Template-Free Synthesis of a Highly Porous Benzimidazole-Linked Polymer for CO₂ Capture and H₂ Storage

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Supporting Information

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The design and synthesis of highly porous organic polymers has attracted considerable attention due to their potential use in gas storage and separation, catalysis, electronics, and chemical sensing. Among these polymers are polybenzimidazoles (PBIs) which have been mainly investigated as membranes in proton-exchange membrane fuel cells (PEMFCs) application. PBIs are usually prepared by polycondensation reactions between aryl-o-diamines and benzene carboxylic acids in the presence of templating agents such as silica nanoparticles or porogen in polyphosphoric acid; other methods also include ionothermal and melt-condensation routes. The resulting polymers possess surface areas up to ∼200 m²/g and pore sizes in the macroporous to microporous ranges. In spite of the great research efforts in this field, the surface area of PBIs remains considerably lower than those observed for purely organic polymers such as polymers of intrinsic microporosity (PIMs), porous aromatic frameworks (PAFs), covalent organic frameworks (COFs), and porous polymer networks (PPNs). The functional nature of PBIs stems from the amphoteric imidazole moieties which are part of the polymer backbone, and consequently, PBIs are attractive for gas storage and separation studies. For example, introducing amine functionality or accessible nitrogen sites into the pore wall of metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), or zeolitic tetrazolate frameworks (ZTFs) can drastically impact their gas uptake and selectivity. In particular, the selective uptake of CO₂ over CH₄ or N₂ is believed to arise from enhanced CO₂-framework interactions through hydrogen bonding and/or dipole–quadrupole interactions. CO₂ is a green house gas which contributes significantly to global warming, hence developing highly efficient materials for its sequestration or separation from natural gas or flue gases will have a direct environmental and economical impact.

With these considerations in mind, we report herein on template-free synthesis of a highly porous benzimidazole-linked polymer (BILP-1) by the condensation reaction between 2,3,6,7,10,11-hexaaminotriphenylene (HATP) and tetrakis(4-formylphenyl)methane (TFPM) (Scheme 1). The resulting polymer was characterized by spectral and analytical methods, while porosity was investigated by argon sorption measurement. A dropwise treatment of a suspension of HATP in N,N-dimethylformamide (DMF) with homogeneous solution of TFPM in DMF over 3 h at −30 °C followed by stirring at room temperature for 6 h afforded a yellow suspension (presumably imine-linked oligomers). The resulting suspension was bubbled with oxygen and then heated in a sealed Schlenk flask at 130 °C for 3 days to afford BILP-1 (70%) as a yellow powder after filtration and drying at 120 °C and 1.0 × 10⁻⁵ Torr for 12 h. The slow addition of TFPM and the use of DMF increase initial oligomer solubility and prevent their premature precipitation which enhances pore formation and, therefore, the overall porosity. The formation of the imidazole ring proceeds through a rapid formation of imine-linkage followed by cyclization assisted by molecular oxygen.

BILP-1 is insoluble in water and common organic solvents such as hexane, methanol, acetone, tetrahydrofuran, and DMF. Storing the material under aerobic conditions for one month or treatment with a 2 M solution of HCl or NaOH lead only to a slight color change from yellow to brown presumably due to the oxidation of unreacted terminal amino groups on the surface of the polymer particles. The chemical composition was determined by elemental analysis which showed that the Lewis basic sites involve in hydrogen bonding with about one water molecule per site. A similar observation has been reported for the imine-linked COF-300.
This was further supported by thermogravimetric analysis (TGA) which showed weight loss between 50 to 100 °C that corresponds to the removal of water molecules followed by decomposition at ∼400 °C (Supporting Information, S1). Scanning electron microscopy (SEM) established phase purity of the polymer and revealed aggregated particles ∼100–300 nm in size (Scheme 1, inset). The material is amorphous as evidenced by powder X-ray diffraction analysis (Supporting Information, S3). The chemical connectivity and the formation of the imidazole ring were confirmed by FT-IR and 13C solid-state NMR spectroscopy. The FT-IR spectrum of BILP-1 (Supporting Information, S4–S5) showed N—H stretching at 3417 (free N—H) and 3185 cm⁻¹ (hydrogen bonded N—H), a characteristic feature of polybenzimidazole NH absorptions.16a,b A new intense band appeared at 1482 cm⁻¹ which corresponds to C≡N stretching of the benzimidazole ring.16c,d The broad band at around 1625 cm⁻¹ is presumably due to the overlap of C=N and C≡N stretching bands. In addition, the absence of a C=O stretching band at 1702 cm⁻¹ indicates a full consumption of the TFPM monomer. The imidazole ring formation and the incorporation of intact triphenylene or tetraphenyldimethane units into the polymer network was examined by 13C CP-MAS NMR measurement. The NMR spectrum (Supporting Information, S9) contains a signal at 151 ppm which corresponds to the NC(Ph)N in benzimidazole units. This is in sharp contrast to the reported signals for Ph—N in imine-linked frameworks such as COF-300,14c polymer organic frameworks (POFs),14d and diimide-based polymers (750–1407 m² g⁻¹).17e Pore size distribution was examined by fitting the uptake branch of the argon isotherm with nonlocal density functional theory (NLDFT) and was found to be centered at 6.8 Å (Figure 1, inset), while the total pore volume calculated at P/P₀ = 0.95 is 0.70 cm³ g⁻¹.

To investigate the impact of microporosity and the amphoteric pore walls of BILP-1 on the uptake of small gases and selectivity, we collected CO₂, CH₄, and H₂ isotherms and calculated their respective isosteric enthalpies of adsorption (Qₑ). CO₂ isotherms were measured at 273 and 298 K from 0 to 1 bar (Figure 2A). The isotherms are fully reversible and exhibit a steep rise at low pressures then reach 188 and 131 mg/g at 273 and 298 K, respectively. The Qₑ for CO₂ was estimated from adsorption data collected under these conditions using the virial method. At zero coverage, the Qₑ is 26.5 kJ/mol and drops to 19.7 kJ/mol as the uptake reaches 188 mg/g (Supporting Information, S17). The CO₂ uptake and Qₑ are higher than the values reported for COFs15,17 imine-linked organic cages,11d or diimide polymers7,10e and comparable to CO₂ selective MOFs8 or ZTF10d which generally feature —NH₂ or —OH functionalized pores. The relatively high CO₂ uptake and binding by BILP-1 are most likely due to favorable interactions of the polarizable CO₂ molecules through hydrogen bonding and/or dipole–quadrupole interactions that utilize the protonated- and proton-free nitrogen sites of imidazole rings, respectively.10b,c

The readily reversible sorption/desorption behavior indicates that CO₂ interactions with pore walls are weak enough to allow for material regeneration without applying heat. This is attractive because materials that have strong acidic or basic sites usually display high CO₂ affinities and require energy input (in the form of heat) to regenerate their active sites as in the case of primary alkylamine MEA.21 This drawback remains one of the great challenges in current CO₂ capture technologies.

Figure 1. Argon uptake isotherm at 87 K; adsorption (filled) and desorption (empty). Inset NLDFT pore size distribution.

Brunauer–Emmett–Teller (BET) model within the pressure range of P/P₀ = 0.05–0.15 resulted in an apparent surface area of 1172 m² g⁻¹ which makes BILP-1 the most porous purely organic benzimidazole-linked polymer reported to date.22 This surface area is comparable to the reported values for 3-D crystalline imine-linked COF-300 (1360 m² g⁻¹),16b POFs (466–1521 m² g⁻¹),14a and diimide-based polymers (750–1407 m² g⁻¹).17e
In addition to CO$_2$ capture and separation by porous materials, extensive studies on hydrogen and methane storage have been reported because of their potential in automotive applications. The hydrogen isotherms depicted in Figure 2B are fully reversible and the uptake reaches 19 and 14 mg/g at 77 and 87 K, respectively. The $Q_d$ for H$_2$ was calculated from adsorption data collected at 77 and 87 K. At zero-coverage, the $Q_d$ is 7.9 kJ/mol which shows a gradual drop as more hydrogen gets adsorbed and reaches 5.8 kJ/mol at 1.9 wt % loading (Supporting Information, S18). The $Q_d$ value is higher than the values reported for organic polymers such as of COFs (6.0–7.0 kJ/mol),$^{19}$ PAF-1 (4.6 kJ/mol),$^5$ polyimide networks (5.3–7.0 kJ/mol),$^{17a}$ and PPNs (5.5–7.6 kJ/mol).$^7$ Similarly, we recorded CH$_4$ uptake at 273 and 298 K up to 1 bar (Figure 2C). Again, both isotherms are completely reversible and exhibit a step rise at low pressure and then reach maxima of 23 and 16 mg/g at 273 and 298 K, respectively. The $Q_d$ for CH$_4$ was calculated by using adsorption data collected at 273 and 298 K. At zero coverage, the $Q_d$ is 16.3 kJ/mol which drops to 10.0 kJ/mol at 23.0 mg/g loading (Supporting Information, S19). A noticeable lower $Q_d$ value of CH$_3$O than that of CO$_2$ is due to the nonpolar nature of methane. We have also considered the selective uptake of small gases (CO$_2$, CH$_4$, N$_2$) to evaluate the potential use of BILP-1 in gas separation applications. The selectivity of BILP-1 toward CO$_2$ over N$_2$ and CH$_4$ was investigated by collecting isotherms at 273 and 298 K (Supporting Information, S20). At 273 K and 0.1 bar, which is a typical partial pressure of CO$_2$ in flue gases, the CO$_2$ uptake is 1.28 mmol/g whereas that of N$_2$ is only 0.03 mmol/g. On the basis of initial slope calculations in the pressure range of 0 to 0.1 bar, the estimated adsorption selectivity for CO$_2$ over N$_2$ is 70 (Figure 2D). This selectivity surpasses carbon-based materials$^{23}$ or ZIFs$^9$ and is comparable to Bio-MOF-11 (81)$^{30}$ and non-covalent porous materials (NPMs) (74).$^{54}$ Furthermore, the CO$_2$ selectivity of BILP-1 over CH$_4$ was calculated using initial slopes calculations (10 at 273 K and 7 at 298 K). Again, these values exceed those reported for activated carbon and ZIFs, as well as that of the recently reported dimide polymer. The high selectivity of CO$_2$ over N$_2$ and CH$_4$ stems from the fact that under the above-mentioned conditions, the imidazole moieties of BILP-1 interact more favorably with the polarizable CO$_2$ molecules through hydrogen bonding and/or dipole–quadrupole interactions involving the protonated- and proton-free nitrogen sites, respectively.

In conclusion, we have proved that a simple template-free synthesis of BILP-1 makes it attractive for use in proton-ion exchange membrane fuel cells (PEMFCs) or to enhance selective gas uptake. These aspects are currently being addressed in our laboratory.

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**References**


(15) Elemental analysis for $\text{C}_{119}\text{H}_{84}\text{N}_{24} \cdot 12\text{H}_2\text{O}$. Calculated: C, 74.99; H, 4.27; N, 13.20%. Found: C, 73.81; H, 4.97; N, 12.65%.


