Pyrene-Derived Porous Organic Polymers: Design, Synthesis, and Application to Gas Storage and Separation

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PYRENE-DERIVED POROUS ORGANIC POLYMERS: DESIGN, SYNTHESIS, AND APPLICATION TO GAS STORAGE AND SEPARATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

by

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List of Abbreviations

BILP ........................................................................................................ Benzimidazole-Linked Polymer
COF ........................................................................................................ Covalent Organic Framework
ILCOF .................................................................................................... Imine-Linked Covalent Organic Framework
DFT .......................................................................................................... Density Functional Theory
IAST ........................................................................................................ Ideal Adsorbed Solution Theory
IR ............................................................................................................. Infrared Spectroscopy
LDA ........................................................................................................ Local Density Approximation
MOF ........................................................................................................ Metal Organic Framework
NLDFT ..................................................................................................... Non-Local Density Functional Theory
NMR ......................................................................................................... Nuclear Magnetic Resonance Spectroscopy
SEM ......................................................................................................... Scanning Electron Microscopy (Microscope)
XRD ......................................................................................................... X-Ray Diffraction
Abstract

PYRENE-DERIVED POROUS ORGANIC POLYMERS: DESIGN, SYNTHESIS, AND APPLICATION TO GAS STORAGE AND SEPARATION

By Ali Kemal Sekizkardes, Ph.D.

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

Virginia Commonwealth University, 2014

Director: Hani M. El-Kaderi, Associate Professor, Department of Chemistry

Porous organic polymers (POPs) received great attention in recent years because of their novel properties such as permanent porosity, adjustable chemical nature, and remarkable thermal and chemical stability. These attractive features make POPs very promising candidates for use in gas separation and storage applications. In particular, CO₂ capture and separation from gas mixtures by POPs have been intensively investigated in recent years because of the greenhouse nature of CO₂, which is considered a leading cause for global warming. CO₂ chemical absorption by amine solutions from the flue gas of coal-fired power plants suffers from several challenges such as high-energy consumption in desorption, chemical instability, volatility, and corrosive nature, limiting the widespread use of this technology. To mitigate these limitations, new adsorbents with improved CO₂ capturing properties need to be designed, synthesized, and tested. Alternatively, the use of cleaner fuels such as methane can reduce CO₂ release or completely
eliminates it in the case of hydrogen. However, the on-board storage of methane and hydrogen for automotive applications remains a great challenge.

With these considerations in mind, our research goals in this dissertation focus on the systematic design and synthesis of N-rich POPs and their use in small gas (H₂ and CH₄) storage as well as selective CO₂ capture from gas mixtures. In particular, we have studied the effect of integrating pyrene and triazine building units into benzimidazole-linked polymers (BILPs) and covalent organic frameworks (COFs) on gas storage and separation. We have found that pyrene-based BILPs exhibit remarkable selective CO₂ capturing capacities under industrial settings (VAS, PSA). However, the methane and hydrogen storage capacities of BILPs were found to be only modest especially at high pressure due to their moderate surface area and pore volume. We addressed these limitations by the synthesis of a highly porous imine-linked COF (ILCOF-1), which has very high surface area and improved hydrogen and methane uptakes when compared to BILPs. We have demonstrated that the use of pyrene in BILPs and COFs can direct frameworks growth through \(\pi-\pi\) stacking and improve porosity and pore volume whereas the use of triazine is instrumental in improving the binding affinity of the frameworks towards CO₂.
CHAPTER 1

Introduction

1.1 Porous Polymers

Developments on the synthesis of polymers such as plastics, polyvinyl chloride, polyester, nylon and polyethylene reestablished and dominated material design used in every aspect of human life. Polymers are macromolecules consisting of repeating units known as monomers, which are linked to each other by covalent bonds. They exhibit unique properties such as lightweight, viscoelasticity, and toughness, among others. Numerous types of polymerization methods have been studied to date and most of these studies have been applied in industry. In general, polymerization of monomers takes place in chain growth through either copolymerization or block polymerization. In the past two decades, porous polymers have emerged as a new class of polymers. Porous polymers have quickly gained research interest due to their novel properties such as high surface area, permanent porosity, and adjustable chemical structure. The resulting porous architectures have been considered for a wide range of applications including gas storage and separation, energy harvesting, optoelectronics, sensing, drug delivery, and catalysis. In general, porous polymers can be classified in two types of polymers: porous coordination polymers (or metal organic frameworks) and porous organic polymers.
1.2 Porous Coordination Polymers

In the early 1990s, research interest in porous materials was accelerated by the introduction of porous coordination polymers (PCPs).\textsuperscript{5} PCPs, also known as metal organic frameworks (MOFs), have evolved from porous materials such as prussian blue, mesoporous silicate, and zeolites, which have been used in many applications over decades. Structurally, MOFs are constructed from metal ions and organic bridging ligands linked together to create porous frameworks.\textsuperscript{6} The unprecedented level of permanent porosity enables MOFs to reach ultrahigh surface areas up to 6000 m\textsuperscript{2}/g.\textsuperscript{7} Following several hundred types of MOFs synthesized in a few years, Yaghi and his coworkers developed the concept of “reticular chemistry”, which involves the construction of porous materials from predesigned molecular building blocks.\textsuperscript{8}

\textbf{Figure 1.1:} Representation of a typical porous coordination polymer (MOF-5).
Because of the highly crystalline nature of MOFs, the place of atoms and their connecting sites within the framework can be easily predicted by materials modeling or determined from x-ray crystallography. Consequently, properties of MOFs can be correlated to their chemical structure and physical nature and hence, desired application requirements can be addressed by targeted synthesis of MOFs.\(^9\) Using this so-called “crystal-engineering technique”, an enormous amount of different types of MOFs has been reported to date. In a typical MOF design; topology, size and chemical functionality of metal units (inorganic secondary building units) and organic ligands play a predominant role in the final framework structure.\(^{10}\) Geometry and chemical attributes of inorganic and organic building units influence the final MOF structure.\(^{11}\) According to the metal type used in secondary building units (SBUs) and its oxidation number, different geometries such as linear, tetrahedral, octahedral, square-planar, square-pyramidal and trigonal-biprymidal can be obtained. The combination between organic linkers and SBUs can lead to almost an infinite number of MOF structures.

1.3 Porous Organic Polymers

As discussed in the previous section, intensive research efforts have been dedicated to studying porous coordination polymers. On the other hand, assembling building blocks through covalent bonds has been widely studied in polymer chemistry as well. Conventionally, organic polymers such as polystyrenes, polyvinylchloride and nylon have been mostly synthesized by the chain growth of linear (1D) disordered monomers. Recently, hypercrosslinked polymers (HCPs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), porous polymeric networks (PPNs), conjugated microporous polymers (CMPs) etc. have emerged as new classes of organic polymers which have been commonly generalized as porous organic polymers (POPs) due to their permanent porosity.\(^3\)
In POPs, monomer assembly is driven by strong covalent bond formation between the functional groups of rigid building blocks. However, unlike conventional polymers, porous polymers are constructed from rigid monomer building blocks in various dimensionality (2D or/and 3D), which are essential for gaining porosity. Building blocks can be tuned and functionalized according to the target application as in gas separation, gas storage, light harvesting, optoelectronics, sensing, heterogeneous catalysis and drug delivery. Rapidly growing research interest has focused on the synthesis and design of different types of 2D and 3D
building blocks to be used in versatile polymerization methods to prepare porous polymers. POPs can be classified as crystalline and amorphous based on their solid-state packing.

1.3.1 Amorphous Porous Organic Polymers

Amorphous or non-crystalline POPs have attracted considerable attention recently, due to their high chemical and thermal stabilities. Amorphous POPs exhibit many desirable properties such as lightweight, high surface area, permanent microporosity, and adjustable pore size.\textsuperscript{12} The design and functionality of building blocks and their polymerization reactions are very important parameters that dictate the chemistry of amorphous POPs. Functional groups in 2D and/or 3D building blocks are covalently connected to each other through the formation of C-C, C-N, N=N, B-N, and B-O covalent bonds.\textsuperscript{13} A selected list of building units used in copolymerization and self-condensation reactions of POPs is depicted in Figure 1.3.

1.3.1.1 Synthesis of Amorphous Porous Organic Polymers

Several synthetic methods have been commonly applied in POP synthesis, most of which have been already used in polymer chemistry for decades. Polymerization of POPs has been dominantly performed by: Yamamoto coupling, Sonogashira coupling, Friedel-Craft, Schiff-base, and cylotrimerization reactions.\textsuperscript{3} The use of versatile building blocks in such reactions, gives a virtually unlimited number of different potential porous polymers. In a typical POP synthesis; monomers (building blocks), solvent systems, and catalysts are mixed then heated for a certain period of time. Then the precipitate is filtrated off after the removal of catalyst and unreacted monomers. Finally, the residual solvent can be removed from the pores of the polymer by heating under reduced pressure or by supercritical CO\textsubscript{2} drying techniques.
Figure 1.3: Schematic representations of common reactions and building blocks used in POPs.

This figure used with permission from RSC.\textsuperscript{12}

Alternatively, microwave irradiation assisted reaction has been proven to offer less reaction time and enhanced product porosity compared to the conventional solvothermal polymerization method described above. Khun \textit{et al.} developed another synthetic avenue involving trimerization reaction of nitrile functionalized building blocks under ion thermal reaction conditions (molten ZnCl\textsubscript{2}).\textsuperscript{14} One of the most known POPs; intrinsically microporous hypercrosslinked polymers have been synthesized by Friedel-Craft alkylation reaction, in which dissolved monomers are cross-linked to each other in the presence of a catalyst to create porous networks.\textsuperscript{15} Despite the well-established reaction route, Friedel-Craft reactions usually tend to initiate a rapid polymerization (less than 1 hr), which complicates porosity control.
Cooper and his coworkers reported another type of POPs termed conjugated microporous organic polymers (CMPs). Because of their highly \( \pi \)-conjugated nanoporous skeletons, CMPs have attracted great attention recently. Different kinds of building blocks have been exploited in various metal-catalyzed cross-coupling (or homo-coupling) reactions such as Sonogashira-Hagihara and Yamamoto reaction (Figure 1.3). For example, porous poly(eryleneethylene) networks CMP-1 was synthesized by the palladium-catalyzed Sonogashira-Hagihara cross-coupling reaction, in which 1,3,5 substituted benzene building blocks are connected to each by phenylene and ethylene groups.

In a recent study, porous aromatic framework (PAF-1) was reported by Zhu and his coworkers. The Yamamoto homo coupling reaction of tetrakis(4-bromophenyl) methane using nickel(0) catalysis afforded PAF-1 which has a very high surface area of 5640 m\(^2\) g\(^{-1}\). In a similar study, Yamamoto homo coupling has been used in the synthesis of porous polymer networks (PPNs), but this time, by slowing down the polymerization at reduced reaction temperature eliminating potential side reactions. The homocoupling of 3D tetrahedral tetrakis(4-bromophenyl)silane monomer afforded PPN-4, which exhibited the highest surface area (6461 m\(^2\) g\(^{-1}\)) reported to date for organic polymers. The distinguished characteristics of CMPs are \( \pi \) conjugation and 3D rigid building blocks, which are able to create more surface area and free space within the polymer network. On the other hand, most of the reaction methods used in CMP utilize metal catalysts, raising concerns over cost-efficiency and trace amounts of metals left over in the pores.

Recently, metal-free polymerization efforts involving Schiff-Base imine-condensation reactions provided new POPs. The synthetic avenue is based on imine-linkage formation from condensation reactions between amine and aldehyde functionalized building blocks, eliminating
the use of metal catalysts. Numerous POPs have been reported in high yields and chemical stability as well as high microporosity by using Schiff-Base reactions. For example, polymer organic frameworks (POFs) were prepared by the condensation reaction of trialdehydes and diamines under solvothermal conditions. More recently, a series of benzimidazole-linked polymers (BILPs) were reported by metal-free condensation reactions between aryl-o-diamine and aryl-aldehyde building blocks that lead to the formation of imidazole linkages. The proposed mechanism for the formation of the imidazole linkage consists of two steps; the formation of an *in situ* aniline Schiff's base and subsequent cyclo-dehydrogenation of the base in the presence of molecular oxygen to afford the imidazole ring. This effective and metal-free avenue facilitates the purification processes of the resultant polymers as it eliminates metal ion trapping and leads to highly porous benzimidazole-based polymers. This method also avoids the use of metal catalysts, which can be very expensive for large scale production of CO$_2$ adsorbents.

![Schematic representation for the synthesis of BILP-1.](image)

**Figure 1.4:** Schematic representation for the synthesis of BILP-1.
1.3.1.2 Functionalization Studies of Porous Organic Polymers

Novel properties such as intrinsic porosity, thermal and chemical stability, create remarkable potential for POPs to be studied in gas capture and selectivity applications.\textsuperscript{23} In POPs chemistry, one of the addressed strategies to improve gas uptake is to increase the interaction energy between guest molecules and the host sorbent. It is now widely accepted that the higher surface area in polymers is very relevant to accommodate more gas molecules within the pores, especially at high pressure.\textsuperscript{24} The gas uptake performance of POPs can also be enhanced by increasing pressure, which is highly desired for gas storage and pre-combustion gas separation applications. Unfortunately, at low-pressure settings as in the case of flue gas of post-combustion power plants, CO\textsubscript{2} capture by POPs would diminish drastically due to the weak CO\textsubscript{2}/POPs interaction energy.\textsuperscript{25} Such limitation has been addressed by several recent studies aimed at pore functionalization of POPs with -COOH, -OH, -NO\textsubscript{2}, -NH\textsubscript{2}, or polyamines.\textsuperscript{25,26} These functional groups provide enhanced electrostatic interaction with polarizable gas molecules such as CO\textsubscript{2} and SO\textsubscript{2}. Furthermore, functionalized POPs tend to provide more selective gas uptake via the preferential binding affinity towards more polarized gas molecules rather than less polar or non-polar gases like N\textsubscript{2}, H\textsubscript{2}, and CH\textsubscript{4}.\textsuperscript{20} Functionalization efforts in POPs can be classified as pre- and post-functionalization based on the step that leads to pore functionalization.
Figure 1.5: The basicity of the functional units used in POPs.

For example, previously discussed porous polymer network, PPN-6 has been sulfonated to afford PPN-6-SO$_3$H. The post-functionalized PPN-6-SO$_3$H has a CO$_2$ uptake of 3.60 mmol g$^{-1}$ which is drastically higher than the pristine PPN-6. Following the CO$_2$ uptake trend, the heat of adsorption for CO$_2$ increased from 17 to 30.4 kJ mol$^{-1}$ for PPN-6 and PPN-6-SO$_3$H, respectively.\textsuperscript{27} In a similar study, Cooper and coworkers used post-synthesis functionalization of the conjugated microporous polymer CPM-1.\textsuperscript{28} They have investigated CPM-1 analogues substituted with various functional groups such as –COOH, -NH$_2$, (OH)$_2$, (CH$_3$)$_2$. The study revealed that more polar carboxylic acid (CMP-1-COOH), amine (CMP-1-(CH$_3$)$_2$) and alcohol (CMP-1-(OH)$_2$) afford higher heats of adsorption than methyl substituted CMP-1(CH$_3$)$_2$.

There have also been several studies on the incorporation of multiple nitrogen groups into various porous polymer networks.\textsuperscript{29} For example, N-functionalized benzimidazole-linked polymers (BILPs) have been studied for gas storage and selectivity. In a BILP, highly Lewis basic imidazole sites provide high interaction energy (28-38 kJ mol$^{-1}$) for acidic guest molecules like CO$_2$.\textsuperscript{21b} Similarly, N-functional units of various basicity, have also been appended
in several types of POPs to improve CO$_2$ (Figure 1.5). In summary, amorphous POPs have promising properties for desired versatile applications. However, the disordered polymer network constitutes a wide range of pore size distribution and irregularity, complicating structural characterization. Therefore, reversible bond formation under thermal control reaction conditions is necessary to generate ordered POPs like COFs.

### 1.3.2 Crystalline Porous Organic Polymers

Covalent-bond formation between the repeating monomers (building blocks) is essential for organic polymers synthesis and stability. Congregation of building blocks in a regular structural fashion, however, has been an obstacle most of organic polymerization processes.$^{30}$ As mentioned above, crystallinity of porous coordination polymers can be easily adjusted due to coordination bonds between building blocks. In contrast to PCPs, amenability of covalent bonds is much harder in POPs as bond formation is mostly irreversible. Crystalline porous organic polymers (COFs) were first reported by Yaghi.$^{31}$ The discovery presented the synthesis of rigid crystalline polymers composed of light elements such as H, B, C, Si, N and O. This new class of porous architectures is constructed by covalent bond formation between building blocks in a fashion similar to linkage found in covalent nets such as diamond and graphite.

With the systematic synthesis of COFs, the difficulty in the control over covalent bond formation rates was overcome by reversible B-O bond formation. Subsequent studies in the COFs field utilized other covalent reversible bonds such as B-N and C-N.$^{32}$
There are two main contributors in this controlled bond formation: (i) monomer assembly under dynamic covalent bond formation that leads to polymerization, and (ii) “error correction step”. In the latter step, bond formation and brakeage of the bonds occur simultaneously as monomers reorganize their position to be assembled in an ordered structure (Figure 1.6).

**Figure 1.6:** Schematic illustrations of the structures of one- and two-dimensional polymers, and strategies for 2D polymerization. This figure used with the permission from Nature Publisher.
Yaghi et al. reported COF-1 through the reversible bond formation of boronate anhydride bonds within a planar six member B$_3$O$_3$ (boroxine) ring. The self-condensation of 1,4-benzenediboronic acid under solvothermal reaction conditions yielded COF-1. In a similar fashion, different types of boronic acids have been dehydrated into the reversible boron-ester or boron-silicate bond formation affording various COFs such as COF-5 (Figure 1.7). Porosity measurements of these crystalline porous polymers showed that 2D COFs possess high surface areas (up to 1590 m$^2$ g$^{-1}$) calculated by Brunette-Emmitt-Theiler (BET) method. The pore size distribution (PSD) of COFs has been reported to range from ~9 to 40 Å. Moreover, they exhibit high thermal stabilities (up to 600 °C) due to the strong covalent bonding between the building blocks. In 2007, another breakthrough was achieved by Yaghi group via the introduction of 3D COFs. The study demonstrated that triangular and tetrahedral building blocks could be polymerized into 3D networks. In general, tetrahedral building blocks such as tetra(4-dihydroxyborylphenyl)methane have been preferred to create 3D COFs with exceptionally porous nature. The use of extremely light elements coupled with 3D crystalline topology rendered 3D COFs highly porous (COF-103 = 4210 m$^2$ g$^{-1}$).
Alternatively, Khun et al. developed a series of COFs based on covalent triazine-based frameworks (CTFs). The trimerization of a nitrile compound 1,4-decyanobenzene under ionothermal conditions afforded C₃N₃ member rings orderly connected in CTF-1. In addition to solvothermal and ionothermal reaction routes, Schiff-base chemistry has been applied in COF polymerization reactions as well. Condensation reactions between aldehyde and amine functionalized building blocks led to imine-linked COFs (ILCOFs). For example: COF-300 has been synthesized by co-condensation of tetrahedral aniline-like building unit with 1,4 benzene dialdehyde in the presence of acetic acid that modulates imine-bond formation rates and reversibility. Moreover, the solvent-free mechanical grinding, microwave and surface mediated growth methods have been recently reported for the synthesis of COFs.

1.3.2.1 Design Strategies for Covalent Organic Frameworks

Similar to PCPs, pore structure and functionality of COFs can be tailored according to the target application. Reticular chemistry approach has been extended to COFs as well. The systematic design of composition, structure, and porosity of polymers has afforded several COFs possessing pore sizes that range from 9–32 Å. Another study has reported that, building blocks in different lengths can tune the pore size of COFs from 1.1 nm to 1.8 nm. Ditchel and co-workers have engineered the pore size of several COFs ranging from 2.7 to 4.4 nm using different sizes of diboronic acids. In another study, Jiang et al. have functionalized COFs by introducing pyrene units within the diboronic building blocks. Structural topology also can be adjusted based on the dimension of building blocks used in the construction of COFs. For example, 3D COFs such as COFs(102, 103, 105, 108) have been synthesized by B-O linking of
tetrahedral and triangular building blocks.\textsuperscript{30} As such, COFs explicitly amenable for unlimited design strategies just like porous coordination polymers.

There are three important properties that play a crucial role in the function of designed COFs: porosity, structural crystallinity, and chemical functionality.\textsuperscript{38} Porosity is perhaps the most critical property for COFs to be classified as a POP. Two main synthetic methods used in porous materials for establishing porosity: The temple method, which is widely applied in the synthesis of porous zeolite and silica and utilizes structure-controlling agents. These agents connect building blocks by creating pores. In the second method, which has been mostly applied in COFs, rigid building blocks predominantly direct the porosity. While the molecular metrics of building blocks manage pore size, the geometry of building units determines the topology of COFs.\textsuperscript{3} The structural regularity is another important property in the COF design. As discussed at the beginning of this section, the uncontrollable formation of the covalent bonding impedes organic polymers from forming ordered structures. COFs, however, have surmounted this barrier by introducing the reversible bond formation concept.\textsuperscript{41} However, it is ambiguous whether the reversible bond formation between rigid buildings blocks is always completed in an ordered form. At this point, the angle of building blocks should be taken into consideration in addition to the shape and rigidity of the building units. For example, the recent study by Kuhn \textit{et al.} showed that reversible cyclomerization reactions between bended nitrile building blocks have resulted in porous polymers which show amorphous morphology.\textsuperscript{14}

The tunable chemical functionality is a prominent property of COFs and thus post-synthetic modification methods have been employed to alter the chemical nature of 2D COFs. Jiang and co-workers reported modified 2D N3-COF-5 which has appended azide groups to incorporate triazole-functional groups.\textsuperscript{42} Another functionalization study has been reported by
Wang and his co-workers which entailed Pd(II) immobilization within a 2D imine-linked COF (Pd/COF-LZU-1) for use in C-C bond formation catalytic studies as illustrated in Figure 1.8.\(^{43}\)

**Figure 1.8:** Chemical structures of COF-LZU1 and Pd/COF-LZU1. This figure used with permission from ACS.\(^{43}\)
1.4 Applications of Porous Organic Polymers

Porous organic polymers have been one of the landmarks in polymers chemistry due to their aforementioned novel properties. Above all, diverse synthetic conditions and the adjustable pore functionality allowed POPs to function in various applications such as gas storage, gas separation, energy harvesting, optoelectronics and catalysis.\(^{44}\)

1.4.1 Gas Storage

Porous organic polymers have been widely investigated as solid adsorbent material in capture and storage of gases such as H\(_2\), CO\(_2\), CH\(_4\) and NH\(_3\). As part of the effort to solve the ongoing global warming issue, hydrogen energy is considered to be one of the green alternatives to mitigate greenhouse gas emissions from the burning of fossil fuels.\(^{45}\) One of the merits of hydrogen is the higher energy density compared to fossil fuels and more importantly zero carbon emission.\(^{46}\) However, the very low density of H\(_2\) makes it very difficult to store hydrogen in a cost-effective manner, especially for on-board applications.\(^{47}\) The conventional methods such as high-pressure and cryogenic gas storage tanks are undesirable due to cost and safety concerns. According to the 2015 U.S. Department of Energy (DOE) targets for cost-efficient hydrogen energy consumption; H\(_2\) needs to be stored at no less than 5.5 wt.% gravimetrically and 40 g L\(^{-1}\) volumetrically under operation temperatures in the range of 40 to 60 °C and a maximum delivery pressure of 100 atm.\(^{48}\) In the last decade, metal hydrides and chemical hydrides have been considered for H\(_2\) storage applications.\(^{48}\) However, high thermodynamics, slow kinetics, high weight and poor reversibility of hydrides kept them away from practical H\(_2\) storage.\(^{49}\)

More recently, porous polymers have emerged as alternative materials for hydrogen storage as well as other gas storage applications such as methane and ammonia. H\(_2\) storage research in porous polymers has been vastly dedicated to MOFs and COFs.\(^{38,50}\) In these systems,
H₂ is physisorbed at cryogenic temperatures and ambient to high pressure conditions (100-150 bar). The H₂ uptake is usually correlated with the physical properties of the host such as surface area and free volume. For example, MOF-5 possesses 3800 m² g⁻¹ surface area (SA_BET) and adsorbs 7.1 wt.% excess H₂ at 40 bar and 77 K. Another study reported MOF-210 to have hydrogen uptake (excess) of 8.7% at 77 K and 60 bar. The higher H₂ uptake by MOF-210 was ascribed to its higher surface area (6240 m² g⁻¹).

H₂ storage research in porous organic polymers has been initiated simultaneously by the introduction of COFs. Similar to MOFs, H₂ storage in POPs occur through the van der Waals forces between H₂ molecules and the surface of POPs. As such, both high pressure and low temperatures are needed to attain significant H₂ storage capacities.

Usually, 3D POPs exhibit higher H₂ uptake at elevated pressure than 2D POPs, due to their larger surface area properties. For example, the H₂ uptake (1.55 wt % at 1 bar and 77K) of COF-18 (SA_BET: 1710 m² g⁻¹) surpasses other COFs like COF-11,14 and 16 which have lower surface areas, 105, 805, and 753 m² g⁻¹, respectively. Also, the higher surface area enables 3D COFs to adsorb more H₂ at elevated pressures. Currently COF-102 (SA_BET: 3620 m² g⁻¹) has one of the highest H₂ uptakes (7.24 wt% at 35 bar and 77 K) reported for organic materials. Similarly, the amorphous POP, PAF-1, also showed very high H₂ uptake (7.0% at 77 K and 48 bar).

Besides fast kinetics and high regenerability properties, the physisorption of H₂ in porous polymers offers limited adsorption capacity because of the weak H₂-host interactions. Several theoretical studies have been conducted to increase the interaction energy (5-10 kJ mol⁻¹) between the sorbent and H₂. It should also be noted that the interaction energy should not exceed the physisorption limits (15-20 kJ mol⁻¹) to avoid reversibility problems, which have been
confronted in H₂ storage in metal and chemical hydrides.⁵⁴ Recently, Yaghi and his coworkers have theoretically demonstrated that DOE hydrogen storage targets can actually be exceeded by PdCl₂-doped COFs.⁵⁴b The incorporation of PdCl₂ into imine-linked COF-301 has been suggested (theoretically) to lead to a remarkably high H₂ storage at room temperature and 100 bar. At such conditions PdCl₂@COF-301 would store 4.2 wt % H₂ (excess).

Porous polymers have been also considered for other gas storage applications such as methane, carbon dioxide, and ammonia storage.³⁰, ⁵²b Methane storage materials have attracted great attention due to the drastic increase in worldwide natural gas consumption and production. Although methane is abundant, relatively inexpensive and clean, methane storage in cost-effective and safe manners is still a challenge for on-board applications. Methane is considered to be greener than other fossil fuels because of its lower carbon footprint. Therefore, POPs have been tested for methane storage applications. High surface area and pore volume properties are highly desired for methane storage at high pressure.⁵⁵ 3D COFs such as COF-102 and COF-103 showed high methane uptakes of 187 mg g⁻¹ and 175 mg g⁻¹, respectively at 35 bar and 298 K. Whereas, 2D COF-5 adsorbed only 89 mg g⁻¹ methane under similar conditions.³⁰ However, the shortcoming of porous materials in general and COFs/POPs in particular, is their low volumetric CH₄ capacities, which is due to their inherent low-density nature. Consequently, the textural and physical parameters of porous adsorbents still need significant improvements prior to their application in methane storage. Nevertheless, porous polymers stand as promising alternative to high-pressure compressed CH₄ storage (at around 250 bar), which suffers from high cost and safety risks in practical applications.⁵⁶ According to DOE, 180 v(STP)/v(STP) equivalent of methane per volume of adsorbent material storage system under 35 bar and near ambient temperature is required for methane storage.
CO₂ capture is another important application for porous adsorbents. Cost-effective CO₂ separation from combustion gas flow is crucial. Although the use of alkanolamine absorbents is currently the state-of-the-art technology to capture CO₂, the large amounts of energy (up to 30% of the output of the power plant) associated with aqueous amine recycling as well as their corrosive, toxic, and volatile nature makes them less desirable.⁵⁷ Thus, to overcome these limitations, numerous types of POPs have been reported such as COFs,¹¹ PAFs,¹⁸ CMPs,¹² HCPs, PIMs,⁵⁸ and BILPs,²¹b among others. For example, PPN-4 has a very high CO₂ storage capacity as high as 2121 mg g⁻¹ (295 K and 50 bar).¹⁹ The inclusion of CO₂-philic functional groups in POPs is vitally important for enhancing their interactions with polarizable CO₂ molecules.⁵⁹

1.4.2 Gas Separation

In industrial applications, gas flows are composed of different types of gases such as H₂O, N₂, H₂, CH₄, CO₂, SO₂, and NO₂. The selective removal of gases from the gas flow is crucial to obtain the target gas purity. This section mainly encompasses CO₂ capture and separation from CH₄ and N₂ under practical conditions. Capture and separation of CO₂ (CCS), has been applied in industrial applications such as natural gas purification for decades. In recent years, CCS has gained great attention due its potential role in reducing CO₂ emissions from the combustion of fossil fuels.⁵⁷b CCS processes are designed to capture and separate CO₂ from the gas flow of combustional systems like power plants. There are three stationary processes currently developed and investigated for capturing CO₂:
Figure 1.9: CO$_2$ capture process in absorption and desorption columns.
(i) The post-combustion process which separates CO$_2$ by chemical solvents such as amine scrubbers, (ii) The pre-combustion process that chemically captures CO$_2$ before converting methane rich fuels into hydrogen, and (iii) the oxyfuel combustion process which removes nitrogen prior to combustion resulting in only water and CO$_2$ in the output gas flow.$^{57b, 57a}$

Conventionally, chemical absorption technology utilizing liquid absorbents, so-called “wet scrubbers”, has been implemented in CO$_2$ capture for over 50 years. The capture process involves the introduction of CO$_2$ containing gas flow from the bottom of the absorption column where CO$_2$ reacts with amine-based solvents through the Zwitterion mechanism to form carbamates at around 40 °C. The resulting CO$_2$ containing amine solutions are then regenerated by heating and finally the captured CO$_2$ is released in the desorption column (Figure 1.9).$^{23}$ However, the existing CCS method shows drastic limitations such as high energy consumption (heat employed in solvent regeneration), chemical degradation of absorbents, corrosiveness, and high toxicity of byproducts generated during the regeneration process.$^{60}$
Figure 1.10: Overall categorization of materials in gas separation and capture.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Flue Gas</th>
<th>Pre-combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>70-75%</td>
<td>0.25%</td>
</tr>
<tr>
<td>CO₂</td>
<td>15-16%</td>
<td>35.5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5-7%</td>
<td>0.2%</td>
</tr>
<tr>
<td>O₂</td>
<td>3-4%</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>61.5%</td>
</tr>
<tr>
<td>SOₓ</td>
<td>&lt; 800 ppm</td>
<td>-</td>
</tr>
<tr>
<td>NOₓ</td>
<td>500 ppm</td>
<td>-</td>
</tr>
<tr>
<td>H₂S</td>
<td>100 ppm</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

Conditions : Temperature and pressure
50-75 ºC, 1 bar
40 ºC, 30 bar

Table 1.1 Typical gas composition of flue gas, natural gas, and landfill gas.

Substantial research efforts have been directed towards the development of porous architectures that enable CO₂ capture and separation from flue gas and methane-rich gasses (natural gas, landfill gas). To be competitive with the state-of-the-art technology, solid-state adsorbents must capture at least 3-4 mmol g⁻¹ of CO₂ at 40 and 80 ºC and atmospheric pressure. Functional groups such as COOH, -(OH)₂, -NH₂, -H, -(CH₃)₂ have been incorporated into porous adsorbents through various synthetic methods creating more attractive sites CO₂ to improve the capturing capacity. For example, triazine-functionalized POPs have been synthesised by the incorporation of 1,3,5-traizine units into various polymer structures. Cooper and his co-workers developed several types of triazine-based conjugated microporous polymers (TCMPs) and showed that π-conjugated 1,3,5 triazine functionalities can act as an electron donor, which play an essential role in the enhanced CO₂ capture performance.
El-Kaderi and co-workers have introduced imidazole functionalities in several POPs known as benzimidazole-linked polymers (BILPs) to conduct gas storage and separation studies. BILP-1 exhibited very high gas selectivity $\text{CO}_2/\text{N}_2$ (70) and $\text{CO}_2/\text{CH}_4$ (10), and stored high amount of $\text{CO}_2$ (19 wt %, 273 K, 1 bar). On the other hand, post-synthetic modification processes have been successfully implemented in POPs such as nanoporous organic frameworks (NPOFs). NPOFs functionalized with $-\text{NO}_2$ and $-\text{NH}_2$ functionalities have been investigated by El-Kaderi’s group. After post-synthetic functionalization, NPOF-4 exhibited a significant enhancement in $\text{CO}_2$ binding affinity and selective binding over nitrogen and methane: $\text{CO}_2/\text{N}_2$ (139) and $\text{CO}_2/\text{CH}_4$ (15) at 273 K. Overall, $\text{CO}_2$ capture studies using POPs have mainly focused on (i) enhancing the surface area to provide more interaction sites for $\text{CO}_2$, (ii) adjusting pore size to preferentially adsorb $\text{CO}_2$, and (iii) increasing interaction strength between the pores and $\text{CO}_2$ by incorporating more polar groups (i.e. $-\text{NH}_2$, $-\text{NO}_2$, $-\text{COOH}$, etc.).
1.5 Statement of the Problem

It is estimated that about 87% of the world’s energy is still fossil fuel-based and as such, CO₂ capture and sequestration (CCS) received great attention in recent years to reduce CO₂ concentration. Although the use of amine-solutions is the current capturing method of CO₂ from flue gas, they consume large amount of energy about 30% of the output of the power plant associated with the aqueous amine cycle. Additionally, the corrosive, toxic and volatile nature of the amine solutions restricts their widespread use. As an alternative energy source, on the other hand, hydrogen (H₂) energy is being considered due to its renewable and clean chemical nature. However due to inherent volumetric energy density problem, its on-board storage remains a great challenge. Porous materials such as Metal-Organic Frameworks and Covalent Organic Frameworks have been widely studied for gas capture and storage applications; CO₂ capture, and hydrogen and methane storage. However, some drawbacks of these adsorbent materials such as weak stability and limited scale production have impeded their use in industrial applications. Recent studies on porous organic polymers (POPs) have designated that POPs exhibit very high physicochemical and thermal stability as well as other advanced properties such as high surface area, adjustable pore formation, low framework density, recyclability and chemical tunability, which allow them to be applicable for practical gas storage and separation. Numerous reports demonstrated that enhancing surface area and number of functional sites of materials provide more improved gas storage properties. At this point, the chemical robustness of such materials is vitally important for the practical usage. Concerns over the stability and cost associated with MOFs accelerated the focus on porous organic polymers (POPs) to overcome the challenges with gas storage and separation applications. The goal of this dissertation is to design and synthesize POPs showing high physiochemical stability, permanent porosity, adjustable pore metrics, and
chemical nature tunability. While the latter property is immensely investigated for gas separation such as CO₂ separation from the flue gas, natural gas and landfill gas, polymers which show high porosity and surface area properties are expected to offer more potential use in gas storage applications such as hydrogen, methane and carbon dioxide storage. Recent studies have documented that selection of building blocks and developing efficient chemical synthesis routes are two key parameters to meet the desired POP material. Accordingly, the use of pyrene-based rigid building blocks in well-developed reversible and irreversible imine-condensation reactions can afford POPs exhibiting great potential for the target applications. The strong π-π stacking interactions of the pyrene moieties is not only able to direct the solid-state packing but also prevents network interpenetration and thereby enhances the porosity and controls the pore size distribution of polymers.
Chapter 2

Pyrene-Directed Growth of Nanoporous Benzimidazole-Linked Polymers and their Application to Selective CO$_2$ Capture and Separation

2.1 Introduction

Porous organic polymers (POPs) has been considered for a versatile applications such as catalysis, sensing, and gas storage and separation due to their novel features such as high surface area, remarkable physiochemical stability, adjustable pore metrics, and chemical nature tunability.$^3$ $^{64}$ Specifically, the latter property is highly desired for selective gas binding and separation, enabling pore modification processes.$^{65}$ Chemical heterogeneities have been incorporated into polymers through the formation of heterocyclic building units such as benzimidazole and triazoles or ether- and imine-linkages.$^{66}$

In this chapter, we show that integrating pyrene into the framework of BILPs leads to the formation of self-assembled nanofibers that have one of the highest CO$_2$ and H$_2$ binding affinities by unmodified porous organic polymers known to date. Additionally, the same polymer exhibits excellent CO$_2$ selectivity over CH$_4$ and N$_2$. The pyrene units presumably facilitate the formation of nanofiber morphology and growth as a result of their ability to form strong $\pi$-$\pi$ stacking interactions.

2.2 Experimental Section

2.2.1 Materials and Methods
All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Acros Organics, or Frontier Scientific) and used without further purification, unless otherwise noted. 1,3,6,8-Tetrabromopyrene was synthesized using published procedure. Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Acros Organics (60 Å, 35-70 µm). Elemental microanalyses were performed at the Midwest Microlab, LLC. Solution $^1$H and $^{13}$C NMR spectra were obtained on a Varian Mercury-300 MHz NMR spectrometer. $^{13}$C cross-polarization magic angle spinning (CP-MAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Spectra were obtained with samples on a Tecmag-based NMR spectrometer, operating at a H-1 frequency of 363 MHz, using a contact time of 1 ms and a delay of three seconds for the CPMAS experiment; samples were spun at 7.0 kHz. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 µL platinum pans under atmosphere of air (heating rate 5 °C/min). For Scanning Electron Microscopy Imaging (SEM), the sample was prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The sample was then coated with platinum at $1 \times 10^{-5}$ mbar of pressure in a nitrogen atmosphere for 90 seconds before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope. Powder X-ray diffraction data were collected on a Panalytical X’pert pro multipurpose diffractometer (MPD). Samples were mounted on a sample holder and measured using Cu Kα radiation with a 2θ range of 1.5-35. FT-IR spectra were obtained as KBr pellets using a Nicolet-Nexus 670 spectrometer. Porosity and gas sorption experiments were collected using a Quantachrome Autosorb 1-C volumetric analyzer using adsorbates of UHP grade. In a typical experiment, a sample was loaded into a 9 mm large bulb cell
(Quantachrome) of known weight and then hooked up to Autosorb 1-C and degassed at 120 °C for 12 h. The degassed sample was refilled with nitrogen, weighed precisely and then transferred back to the analyzer. The temperatures for adsorption measurements were controlled by using refrigerated bath of liquid nitrogen (77 K), liquid argon (87 K), or temperature controlled water bath (273 K and 298 K). Hydrogen isotherms were collected at 77 K and 87 K. Carbon dioxide and methane isotherms were collected at 273, 288 and 298 K. Pore Size Distribution (PSD) was calculated using spherical/cylindrical pore (zeolite) NLDFT adsorption model. High pressure sorption isotherms were run using a VTI HPVA-100 volumetric analyzer. Free space measurements were performed prior to data collection utilizing ultra-high purity helium to establish the appropriate cold zone compensation factors. The skeletal density of the material was found in the course of analysis for appropriate density correction factorization.
2.2.3 Synthesis of Building block, 1,3,6,8-tetrakis($\rho$-formylphenyl)pyrene (TFPPy)

A mixture of 1,3,6,8-tetrabromopyrene (1.00 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol%), and potassium carbonate (2.1 g, 15 mmol) in dry dioxane (30 mL) was stirred under nitrogen for 3 days at 85 °C. The yellow suspension reaction mixture was poured into a solution of ice containing concentrated hydrochloric acid. The yellow solid was filtered, washed with 2 M HCl (20 mL) for three times. The product was extracted with CHCl₃ (3x100 mL) and dried over MgSO₄. After filtration, the solvent was removed under reduced pressure and the resultant solid residue was recrystallized from hot CHCl₃ to afford TFPPy as a bright yellow powder (0.85 g, 72%). H NMR (300 MHz, CDCl₃, $\delta$): 10.17 (s, 4H, Ar H), 8.18 (s, 4H, Ar H), 8.09 (d, $J = 6$ Hz, 8H, Ar H), 8.05 (s, 2H, Ar H), 7.86 (d, $J = 6$ Hz, 8H, Ar H); UV-vis (CHCl₃): $\lambda_{\text{max}} = 259, 290$ (sh) 303, 402 nm; IR (KBr): $\nu = 3061$ (w), 2921 (w), 2812 (w), 2721 (w), 1700 (s), 1601 (s), 1566 (w), 1305 (w), 1215 (m), 1169 (m), 1006 (w), 832 (m), 757 (w), 734 (w); MALDI-TOF MS for C₄₄H₂₆O₄: [M]$^+$ found 618.11, calcd 618.18. Anal. Calcd for C₄₄H₂₆O₄: C 78.95, H 4.05, O 10.66; Found: C 78.96, H 4.09, O 10.89.²¹d
Figure 2.1 $^1$H NMR spectra for 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) in CDCl$_3$: Note that $^{13}$C NMR spectrum could not be measured due to the low solubility of TFPPy.
2.2.4 Synthesis of Benzimidazole-Linked Polymer, BILP-10

A 250 mL Schlenk flask was charged with 1,2,4,5-benzenetetramine tetrahydrochloride (113 mg, 0.39 mmol), 50 mL of anhydrous DMF, and a stir-bar. The resultant homogeneous solution was cooled to ca. -30 °C and treated drop-wise with TFPPy (120 mg, 0.19 mmol) dissolved in anhydrous DMF (115 mL). The temperature was maintained around -30 °C for 6 hours during which a yellowish brown solid formed then the resultant slurry solution was left to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 10 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 °C (0.5 °C/min) and kept for 3 days to afford a fluffy yellow powder. The solid was isolated by filtration over a medium glass frit and subsequently washed with DMF, acetone, water, 2M HCl, 2M NaOH, water, and acetone. The product was then immersed in acetone/CHCl₃ (1:1 v/v) for one day, during which the activation solvent was decanted and freshly replenished twice. After filtration, the product was dried at 120 °C under vacuum (150 mTorr) to give BILP-10 as a fluffy yellow powder (130 mg, 84%). Anal. Calcd. for C₅₆H₃₀N₈.8H₂O: C 70.13, H 4.83, N 11.68; Found: C 68.70, H 3.85, N 10.47.21d
2.3. Results and Discussion

2.3.1 Synthesis and Characterization of BILP-10

The synthesis of the pyrene-derived BILP-10 was accomplished by using the condensation method we have reported recently for BILPs.\textsuperscript{21a} The proposed mechanism for the formation of the imidazole linkage consists of two steps; the formation of in-situ aniline Schiff’s base that undergoes subsequent cyclo-dehydrogenation in the presence of molecular oxygen to afford the imidazole ring as illustrated in Scheme 2.1.\textsuperscript{22} This effective and metal-free avenue facilitates the purification processes of the resultant polymers as it eliminates metal ion trapping and leads to the most porous benzimidazole-based polymers. This method also avoids the use of metal catalysts which can be too expensive for the production of CO\textsubscript{2} adsorbents on a large scale.

![Scheme 2.1 Proposed mechanism for the formation of imidazole via condensation reaction between a 1,2-benzenediamine and an aryl-aldehyde.](image-url)
Scheme 2.2 Synthesis of 1,3,6,8-tetrakis(4-formylphenyl)pyrene and its subsequent use in the preparation of BILP-10 by condensation with 1,2,4,5-benzenetetramine tetrahydrochloride.
A schematic representation for the synthesis of BILP-10 is shown in Scheme 2.2. A homogeneous solution of 1,2,4,5-benzenetetramine tetrahydrochloride (BTA) in dimethylformamide (DMF) was cooled to -30 °C then treated dropwise with 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) dissolved in DMF to afford a yellow suspension which is most likely imine-linked networks. The resultant suspension was bubbled with air for 10 minutes then heated for three days at 130 °C to afford BILP-10 as a yellow powder in a good yield (84%). We have noticed previously that the slow addition of aldehyde and the use of low temperatures during the initial polymerization stages were important factors that affect the overall porosity of BILPs. The first step is acid-catalyzed (HCl in this case) even at low temperature (-30 °C) whereas exposure to molecular oxygen and heating over an extended period of time are required for imidazole ring formation. BILP-10 is insoluble in common organic solvents and was purified by washing with a 2 M aqueous solutions of HCl, NaOH, water, and acetone. The chemical composition and connectivity between building units were established using spectral and analytical methods while porosity was investigated by argon sorption-desorption measurements. The chemical connectivity and the formation of the imidazole ring were confirmed by FT-IR and \(^{13}\text{C}\) CP-MAS NMR studies. The FT-IR spectrum of BILP-10 (Figure 2.2) reveals N-H stretching at around 3412 cm\(^{-1}\) (free N-H) and 3205 cm\(^{-1}\) (hydrogen bonded N-H), while intense new bands appeared at 1638 cm\(^{-1}\) (C=N), and 1484, 1435, 1370 and 1275 cm\(^{-1}\) which can be assigned to skeleton vibration of the benzimidazole ring.\(^{21b}\) The intensity of C=O band at 1700 cm\(^{-1}\) in TFPPy is substantially attenuated in BILP-10 which suggested the full consumption of TFPPy monomer in the polymerization.
Figure 2.2 FT-IR spectra of activated BILP-10, and monomers TFPPy and BTA.
The $^{13}$C CP-MAS NMR spectrum for BILP-10 (Figure 2.4) contains a signal around 151 ppm that corresponds to NC(Ph)N in the benzimidazoles units as well as other signals in the aromatic range that arise from the TFPPy and BTA units.$^{21d}$

**Figure 2.3** $^{13}$C NMR for 1,2,4,5-Benzenetetramine tetrahydrochloride (BTA) (in $d_6$ DMSO).

**Figure 2.4** Solid state $^{13}$C CP-MAS NMR spectrum of BILP-10. Asterisks denote spinning side bands.
The thermal stability of BILP-10 was confirmed by thermogravimetric analysis (TGA) which indicates that the polymer remains stable up to ~450 °C (Figure 2.5).

**Figure 2.5** TGA trace of BILP-10.

The material is amorphous as indicated by the powder X-ray diffraction profile of BILP-10 shown in the Figure 2.6.

**Figure 2.6** X-ray diffraction pattern for BILP-10.
Scanning electron microscopy (SEM) revealed a unique morphology of nanofibers of around 0.2 μm in diameter and up to ~7.5 μm in length (Figure 2.7).

**Figure 2.7:** Scanning electron microscopy imaging (SEM) for BILP-10.

Worth mentioning is that such directional growth was not observed for the previously reported BILPs. As mentioned above, the nanofiber morphology of BILP-10 is most likely driven by the strong π-π stacking interactions of the rigid and electron-rich pyrene cores. In addition to the π-π stacking interactions, the hydrogen bonding interactions originated from the benzimidazole moieties which are in the same plane of pyrene cores can also facilitate the longitudinal directed self-assemblies of the nanofibers.
2.3.2 Porosity Studies of BILP-10

The porosity of BILP-10 was investigated by argon sorption-desorption measurements. The dry polymer was degassed at 140 °C for 12 h to remove any remaining guest molecules before sorption measurements. Figure 2.8 shows the argon isotherm for BILP-10 at 87 K. The fully reversible isotherm exhibits a rapid uptake at low pressure ($P/P_o = 0-0.05$ bar) followed by a somewhat steep uptake until saturation pressure which indicate the presence of microporos in addition to a minor pore size distribution in the mesoporous range.

![Figure 2.8](image)

**Figure 2.8:** Argon adsorption isotherm for BILP-10 measured at 87 K. The filled circles are adsorption points and the empty circles are desorption points.
Figure 2.9: N₂ adsorption isotherm for BILP-10 measured at 77K. The filled circles are adsorption points and the empty circles are desorption points.

Figure 2.10: BET plot for BILP-10 calculated from the Ar adsorption isotherm at 87 K. The model was applied from P/P₀ = 0.04–0.16. The correlation factor is indicated. (W= Weight of gas absorbed at a relative pressure P/P₀).
Figure 2.11: BET plot for BILP-10 calculated from the N$_2$ adsorption isotherm at 77 K. The model was applied from P/P$_0$ = 0.05-0.15. The correlation factor is indicated. (W= Weight of gas absorbed at a relative pressure P/P$_0$).

Applying the Brunauer-Emmett-Teller (BET) model to the sorption branch within the pressure range of $P/P_o = 0.05$-0.15 resulted in a specific surface area $S_{A_{BET}} = 787$ m$^2$/g.

Pore size distribution was estimated from the argon isotherm by nonlocal density functional theory (NLDFT) and was found to be centered around 7.6 Å (Figure. 2.12), while pore volume ($P_{vol} = 0.40$ cc g$^{-1}$) was calculated from a single point measurement at $P/P_o = 0.95$. It should be noted that NLDFT investigations also resulted in minor domains of larger pores (10 to 20 Å) which possibly result from a lack of a uniform growth of the polymer’s network or solid-state packing. In contrast, calculating the corresponding properties from the nitrogen isotherm leads to a much broader PSD range with pore size ranges centered about 12.6 Å and 20-50 Å and a cumulative pore volume of 0.457 cc g$^{-1}$ with ~23% contribution from mesopores.
Figure 2.12: The Pore Size Distribution of BILP-10 was calculated from the Ar adsorption isotherm using oxygen (zeolite) model, spherical/cylindrical pore, NLDFT adsorption model (A) and from N\textsubscript{2} isotherm (B) using silica as adsorbent and cylindr./sphere. pore, NLDFT adsorption model. The use of N\textsubscript{2} to probe porosity leads to PSD $\sim$12.6 Å and to a broad distribution of mesopores in the range of $\sim$20 to 50 Å that contributes $\sim$23\% of the cumulative pore volume.
Figure 2.13: Experimental Ar adsorption isotherm for BILP-10 measured at 87 K is shown as filled circle. The calculated NLDFT isotherm is overlaid as open circle. Note that a fitting error of less than 1% indicates the validity of using this method for assessing the porosity of BILP-10. The fitting error is indicated.
2.3.3 Gas Storage Studies of BILP-10

In addition to the subnanometer porosity of BILP-10, altering the chemical heterogeneity of pore walls by introducing nitrogen-rich moieties as in the case of imidazole units was proven to be very important in selective gas uptake and enhanced binding affinities.\textsuperscript{21c} The effectiveness of this approach has been documented for porous materials such as metal-organic frameworks (MOFs) and organic polymers especially for targeted applications directed towards CO\textsubscript{2} storage or separation.\textsuperscript{68} For example, several polymeric systems that contain N-functionalized pore walls, including those of BILPs, we have reported recently have shown enhanced CO\textsubscript{2} uptakes and selectivity.\textsuperscript{29} Accordingly, the impact of these factors on the uptake of H\textsubscript{2} and CO\textsubscript{2} and the preferential CO\textsubscript{2} binding over N\textsubscript{2} and CH\textsubscript{4} were investigated. H\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4} gas isotherms were collected and their respective isosteric enthalpies of adsorption (\(Q_{st}\)) were calculated. The CO\textsubscript{2} isotherms depicted in Figure 2.14 are fully reversible and exhibit a steep rise at low pressures. The absence of adsorption-desorption hysteresis indicates that CO\textsubscript{2} is reversibly adsorbed by BILP-10. The CO\textsubscript{2} uptake (177 mg g\textsuperscript{-1}, 4.0 mmol g\textsuperscript{-1}) at 273 K and 1.0 bar is slightly lower than those of BILPs that have high CO\textsubscript{2} uptakes (188-235 mg g\textsuperscript{-1}), but higher than the values reported for BILPs that were constructed from 2D building units such as BILP-2 and BILP-5 (128-149 mg g\textsuperscript{-1}). To the best of our knowledge, this CO\textsubscript{2} uptake by BILP-10 is among the highest by porous organic polymers such as BILPs (5.3 mmol g\textsuperscript{-1}), carbazole-based porous organic polymers (CPOPs, 4.82 mmol g\textsuperscript{-1}) and -OH functionalized porous organic frameworks (POFs: 4.2 mmol g\textsuperscript{-1}), and rivals those of the best performing MOFs under similar experimental settings.\textsuperscript{12,57c}
Figure 2.14: Gas uptake isotherms of BILP-10.
2.4.1 Calculation of Isosteric Heats of Adsorption for BILP-10

Virial Equation

The virial equation was used to determine the binding affinity and isosteric heats of adsorption. The virial equation can be written in the form

\[
\ln\left(\frac{N}{P}\right) = A_0 N^0 + A_1 N^1 + A_2 N^2 + \ldots \quad (I)
\]

Where \(N\) is the amount adsorbed at pressure \(P\) and \(A_0, A_1, \ldots\) are virial coefficients. \(A_0\) is related to adsorbate-adsorbent interactions, whereas describes adsorbate-adsorbate interactions. Under condition of low surface coverage, the higher terms (\(A_2, \ldots\)) in the virial equation can be neglected.

A virial-type expression in the following form can also be used to fit the experimental isotherm data for a given material at different temperatures:

\[
\ln(P) = \ln(N) + \frac{1}{T} \sum_{i=1}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad (II)
\]

Where \(N\) is the amount adsorbed at pressure \(P\), \(T\) is the temperature, \(a_i\) and \(b_i\) are temperature independent empirical parameters, and \(m\) and \(n\) determine the number of terms required to adequately describe the isotherm. The resulting virial coefficients \(a_0\) through \(a_m\) can then be used to calculate the isosteric heats of adsorption as function of uptake:

\[
Q_{st} = -R \sum_{i=0}^{m} a_i N^i \quad (III)
\]

Where \(R\) is the universal gas constant (8.314 J K\(^{-1}\) Mol\(^{-1}\))

It follows that the zero-coverage isosteric heats of adsorption is given by

\[
Q_{st} = -Ra_0 \quad (IV)
\]
Isosteric heats of adsorption can also be calculated from the Clausius-Clapeyron equation.

\[ Q_{st} = RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_N \]  

(\text{V})

Where \( T \) is the temperature, \( R \) is the universal gas constant and \( P \) is the pressure for given quantity of gas adsorbed (\( N \)). The temperature dependent experimental data are fit to model isotherms to obtain \( P \) for given \( N \). Adsorption isotherms for CO\(_2\) and CH\(_4\) collected at 273 K, 288 K and 298 K were fitted here using the Tóth equation.\(^{21b}\) Tóth equation has the advantage that it appears to satisfy both limits of the isotherm, at \( p \to 0 \) and \( p \to \infty \). It is given by,

\[ N = N_s \left( \frac{(kP)^t}{1 + (kP)^t} \right)^{1/t} \]  

(\text{VI})

\( N \) = Gas adsorbed (mmol/g) at a given pressure
\( N_s \) = Gas adsorbed (mmol/g) at saturation
\( P \) = Pressure (atm)
\( k \) and \( t \) are constants.

Equation (\text{VI}) can be rearranged to the following form to calculate \( P \) for equation (\text{V}).

\[ P = \frac{N}{N_s} \left( \frac{1}{k \left( 1 - \frac{N}{N_s} \right)^t} \right)^{1/t} \]  

(\text{VII})

\( Q_{st} \) was then obtained from the slope of \( \ln(\text{P}) \) vs. \( 1/T \) plot in the following form of equation (\text{V}):  

\[ (\ln P)_N = -\left( Q_{st} / R \right)(1/T) + C \]  

(\text{VIII})

For the Clausius-Clapeyron equation, CO\(_2\) isotherms at 273, 288 and 298 K were collected and the resulting data were fitted using the Tóth model (Figure 2.15).
This model has been reported to be superior to the Langmuir or Freundlich models in providing a more extensive data fitting at both low and high surface coverage. The $Q_{st}$ values obtained from the Clausius-Clapeyron equation and the virial method resulted in a very similar trend with increasing surface coverage.

Figure 2.15: CO$_2$ gas adsorption for BILP-10 at 273 K (A), 288 K (B), and 298 K (C). The continuous solid line corresponds to a Tóth isotherm fit to the experimental data.
Figure 2.16: CH₄ gas adsorption for BILP-10 at 273 K (A), 288 K (B), and 298 K (C). The continuous solid line corresponds to a Tóth isotherm fit to the experimental data.
The \( Q_{st} \) values obtained from the Clausius-Clapeyron equation and the virial method resulted in a very similar trend with increasing surface coverage. As stated above, the CO\(_2\) \( Q_{st} \) value is much higher than those of unmodified organic polymers including nitrogen-rich networks PECONFs (26-34) or PI-1 (34) but are lower than CO\(_2\) selective MOFs or functionalized PPNs which generally feature –NH\(_2\) or –OH functionalized pores\(^{25,72}\). The high CO\(_2\) uptake and binding affinity by BILP-10 are expected to arise from strong interactions of the polarizable CO\(_2\) molecules through hydrogen bonding and/or dipole-quadrupole interactions that utilize the nitrogen sites of imidazole rings\(^{73}\). Other attractive features of BILP-10 are the readily reversible CO\(_2\) sorption/desorption behavior and the moderate \( Q_{st} \) value which indicate that CO\(_2\) evacuation from the pores can be performed rapidly and simply by reducing the pressure without heating the polymer. This energy-saving step in post-combustion CO\(_2\) capture is highly desirable because it eliminates energy consumption during adsorbent regeneration as in the case of primary alkanolamines that require significant amounts of heat because of the high heat capacity of water\(^ {60}\).

Since most BILPs reported thus far show high CO\(_2\) uptakes as a result of their imidazole functionalized pore walls, it is expected that their CO\(_2\) uptake capacity will depend on the number of accessible nitrogen sites that can preferentially bind CO\(_2\). This may be due to the CO\(_2\) interaction with the imidazole moiety through the nitrogen lone-pair of \(-C=N–\) and the carbon atom in O=C=O as well as via the N-H···O hydrogen bonding interaction\(^{74}\). In order to investigate this factor, a quantitative correlation between the number of available nitrogen adsorption sites versus those that would be occupied upon CO\(_2\) adsorption was performed by considering the repeating unit of BILP-10 (C\(_{56}\)H\(_{30}\)N\(_8\)).
Figure 2.17: Virial analysis of CO₂ adsorption data (A) (circles: 273 K, squares: 298 K) and isosteric heats of adsorption ($Q_{st}$) (B) for BILP-10. $a_0 = -4587.4755$, $a_1 = 292.432275$, $a_2 = 116.288873$, $a_3 = -18.315564$, $b_0 = 20.60912903$, $b_1 = -1.368179285$. 
Assuming that each imidazole unit can potentially interact with one CO$_2$ molecule on average, the calculation predicts that BILP-10 would adsorb 216 mg of CO$_2$ (i.e. 21.6 wt%). Interestingly, at 273 K and 1.0 bar, BILP-10 shows an experimental uptake of 177 mg g$^{-1}$ which indicates that ~82% of the available nitrogen centers are associated with CO$_2$. The remaining vacant nitrogen sites (18%) may not be accessible under the current experimental settings (1.0 bar/273 K) due to the amorphous nature of BILP-10 and its small pores (PSD = 7.6 Å). In addition, the adsorbed CO$_2$ molecules in narrow pore channels may impede the diffusion of additional CO$_2$ towards the remaining available nitrogen sites. In order to understand the nature of the adsorbate/adsorbent and adsorbate/adsorbate interactions at different temperatures, the CO$_2$ isotherms collected at 273 and 298 K were analyzed by virial type equation (I). The less negative value of the first virial coefficient ($A_0$) at 273 K (-15.31 mol g$^{-1}$ Pa$^{-1}$) compared to that of 298 K (-16.59 mol g$^{-1}$ Pa$^{-1}$) suggests a stronger CO$_2$-surface interactions at 273 K. In contrast, the more negative value of the second virial parameter ($A_1$) at 273 K (-439.54 g mol$^{-1}$) compared to that of 298 K (-373.52 g mol$^{-1}$) indicates stronger CO$_2$-CO$_2$ interactions inside the pores of the polymer.$^{73a}$

Similarly, we recorded CH$_4$ uptakes at 273 and 298 K up to 1 bar in order to evaluate the potential use of BILP-10 in CO$_2$/CH$_4$ separation. Both isotherms are completely reversible and exhibit adsorption maxima of 16.7 and 11.1 mg g$^{-1}$ at 273 and 298 K, respectively. The $Q_{st}$ for CH$_4$ was calculated by using adsorption data collected at 273 and 298 K using the virial method. At zero coverage, the $Q_{st}$ is 17.5 kJ mol$^{-1}$ (Figure 2.18). The $Q_{st}$ was also calculated using the Clausius-Clapeyron equation by fitting the data collected at 273, 288 and 298 K to Tóth model and the result was compared to that obtained by the virial method.
It was noticeable that the Tóth model gave a slightly higher initial $Q_{st}$ value (20.0 kJ mol$^{-1}$), however both trends become very similar as the methane loading increases with pressure.

**Figure 2.18:** Virial analysis of CH$_4$ adsorption data (A) (circles: 273 K, squares: 298 K) and isosteric heats of adsorption ($Q_{st}$) (B) for BILP-10. $a_0 = -2097.0147$, $a_1 = -663.62494$, $a_2 = 2330.59193$, $a_3 = -1300.4415$, $b_0 = 14.40926906$, $b_1 = -1.535465808$. 

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The gas storage capacity of BILP-10 was also examined for hydrogen which is a very promising candidate for use in automotive applications due to its abundance and clean aspect. The hydrogen uptake for BILP-10 (1.6 wt%) at 77 K and 1 bar is among the highest values reported for microporous organic polymers. The isotherms are fully reversible and exhibit relatively steep initial uptakes at low pressure, which indicate strong affinity for H₂ gas. The \( Q_{st} \) for H₂ was calculated from adsorption data collected at 77 and 87 K (Figure 2.19). At zero-coverage, the \( Q_{st} \) value for BILP-10 is 9.3 kJ mol\(^{-1}\) which is higher than all values reported recently for BILPs (7.8-8.3 kJ mol\(^{-1}\)) and other organic polymers such as polyimide networks (5.3-7.0 kJ mol\(^{-1}\)), COFs (3.9-7.0 kJ mol\(^{-1}\)), porous aromatic frameworks (PAF-1, 4.6 kJ mol\(^{-1}\)), porous polymer networks (PPNs, 5.5-7.6 kJ mol\(^{-1}\)), –OH functionalized POFs (8.3 kJ mol\(^{-1}\)) and tetrazine-based organic frameworks (TzFs, 7.8-8.2 kJ mol\(^{-1}\)).
Figure 2.19: Virial analysis of H₂ adsorption data (A) (circles: 77 K, squares: 87 K) and isosteric heats of adsorption (\(Q_{st}\)) (B) for BILP-10. \(a_0 = -1119.5137, a_1 = 92.497322, a_2 = 13.2175119, a_3 = -3.4022173, a_4 = 0.20427007, b_0 = 15.64281359, b_1 = -1.114735826, b_2 = 0.058628009\).
2.3.4 High Pressure Gas Storage Studies of BILP-10

Hydrogen and Methane gases have been studied for practical use such as onboard storage in automotive applications, and these gases need to be stored under high pressure conditions in order to meet both volumetric and gravimetric targets. The U.S. Department of Energy (DOE) has set a target for onboard methane storage at 180 v/v at room temperature and 35 bar. While for hydrogen storage, the gravimetric/volumetric system targets for near-ambient temperature (-40 to 85 °C) and moderate pressure (less than 100 bar) are 5.5 wt% and 40 g L⁻¹, respectively, for 2017.⁴⁸ Additionally carbon dioxide is usually separated at ambient pressure and then sequestered at a much higher pressure. Given the low density of porous organic polymers, meeting volumetric constrains by organic polymers and other low density materials such as COFs and MOFs has been a considerable challenge especially for methane and hydrogen storage.⁷⁶ Accordingly, high pressure gas isotherms were collected to evaluate the performance of BILP-10 in gas storage under high pressure conditions and the data for gravimetric and volumetric uptakes is presented in Figure 2.20.

![Figure 2.20: High pressure gas uptake isotherms of BILP-10.](image-url)
High-pressure sorption isotherms were run using a VTI HPVA-100 volumetric analyzer. Ultrahigh purity helium (99.999\%) was used to calibrate the free volume in the sample cell before each measurement. The skeletal density ($d_{sk}$) of BILP-10 was found in the course of analysis for appropriate density correction factorization.\(^7\) High-pressure data was collected using ultrahigh purity H\(_2\) (99.999\%), CO\(_2\) (99.99\%) and CH\(_4\) (99.999\%) obtained from Airgas Inc. (Radnor, PA). Free space measurements were performed prior to data collection utilizing ultra-high purity helium to establish the appropriate cold zone compensation factors. Absolute gas uptakes were calculated according to literature methods using NIST Thermochemical Properties of Fluid Systems.\(^7\) Bulk phase gas densities up to 40 bar were fit using a sixth-order polynomial, then multiplied by the pore volume obtained from the Ar isotherm.

Although the surface excess adsorption and absolute adsorption are nearly identical under low pressure up to 1 bar, they are different under high-pressure conditions because the void space of the pores of adsorbent can hold significant amount of compressed gas under high pressure.

The absolute amount of adsorbed gas is then expressed as

$$N_{abs} = N_{exc} + d_{gas}V_p$$

Where $N_{abs}$ is the absolute adsorption in mg g\(^{-1}\); $N_{exc}$ is the excess adsorption which is experimentally measured; $d_{gas}$ is the density of the compressed gas at a given temperature and pressure in cm\(^3\) g\(^{-1}\),\(^7\) and $V_p$ is the pore volume in cm\(^3\) g\(^{-1}\).

The $V_p$ can be calculated from $d_{sk}$ and $d_{bulk}$ using the following expression

$$V_p = \frac{d_{sk} - d_{bulk}}{d_{sk}d_{bulk}}$$

Where $d_{sk}$ is the skeletal density of the material obtained from He experiment and $d_{bulk}$ is the bulk density of the sample which is, typically, obtained from available crystallographic model.
Ideally, above calculated pore volume should be comparable to the pore volume obtained from low-pressure Ar or N₂ isotherms. However, they deviate each other in many cases even for crystalline materials due to the partial decomposition of crystals or the presence of any other impurities. Consequently, it is more relevant to recalculate the $d_{\text{bulk}}$, particularly for noncrystalline amorphous materials, using the experimental obtained $V_p$ and $d_{sk}$.

The volumetric density of adsorbed gas inside the sample can be obtained simply by multiplying the adsorbed quantity with the bulk density of the sample.

$$N_v = N_g \times d_{\text{bulk}}$$

Where $N_v$ is the volumetric uptake in g L$^{-1}$, and $N_g$ is the gravimetric uptake in mg g$^{-1}$, and $d_{\text{bulk}}$ is the bulk density of the sample in g cm$^{-3}$.

Figure 2.21: H$_2$ isotherms for BILP-10 measured at 77 (black) and 87 K (red). Circles and squares represent surface excess ($N_{\text{Exc}}$) and absolute adsorbed ($N_{\text{Abs}}$) amounts, respectively.
**Figure 2.22:** H₂ isotherms for BILP-10 measured at 77 (black) and 87 K (red). Circles and squares represent surface excess (N_{Exc}) and absolute adsorbed (N_{Abs}) amounts, respectively.

**Figure 2.23:** CO₂ isotherms for BILP-10 measured at 275 (black) and 298 K (red). Circles and squares represent surface excess (N_{Exc}) and absolute adsorbed (N_{Abs}) amounts, respectively.
Figure 2.24: CH₄ isotherms for BILP-10 measured at 275 (black) and 298 K (red). Circles and squares represent surface excess (N_{exc}) and absolute adsorbed (N_{abs}) amounts, respectively.

The gravimetric excess uptake for hydrogen was found to be 3.4 wt% (17.3 mmol g⁻¹) at 77 K/40 bar which is higher than most of organic polymers of similar surface area but less than those of high surface area 3D COFs (~7.0 wt%), PAFs (4.2-7.0 wt%), and PPN-4 (8.34 wt%) collected at a higher pressure (up to 60 bar). The CO₂ uptake was significant at 298 K/40 bar (12.4 mmol g⁻¹) and in the range of reported uptakes for HCPs (10.6-13.3) but falls short of high surface area COFs, PPNs, and PAFs that can reach ~39 mmol g⁻¹ at 298 K/55 bar. Similarly, the excess methane uptake at 298 K/40 bar was 4.1 mmol g⁻¹ which compares well with values reported for porous organic materials of similar surface areas. However the storage capacity for methane remains below those of high surface area networks mentioned above. The volumetric storage capacity which determines how densely the gas molecules are stored within the materials is also relevant to express the efficiency of adsorbents. The absolute volumetric (v:v) uptakes for hydrogen is (303 L L⁻¹) which is comparable to many of the MOFs.
adsorbed amounts for CH\textsubscript{4} in volumetric units were also estimated to be 72 L L\textsuperscript{-1} which is slightly lower than COF-102 (136 L L\textsuperscript{-1}).\textsuperscript{52b} The volumetric hydrogen and methane uptakes are still short of targets set by the US DOE. The volumetric CO\textsubscript{2} adsorption capacity at 298 K and 35 bar is 175 L L\textsuperscript{-1} which is lower than that of the best performing MOF-177 (320 v/v at 35 bar) but approximately 5 times higher than the quantity stored at this pressure in an empty container.\textsuperscript{81}

**2.3.5 Gas Selectivity Studies for BILP-10**

The gas selectivity of porous materials consisting of pore sizes within the kinetic diameters of small gas molecules solely depends on the difference in affinity of gas components to be adsorbed on the surface of porous architectures. Selective adsorption and separation of small gas molecules such as CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} has received considerable attention because CO\textsubscript{2} is a major contaminant of natural gas and its release to the atmosphere by anthropogenic activity is a major concern. Given the similar kinetic diameter of these gases, it has been very difficult to develop effective materials for small gas separation that possess the needed physicochemical stability under practical conditions. In order to investigate the potential use of BILP-10 in gas separation applications, isotherms for CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} were collected at 273 and 298 K up to 1.0 bar (Figure 2.25).

The initial steep rise in CO\textsubscript{2} compared to N\textsubscript{2} and CH\textsubscript{4} can be attributed to the more favourable interactions between CO\textsubscript{2} and the accessible nitrogen sites of imidazole moieties.\textsuperscript{73b} Preferential and higher affinity of CO\textsubscript{2} compared to N\textsubscript{2} and CH\textsubscript{4} would be very instrumental in CO\textsubscript{2} capture and separation processes.
The CO₂/N₂ and CO₂/CH₄ selectivities were calculated from single-component adsorption isotherms using the Henry Law constants. These constants can be calculated from the initial slopes of the isotherms in the linear low pressure range (P < 0.1 bar).

Figure 2.25: Gas uptake isotherms of BILP-10 for CO₂ over CH₄ and N₂ at 273 K and at 298 K.
The selectivities for CO\textsubscript{2}/N\textsubscript{2} were found to be 107 (273 K) and 59 (298 K) (Figure 2.26). The selectivity value 107 at 273 K is among the highest for reported organic or inorganic-hybrid porous materials that employed the same method for selectivity calculations; for examples, BILPs (59-113), PECONF-2 (109), BPL carbon (17.8) and ZIFs (17-50), Bio-MOF-11 (81) and noncovalent porous materials (NPMs) (74).\textsuperscript{21b, 25} In addition to this method, recent reports have reported selectivity studies using below:

\[ S = \frac{q_1}{q_2} \left( \frac{p_1}{p_2} \right) \]

where \( S \) is the selectivity factor, \( q_i \) represents the quantity adsorbed of component \( i \), and \( p_i \) represents the partial pressure of component \( i \).\textsuperscript{81}

\textbf{Figure 2.26:} Adsorption selectivity of BILP-10 for CO\textsubscript{2} over CH\textsubscript{4} and N\textsubscript{2} at 273 K from low-pressure data.
Figure 2.27: Adsorption selectivity of BILP-10 for CO$_2$ over CH$_4$ and N$_2$ at 298 K from low-pressure data.

For post-combustion CO$_2$ capture, the partial pressure of CO$_2$ and N$_2$ are 0.15 bar and 0.75 bar, respectively. According to gas uptakes at these partial pressures, the calculated CO$_2$/N$_2$ selectivity values (S) for BILP-10 were found to be 128 (273 K) and 107 (298 K). Interestingly, the latter selectivity is one of the highest by purely organic materials.$^{82}$ Although the use of single-component gas isotherms to investigate selectivity has been well documented in recent literature, it should be noted that this approach may not reflect the actual selectivity of the material because this method does not take into consideration the competition between adsorbate molecules for pore binding sites.
Nevertheless, this simple method is a convenient, rapid and useful tool to compare the performance of different porous materials in selective adsorption studies.

Following the same procedures described above, we have also studied CO$_2$/CH$_4$ selectivity for BILP-10 by collecting isotherms at 273 and 298 K and by subjecting the data to initial slope calculations (Figure 2.27). While the CO$_2$ isotherms exhibit steep uptakes at low pressure, the CH$_4$ isotherms lead to much lower uptakes (Figure 2.25). The CO$_2$/CH$_4$ selectivities of BILP-10 were found to be 14 (273 K) and 7 (298 K). These values are similar to those of diimide-based organic polymers, and exceeds reported values for BPL carbon,$^{52b}$ ZIFs,$^{83}$ and most MOFs.$^{84}$ This selective nature of BILP-10 makes it promising candidate for use in CO$_2$ removal from methane-rich gases (natural gas and landfill gas) where CO$_2$ has to be removed to avoid pipeline corrosion, enhance storage efficiency and increase the heat value. In a typical natural gas purification process, the mole fractions of CO$_2$ and CH$_4$ are 0.05 and 0.95, respectively, and the total pressure is maintained at 2 bar, resulting in CO$_2$ having a partial pressure of only 0.1 bar.$^{85}$ The CO$_2$/CH$_4$ selectivity was then calculated according to Eq. 1 by using the CO$_2$ and CH$_4$ uptakes at 0.1 bar and 1.9 bar, respectively. These calculations resulted in relatively high selectivity levels; $S = 18$ (273 K) and 10 (298 K) that are in good agreement with those obtained from initial slope calculations. Because gas storage and selective uptake can vary at high pressure, we evaluated the performance of BILP-10 in high pressure gas storage and used the resulting isotherms to investigate selectivities of CO$_2$ over CH$_4$ and N$_2$ by the ideal adsorbed solution theory as described below.
2.3.6 High Pressure Gas Selectivity Studies

We applied the ideal adsorbed solution theory (IAST)\textsuperscript{86} to estimate the selectivity of CO\textsubscript{2} over CH\textsubscript{4} and N\textsubscript{2} as a function of pressure (up to 40 bar) by using the sorption data collected from high pressure gas sorption measurements. The IAST method predicts the adsorption selectivity for gas mixtures based on pure component gas isotherms and has been used to investigate adsorbents such as MOFs, zeolites and organic polymers.\textsuperscript{23, 79a}

According to Myers and Prausnitz,\textsuperscript{86} the ideal adsorbed solution theory can be reduced to the mathematical integration:

\[
\int_{t=0}^{x_1} F_1(t) \, d \ln t = \int_{t=0}^{x_2} F_2(t) \, d \ln t
\]

In this equation, \( P \) is the total pressure, \( y_i \) is the bulk phase molar ratio of gas \( i \), \( x_i \) is the adsorbed phase molar ratio of gas \( i \), and the function, \( F_i (t) \), is a fitting function for the pure component \( i \) based on the Langmuir-Freundlich model:

\[
n = \frac{a \cdot b \cdot p^{1/c}}{1 + b \cdot p^{1/c}} + \frac{d \cdot e \cdot p^{1/f}}{1 + d \cdot p^{1/f}}
\]

In this equation, \( n \) is the gas uptake in mmol/g, \( p \) is the pressure in bar, and \( a, b, c, d, e, \) and \( f \) are the fitting parameters. Since \( x_1 = 1 - x_2 \) and \( y_1 = 1 - y_2 \), the integrated equation nets only three unknowns. Therefore, by specifying one value and varying a second, the third value can be calculated. Selectivity can then be calculated as:

\[
S_{1,2} = \frac{x_1/y_1}{x_2/y_2}
\]
Figure 2.28: Pure component isotherms for CO$_2$ (black circle), CH$_4$ (red square) and N$_2$ (blue diamond) at 298 K. The solid lines are the dual-site Langmuir-Freundlich fits for CO$_2$ (black), CH$_4$ (red) and N$_2$ (blue).

The predicted CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity for binary gas mixtures of various molar composition as a function of pressure are shown in Figure 2.28. At the very low-pressure region, the CO$_2$/CH$_4$ selectivity starts to drop rapidly until the pressure reaches ~2 bar and then the selectivity increases steadily. For instance, the selectivity for a gas mixture of CO$_2$ and CH$_4$ with a mole fraction ratio of 0.5:0.5 (typical feed composition of landfill gas) at 298 K and 0.1 bar is 10.0 that drops to 8.5 at 0.5 bar, then increases to reach 13.7 at 40 bar. The latter value is consistent with that calculated by the initial slope calculation method described above. Most likely at low pressure the nitrogen functional sites of the polymer have much higher binding affinity for CO$_2$ because of its large quadrupolar moment and with increasing pressure (0 to 2 bar) these sites get saturated and become less available for CO$_2$ molecules. However, as the pressure increases beyond 2 bar, the selectivity increases due to the higher adsorption potential
of CO$_2$. The observed initial drop in selectivity at low pressures is consistent with the reported trends for diimide-based polymers in the pressure range of 0.1 to 5 bar,\textsuperscript{85} while the steady increase of CO$_2$/CH$_4$ selectivity upon pressure increase has been reported for PPNs.\textsuperscript{79a} Notably, the selectivity by BILP-10 at high pressure is more than double those of PPNs. In a similar fashion, we investigated the selectivity of CO$_2$ over N$_2$ (Figure 2.29). The overall trend indicates that selectivity increases with pressure and the highest levels were observed for gas mixtures that have high CO$_2$ compositions. The selectivity approaches 120 and 71 for gas mixtures of (0.5:0.5) and (0.15:0.85; typical composition for flue gas from power plants) molar ratios, respectively, at 298 K and 40 bar. At low pressure, IAST predicts the selectivity to be \( \sim 57 \) which agrees very well with that obtained from initial slope calculations (59). Again, the higher selectivity is observed at high-pressure region for gas mixtures that contain higher CO$_2$ mole fractions due to the higher adsorption potential of CO$_2$. The overall results are consistent with the fact that CO$_2$ is the most strongly adsorbed molecule due to its large quadrupolar moment while methane is more strongly adsorbed than N$_2$ because of the higher polarizability of CH$_4$ (\( 26 \times 10^{-25} \text{ cm}^3 \)) vs. N$_2$ (\( 17.6 \times 10^{-25} \text{ cm}^3 \)).\textsuperscript{49}
Figure 2.29: IAST selectivities of CO$_2$ over CH$_4$ at 298 K, the low pressure region is expanded in the bottom figure.
Figure 2.30: IAST selectivities of CO₂ over N₂ at 298 K, low pressure region is expanded in the bottom figure.
4. Conclusions

We have successfully developed a simple synthetic route to incorporate pyrene into the backbone of benzimidazole-linked polymers. The impact of this electron-rich building unit on the solid-state packing of the polymer leads to the formation of a unique nanofiber morphology prompted by the ability of the pyrene units to interact through strong π-π stacking interactions. The formation of such morphology and the predominant microporous mature lead to high CO$_2$ (18 wt%, 273 K/1.0 bar) and H$_2$ (1.6 wt% at 77 K/1.0 bar) uptakes. However, BILP-10 stores moderate absolute volumetric amounts of H$_2$ (27.3 g L$^{-1}$) and methane (72 L L$^{-1}$) under high pressure conditions which can limit its use in onboard gas storage applications. While the low pressure gas storage capacities have been exceeded by other recently reported BILPs; IAST studies indicate that at high pressure, BILP-10 exhibits high selectivity of CO$_2$ over CH$_4$ and N$_2$ which makes BILP-10 a promising material for use in gas separation processes. Additionally, the high isosteric heats of adsorption for H$_2$ (9.3 kJ mol$^{-1}$) and CO$_2$ (38.2 kJ mol$^{-1}$) was observed are among the highest values reported to date for unmodified porous organic polymers or discrete molecules.
Chapter 3

Application of Pyrene-Derived Benzimidazole-Linked Polymers to CO₂ Separation under Pressure and Vacuum Swing Adsorption Settings

3.1 Introduction

Porous adsorbents are promising candidates for CO₂ capture because of their high porosity, tunable pore metrics, and high CO₂ uptake properties. ⁷²b Tailoring the chemical and physical properties of porous adsorbents to make them suitable for CO₂ capture from flue gas has been proven essential as these physicochemical properties are central to effective CO₂ capture and separation processes. ²⁹, ⁸⁷ Recently, Wilmer et al. ²⁴ have studied over 130,000 structures of metal-organic frameworks (MOFs) and investigated the chemical and structural properties of MOFs that are relevant to CO₂ capture from flue gas and methane-rich gases (i.e. natural gas and landfill gas). The study offered set of criteria relating structural features of adsorbents to separation processes; vacuum and pressure swing methods. Five evaluation criteria (Table 3.1) were taken from the chemical engineering field to study the capability of porous adsorbents: CO₂ uptake, working capacity for CO₂, adsorbent regenerability, selectivity under adsorption conditions, and sorbent selection parameter. These criteria, although not perfect, provide a more comprehensive approach for assessing the suitability of porous adsorbents in CCS processes. ⁵⁷c

In this chapter, we extend the synthesis of porous pyrene-derived BILPs and use the five criteria discussed above to demonstrate the remarkable performance of BILPs in CO₂ capture and separation from N₂ and CH₄ under pressure swing adsorption (PSA) and vacuum
swing adsorption (VSA) conditions. The study shows that the performance of the reported BILPs in CO$_2$/N$_2$ and CO$_2$/CH$_4$ separations is among the best in the field of porous organic and inorganic-organic hybrid materials, which make BILPs very attractive candidates for CO$_2$ capture and separation applications.

<table>
<thead>
<tr>
<th>CO$_2$ uptake under adsorption conditions (mol kg$^{-1}$)</th>
<th>$N_{1}^{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working CO$<em>2$ capacity (mol kg$^{-1}$), $N</em>{1}^{ads} - N_{1}^{des}$</td>
<td>$\Delta N_{1}$</td>
</tr>
<tr>
<td>Regenerability (%), $(\Delta N_{1}/N_{1}^{ads}) \times 100$</td>
<td>R</td>
</tr>
<tr>
<td>Selectivity under adsorption conditions, $(N_{1}^{ads}/N_{2}^{ads}) \times (y_{2}/y_{1})$</td>
<td>$\alpha_{12}^{ads}$</td>
</tr>
<tr>
<td>Sorbent selection parameter, $(\alpha_{12}^{ads})^{2}/(\alpha_{21}^{des}) \times (\Delta N_{1}/\Delta N_{2})$</td>
<td>S</td>
</tr>
</tbody>
</table>

**Table 3.1.** Adsorbent evaluation criteria suggested by Bae and Snurr.$^{5/c}$

$N$: adsorbed amount, $y$: molar fraction in the bulk phase. Subscripts 1 and 2 correspond to the strongly adsorbed component (CO$_2$) and the weakly adsorbed component (CH$_4$ or N$_2$), respectively. $\alpha_{12}$: Selectivity of gas component 1 over 2. ads and des correspond to adsorption and desorption conditions, respectively.
3.2 Experimental Section

3.2.1. Materials, and Methods. All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Acros Organics and Frontier Scientific) and used without further purification, unless otherwise noted. 3,3’diaminobenzidine was purchased from Acros Organics. 2,3,6,7,10,11-hexaaminotriphenylene (HATP),\textsuperscript{21a} and 2,3,6,7,14,15-hexaaminotriptycene (HATT),\textsuperscript{21c} were synthesized using reported procedure. Air-sensitive samples and reactions were handled under an inert atmosphere of nitrogen using either glovebox or Schlenk line techniques. Chromatographic separations were performed using standard flash column chromatography methods using silica gel (60 Å, 35-70 µm). Elemental microanalyses were performed at the Midwest Microlab, LLC. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were obtained on a Varian Mercury-300 MHz NMR spectrometer. \textsuperscript{13}C cross-polarization magic angle spinning (CPMAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Thermogravimetric analysis (TGA) were carried out using a TA Instruments Q-5000IR series thermal gravimetric analyser with samples held in 50 µL platinum pans under atmosphere of air (heating rate 5 °C/min). For Scanning Electron Microscopy Imaging (SEM), sample was prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminium sample holder. The sample was then coated with platinum at 7x10\textsuperscript{-5} bar of pressure in a nitrogen atmosphere for 50 seconds before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope. Powder X-ray diffraction data were collected on a Panalytical X’pert pro multipurpose diffractometer (MPD). Samples were mounted on a sample holder and measured using Cu Kα radiation with a 2\(\theta\) range of 1.5-35. FT-IR spectra were obtained as KBr pellets using Nicolet-Nexus 670 spectrometer. Sorption experiments were run using a Quantachrome Autosorb 1-C analyser. High pressure gas sorption
measurements were performed by using VTI-HPVA-100 volumetric analyser. High pressure total gas uptakes were calculated by reported literature methods and NIST Thermochemical Properties of Fluid Systems were applied to the calculations.  

3.2.2 Synthesis of Polymers

*Synthesis of BILP-11*

A 250 mL Schlenk flask was charged with 3,6,7,10,11-hexaaminotriphenylene hexahydrochloride salt (58 mg, 0.11 mmol), 70 mL of anhydrous DMF, and a stir-bar. The resultant homogeneous solution was cooled to -30 °C and treated with TFPPy (50 mg, 0.08 mmol) dropwise dissolved in anhydrous DMF (115 mL). The temperature was maintained around -30 °C for 6 hours during which a brown solid formed then the resultant slurry solution was allowed to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 20 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 °C (0.5 °C/min) and kept for 3 days to afford a fluffy yellow powder. The solid was isolated by filtration over a medium glass frit and washed with acetone, CHCl₃, water, 2 M HCl, 2 M NaOH, water, and acetone. The product was then immersed in acetone/CHCl₃ (1:1 v/v) for 18 hours, during which the activation solvent was decanted and refreshed twice. After filtration, the product was dried at 120 °C under vacuum (150 mTorr) to give BILP-11 as a brown powder (70 mg, 81%). Anal. Calcd. (%) for C₁₀₂H₆₃N₁₂H₂O: C, 73.23; H, 5.24; N, 10.05. Found: C, 75.55; H, 4.37; N, 11.00.
Synthesis of BILP-12

BILP-12 was synthesized following the procedure described above for BILP-11 from 2,3,6,7,14,15 hexaaminotriptycene hexahydrochloride salt (65 mg, 0.12 mmol) and TFPPy (50 mg, 0.08 mmol). After drying, the final product BILP-12 was obtained as a yellowish brown fluffy solid (73 mg, 79% yield). Anal. Calcd (%) for C_{106}H_{67}N_{12}12H_2O: C, 74.25; H, 5.31; N, 9.80. Found: C, 77.57; H, 4.32; N, 10.35.

Synthesis of BILP-13

BILP-13 was synthesized following the methods mentioned above for BILP-11 and BILP-12 using 3,3’ Diaminobenzidine tetrahydrochloride salt (58 mg, 0.16 mmol) and TFPPy (50 mg, 0.08 mmol). After drying, the final product BILP-13 was obtained as a brown fluffy solid (67 mg, 75% yield). Anal. Calcd. (%) for C_{68}H_{46}N_{8}8H_2O: C, 72.97; H, 5.58; N,10.01. Found: C, 73.51; H, 4.86; N, 10.09.
Figure. 3.1 Synthesis of BILPs, (i) DMF, -30 °C, 3 hr, (ii) DMF, RT, 6 hr under N₂, (iii) DMF, 130 °C, 72 hr under O₂.
3. 3 Results and Discussion

3.3.1 Synthesis and Characterisation of BILPs

The synthesis of BILPs reported in this study was performed according to the method we reported recently, which is based on acid-catalysed condensation reactions between aryl-\(o\)-amine and aryl-aldehyde building blocks as depicted in the Figure 3.1. Briefly, a solution of TFPPy in DMF was added dropwise to solutions of the corresponding aryl-\(o\)-diamine building unit dissolved in DMF and stirred for 4 hours at -30 °C. The resulting mixture was stirred under nitrogen at room temperature to afford an orange suspension, presumably, imine-linked oligomers.\(^{22}\) Finally, the reaction mixture were gradually heated up to 130 °C in the presence of oxygen and kept for 3 days to afford the corresponding BILP as a yellowish brown suspension. Purification steps involved washing the polymers with 2M aqueous solutions of HCl and NaOH as well as a combination of water, acetone, and chloroform. All polymers are insoluble in common organic solvents such as tetrahydrofuran, DMF, dichloromethane, methanol, and acetone consistent with their expected hypercrosslinked networks. Chemical compositions were confirmed by micro-elemental analysis while thermogravimetric analysis (TGA) of as-prepared BILPs showed initial weight loss of adsorbed water (up to 100 °C) followed by frameworks decomposition at about 400 °C (Figure 3.2).
Figure 3.2: TGA traces of BILP-11, BILP-12, BILP-13.
The formation of the imidazole ring was verified by FT-IR studies (Figure 3.3 and 3.4), which revealed new characteristic stretching bands at 1625 (C=N) 1482 and 1433 cm\(^{-1}\) in addition to bands at 3410 and 3180 cm\(^{-1}\) for free N-H and hydrogen-bonded N-H, respectively.\(^{21a, 88}\) The consummation of the aldehyde functionality is evidenced by a significant decrease in the intensity of the aldehyde band at 1700 cm\(^{-1}\) (C=O).

**Figure 3.3:** FT-IR spectra of BILP-11, BILP-12, BILP-13 and their starting building units. Lower panel is an expanded region from 400 to 2000 cm\(^{-1}\).
**Figure 3.4**: FT-IR spectra (400-4000 cm$^{-1}$) of starting materials and polymers.
Figure 3.5. FT-IR Spectra of TFPPy and BILPs.
Furthermore, the $^{13}$C CP-MAS NMR spectra of BILP-11, BILP-12 and BILP-13 showed NC(Ph)N characteristic peaks in the range of 152-153 ppm in line with reported shifts for benzimidazole units in other BILPs. The remaining signals in $^{13}$C CP-MAS NMR spectra are assigned to other carbons of the building units (Table 3.3).

Table 3.2 Assignments of the $^{13}$C CP-MAS NMR peaks for BILPs.

<table>
<thead>
<tr>
<th>Peaks (ppm)</th>
<th>Peaks (ppm)</th>
<th>Peaks (ppm)</th>
<th>Assignments/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-11</td>
<td>BILP-12</td>
<td>BILP-13</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td></td>
<td></td>
<td>Triptycene aliphatic CH.</td>
</tr>
<tr>
<td>104</td>
<td></td>
<td></td>
<td>Triphenylene aromatic CH(1) which is observed at 107 ppm in HATP,$^{21b}$ (d$_6$-DMSO)</td>
</tr>
<tr>
<td>107</td>
<td></td>
<td></td>
<td>Triptycene aromatic CH(2). The peak is observed at 111 ppm in HATT,$^{21c}$ (d$_6$-DMSO)</td>
</tr>
<tr>
<td>111</td>
<td></td>
<td></td>
<td>Triphenylene aromatic C(2). The peak is observed at 121 ppm in HATT,$^{21c}$ (d$_6$-DMSO)</td>
</tr>
<tr>
<td>113</td>
<td></td>
<td></td>
<td>Triptycene aromatic C(3). The peak is observed at 131 ppm in HATT,$^{21c}$ (d$_6$-DMSO)</td>
</tr>
<tr>
<td>153</td>
<td>152</td>
<td>152</td>
<td>Benzimidazole ring C in C=N. There is no peak was observed at around 160 for imine C=N showing formation of benzimidazole ring.$^{21a}$</td>
</tr>
</tbody>
</table>
Figure 3.6: Solid-state $^{13}$C CP-MAS NMR spectra of BILP-11, BILP-12 and BILP-13.
The rapid and irreversible imidazole ring formation leads to amorphous polymers according to powder X-ray diffraction (PXRD) studies (Figure 3.7). Interestingly, based on SEM images (Figure 3.8) of all three networks form nanofiber morphologies similar to the pyrene-derived BILP-10. This unique formation of nanofibers is presumably driven by the strong π-π stacking interactions between the pyrene cores, which can assist in solid-state packing of highly porous 2D covalent organic frameworks and thereby enhance gas uptake properties.\textsuperscript{21d, 90}

\textbf{Figure 3.7:} Powder XRD patterns for BILP-11, BILP-12, BILP-13, indicating the amorphous characteristics of the polymers.
Figure 3.8: SEM images of BILP-11, BILP-12, BILP-13.
3.3.2 Low-Pressure (0 – 1.0 bar) Gas Adsorption Measurements.

A sample was loaded into a 9 mm large bulb cell (from Quantachrome) of known weight and then hooked up to MasterPrep. The sample was degassed at 120 °C for 12 hours. The degassed sample was weighed precisely and then transferred back to the analyzer. The temperature for adsorption measurements was controlled by using refrigerated bath of liquid nitrogen (77 K) or liquid argon (87 K), and the temperature controlled water bath (273 K and 298 K). Adsorption measurements were performed on an Autosorb-1 C (Quantachrome) volumetric analyzer using adsorbates of UHP grade. The porosity of BILPs was investigated by argon sorption/desorption measurements at 87 K on activated samples (Figure 3.9). The fully reversible argon isotherms show rapid argon uptake at low relative pressures ($P/P_0 < 0.1$ bar), which is indicative of their microporous nature. The isotherms for BILP-12 and BILP-13 show gradual increase in the Ar uptake after $P/P_0 = 0.90$ bar due to argon condensation in interparticle voids.
Figure 3.9 Argon uptake isotherms at 87 K (A) and pore size distribution from NLDFT (B). Adsorption (filled) and desorption (empty).
Figure 3.10: Experimental Ar adsorption isotherms for, BILP-11 (orange circles), BILP-12 (blue circles) and BILP-13 (red circles) measured at 87 K. The calculated NLDFT isotherm is overlaid as open circle.
Figure 3.11: Pore size distribution of BILP-11, BILP-12, and BILP-13.
The specific BET surface areas were calculated from the argon sorption branch in the range of $P/P_0 = 0.05-0.10$ bar and found to be 658 m$^2$ g$^{-1}$ (BILP-11), 1497 m$^2$ g$^{-1}$ (BILP-12), 677 m$^2$ g$^{-1}$ (BILP-13). The high surface area of BILP-12 can be attributed to the unique structural features of the triptycene building unit which has high internal molecular free volume (IMFV).\textsuperscript{21c} It is worth noting that the surface area and pore width values of BILPs are within the desirable range predicted by Wilmer \textit{et. al.} for efficient CO$_2$ capture and separation processes.\textsuperscript{91}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_12.png}
\caption{Plot of the term $V(1-P/P_0)$ vs. $P/P_0$ for BILP-11. Only the range below $P/P_0 = 0.10$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.}
\end{figure}
Figure 3.13: Plot of the term $V(1 - P/P_0)$ vs. $P/P_0$ for BILP-12. Only the range below $P/P_0 = 0.09$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.
Figure 3.14: Plot of the term $V(1 - P/P_0)$ vs. $P/P_0$ for BILP-13. Only the range below $P/P_0 = 0.11$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

BILP-13, Ar at 87 K
$S_{BET} = 677 \text{ m}^2\text{g}^{-1}$
Motivated by these observations, we set out to measure the CO$_2$ uptake and its selective capture over N$_2$ and CH$_4$; the major gaseous components in flue gas and methane-rich gases (natural gas and landfill gas), respectively. We collected low-pressure sorption isotherms for CO$_2$, CH$_4$, and N$_2$ at 273 K and 298 K to investigate the capture capacity and enthalpies of adsorption ($Q_{st}$) for CO$_2$ and CH$_4$. Both parameters have been identified as key factors in CO$_2$ separation applications.$^{12, 29}$ Both parameters have been identified as key factors in CO$_2$ separation applications.$^{12, 29}$ The CO$_2$ uptake was significant for BILP-12 (223 mg g$^{-1}$; 5.06 mmol g$^{-1}$) at 273 K and 1 bar, competing with the best performing porous organic polymers such as BILP-4 (5.34 mmol g$^{-1}$),$^{21b}$ Azo-Linked Polymers (ALPs, 3.52 - 5.37 mmol g$^{-1}$),$^{92}$ hyper-crosslinked polymers HCPs (3.01-3.92 mmol g$^{-1}$),$^{79b}$ functionalized conjugated microporous polymers CMPs (1.6–1.8 mmol g$^{-1}$),$^{25}$ porous aromatic frameworks PAFs (3.01-3.92 mmol g$^{-1}$).$^{56}$ On the other hand, BILP-11 and BILP-13 adsorb moderate amounts of CO$_2$ (136 and 113 mg g$^{-1}$), respectively.
Figure 3.15: Gas uptake isotherms for BILP-11 (orange circles), BILP-12 (blue pentagons) and BILP-13 (red triangle) at 273 and 298 K.
Figure 3.16: Gas uptake isotherms for BILP-11 (orange circles), BILP-12 (blue pentagons) and BILP-13 (red triangle) at 273 and 298 K.
3.3.3 Calculation of Isosteric Heats of Adsorption for BILPs

As stated above, approaching the desirable range for CO$_2$ binding affinities would be advantageous for selective CO$_2$ capture and thus, we calculated the $Q_{st}$ for CO$_2$ from data collected at 273 K and 298 K by the virial method and the Clausius-Clapeyron equation as summarized in Table 3.4 and illustrated in Figure 3.23. The calculated values indicate that at low coverage, BILPs have strong interaction with CO$_2$ leading to $Q_{st}$ values in the range of 31.2 to 35.8 kJ mol$^{-1}$. Such high values were observed because of the narrow pores of BILPs coupled with their N-functionalized pore walls.$^{73b}$ The $Q_{st}$ drops initially with increased loading and highlights the significance of the CO$_2$ preferred binding sites, which become less accessible as CO$_2$ loading increases with pressure increase.$^{44}$ BILP-12 has a uniform $Q_{st}$ values over CO$_2$ loading of 20 to 160 mg g$^{-1}$. Although the binding affinities are high, all BILPs are easily regenerated by CO$_2$ desorption through pressure drop as clearly seen from the fully reversible nature of all isotherms at 273 K and 298 K (Figure 3.23). The CH$_4$ uptakes at 273 K and 298 K and for BILPs revealed a linear correlation with surface area and $Q_{st}$ values (Figure 3.24).$^{21b}$ Methane uptakes at 1.0 bar were in the range of 0.78 to 1.47 mmol g$^{-1}$ and as expected, drop to 0.59-0.91 mmol g$^{-1}$ at 298 K. The binding affinities for CH$_4$ fall in the range of 13.7 to 18.7 kJ mol$^{-1}$. In contrast to CO$_2$ and CH$_4$, the N$_2$ uptake at 273 K was very low for all polymers (2.17 to 4.00 cc g$^{-1}$). For all BILPs, CO$_2$ is the most strongly adsorbed gas when compared to CH$_4$ and N$_2$. This is expected as CO$_2$ has high quadruple moment and polarizability and as hence, it interacts more favourably with polar functionalities present in the pores of BILPs.$^{28,63,65,93}$
We have fitted the pure gas isotherms collected at 237 and 298 K with both viral-type and Langmuir-Freundlich equation. In both cases, Clausius-Clapeyron equation was employed in order to calculate isosteric heat of adsorptions of BILPs.

\[
Q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_n
\]

where \( T \) is the temperature, \( R \) is the universal gas constant and \( p \) is the pressure for given quantity of gas adsorbed (\( n \)). Pressure for a given \( n \) calculated from fitted isotherms.

The virial equation can be written in the form of

\[
\ln p = \ln n + \frac{1}{T} \sum_{i=0}^{M} a_i n^i + \sum_{i=0}^{N} b_i n^i
\]

where \( n \) is the amount adsorbed in mmol g\(^{-1}\), \( p \) is the pressure in Torr, \( T \) is the temperature, \( a_i \) and \( b_i \) are temperature independent empirical parameters, and \( M \) and \( N \) determine the number of terms required to adequately describe the isotherm. By applying Clausius-Clapeyron equation to virial equation, \( Q_{st} \) can be calculated according to following equation as a function of loading:

\[
Q_{st} = -R \sum_{i=0}^{M} a_i n^i
\]

where \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)).

Zero-coverage (loading independent) isosteric heats of adsorption is given by

\[
Q_{st} = -Ra_0
\]

Langmuir-Freundlich isotherm model was also used to describe single component gas uptakes measured at 273 and 298 K. Fitting parameters obtained were then used to calculate the pressures required for the same loadings (\( n \)) at 273 and 298 K, then Clausius-Clapeyron equation were applied in order to calculate isosteric heats of adsorption.\(^{94}\)
Figure 3.17: Experimental data (symbol) and corresponding fittings (solid line) of CO$_2$ adsorption isotherms in BILP-11 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.

Figure 3.18: Experimental data (symbol) and corresponding fittings (solid line) of CO$_2$ adsorption isotherms in BILP-12 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.
Figure 3.19: Experimental data (symbol) and corresponding fittings (solid line) of CO$_2$ adsorption isotherms in BILP-13 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.

Figure 3.20: Experimental data (symbol) and corresponding fittings (solid line) of CH$_4$ adsorption isotherms in BILP-11 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.
Figure 3.21: Experimental data (symbol) and corresponding fittings (solid line) of CH\textsubscript{4} adsorption isotherms in BILP-12 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.

Figure 3.22: Experimental data (symbol) and corresponding fittings (solid line) of CH\textsubscript{4} adsorption isotherms in BILP-13 at 273 and 298 K. Fitted curves are obtained by the virial-type expansion.
Figure 3.23: Isosteric heats of adsorption of CO$_2$ in BILP-11, BILP-12, and BILP-13 calculated using viral-type isotherm and Langmuir-Freundlich isotherm fitting.
Figure 3.24: Isosteric heats of adsorption of methane in BILP-11, BILP-12, and BILP-13 calculated using virial-type isotherm (A) and Langmuir-Freundlich isotherm (B) fitting.

3.3.4 CO₂/N₂ and CO₂/CH₄ Selectivity Studies

Once the uptake and binding affinity for CO₂ and CH₄ were established, we investigated the potential use of BILPs in CO₂/N₂ and CO₂/CH₄ separation. The CO₂/N₂ and CO₂/CH₄ selectivity of BILPs were studied by using single-component gas adsorption experiments collected under equilibrium settings. The selectivity of CO₂ over CH₄ and N₂ were calculated
by using Henry’s Law which can estimate the initial slope ratios of single-component gas adsorption isotherms at 273 K and 298 K (Figure 3.26).\textsuperscript{95}

Initial slope calculations revealed that both BILP-11 and BILP-13 exhibited high selectivity (103) for CO\textsubscript{2} over N\textsubscript{2} at 273 K. As expected, BILP-12 showed a lower selectivity (56 at 273 K) confirming the findings of several studies that indicated a trade off between porosity and selectivity levels.\textsuperscript{26} In addition to CO\textsubscript{2}, high surface area materials with large pores can also accommodate other gas molecules accompanying CO\textsubscript{2} (i.e. N\textsubscript{2} and CH\textsubscript{4}), which make the material less effective in gas separation processes.\textsuperscript{20, 91, 93} Besides initial slope calculations, we evaluated the gas mixture adsorption behaviour of BILPs by applying the Ideal Adsorbed Solutions Theory (IAST) wherein selectivity of binary gas mixtures can be predicted by single component adsorption isotherms as a function of pressure.\textsuperscript{86}

Although the validity of IAST calculations is dependent on the ideality of the polymer,\textsuperscript{96} this method has been widely used to investigate amorphous organic polymers such as BILPs,\textsuperscript{21b} MOPs,\textsuperscript{97} POPs,\textsuperscript{85} COPs,\textsuperscript{98} APOPs,\textsuperscript{99} NPOFs,\textsuperscript{59} BLP-10(Cl)\textsuperscript{100} and azo-COPs\textsuperscript{101}. Three main industrial CO\textsubscript{2} capture separation processes; post-combustion flue gas, natural gas and landfill gas were examined to predict the selectivity of CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4}, for gas compositions of 10/90 and 50/50, respectively. Single component adsorption isotherms at 298 K were fitted by either dual-site Langmuir Freundlich (DSLF) or single-site Langmuir Freundlich (SSLF) model. The IAST selectivity levels are in good agreement with data obtained from initial slope studies (Table 3.4). In particular, BILP-11 exhibits high CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivity of 56 and 7.6 at 298 K, respectively. On the other hand, BILP-12 and BILP-13 show lower CO\textsubscript{2}/N\textsubscript{2} (31-32) and CO\textsubscript{2}/CH\textsubscript{4} (6.6-7.2) selectivity.
Figure 3.25: CO$_2$, CH$_4$ and N$_2$ uptakes of BILP-11, BILP-12 and BILP-13 at 273 K and 298 K.
Figure 3.26: Gas uptake selectivity studies for BILP-11, BILP-12 and BILP-13 at 273 and 298 K (CO$_2$ over CH$_4$ and N$_2$).
Table 3.3 Porosity properties of pyrene-based BILPs calculated from argon adsorption isotherms measured at 87 K.

<table>
<thead>
<tr>
<th>Network</th>
<th>$S_{BET}$ (m² g⁻¹)</th>
<th>$S_{Langmuir}$ (m² g⁻¹)</th>
<th>$V_{total}$ (cm³ g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-10</td>
<td>787</td>
<td>1039</td>
<td>0.40</td>
<td>0.76</td>
</tr>
<tr>
<td>BILP-11</td>
<td>658</td>
<td>813</td>
<td>0.32</td>
<td>0.72</td>
</tr>
<tr>
<td>BILP-12</td>
<td>1497</td>
<td>1825</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>BILP-13</td>
<td>677</td>
<td>862</td>
<td>0.42</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Table 3.4 CO$_2$ and CH$_4$ uptakes, isosteric heats of adsorption and selectivity (CO$_2$/N$_2$ and CO$_2$/CH$_4$) for BILPs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$^a$CO$_2$ at 1 bar</th>
<th></th>
<th>$^b$CH$_4$ at 1 bar</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>273K</td>
<td>298K</td>
<td>$Q_{st1}$</td>
<td>$Q_{st2}$</td>
</tr>
<tr>
<td>BILP-10</td>
<td>177</td>
<td>111</td>
<td>38.2</td>
<td>38.0</td>
</tr>
<tr>
<td>BILP-11</td>
<td>136</td>
<td>88</td>
<td>32.0</td>
<td>35.8</td>
</tr>
<tr>
<td>BILP-12</td>
<td>223</td>
<td>140</td>
<td>27.6</td>
<td>31.2</td>
</tr>
<tr>
<td>BILP-13</td>
<td>113</td>
<td>79</td>
<td>26.7</td>
<td>32.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$^c$Selectivity at 273 K</th>
<th>$^c$Selectivity at 298 K</th>
<th>$^d$IAST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO$_2$/N$_2$</td>
<td>CO$_2$/CH$_4$</td>
<td>CO$_2$/N$_2$</td>
</tr>
<tr>
<td>BILP-10</td>
<td>111</td>
<td>14</td>
<td>59</td>
</tr>
<tr>
<td>BILP-11</td>
<td>103</td>
<td>11</td>
<td>55</td>
</tr>
<tr>
<td>BILP-12</td>
<td>56</td>
<td>8</td>
<td>31</td>
</tr>
<tr>
<td>BILP-13</td>
<td>103</td>
<td>9</td>
<td>38</td>
</tr>
</tbody>
</table>

$^a$ Gas uptake in mg g$^{-1}$ and the isosteric enthalpies of adsorption ($Q_{st}$) in kJ mol$^{-1}$ calculated by virial model ($Q_{st1}$) reported at zero coverage and DSLF model ($Q_{st2}$) reported at 0.05 mmol/g loading for CH$_4$ and 0.04 mmol/g loading for CO$_2$. $^c$ Selectivity (mol mol$^{-1}$) was calculated initial slope method at 273 and 298 K. $^d$ Selectivity (mol mol$^{-1}$) was calculated from IAST method at 0.05 bar and 298 K.
The pure component isotherms of CO\textsubscript{2} measured at 273 and 298 K were fitted with the dual-site Langmuir-Freundlich (DSLF) model

\[ q = q_A + q_B = q_{sat,A} \frac{b_A p^\alpha_A}{1 + b_A p^\alpha_A} + q_{sat,B} \frac{b_B p^\alpha_B}{1 + b_B p^\alpha_B} \]

where, \( q \) is molar loading of adsorbate (mmol g\textsuperscript{-1}), \( q_{sat} \) is saturation capacity (mmol g\textsuperscript{-1}) , \( b \) is Langmuir-Freundlich parameter (bar\textsuperscript{α}), \( p \) is bulk gas phase pressure (bar), \( \alpha \) is the Langmuir–Freundlich exponent (dimensionless) subscripts \( A \) and \( B \) refers to site \( A \) and site \( B \), respectively. Since the pure component isotherms of CH\textsubscript{4} and N\textsubscript{2} do not show any inflection characteristic they were fitted with the single-site Langmuir-Freundlich (SSLF) model.

\[ q = q_{sat,A} \frac{b_A p^\alpha_A}{1 + b_A p^\alpha_A} \]

Pure-component isotherm fitting parameters were then used for calculating Ideal Adsorbed Solution Theory (IAST) binary-gas adsorption selectivities, \( S_{ads} \), defined as

\[ S_{ads} = \frac{x_1/x_2}{p_1/p_2} \]

where \( x_i \) is the mole fraction of component \( i \) in the adsorbed phase and \( p \) is the mole fraction of component \( i \) in the bulk. \textsuperscript{86}

\( x_i \) values were then used for calculating total amount adsorbed under mixture conditions according to following equation.
\[ \frac{1}{n_t} = \sum_{i=1}^{N} \left[ \frac{x_i}{n_i^0} \right] \]

where \( n_t \) is the total number of adsorbed moles of gas per unit mass of adsorbent and \( n_i^0 \) is the number of moles of component \( i \) in the adsorbed phase per unit mass of adsorbent at temperature \( T \) in the absence of competing component. \(^{86}\)

The adsorption amount for the component \( i \) (\( n_i^{ads} \)) in the binary mixture adsorption is calculated by employing the following equation:

\[ n_i^{ads} = n_t x_i \]

Using the sorbent evaluation criteria one can easily evaluate the material for possible pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) applications. Recent cases that have been used in literature\(^{24, 57c}\) are listed below:

1. Natural gas purification using PSA (\( \text{CO}_2/\text{CH}_4 : 10/90, p^{ads} = 5 \text{ bar}, p^{des} = 1 \text{ bar} \))

2. Landfill gas separation using PSA (\( \text{CO}_2/\text{CH}_4 : 50/50, p^{ads} = 5 \text{ bar}, p^{des} = 1 \text{ bar} \))

3. Landfill gas separation using VSA (\( \text{CO}_2/\text{CH}_4 : 50/50, p^{ads} = 1 \text{ bar}, p^{des} = 0.1 \text{ bar} \))

4. Flue gas separation using VSA (\( \text{CO}_2/N_2 : 10/90, p^{ads} = 1 \text{ bar}, p^{des} = 0.1 \text{ bar} \))
Table 3.5: Langmuir-Freundlich fitting parameters of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} adsorption isotherms in BILP-11 at 298 K and low pressures (0-1 bar).

<table>
<thead>
<tr>
<th></th>
<th>$q_{\text{sat},A}$ (mmol/g)</th>
<th>$b_A$ (bar$^\alpha$)</th>
<th>$\alpha_A$ dimensionless</th>
<th>$q_{\text{sat},B}$ (mmol/g)</th>
<th>$b_B$ (bar$^\alpha$)</th>
<th>$\alpha_B$ dimensionless</th>
<th>Reduced $\chi^2$</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>4.63186</td>
<td>0.38932</td>
<td>0.99595</td>
<td>0.86275</td>
<td>4.58749</td>
<td>0.98666</td>
<td>1.86E-06</td>
<td>1</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>2.39111</td>
<td>0.36226</td>
<td>1.03824</td>
<td>2.14E-06</td>
<td>0.99995</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>7.00487</td>
<td>0.01702</td>
<td>1.04926</td>
<td>1.67E-07</td>
<td>0.9999</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.27: Experimental data and corresponding fittings of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} adsorption isotherms in BILP-11 at 298 K and low pressures (0-1 bar).
Table 3.6: Langmuir-Freundlich fitting parameters of CO₂, CH₄, and N₂ adsorption isotherms in BILP-12 at 298 K low pressures (0-1 bar).

<table>
<thead>
<tr>
<th></th>
<th>q_sat_A (mmol/g)</th>
<th>b_A (bar⁻¹)</th>
<th>α_A dimensionless</th>
<th>q_sat_B (mmol/g)</th>
<th>b_B (bar⁻¹)</th>
<th>α_B dimensionless</th>
<th>Reduced χ²</th>
<th>Adj. R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>11.53246</td>
<td>0.24064</td>
<td>1.03760</td>
<td>1.22272</td>
<td>3.59695</td>
<td>1.01274</td>
<td>1.86E-06</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.84089</td>
<td>0.30965</td>
<td>1.06675</td>
<td></td>
<td></td>
<td></td>
<td>2.14E-06</td>
<td>0.9995</td>
</tr>
<tr>
<td>N₂</td>
<td>12.48505</td>
<td>0.01789</td>
<td>1.03264</td>
<td></td>
<td></td>
<td></td>
<td>1.67E-07</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

Figure 3.28: Experimental data and corresponding fittings of CO₂, CH₄, and N₂ adsorption...
Table 3.7: Langmuir-Freundlich fitting parameters of CO$_2$, CH$_4$, and N$_2$ adsorption isotherms in BILP-13 at 298 K low pressures (0-1 bar).

<table>
<thead>
<tr>
<th></th>
<th>$q_{sat,A}$ (mmol/g)</th>
<th>$b_A$ (bar$^a$)</th>
<th>$\alpha_A$ dimensionless</th>
<th>$q_{sat,B}$ (mmol/g)</th>
<th>$b_B$ (bar$^a$)</th>
<th>$\alpha_B$ dimensionless</th>
<th>Reduced $\chi^2$</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>4.31374</td>
<td>0.41225</td>
<td>1.05511</td>
<td>0.62258</td>
<td>6.56056</td>
<td>1.09024</td>
<td>3.22E-06</td>
<td>0.99999</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.73943</td>
<td>0.50917</td>
<td>1.17534</td>
<td></td>
<td></td>
<td></td>
<td>1.29E-05</td>
<td>0.99966</td>
</tr>
<tr>
<td>N$_2$</td>
<td>15.47574</td>
<td>0.00859</td>
<td>1.06806</td>
<td></td>
<td></td>
<td></td>
<td>3.55E-07</td>
<td>0.99984</td>
</tr>
</tbody>
</table>

Figure 3.29: Experimental data and corresponding fittings of CO$_2$, CH$_4$, and N$_2$ adsorption isotherms in BILP-13 at 298 K and low pressures (0-1 bar).
**Table 3.8:** Langmuir-Freundlich fitting parameters of CO$_2$ adsorption isotherms in BILP-11, BILP-12 and BILP-13 at 273 K and low pressures (0-1 bar).

<table>
<thead>
<tr>
<th></th>
<th>$q_{sat,A}$</th>
<th>$b_A$</th>
<th>$\alpha_A$</th>
<th>$q_{sat,B}$</th>
<th>$b_B$</th>
<th>$\alpha_B$</th>
<th>Reduced $\chi^2$</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-11</td>
<td>2.55473</td>
<td>3.92609</td>
<td>0.87342</td>
<td>2.55473</td>
<td>0.71021</td>
<td>1.31074</td>
<td>9.58E-06</td>
<td>0.99999</td>
</tr>
<tr>
<td>BILP-12</td>
<td>11.71108</td>
<td>0.47642</td>
<td>0.93745</td>
<td>1.52437</td>
<td>5.59862</td>
<td>0.94541</td>
<td>7.01E-06</td>
<td>1</td>
</tr>
<tr>
<td>BILP-13</td>
<td>2.15718</td>
<td>3.79148</td>
<td>0.91630</td>
<td>2.15718</td>
<td>0.65884</td>
<td>1.40823</td>
<td>8.59E-06</td>
<td>0.99999</td>
</tr>
</tbody>
</table>

**Figure 3.30.** Experimental data and corresponding fittings of CO$_2$ adsorption isotherms in BILP-11, BILP-12 and BILP-13 at 273 K and low pressures (0-1 bar).
Table 3.9. Langmuir-Freundlich fitting parameters of CH₄ adsorption isotherms in BILP-11, BILP-12 and BILP-13 at 273 K and low pressures (0-1 bar).

<table>
<thead>
<tr>
<th></th>
<th>( q_{sat,A} ) (mmol/g)</th>
<th>( b_A ) (bar(^a))</th>
<th>( \alpha_A ) dimensionless</th>
<th>Reduced ( \chi^2 )</th>
<th>Adj. ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-11</td>
<td>2.53960</td>
<td>0.61492</td>
<td>0.98134</td>
<td>5.01E-06</td>
<td>0.99995</td>
</tr>
<tr>
<td>BILP-12</td>
<td>4.87729</td>
<td>0.43123</td>
<td>0.99132</td>
<td>1.67E-05</td>
<td>0.99993</td>
</tr>
<tr>
<td>BILP-13</td>
<td>1.81128</td>
<td>0.73637</td>
<td>1.07923</td>
<td>2.21E-05</td>
<td>0.99967</td>
</tr>
</tbody>
</table>

Figure 3.31: Experimental data and corresponding fittings of CH₄ adsorption isotherms in BILP-11, BILP-12 and BILP-13 at 273 K and low pressures (0-1 bar).
Table 3.10. Langmuir-Freundlich fitting parameters of CO$_2$ and CH$_4$ total adsorption isotherms in BILP-11 at 298 K and high pressures (1-10 bar).

<table>
<thead>
<tr>
<th></th>
<th>$q_{sat,A}$ (mmol/g)</th>
<th>$b_A$ (bar$^{-\alpha}$)</th>
<th>$\alpha_A$ dimensionless</th>
<th>$q_{sat,B}$ (mmol/g)</th>
<th>$b_B$ (bar$^{-\alpha}$)</th>
<th>$\alpha_B$ dimensionless</th>
<th>Reduced $\chi^2$</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>8.78923</td>
<td>0.23720</td>
<td>0.58989</td>
<td>1.13471</td>
<td>0.00027</td>
<td>3.48432</td>
<td>1.02E-04</td>
<td>0.99985</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>82.17967</td>
<td>0.00611</td>
<td>0.63652</td>
<td></td>
<td></td>
<td></td>
<td>9.22E-05</td>
<td>0.99955</td>
</tr>
</tbody>
</table>

Figure 3.32. Experimental data and corresponding fittings of CO$_2$ and CH$_4$ total adsorption isotherms in BILP-11 at 298 K and high pressures (1-10 bar).
Table 3.11. Langmuir-Freundlich fitting parameters of CO₂ and CH₄ total adsorption isotherms in BILP-12 at 298 K and high pressures (1-10 bar).

<table>
<thead>
<tr>
<th></th>
<th>q_{sat,A} (mmol/g)</th>
<th>b_A (bar^{α_A})</th>
<th>α_A dimensionless</th>
<th>q_{sat,B} (mmol/g)</th>
<th>b_B (bar^{α_B})</th>
<th>α_B dimensionless</th>
<th>Reduced χ²</th>
<th>Adj. R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.11207</td>
<td>0.10000</td>
<td>25.96054</td>
<td>21.42649</td>
<td>0.16300</td>
<td>0.68351</td>
<td>5.84E-04</td>
<td>0.99982</td>
</tr>
<tr>
<td>CH₄</td>
<td>12.02378</td>
<td>0.08736</td>
<td>0.80664</td>
<td></td>
<td></td>
<td></td>
<td>6.83E-05</td>
<td>0.99993</td>
</tr>
</tbody>
</table>

Figure 3.33. Experimental data and corresponding fittings of CO₂ and CH₄ total adsorption isotherms in BILP-12 at 298 K and high pressures (1-10 bar).
Table 3.12. Langmuir-Freundlich fitting parameters of CO\textsubscript{2} and CH\textsubscript{4} total adsorption isotherms in BILP-13 at 298 K and high pressures (1-10 bar).

<table>
<thead>
<tr>
<th></th>
<th>(q_{\text{sat,A}}) (mmol/g)</th>
<th>(b_A) (bar\textsuperscript{\alpha})</th>
<th>(\alpha_A) dimensionless</th>
<th>(q_{\text{sat,B}}) (mmol/g)</th>
<th>(b_B) (bar\textsuperscript{\alpha})</th>
<th>(\alpha_B) dimensionless</th>
<th>Reduced (\chi^2)</th>
<th>Adj. (R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>4.93109</td>
<td>0.00418</td>
<td>1.87579</td>
<td>4.93109</td>
<td>0.50425</td>
<td>0.80475</td>
<td>9.13E-05</td>
<td>0.99988</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>16.90487</td>
<td>0.03233</td>
<td>0.68995</td>
<td></td>
<td></td>
<td></td>
<td>3.13E-05</td>
<td>0.99987</td>
</tr>
</tbody>
</table>

Figure 3.34: Experimental data and corresponding fittings of CO\textsubscript{2} and CH\textsubscript{4} total adsorption isotherms in BILP-13 at 298 K and high pressures (1-10 bar).
3.3.5 CO₂ Separation from flue gas using VSA

We assessed the potential of all pyrene-based BILPs in CO₂ capture from flue gas (CO₂/N₂: 10/90) using VSA at 298 K and compared their performance with commercially available activated carbon and zeolites as well as the best performing porous materials in the field as listed in Tables below. The working capacities (ΔN₁) were determined by calculating the CO₂ adsorption difference between 1.0 and 0.1 bar. BILPs showed high working capacities comparable to those of the top performing adsorbents (Table 3.13). BILP-12 exhibits the highest ΔN₁ (0.49 mol kg⁻¹) followed by BILP-10 (0.41 mol kg⁻¹), BILP-11 (0.38 mol kg⁻¹), and BILP-13 (0.30 mol kg⁻¹). In the case of flue gas separation under VSA, the level of CO₂ uptake at 0.1 bar, which is influenced by isosteric heat of adsorption of CO₂ can significantly alter the working capacity of adsorbents. For example, BILP-12 has ~90% more specific surface area than BILP-10; however the working capacity of BILP-12 is only ~20% higher than that of BILP-10 due to higher CO₂ binding affinity of latter. For this reason, MOFs that possess open metal cites (i.e. Ni-MOF-74) outperform POPs especially at lower CO₂ concentrations.

In addition to high working capacities, all BILPs showed excellent regenerability (R) levels (87.2 to 91) similar to those of ZIF-78 (96.3), ZIF-82 (92.5) and SNU-Cl-va (87.3). Regenerabilities of BILPs surpassed porous Zeolite-13X and Ni-MOF-74, which show higher N_ads values than BILPs. However, this trend is associated with much lower regenerability levels (54.2-73.7). Although BILPs have favourable binding sites for CO₂ (imidazole N-sites), their regeneration processes are more favourable than MOFs that have strong interactions between CO₂ and open-metal sites. Another important criterion is the sorbent selection parameter (S), which varies from one BILP to another (72.6 to 157.3). The highest
sorbent selection parameter was recorded for BILP-11 (157.3), which can be attributed to its high selectivity factor ($\alpha_{\text{ads}}^{12} = 42.9$).

Table 3.13: Adsorbents for VSA in flue gas (CO$_2$/N$_2$ : 10/90) separation at 298K, $P_{\text{ads}} = 1$ bar and $P_{\text{des}} = 0.1$ bar.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$N_1^{\text{ads}}$</th>
<th>$\Delta N_1$</th>
<th>$R$</th>
<th>$\alpha_{\text{ads}}^{12}$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-10 $^{21d}$</td>
<td>0.45</td>
<td>0.41</td>
<td>90.8</td>
<td>35.5</td>
<td>109.0</td>
</tr>
<tr>
<td>BILP-11</td>
<td>0.44</td>
<td>0.38</td>
<td>87.2</td>
<td>42.9</td>
<td>157.3</td>
</tr>
<tr>
<td>BILP-12</td>
<td>0.55</td>
<td>0.49</td>
<td>88.7</td>
<td>27.1</td>
<td>72.6</td>
</tr>
<tr>
<td>BILP-13</td>
<td>0.34</td>
<td>0.30</td>
<td>89.2</td>
<td>28.6</td>
<td>79.0</td>
</tr>
<tr>
<td>Zeolite-13X $^{57c}$</td>
<td>2.49</td>
<td>1.35</td>
<td>54.2</td>
<td>86.2</td>
<td>128</td>
</tr>
<tr>
<td>SNU-Cl-v$a^{66}$</td>
<td>0.47</td>
<td>0.41</td>
<td>87.3</td>
<td>38.0</td>
<td>262</td>
</tr>
<tr>
<td>ZIF-78 $^{57c}$</td>
<td>0.6</td>
<td>0.58</td>
<td>96.3</td>
<td>34.5</td>
<td>396</td>
</tr>
<tr>
<td>ZIF-82 $^{57c}$</td>
<td>0.41</td>
<td>0.38</td>
<td>92.5</td>
<td>22.7</td>
<td>101</td>
</tr>
<tr>
<td>HKUST-1 $^{57c}$</td>
<td>0.62</td>
<td>0.55</td>
<td>89.0</td>
<td>20.4</td>
<td>46.2</td>
</tr>
<tr>
<td>Ni-MOF-74 $^{57c}$</td>
<td>4.34</td>
<td>3.2</td>
<td>73.7</td>
<td>41.1</td>
<td>83.5</td>
</tr>
<tr>
<td>NoritR1 extra $^{57c}$</td>
<td>0.38</td>
<td>0.28</td>
<td>73.7</td>
<td>10.7</td>
<td>5.09</td>
</tr>
</tbody>
</table>
3.3.6 CO\textsubscript{2} Separation from landfill gas using VSA

Landfill gas is an important source of methane gas, however, it usually contains significant levels of CO\textsubscript{2} (CO\textsubscript{2}/CH\textsubscript{4}: 50/50) and thus requires processing before transport or use because of the acidic nature of CO\textsubscript{2}. Because landfill gas has much higher CO\textsubscript{2} concentration than flue gas or natural gas, the use of the same CO\textsubscript{2} adsorbents may not be always effective in all cases.\textsuperscript{24} Therefore, we assessed BILPs performance in landfill gas purification from CO\textsubscript{2} under VSA conditions at 298 K. All polymers showed good working capacity values of 1.44 (BILP-10), 1.11 (BILP-11), 1.71 (BILP-12), and 1.01 (BILP-13) mol kg\textsuperscript{-1}. It is worth noting that the effect of having high surface area becomes more significant as partial pressure of CO\textsubscript{2} increases in gas mixtures. For example, BILP-12 exhibited ~54\% enhancement in working capacity compared to BILP-11, whereas this difference is only ~29\% for flue gas case. The working capacities of BILP-10 and BILP-12 exceed those of SNU-Cl-va and ZIF-82 listed in the Table 3.13. These values indicate that BILPs compete with top adsorbent candidates in the field for CO\textsubscript{2} removal form landfill gas by VSA. The regenerability and selectivity factor trends for all BILPs are somewhat similar (81.6–85.3) and (6.0–7.6), respectively, unlike the sorbent selection parameter (S) which varies from 31.8 (BILP-13) to 59.3 (BILP-10). The S value of the latter is very significant but lower than that of SNU-Cl-va (84) and much higher than the levels reported for Mg-MOF-74, ZIF-82, and zeolite-13X (19.1-23.5). Both Mg-MOF-74 and zeolite-13X have higher selectivity factors, however, their regenerability values fall much below those of BILPs.
Table 3.14 Adsorbents for VSA in landfill gas (CO$_2$/CH$_4$ : 50/50) separation at 298K, $P_{\text{ads}} = 1$ and $P_{\text{des}} = 0.1$ bars.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$N_{1}^{\text{ads}}$</th>
<th>$\Delta N_{1}$</th>
<th>R</th>
<th>$\alpha_{12}^{\text{ads}}$</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-10$^{21d}$</td>
<td>1.70</td>
<td>1.44</td>
<td>84.3</td>
<td>7.6</td>
<td>59.3</td>
</tr>
<tr>
<td>BILP-11</td>
<td>1.36</td>
<td>1.11</td>
<td>81.6</td>
<td>6.7</td>
<td>39.8</td>
</tr>
<tr>
<td>BILP-12</td>
<td>2.01</td>
<td>1.71</td>
<td>85.3</td>
<td>6.0</td>
<td>33.7</td>
</tr>
<tr>
<td>BILP-13</td>
<td>1.19</td>
<td>1.00</td>
<td>84.2</td>
<td>6.0</td>
<td>31.8</td>
</tr>
<tr>
<td>SNU-Cl-v$^{66}$</td>
<td>1.51</td>
<td>1.21</td>
<td>80.6</td>
<td>9.7</td>
<td>84.0</td>
</tr>
<tr>
<td>Mg-MOF-74$^{57c}$</td>
<td>7.23</td>
<td>2.32</td>
<td>32.1</td>
<td>12.5</td>
<td>23.5</td>
</tr>
<tr>
<td>ZIF-82$^{57c}$</td>
<td>1.42</td>
<td>1.2</td>
<td>84.9</td>
<td>5.6</td>
<td>20.5</td>
</tr>
<tr>
<td>Zeolite-13X$^{57c}$</td>
<td>3.97</td>
<td>1.97</td>
<td>49.6</td>
<td>13.2</td>
<td>19.1</td>
</tr>
<tr>
<td>UiO-66-AD6$^{102}$</td>
<td>1.59</td>
<td>1.41</td>
<td>88.5</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>NoritR1 extra$^{2,3c}$</td>
<td>1.4</td>
<td>1.17</td>
<td>83.6</td>
<td>2.19</td>
<td>4.5</td>
</tr>
</tbody>
</table>
3.3.7 CO₂ Separation from natural gas and landfill gas using PSA

Unlike VSA, PSA operates on pressure swing between \( P_{\text{ads}} = 5 \) bar and \( P_{\text{des}} = 1 \) bar, therefore, gas uptake measurements were collected in the pressure range of 1.0 to 5.0 bar (Figure 3.35). The PSA working capacities (\( \Delta N_1 \)) of BILPs were determined by CO₂ uptake difference between 5.0 and 1.0 bar. Because high surface area hypothetical MOFs were superior in PSA processes; we anticipated BILP-12 to be more applicable than the other BILPs in both flue gas and landfill gas PSA separation. \(^{24}\) PSA working capacities of BILP-10, -11, -12 and -13 were found to be 0.80, 0.53, 0.92 and 0.50 mol kg\(^{-1}\), respectively, when natural gas composition (CO₂/CH₄ : 10/90) was considered.

Table 3.15: Adsorbents for PSA in natural gas (CO₂/CH₄ : 10/90) separation at 298K, \( P_{\text{ad}} = 5 \) and \( P_{\text{des}} = 1 \) bars.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( N_1 \text{ads} )</th>
<th>( \Delta N_1 )</th>
<th>R</th>
<th>( \alpha_{12} \text{ads} )</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-10 (^{21d})</td>
<td>1.26</td>
<td>0.80</td>
<td>63.4</td>
<td>8.8</td>
<td>9.3</td>
</tr>
<tr>
<td>BILP-11</td>
<td>0.99</td>
<td>0.53</td>
<td>53.7</td>
<td>9.1</td>
<td>6.3</td>
</tr>
<tr>
<td>BILP-12</td>
<td>1.52</td>
<td>0.92</td>
<td>60.1</td>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td>BILP-13</td>
<td>0.76</td>
<td>0.50</td>
<td>65.5</td>
<td>5.8</td>
<td>4.2</td>
</tr>
<tr>
<td>55% Li red. diimide-POP (^{57c})</td>
<td>1.11</td>
<td>0.63</td>
<td>56.3</td>
<td>16.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Zeolite-13X (^{57c})</td>
<td>3.97</td>
<td>1.48</td>
<td>37.3</td>
<td>18.9</td>
<td>9.0</td>
</tr>
<tr>
<td>Diimide-POP (^{57c})</td>
<td>1.39</td>
<td>0.86</td>
<td>62.2</td>
<td>9.7</td>
<td>7.5</td>
</tr>
<tr>
<td>HKUST-1 (^{57c})</td>
<td>2.7</td>
<td>1.7</td>
<td>63.0</td>
<td>10.0</td>
<td>9.6</td>
</tr>
<tr>
<td>Norit R1 extra (^{57c})</td>
<td>1.40</td>
<td>1.02</td>
<td>72.9</td>
<td>4.75</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Landfill gas separation performances of BILPs were also evaluated between 1-5 bar and 298 K. The highest working capacity was observed for BILP-12 (3.02 mol kg\(^{-1}\)) for a gas composition of CO\(_2\)/CH\(_4\): 50/50. The other polymers exhibited lower working capacities: BILP-10 (2.18 mol kg\(^{-1}\)), BILP-11 (1.31 mol kg\(^{-1}\)), and BILP-13 (1.44 mol kg\(^{-1}\)). Remarkably, BILP-12 outperforms most adsorbents in terms of \(\Delta N_1\) listed in Table 7 and only exceeded by HKUST-1 (5.34 mol kg\(^{-1}\)) and MIL-101 (3.2 mol kg\(^{-1}\)). Notably, the working capacities of BILPs are higher for landfill gas separation than natural gas separation. This is reasonable because of the high CO\(_2\) content in landfill gas that can reach ~50%. These results suggested that, adsorbents with higher porosity rather than effective than their heat of adsorption property at higher CO\(_2\) partial pressures. High pressure CO\(_2\) sorption of BILPs under landfill gas composition showed relevant correlation between \(\Delta N_1\) of BILPs and surface area properties. In the case of flue gas, however, CO\(_2\) heats of adsorption and pore size of BILPs were found more related with the \(\Delta N_1\) values, most probably, due to low CO\(_2\) composition in the gas mixture (Figure 3.35). We also examined other CO\(_2\) capture evaluation criteria such as regenerability and sorbent selection parameters. BILPs exhibited high R values (Table 3.16). The regenerability of BILP-12 found to be higher than other BILPs. Another important observation is that the \(\alpha_{12}^{ads}\) and S parameters of all BILPs exceed those of MOFs and other adsorbents. BILPs resulted in very high S value (29.7-115.3). The remarkable S values of BILPs in general, and BILP-10 in particular, stem from the large difference between the working capacities of pure gas components; CO\(_2\) and CH\(_4\) in this case.\(^{57c}\)
Table 3.35: CO₂ working capacity under PSA conditions for natural gas (A) and landfill gas (B) at 298 K.
Table 3.16: Adsorbents for PSA in Landfill gas (CO₂/CH₄ : 50/50) separation at 298 K, P_{ads} = 5 bar and P_{des} = 1 bar.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>N₁^{ads}</th>
<th>ΔN₁</th>
<th>R</th>
<th>α₁₂^{ads}</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-10_{21d}</td>
<td>3.84</td>
<td>2.18</td>
<td>56.7</td>
<td>9.6</td>
<td>115.3</td>
</tr>
<tr>
<td>BILP-11</td>
<td>2.57</td>
<td>1.31</td>
<td>51.1</td>
<td>7.5</td>
<td>35.3</td>
</tr>
<tr>
<td>BILP-12</td>
<td>5.04</td>
<td>3.02</td>
<td>59.8</td>
<td>5.8</td>
<td>29.7</td>
</tr>
<tr>
<td>BILP-13</td>
<td>2.51</td>
<td>1.44</td>
<td>57.3</td>
<td>5.6</td>
<td>30.1</td>
</tr>
<tr>
<td>Zeolite-13 X^{57c}</td>
<td>5.37</td>
<td>1.4</td>
<td>26.1</td>
<td>4.2</td>
<td>2.0</td>
</tr>
<tr>
<td>HKUST-1^{57c}</td>
<td>8.01</td>
<td>5.34</td>
<td>66.7</td>
<td>4.9</td>
<td>21.0</td>
</tr>
<tr>
<td>MIL-101^{57c}</td>
<td>6.7</td>
<td>3.2</td>
<td>47.8</td>
<td>5</td>
<td>9.5</td>
</tr>
<tr>
<td>35% Li-reduced diimide-POP^{57c}</td>
<td>2.93</td>
<td>1.44</td>
<td>49.2</td>
<td>3.6</td>
<td>11.5</td>
</tr>
<tr>
<td>Zn-Atz^{103}</td>
<td>3.55</td>
<td>0.63</td>
<td>-</td>
<td>10.63</td>
<td>46.15</td>
</tr>
<tr>
<td>MOF-508b^{57c}</td>
<td>3.6</td>
<td>2.58</td>
<td>71.7</td>
<td>2.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Norit R1 extra^{57c}</td>
<td>3.53</td>
<td>2.13</td>
<td>60.3</td>
<td>2.02</td>
<td>3.58</td>
</tr>
</tbody>
</table>
3.4 Conclusions

We have extended our study on pyrene-derived BILPs by synthesising three new BILPs having enhanced textural properties. The most porous polymer, BILP-12, has pyrene and triptycene building units that lead to high surface area ($S_{BET} = 1497 \text{ m}^2 \text{ g}^{-1}$) and CO$_2$ uptake (5.06 mmol g$^{-1}$ at 273 K and 1 bar). The implication of different physical properties (pore size and surface area) on selective CO$_2$ uptake or separation from N$_2$ and CH$_4$ under PSA and VSA were investigated. The IAST data show that BILPs exhibit high CO$_2$/N$_2$ selectivity values (32-56 at 298 K). Furthermore, the optimal porosity and CO$_2$ enthalpy of adsorption render BILP-12 very efficient in landfill and natural gas separation by PSA. On the other hand, the moderate porosities and higher CO$_2$ binding affinities of BILP-11 and BILP-13 make them better fit for flue gas separation by VSA. Interestingly, the diverse physical properties of BILPs and their N-rich pores enable them to be among the top performing materials for landfill gas and flue gas separation by VSA and PSA. Tailoring such properties within one class of materials has been a challenge especially when chemical stability is not compromised. We are currently investigating the use of BILPs in binary gas mixtures separation under dynamic gas flow.
Chapter 4

Highly Selective CO₂ capture by Triazine-Based Benzimidazole-Linked Polymers

4.1 Introduction

Recently, triazine-functionalized POPs were synthesized by incorporating 1,3,5-triazine units into various polymer networks. In general, triazine-based POPs exhibit high thermal and chemical stability as well as permanent microporosity. Khun et al., reported covalent triazine-based framework (CTF) by trimerization of dicyanobenzene under ionothermal conditions. Subsequently, Cooper and his coworkers developed several triazine-based conjugated microporous polymers (TCMPs) by a palladium-catalysed Sonogashira-Hagihara cross coupling reaction. These studies demonstrated that the π-conjugated 1,3,5 triazine core acts as an electron donor enhancing the CO₂-polymer interaction.

With these considerations in mind, this chapter focuses on the synthesis of BILPs constructed from triazine-containing building units and assess their potential use in CO₂ capture from flue gas and methane-rich gases under vacuum swing adsorption (VSA) and pressure swing adsorption (PSA) conditions. The CO₂ uptake, selectivity, heat of adsorption and the CO₂ capture performance of TBILPs using a set of CO₂ sorbent evaluation criteria suggested by Bae and Snurr, were studied in this chapter.
4.2 Experimental Section

4.2.1 General techniques, Materials, and Methods

All chemicals were purchased from commercial suppliers (Sigma Aldrich, Acros Organics and Frontier Scientific) and used without further purification, unless otherwise noted. Air-sensitive samples and reactions were handled under an inert atmosphere of nitrogen using either glovebox or Schlenk line techniques. Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Acros Organics (60 Å, 35–70 µm). Elemental microanalyses were performed at the Midwest Microlab, LLC. 

H and 13C NMR spectra were obtained on a Varian Mercury-300 MHz NMR spectrometer. 

C cross-polarization magic angle spinning (CPMAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-5000IR series thermal gravimetric analyser with samples held in 50 µL platinum pans under nitrogen (heating rate 10 °C/min). For scanning electron microscopy imaging (SEM), samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminium sample holder. The sample was then coated with platinum at 6x10⁻⁵ mbar for 60 seconds before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope. Powder X-ray diffraction data were collected on a Panalytical X’pert pro multipurpose diffractometer (MPD). Samples were mounted on a sample holder and measured using Cu Kα radiation with a 2θ range of 1.5-35. FT-IR spectra were obtained as KBr pellets using Nicolet - Nexus 670 spectrometer. Sorption experiments were collected using a Quantachrome Autosorb IQ analyser. 2,4,6-tris(4-bromophenyl)-1,3,5-triazine and 2,3,6,7,14,15–hexaaminotriptycene hexahydrochloride were prepared according to literature procedures. High-pressure gas sorption measurements were performed by
using VTI-HPVA-100 volumetric analyser. High pressure total gas uptakes were calculated by reported literature methods and NIST Thermochemical Properties of Fluid Systems were applied to the calculations.\textsuperscript{76}
4.2.2 Synthesis of 2,4,6-Tris-(4-formylphenyl) 1,3,5 Triazine (TFPT)

2,4,6-Tris-(4-bromophenyl)-1,3,5-triazine (1.48 g, 2.71 mmol) was dissolved in dry THF (200 mL) under a N$_2$ atmosphere. To the stirred solution, n-BuLi was added dropwise (2.5 M in n-hexane, 11 mL, 27.5 mmol) at −78 °C. The temperature was allowed to rise to −60 °C and stirred for 3 h. The obtained green solution was treated with anhydrous N,N-dimethylformamide (DMF) (4.19 mL, 54.2 mmol) at −78 °C. The mixture was stirred overnight, while the temperature was allowed to rise to 25 °C. The milky opaque mixture was acidified with aqueous 3 M HCl (46 mL). The organic volatiles were partially removed by evaporation under reduced pressure and the product was extracted with CHCl$_3$. The organic phase was washed with water, dried over MgSO$_4$, and filtered. Volatiles were removed under reduced pressure, and the crude light yellow product was further purified by silica gel column using CH$_2$Cl$_2$ as eluent to afford colourless crystals (800 mg, 74% yield). $^1$H NMR (CDCl$_3$, 300 MHz) δ (ppm) 10.19 (s, 3H, CHO), 8.95 (d, J = 8.4 Hz, 6H, ArH), 8.11 (d, J = 8.1 Hz, 6H, ArH).

4.2.3 Synthesis of TBILP-1

A 250 mL Schlenk flask was charged with 1,2,4,5-benzenetetramine tetrahydrochloride (64 mg, 0.23 mmol), 65 mL of anhydrous DMF, and a stir-bar. The resultant homogeneous solution was cooled to −30 °C and treated dropwise with TFPT (60 mg, 0.152 mmol) dissolved in anhydrous DMF (50 mL). The temperature was maintained around −30 °C for 6 hours during which a yellowish brown solid is formed and the resultant slurry solution was left to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 10 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 °C (0.5 °C/min) and kept for 3 days to afford a fluffy yellow powder. The solid
was isolated by filtration over a medium glass frit and subsequently washed with DMF, acetone, water, 0.5 M HCl, 0.5 M NaOH, water, and acetone. The product was then immersed in acetone/chloroform (1:1 v/v) for one day, during which the activation solvent was decanted and freshly replenished twice. After filtration, the product was dried at 120 °C under vacuum (150 mTorr) to give TBILP-1 as a fluffy brown powder (50 mg, 81% yield). Anal. Calcd. (%) for C_{34}H_{17}N_{4}.4H_{2}O: C, 75.55; H, 4.37; N, 11.00; Found: C, 73.78; H, 4.52; N, 10.12.

### 2.2.4 Synthesis of TBILP-2

TBILP-2 was prepared according to the method described above for TBILP-1. 2,3,6,7,14,15-hexaaminotriptycene hexahydrochloride (58 mg, 0.10 mmol) in 90 mL anhydrous DMF and TFPT (40 mg, 0.10 mmol) in 45 mL anhydrous DMF were used. After drying, the final product TBILP-2 was obtained as a light brown fluffy solid (45 mg, 79% yield). Anal. Calcd. (%) for C_{68}H_{38}N_{8}.8H_{2}O: C, 74.47; H, 3.97; N,11.32. Found: C, 73.51; H, 4.86; N, 10.09.
4.3 Results and Discussion

In this study, TBILP-1 and TBILP-2 were synthesized by a template-free polycondensation reaction between 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TFPT) and 1,2,4,5-benzenetetraamine tetrahydrochloride (BTA) and 2,3,6,7,14,15-hexaaminotriptycene hexahydrochloride (HATT), respectively, in good yields (Figure 4.1). The chemical connectivity of the polymers was investigated by FT-IR and $^{13}$C CP-MAS NMR, while chemical composition was confirmed by microelemental analysis. The characteristic stretching bands from the imidazole ring were clearly visible in FT-IR spectra at 3415 cm$^{-1}$ due to free N-H and hydrogen-bonded N-H, respectively (Figure 4.2). The new bands located around 1625 (C=N), also confirm the formation of imidazole rings. A significant depletion in the intensity of the peak located at 1700 cm$^{-1}$, corresponds to the aldehyde carbonyl, suggests a complete conversion of aldehyde functional groups. The strong absorption band at 1515 cm$^{-1}$ supports the formation of the 1,3, 5 triazine unit. The $^{13}$C CP-MAS NMR spectra of TBILPs showed characteristic peaks assigned in Figure 4.4, representing NC(Ph)N in benzimidazole units. Thermogravimetric analysis (TGA) of as prepared TBILPs revealed high thermal stability without any decomposition up to 500 °C (Figure 4.5). The expected amorphous nature of the polymers was established by powder X-ray diffraction studies (Figure 4.6).
Figure 4.1: Structural representations of TFPT monomer and TBILPs.
Figure 4.2: FT-IR spectra of TBILPs and their corresponding building units.
Figure 4.3: $^1$H NMR spectrum of TFPT in DMSO.
Figure 4.4: Solid-state $^{13}$C CP-MAS NMR spectra of TBILPs.
Figure 4.5: TGA traces of TBILPs.
Figure 4.6: XRD-patterns for TBILPs.
Figure 4.7: Scanning electron microscopy (SEM) images of TBILP-1 (A) and TBILP-2 (B).
4.3.1 Porosity and Gas Adsorption Study

The porosity of the polymers was studied by Argon sorption-desorption isotherms collected at 87 K as shown in Figure 4.8. The Brunner-Emmett-Teller (BET) surface area calculation resulted in values of 330 m$^2$ g$^{-1}$ (TBILP-1) and 1080 m$^2$ g$^{-1}$ (TBILP-2). Argon isotherms were fitted by non-local density functional theory (NLDFT) model to calculate pore size distribution (PSD). The dominant PSDs of TBILP-1 and TBILP-2 were found to centre around 0.92 and 1.1 nm, respectively, (Figure 4.8). Pore volumes were calculated at $P/P_o = 0.90$ and resulted in 0.30 cc g$^{-1}$ (TBILP-1) and 0.60 cc g$^{-1}$ (TBILP-2). The higher surface area and pore volume of TBILP-2 are most likely attributed to the unique structural features of triptycene core, which has been reported to provide structures of high internal free volume and could probably disfavour the formation of interpenetrated networks.\(^{109}\)

Gas isotherms (N$_2$, CO$_2$, and CH$_4$) were collected at 273 K and 298 K to study the gas uptake capacity and selective nature of the polymers. The CO$_2$ uptake of TBILP-2 (5.19 mmol g$^{-1}$ at 273 K and 1 bar) is much higher than TBILP-1 (2.65 mmol g$^{-1}$) and competes with the best performing porous materials such as ALP-1 (5.37 mmol g$^{-1}$),\(^{92}\) BILP-4 (5.34 mmol g$^{-1}$),\(^{21b}\) HCPs (3.01-3.92 mmol g$^{-1}$),\(^{79b}\) functionalized CMPs (1.6-1.8 mmol g$^{-1}$),\(^{28}\) fluorinated FCTFs (4.67-5.53 mmol g$^{-1}$)\(^{110}\) and PAFs (3.01-3.92 mmol g$^{-1}$).\(^{111}\) The high CO$_2$ uptake of TBILPs can be attributed to the combined effects of the Lewis basic 1,3,5 triazine and imidazole-building units of the polymers. Consequently, TBILPs revealed improved CO$_2$ uptake compared to triazine-free BILP analogues. For instance, TBILP-2 (3.32 mmol g$^{-1}$) showed around 20% more CO$_2$ uptake than BILP-7 (2.77 mmol g$^{-1}$) at 298 K. Meanwhile, the CO$_2$ uptake of TBILP-1 (1.77 mmol g$^{-1}$) was comparable with BILP-5 (1.98 mmol g$^{-1}$) at 298 K and 1 bar, despite the much higher surface area of the latter (Table 4.1). The CO$_2$ uptake of TBILP-1 (2.65 mmol g$^{-1}$) also
competes with triazine-based POPs such as, CTFs (0.94-4.17 mmol g⁻¹),⁶²a TCMPs (1.22-2.62 mmol g⁻¹),¹⁰⁵ triazine-based polyimide (TPIs) (0.68-2.45 mmol g⁻¹),¹¹² porous covalent triazine frameworks (PCTFs) (1.88-3.31 mmol g⁻¹),¹¹³ nanoporous organic polymer (NOP-6) (2.51 mmol g⁻¹),¹¹⁴ and fluorine-based covalent triazine frameworks (fl-CTFs) (1.27-4.28 mmol g⁻¹).¹¹⁰
Figure 4.8 (A) Argon uptake isotherms at 87 K and (B) Pore size distribution by using NLDFT method. Adsorption (filled) and desorption (empty).
Figure 4.9: BET plot for TBILPs calculated from the Ar adsorption isotherm at 87 K. The model was applied from $P/P_0 = 0.04$-0.25. The correlation factor is indicated. ($W =$ Weight of gas absorbed at a relative pressure $P/P_0$).
Figure 4.10: Langmuir plot for TBILPs calculated from the Ar adsorption isotherm at 87 K. The model was applied from $P/P_0 = 0.04$-0.20. The correlation factor is indicated. ($W =$ Weight of gas absorbed at a relative pressure $P/P_0$).
Figure 4.11: Nitrogen and methane gas uptake isotherms for TBILP-1 at 273 and 298 K.
Figure 4.12: Nitrogen and methane gas uptake isotherms for TBILP-2 at 273 and 298 K.
**Figure 4.13:** \( \text{CO}_2 \) uptake isotherms for TBILP-1 (A) and TBILP-2 (B) at 273 and 298 K, and \( \text{CO}_2 \) heats of adsorption calculated by the virial method (B). Adsorption (filled) and desorption (empty).
Figure 4.14: CO$_2$, CH$_4$ and N$_2$ gas adsorption isotherms for TBILPs at 273 K (A, B) and 298 K (C, D).
4.3.2 Calculation of Isosteric Heats of Adsorption for TBILPs

The CO$_2$ binding affinity is a key parameter for effective adsorbent design. CO$_2$ isosteric heats of adsorption ($Q_{st}$) were calculated by using the Clausius-Clapeyron equations. TBILP-1 has a much higher $Q_{st}$ (35 kJ mol$^{-1}$) than TBILP-2 (29 kJ mol$^{-1}$) (Figure 4.17). The difference in $Q_{st}$ values can be reasoned by the pore size distribution of TBILPs, which can play a predominant role in determining the binding affinity of CO$_2$. For instance, while both polymers have the same N-rich building units (i.e. triazine and imidazole), the smaller pores of TBILP-1 can lead to CO$_2$-multi pore wall interactions and hence higher CO$_2$ binding affinity. Both theoretical and experimental studies have revealed that CO$_2$ binding affinity can be enhanced through pore functionalization that enhances adsorbent-CO$_2$ interactions.$^{24-25}$ However, such interactions should be maintained in the physisorption regime to facilitate adsorbent regeneration with minimal energy input.$^93$ It is evident from the CO$_2$ isotherms that the binding is fully reversible at 273 and 298 K in spite of the high $Q_{st}$ values (Table 4.1). We have noticed from our recent studies that BILPs in general exhibit desirable $Q_{st}$ values (25-38 kJ mol$^{-1}$) where CO$_2$ can strongly and only physically interact with N-imine functionalities of the polymers.$^{115}$ Additional CO$_2$ interactions with aromatic C-H sites were also predicted recently by DFT studies, however, these interactions are considerably lower than those involving the N-imine sites.$^{73b}$
Figure 4.15: Virial analysis of CO$_2$ adsorption data TBILPs and their isosteric heat of adsorption ($Q_s$).
Figure 4.16: Virial analysis of CH₄ adsorption data TBILPs and their isosteric heat of adsorption ($Q_{st}$).
Figure 4.17: Isosteric heats of adsorption of CO$_2$ and CH$_4$ for TBILP-1 and TBILP-2 calculated by using DSL fitting.
4.3.3 Selectivity Studies and Adsorbent Evaluation Criteria

Given the high CO$_2$ uptake and desirable binding affinity, we studied the use of TBILPs in selective CO$_2$ capture over CH$_4$ and N$_2$ (Figure 4.19 and 4.20). The initial steep increase in CO$_2$ uptake can be explained by dipole-quadrupole interactions between CO$_2$ and the N-imine sites of TBILPs. In contrast, both CH$_4$ and N$_2$ adsorption isotherms revealed almost linear correlation between gas uptake and pressure (Figure 4.18). Henry’s law initial slope calculations were applied to single component gas adsorption isotherms at 298 K. TBILP-1 showed high selectivity for CO$_2$/N$_2$ (63) and CO$_2$/CH$_4$ (9) at 298 K. The observed selectivity at 298 K for CO$_2$/N$_2$ (63) of TBILP-1 is the highest among the reported triazine-based POPs and BILPs except BILP-2 (71).$^{21b}$ As expected, TBILP-2 exhibited relatively lower selectivity for CO$_2$/N$_2$ (40) and CO$_2$/CH$_4$ (7) at 298 K, which is most likely due to its larger pores that are more accessible by CH$_4$ and N$_2$. To evaluate the performance of the polymers in CO$_2$ separation from gas mixtures (CO$_2$/N$_2$ and CO$_2$/CH$_4$), the Ideal Adsorbed Solutions Theory (IAST) was applied wherein selectivity of binary gas mixtures can be predicted from single component adsorption isotherms as a function of pressure.$^{86}$ Two industrial waste gas compositions: post-combustion flue gas and landfill gas were used to predict selectivity of CO$_2$/N$_2$ (10/90) and CO$_2$/CH$_4$ (50/50), respectively. Single component gas adsorption isotherms at 298 K were fitted by either single-site or dual-site Langmuir Freundlich models. The IAST selectivity results (Table 4.1) are in good agreement with those reported above from initial slope selectivity calculations. The gas mixture adsorption behaviour of TBILP-1 and TBILP-2 showed high CO$_2$/N$_2$ selectivity of 62 and 43 at 298 K and CO$_2$/CH$_4$ selectivity of 9 and 7 at 298 K, respectively.
Table 4.1: Gas uptake, binding affinity, and selectivity (CO$_2$/N$_2$ and CO$_2$/CH$_4$) for TBILP-1 and TBILP-2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>aCO$_2$ at 1 bar</th>
<th>bSelectivity</th>
<th>cSelectivity</th>
<th>dSurface Area</th>
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<tbody>
<tr>
<td></td>
<td>273 K</td>
<td>298 K</td>
<td>$Q_a$</td>
<td>CO$_2$/N$_2$</td>
</tr>
<tr>
<td>BILP-5$^{11b}$</td>
<td>128</td>
<td>87</td>
<td>29</td>
<td>36</td>
</tr>
<tr>
<td>BILP-7$^{11b}$</td>
<td>193</td>
<td>122</td>
<td>28</td>
<td>34</td>
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<tr>
<td>TBILP-1$^{10a}$</td>
<td>117</td>
<td>78</td>
<td>35</td>
<td>63</td>
</tr>
<tr>
<td>TBILP-2$^{10a}$</td>
<td>228</td>
<td>146</td>
<td>29</td>
<td>40</td>
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<tr>
<td>TFM-1$^{11b}$</td>
<td>76.1</td>
<td>N/A</td>
<td>27</td>
<td>29</td>
</tr>
<tr>
<td>TCMP-0$^{10s}$</td>
<td>105</td>
<td>59</td>
<td>N/A</td>
<td>N/A</td>
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<td>APOP-1$^{117}$</td>
<td>188</td>
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<td>27</td>
<td>20</td>
</tr>
<tr>
<td>PCTF-1$^{113}$</td>
<td>145</td>
<td>89</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TPI-1$^{112}$</td>
<td>107</td>
<td>55</td>
<td>34</td>
<td>31</td>
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</table>

$^a$Gas uptake in mg g$^{-1}$ and isosteric enthalpies of adsorption ($Q_a$) in kJ mol$^{-1}$ calculated by virial model reported at zero coverage for CO$_2$. $^b$Selectivity (mol mol$^{-1}$) was calculated by initial slope method at 298 K. $^c$Selectivity (mol mol$^{-1}$) was calculated by IAST method at 298 K. $^d$Surface area (BET) in m$^2$ g$^{-1}$. 

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Figure 4.18: CO₂, CH₄ and N₂ gas adsorption isotherms for TBILPs at 273 K (A, B) and 298 K (C, D).
**Figure 4.19:** Gas uptake selectivity studies for TBILP-1 at 298 K (CO$_2$ over CH$_4$ and N$_2$).
Figure 4.20: Gas uptake selectivity studies for TBILP-2 at 298 K (CO₂ over CH₄ and N₂).
Figure 4.21: IAST selectivity of CO$_2$ over N$_2$ in TBILP-1 and TBILP-2 at 298 K and CO$_2$ over CH$_4$ in TBILP-1 and TBILP-2 at 298 K.
Table 4.2: Langmuir fitting parameters of CO\(_2\), CH\(_4\), and N\(_2\) adsorption isotherms of TBILP-1 measured at 273 and 298 K.

<table>
<thead>
<tr>
<th></th>
<th>(q_{\text{sat},A}) (mol/kg)</th>
<th>(b_{A0}) (bar(^{-1}))</th>
<th>(E_A) (J/mol)</th>
<th>(q_{\text{sat},B}) (mol/kg)</th>
<th>(b_{B0}) (bar(^{-1}))</th>
<th>(E_B) (J/mol)</th>
<th>Reduced (\chi^2)</th>
<th>Adj. (R^2)</th>
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</thead>
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<tr>
<td>CO(_2)</td>
<td>3.28966</td>
<td>9.36E-11</td>
<td>26535.19</td>
<td>0.95410</td>
<td>8.15E-12</td>
<td>38337.67</td>
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<td>0.99993</td>
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<tr>
<td>CH(_4)</td>
<td>1.74239</td>
<td>2.33E-10</td>
<td>23796.67</td>
<td></td>
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<td></td>
<td>1.36E-05</td>
<td>0.99974</td>
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<td>N(_2)</td>
<td>11.84105</td>
<td>2.16E-13</td>
<td>31383.56</td>
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<td></td>
<td></td>
<td>9.69E-06</td>
<td>0.99831</td>
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Figure 4.22: Experimental data and corresponding DSL fits for CO\(_2\) adsorption in TBILP-1 at 273 and 298 K.
**Figure 4.23:** Experimental data and corresponding SSL fits for CH$_4$ adsorption in TBILP-1 at 273 and 298 K.

**Figure 4.24:** Experimental data and corresponding SSL fits for N$_2$ adsorption in TBILP-1 at 273 and 298 K.
Table 4.3: Langmuir fitting parameters of CO₂, CH₄, and N₂ adsorption isotherms of TBILP-2 measured at 273 and 298 K.

<table>
<thead>
<tr>
<th></th>
<th>q_{sat,A} (mol/kg)</th>
<th>b_{A0} (bar⁻¹)</th>
<th>E_A (J/mol)</th>
<th>q_{sat,B} (mol/kg)</th>
<th>b_{B0} (bar⁻¹)</th>
<th>E_B (J/mol)</th>
<th>Reduced χ²</th>
<th>Adj. R²</th>
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</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.32471</td>
<td>5.77E-11</td>
<td>33147.94</td>
<td>8.18690</td>
<td>2.21E-10</td>
<td>24162.45</td>
<td>4.82E-05</td>
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<tr>
<td>CH₄</td>
<td>3.66799</td>
<td>5.26E-10</td>
<td>21514.09</td>
<td></td>
<td></td>
<td></td>
<td>2.20E-05</td>
<td>0.99988</td>
</tr>
<tr>
<td>N₂</td>
<td>4.53019</td>
<td>1.64E-11</td>
<td>25103.00</td>
<td></td>
<td></td>
<td></td>
<td>5.15E-06</td>
<td>0.99965</td>
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</table>

Figure 4.25: Experimental data and corresponding DSL fits for CO₂ adsorption in TBILP-2 at 273 and 298 K.
Figure 4.26: Experimental data and corresponding SSL fits for $\text{N}_2$ adsorption in TBILP-2 at 273 and 298 K.

Figure 4.27: Experimental data and corresponding SSL fits for $\text{CH}_4$ adsorption in TBILP-2 at 273 and 298 K.
Furthermore, the promising results of CO$_2$ adsorption and selectivity studies motivated us to follow the set of CO$_2$ capture evaluation criteria proposed by Bae and Snurr to provide a more comprehensive approach for CO$_2$ adsorbent evaluation. The criteria include CO$_2$ uptake using single-component gas isotherm ($N_1^{\text{ads}}$), working capacity ($\Delta N_1$), regenerability (R), selectivity ($\alpha_{12}^{\text{ads}}$) and sorbent selection parameter (S). The CO$_2$ capture performance of the polymers was evaluated by applying vacuum swing adsorption (VSA) conditions (adsorption at 1 bar and desorption at 0.1 bar) to typical post-combustion flue gas (CO$_2$:N$_2$ = 10:90) and landfill gas (CO$_2$:CH$_4$ = 50:50) compositions. The working capacities of TBILP-1 were found to be 0.35 and 1.02 mol kg$^{-1}$ in the case of flue gas and landfill gas separation, respectively. In contrast, TBILP-2 showed higher $\Delta N_1$ values of 0.59 and 1.84 mol kg$^{-1}$ for flue gas and landfill separation, respectively. The observed $\Delta N_1$ values of TBILP-1 and TBILP-2 are similar to those of ZIF-78, -81, and -82, SNU-Cl-va, UiO-66-AD6, BILPs, and commercial Norit R1 extra. TBILPs show favourable regenerabilities (R >80) for both VSA gas separation cases, which point out the reversibility of CO$_2$ adsorption-desorption under ambient conditions. Recent studies also reported that $Q_{st}$ has an inverse correlation with the R factor of polymers. Sorbent selection parameter of TBILP-1 (335) in VSA flue gas outperformed all reported porous polymers except ZIF-78 (396), due to the high CO$_2$/N$_2$ selectivity of TBILP-1. VSA landfill gas and flue gas performance of TBILP-2 also competes with top adsorbent candidates in terms of S factor.

For PSA application, the use of high surface area adsorbents has been suggested to be more effective and as such, we selected only TBILP-2 for landfill gas separation since TBILP-1 has much lower surface area (330 m$^2$ g$^{-1}$). We collected high pressure CO$_2$ and CH$_4$ isotherms because PSA operates in a pressure range of 1 to 5 bar (Table 4.4). The working capacity of TBILP-2 was calculated to be 2.32 mol kg$^{-1}$ which exceeds the working capacities of Zeolite-
13X (1.4 mol kg\textsuperscript{-1}), diimide-POP (1.62 mol kg\textsuperscript{-1}) and IRMOF-16 (2.18 mol kg\textsuperscript{-1}). Notably, the combination of high CO\textsubscript{2} working capacity and good CO\textsubscript{2}/CH\textsubscript{4} selectivity (7.2) of TBILP-2 leads to a remarkably high S factor (31.9) that is among the highest for reported porous materials in the field.\textsuperscript{57c}

**Table 4.4** CO\textsubscript{2} Sorption Evaluation of TBILP by using reported set of criteria.

<table>
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<tr>
<th>Adsorbents</th>
<th>N\textsubscript{1}\textsuperscript{ads}</th>
<th>ΔN\textsubscript{1}</th>
<th>R</th>
<th>α\textsubscript{12}\textsuperscript{ads}</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBILP-1</td>
<td>0.40</td>
<td>0.35</td>
<td>87.0</td>
<td>58.7</td>
<td>334.6</td>
</tr>
<tr>
<td>TBILP-2</td>
<td>0.67</td>
<td>0.59</td>
<td>88.3</td>
<td>42.1</td>
<td>192.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>N\textsubscript{1}\textsuperscript{ads}</th>
<th>ΔN\textsubscript{1}</th>
<th>R</th>
<th>α\textsubscript{12}\textsuperscript{ads}</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>TBILP-1</td>
<td>1.25</td>
<td>1.02</td>
<td>81.3</td>
<td>9.8</td>
<td>107.0</td>
</tr>
<tr>
<td>TBILP-2</td>
<td>2.20</td>
<td>1.84</td>
<td>83.7</td>
<td>7.6</td>
<td>62.5</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>N\textsubscript{1}\textsuperscript{ads}</th>
<th>ΔN\textsubscript{1}</th>
<th>R</th>
<th>α\textsubscript{12}\textsuperscript{ads}</th>
<th>S</th>
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<tbody>
<tr>
<td>TBILP-2</td>
<td>4.28</td>
<td>2.32</td>
<td>54.33</td>
<td>7.2</td>
<td>31.9</td>
</tr>
</tbody>
</table>
4.4 Conclusion

In this study, we have successfully integrated both triazine and benzimidazole building units into porous organic polymers and investigated their impact on CO$_2$ separation from flue and landfill gases. TBILP-2 adsorbs very high CO$_2$ uptake (5.19 mmol g$^{-1}$) at 1 bar and 273 K. IAST selectivity calculations revealed high CO$_2$/N$_2$ selectivity of 62 and 43 for TBILP-1 and TBILP-2, respectively, at 298 K. CO$_2$/N$_2$ selectivity of TBILP outperforms all triazine-based porous organic polymers reported to date. CO$_2$ heats of adsorption and selectivity studies showed incorporation of triazine units into BILPs could improve selective CO$_2$ adsorption over N$_2$ and CH$_4$. TBILPs also exhibit promising working capacity, regenerability and sorbent selection parameter values for CO$_2$ capture from flue and landfill gases under VSA and PSA processes making them attractive candidates for use in CO$_2$ capture and separation applications.
Chapter 5

A 2D Mesoporous Imine-Linked Covalent Organic Framework for High Pressure Gas Storage Applications

5.1 Introduction

The research on the crystalline porous organic polymers have inaugurated by the introduction of covalent organic frameworks (COFs) in the last decade.\textsuperscript{30, 38} Yaghi and his co-workers have achieved to generate dynamic covalent bond formation between 2D and 3D rigid building blocks affording many different types of COFs.\textsuperscript{34} This new class of porous crystalline materials has been fabricated by designed synthesis to have high surface area, very low densities, and tunable pore dimensions.\textsuperscript{30, 119} COFs have been considered for wide range of applications among which, gas storage have been intensively studied in COFs because of their inherent low density (i.e. made of H, C, N, B, O, Si) and high surface area which can mitigate gravimetric and volumetric constrains for the onboard storage of hydrogen and methane.\textsuperscript{52b, 120} Although COFs derived from B-O bond formation have been widely investigated, their low chemical stability leads to a rapid decomposition upon exposure to moisture and limits their effective use in gas storage under practical conditions. This drawback has been addressed in new COF materials constructed through the formation of C-N bonds and found to have enhanced chemical robustness. Up to date, C-N linked COFs such as triazine, imine, and hydrazones linked COFs typically possess moderate specific surface areas that can hinder their application in gas storage.\textsuperscript{38} One of the effective methods for attaining high porosity in organic materials has been the use of rigid or expanded 3D building units, however, extrapolating this approach to imine-linked COFs resulted in framework interpenetration and only moderate surface area for the 3D COF-300 ($SA_{BET} = 1360 \text{ m}^2 \text{ g}^{-1}$).\textsuperscript{37} Likewise, the use of $\pi$-electron rich building units has also afforded low surface
area for the 2D COF-66 \((S_{BET} = 360 \text{ m}^2\text{g}^{-1})\) and to the best of our knowledge, the use of imine-linked COFs in gas storage has been only investigated theoretically.\(^{38}\)

In this chapter, we describe the synthesis of a high surface area mesoporous imine-linked COF (ILCOF-1) and demonstrate that the use of expanded pyrene cores in the construction of imine-linked COFs can significantly enhance porosity and performance in high pressure H\(_2\), CH\(_4\), and CO\(_2\) storage.

### 5.2 Synthesis of ILCOF-1

Tetrakis\((p\text{-formylphenyl})\)pyrene (20 mg, 32 µmol) and 1,4- \(p\)-phenylenediamine (7.0 mg, 64 µmol) were suspended in anhydrous 1,4-dioxane (3.0 mL) in the presence of aqueous acetic acid (0.6 mL, 3.0 M) in a Pyrex tube. The mixture was then degassed by freeze-pump-thaw technique twice using liquid nitrogen bath. Finally the tube was frozen using liquid nitrogen then flame sealed under reduced pressure (150 mtorr). The sealed tube was heated at 120 °C for 3 days to yield a yellow solid which was filtered and washed with THF. The resulting powder was soaked in THF/chloroform mixture (1:1) for 1 day during which the solvents were replenished twice then filtered over a medium glass frit and dried at 120 °C/150 mtorr to give ILCOF-1 as a yellow powder (19 mg, 78% based on TFPPy). Solid state \(^{13}\)C NMR: \(\delta = 156 \text{ (C=N)}, 148, 141, 135, 133, 129, 125, 121, 118, 113 \text{ ppm};\) FTIR (KBr): \(\nu \text{ bar} = 3410, 3027, 2920, 2860, 1700, 1621 \text{ (C=N), 1602, 1558, 1491, 1460, 1409, 1305, 1194, 1173, 1105, 1005, 980, 880, 838, 814 cm}^{-1};\) elemental analysis calcd (%) for C\(_{56}H_{34}N_4.4H_2O\): C 80.55, H 5.07, N 6.71; found: C 80.45, H 6.40, N 4.23.
5.3 Results and Discussion

5.3.1 Synthesis and Characterization of ILCOF-1

ILCOF-1 was synthesized by the condensation reaction between 1,3,6,8-tetrakis(p-formylphenyl)pyrene and p-phenylenediamine in 1,4-dioxane in the presence of aqueous acetic acid at 120 °C over 3 days and was isolated in good yields (Figure 5.1). ILCOF-1 was purified by washing with acetone then soaked in a solvent mixture of acetone/chloroform (v:v ; 1:1) for one day to remove trapped guest molecules such as solvents and unreacted monomers from the pores followed by drying at 120 °C/1.0 x 10⁻³ torr prior to characterization studies.

The thermal stability of ILCOF-1 was confirmed by thermogravimetric analysis (TGA) which indicated that this COF remains stable up to ~ 400 °C under air (Figure 5.2). The formation of a uniform morphology consistent with the expected crystalline nature of the COF was evidenced by scanning electron microscopy (SEM) which indicates the formation of aggregated cubes ~30-70 nm in size (Figure 5.3). The formation of imine linkage was confirmed by FT-IR and ¹³C cross-polarization with magic angle spinning (CP-MAS) NMR spectroscopic methods. The FT-IR spectra (Figure 5.4) contains a characteristic C=N stretch band at 1621 cm⁻¹. The spectrum also showed a strongly attenuated C=O and N-H stretches that are present in the aldehyde- and amine-functionalized monomers used for the construction of ILCOF-1. The ¹³C CP-NMR spectrum contains a characteristic signal for the C=N bond at 156 ppm while additional signals in the aromatic range arise from the phenyl and pyrene cores of the building units (Figure 5.5).
Figure 5.1 Schematic representation for ILCOF-1 synthesis.
Figure 5.2: TGA trace of ILCOF-1.
Figure 5.3: SEM images of ILCOF-1.
Figure 5.4: FT-IR spectra (400-3600 cm\(^{-1}\)) of starting materials and ILCOF-1.
Figure 5.5: Solid-state $^{13}$C CP-MAS NMR spectrum of ILCOF-1.
5.3.2 Structural Models and Atomic Coordinates for ILCOF-1

To elucidate the solid-state packing of ILCOF-1 and its crystallinity, we collected powder X-ray diffraction (PXRD) patterns for multiple samples and all supported the formation of a highly crystalline material as depicted in Figure 5.6. We examined the experimental PXRD pattern of ILCOF-1 against calculated patterns of potential staggered and eclipsed conformations of the 2D sheets according to literature methods. We have constructed two plausible models in which the AA packing leads to an eclipsed arrangement having an orthorhombic space group \( Cmm2 \) while the staggered AB conformation leads to a structure having orthorhombic space group \( Fmm2 \). These models were constructed using Materials Studio Visualizer and their respective geometries and energies were optimized using the Forcite module.

As shown in Figure 5.6 and in contrast to the calculated pattern of the staggered model, the calculated diffraction pattern of the eclipsed model is consistent with the experimental PXRD pattern of ILCOF-1. The most notable difference is the reflection for the (110) plane at \( 2\theta = 3.32^\circ \) of the eclipsed model and experimental pattern that is absent from the PXRD pattern of the staggered model. Furthermore, the experimental powder XRD pattern of ILCOF-1 was subjected to refinement by the Rietveld method, which produced refined PXRD curves with lattice parameters of \( a = 34.88 \, \text{Å; } b = 32.41 \, \text{Å; } c = 7.88 \, \text{Å} \) that are very similar to the dimensions of the eclipsed model (\( a = 34.7756 \, \text{Å; } b = 34.1644 \, \text{Å and } c = 6.5787 \, \text{Å} \)). The \( wRp \) and \( Rp \) values converged to 5.5% and 4.6%, respectively. The general broadening of the PXRD reflections is most likely due to the deviation from the ideal eclipsed stacking of the 2D layers as predicted by theoretical investigation of 2D COFs that are governed by electrostatic interactions and dispersive forces of the pyrene units. Such interactions have been suggested to lead to small
offsets (1.5-2.8 Å) that cannot be recognized by X-ray diffraction techniques. Furthermore, such packing can reduce pore volume and limit the uptake of large molecules like C\textsubscript{60}, however, it would have a very limited impact on the admission of small gas molecules into the pores of mesoporous COFs.
Figure 5.6: Space-filling models showing: A) solid-state eclipsed and C) staggered models and their corresponding PXRD patterns (B) and (D), E) PXRD pattern of ILCOF-1.
Table 5.1: Fractional atomic coordinates for the eclipsed conformation of *ILCOF-1* calculated from *Materials Studio* modeling.

Space group symmetry

*Cmm2*

\[
a = 34.7756 \text{ Å } b = 34.1644 \text{ Å } c = 6.5787 \text{ Å}
\]

\[
\alpha = \beta = \gamma = 90^\circ
\]

Orthorhombic

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
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<td>C1</td>
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**Table 5.2**: Fractional atomic coordinates for the staggered conformation of ILCOF-1 calculated from *Materials Studio* modeling.

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Space group symmetry

Fmm2

a = 34.2435 Å  \( b = 34.6947 \) Å  \( c = 12.5394 \) Å

\( \alpha = \beta = \gamma = 90^\circ \)
5.3.3 Powder X-ray Diffraction Analysis of ILCOF-1

Panalytical X’pert Pro Multipurpose Diffractometer (MPD) is used to collect the powder X-ray diffraction data of ILCOF-1. Sample was mounted on a zero background sample holder measured in transmission mode using Cu Kα radiation with a 2θ range of 1.5-35°. Rietveld method for powder XRD refinement was applied on ILCOF-1 using the GSAS and EXP-GUI software packages with a general least squares fit. Refinement produced PXRD curve with lattice parameters of $a = 34.8814 \, \text{Å}$, $b = 32.4105 \, \text{Å}$ and $c = 7.8894 \, \text{Å}$ which are close to the theoretical eclipsed conformation model ($a = 34.7756 \, \text{Å}$, $b = 34.1644 \, \text{Å}$ and $c = 6.5787 \, \text{Å}$). The $wR_p$ and $R_p$ values converged to 5.5 % and 4.6 %, respectively.

The positions of atoms in the unit cell were determined using EXP-GUI and are shown as fractional atomic coordinates in Table 5.3.
Figure 5.7: PXRD pattern of ILCOF-1 with the experimental pattern in black, the Reitveld refined profile in red, the difference plot in blue and the eclipsed crystal model is green.
Figure 5.8: XRD pattern of ILCOF-1 with the eclipsed crystal model.
Figure 5.9: XRD pattern of \textit{ILCOF-1} with the staggered crystal model.
Table 5.3: Fractional atomic coordinates for the refined unit cell parameters for ILCOF-1 calculated from GSAS and EXP-GUI software packages.

Refined

\[ \begin{align*}
    a &= 34.88 \text{ Å} \quad b = 32.41 \text{ Å} \quad c = 7.88 \text{ Å} \\
    \alpha &= \beta = \gamma = 90^\circ
\end{align*} \]

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5.3.4 Porosity Studies Measurements for ILCOF-1

Based on the modelling studies discussed above, it was anticipated that ILCOF-1 would have mesopores (pore dimensions $\sim 28.0 \times 24.3$ Å) and high surface area (Connelly surface = 5070 m$^2$g$^{-1}$) that can allow for substantial gas storage capacities especially under high-pressure conditions. Accordingly, the porosity of ILCOF-1 was established by argon sorption-desorption measurements. The fully reversible Type-IV isotherm depicted in Figure 5.10 exhibits a rapid uptake at low pressure followed by a sharp step in the range of $P/P_0 = 0.05-0.15$ that is typical of mesoporous COFs and inline with the predicted mesoporous nature of ILCOF-1 according to the eclipsed model. The Brunauer-Emmett-Teller and Langmuir surface areas were $S_{A\text{BET}} = 2723$ m$^2$g$^{-1}$ and $S_{A\text{Lang}} = 3453$ m$^2$g$^{-1}$, respectively. Pore size distribution was estimated from the argon uptake isotherm by nonlocal density functional theory (NLDFT, Figure 5.13) and revealed two minor ranges that peak at 10 and 17 Å, and a major one centered at around 23 Å that is very similar to the calculated pore width of the model (24.3 Å) defined by the distance between the phenyl linkers. The total pore volume was calculated from a single point measurement at $P/P_0 = 0.96$ and found to be 1.21 cm$^3$g$^{-1}$. 

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Figure 5.10: Ar adsorption isotherms for ILCOF-1 measured at 87 K. The filled circles are adsorption points and the empty circles are desorption points.
Figure 5.11: BET and Langmuir plots for ILCOF-1 calculated from the Ar adsorption isotherm at 87 K. The BET model was applied from $P/P_0 = 0.07-0.1$ and $P/P_0 = 0.12-0.18$. The Langmuir model was applied from $P/P_0 = 0.15-0.28$. The correlation factor is indicated. ($W$ = Weight of gas absorbed at a relative pressure $P/P_0$).
Figure 5.12: Experimental Ar adsorption isotherms (filled circles) for ILCOF-1 measured at 87 K. The calculated NLDFT isotherm is overlaid as open circle. Note that a fitting error of < 1 % indicates the validity of using this method for assessing the porosity of ILCOF-1. The fitting error is indicated.
Figure 5.13: The pore size distribution of ILCOF-1 was calculated from the Ar adsorption isotherm by the Non-Local Density Functional Theory (NLDFT) method using a cylindrical pore model.
5.3.6 Low-Pressure (0–1 bar) Gas Adsorption Measurements for ILCOF-1

![Graphs showing gas uptake isotherms for ILCOF-1](image)

**Figure 5.14:** Low-pressure gas uptake isotherms for ILCOF-1; adsorption (filled) and desorption (empty). (A) H₂ at 77 K (circles) and 87 K (squares); (B) CO₂ at 273 K (circles) and 298 K (squares); (C) CH₄ at 273 K (circles) and 298 K (squares).
5.3.7 Calculation of Isosteric Heats of Adsorption for ILCOF-1

Figure 5.15: Virial analysis of H₂ adsorption data for ILCOF-1 (A) (black circles: 77 K, blue squares: 87 K) and its isosteric heat of adsorption ($Q_{st}$) (B). $a_0 = -707.437711184324$, $a_1 = 69.0214727699308$, $a_2 = 4.88036158643286$, $a_3 = -3.46711359967128$, $a_4 = 0.26708649236963$; $b_0 = 13.0749480216611$, $b_1 = -0.946105245635075$, $b_2 = 0.113732681972982$. 

$\ln \left( \frac{p}{n} \right)$

$H_2$ uptake (mg/g)

$Q_{st}$ for H₂ (from virial method)

ILCOF -1

(A)

Virial fitting for $H_2$ isotherm

Expt at 77 K
Fitted at 77 K
Expt at 87 K
Fitted at 87 K

n (mmol/g)

0 1 2 3 4 5 6 7

0 1 2 3 4 5 6 7 8

10 11 12 13 14
Figure 5.16 Tóth isotherm fitting to the experimental H\textsubscript{2} adsorption isotherm for ILCOF-1 at 77 K (A) and 87 K (B). Isosteric heat of adsorption (\(Q_{st}\)) from Clausius-Clapeyron plot (C) and a comparison of \(Q_{st}\) obtained from virial method and Clausius-Clapeyron plot (D).
Figure 5.17: Virial analysis of CO₂ adsorption data for ILCOF-1 (A) (black circles: 273 K, blue squares: 298 K) and its isosteric heat of adsorption ($Q_{st}$) (B). $a_0 = -2195.76135971482$, $a_1 = -171.207832940695$, $a_2 = 963.047971837978$, $a_3 = -426.962384463087$; $b_0 = 14.5606189951729$, $b_1 = -1.48642469975414$
Figure 5.18: Tóth isotherm fitting to the experimental CO$_2$ adsorption isotherm for ILCOF-1 at 273 K (A), 288 K (B) and 298 K (C). Isosteric heat of adsorption ($Q_{st}$) from Clausius-Clapeyron plot (D) and a comparison of $Q_{st}$ obtained from virial method and Clausius-Clapeyron plot (E).
Figure 5.19: Virial analysis of CH$_4$ adsorption data for ILCOF-1 (A) (black circles: 273 K, blue squares: 298 K) and its isosteric heat of adsorption ($Q_{st}$) (B). $a_0 = -1643.5488852817$, $a_1 = -207.926357659911$, $a_2 = 72.9995061930211$, $a_3 = 53.7908842178909$; $b_0 = 13.437056532264$. 
Figure 5.20 Tóth isotherm fitting to the experimental CH$_4$ adsorption isotherm for ILCOF-1 at 273 K (A), 288 K (B) and 298 K (C). Isosteric heat of adsorption ($Q_{st}$) from Clausius-Clapeyron plot (D) and a comparison of $Q_{st}$ obtained from virial method and Clausius-Clapeyron plot (E).
5.3.8 High-Pressure (0–40 bar) Gas Adsorption Measurements for ILCOF-1

As it is discussed widely in the chapter 1, the on-board applications of methane and hydrogen storage remains a considerable technological challenge to the widespread commercialization of these fuels. In order to meet gravimetric and volumetric targets, both gases need to be stored under high pressure conditions. The US Department of Energy (DOE) has set a target for onboard methane storage at 180 v/v at room temperature and 35 bar, while the gravimetric and volumetric density targets for hydrogen are 5.5 wt% and 40 gL⁻¹, respectively, for 2015.¹²³ The use of porous materials such as porous organic polymers, MOFs, and porous carbon, etc. remains very attractive because of their ability to fuel-defuel at acceptable rates and due to their tailored high surface areas that can enable high storage capacities. In spite of these promising properties the low binding affinity for H₂ necessitates the use of low temperature and high-pressure conditions in order to achieve tangible storage levels. Likewise, meeting the volumetric constrain for on-board methane storage has proven to be very difficult and still needs to be addressed for proper assessment of new adsorbents. Additionally, carbon dioxide is usually separated at ambient pressure and then sequestered at a much higher pressure. With these considerations in mind, we set out to evaluate the gravimetric and volumetric performance of ILCOF-1 in gas storage at high pressure. Accordingly, high pressure (up to 40 bar) gas sorption measurements for H₂, CH₄ and CO₂ were performed and the resulting isotherms are presented in Figure 5.24.

The hydrogen uptake shows a gradual increase with pressure and reaches saturation at ~35 bar; the gravimetric surface excess uptake (4.7 wt%, 77 K / 40 bar) is higher than most of the organic polymers of similar surface area.⁸⁰ In contrast to the nitrogen free frameworks of COFs, PAFs, and HCP, the nitrogen-functionalized pore walls of ILCOF-1 can enhance CO₂ binding
through N···CO₂ interactions which can be one of the reasons behind the observed high CO₂ uptake. The gravimetric surface excess methane uptake was 11.2 mmolg⁻¹ at 298 K/40 bar which is higher than the reported methane uptakes for 2D COFs and inline with those of 3D COFs (~11 mmolg⁻¹). The performance of ILCOF-1 in volumetric (v:v) gas storage at high pressure was also assessed (Figure 5.21). The volumetric storage capacity of an adsorbent determines how densely the gas molecules are stored within the pores and is very relevant to express the efficiency of low density adsorbents like COFs. Under high pressure conditions, the void space of the pores can hold a significant amount of compressed gas and therefore, the absolute amounts adsorbed (total) were calculated from experimentally determined surface excess adsorptions. The absolute gravimetric and volumetric (v:v) uptakes for hydrogen at 77 K / 40 bar is 6.1 wt% and 30 g L⁻¹ (335 LL⁻¹), respectively. Similarly the absolute adsorbed amount for CH₄ in volumetric units was estimated to be 129 LL⁻¹ (92 gL⁻¹) at 298 K / 35 bar which is comparable to that of COF-102 (136 LL⁻¹) but still lower than the DOE target for 2015 (180 ; v:v). The volumetric CO₂ adsorption capacity at 298 K and 35 bar is 587 gL⁻¹ (299 LL⁻¹) which is approximately eight times the density of carbon dioxide at the same temperature and pressure.
**Figure 5.21:** High-pressure $\text{H}_2$ isotherms for ILCOF-1 measured at 77 K. Circles and squares represent surface excess ($N_{\text{Exc}}$) and absolute adsorbed ($N_{\text{Abs}}$) amounts, respectively.
Figure 5.22: CO₂ isotherms for ILCOF-1 measured at 275 (black) and 298 K (red). Circles and squares represent surface excess ($N_{\text{Exc}}$) and absolute adsorbed ($N_{\text{Abs}}$) amounts, respectively.
Figure 5.23: CH$_4$ isotherms for ILCOF-1 measured at 275 (black) and 298 K (red). Circles and squares represent surface excess ($N_{\text{Exc}}$) and absolute adsorbed ($N_{\text{Abs}}$) amounts, respectively.
Figure 5.24: Absolute amount adsorbed of $\text{H}_2$, $\text{CO}_2$ and $\text{CH}_4$ for ILCOF-1 at 298 K.
Table 5.4: Notable gas uptake by porous organic materials.\textsuperscript{21e, 25, 38, 56}

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<td>7.0</td>
<td>1.22</td>
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<td>1760</td>
<td>6.6</td>
<td>0.84</td>
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<tr>
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<td>3620</td>
<td>3.9</td>
<td>1.20</td>
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5.4 Conclusion

We have demonstrated that the use of expanded pyrene building units can be very effective in the preparation of highly crystalline mesoporous imine-linked COFs. The strong $\pi-\pi$ stacking interactions of the pyrene moieties not only direct the 2D solid-state packing but also prevent network interpenetration and thereby enhance the porosity and performance of COFs in gas storage. In addition to the promising gas storage properties of ILCOF-1, this COF is expected to have other potential applications in gas separation or as a catalyst support for heterogeneous catalysis in which the nitrogen functionalized pore walls can facilitate selective gas adsorption and catalyst immobilization, respectively.
Chapter 6
Concluding Remarks

The systematic design and synthesis of porous organic polymers is widely studied and discussed in this dissertation. Two classes of porous organic polymers, benzimidazole-linked and imine-linked porous organic polymers were studied and evaluated for potential use in gas storage and separation applications. The benchmark aspects of the dissertation are summarized below.

Recalling from the first chapter, “Rational Design” of rigid and functional building blocks is the focal point of multifunctional porous polymer synthesis for targeted applications. Seven new porous organic polymers were introduced in the dissertation. Schiff-base chemistry was commonly applied in reversible and irreversible polymerization routes. At this scope, 2D rigid pyrene-based arlyaldehyde, 1,3,6,8-tetrakis(p-formylphenyl)pyrene (TFPPy) was synthesized through Suzuki-coupling reaction between 4-formylphenylboronic acid and 1,3,6,8-tetabromopyrene. The metal catalyst-free imine-condensation between TFPPy, and a variety of aryl-o -diamine building blocks afforded 4 pyrene-derived benzimidazole-linked polymers. Additionally, 1,3,5 triazine functional units were successfully incorporated into new BILPs: TBILP-1 and TBILP-2, through condensation reactions of 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TPPT) with 1,2,4,5-benzenetetraamine tetrachloride (BTA) and 2,3,6,7,14,15 hexaaminotriptycene (HATT), respectively. The template-free reaction route was used for all reported BILP synthesis, in which the formation of in-situ aniline Schiff’s base undergoes the subsequent cyclo-dehydrogenation in presence of molecular oxygen to afford the imidazole ring. More importantly, the metal catalyst-free polymerization avenue dismissed potential metal
residue blocking of the pores as well as high catalyst cost often confronted in a POP synthesis. In addition to BILPs chemistry, crystalline porous polymer formation was studied to prepare a 2D imine-linked covalent organic framework (ILCOF-1). Characterization of building blocks, polymers, chemical compositions and connectivity between building units was performed using spectral and analytical methods such as FT-IR, NMR, and elemental analysis. All polymers showed high thermal (up to 500 °C) and chemical stability. Moreover, the stability of BILPs remained intact after the treatment with 2M HCl and 2M NaOH.

All polymers showed high permanent porosity, which was investigated by argon and nitrogen sorption-desorption measurements. Brunauer-Emmet-Teller surface area (SA\textsubscript{BET}) calculations of BILPs resulted in moderate to high porosity (of 330-1497 m\textsuperscript{2} g\textsuperscript{-1}). The pore size distributions (7.2-12 Å) of polymers confirmed their microporous nature. On the other hand, crystalline porous organic polymer, ILCOF-1 showed unprecedented surface area (SA\textsubscript{BET}: 2750 m\textsuperscript{2} g\textsuperscript{-1}) for 2D crystalline organic polymers. The strong π-π stacking interactions of the pyrene moieties not only directed the 2D solid-state packing but also prevented network interpenetration and thereby enhanced the porosity and controlled the pore size distribution (23 Å) of ILCOF-1. At high pressure, ILCOF-1 exhibited high gas uptake (H\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}) because of its high surface area and pore volume.
The synthesis, characterization, and porosity studies were followed by gas storage and separation studies. It was observed that the higher surface area is very relevant for gas uptake at elevated pressures. For example: The hydrogen uptake of ILCOF-1 (4.7 wt.%, 77 K and 40 bar) exceeded most of porous organic polymers reported in the literature. For CO₂ capture and storage, functional groups which are susceptible to interactions with acidic guest molecules, played a complementary role with the surface area property. The highest CO₂ uptake in pyrene-based BILPs was recorded for BILP-12 (223 mg g⁻¹; 5.06 mmol g⁻¹ at 273 K/1 bar) confirming the effect of surface area on the final CO₂ uptake.

The potential of using of polymers in CO₂/N₂ and CO₂/CH₄ separation systems was thoroughly investigated. The initial slope ratios of single-component gas adsorption isotherms resulted in high selectivity values for all BILPs. BILP-10, 11 and 13 showed higher CO₂/N₂ selectivity (>100 at 273 K) and heats of adsorption values for CO₂ (>32 kJ mol⁻¹), compared to high surface area polymers BILP-12, TBILP-2 and ILCOF-1. This data set is found to be consistent with recent studies, which documented that pore size distribution and heats of adsorption properties play predominant roles in the selectivity (at partial pressure of CO₂ <0.5 bar) rather than surface area values. The study on the incorporation of 1,3,5 triazine functional units in BILPs; TBILP-1 and TBILP-2 also revealed similar correlation between the functionalities and selective CO₂ uptake, showing more selective CO₂ uptake when compared with their corresponding structural analogues: BILP-7 and BILP-5. Furthermore, selectivity data obtained from the prediction of binary gas mixtures (IAST Theory) was consistent with gas selectivity calculations performed by using Henry’s law initial slope calculations. Overall, several new porous organic polymers were successfully designed, synthesized and characterized using analytical and spectral techniques. Gas storage and selective uptake by polymers were studied to unravel structure-function
relationships. More importantly, the performance of BILPs in CO$_2$ removal from flue gas and methane–rich gases (natural gas and landfill gas) under different industrial conditions was investigated according to evaluation criteria recently suggested in the literature. BILPs exhibited high working capacity, regenerability, and sorbent selection parameters. ILCOF-1, on the other hand, showed more promise in gas storage applications such as hydrogen and methane storage due to its higher porosity. The outcome of this doctoral study revealed that BILPs and ILCOF-1 are among the best performing porous materials in the fields of gas separation and storage. Collectively, all these novel properties of reported polymers coupled with the remarkable physicochemical stability, make them potential candidates for widespread practical use.
References


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Publications


Selected Presentations


- Sekizkardes, A. K.; El-Kaderi, H. M. “Pyrene-Based Benzimidazole-Linked Polymers for CO₂ Capture and Separation processes” 247th ACS Meeting, Dallas, TX, March 2014.


• Sekizkardes, A. K.; Rabbani M. G.; El-Kaderi H. M. “Multifunctional Pyrene-Derived Porous Architectures” Virginia Commonwealth University (Richmond, VA), October 2011.

• Sekizkardes, A. K.; Rabbani M. G.; El-Kaderi H. M. “Pyrene-Directed Growth of Multifunctional Porous Organic Polymers ” Virginia Commonwealth University (Richmond, VA), October 2012.


Awards, Scholarships, and Honors

2011  Teaching and Research Assistant Scholarship at Virginia Commonwealth University

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2013  Commonwealth Graduate Studies Award

2013  VCU Chemistry Department Kapp Award

2014  Lidia M. Vallarino Scholarship Award