Porphyrin based porous organic polymers: Novel synthetic strategy and exceptionally high CO₂ adsorption capacity

Arindam Modak, Mahasweta Nandi, John Mondal and Asim Bhaumik*

Supporting Information

Materials and Methods:

Pyrrole was purchased from SRL, India and distilled under Ar prior use. Terephthaldehyde, 4-formyl benzene boronic acid, tetrakis triphenyl phosphine Pd(0) were received from Sigma Aldrich, USA. 4-bromo benzaldehyde was procured from Avra chemicals, India. Glacial acetic acid and all other remaining organic solvents were taken from Merk, India and used after purification. 4,4'-Diformyl-1,1'-biphenyl and 4,4"-diformyl-p-terphenyl were synthesized by employing palladium catalysed Suzuki cross coupling procedure as mentioned elsewhere. After the hydrothermal synthesis materials were filtered and washed extensively with water and THF, and dried in a vacuum oven at 393 K for 48 h.

Carbon, hydrogen and nitrogen contents were determined using a Perkin Elmer 2400 Series II CHN analyzer. Fourier Transform Infra Red (FTIR) spectra of Fe-POPs are recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. ¹H and ¹³C NMR experiments (liquid state) are carried out on a Bruker DPX-300 NMR spectrometer. Mass spectrometric data are acquired by the electron spray ionization (ESI) technique at 25-70 eV in a Micromass Q-tof-Micro Quadruple mass spectrophotometer. X-ray diffraction patterns of the powder samples are obtained with a Bruker AXS D8 Advanced SWAX diffractometer using Cu K α ($\lambda = 0.15406$ nm) radiation. Nitrogen sorption experiments and micropore analysis were conducted at 77 K using a Beckman Coulter, SA 3100 surface area measurement instrument. Prior to adsorption measurement the samples were degassed in vacuum at 180 ⁰C for about 3h. NLDFT pore-size distributions were determined using the carbon/slit-cylindrical pore model of the Autosorb-1 software. CO₂ adsorption experiments were carried out at 273 K by using a Belsorp HP gas adsorption apparatus.

The ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectrum was obtained on a Bruker Avance III600WB 600 MHz at 150.9 MHz and a MAS frequency of 12 kHz.

Thermogravimetry (TGA) and differential thermal analyses (DTA) of the samples are carried out in a TGA Instruments thermal analyzer TA-SDT Q-600. A Hitachi S-5200 field-emission scanning electron microscope was used for the determination of the morphology of the particles.

Experimental Section:

Synthesis of 4, 4'-Diformyl-l, l'-biphenyl:



In a typical synthesis a two neck round bottom flask was charged with 4-bromo benzaldehyde (100.0 mg, 0.54 mmol), 4-formyl benzeneboronic acid (138 mg, 0.92 mmol), Na₂CO₃ (114 mg, 1.08 mmol) in water (5 ml) and THF-Toluene (1:1, 5 ml) mixture. Then the whole mixture was degassed for 30 minutes under an Argon atmosphere with rotation in a magnetic stirrer. To this degassed solution was added Pd (PPh₃)₄ (10 mol%, 35.5 mg) and the whole mixture was heated to reflux at 80⁰C for about 14-18 h. At the conclusion of the reaction TLC was checked and water was added. The whole mixture was then extracted with CH_2Cl_2 (3 x 30 ml). The combined organic parts were thoroughly washed with water (40 ml), brine (20 ml) and dried under sodium sulphate for 20 min. Evaporation of the solvent gave crude product which was purified by silica gel column chromatography. Elution of the column with 5% ethyl acetate-pet ether gave the desired compound 4,4'-Diformyl-1,l'-biphenyl (yield ~ 54 %) as a pale yellow solid ; mp 145-148^oC. Anal. Found: C, 79.0; O, 15.7; H, 5.1. Calcd for 4,4'-Diformyl-1,l'-biphenyl : C, 79.9; O, 15.2; H, 4.8.

¹H NMR (CDCl₃, 300 MHz): δ 8.01 (d, 4H, 8.34 Hz, ArH), 7.81 (d, 4H, 8.19 Hz, ArH), 10.08 (s, 2H, CHO). ¹³C NMR (CDCl₃, 75 MHz): δ 128.161 (4C, C_6 H₄), 130.491 (4C, C_6 H₄), 136.13 (2Cq, C_6 H₄), 145.69 (2Cq, C_6 H₄), 191.83 (2C, CHO) ppm.

Synthesis of 4, 4"-Diformyl-p-terphenyl:



In a typical synthesis a two neck round bottom flask was charged with 4-bromo benzaldehyde (0.555g, 2 mmol), 1,4-benzene di boronic acid (0.166 g, 1 mmol), Na₂CO₃ (0.319 g, 3 mmol) in water (5 ml) and THF-Toluene (1:1, 5 ml) mixture. Then the whole mixture was degassed for 30 minutes under an Argon atmosphere with rotation in a magnetic stirrer. To this degassed solution was added Pd(PPh₃)₄ (9 mol%, 31.5 mg) and the whole mixture was heated to reflux at 80^oC for about 48 h under rapid stirring in presence of Ar atm. At the conclusion of the reaction TLC was checked and water was added. The whole mixture was then extracted with CH₂Cl₂ (3 x 30 mL). The combined organic parts were thoroughly washed with water (40 mL), brine (20 mL) and dried under sodium sulphate for 20 min. Evaporation of the solvent gave crude product which was purified by silica gel column chromatography. Elution of the column with 5% ethyl acetate-pet ether gave the desired compound 4,4"-Diformyl-p-terphenyl (yield ~ 34 %) as a white solid. mp 209–213 °C.

¹H NMR (CDCl₃, 300 MHz): δ 8.00 (d, 4H, 8.34 Hz, ArH), 7.83 (d, 4H, 8.22 Hz, ArH), 7.77 (s, 4H, ArH), 10.08 (s, 2H, CHO). ¹³C NMR (CDCl₃, 75 MHz): δ 191.98, 146.40, 139.912, 135.60, 130.51, 128.129, 127.76 ppm.

Synthesis of Porous Organic Polymers:

Synthesis of Fe-POP-1:

In a typical experimental procedure, a flame dried round bottom flask was charged with freshly distilled pyrrole (0.05 g, 0.74 mmol) and terephthaldehyde (0.1 g, 0.74 mmol). Then 15 ml glacial acetic acid was taken in the flask with constant stirring along with ferric chloride (1.2 equivalent) under inert Argon atmosphere. The whole solution was stirred in a magnetic stirrer with stirring rate of 300 rpm to make the whole solution homogenized. After 6 h the mixture was transferred to a Teflon lined autoclave and kept under hydrothermal treatment for 72 h at 180 $^{\circ}$ C. The complete condensation takes place after 3 days and the oven was slowly cooled to room temperature, resulting a dark brownish product which separates out from the mixture. The precipitated solid was filtered and thoroughly washed with distilled water methanol, acetone, THF, dichloromethane and then vacuum dried in an oven at 80 $^{\circ}$ C for another 48 h. The material was then rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol, and tetrahydrofuran (THF), respectively, to give 0.2g Fe-POP-1, yield 44% based on terephthaldehyde and pyrrole. Elemental analysis (%) Found by combustion: C, 77.0; H, 4.3; N, 7.8. Found by EDX analysis (wt%) C, 88.4; N, 2.3. Calcd. theoretical formula for an infinite Fe-POP-1: {C44H₂₆N₄}_n with C, 86.5; H, 4.2; N, 9.2.

Synthesis of Fe-POP-2:

Similarly for the preparation of Fe-POP-1, Pyrrole (0.05 g, 0.74 mmol), 4, 4'-Diformyl-l, l'biphenyl (0.156 g, 0.74 mmol) and 1.2 equivalent ferric chloride were hydrothermally reacted in 15 ml glac. acetic acid for 72 h at 180 0 C to afford 0.195g Fe-POP-2, yield 28.7% based on 4, 4'-Diformyl-l, l'-biphenyl and pyrrole. Elemental analysis (%) Found by combustion: C, 80.0; H, 4.6; N, 5.3. Found by EDX analysis (wt%) C, 88.9; N, 2.0. Calcd. Theoretical formula for an infinite Fe-POP-2: {C₆₈H₄₂N₄}_n with C, 89.2; H, 4.6; N, 6.1.

Synthesis of Fe-POP-3:

For the preparation of Fe-POP-3, Pyrrole (0.05 g, 0.74 mmol), 4, 4"-Diformyl-p-terphenyl (0.213 g, 0.74 mmol) and 1.2 equivalent ferric chloride were hydrothermally reacted in 15 ml glacial acetic acid for 72 h at 180 0 C to afford 0.185g Fe-POP-3, yield 20.4% based on 4, 4"-Diformyl-p-terphenyl and pyrrole. Elemental analysis (%) Found by combustion: C, 81.9; H, 4.8; N, 4.1. Found by EDX analysis (wt%) C, 90.5; N, 1.9. Calcd. Theoretical formula for an infinite Fe-POP-3: {C₉₂H₅₈N₄}_n with C, 90.6; H, 4.7; N, 4.6.



Fig S1. Powder XRD diffraction of several Fe-POPs at wide angel showing broad diffraction for thick amorphous pore wall.



Fig. S2a. SEM image of Fe-POP-1.



Fig. S2b. SEM image of Fe-POP-2.



Fig. S2c. SEM image of Fe-POP-3.



Fig. S3a. TG (a) and DTA (b) profiles of Fe-POP-1.



Fig. S3b. TG (a) and DTA (b) profiles of Fe-POP-2.



Fig. S3c. TG (a) and DTA (b) profiles of Fe-POP-3.



Fig. S4. FT IR spectra of several microporous porphyrin networks where a, b and c represents Fe-POP-1, -2 and -3, respectively.

Bands corresponding to $1720-1740 \text{ cm}^{-1}$ (C=O stretching) are absent or strongly attenuated, suggesting the absence of carbonyl functional groups of the aldehyde or confirming the near completion of the formation of polymeric networks. The other bands *i.e.* 2986–2952 cm⁻¹ (C–H stretching of the phenyl ring), 1604 cm⁻¹ (C=C stretching of pyrrole ring), 1484 cm⁻¹ (C=C vibration modes of the phenyl rings), 1336 cm⁻¹ (pyrrole deformation), 1072 cm⁻¹ (pyrrole stretching), 801 cm⁻¹ (C–H out-of-plane bending of the phenyl rings) and C–H (trans) out-of-plane bending of the phenyl rings at 719 cm⁻¹ confirm the direct incorporation of the pyrrole moiety and the formation of microporous porphyrin networks with the corresponding aldehydes. New vibration band in the series of Fe-POPs at 1001 cm-1 is due to the strong coordination of Fe(III) with porphyrin units (N-Fe moiety).

Solid State ¹³C MAS NMR spectroscopy:



Fig. S5a. Solid-state ¹³C CP/MAS NMR spectrum of Fe-POP-1, recorded at a MAS rate of 12 kHz.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2011



Figure S5b. Solid-state ¹³C CP/MAS NMR spectrum of Fe-POP-2, recorded at a MAS rate of 12 kHz.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2011



Fig. S5c. Solid-state ¹³C CP/MAS NMR spectrum of Fe-POP-3, recorded at a MAS rate of 12 kHz.

Fig S6. UV-visible diffuse reflectance spectra of several Fe-POPs (a= Fe-POP-1, b= Fe-POP-2, c= Fe-POP-3) were recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO4 was used as background standard.

This UV-Visible absorbance of Fe-POPs shows the existence of several peaks corresponding to 318, 470, 595, 635 and 705 nm. Presence of Porphyrin units in the Fe-POPs have been justified due to the appearance of Soret bands^{1,2,3,4} (450-474 nm) and Q band (595, 635, 705 nm). The large bathochromic shift⁵ of the Soret band is observed here with increasing phenyl rings from Fe-POP-1 to Fe-POP-3 and loading of Fe in these materials.

Fig.S7. Photoluminescence spectrum of of Fe-POP-1 upon excitation at 320 nm.

Material	Composition	BET surface area $(m^2g^{-1})^a$	$PV (cm^3g^{-1})^b$	PD nm ^c	Fe loading (mmolg ⁻¹)
Fe-POP-1	Pyrrole + 1	875	0.365	1.10	0.00267
Fe-POP-2	Pyrrole + 2	855	0.417	1.04	0.00312
Fe-POP-3	Pyrrole + 3	750	0.516	0.75, 1.75, 2,6	0.00324

Table S1. Surface area and pore size analysis of Fe-POPs.

^a Surface area calculated from nitrogen adsorption isotherms using the BET equation.

^b Pore volume calculated from nitrogen adsorption at $p/p_0 = 0.9$.

^c Pore diameter (PD) calculated by employing the NLDFT model.

Fig. S8. NLDFT pore size distributions of different microporous organic polymers are shown here, where Fe-POP-1 (red), Fe-POP-2 (purple) and Fe-POP-3 (blue).

References:

1) L. R. Milgrom, *The Colours of Life: An Introduction to the Chemistry of Porphyrins and Related Compounds*, OUP, Oxford, 1997; *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978.

2) E. Dietel, A. Hirsch, E. Eichhorn, A. Rieker, S. Hackbarth, B. Roder, Chem. Commun., 1998 1981.

3) T. Ishi-i, J. H. Jung, S. Shinkai, J. Mater. Chem., 2000, 10, 2238.

4) a) D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed. *McGraw-Hill: London*, 1987, 23. b) J. D. Spence and T. D. Lash, *J. Org. Chem.*, 2000, 65, 1530. c) J. D. Spence, T. D. Lash, *J. Org. Chem.*, 2000, 65, 1530.

5) L. Chen, Y. Yang and D. Jiang, J. Am. Chem. Soc., 2010, 132, 9138.