

Selective CO₂ capture in an imine linked porphyrin porous polymer†Cite this: *Polym. Chem.*, 2013, **4**, 4566Venkata S. Pavan K. Neti,^a Xiaofei Wu,^b Shuguang Deng^b and Luis Echegoyen^{*a}

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A new microporous imine-linked porous porphyrin polymer, CuPor-BPDC, has been solvothermally synthesized. The CuPor-BPDC showed high CO₂ capture (5.5 wt% at 273 K/1 bar) and very good selectivity for CO₂/CH₄ adsorption (5.6) at 1.0 bar and 273 K, and exhibited a BET surface area of 442 m² g⁻¹ with high thermal stability (up to 400 °C), thus showing good potential for CO₂ capture.

Imine-linked covalent organic frameworks¹ (COFs) and porous organic polymers² (POPs) are crystalline and amorphous porous networks containing robust polymeric C=N bonds. These materials have attracted significant attention due to their ability to capture CO₂ through $R = N(\delta^-) - C(\delta^+)O_2$ interactions.³ C-N linkages can also be found in other types of crystalline and amorphous materials such as hydrazone⁴ and triazine⁵ based frameworks. Boronate ester and boroxine based COFs⁶ are known for the reactivity of the B-O bonds towards moisture, hence C-N based crystalline or amorphous porous materials are better alternatives for practical applications such as CO₂ capture, and for H₂ and CH₄ storage. Although high pressures are typically needed for relatively high gravimetric and volumetric H₂ and CH₄ storage, this is not necessary for CO₂ capture. Metal Organic Frameworks⁷ (MOFs) and some of the POPs⁸ have already achieved enhanced gas storage values at low and high pressures, hence the development of robust π -electron rich and conjugated materials with relatively high gas uptake capacities is a promising endeavor. Porphyrins are stable and intensely colored aromatic macrocyclic compounds that can be found in many co-ordination complexes and optoelectronic devices.⁹ Only one imine-linked porphyrin COF has been reported containing Cu as a central metal ion. A free-base

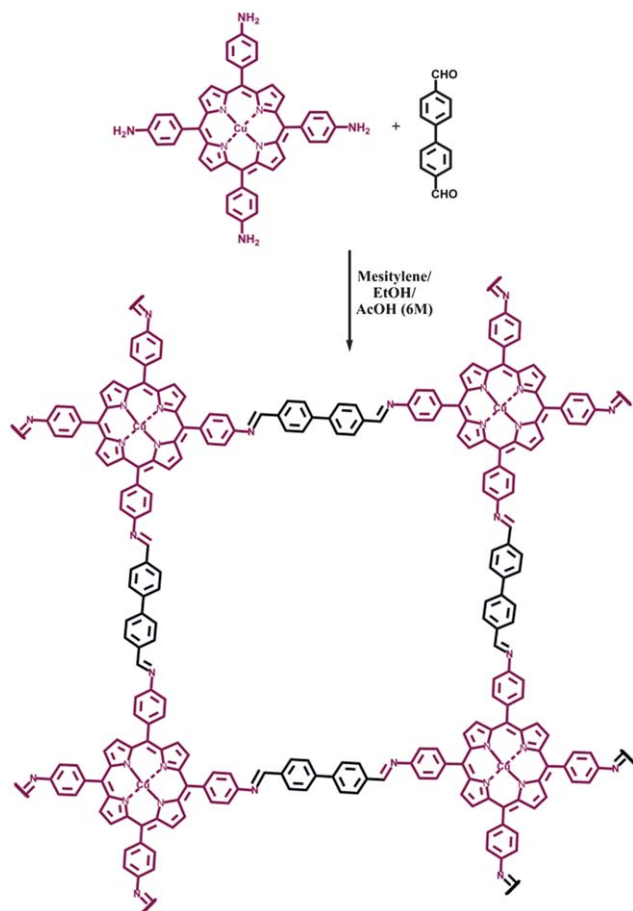
porphyrin imine-linked COF was also used in the development of optoelectronic materials for high charge carrier mobility.^{1b,e} To the best of our knowledge, the use of an imine linked porphyrin COF or porous polymer for CO₂ capture, or for H₂ and CH₄ storage has not been reported. One of the advantages of metallated porphyrin incorporation into a framework is that the metal sites can mimic the function of secondary building units (SBU's) in MOFs. Here we report a new imine-linked porous porphyrin polymer, CuPor-BPDC, which has been synthesized *via* a Schiff base condensation reaction between 5,10,15,20-tetrakis (*p*-tetraphenylamino) porphyrin Cu(II) (**1**) and 4,4'-biphenyl dicarboxaldehyde (**2**) (Scheme 1).

The CuPor-BPDC was synthesized under solvothermal conditions in a mixture of mesitylene and ethanol and acetic acid (6 M) as the catalyst to activate the carbonyl groups (1/1/0.1 v/v) in a sealed glass ampoule at 120 °C for 72 h (see ESI†). The CuPor-BPDC exhibits a CO₂ adsorption capacity of 5.5 wt% and a CH₄ capacity of 0.6 wt% at 273 K, 1 bar and an adsorption capacity of 0.4 wt% for H₂ at 77 K/1 bar. The chemical connectivity and composition of the CuPor-BPDC were characterized by several methods such as infrared spectroscopy, powder X-ray diffraction (PXRD), solid-state ¹³C CP-MAS NMR, surface area measurements, solid-state UV-Vis, thermogravimetric and elemental analysis. The CuPor-BPDC was isolated in 69% yield as a purple powder after thorough washing with dioxane and tetrahydrofuran and was insoluble in other organic solvents such as dimethylsulfoxide, dichloromethane, *N,N*-dimethylformamide, acetone *etc.* The formation of imine bonds between **1** and **2** (see ESI†) was confirmed by FT-IR which exhibited a new characteristic C=N stretching frequency at 1690 cm⁻¹ (Fig. S1 and S2, ESI†). The FT-IR spectrum also showed highly attenuated N-H and C=O stretching frequencies from the meso-tetraphenylamino porphyrin and 4,4'-biphenyl dicarboxaldehyde at 1500 cm⁻¹ and 1740 cm⁻¹. The solid-state ¹³C cross polarization, magic angle spinning (CP-MAS) NMR spectra (Fig. S3 and S4, ESI†) further support the formation of the imine bond formation between **1** and **2** and the incorporation of these monomers into the framework of

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Scheme 1 Synthesis of CuPor-BPDC POP from meso-tetrakis(p-aminophenyl)porphyrin and 4,4'-biphenyl dicarboxaldehyde.

CuPor-BPDC. The solid-state ^{13}C CP-MAS NMR spectrum of the CuPor-BPDC showed a new $\text{C}=\text{N}$ bond characteristic signal at $\delta = 158.41$ which was not present in the solid-state NMR spectrum of the tetrakis(*p*-tetraphenylamino) porphyrin Cu(II). Other peaks at $\delta = 173.56, 137.51, 128.66, 105.85$ ppm, were assigned to the carbon atoms of the CuPor-BPDC by comparison with the spectrum of the porphyrin (see ESI†). The ^{13}C CP-MAS spectra of the CuPor-BPDC and meso-tetrakis(p-aminophenyl)porphyrin copper display similar chemical shifts to those of other reported COFs and starting materials.^{1b} Powder X-ray diffraction (Cu $K\alpha$ radiation) was employed to probe the solid-state packing and crystallinity of the as-synthesized CuPor-BPDC. The diffraction pattern (Fig. 1) displays a low intensity diffraction peak at a $2\theta = 3^\circ$, and another very weak intense peak at 5.8 , reflecting a mostly amorphous or partially crystalline CuPor-BPDC.

The porous morphology of CuPor-BPDC was also observed by scanning electron microscopy (SEM). The SEM image revealed randomly aggregated particles and a flake-like morphology of the purple CuPor-BPDC powder (Fig. 2). The gas uptake capacities of CuPor-BPDC were found by measuring nitrogen and hydrogen adsorption/desorption isotherms at 77 K, 1 bar and 273 K and 298 K, 1 bar in the case of CH_4 and CO_2 .

The rapid nitrogen uptake at low pressure (0–0.1 bar) and the gradual increase at higher pressures (0.1–1 bar) result in a type

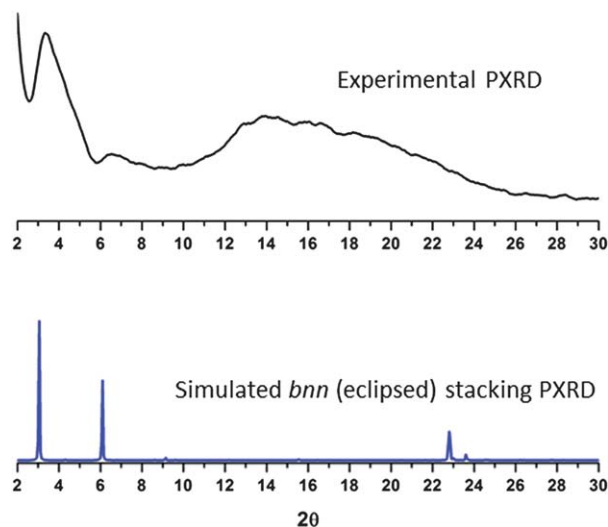


Fig. 1 Powder X-ray diffraction pattern of CuPor-BPDC (above) and eclipsed stacking simulated PXRD pattern (below).

II isotherm (Fig. 3a), which is typical for microporous materials that show permanent microporosity. A surface area of $442 \text{ m}^2 \text{ g}^{-1}$ was obtained by applying the Brunauer–Emmett–Teller (BET) model and a surface area of $933 \text{ m}^2 \text{ g}^{-1}$ was obtained by applying the Langmuir model within the pressure range of $P/P_0 = 0\text{--}1$ bar. These values are comparable to those for other amorphous nanoporous organic polymer networks.² The total pore volume and average pore size were calculated from the nitrogen isotherms by applying the nonlocal density functional theory (NLDFT) method, and found to be approximately $0.41 \text{ cm}^3 \text{ g}^{-1}$ at single point adsorption ($P/P_0 = 0.97$) and 21 \AA , (Fig. S8, ESI†).

Efficient and selective separation of CO_2 from other gases in the atmosphere continues to be a major challenge. At present, organoamine solutions are commercial products used to capture CO_2 . Porous solid adsorbents such as porous organic polymers are an alternative approach to amine solutions, because regeneration of the amine solutions requires considerable energy and they are also highly corrosive. We evaluated the adsorption properties and selectivity of CO_2 , CH_4 and H_2 uptake by CuPor-BPDC at low pressures and different temperatures. At 273 K/298 K, 1.0 bar, CuPor-BPDC stores up to 5.5/3.2 wt% of CO_2 with good selectivity (5.6/4.7) over CH_4 under the same conditions. These likely results by donation of the nitrogen lone pair in the imine bond to carbon dioxide. The electron rich building blocks of CuPor-BPDC, connected by

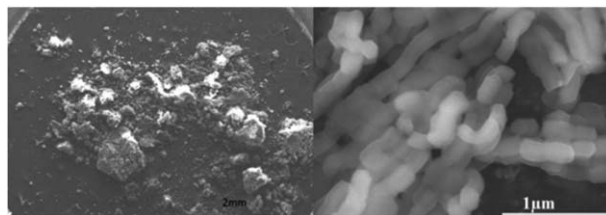


Fig. 2 Scanning electron microscope image of the CuPor-BPDC.

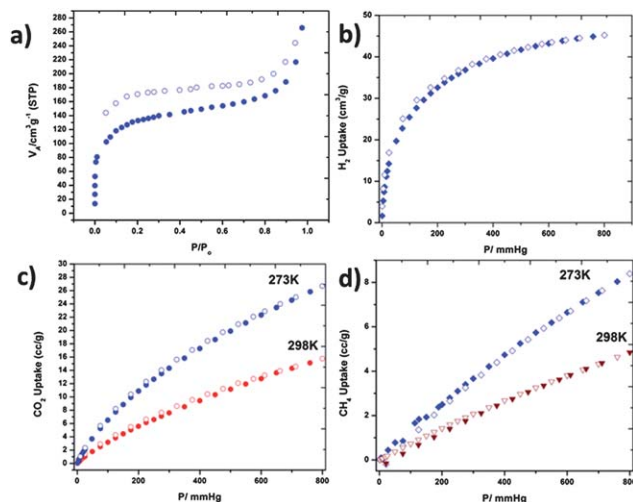


Fig. 3 (a) Nitrogen at 77 K (b) hydrogen at 77 K (c) CO₂ at 273 K and 298 K (d) CH₄ at 273 K and 298 K adsorption (filled symbols) and desorption (empty symbols) isotherm curves.

the imine bond pore walls are also interaction sites for CO₂ binding. Increasing the internal molecular free pore volume by expanding the length of the building blocks could enhance the porosity for the uptake of CO₂. The CuPor-BPDC CO₂ uptake (1.25 mmol g⁻¹) is only slightly lower than for other imine-linked COFs (1.36 mmol g⁻¹/273 K, 1 bar), and significantly lower than for benzimidazole polymers which can store up to 5.12 mmol g⁻¹ at 273 K/1 bar. Low adsorption levels for H₂ (0.4 wt%, 77 K) and CH₄ (0.32 wt%, 298 K), as shown in Fig. 3b and d, preclude its use as an energy storage material. The hydrogen uptake is lower than for many of the reported imine linked porous organic polymers under similar conditions, but considerably lower than those of the best performing metal organic frameworks and metal doped 2D or 3D COFs. The lower H₂ and CH₄ uptake capacity of CuPor-BPDC is consistent with its microporous nature that does not facilitate gas storage under low pressure. The isosteric heats of adsorption (Q_{st}) values were calculated (Fig. S9, ESI[†]) at zero coverage by calculating Henry's constants and using the Van't Hoff equation from the CO₂ and CH₄ isotherms at 273 K and 298 K. The Q_{st} values for CO₂ and CH₄ are 20.6 kJ mol⁻¹ and 15.7 kJ mol⁻¹, slightly higher than for other reported imine linked polymers and COFs.^{1d} The reversible adsorption/desorption behavior and moderate Q_{st} values of CuPor-BPDC indicate that CO₂ and CH₄ interactions with the pore walls are weak enough to allow for material regeneration without applying heat. The relatively lower adsorption of CH₄ relative to the value obtained for H₂ may be size related. The solid-state UV-vis diffuse reflectance spectra of CuPor-BPDC provides an insight of the molecular organization of the porphyrin chromophores in the CuPor-BPDC polymer network which is evident from the slightly faded purple color of the polymer samples. The UV-vis diffuse reflectance spectra (Fig. S6, ESI[†]) of CuPor-BPDC showed broad peaks from 200 to 800 nm with maxima at 410 nm, whereas two separated bands with maxima at 474 and 560 nm were observed. To measure the

thermal stability of CuPor-BPDC, the as-synthesized sample was subjected to thermogravimetric analysis under a flow of nitrogen (Fig. S7, ESI[†]). The TGA trace is similar to those of other reported imine linked porous organic polymers and COFs, retaining 80% of the mass at 400 °C.

Conclusions

In conclusion, we have synthesized, characterized and described the use of an imine linked porphyrin based porous polymer framework, CuPor-BPDC, for CO₂ capture. In addition to the promising selective CO₂ capture properties, CuPor-BPDC also showed some storage properties for H₂ at 77 K and for CH₄ at 273 and 298 K. Other potential heterogeneous catalytic properties of CuPor-BPDC are under investigation.

Acknowledgements

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References

- (a) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 4570; (b) S. Wan, F. Gándara, A. Asano, H. Furukawa, A. Saeki, S. K. Dey, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. F. Duan, S. Seki, J. F. Stoddart and O. M. Yaghi, *Chem. Mater.*, 2011, **23**, 4094; (c) S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su and W. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 19816; (d) M. G. Rabbani, A. K. Sekizkardes, Z. Kahveci, T. E. Reich, R. Ding and H. M. El-Kaderi, *Chem.-Eur. J.*, 2013, **19**, 3324; (e) X. Chen, M. Addicoat, S. Irle, A. Nagai and D. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 546.
- (a) P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Wu, M. G. Kanatzidis and S. T. Nguyen, *Chem. Mater.*, 2010, **22**, 4974; (b) J. Ma, M. Wang, Z. Du, C. Chen, J. Gao and J. Xu, *Polym. Chem.*, 2012, **3**, 2346; (c) E. Verde-Sesto, E. M. Maya, A. E. Lozano, J. G. de la Campa, F. Sanchez and M. Iglesias, *J. Mater. Chem.*, 2012, **22**, 24637; (d) Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630; (e) Y. Jin, Y. Zhu and W. Zhang, *CrystEngComm*, 2013, **15**, 1484; (f) J. Wang, I. Senkowska, M. Oschatz, M. R. Lohe, L. Borchardt, A. Heerwig, Q. Liu and S. Kaskel, *ACS Appl. Mater. Interfaces.*, 2013, **5**, 3160.
- M. Schröder, *et al.*, *Nat. Chem.*, 2012, **4**, 887.
- F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478.
- P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450.
- (a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science.*, 2005, **310**, 1166; (b) R. W. Tilford, W. R. Gemmill, H.-C. zur Loye and J. J. Lavigne, *Chem. Mater.*, 2006, **18**, 5296; (c) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côté,

- R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268; (d) E. L. Spitler and W. R. Dichtel, *Nat. Chem.*, 2010, **2**, 672; (e) X. Ding, J. Guo, X. Feng, Y. Honsho, J. Guo, S. Seki, P. Maitarad, A. Saeki, S. Nagase and D. Jiang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1289; (f) M. Dogru, A. Sonnauer, A. Gavryushin, P. Knochel and T. Bein, *Chem. Commun.*, 2011, **47**, 1707.
- 7 (a) J. Sculley, D. Yuan and H.-C. Zhou, *Energy Environ. Sci.*, 2011, **4**, 2721; (b) M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782; (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
- 8 (a) M. G. Rabbani, T. E. Reich, R. M. Kassab, K. T. Jackson and H. M. El-Kaderi, *Chem. Commun.*, 2012, **48**, 1141; (b) T. E. Reich, S. Behera, K. T. Jackson, P. Jena and H. M. El-Kaderi, *J. Mater. Chem.*, 2012, **22**, 13524; (c) K. V. Rao, R. Haldar, C. Kulkarni, T. K. Maji and S. J. George, *Chem. Mater.*, 2012, **24**, 969; (d) M. R. Liebl and J. Senker, *Chem. Mater.*, 2013, **25**, 970.
- 9 X. Feng, L. Chen, Y. Dong and D. Jiang, *Chem. Commun.*, 2011, **47**, 1979.