

A porous covalent porphyrin framework with exceptional uptake capacity of saturated hydrocarbons for oil spill cleanup†

Cite this: *Chem. Commun.*, 2013, **49**, 1533

Received 7th November 2012,
Accepted 2nd January 2013

DOI: 10.1039/c2cc38067f

www.rsc.org/chemcomm

Xi-Sen Wang,^a Jian Liu,^b Jean M. Bonfont,^a Da-Qiang Yuan,^c
Praveen K. Thallapally^b and Shengqian Ma^{*a}

A highly porous porphyrin-based organic polymer, PCPF-1, was constructed via homo-coupling reaction of the custom-designed porphyrin ligand, 5,10,15,20-tetrakis(4-bromophenyl)porphyrin. PCPF-1 possesses a large BET surface area of over 1300 m² g⁻¹ (Langmuir surface area of over 2400 m² g⁻¹) and exhibits strong hydrophobicity with a water contact angle of 135°, and these features afford it the highest adsorptive capacities for saturated hydrocarbons and gasoline among sorbent materials reported thus far, as well as render it the capability to remove oil from water.

The adverse environmental impacts of oil spill in water and organic chemical pollutants in air,¹ particularly the recent Deepwater Horizon oil spill devastation,² have urged the development of effective technologies for removing oils and organic pollutants from water and air. Physical adsorption using porous materials as adsorbents has been proved to be a very promising way to address such severe issues,³ and several types of porous materials have been widely explored including mesoporous silica,⁴ resins,⁵ and activated carbons.⁶ However, these adsorbents usually suffer from low adsorptive capacity due to limited pore volume³ or poor effectiveness because of their hydrophilic nature.⁷ Therefore, there is still an urgent need for new types of adsorbents that are water-stable/-proof and highly efficient and effective in removing oil residues under different conditions.

Metal-organic frameworks (MOFs)⁸ have recently been exploited as a new type of sorbents for hydrocarbon storage;⁹ but the poor water/moisture stability of most MOFs casts a

shadow on their application in removing oil residues from water and organic pollutants from air.

Over the past several years, porous organic polymers including crystalline covalent boron oxide-based frameworks (COFs),¹⁰ triazine-based organic frameworks (CTFs),¹¹ amorphous polymers of intrinsic microporosity (PIMs),¹² hyper-crosslinked polymers (HCPs),¹³ conjugated microporous polymers (CMPs),¹⁴ porous aromatic frameworks (PAFs),¹⁵ and porous polymer networks (PPNs)¹⁶ have been advanced as a new type of porous materials for various applications particularly gas storage and CO₂ capture.^{10–16} Compared with MOFs, porous organic polymers possess high thermal, chemical and water stabilities as well as hydrophobic components in their structures. These features make them promising candidates for removing oil spill from water and organic chemical pollutants from air, which however has rarely been explored.¹⁷ Among various types of porous organic polymers, CMPs feature elaborate integration of π -electronic components, and their surface areas and surface wettabilities could be altered by functionalizing the conjugated monomers. Porphyrins represent an interesting type of large conjugated macrocycles with 18-electron π systems,¹⁸ and they have recently been employed as building blocks for the construction of highly porous COFs.¹⁹ In this contribution, we report the construction of a porphyrin-based CMP utilizing the custom-designed porphyrin ligand, 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (tbpp) (Scheme 1), as a building block. We hypothesize that the homo-coupling of tbpp building blocks could lead to a 2D layered structure with high surface area, and the exposed conjugated porphyrin and phenyl rings could render strong hydrophobicity. As expected, the resulted material named PCPF-1 (PCPF denotes porous covalent porphyrin framework) possesses a large surface area and exhibits strong hydrophobicity, and these features afford it exceptional uptake capacities for saturated hydrocarbons and gasoline.

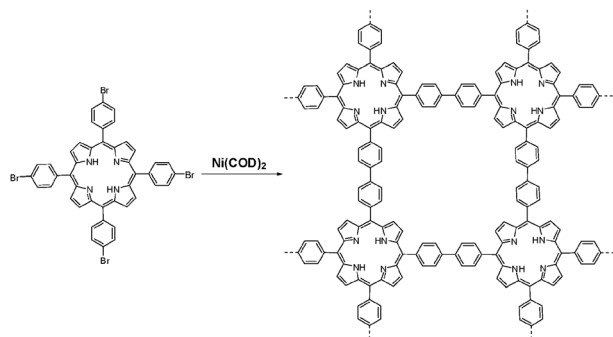
PCPF-1 was synthesized by the well-established Yamamoto homo-coupling reaction²⁰ (Scheme 1) as dark red powder, which has a low density and is insoluble in common organic solvents. The success of the phenyl-phenyl coupling was

^a Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620, USA. E-mail: sqma@usf.edu; Fax: +1-813-974-3203; Tel: +1-813-974-5217

^b Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou 350002, People's Republic of China

† Electronic supplementary information (ESI) available: IR and NMR spectra, modeled structure of PCPF-1, plots of TGA, Ar adsorption isotherms, and pore size distribution, PXRD patterns, photo of PCPF-1 floating on the surface of water. See DOI: 10.1039/c2cc38067f



Scheme 1 Synthetic route for PCPF-1 using 5,10,15,20-tetrakis(4-bromophenyl)porphyrin as a building block.

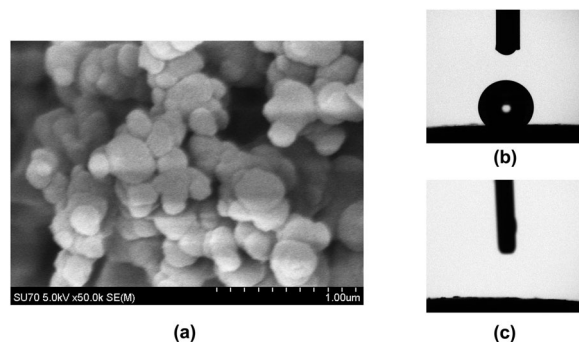


Fig. 1 (a) SEM image of the PCPF-1; (b) photo of a water droplet, and (c) photo of a salad oil droplet on a tablet of the PCPF-1 sample.

confirmed by FTIR measurements, which indicated the disappearance of the C–Br vibration band in the spectra of PCPF-1 (Fig. S1, ESI[†]). The local structure of PCPF-1 was characterized by ¹³C CP/MAS NMR studies. The signal assignments for the spectra displayed in Fig. S2 (ESI[†]) were made on the basis of a compound with similar structural elements reported before,^{19a} together with a comparison with the solution NMR data of the tbbp ligand in CDCl₃.²¹ The tbbp ligand resonance at 118.1 ppm for the *ipso*-C bound to Br was absent whereas a new signal at 139.1 ppm for the *ipso*-C bound to a phenyl ring appeared. The NMR spectra of PCPF-1 proved the homogeneity of the material and further confirmed the completion of the Yamamoto coupling reaction.

To analyze the possible structure of PCPF-1, we modeled the structure through Focite force-field calculations using Accelrys' Materials Studio (MS) v.6.1 software.²² The optimum simulation generated a structure with the *Pbcn* space group and a unit cell with $a = 24.1281$ Å, $b = 24.0961$ Å, $c = 11.5069$ Å. The model indicated that the planar porphyrin rings and chair-formed phenyl rings are connected to extend into wave-like sheets and the sheets prefer AA stacking to form aligned tubular channels with a diameter of 11.739 Å \times 11.739 Å (atom to atom distance) along the c direction (Fig. S3, ESI[†]).

Thermogravimetric analysis (TGA) indicates that PCPF-1 is thermally stable up to ~ 400 °C (Fig. S4, ESI[†]). PCPF-1 shows high chemical stability, and it is insoluble in strong acidic and basic solutions (e.g. 6 M HCl solution and 6 M NaOH solution). Powder X-ray diffraction (PXRD) studies on PCPF-1 indicated certain accordance between experimental patterns and the simulated patterns based on the modeled structure, although the poor overall crystallinity suggests that PCPF-1 is almost amorphous (Fig. S5, ESI[†]). Field-emission scanning electron microscopy (FE-SEM) images revealed that PCPF-1 is composed of agglomerated ball-shaped particles with sizes of 100–500 nm in diameter (Fig. 1a), which also indicates the roughness of its surface. The surface wettability of PCPF-1 was investigated by water contact angle (CA) measurements. It was observed that PCPF-1 is strongly hydrophobic with a water CA of 135° (Fig. 1b), which should mainly originate from its hydrophobic compositions of conjugated porphyrin and phenyl rings. In contrast, when a salad oil droplet was placed on the surface of the PCPF-1 sample, the oil was quickly adsorbed and a CA

with oil of nearly 0° was obtained (Fig. 1c), indicating that PCPF-1 is strongly oleophilic. We reasoned that the strong oleophilicity of PCPF-1 should be attributed to its hydrophobic surface and nanoporous structure. The hydrophobic nature of PCPF-1 was further confirmed by water vapor sorption isotherms at 298 K (Fig. S6, ESI[†]), which revealed a very low water uptake capacity of less than 4.0 wt% below the relative humidity of 60% and an abrupt increase of water adsorption above the relative humidity of 70% due to water vapor condensation on the exterior surface.

To assess the permanent porosity of PCPF-1, gas sorption measurements were performed on the activated PCPF-1 sample. The N₂ adsorption isotherm at 77 K (Fig. S7, ESI[†]) reveals that PCPF-1 exhibits an uptake capacity of 538 cm³ g⁻¹ at the saturation pressure with typical type-I sorption behavior, as expected for microporous materials. Derived from the N₂ adsorption data, PCPF-1 has a BET surface area of 1333 m² g⁻¹ ($P/P_0 = 0.02$ – 0.2) (Langmuir surface area: 2426 m² g⁻¹ ($P/P_0 = 0.9$)) and a pore volume of 0.86 cm³ g⁻¹. The surface area of PCPF-1 was further confirmed by Ar adsorption isotherms at 87 K (Fig. S8, ESI[†]), which revealed similar surface area values. Density functional theory (DFT) pore size distribution analysis based on the Ar adsorption data at 87 K indicated that the pore size of PCPF-1 is narrowly distributed around 9.0 Å (Fig. S9, ESI[†]), which is in good agreement with the pore size observed in the modeled structure when van der Waals radii are taken into account.

The high surface area and strong surface hydrophobicity of PCPF-1 prompted us to evaluate its performances in adsorbing saturated C5–C8 hydrocarbons, which embody the components of petroleum oil. The vapor adsorption isotherms of PCPF-1 for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and cyclohexane at 298 K are displayed in Fig. 2a. At their individual saturation pressures, the adsorbed amounts by PCPF-1 for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and cyclohexane are 456, 623, 752, 737, 909, and 1030 mg g⁻¹, respectively (Table 1). This means that the hexane and cyclohexane uptake capacities of PCPF-1 are about 5 times higher than that of the hydrophobic MOF, FMOF-1 (99 mg g⁻¹ for hexane; 156 mg g⁻¹ for cyclohexane),^{9b} and also far exceed that of the widely used activated carbon material, BPL (300 mg g⁻¹ for hexane).²³ We also assessed the adsorptive capacities of

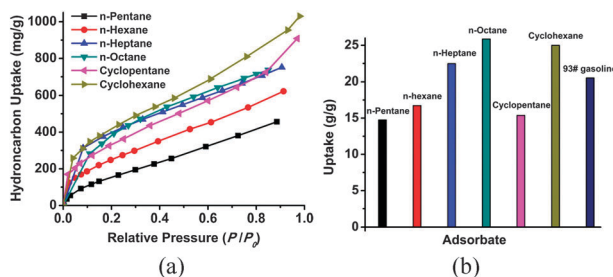


Fig. 2 (a) Adsorption isotherms of PCPF-1 for the vapors of various saturated hydrocarbons at 298 K (the saturation pressures of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and cyclohexane are 684.8, 203.5, 60.7, 18.7, 423.6, 131.3 mbar, respectively); (b) uptake amounts of various saturated hydrocarbons and gasoline (93#) in the liquid phase at 298 K by PCPF-1.

Table 1 Adsorptive capacities of PCPF-1 for various saturated hydrocarbons and gasoline in vapor and liquid phases at 298 K

	Vapor-phase adsorptive capacity (mg g ⁻¹)	Liquid-phase adsorptive capacity (g g ⁻¹)
<i>n</i> -Pentane	456	14.7
<i>n</i> -Hexane	623	16.7
<i>n</i> -Heptane	752	22.5
<i>n</i> -Octane	737	25.9
Cyclopentane	909	15.4
Cyclohexane	1030	25.1
Gasoline (93#)	N/A	20.5

PCPF-1 for the saturated C5–C8 hydrocarbons in the liquid phase and for liquid gasoline. As shown in Fig. 2b, 1 g of the PCPF-1 sample can adsorb around 14.7 g of *n*-pentane, 16.7 g of *n*-hexane, 22.5 g of *n*-heptane, 25.9 g of *n*-octane, 15.4 g of cyclopentane, 25.1 g of cyclohexane, and also about 20.5 g of gasoline (Table 1), outperforming the recently reported porous organic polymer materials PDVB-0.1^{17a} and HCMP-1/2.^{17b} PCPF-1 can be readily cycled over 20 times without drop in uptake capacities for hydrocarbons (Fig. S10, ESI†). Indeed, to the best of our knowledge, the adsorptive capacities of PCPF-1 for both vapors and liquids of saturated hydrocarbons as well as liquid gasoline are the highest among sorbent materials reported thus far.^{3–7,9,17} It is worth noting that due to the low density as well as strong hydrophobicity and oleophilicity, PCPF-1 floats on the surface of water (Fig. S11, ESI†) and almost does not adsorb the liquid-phase water. This together with its exceptional uptake capacities for saturated hydrocarbons and gasoline affords PCPF-1 great potential for use in the cleanup of oil spill in water and air. Indeed, PCPF-1 can remove oil from water as evidenced by the experiment of using PCPF-1 to separate the mixed corn oil and water solution (Fig. S12, ESI†). We are currently investigating the efficiency and effectiveness of PCPF-1 in removing saturated hydrocarbons and different types of oils from water.

In summary, a porphyrin-based porous organic polymer material, PCPF-1, has been synthesized *via* the Yamamoto homo-coupling reaction of the custom-designed porphyrin building block, 5,10,15,20-tetrakis(4-bromophenyl)porphyrin.

PCPF-1 is highly porous with a large BET surface area of over 1300 m² g⁻¹ (Langmuir surface area of over 2400 m² g⁻¹). It features strong hydrophobicity and oleophilicity, and demonstrates by far the highest adsorptive capacities for saturated hydrocarbons and gasoline among reported porous materials, and is capable of removing oil from water. This work thus lays a solid foundation for developing conjugated porous polymer materials as a new type of sorbents for removal of oil residues from water and organic pollutants from air as well as for hydrocarbon storage and waste water purification. Ongoing work in our laboratory includes the design and synthesis of new porous PCPFs and other types of conjugated porous organic polymers for energy and environmental-related applications.

S. Ma acknowledges the University of South Florida for financial support of this work. This work was also supported, in part, by US Department of Energy (contract DE-AR0000177). P. K. T. and J. L. would like to acknowledge the support from US-DOE-EERE through the Geothermal Technologies Program.

Notes and references

- 1 A. Godduhn and L. K. Duffy, *Environ. Sci. Policy*, 2003, **6**, 341.
- 2 United States Environmental Protection Agency. *Deepwater Horizon Response April 2010*.
- 3 M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas and A. M. Mayes, *Nature*, 2008, **452**, 301.
- 4 A. Sayari, S. Hamoudi and Y. Yang, *Chem. Mater.*, 2005, **17**, 212.
- 5 V. Janout, S. B. Myers, R. A. Register and S. L. Regan, *J. Am. Chem. Soc.*, 2007, **129**, 5756.
- 6 A. B. Fuertes, G. Marban and D. M. Nevskaja, *Carbon*, 2003, **41**, 87.
- 7 T. Ono, T. Sugimoto, S. Shinkai and K. Sada, *Nat. Mater.*, 2007, **6**, 429.
- 8 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673.
- 9 (a) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836; (b) C. Yang, U. Kaipa, Q. Z. Mather, X. P. Wang, V. Nesterov, A. F. Venero and M. A. Omary, *J. Am. Chem. Soc.*, 2011, **133**, 18094.
- 10 A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.
- 11 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450.
- 12 N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675.
- 13 C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou and A. I. Cooper, *Adv. Mater.*, 2008, **20**, 1916.
- 14 A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291.
- 15 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457.
- 16 D. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, **23**, 3723.
- 17 (a) Y. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoib, T. Tatsumib and F.-S. Xiao, *Nano Today*, 2009, **4**, 135; (b) A. Li, H.-X. Sun, D.-Z. Tan, W.-J. Fan, S.-H. Wen, X.-J. Qing, G.-X. Li, S.-Y. Li and W.-Q. Deng, *Energy Environ. Sci.*, 2011, **4**, 2062.
- 18 *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000–2003.
- 19 (a) L. Chen, Y. Yang and D. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 9138; (b) S. Wan, F. Gandara, 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.
- 20 T. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 621.
- 21 H. Sharghi and A. Hassani Nejad, *Tetrahedron*, 2004, **60**, 1863.
- 22 *Accelrys Materials Studio Release Notes, 6.1*, Accelrys Software, Inc., San Diego, 2012.
- 23 E. N. Rudisill, J. J. Hacskaylo and M. Douglas Levan, *Ind. Eng. Chem. Res.*, 1992, **31**, 112.