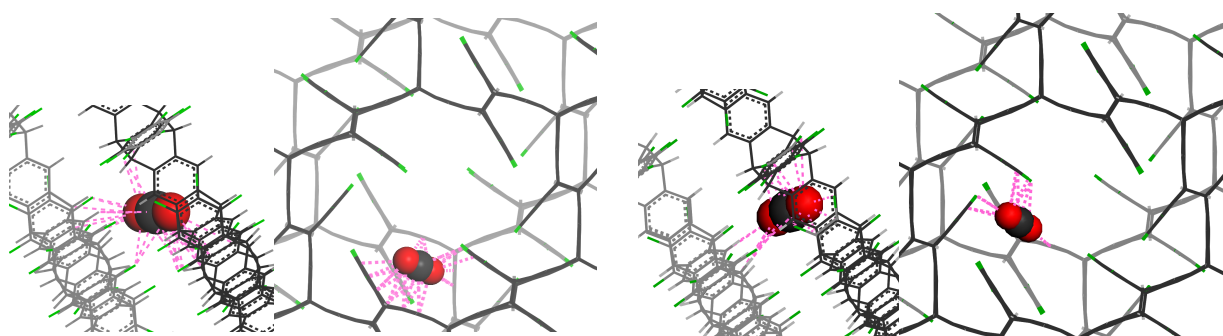


Figure 7.8. Representative CO₂ molecule position in poly(fantrip) with QEq charges.

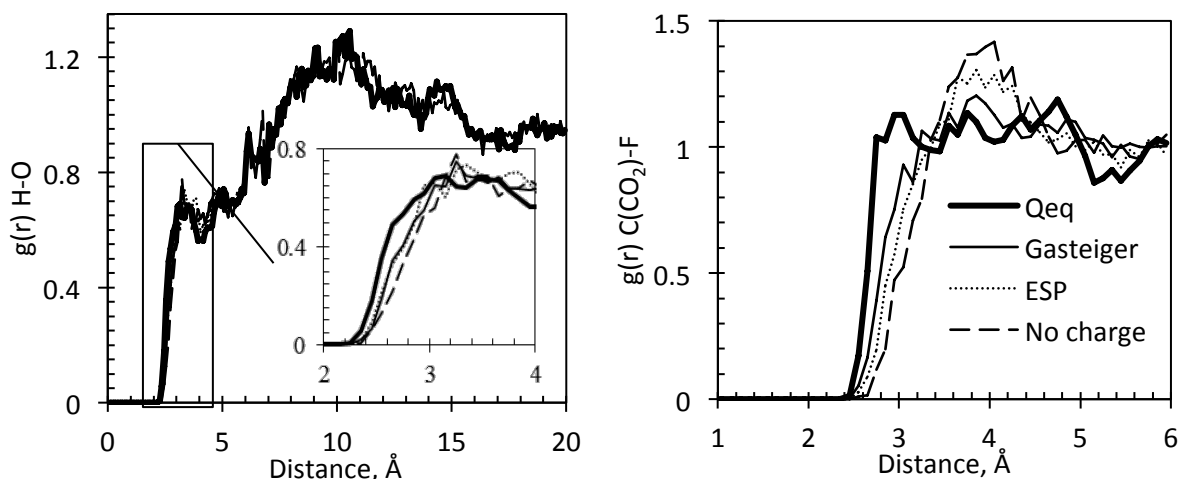


Figure 7.9. RDF (left) between oxygen atoms of CO₂ and hydrogen atoms located on tetrahedral carbons of the framework and (right) between carbon atoms of CO₂ and fluorine atoms.

In poly(fantrip)-QEq, more ordered adsorption of CO₂ molecules seems to be promoted compared to CO₂ positions in differently charged frameworks. Figure 7.10 shows spatial orientation parameter P_x , P_y and P_z of CO₂ molecules in poly(fantrip) at 10 bar pressure. In poly(fantrip)-QEq, there is larger fraction of molecules that are perpendicular to x and y axis and almost none that are parallel to x , i. e. there are no molecules with P_x between 0.5 to 1. There are more molecules that are parallel to y and z axis in QEq case than in differently charged frameworks (see P_y and P_z ranges from 0.5 to 1). CO₂ molecules tend to favour the same orientation at specific pore location as can be seen from Figure 7.11, which shows the merged positions of CO₂ molecules in the pore from five different snapshots. For example, CO₂ molecules defined as red sticks are located in the middle of the pore in between two blades. These CO₂ molecules orient to favour the interactions between the positive carbon atom and negative fluorine atoms. The green coloured CO₂ align so that one oxygen atom is between two blades and the other points to hydrogen atom of the other layer similarly to orientation shown in Figure 7.8.

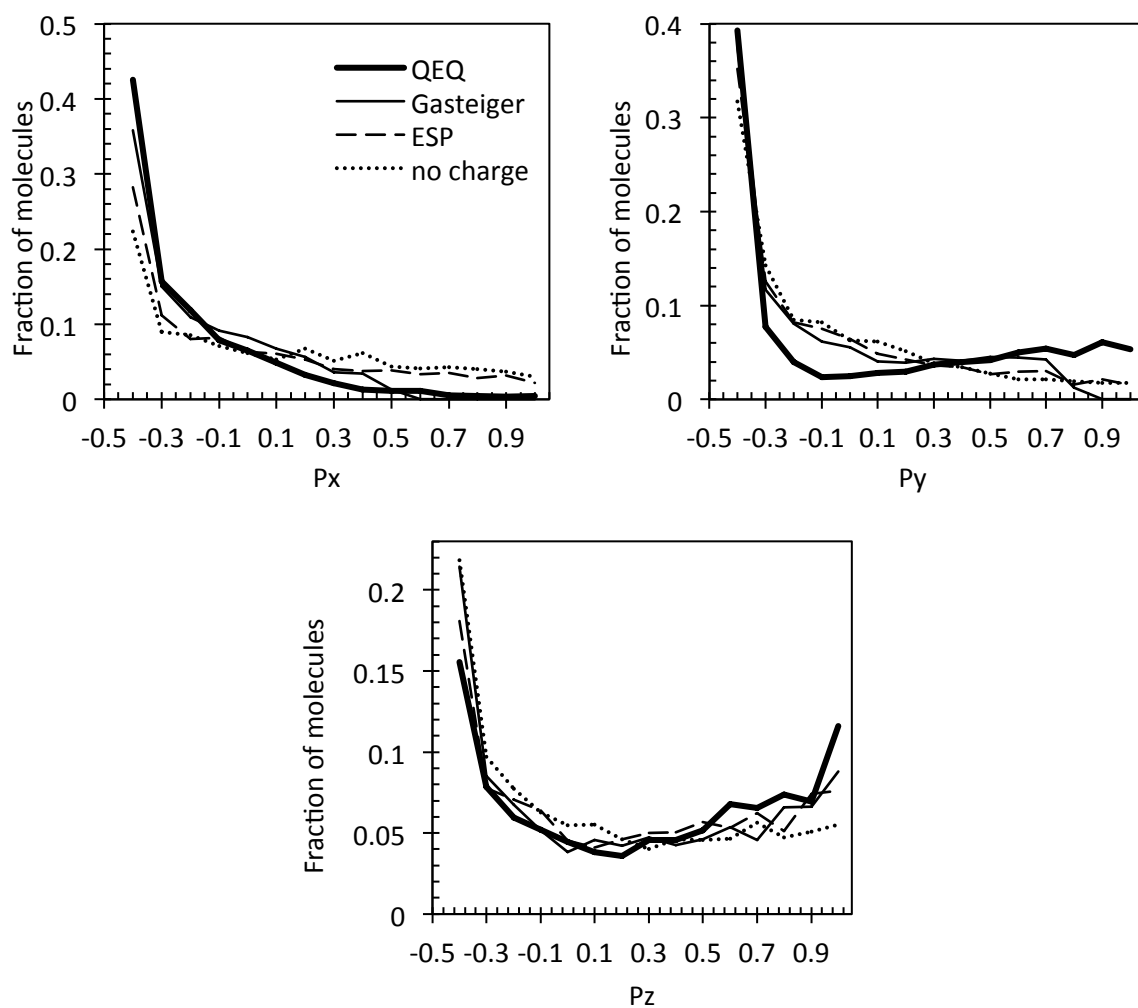


Figure 7.10. Fraction of CO₂ molecules that have a given orientation expressed as order parameter P_i with respect to i (x, y or z) axis.

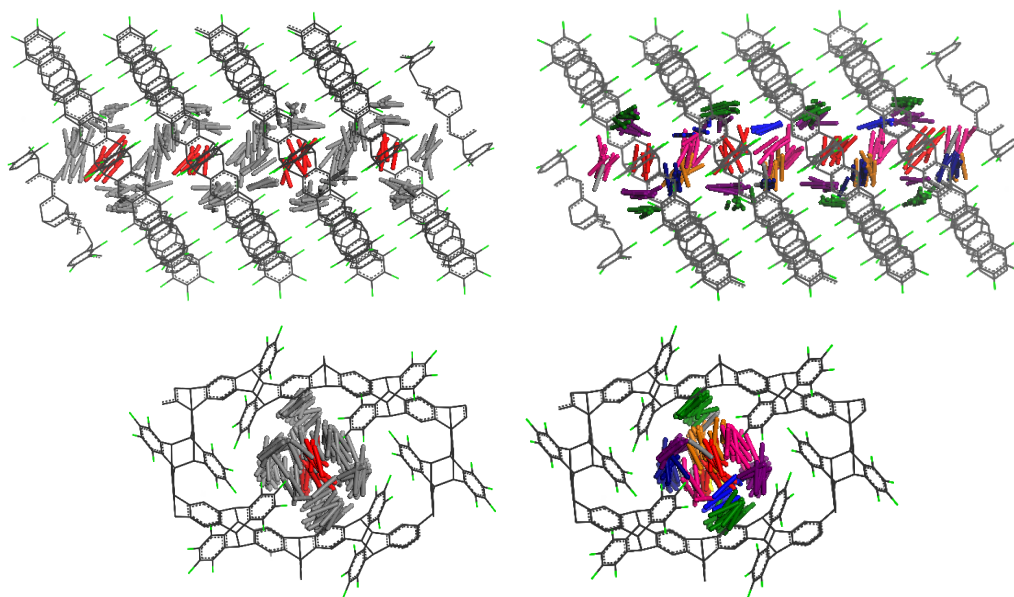


Figure 7.11. CO₂ molecules in poly(fantrip) with QEq charges.

7.3.3 Mixture Adsorption

Figure 7.12 shows adsorption isotherms at 298K of equimolar CO_2/CH_4 , CO_2/N_2 and CH_4/N_2 mixtures. Poly(fantrip) preferentially adsorbed CO_2 from mixtures; at lower than atmospheric pressures CO_2 loading remained unaffected compared to single-component adsorption, but at higher pressure poly(fantrip) took up slightly less CO_2 compared to pure gas adsorption at the same partial pressure. N_2 and CH_4 adsorption from mixture with CO_2 was dramatically weakened compared to the pure component isotherms at the same partial pressure. This can be due to very strong CO_2 -solid interactions and/or extremely unfavourable fluid-fluid interactions, although the first case seems to be more important since the behaviour of CO_2 mixture with N_2 and CH_4 in poly(fantrip)-Gasteiger (Figure 7.13) is slightly different even though the interactions parameters for all gases were kept the same. Nevertheless, zero coverage selectivity in poly(fantrip)-QEq (Table 7.8) remained of the same order of magnitude as pure component selectivity in spite of slight increase. It is worth noting that it is difficult to sample accurately such a small adsorbed amount in GCMC simulation leading to poor statistics and amplified selectivity that is most notable in CO_2/N_2 case.

Despite CH_4 being the component adsorbed more strongly than N_2 , its adsorption from the CH_4/N_2 mixture decreased significantly from what is observed for the pure component indicating competitive adsorption due to fluid-fluid interactions. Zero coverage selectivity calculated from mixture adsorption in poly(fantrip)-QEq as well as -Gasteiger also remained comparable to the pure gas selectivity and the same would be expected in cases where other charge calculation methods were used due to very similar single component adsorption isotherms.

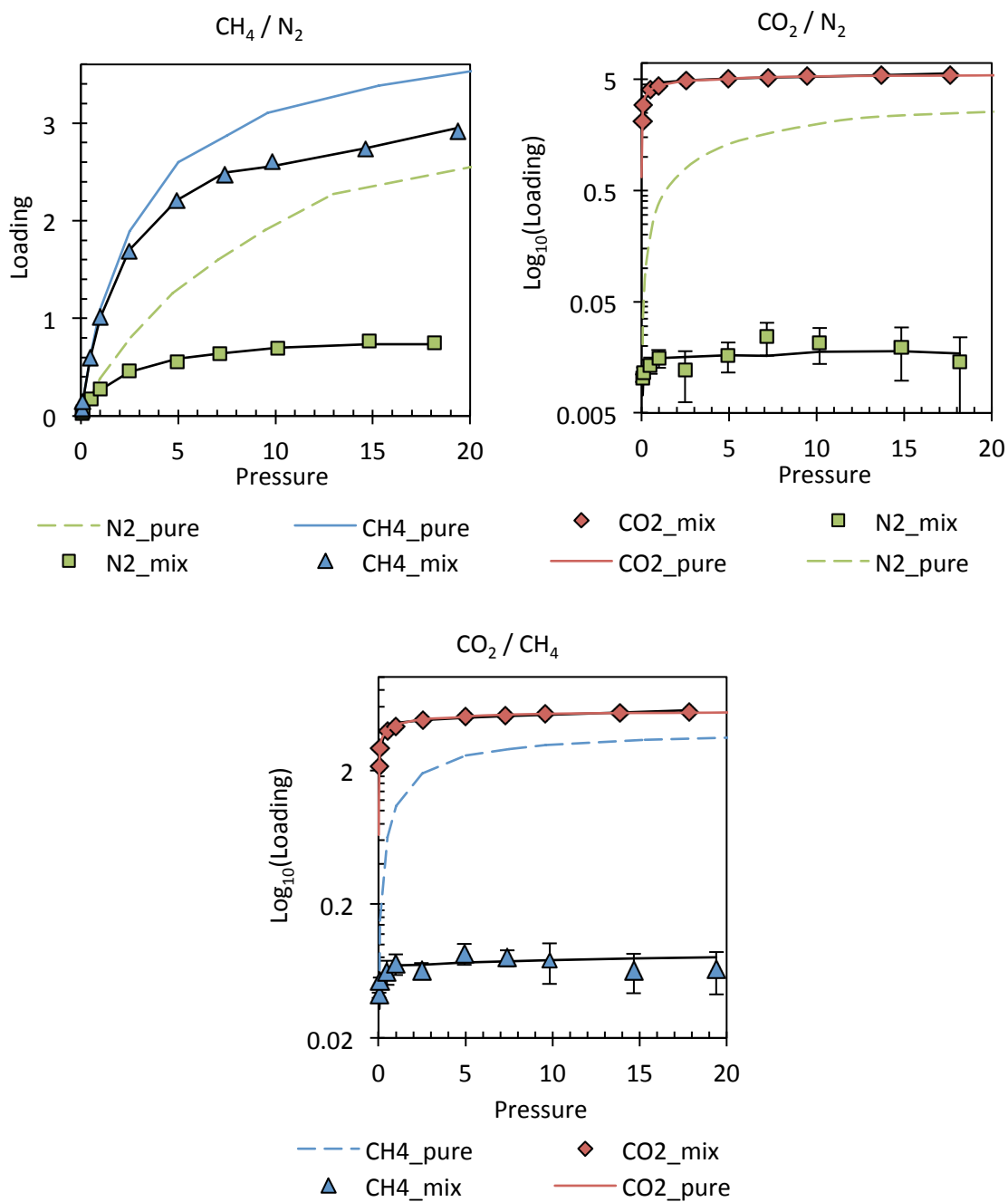


Figure 7.12. Adsorption isotherms for equimolar gas mixtures at 298K in poly(fantrip) with QEq charges. Solid black lines are fits to isotherm models. Loading are in mmol g⁻¹ and pressure in bar.

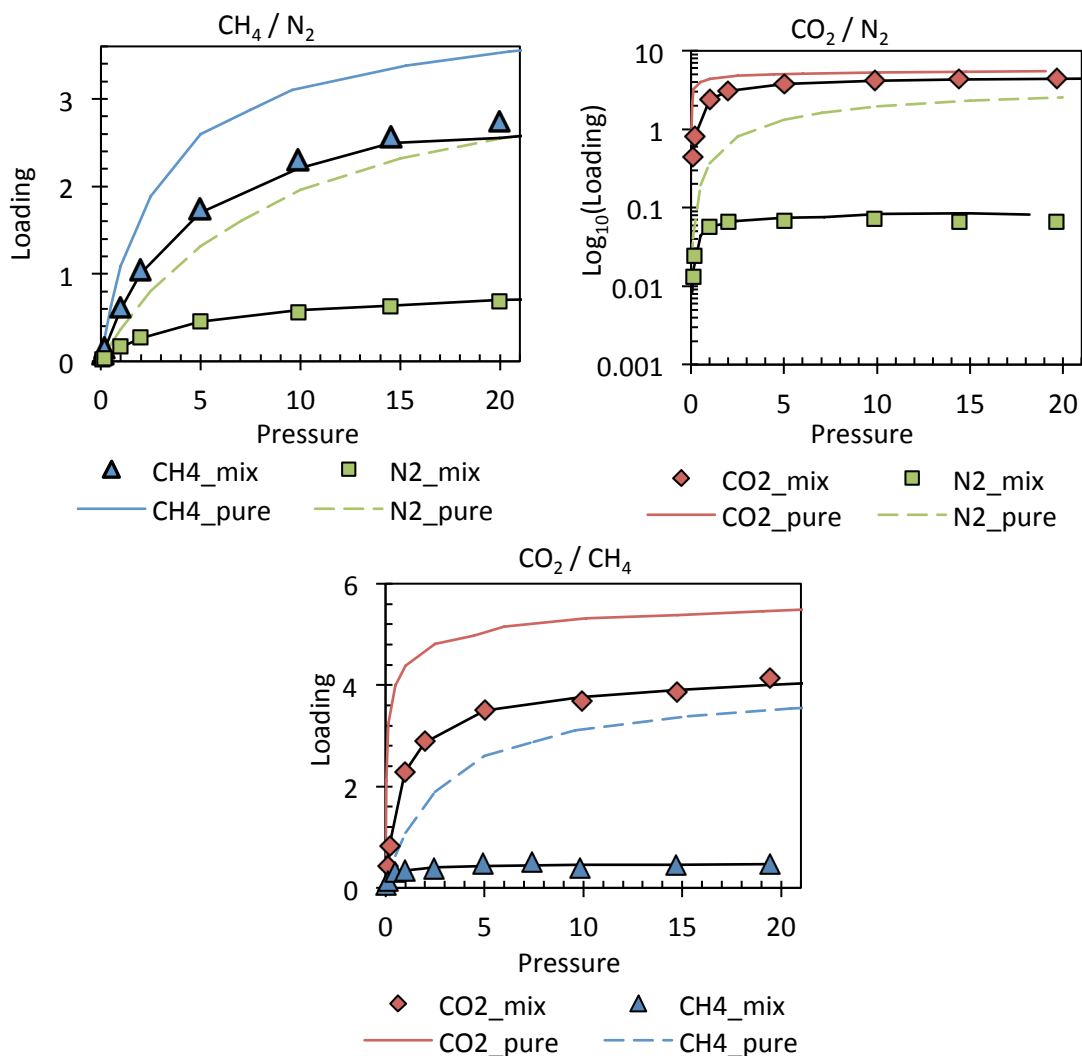


Figure 7.13. Adsorption isotherms for equimolar gas mixtures at 298K in poly(fantrip) with Gasteiger charges. Solid black lines are fits to isotherm models. Loading are in mmol g⁻¹ and pressure is in bar.

Table 7.8. Binary mixture selectivity at 298K in poly(fantrip).

	CO ₂ / CH ₄	CO ₂ / N ₂	CH ₄ / N ₂
QEq	64	294	3.8
Gasteiger	8	53	5.1

The selectivity of poly(fantrip) for gas A over gas B is defined as $S = (x_A/x_B)(y_B/y_A)$ and is presented as a function of total pressure in Figure 7.14. The CH₄/N₂ selectivity is almost independent of pressure and can be well-predicted using IAS theory. CO₂/N₂ and CO₂/CH₄ selectivity follows similar trend considering wide error bars. Poly(fantrip) contains fairly smooth pore channels with no prominent pockets as seen in unimodal PSD. Considering that the adsorption sites are similar for all molecules, the large selectivity is solely due to energetic effect. The retained large selectivity at elevated pressures is probably due to ordered packing of CO₂ molecules and increased gas-gas interactions. At low pressures, all the calculated selectivities from mixture GCMC simulations converge to the IAST predictions, however for CO₂ mixtures IAST fails at higher pressures where it predicts selectivity increase, while mixture selectivity reaches plateau. This is explained by the non ideality of the system, which is not taken into account by IAST; similar deviations were observed for CO₂/N₂ mixture adsorption in zeolites [77]. In both systems with QEq and Gasteiger charges, the selectivity trends are very similar over the pressure range.

Returning to the problem regarding too small amount of N₂ molecules being adsorbed from the mixture with CO₂, we have also simulated adsorption of mixture with higher N₂ concentration (15:85 CO₂:N₂), which mimics flue gas composition and should allow greater amount of N₂ molecules being adsorbed. However, selectivity decreases only slightly in poly(fantrip)-QEq despite smaller CO₂ concentration. The selectivity variations over the pressure range up to 20 bar is similarly independent of pressure compared to 50:50 mixture (Figure 7.15). IAST predicts only about 15 – 20 % increase in CO₂/N₂ selectivity at 1 bar with CO₂ fraction increase from 0.15 to 0.75 in both frameworks with QEq or Gasteiger charges (Figure 7.16).

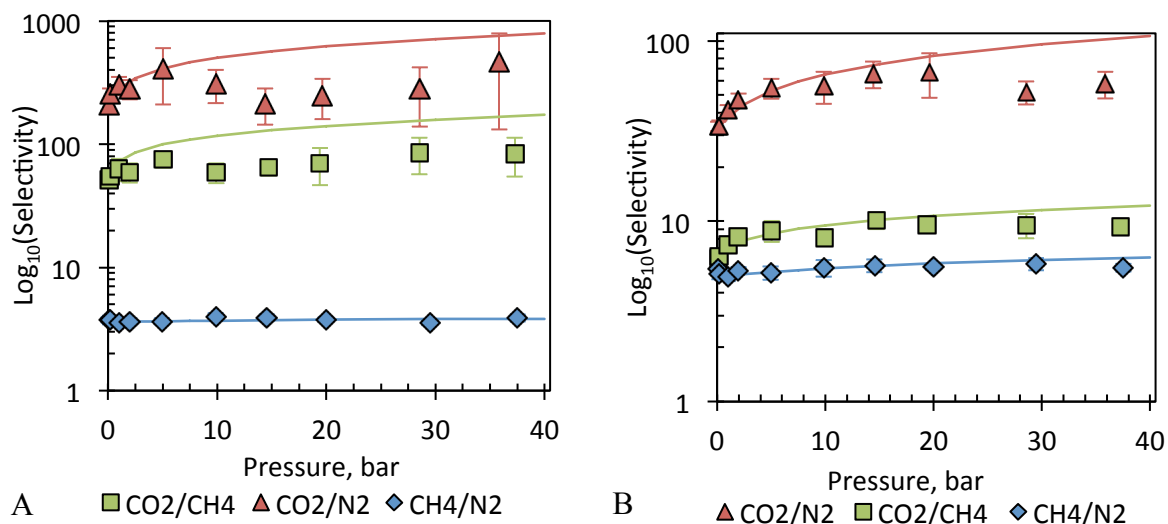


Figure 7.14. Selectivity of (A) poly(fantrip)-QEq and (B) -Gasteiger at 298 K. Symbols represent selectivity calculated from adsorption isotherms and lines are IAST selectivity.

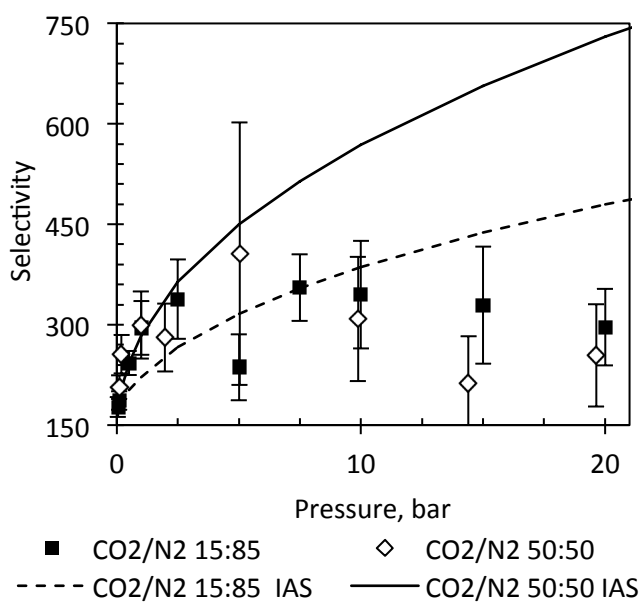


Figure 7.15. 15:85 and 50:50 CO₂/N₂ selectivity in poly(fantrip)-QEq.

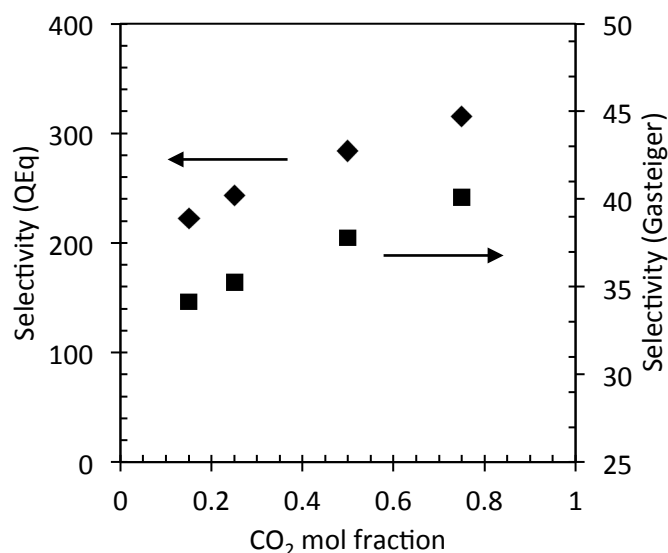


Figure 7.16. CO₂/N₂ selectivity in poly(fantrip)-QEq (diamonds) and –Gasteiger (squares) as a function of CO₂ composition at 1 bar as predicted by IAST.

7.3.4 Permeability

Permeability and permselectivity for poly(fantrip) and poly(antrip) was calculated (Table 7.9) and put into context with other membranes by plotting the data on Robeson graph [78] (Figure 7.17). The plot describes relationship between selectivity and permeability and reflects trade-off between these two parameters observed in polymeric materials, i.e. selective polymers are usually poorly permeable and vice versa. Plotting the selectivity of various gas pairs versus permeability of many polymers reported in the literature draws an upper bound, the limit of membrane performance and it is desirable to achieved or surpass it.

Our materials either surpass the upper bound or overlay it. Due to larger percentage of free volume, the materials have very high diffusion coefficients. Poly(fantrip) approached high diffusivity observed in benchmark polymer PTMSP ($4167 \times 10^{-8} \text{ cm}^2/\text{s}$ [79]), while poly(antrip) exceeds this value. Even the solubility is considerably higher than in PIMs [39], which are known for high solubility of CO₂, CH₄ and N₂ gases. Both of these values contribute to very good permeability performance indicating that these materials could be potential membranes for multipurpose separations.

Table 7.9. Porosity and separation parameters calculated using equations (7.9), (7.10) and (7.12).

	Poly(fantrip)			Poly(antrip)		
$V_{pore}, \text{cm}^3 \text{g}^{-1}$	0.271			0.417		
$f, \%$	0.341			0.369		
$D, 10^{-8} \text{cm}^2 \text{s}^{-1}$	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂
$S, 10^{-2} \text{cm}^3(\text{STP})\text{cm}^{-3} \text{cmHg}^{-1}$	2115	1642	1888	6105	6226	6018
QEq	250	62.2	21.0	111		
Gasteiger	182	62.9	15.9	117	48	11.7
ESP	160	62.5	15.4	121		
No charge	134	62.3	14.5	99		
p, barrer^*						
QEq	529239	102071	39673	675351		
Gasteiger	384374	103211	30076	715436	78654	22059
ESP	338501	102664	29065	739794		
No charge	283026	102334	27332	602891		

* barrer = $10^{-10} (\text{cm}^3(\text{STP})\text{cm})/(\text{cm}^2 \text{s cmHg})$

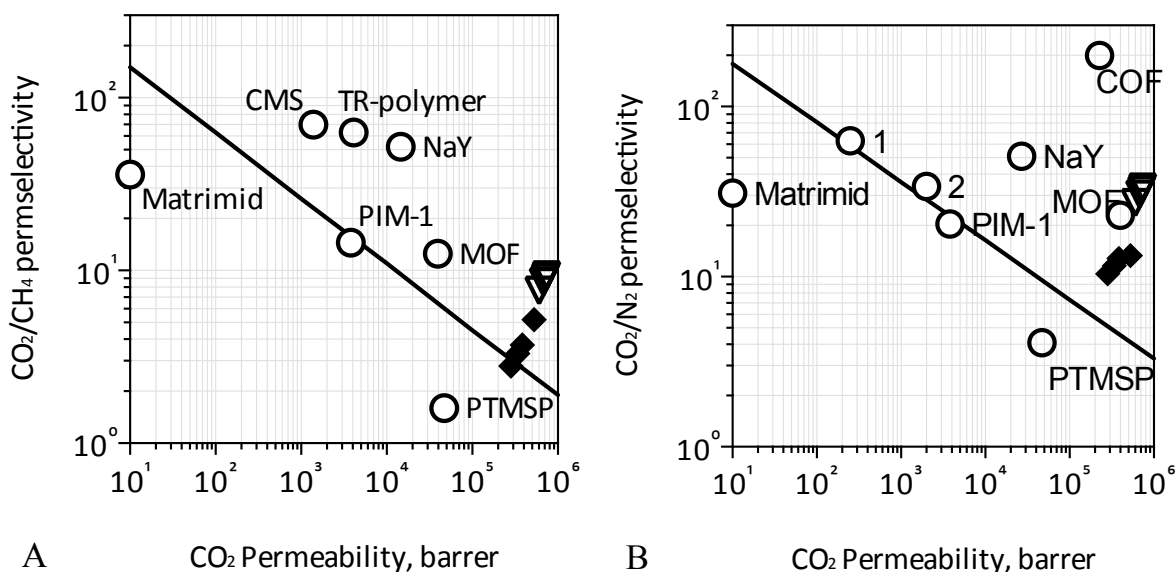


Figure 7.17. Robeson plots of (A) CO₂/CH₄ and (B) CO₂/N₂. Filled diamonds correspond to poly(fantrip) with different charges and open triangles are poly(antrip). References for examples: CMS (carbon molecular sieve) [80], PIM-1 [39], PTMSP [81], Matrimid [82], TR-polymer (thermally rearranged polymer) [83], 1 (poly[bis(2-(2-methoxyethoxy)ethoxy) phosphazene]) [84], 2 (modified poly(dimethylsiloxane) [85], NaY and MOF [86], COF [87].

Interestingly, nonfluorinated poly(antrip) overall performed better than poly(fantrip) showing even larger CO₂ permeability as well as selectivity. This can be attributed to the difference in

fractional free volume. The presence of fluorine atoms reduces fractional free volume by about 8% leading to diffusivity reduction by more than 60%. The solubility is less significantly affected from polymer to polymer.

7.4 Conclusions

Initial simulations indicate that fluorinated porous framework have a significantly high selectivity for CO₂ over CH₄ and N₂. However, we observed considerable differences between results obtained for fluorinated polymers with different charge assignment methods. Encouragingly, even the lowest calculated selectivities and gas uptake capacities are comparable to the reported values of structurally and chemically analogous microporous organic materials. The CH₄/N₂ selectivity is not influenced by the charge calculation method nor to the presence of fluorine atoms and the values are comparable to currently most selective MOF. Selectivities obtained from mixture adsorption simulations are very similar to those calculated from pure gas adsorption isotherms. Ideal adsorbed solution theory is capable to predict equimolar gas mixture selectivity up to about 20 bars, although there are larger deviations when QEq charges are used for fluorinated framework. Permeability calculations show that both poly(fantrip) and poly(antrip) are potential membranes for CO₂/N₂ and CO₂/CH₄ separations as they either overlay or surpass Robeson upper bound exhibiting very large CO₂ permeability. Validation of simulation results with experimental data would be important to refine the models and select appropriate charge calculation method.

7.5 Supplementary Information

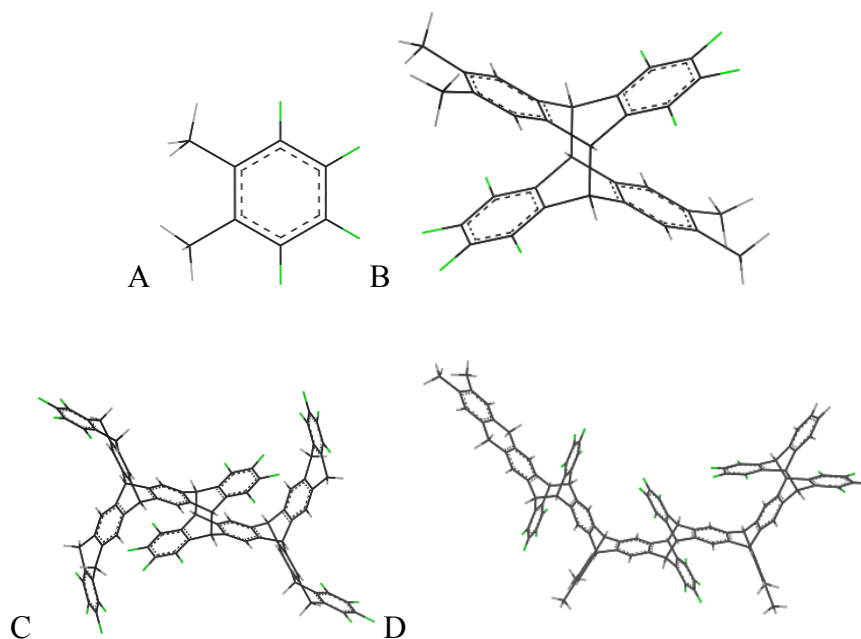


Figure 7.18. Poly(fantrip) fragments used to calculated ESP charges.

Table 7.10. The xyz coordinates and charges of the A fragment presented in Figure 7.18.

Atom	x	y	z	Charge
C	4.799	44.929	31.924	0.117
C	5.997	44.305	31.572	0.044
C	6.169	42.938	31.719	0.010
C	5.104	42.160	32.207	0.041
C	3.906	42.777	32.527	0.021
C	3.744	44.158	32.404	0.095
F	4.671	46.263	31.817	-0.109
F	6.994	45.076	31.071	-0.101
C	7.435	42.211	31.340	-0.194
C	5.327	40.671	32.308	-0.254
F	2.848	42.048	32.962	-0.096
F	2.588	44.741	32.766	-0.100
H	8.056	42.857	30.755	0.074
H	7.189	41.340	30.770	0.081
H	7.959	41.920	32.227	0.088
H	4.817	40.292	33.169	0.097
H	6.375	40.473	32.398	0.085
H	4.947	40.193	31.429	0.102

Table 7.11. The xyz coordinates and charges of the B fragment presented in Figure 7.18.

Atom	x	y	z	Charge	Atom	x	y	z	Charge
C	10.245	33.280	31.528	0.061	C	13.559	34.009	31.024	0.051
C	10.456	33.397	30.008	-0.096	C	13.325	33.920	32.542	-0.082
C	9.478	32.712	29.037	0.128	C	14.273	34.643	33.516	0.136
C	9.657	32.886	27.517	0.079	C	14.064	34.506	35.036	0.081
C	10.807	33.754	26.971	0.071	C	12.913	33.640	35.580	0.074
C	11.779	34.446	27.945	0.140	C	11.970	32.909	34.606	0.166
C	11.606	34.262	29.463	-0.179	C	12.174	33.054	33.087	-0.235
C	12.535	35.001	30.444	0.318	C	11.268	32.286	32.107	0.252
C	11.673	35.528	31.605	-0.134	C	12.166	31.737	30.983	-0.023
C	11.917	36.941	32.171	-0.307	C	11.982	30.289	30.484	-0.349
C	10.980	37.488	33.262	0.151	C	12.985	29.706	29.473	0.150
C	8.879	37.288	34.819	-0.410	C	15.140	29.884	27.988	-0.335
C	8.747	34.570	33.675	0.188	C	15.143	32.666	28.973	0.186
C	9.182	32.939	31.760	0.072	C	14.621	34.359	30.804	0.073
C	8.357	31.887	29.567	-0.137	C	15.392	35.471	32.987	-0.142
H	8.714	32.221	26.575	-0.113	H	14.979	35.208	35.979	-0.117
H	10.976	33.928	25.501	-0.112	H	12.715	33.503	37.051	-0.117
F	12.882	35.298	27.419	-0.140	F	10.863	32.062	35.131	-0.142
F	13.066	35.862	29.919	0.025	F	10.735	31.433	32.644	0.043
F	12.781	37.579	31.789	0.190	F	11.110	29.662	30.863	0.194
F	11.093	38.926	33.800	-0.374	F	12.930	28.240	29.007	-0.375
H	11.687	38.923	34.772	0.127	H	13.470	27.580	29.764	0.124
H	10.049	39.342	33.993	0.112	H	13.436	28.145	27.990	0.116
C	11.625	39.579	33.031	0.116	C	11.842	27.908	28.923	0.119
H	9.486	37.924	35.545	0.127	H	16.199	30.213	28.251	0.106
H	8.128	37.948	34.271	0.130	H	15.055	28.752	28.097	0.108
H	8.322	36.479	35.397	0.129	H	14.906	30.180	26.912	0.114
H	9.486	37.924	35.545	0.127	H	16.199	30.213	28.251	0.106
H	8.128	37.948	34.271	0.130	H	15.055	28.752	28.097	0.108
H	8.322	36.479	35.397	0.129	H	14.906	30.180	26.912	0.114
H	8.3216	36.478	35.397	0.1289	H	14.905	30.180	26.912	0.1138
	5	66	36	09		78	41	36	53

Table 7.12. The xyz coordinates and charges of the C fragment presented in Figure 7.18.

Atom	x	y	z	Charge	Atom	x	y	z	Charge
C	8.900	38.012	29.865	0.021	C	4.799	44.929	31.924	0.077
C	7.846	37.242	30.346	0.075	C	5.997	44.305	31.572	0.248
C	6.636	37.861	30.663	0.222	C	6.169	42.938	31.719	-0.281

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Table 7.12 Continued

C	6.453	39.223	30.486	-0.271	C	7.435	42.211	31.340	0.256
C	5.185	39.950	30.856	0.275	C	7.750	41.204	32.415	0.019
C	4.869	40.962	29.788	-0.026	C	9.060	40.937	32.816	-0.307
C	3.556	41.249	29.410	-0.268	C	9.301	39.875	33.674	0.051
C	3.312	42.328	28.575	0.017	C	10.664	39.351	34.094	0.136
C	1.947	42.880	28.195	0.159	C	10.641	39.256	35.608	-0.025
C	1.938	43.013	26.683	0.020	C	11.552	39.824	36.485	-0.272
C	0.997	42.487	25.812	-0.313	C	11.404	39.626	37.862	0.077
C	1.111	42.730	24.439	0.073	C	12.371	40.233	38.844	-0.049
C	0.106	42.174	23.464	0.025	C	12.636	39.303	39.998	-0.067
C	-0.173	43.151	22.352	-0.060	C	13.889	39.191	40.587	0.111
C	-1.441	43.304	21.803	0.089	C	14.120	38.317	41.648	0.078
C	-1.689	44.224	20.786	0.103	C	13.071	37.541	42.134	0.106
C	-0.640	45.001	20.299	0.103	C	11.811	37.651	41.546	0.098
C	0.634	44.847	20.843	0.105	C	11.578	38.517	40.485	-0.067
C	0.883	43.936	21.862	-0.115	C	10.224	38.646	39.836	-0.012
C	2.251	43.768	22.470	0.051	C	10.349	38.846	38.348	0.070
C	2.165	43.510	23.951	0.044	C	9.438	38.267	37.458	-0.292
C	3.109	44.043	24.836	-0.272	C	9.582	38.476	36.095	-0.024
C	2.997	43.792	26.194	-0.058	C	8.702	37.912	34.993	0.210
C	3.912	44.313	27.289	0.237	C	8.240	39.096	34.159	-0.028
C	4.374	43.104	28.086	-0.028	C	6.933	39.381	33.790	-0.287
C	5.682	42.799	28.430	-0.280	C	6.690	40.428	32.900	0.154
C	5.928	41.737	29.301	0.135	C	5.327	40.671	32.308	-0.097
C	7.293	41.489	29.890	-0.056	C	5.104	42.160	32.207	-0.154
C	7.519	40.002	30.000	-0.129	C	3.906	42.777	32.527	0.278
C	8.727	39.389	29.710	0.241	C	3.744	44.158	32.404	-0.013
C	1.953	44.301	28.745	0.040	C	10.688	37.919	33.576	0.035
C	1.083	44.821	29.688	-0.306	C	11.578	37.394	32.654	-0.302
C	1.266	46.130	30.151	-0.013	C	11.414	36.078	32.208	0.050
C	0.365	46.713	31.206	0.076	C	12.342	35.487	31.180	-0.031
C	1.143	47.568	32.172	-0.149	C	11.589	34.614	30.211	-0.054
C	0.860	47.589	33.532	0.101	C	11.900	34.577	28.857	0.080
C	1.606	48.363	34.418	0.114	C	11.177	33.787	27.966	0.131
C	2.658	49.136	33.932	0.115	C	10.119	33.015	28.440	0.083
C	2.943	49.120	32.568	0.062	C	9.806	33.046	29.797	0.130
C	2.202	48.348	31.682	-0.022	C	10.523	33.836	30.688	-0.103
C	2.527	48.290	30.213	-0.017	C	10.172	33.907	32.151	-0.068
C	2.324	46.902	29.664	0.116	C	10.354	35.303	32.686	0.107
C	3.206	46.368	28.717	-0.346	C	9.455	35.840	33.614	-0.332
C	3.016	45.076	28.257	0.025	C	9.626	37.140	34.060	0.021
F	10.069	37.433	29.541	-0.067	F	4.671	46.263	31.817	-0.071
F	7.989	35.913	30.491	-0.075	F	6.994	45.076	31.071	-0.161

Table 7.12 Continued

F	5.640	37.093	31.170	-0.153	H	8.263	42.916	31.235	0.033
H	4.357	39.245	30.961	0.033	H	9.883	41.523	32.407	0.136
H	2.733	40.667	29.826	0.132	H	11.491	39.957	33.712	0.048
H	1.120	42.277	28.580	0.038	H	12.385	40.419	36.111	0.138
H	0.163	41.895	26.188	0.144	H	11.945	41.169	39.243	0.064
H	-0.817	41.897	23.983	0.055	H	13.303	40.512	38.342	0.072
H	0.501	41.245	23.021	0.045	F	14.929	39.935	40.136	-0.119
F	-2.479	42.557	22.254	-0.118	F	15.342	38.219	42.204	-0.098
F	-2.923	44.361	20.270	-0.103	F	13.278	36.696	43.160	-0.103
F	-0.864	45.889	19.313	-0.105	F	10.808	36.884	42.040	-0.120
F	1.634	45.618	20.351	-0.119	H	9.709	39.514	40.280	0.056
H	2.879	44.641	22.270	0.054	H	9.600	37.774	40.055	0.064
H	2.748	42.913	21.979	0.042	H	8.626	37.648	37.840	0.142
H	3.917	44.667	24.453	0.135	H	7.872	37.306	35.369	0.031
H	4.741	44.917	26.910	0.026	H	6.107	38.759	34.135	0.135
H	6.508	43.422	28.088	0.134	H	4.560	40.212	32.936	0.093
H	8.059	41.947	29.261	0.084	F	2.848	42.048	32.962	-0.158
F	9.786	40.120	29.282	-0.157	F	2.588	44.741	32.766	-0.057
H	0.279	44.211	30.099	0.150	H	12.384	38.006	32.249	0.145
H	-0.165	45.914	31.733	0.045	H	13.108	34.874	31.684	0.069
H	-0.407	47.337	30.727	0.053	H	12.878	36.282	30.654	0.067
F	-0.154	46.844	34.034	-0.116	F	12.920	35.323	28.366	-0.118
F	1.321	48.370	35.733	-0.112	F	11.490	33.765	26.657	-0.113
F	3.387	49.887	34.778	-0.109	F	9.413	32.248	27.589	-0.107
F	3.975	49.877	32.122	-0.114	F	8.769	32.289	30.231	-0.122
H	3.554	48.620	30.028	0.055	H	10.824	33.212	32.706	0.078
H	1.872	48.998	29.677	0.058	H	9.145	33.570	32.321	0.075
H	4.050	46.964	28.372	0.152	H	8.609	35.242	33.953	0.151
C	8.900	38.012	29.865	0.021	C	4.799	44.929	31.924	0.077

Table 7.13. The xyz coordinates and charges of the D fragment presented in Figure 7.18.

Atom	x	y	z	Charge	Atom	x	y	z	Charge
C	4.814	45.019	31.999	0.123	H	13.702	19.451	14.806	0.108
C	6.148	44.358	31.603	0.152	H	12.118	19.305	15.775	0.113
C	6.310	42.831	31.710	-0.254	C	4.246	43.422	28.136	-0.153
C	7.635	42.165	31.299	0.272	C	5.696	43.091	28.535	-0.168
C	7.930	40.976	32.230	-0.022	C	5.982	41.910	29.481	0.017
C	9.383	40.642	32.617	-0.299	C	7.429	41.581	29.892	0.010
C	9.664	39.403	33.481	0.046	C	7.600	40.055	30.001	-0.134
C	11.093	38.926	33.800	0.126	C	8.921	39.391	29.570	0.198
C	10.980	37.488	33.262	-0.010	C	9.093	37.865	29.696	0.024
C	11.917	36.941	32.171	-0.255	C	7.933	37.000	30.223	0.119

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Table 7.13 Continued

C	11.673	35.528	31.605	0.007	C	6.600	37.662	30.626	0.122
C	12.535	35.001	30.444	0.136	C	6.441	39.191	30.530	-0.157
C	13.559	34.009	31.024	0.023	C	5.116	39.860	30.944	0.165
C	13.322	32.604	30.439	0.096	C	4.822	41.047	30.008	-0.010
C	14.303	32.025	29.399	-0.293	C	3.375	41.361	29.589	-0.196
C	14.139	30.567	28.938	-0.091	C	3.086	42.557	28.663	-0.121
C	15.140	29.884	27.988	0.235	H	4.032	44.305	27.448	0.153
C	14.228	29.212	26.946	0.041	H	6.556	43.726	28.140	0.153
C	14.499	29.303	25.435	-0.348	H	8.177	42.023	29.153	0.087
C	13.655	28.453	24.466	0.076	F	10.038	40.226	29.045	-0.149
C	14.003	28.421	22.967	0.048	F	10.382	37.223	29.307	-0.115
C	14.841	27.149	22.757	0.177	F	8.099	35.524	30.344	-0.125
C	14.041	26.259	21.788	-0.013	F	5.472	36.826	31.125	-0.138
C	14.402	26.226	20.293	-0.330	H	4.260	39.107	30.933	0.066
C	13.563	25.381	19.317	0.085	H	2.517	40.716	29.974	0.155
C	13.931	25.339	17.823	-0.045	H	2.013	42.800	28.365	0.150
C	13.719	23.913	17.284	0.010	C	9.852	37.875	35.858	-0.084
C	14.713	23.322	16.267	-0.369	C	9.674	37.659	37.370	-0.310
C	14.535	21.875	15.769	0.148	C	10.660	38.326	38.350	0.149
C	13.403	21.001	16.336	0.121	C	11.850	39.150	37.813	0.157
C	12.403	21.594	17.346	-0.356	C	12.020	39.366	36.295	-0.305
C	12.560	23.051	17.818	0.004	C	11.011	38.728	35.325	-0.061
C	11.607	23.619	18.885	-0.044	H	8.814	37.023	37.764	0.176
C	12.400	24.521	19.848	0.082	C	10.504	38.107	39.867	-0.394
C	12.076	24.510	21.354	-0.316	C	12.827	39.817	38.799	-0.467
C	12.877	25.402	22.319	-0.023	H	12.881	39.998	35.897	0.178
C	12.518	25.440	23.816	0.142	H	9.800	38.896	40.293	0.121
C	11.682	26.712	24.030	0.092	H	11.523	38.197	40.368	0.115
C	12.491	27.591	25.001	0.009	H	10.074	37.069	40.060	0.130
C	12.168	27.575	26.508	-0.308	H	13.397	40.647	38.265	0.138
C	13.071	28.353	27.478	-0.021	H	12.240	40.258	39.672	0.138
C	12.930	28.240	29.007	0.216	H	13.562	39.039	39.191	0.152
C	12.985	29.706	29.473	-0.001	C	11.606	34.262	29.463	-0.241
C	11.982	30.289	30.484	-0.343	C	11.779	34.446	27.945	0.195
C	12.166	31.737	30.983	0.097	C	10.807	33.754	26.971	0.067
C	11.268	32.286	32.107	0.169	C	9.657	32.886	27.517	0.094
C	10.245	33.280	31.528	-0.031	C	9.478	32.712	29.037	0.140
C	10.516	34.663	32.149	0.195	C	10.456	33.397	30.008	-0.072
C	9.594	35.209	33.257	-0.369	F	12.882	35.298	27.419	-0.147
C	9.825	36.630	33.798	0.062	F	10.976	33.928	25.501	-0.118
C	8.879	37.288	34.819	0.182	F	8.714	32.221	26.575	-0.121
C	8.506	38.545	34.013	0.001	F	8.357	31.887	29.567	-0.144
C	7.051	38.911	33.684	-0.273	C	12.174	33.054	33.087	-0.281

Table 7.13 Continued

C	6.767	40.111	32.761	0.000	C	11.970	32.909	34.606	0.195
C	5.321	40.442	32.352	0.050	C	12.913	33.640	35.580	0.071
C	5.150	41.968	32.239	-0.069	C	14.064	34.506	35.036	0.091
C	3.827	42.630	32.661	0.118	C	14.273	34.643	33.516	0.152
C	3.654	44.155	32.528	0.085	C	13.325	33.920	32.542	-0.131
F	4.646	46.493	31.867	-0.131	F	10.863	32.062	35.131	-0.147
F	7.274	45.192	31.098	-0.144	F	12.715	33.503	37.051	-0.119
H	8.492	42.917	31.309	0.055	F	14.979	35.208	35.979	-0.120
H	10.244	41.286	32.236	0.159	F	15.392	35.471	32.987	-0.144
H	11.947	39.564	33.396	0.094	C	15.515	28.643	28.819	-0.005
H	12.768	37.584	31.768	0.152	C	16.974	28.249	29.103	-0.372
H	13.064	35.862	29.917	0.085	C	17.268	26.980	29.927	0.178
H	14.622	34.360	30.809	0.095	C	16.107	26.091	30.423	0.112
H	15.161	32.661	29.001	0.163	C	14.646	26.507	30.160	-0.332
H	16.005	30.514	27.595	0.064	C	14.359	27.781	29.349	-0.046
H	15.348	29.953	25.041	0.172	H	17.830	28.889	28.706	0.190
H	14.582	29.352	22.655	0.101	C	18.724	26.550	30.184	-0.376
H	15.869	27.401	22.333	0.066	C	16.410	24.826	31.247	-0.359
H	15.280	26.841	19.905	0.183	H	13.787	25.870	30.553	0.185
H	15.024	25.638	17.692	0.066	H	18.757	25.429	30.386	0.117
H	13.267	26.066	17.247	0.071	H	19.131	27.111	31.089	0.117
H	15.580	23.954	15.883	0.195	H	19.359	26.792	29.269	0.115
C	15.543	21.274	14.773	-0.327	H	16.483	23.929	30.548	0.116
C	13.228	19.554	15.838	-0.365	H	15.574	24.654	32.003	0.116
H	11.553	20.952	17.750	0.197	H	17.400	24.961	31.797	0.106
H	11.134	22.762	19.470	0.065	C	12.730	28.245	22.119	-0.161
H	10.789	24.229	18.377	0.073	C	12.626	28.910	20.735	0.149
H	11.231	23.855	21.750	0.177	C	11.367	28.700	19.874	0.099
H	11.936	24.509	24.123	0.079	C	10.203	27.844	20.408	0.058
H	10.654	26.462	24.455	0.090	C	10.298	27.198	21.802	0.158
H	11.300	26.951	26.904	0.171	C	11.567	27.388	22.652	-0.132
H	12.078	27.594	29.405	0.073	F	13.755	29.734	20.220	-0.146
H	11.131	29.647	30.885	0.166	F	11.278	29.320	18.522	-0.122
H	10.736	31.435	32.648	0.074	F	8.987	27.636	19.572	-0.114
H	9.181	32.941	31.758	0.100	F	9.176	26.365	22.318	-0.148
H	8.733	34.575	33.653	0.170	C	13.795	25.603	24.660	-0.153
H	8.014	36.654	35.206	0.077	C	13.910	24.911	26.030	0.160
H	6.192	38.281	34.090	0.157	C	15.176	25.104	26.886	0.051
H	4.573	40.000	33.090	0.094	C	16.339	25.963	26.357	0.063
F	2.709	41.794	33.180	-0.138	C	16.237	26.630	24.972	0.143
F	2.363	44.794	32.909	-0.121	C	14.959	26.462	24.130	-0.147
H	15.575	20.141	14.903	0.101	F	12.787	24.073	26.536	-0.151
H	15.219	21.524	13.709	0.103	F	15.277	24.457	28.224	-0.086
H	16.579	21.710	14.967	0.104	F	17.564	26.149	27.185	-0.094

Table 7.13 Continued

H	13.739	18.837	16.562	0.119	F	17.365	27.454	24.455	-0.146
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7.6 References

1. Kissel, P., et al., *A nanoporous two-dimensional polymer by single-crystal-to-single-crystal photopolymerization*. Nat Chem, 2014. **6**(9): p. 774-778.
2. Bhola, R., et al., *A Two-Dimensional Polymer from the Anthracene Dimer and Triptycene Motifs*. Journal of the American Chemical Society, 2013. **135**(38): p. 14134-14141.
3. Makhseed, S., et al., *Synthesis and characterization of fluoropolymers with intrinsic microporosity and their hydrogen adsorption studies*. Journal of Applied Polymer Science, 2008. **109**(4): p. 2591-2597.
4. Michl, J. and T.F. Magnera, *Two-dimensional supramolecular chemistry with molecular Tinkertoys*. Proceedings of the National Academy of Sciences, 2002. **99**(8): p. 4788-4792.
5. Yang, Z.-Z., et al., *Fluorinated microporous organic polymers: design and applications in CO₂ adsorption and conversion*. Chemical Communications, 2014. **50**(90): p. 13910-13913.
6. Zhao, Y., et al., *A perfluorinated covalent triazine-based framework for highly selective and water-tolerant CO₂ capture*. Energy & Environmental Science, 2013. **6**(12): p. 3684-3692.
7. Peikert, K., F. Hoffmann, and M. Froba, *Fluorine magic: one new organofluorine linker leads to three new metal-organic frameworks*. CrystEngComm, 2015. **17**(2): p. 353-360.
8. Guzmán-Gutiérrez, M.T., et al., *Structure-properties relationship for the gas transport properties of new fluoro-containing aromatic polymers*. Journal of Membrane Science, 2011. **385-386**(0): p. 277-284.
9. Burch, N.C., et al., *Molecular-level Insight into Unusual Low Pressure CO₂ Affinity in Pillared Metal-Organic Frameworks*. Journal of the American Chemical Society, 2013. **135**(19): p. 7172-7180.
10. Kharitonov, A.P., *Practical applications of the direct fluorination of polymers*. Journal of Fluorine Chemistry, 2000. **103**(2): p. 123-127.
11. Ruthven, D.M., *Past Progress and Future Challenges in Adsorption Research*. Industrial & Engineering Chemistry Research, 2000. **39**(7): p. 2127-2131.
12. Sircar, S., *Basic Research Needs for Design of Adsorptive Gas Separation Processes*. Industrial & Engineering Chemistry Research, 2006. **45**(16): p. 5435-5448.
13. Ghanem, B.S., et al., *Triptycene-Based Polymers of Intrinsic Microporosity: Organic Materials That Can Be Tailored for Gas Adsorption*. Macromolecules, 2010. **43**(12): p. 5287-5294.
14. Swaidan, R., et al., *Effects of hydroxyl-functionalization and sub-T_g thermal annealing on high pressure pure- and mixed-gas CO₂/CH₄ separation by polyimide membranes based on 6FDA and triptycene-containing dianhydrides*. Journal of Membrane Science, 2015. **475**(0): p. 571-581.

15. Del Regno, A., et al., *Polymers of Intrinsic Microporosity Containing Troger Base for CO₂ Capture*. Industrial & Engineering Chemistry Research, 2013. **52**(47): p. 16939-16950.
16. Ghanem, B.S., et al., *A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption*. Chemical Communications, 2007(1): p. 67-69.
17. Crane, A.K., B.O. Patrick, and M.J. MacLachlan, *New metal-organic frameworks from triptycene: structural diversity from bulky bridges*. Dalton Transactions, 2013. **42**(22): p. 8026-8033.
18. Kahveci, Z., et al., *Targeted synthesis of a mesoporous triptycene-derived covalent organic framework*. CrystEngComm, 2013. **15**(8): p. 1524-1527.
19. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: A Generic Force Field for Molecular Simulations*. J. Phys. Chem. , 1990. **94**: p. 8897-8909.
20. Fraccarollo, A., et al., *Monte Carlo Modeling of Carbon Dioxide Adsorption in Porous Aromatic Frameworks*. Langmuir, 2014. **30**(14): p. 4147-4156.
21. Duren, T., Y.-S. Bae, and R.Q. Snurr, *Using molecular simulation to characterise metal-organic frameworks for adsorption applications*. Chemical Society Reviews, 2009. **38**(5): p. 1237-1247.
22. Rappe, A.K. and W.A. Goddard, *Charge equilibration for molecular dynamics simulations*. J. Phys. Chem, 1991. **95**: p. 3358-3363.
23. Harris, J.G. and K.H. Yung, *Carbon Dioxide's Liquid-Vapor Coexistence Curve And Critical Properties as Predicted by a Simple Molecular Model*. The Journal of Physical Chemistry, 1995. **99**(31): p. 12021-12024.
24. Potoff, J.J. and J.I. Siepmann, *Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen*. AIChE Journal, 2001. **47**(7): p. 1676-1682.
25. Möller, D., et al., *Prediction of thermodynamic properties of fluid mixtures by molecular dynamics simulations: methane-ethane*. Molecular Physics, 1992. **75**(2): p. 363-378.
26. Gasteiger, J. and M. Marsili, *Iterative partial equalization of orbital electronegativity—a rapid access to atomic charges*. Tetrahedron, 1980. **36**(22): p. 3219-3228.
27. Hamad, S., et al., *Atomic charges for modeling metal-organic frameworks: Why and how*. Journal of Solid State Chemistry, 2015. **223**(0): p. 144-151.
28. Singh, U.C. and P.A. Kollman, *An approach to computing electrostatic charges for molecules*. Journal of Computational Chemistry, 1984. **5**(2): p. 129-145.
29. M. J. Frisch, G.W.T., H. B. Schlegel, G. E. Scuseria, , et al., *Gaussian 09*. 2010, Gaussian, Inc.: Wallingford CT.
30. Pérez-Pellitero, J., et al., *Adsorption of CO₂, CH₄, and N₂ on Zeolitic Imidazolate Frameworks: Experiments and Simulations*. Chemistry – A European Journal, 2010. **16**(5): p. 1560-1571.
31. Ramsahye, N.A., et al., *Charge distribution in metal organic framework materials: transferability to a preliminary molecular simulation study of the CO₂ adsorption in the MIL-53 (Al) system*. Physical Chemistry Chemical Physics, 2007. **9**(9): p. 1059-1063.
32. Mellot, C.F. and A.K. Cheetham, *Energetics and Structures of Fluoro- and Chlorofluorocarbons in Zeolites: Force Field Development and Monte Carlo Simulations*. The Journal of Physical Chemistry B, 1999. **103**(19): p. 3864-3868.
33. Martin, M.G., *MCCCS Towhee: a tool for Monte Carlo molecular simulation*. Molecular Simulation, 2013. **39**(14-15): p. 1212-1222.

34. Myers, A.L. and J.M. Prausnitz, *Thermodynamics of mixed-gas adsorption*. AIChE Journal, 1965. **11**(1): p. 121-127.
35. Krishna, R. and J.M. van Baten, *In silico screening of metal-organic frameworks in separation applications*. Physical Chemistry Chemical Physics, 2011. **13**(22): p. 10593-10616.
36. Bae, Y.-S., et al., *Separation of CO₂ from CH₄ Using Mixed-Ligand Metal–Organic Frameworks*. Langmuir, 2008. **24**(16): p. 8592-8598.
37. Larsen, G.S., et al., *Methane adsorption in PIM-1*. Adsorption, 2011. **17**: p. 21–26.
38. Thornton, A.W., et al., *New relation between diffusion and free volume: I. Predicting gas diffusion*. Journal of Membrane Science, 2009. **338**(1–2): p. 29-37.
39. Hart, K.E. and C.M. Colina, *Estimating gas permeability and permselectivity of microporous polymers*. Journal of Membrane Science, 2014. **468**: p. 259-268.
40. Hofmann, D., et al., *Molecular Modeling Investigation of Free Volume Distributions in Stiff Chain Polymers with Conventional and Ultrahigh Free Volume: Comparison between Molecular Modeling and Positron Lifetime Studies*. Macromolecules, 2003. **36**(22): p. 8528-8538.
41. Siriwardane, R.V., et al., *Adsorption of CO₂ on Molecular Sieves and Activated Carbon*. Energy & Fuels, 2001. **15**(2): p. 279-284.
42. Casco, M.E., et al., *High-Pressure Methane Storage in Porous Materials: Are Carbon Materials in the Pole Position?* Chemistry of Materials, 2015. **27**(3): p. 959-964.
43. Ahmadpour, A. and D.D. Do, *The preparation of active carbons from coal by chemical and physical activation*. Carbon, 1996. **34**(4): p. 471-479.
44. Anson, M., et al., *ABS copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation*. Journal of Membrane Science, 2004. **243**(1–2): p. 19-28.
45. Otowa, T., R. Tanibata, and M. Itoh, *Production and adsorption characteristics of MAXSORB: High-surface-area active carbon*. Gas Separation & Purification, 1993. **7**(4): p. 241-245.
46. Dirar, Q. and K. Loughlin, *Intrinsic adsorption properties of CO₂ on 5A and 13X zeolite*. Adsorption, 2013. **19**(6): p. 1149-1163.
47. Azizi, S.N., S. Ghasemi, and S. Kaviani, *Synthesis and characterization of NaX nanozeolite using stem sweep as silica source and application of Ag-modified nanozeolite in electrocatalytic reduction of H₂O₂*. Biosensors and Bioelectronics, 2014. **62**(0): p. 1-7.
48. Yi, H., et al., *Adsorption equilibrium and kinetics for SO₂, NO, CO₂ on zeolites FAU and LTA*. Journal of Hazardous Materials, 2012. **203–204**(0): p. 111-117.
49. Ngoc, D.T., T.H. Pham, and K.D.H. Nguyen, *Synthesis, characterization and application of nanozeolite NaX from Vietnamese kaolin*. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2013. **4**(4): p. 045018.
50. Du, X. and E. Wu, *Porosity of microporous zeolites A, X and ZSM-5 studied by small angle X-ray scattering and nitrogen adsorption*. Journal of Physics and Chemistry of Solids, 2007. **68**(9): p. 1692-1699.
51. Mastalerz, M. and I.M. Oppel, *Rational Construction of an Extrinsic Porous Molecular Crystal with an Extraordinary High Specific Surface Area*. Angewandte Chemie International Edition, 2012. **51**(21): p. 5252-5255.
52. Abbott, L.J., et al., *Characterizing the Structure of Organic Molecules of Intrinsic Microporosity by Molecular Simulations and X-ray Scattering*. The Journal of Physical Chemistry B, 2012. **117**(1): p. 355-364.
53. Chong, J.H., et al., *Triptycene-Based Metal Salphens—Exploiting Intrinsic Molecular Porosity for Gas Storage*. Chemistry – A European Journal, 2009. **15**(44): p. 11824-11828.

-
54. Heuchel, M., et al., *Adsorption of Carbon Dioxide and Methane and Their Mixtures on an Activated Carbon: Simulation and Experiment*. Langmuir, 1999. **15**(25): p. 8695-8705.
55. Rufford, T.E., et al., *Adsorption Equilibria and Kinetics of Methane plus Nitrogen Mixtures on the Activated Carbon Norit RB3*. Industrial & Engineering Chemistry Research, 2013. **52**(39): p. 14270-14281.
56. Sievers, W. and A. Mersmann, *Single and multicomponent adsorption equilibria of carbon dioxide, nitrogen, carbon monoxide and methane in hydrogen purification processes*. Chemical Engineering & Technology, 1994. **17**(5): p. 325-337.
57. Ren, X., et al., *Highly enhanced selectivity for the separation of CH₄ over N₂ on two ultra-microporous frameworks with multiple coordination modes*. Microporous and Mesoporous Materials, 2014. **186**(0): p. 137-145.
58. Ren, X., et al., *Synthesis optimization of the ultra-microporous [Ni₃(HCOO)₆] framework to improve its CH₄/N₂ separation selectivity*. RSC Advances, 2014. **4**(80): p. 42326-42336.
59. *Chemical Composition of Discovered and Undiscovered Natural Gas in the Continental United States - 1998 Update, Project Summary*. 1999, Energy and Environmental Analysis, Inc., Arlington, VA.
60. Kumar, K.V. and F. Rodríguez-Reinoso, *Co-adsorption of N₂ in the presence of CH₄ within carbon nanospaces: evidence from molecular simulations*. Nanotechnology, 2013. **24**(3): p. 035401.
61. Kumar, K.V., E.A. Müller, and F. Rodríguez-Reinoso, *Effect of Pore Morphology on the Adsorption of Methane/Hydrogen Mixtures on Carbon Micropores*. The Journal of Physical Chemistry C, 2012. **116**(21): p. 11820-11829.
62. Service, R.F., *Stepping on the gas*. Science, 2014. **346**(6209): p. 538-541.
63. Palomino, M., et al., *Zeolite Rho: a highly selective adsorbent for CO₂/CH₄ separation induced by a structural phase modification*. Chemical Communications, 2012. **48**(2): p. 215-217.
64. Xiong, S., et al., *A new tetrazolate zeolite-like framework for highly selective CO₂/CH₄ and CO₂/N₂ separation*. Chemical Communications, 2014. **50**(81): p. 12101-12104.
65. Kong, L., et al., *Selective adsorption of CO₂/CH₄ and CO₂/N₂ within a charged metal-organic framework*. Journal of Materials Chemistry A, 2014. **2**(42): p. 17771-17778.
66. Liu, Q., et al., *NaKA sorbents with high CO₂-over-N₂ selectivity and high capacity to adsorb CO₂*. Chemical Communications, 2010. **46**(25): p. 4502-4504.
67. Li, J.-R., et al., *Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks*. Coordination Chemistry Reviews, 2011. **255**(15–16): p. 1791-1823.
68. Dawson, R., et al., *Microporous organic polymers for carbon dioxide capture*. Energy & Environmental Science, 2011. **4**(10): p. 4239-4245.
69. Wilmer, C.E., K.C. Kim, and R.Q. Snurr, *An Extended Charge Equilibration Method*. The Journal of Physical Chemistry Letters, 2012. **3**(17): p. 2506-2511.
70. Wilmer, C.E. and R.Q. Snurr, *Towards rapid computational screening of metal-organic frameworks for carbon dioxide capture: Calculation of framework charges via charge equilibration*. Chemical Engineering Journal, 2011. **171**(3): p. 775-781.
71. Babarao, R. and J. Jiang, *Molecular Screening of Metal–Organic Frameworks for CO₂ Storage*. Langmuir, 2008. **24**(12): p. 6270-6278.
72. Fried, J.R. and N. Hu, *The molecular basis of CO₂ interaction with polymers containing fluorinated groups: computational chemistry of model compounds and*

- molecular simulation of poly[bis(2,2,2-trifluoroethoxy)phosphazene]*. Polymer, 2003. **44**(15): p. 4363-4372.
73. Raveendran, P. and S.L. Wallen, *Exploring CO₂-Philicity: Effects of Stepwise Fluorination*. The Journal of Physical Chemistry B, 2003. **107**(6): p. 1473-1477.
 74. Baradie, B., et al., *Synthesis and Solubility of Linear Poly(tetrafluoroethylene-co-vinyl acetate) in Dense CO₂: Experimental and Molecular Modeling Results*. Macromolecules, 2004. **37**(20): p. 7799-7807.
 75. Torrisi, A., C. Mellot-Draznieks, and R.G. Bell, *Impact of ligands on CO₂ adsorption in metal-organic frameworks: First principles study of the interaction of CO₂ with functionalized benzenes. I. Inductive effects on the aromatic ring*. The Journal of Chemical Physics, 2009. **130**(19): p. -.
 76. Diep, P., et al., *CO₂-Fluorocarbon and CO₂-Hydrocarbon Interactions from First-Principles Calculations*. The Journal of Physical Chemistry A, 1998. **102**(12): p. 2231-2236.
 77. Goj, A., et al., *Atomistic Simulations of CO₂ and N₂ Adsorption in Silica Zeolites: The Impact of Pore Size and Shape†*. The Journal of Physical Chemistry B, 2002. **106**(33): p. 8367-8375.
 78. Robeson, L.M., *The upper bound revisited*. Journal of Membrane Science, 2008. **320**(1-2): p. 390-400.
 79. Merkel, T.C., et al., *Sorption and transport of hydrocarbon and perfluorocarbon gases in poly(1-trimethylsilyl-1-propyne)*. Journal of Polymer Science Part B: Polymer Physics, 2000. **38**(2): p. 273-296.
 80. Steel, K.M. and W.J. Koros, *Investigation of porosity of carbon materials and related effects on gas separation properties*. Carbon, 2003. **41**(2): p. 253-266.
 81. Hu, Y., et al., *Synthesis and Properties of Indan-Based Polyacetylenes That Feature the Highest Gas Permeability among All the Existing Polymers*. Macromolecules, 2008. **41**(22): p. 8525-8532.
 82. Sanders, D.F., et al., *Energy-efficient polymeric gas separation membranes for a sustainable future: A review*. Polymer, 2013. **54**(18): p. 4729-4761.
 83. Park, H.B., et al., *Polymers with Cavities Tuned for Fast Selective Transport of Small Molecules and Ions*. Science, 2007. **318**(5848): p. 254-258.
 84. Orme, C.J., et al., *Characterization of gas transport in selected rubbery amorphous polyphosphazene membranes*. Journal of Membrane Science, 2001. **186**(2): p. 249-256.
 85. Senthilkumar, U. and B.S.R. Reddy, *Polysiloxanes with pendent bulky groups having amino-hydroxy functionality: Structure-permeability correlation*. Journal of Membrane Science, 2007. **292**(1-2): p. 72-79.
 86. Pera-Titus, M., *Porous Inorganic Membranes for CO₂ Capture: Present and Prospects*. Chemical Reviews, 2014. **114**(2): p. 1413-1492.
 87. Tong, M., et al., *Few-layered ultrathin covalent organic framework membranes for gas separation: a computational study*. Journal of Materials Chemistry A, 2016. **4**(1): p. 124-131.

8 CONCLUSIONS

We investigated three types of materials: composites of amorphous polymer and carbons, pure amorphous carbon system and crystalline network polymer in terms of structural properties and adsorption characteristics using atomistic molecular modeling and theoretical data analysis methods and, in some cases, experimental technique. Amorphous virtual materials were packed in a simulation cell following well-established several-step MD procedures; crystalline system was constructed based on reported crystallographic data. Structural property data such as density, surface area, free volume and pore size distribution was extracted from the models. Most of the materials were studied for CO₂ adsorption, however other gases (CH₄, N₂ and C₆F₁₄) were also tested in some cases. In the cases where adsorption isotherms were calculated and/or measured, they were fitted to either dual-mode or Langmuir isotherm model whose parameters were then employed to calculate heat of adsorption or solubility at infinite dilution and selectivity. Adsorption in virtual models was calculated using grand canonical Monte Carlo simulation, while experimental isotherms were measured using gravimetric method.

In the case of polymer and carbon composite (PIM-1-graphene), virtual model showed that graphene does not alter significantly structural properties of bulk polymer, although experimental composite sample had rougher surface. However, polymer chains align onto graphene surface due to possible π - π interactions and no additional pores are created, which potentially can obstruct gas adsorption. Therefore graphene sheets were connected via triptycene molecule and other rigid cores to eliminate graphene planarity and possibly hinder PIM-1 packing around the additive. Although some increase in surface area was observed in some composite cases compared to pure PIM-1, the difference was considered insignificant for further studies. Experimental CO₂ adsorptions were also very similar between pure PIM-1 and composite, indicating unchanged affinity.

Network poly(fantrip) polymer was found to be a potential CO₂ adsorbent with comparable selectivity to many similar microporous materials. It could also be an alternative for CH₄/N₂

separation due to high selectivity. Experimental measurement data is needed to validate the model as the different charges assigned to electronegative fluorine affect significantly CO₂ packing inside the pore and subsequent selectivity.

The 3D graphenes connected through triptycene core are interesting materials. Although the presence of triptycene core was not sufficient to achieve greater free volume in a composite, we showed that packing of these discrete macromolecule create microporous amorphous systems, that can be used to study activated carbons. The model is simple to construct and does not require any experimental data feed.

In light of overall work performed for this thesis on different materials, few generalised conclusions can be made:

- 3D shape restricts molecule packing generating free volume. Rigidity and shape persistency provided by triptycene molecules promotes larger volume than more flexible cores. However the mere presence of cores such as triptycene molecule does not necessarily increase free volume in amorphous materials, simply because intramolecular volume of triptycene cavity can be penetrated by smaller or narrower structures, it can also be occupied by structures that resemble its concave angle as seen in Chapter 4.
- Bare graphene based structures are not suitable as an additive to increase surface area for ladder-like polymers because of the planar polycyclic aromatic structure that can be observed in both of these materials.
- As expected, confined complex pores are most attractive for CO₂ adsorption as evidenced by higher selectivity in model carbons than in slit pore model.
- Electronegative chemical groups such as fluorine atoms increase affinity towards CO₂ and subsequently materials selectivity.
- Computational techniques compliment experimental methods and allow understanding the adsorption phenomenon on molecular level. In cases where no experimental data is available, it can be used as a faster and cheaper tool for screening potential properties and applications. However care must be taken in selecting appropriate techniques for each special case to provide valid predictions, as was the case with difficulty to calculate chemical potential in Chapter 6 and choose appropriate charge assignment method in Chapter 7.

Although it was not our aim to compare the studied materials among themselves nor to investigate their efficiency for specific industrial separations, we found that all of the virtual materials, despite of differences in bulk state (crystalline or amorphous) and chemistry, exhibit very similar general structural properties and adsorption properties (see Figure 8.1 and Table 8.1). This shows that there exists variety of different materials that could serve the same purpose adopting material based on secondary requirements such as stability.

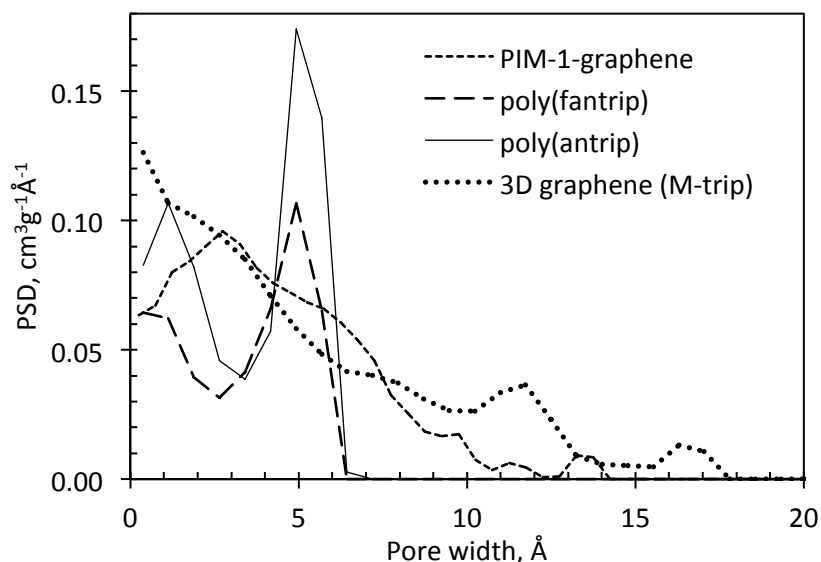


Figure 8.1. Pore size distribution of materials studied in this work, M-trip is selected as a representative structure of 3D graphenes.

Table 8.1. Structural and adsorption properties of materials studied in this thesis.

	PIM-1-graphene ^{IV}	PIM-1-3D graphenes	Poly(fantrip) ^V , ^{VI}	Poly(antrip)	3D graphenes
SA ^I	790 – 980	760 – 1040	544	830	200 – 400
n ^{II} (0.05 bar)	0.38	-	0.35, 2.16	0.20	0.29 - 0.44
n (1 bar)	3.05	-	2.80, 4.38	2.80	-
n (20 bar)	4.87	-	4.61, 5.56	6.41	-
S ^{III} (CO ₂ /CH ₄)	-	-	4.80, 52	3.7	~ 8
ΔH(CO ₂)	26	-	24, 31	19.5	~ 33

^I Nitrogen surface area, m² g⁻¹, ^{II} CO₂ capacity, mmol g⁻¹ at 293K for PIM-1-graphene and 298K for other materials, ^{III} at infinite dilution, ^{IV} using unmodified DREIDING with QEq charges, ^V and ^{VI} using ESP and QEq charges, respectively.

Design of materials with large surface area is one of the main research directions. Large surface area provides large amount of adsorption sites affecting separation kinetics and

selectivity. The predicted surface areas of polymers studied in this work are similar to other highly porous organic materials such as conjugated microporous polymers [1], some COFs [2-4], PIMs [4], hypercrosslinked polymers [5, 6], activated carbons [7, 8] and zeolites (also see Table 3.1 and 7.5). This leads to moderate adsorption capacities up to 3 mmol g^{-1} at ambient conditions comparable to many organic microporous materials, activated carbons, zeolites [9]. However much larger surface areas, in excess of $1000 \text{ m}^2\text{g}^{-1}$, can be reached in other state-of-the-art materials such as triptycene containing PIMs [10], porous aromatic framework (PAF-1) [11] and especially hybrid organic-inorganic MOFs [12] that absorb substantial amounts of CO_2 at high pressures well exceeding those observed in our materials.

It is well known that large surface area itself does not guarantee good separation characteristics as pore size and surface affinity plays important role, especially considering low-pressure applications. For example, poly(antrip) adsorbs slightly less CO_2 than poly(fantrip) at very low pressure presumably because of the lack of fluorine groups. However, PIM-1 composite and 3D graphenes adsorb slightly more CO_2 than poly(antrip) probably due to larger amount of confined pores as evidenced by the larger peak at $3.3 \text{ \AA}$ in PSD that commensurate with CO_2 diameter. All of the materials have pore size distribution showing high concentration of ultramicropores ($< 1 \text{ nm}$) suggesting that these polymers can potentially compete with materials, which separate based on molecular sieving.

The studied materials have isosteric heats of adsorption of about $20\text{-}33 \text{ kJ mol}^{-1}$. This is lower than $30 - 90 \text{ kJ mol}^{-1}$ observed in zeolites and MOFs and comparable to activated carbons and many other organic materials. This suggests that materials provide sufficient affinity towards CO_2 and would result in less energy intensive regeneration.

PIM-1 composite can form flexible films while poly(fantrip) and poly(antrip) can be exfoliated into 2D molecular-sized sheets which is advantageous in membrane CO_2 separation. To this point, only poly(fantrip) and poly(antrip) were analysed in terms of membrane applications. The predictions suggest that these polymers would not be sufficient for industrial CO_2/CH_4 membrane separation solely based on selectivity as they could not compete with common commercial membranes, selectivity of which generally ranges from 10 to 30, while predicted CO_2/N_2 selectivity of 18-32 is more promising and falls into the 10-50 range obtained in commercial membranes [13-16]. Moreover it was shown, that increased permeability decreases capital cost more substantially than increased selectivity [15]. Thus the polymer could potentially compete with commercial materials due to significantly larger

permeability. Furthermore chemistry of poly(fantrip) is hydrophobic thus hydrostability in humid conditions often present in industrial processes can be expected. However, other secondary parameters such as thermal-stability, processability and scaleability could disregard the material from its use or make it a stronger candidate, thus additional efficiency studies are necessary.

Outlook

This work contributes to the scientific community by presenting structural and adsorption properties of novel materials that have never been studied before as well as proposing the new simple approach to study adsorption in activated carbons. It was shown that these materials have strong affinity towards CO₂ or could be beneficial to study adsorption. Nevertheless, this work is still only a first step towards targeted development of efficient adsorbents.

Polymeric materials, PIM-1 composites and poly(fantrip), are intended to be used as separation membranes, thus gas diffusion study is important to characterise permeability properties. Althumayri *et al.* [17] has just recently reported experimental permeation study showing more than doubled enhancement in CO₂ permeation of PIM-1/few-layer-graphene membrane compared to pure PIM-1 membrane at graphene filling of only 0.05%. The enhancement was also retained even after 8 month of storage although both mixed matrix membrane and pure PIM-1 membrane lost the same percentage of permeability over that time. It would be interesting to model PIM-1 packing around infinite graphene sheet as it is considered that much larger graphene sheets are obtained experimentally than what was used in virtual model in this work. The model with infinite graphene sheet will eliminate edge effect, hindering polymer chains from wrapping around the sheet. This may reveal different structural properties such like larger separation between polymer and filler allowing less hindered passage of gas molecules through the interface thus increasing permeability.

For poly(fantrip) permeation case, it would be interesting to see whether the channel size is small enough and interactions with CO₂ are strong enough to pass though only CO₂ and retain other gases as it was recently shown that fluorine functionalised hole in graphene of only slightly larger size has dramatically lower selectivity than the similar larger hole [18].

Both of polymeric materials are prone to swelling which is an undesirable phenomenon due to possibly reduced selectivity and poor reproducibility, faster aging and contamination. Although graphene did not seem to improve CO₂ adsorption of PIM-1, it could be still used as a stiffening agent. Due to seemingly good polymer-graphene adhesion, graphene may help to control polymer chain movement, which should reduce swelling and at least slow down the ageing. Measuring and calculating mechanical properties could test this hypothesis. Although time-scale of swelling is much longer than can be captured by simulations there have been reported indirect approaches to simulate swelling that can help in understanding what governs the process and how it affects sorption properties [19]. Swelling in poly(fantrip) could only occur due to delamination of layers, thus the study would be more straightforward than in PIM-1-graphene case.

The further step in PIM-1-graphene composite study could be graphene functionalization to decrease in-plane attraction between the polymer chains and graphene potentially introducing access to the larger surface of graphene and creation of additional adsorption sites.

The adsorption of other gases in these materials should also be studied to obtain selectivity characteristics and gas mixture behavior, which is known to be sometimes different compared to those predicted from pure gas results. The effect of other contaminants (e.g. NO_x and SO_x) and moisture, often present in industrial streams, is also important factor in material design as well as reproducibility, which were not assessed here.

References

1. Dawson, R., D.J. Adams, and A.I. Cooper, *Chemical tuning of CO₂ sorption in robust nanoporous organic polymers*. Chemical Science, 2011. **2**(6): p. 1173-1177.
2. Dawson, R., A.I. Cooper, and D.J. Adams, *Nanoporous organic polymer networks*. Progress in Polymer Science, 2012. **37**(4): p. 530-563.
3. Tilford, R.W., et al., *Tailoring Microporosity in Covalent Organic Frameworks*. Advanced Materials, 2008. **20**(14): p. 2741-2746.
4. Dawson, R., et al., *Microporous organic polymers for carbon dioxide capture*. Energy & Environmental Science, 2011. **4**(10): p. 4239-4245.
5. Luo, Y., et al., *Hypercrosslinked Aromatic Heterocyclic Microporous Polymers: A New Class of Highly Selective CO₂ Capturing Materials*. Advanced Materials, 2012. **24**(42): p. 5703-5707.

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6. Tsyurupa, M.P. and V.A. Davankov, *Hypercrosslinked polymers: basic principle of preparing the new class of polymeric materials*. Reactive and Functional Polymers, 2002. **53**(2–3): p. 193-203.
 7. Sun, N., et al., *Surface-modified spherical activated carbon materials for pre-combustion carbon dioxide capture*. RSC Advances, 2015. **5**(42): p. 33681-33690.
 8. Plaza, M.G., et al., *Post-combustion CO₂ capture with a commercial activated carbon: Comparison of different regeneration strategies*. Chemical Engineering Journal, 2010. **163**(1–2): p. 41-47.
 9. Wang, J., et al., *Recent advances in solid sorbents for CO₂ capture and new development trends*. Energy & Environmental Science, 2014. **7**(11): p. 3478-3518.
 10. Ghanem, B.S., et al., *A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption*. Chemical Communications, 2007(1): p. 67-69.
 11. Ben, T., et al., *Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area*. Angewandte Chemie International Edition, 2009. **48**(50): p. 9457-9460.
 12. Farha, O.K., et al., *Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit?* Journal of the American Chemical Society, 2012. **134**(36): p. 15016-15021.
 13. Baker, R.W. and K. Lokhandwala, *Natural Gas Processing with Membranes: An Overview*. Industrial & Engineering Chemistry Research, 2008. **47**(7): p. 2109-2121.
 14. Robeson, L.M., *The upper bound revisited*. Journal of Membrane Science, 2008. **320**(1–2): p. 390-400.
 15. Abetz, V., et al., *Polymer Membranes for Separation of CO₂ - An Overview*, in *2nd International Conference on Energy Process Engineering. Efficient Carbon Capture for Coal Power Plants*. 2011: Frankfurt/Main, Germany.
 16. Ritter, J.A. and A.D. Ebner, *Carbon Dioxide Separation Technology: R&D Needs For the Chemical and Petrochemical Industries*. 2007, Chemical Industry Vision2020 Technology Partnership.
 17. Althumayri, K., et al., *The influence of few-layer graphene on the gas permeability of the high-free-volume polymer PIM-1*. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2016. **374**(2060).
 18. Wu, T., et al., *Fluorine-Modified Porous Graphene as Membrane for CO₂/N₂ Separation: Molecular Dynamic and First-Principles Simulations*. The Journal of Physical Chemistry C, 2014. **118**(14): p. 7369-7376.
 19. Hölck, O., et al., *Gas sorption isotherms in swelling glassy polymers—Detailed atomistic simulations*. Journal of Membrane Science, 2013. **428**: p. 523–532.