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Selective CO₂ adsorption in a porphyrin polymer with benzimidazole linkages†

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Venkata S. Pavan K. Neti,^a Jun Wang,^b Shuguang Deng^b and Luis Echegoyen^{*a}

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A new nanoporous porphyrin-based benzimidazole linked polymer, PBILP, was synthesized. The use of porphyrin monomers as molecular building units led to the formation of a rigid amorphous network that has a moderate surface area ($S_{\text{BET}} = 557 \text{ m}^2 \text{ g}^{-1}$). The CO₂ adsorption ability of PBILP is 12.1 wt% (2.76 mmol g⁻¹) and it has a CO₂/CH₄ selectivity of 7.2 at 273 K/1 bar and a CO₂/N₂ selectivity of 72 at 273 K/1 bar.

The synthesis of nitrogen rich microporous materials has gained significant attention due to their potential as solid adsorbents for CO₂ capture. These microporous materials include, but are not limited to, metal-organic frameworks (MOFs),¹ zeolitic imidazolate frameworks (ZIFs),² and hypercross-linked microporous polymers (BILPs, POPs, *etc.*).³⁻⁶ The key strategy to develop new and efficient POPs mainly relies on the design of nitrogen rich building blocks that possess high surface areas. In fact, many examples of new ligands and linkages have expanded the versatility of the resulting functional microporous materials. These materials have found a wide variety of applications in gas storage and separation,³⁻⁶ heterogeneous catalysis,⁶ *etc.* POPs and their membranes are best suited for selective gas adsorption and gas separation applications due to their physical, chemical, high temperature and pressure stabilities, and their resistance towards moisture, and basic and acidic conditions.^{4a,5a} Recently, Hupp and Nguyen *et al.* reported an Al-porphyrin based POP for supercritical CO₂ processing and for the degradation of nerve agents.^{6d} El-Kaderi *et al.* developed benzimidazole-linked polymers (BILPs),^{5a} azo-linked polymers (ALPs),^{5e} and Zhang *et al.* reported imine linked polymers (ILPs),^{4b} and Uyama *et al.* reported N-doped activated carbon monoliths for selective CO₂ capture. Some

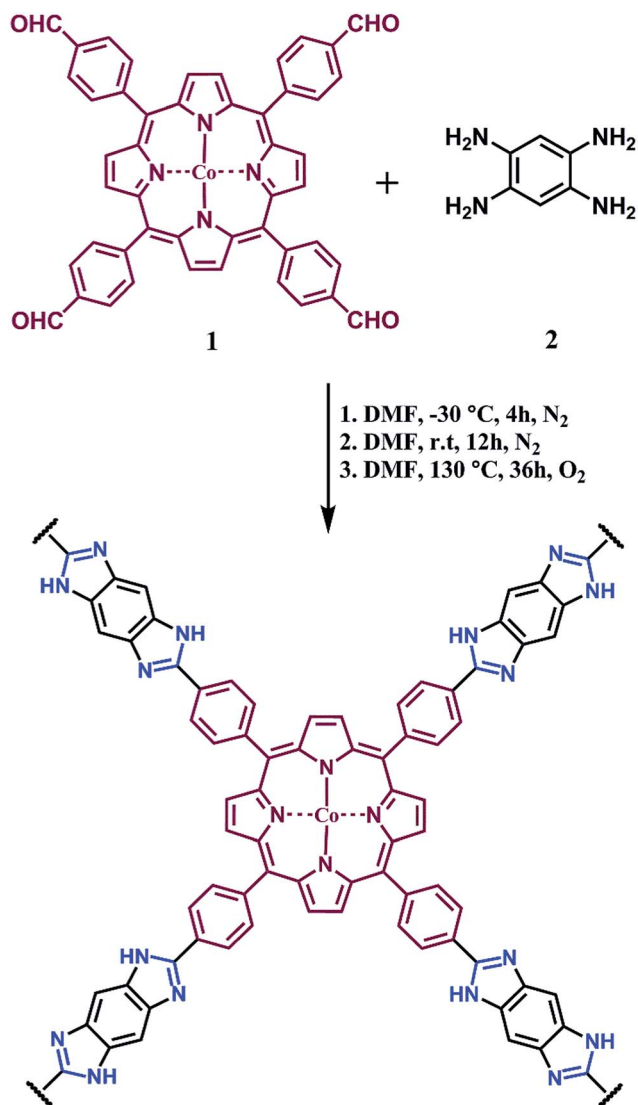
advantages of porous polymers over activated carbons are higher CO₂/N₂ selectivity and efficient and reversible capture of CO₂. On the other hand, advantages of the micro- and mesoporous activated carbons over the porous polymers are the low cost of the raw material and the high CO₂ uptake. The selective CO₂ adsorption in these frameworks over CH₄ or N₂ is believed to arise as a consequence of CO₂-framework interactions through R-N(δ^-)-C(δ^+)O₂.

In order to expand the BILP chemistry to porphyrins, we focused on carboxaldehyde based porphyrin, specifically *meso*-tetra-(4-phenylformyl) porphyrin (TCPP, **1**), and benzene-1,2,4,5-tetramine (BTA, **2**). We have prepared a porphyrin benzimidazole linked polymer (PBILP) containing polybenzimidazole linkages as shown in Scheme 1. Part of the motivation behind this work is to demonstrate the capture of high amounts of CO₂ in a metalloporphyrin porous polymer. In the future we want to convert the captured CO₂ to polycarbonates or other polymers, similar to a report using cobalt-porphyrins to effect this catalytic transformation.^{7a} High nitrogen and cobalt content of PBILP can be used for selective CO₂ adsorption and also for catalytic transformations. In this report, we describe the synthesis and characterization of PBILP and the selective CO₂ adsorption properties. The synthesis of PBILP was accomplished by the condensation reaction between **1** and **2**, which is similar to a BILP synthesis reported by El-Kaderi *et al.* with a slight modification (see ESI†).^{5a} Compound **1** was synthesized following a similar literature procedure.^{7b} A homogeneous solution of **1** was added drop-wise to the suspension of **2** in *N,N*-dimethylformamide (DMF) over 4 h while stirring at the -30 °C, followed by stirring at room temperature for 12 h. The reaction yielded a purple suspension which was bubbled with O₂, and then heated at 130 °C for 36 h. The slow addition of **1** to **2** yielded the PBILP in a 60% yield as a purple solid. The resulting purple polymeric solid was unambiguously characterized by spectral and analytical methods. The PBILP was designed to possess a 2D network structure arising from the four benzimidazole-linkages (Scheme 1). It is well known that during the course of polymerization, planar

^aDepartment of Chemistry, University of Texas at El Paso, El Paso, TX 79968, USA. E-mail: echegoyen@utep.edu; Fax: +1-915-747-8807; Tel: +1-915-747-7573

^bDepartment of Chemical Engineering, New Mexico State University, Las Cruces, NM 88003, USA

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Scheme 1 Synthesis of PBILP from *meso*-tetra(4-formylphenyl)porphyrine and benzene-1,2,4,5-tetramine.

porphyrins have a tendency to stack *via* π - π interactions. Consequently, the majority of porphyrin porous polymers are interpenetrating networks with relatively low total pore volumes.⁶ Thus we chose one large porphyrin building unit and one small building unit to reduce interpenetration. In fact, a small degree of interpenetration is observed in the polymeric skeleton (Fig. 2a).

The PBILP is stable and insoluble in common organic solvents, water. PBILP is also stable in a 2 M solution of HCl or NaOH and its elemental analysis did not indicate any decomposition, moreover the color of the material was unchanged. Due to the insoluble nature of the PBILP in organic solvents, FT-IR and solid-state ¹³C cross polarization, magic angle spinning (CP-MAS) NMR characterization was performed. A peak at about 1000 cm⁻¹ in the FT-IR spectra of TCPP and PBILP is assigned to the Co-N stretching frequency, indicating the presence of Coporphyrin units in the PBILP polymer. A new stretch appeared

at 1482 cm⁻¹, which is assigned to the C=N stretching of the benzimidazole ring.^{5a} The broad band at around 1630 cm⁻¹ is presumably due to the overlap of C=C and C=N stretching bands, which is in good agreement with previous reports.^{5a} In addition, the absence of a C=O stretching band at ~1700 cm⁻¹ in PBILP indicates the full consumption of compound 1 (Fig. S1, ESI[†]). The ¹³C CP-MAS NMR spectrum exhibited a signal at δ = 153 ppm which corresponds to benzimidazole linkages and this is in good agreement with other reported benzimidazole frameworks.^{5a} Other peaks at δ = 131.3 and 93.7 ppm were assigned to the aromatic carbon atoms of the PBILP (Fig. S2, ESI[†]).

A scanning electron microscopy (SEM) image of PBILP (Fig. S3, ESI[†]) shows spherical-shaped irregular submicrometer particles with sizes between 50 and 100 nm. To evaluate the porosity of PBILP, N₂ adsorption-desorption isotherms were measured at 77 K (Fig. 1). The N₂-adsorption isotherms indicated Brunauer-Emmett-Teller (BET) and Langmuir surface areas of 557 and 1077 m² g⁻¹, respectively. The BET surface area of PBILP is lower than for other porphyrin polymers obtained by triazine/carbazole linkages (Table 2).^{9f,i} The increase in the N₂ adsorption at P/P_0 = 0.9 may arise in part from interparticulate porosity associated with the intertwined nano- and microporous nature of PBILP. The pore size distribution analyzed by using non-local density functional theory (NLDFT) further confirmed the nanoporosity nature of the material. The dominant pore size of PBILP is around 6 Å (Fig. 2a). Conjugated polymers with nanopores interact effectively with small gas molecules through improved molecular interactions.

The reasonably high surface area and nitrogen rich functional groups of PBILP are conducive to CO₂ adsorption. The CO₂, CH₄, N₂ and H₂ adsorption isotherms of PBILP were measured at 77, 273, and 298 K, 1 atm and the data are summarized in Table 1. The isotherms show slight hystereses on desorption (Fig. 2). The PBILP shows a CO₂ uptake of 2.76 mmol g⁻¹ (12.1 wt%) at 273 K and 1.8 mmol g⁻¹ (7.9 wt%) at 298 K, 1 atm (Fig. 2b). The isosteric heat (Q_{st}) of the CO₂ adsorption at low coverage is 25.7 kJ mol⁻¹, calculated using the Clausius-

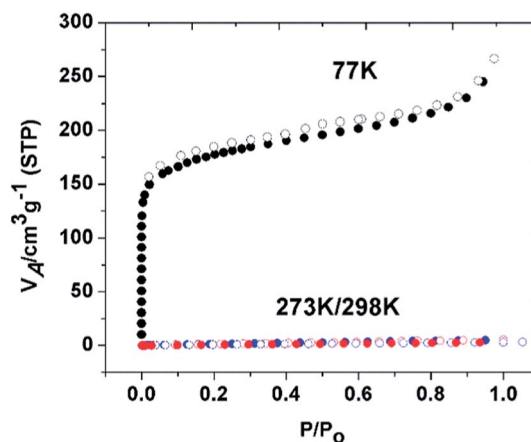


Fig. 1 Adsorption (filled circles) and desorption (empty circles) for N₂ at 77 K (black), 273 K (blue), and 298 K (red).

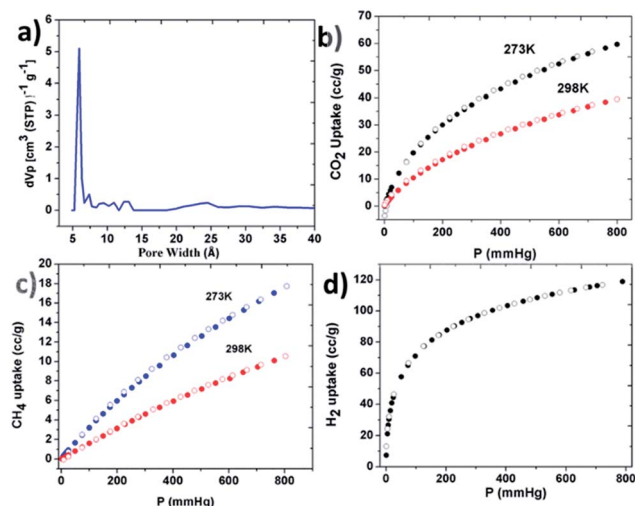


Fig. 2 (a) NLDFT pore width analysis (b) CO₂ at 273 K and 298 K (c) CH₄ at 273 K and 298 K (d) H₂ at 77 K. Adsorption (filled symbols) and desorption (empty symbols).

Clapeyron equation (Fig. S6, ESI†) fitting the parameters obtained from the adsorption data measured at 273, and 298 K.^{4f} The data suggest that strong physisorption (<40 kJ mol⁻¹) rather than chemisorption of CO₂ is in effect. According to previous reports, BILPs could be fully reactivated under vacuum at room temperature after CO₂ adsorption and then re-adsorb the same amount of gas.^{5a} The low-coverage Q_{st} values of PBILP are comparable with those for MCTFs [24.5 kJ mol⁻¹] and BILPs (26.5 kJ mol⁻¹),^{6f,i} and are lower than those previously reported for imine, benzothiazole and triazole containing porous polymers, and COFs.^{4,6} Although the BET surface area of PBILP is moderate, the CO₂ adsorption capacity of PBILP is comparable to those for previously reported porphyrin based CPOPs and triazine porphyrin POPs, which had much higher surface areas (Table 2),^{6f,i} and lower than activated carbons.^{6j}

Based on the measured physisorption isotherms with a pressure of up to 1 bar (Fig. 2), we found that PBILP showed a moderate uptake capacity for H₂ (1 wt%) and for CH₄ (1.3 wt%),

Table 1 Gas adsorption properties of PBILP

Polymer	Selectivity	CO ₂ (wt%)	CH ₄ (wt%)
PBILP	72 (CO ₂ /N ₂)	12.1 (273 K)	1.3 (273 K)
	7.2 (CO ₂ /CH ₄)	7.9 (298 K)	0.8 (298 K)

Table 2 Gas adsorption properties of porphyrin polymers

Polymer	CO ₂	CH ₄	S_{BET} (m ² g ⁻¹)
PBILP	12.1 wt%	1.3 wt%	557
MCTF	13.9 wt%	—	1520
CPOP	13.8 wt%	4.7 wt%	1320
BILP-1	18.8 wt%	2.3 wt%	1172
Fe-POP-1	19 wt%	—	875

which are similar to those for some reported porous porphyrins and COFs measured under similar conditions.^{4,6} At zero coverage, the Q_{st} for CH₄ is 18.3 kJ mol⁻¹. A higher Q_{st} value for CO₂ compared to that for CH₄ is likely due to R-N(δ^-)=C(δ^+) O₂ interactions. Furthermore, the selectivity of PBILP towards CO₂ over N₂ and CH₄ was investigated (Fig. S5, ESI†). On the basis of Langmuir model fits and Henry's constant values in the pressure range between 0 and 1 bar, the estimated adsorption selectivity for CO₂/CH₄ is 7.2 and 72 for CO₂/N₂ at 273 K/298 K/1 bar. The thermal stability of the PBILP was examined by thermogravimetric analysis (TGA). The porphyrin monomer appears to have more than a 50% mass loss at around 600 °C, while the cross-linked polymer yields high residual masses of 70% at the same temperature (Fig. S7, ESI†). Comparing the thermogravimetric results of the polymer-network and the corresponding monomer, it is evident that Co-porphyrin oxidative coupling polymerization occurs. The powder X-ray diffraction pattern of the synthesized PBILP revealed no diffraction peaks, indicating that it is amorphous.

Conclusions

In conclusion, we have synthesized, characterized, and described the use of a benzimidazole-linked porphyrin-based porous polymer, PBILP, for CO₂ capture. Similar to Wang's cobalt porphyrin catalyst, the BILP could be used as a heterogeneous catalyst to convert the captured CO₂ to poly(propylene carbonate) and other carbonate based polymers. In addition to the promising selective CO₂ adsorption, PBILP also showed some storage capacity for H₂ at 77 K and for CH₄ at 273 K. The PBILP possesses high thermal and chemical stability, relatively high surface area, and its porosity can be tuned by changing the reaction conditions.

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