

Synthesis of a phthalocyanine 2D covalent organic framework†

Cite this: *CrystEngComm*, 2013, 15, 7157

Received 10th June 2013,

Accepted 19th July 2013

DOI: 10.1039/c3ce41091a

www.rsc.org/crystengcomm

Venkata S. Pavan K. Neti,^a Xiaofei Wu,^b Mahsa Hosseini,^a Ricardo A. Bernal,^a Shuguang Deng^b and Luis Echegoyen^{*a}

A new two-dimensional cobalt based phthalocyanine covalent organic framework (CoPc-BPDA COF) has been synthesized under solvothermal conditions. CoPc-BPDA COF exhibits a high surface area ($S_{\text{BET}} = 1087 \text{ m}^2 \text{ g}^{-1}$), and it can store up to 1.2 wt% of hydrogen at 77 K and 1 bar.

Covalent organic frameworks¹ (COFs) are structurally precise, crystalline materials that have attracted significant attention due to their potential applications in efficient gas adsorption² (H_2 , N_2 , CO_2 , NH_3), in catalysis,³ and importantly, in optoelectronic devices.⁴ Dichtel *et al.* and Jiang *et al.* reported octahydroxyphthalocyanine based COFs for photocurrent generation by attaching appropriate boronic acid groups to the phthalocyanine with well-defined geometries.⁵ Recently, Pd@COF-102 (9.5 wt%) and PdCl₂@COF-301 (4.2 wt%) were shown to possess higher hydrogen storage properties at 298 K than the metal-free COF-102 (5.2 wt%) and COF-301 (0.44 wt%) by themselves.⁶ Using density functional theory (DFT) calculations it was also shown that lithium-doped free base phthalocyanine COF (5.3 wt%)⁷ and lithium-doped fullerene intercalated 2D layered free base phthalocyanine COFs (12 wt%)⁸ should exhibit superior hydrogen storage capabilities at 77 K, 298 K and 100 bar compared to lithium-free (3.7 wt%) and Li@fullerene free phthalocyanine COFs (4.2 wt%). Iron containing nanoporous porphyrin polymers with high surface areas were shown to possess high hydrogen storage capacities (5 wt%) when compared to free-base porphyrin polymers due to the presence of metal–hydrogen interactions in the former.⁹ Although 2D layered COFs show lower hydrogen storage capacities when compared to 3D COFs,² metallated phthalocyanine based 2D COFs exhibit the advantage of hosting a variety of metals in the core of the phthalocyanines. Phthalocyanines are ubiquitous in many applications such as in liquid crystals, luminescent devices and organic light emitting diodes¹⁰ (OLEDs), mainly due to their stability,

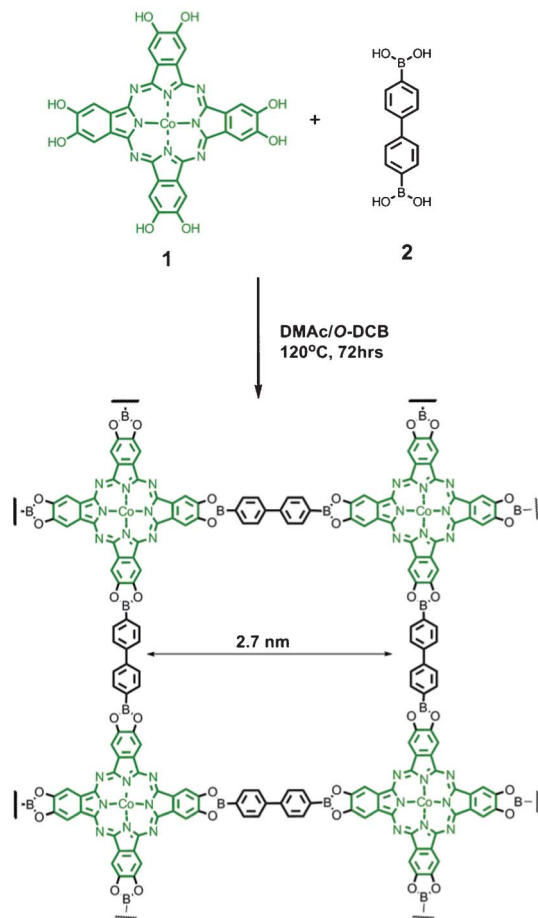
planarity, and rigidity. Phthalocyanines can also bind a wide variety of metals such as Pd, Fe, Co *etc.* Incorporation of these transition metal ions into the core of the phthalocyanine should increase the hydrogen storage capacities of metallated phthalocyanine COFs due to the presence of metal–H₂ interactions. A few metallophthalocyanine COFs have been reported with Zn, Ni, or Co central ions, but the hydrogen and methane storage properties at low or high pressure have not been reported. Thus we decided to investigate the hydrogen and methane storage properties of a cobalt based phthalocyanine COF having Co–H₂ interactions at low pressure and at different temperatures. Here we report a new boronate ester based metallated phthalocyanine COF that exhibits high surface area and hydrogen and methane storage properties. The COF is based on octahydroxy phthalocyanine Co(II) (**1**) and 4,4'-biphenyl bisboronic acid (**2**) (Scheme 1).

The CoPc-BPDA COF was synthesized under solvothermal conditions in a mixture of *o*-dichlorobenzene and dimethylacetamide (1/2 v/v) in a sealed glass ampoule at 120 °C for 72 h (see, ESI†). The CoPc-BPDA COF was characterized by solid-state ¹¹B and ¹³C CP-MAS NMR, Powder X-ray diffraction, infrared spectroscopy, surface area measurements and elemental analysis. The COF was isolated in 80% yield as a green powder and was insoluble in a variety of common organic solvents (such as dichloromethane, tetrahydrofuran, *N,N*-dimethylformamide, dimethylsulfoxide *etc.*). The formation of boronate ester bonds between **1** and **2** (see ESI†) was first established by FT-IR which exhibited a new stretching frequency at 1330 cm⁻¹ including attenuation of peaks at 3400 cm⁻¹ and 3350 cm⁻¹, which correspond to hydroxyl groups of the phthalocyanine and boronic acids, respectively. Powder X-ray diffraction (Cu K α radiation) was employed to find out the crystalline nature of the as-synthesized CoPc-BPDA COF. The experimental diffraction pattern (Fig. 1) displays an intense diffraction peak at a 2θ angle (d -spacing) of 3.23° (27.3 Å), less intense peaks at 4.56° (19.3 Å), 6.46° (13.66 Å), 9.7° (9.10 Å), 12.95° (6.83 Å) and a broad peak at 24.4° (3.55 Å). With cell parameters of $a = 27.322 \text{ \AA}$ and $c = 3.55 \text{ \AA}$, this pattern was indexed into a primitive tetragonal unit cell similar to other primitive tetragonal reported NiPc and ZnPc COFs.⁵ Using the Materials Studio modeling suite of programs, crystal models were

^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

† Electronic supplementary information (ESI) available: Experimental details, Fig. S1–S10. See DOI: 10.1039/c3ce41091a



Scheme 1 Synthesis of CoPc-BPDA COF from 4,4'-biphenylboronic acid and (OH)₈Pc Co(II).

generated, from eclipsed stacking sheets of CoPc-BPDA COF (Fig. 1 inset) in a *sql* topology¹¹ using the space group *P4/mmm*, resulting in simulated cell parameters of $a = 27.30 \text{ \AA}$ and $c = 3.652 \text{ \AA}$, which match the indexed values. The simulated powder X-ray diffraction pattern also matched well the measured pattern (Fig. 1). The powder XRD pattern of CoPc-BPDA COF was subjected to Pawley refinement which produced refined PXRD curves with lattice parameters of $a = 26.65 \text{ \AA}$ and $c = 3.55 \text{ \AA}$ with good residuals (see ESI†).

The solid-state ¹¹B and ¹³C cross polarization with magic angle spinning (CP/MAS) NMR spectra (Fig. S3–S6, ESI†) further support the formation of the boronate ester bond between **1** and **2** and the incorporation of these monomers into the CoPc-BPDA COF framework. Solid-state ¹³C CP-MAS NMR spectra of the CoPc-BPDA COF show five signals at $\delta = 172.34, 155.94, 144.34, 127.94,$ and 105.28 ppm , which were assigned to the carbon atoms of the phthalocyanine and phenyl groups by comparing to the spectrum of octahydroxy phthalocyanine Co(II) (see ESI†). The ¹¹B MAS NMR spectra of the CoPc-BPDA COF and BPDA display similar features to those of other COFs and starting materials.¹ The layered structure of the COF was also observed by scanning electron microscopy (SEM) and Cryo electron microscope (Cryo-EM). The SEM image revealed the layered sheet structure (Fig. 2a) and the

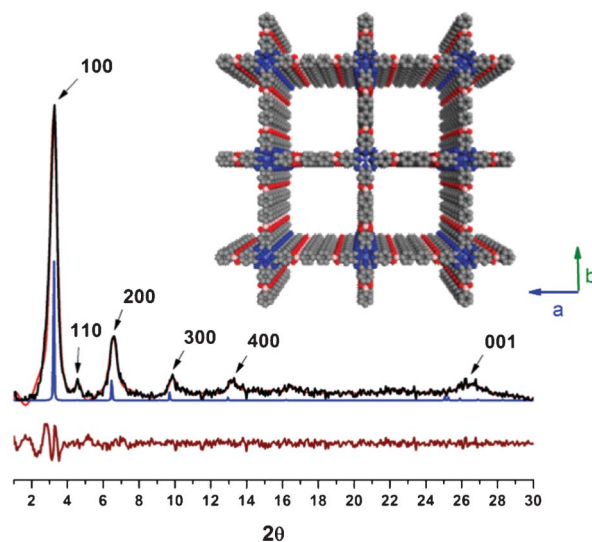


Fig. 1 XRD pattern of CoPc-BPDA COF in black, Pawley refined profile in red, and the difference plot in purple (observed minus refined profiles). The calculated XRD pattern from the proposed models is shown in blue. Inset: eclipsed stacking representation of CoPc-BPDA COF based on powder diffraction and modeling projected along the *c*-axis view (H atoms are omitted).

Cryo-EM measurements showed the porous nature of the CoPc-BPDA COF (Fig. S9, ESI†).

To measure the thermal stability of CoPc-BPDA COF, the as-synthesized sample was subjected to thermogravimetric analysis under a flow of nitrogen (Fig. S8, ESI†). The TGA trace is typical of other reported boronate ester based COFs, retaining 80% of the mass at 300 °C. To investigate the permanent porosity we measured the surface area of the CoPc-BPDA COF, nitrogen adsorption isotherms were measured at 77 K. The N₂ uptake displays a type IV isotherm (Fig. 3a), typical of mesoporous materials and with reversible sorption profiles with a Brunauer–Emmet–Teller (BET) surface area of 1087 m² g⁻¹. The total pore volume was calculated to be 0.573 cm³ g⁻¹ and the average pore size was calculated using nonlocal density functional theory (NLDFT), and found to be approximately 2.26 nm (see ESI†). As we have stated earlier, metallated or metal-doped COFs are among the most promising materials for gas storage, hydrogen in particular. We evaluated the physisorption of H₂ and CH₄ on CoPc-BPDA COF at low pressures and different temperatures. The



Fig. 2 (a) Scanning electron microscope (SEM) image CoPc-BPDA COF powder.

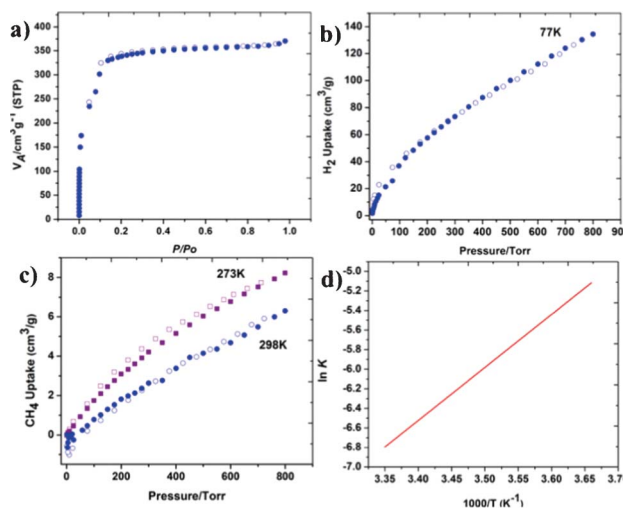


Fig. 3 (a) Nitrogen at 77 K (b) hydrogen at 77 K (c) methane at 273 K and 298 K. Adsorption (filled symbols) and desorption (empty symbols) isotherm curves (d) Van't Hoff plot for CH_4 isotherms.

hydrogen uptake of CoPc-BPDA COF at 77 K, 1 bar is 1.2 wt% (Fig. 3b) which is comparable to other crystalline 2D COFs such as COF-10² (0.8 wt% at 77 K and 1 bar). The hydrogen isotherms are fully reversible with uptake ranges between 0.15–1.20 wt% at 77 K. We also measured CH_4 storage properties with CoPc-BPDA COF at 273 K and 298 K, which revealed an uptake of 0.59 wt% at 273 K and 0.45 wt% at 298 K and 1 bar (Fig. 3c). The isosteric heat of adsorption (Q_{st}) value was calculated (Fig. 3d) at zero coverage by calculating Henry's constants and using the Van't Hoff equation (see ESI†) from the CH_4 isotherms at 273 K and 298 K. The calculated isosteric heat of adsorption (Q_{st}) value is 44.9 kJ mol^{-1} . The Q_{st} value is higher than those reported for 2D and 3D non-phthalocyanine based COFs.^{1d} The reversible adsorption–desorption behavior and moderate Q_{st} values of CoPc-BPDA COF, indicate that CH_4 interactions with pore walls are sufficiently high to allow for material regeneration without applying heat. The relatively lower adsorption of CH_4 relative to the value obtained for H_2 may be due to size related effect.

Conclusions

In conclusion, we have synthesized and characterized a new cobalt based phthalocyanine based covalent organic framework. The impact of the phthalocyanine building units on the solid-state crystalline packing of the CoPc-BPDA COF leads to the formation of a 2D layered structure through strong π – π interactions. The formation of such a flake-like morphology and the predominant mesoporous nature lead to high surface area ($S_{\text{BET}} = 1087 \text{ m}^2 \text{ g}^{-1}$) and moderate H_2 (1.2 wt% at 77 K/1.0 bar) and CH_4 (0.59 wt% at 273 K/1.0 bar) uptake.

Acknowledgements

This work was generously supported by NSF grants CHE-1110967 and DMR-1205302, and the Robert A. Welch founda-

tion, grant # AH-0033. We are very thankful to Professor William R. Dichtel (Cornell University) for providing us the PXRD simulation of CoPc-BPDA COF and Professor Ricardo Bernal thank NSF-MRI funded TEM Grant # 0923437.

References

- (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) A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt and O. M. Yaghi, *J. Am. Chem. Soc.*, 2007, **129**, 12914; (d) 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; (e) J. R. Hunt, C. J. Doonan, J. D. LeVangie, A. P. Côté and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 11872; (f) P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450; (g) 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; (h) F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478; (i) M. Dogru, A. Sonnauer, A. Gavryushin, P. Knochel and T. Bein, *Chem. Commun.*, 2011, 47, 1707; (j) A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding and D. Jiang, *Nat. Commun.*, 2011, **2**, 536; (k) K. T. Jackson, T. E. Reich and H. M. El-Kaderi, *Chem. Commun.*, 2012, **48**, 8823; (l) D. N. Bunck and W. R. Dichtel, *Angew. Chem., Int. Ed.*, 2012, **51**, 1855.
- H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875.
- (a) 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; (b) H. J. Mackintosh, P. M. Budd and N. B. McKeown, *J. Mater. Chem.*, 2008, **18**, 573.
- (a) S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2008, **46**, 8826; (b) S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5439; (c) 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; (d) J. W. Colson, A. R. Woll, A. Mukherjee, M. P. Levendorf, E. L. Spitler, V. B. Shields, M. G. Spencer, J. Park and W. R. Dichtel, *Science*, 2011, **332**, 228; (e) J. F. Dienstmaier, A. M. Gigler, A. J. Goetz, P. Knochel, T. Bein, A. Lyapin, S. Reichlmaier, W. M. Heckl and M. Lackinger, *ACS Nano*, 2011, **5**, 9737; (f) T. Fauray, S. Clair, M. Abel, F. Dumur, D. Gigmes and L. Porte, *J. Phys. Chem. C*, 2012, **116**, 4819; (g) A. C. Marele, R. B. Mas, L. Terracciano, J. F. Rodriguez, I. Berlanga, S. S. Alexandre, R. Otero, J. M. Gallego, F. Zamora and J. M. Gomez, *Chem. Commun.*, 2012, **48**, 6779; (h) X. Ding, X. Feng, A. Saeki, S. Seki, A. Nagai and D. Jiang, *Chem. Commun.*, 2012, **48**, 8952.
- (a) E. L. Spitler and W. R. Dichtel, *Nat. Chem.*, 2010, **2**, 672; (b) 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; (c) E. L. Spitler, J. W. Colson, F. J. Uribe-Romo, A. R. Woll, M. R. Giovino, A. Saldivar and W. R. Dichtel, *Angew. Chem., Int. Ed.*, 2012, **51**, 2623.
- (a) S. B. Kalidindi, H. Oh, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo and R. A. Fischer, *Chem.–Eur. J.*, 2012, **18**, 10848; (b) J. L. Mendoza-Cortes, W. A. Goddard,

- H. Furukawa and O. M. Yaghi, *J. Phys. Chem. Lett.*, 2012, **3**, 2671.
- 7 J.-H. Guo, H. Zhang, Z.-P. Liu and X.-L. Cheng, *J. Phys. Chem. C*, 2012, **116**, 15908.
- 8 J.-H. Guo, H. Zhang and Y. Miyamoto, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8199.
- 9 J. Xia, S. Yuan, Z. Wang, S. Kirklin, B. Dorney, D.-J. Liu and L. Yu, *Macromolecules*, 2010, **43**, 3325.
- 10 J. Metz, O. Schneider and M. Hanack, *Inorg. Chem.*, 1984, **23**, 1065.
- 11 M. O'Keeffe, M. A. Peskov, S. J. Ramsen and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.