Supplementary information

Supramolecular porous materials with robust and tunable 1D channels constructed from tin(IV)porphyrin phenolates

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Synthesis:

Solvents were obtained as AR grade or HPLC grade reagents and were used as received with the following exceptions. Tetrahydrofuran (THF) was stored over sodium wire and redistilled prior to use. Dichloromethane and chloroform were distilled from calcium hydride. Distilled water was used for all aqueous manipulations. Melting points (M.p.) were measured on a Stuart Scientific SMP 3 melting point apparatus. The ¹H nuclear magnetic resonance (NMR) spectra was recorded using a Bruker DPX 400 MHz spectrometer (400 MHz for ¹H NMR). TGA analyses were performed on a Mettler Toledo instrument heated from 80 to 450 °C with a scan rate of 2° C min⁻¹ in flowing of nitrogen. Analytical thin layer chromatography (TLC) is performed on Merck aluminium oxide 60 F₂₅₄ coated on an aluminium sheet. The components are visualized by either UV exposure (254 nm, 356 nm) or by direct visualization (porphyrin derivatives).

Synthesis of TTP:



Pyrrole (9.73 g, 145 mmol) and 4-methyl-benzaldehyde (15.77 g, 131 mmol) were added to propionic acid (400 mL) refluxed for 2 h. The reaction mixture was stirred overnight at room temperature, followed by filtration to obtain a crystalline purple solid, which was washed with CH₃OH (3×50 mL) and hexane (2×50 mL) and air dried. M.p. >300 °C. ¹H NMR (300 MHz, CDCl₃, 300 K) δ = -2.76 (s, 2H, *centro*-pyrrolic H_{Sn}), 2.71 (s, 12H, *meso*-ArCH₃), 7.53 (d, *J* = 7.6 Hz, 8H, *meso*-ArH), 8.10 (d, *J* = 7.6 Hz, 8H, *meso*-ArH), 8.85 (s, 8H, β -pyrrolic H).

Synthesis of Sn(IV)TTPCl₂



5,10,15,20-tetra-*p*-tolyl-porphyrinato (500 mg, 0.813 mmol) and SnCl₂·2H₂O (400 mg, 1.771 mmol) were stirred and refluxed in pyridine (50 mL) for 3 h. Excess water was added to precipitate the product which was then filtered, washed with water and air dried to give dichloro-(5,10,15,20-tetra-*p*-tolyl-porphyrinato)tin(IV) **2** (520 mg, 80%) as an amorphous solid, M.p. >300°C. The compound had identical ¹H NMR properties to those reported by Arnold.^[36] ¹H NMR (400 MHz, CDCl₃, 300 K) δ = 7.81 (m, *J* = 3.2 Hz, 12H, *meso*-ArH), 8.30 (d, *J* = 6.4 Hz, 8H, *meso*-ArH), 9.22 (s, 8H, *β*-pyrrolic H).

Synthesis of Sn(IV)tTTP(OH)₂:



Potassium carbonate (400 mg, 2.9 mmol) and dichloro-(5,10,15,20-tetra-*p*-tolyl-porphyrinato)tin(IV) (140 mg, 0.163 mmol) were dissolved in a mixture of tetrahydrofuran (80 mL) and water (20 mL) and heated at reflux for 3 h. The organic solvent was removed and the aqueous layer was extracted into dichloromethane (60 mL). The organic layer was washed with water (2 × 40 mL) and then dried over anhydrous sodium sulfate, filtered and then the solvent was removed to give the crude product, which was then recrystallised (hexane– dichloromethane, 1 : 1) to give dihydroxo-(5,10,15,20-tetra-*p*-tolyl-porphyrinato) tin(IV) **3** (120 mg, 90%) as a metallic purple crystalline solid. M.p. >350°C. ¹H NMR (400 MHz, CDCl₃, 300 K) δ = 2.171 (s, 1H, hydroxyl-H_{sn}), 2.273 (s, 1H, hydroxyl-H_{sn}), 2.74 (s, 12H, *meso*-ArCH3), 7.62 (d, *J* = 7.6 Hz, 8H, *meso*-ArH), 8.21 (d, *J* = 8.0 Hz, 8H, *meso*-ArH), 9.13 (s, 8H, *β*-pyrrolic H).

Synthesis of Sn(IV)tTTP(2-methylphenolate)₂ 1

Dihydroxo-(5,10,15,20-tetra-*p*-tolyl-porphyrinato) tin(IV)²⁰ (82.2 mg, 0.1 mmol) was added to 2 equivalents of 2-methylphenol (21.6 mg, 0.2 mmol) in base-washed CHCl₃ and the solution was left to stir at room temperature for 2 days, monitored for completion by taking aliquots for NMR analysis. M.p. >350°C. ¹H NMR (400 MHz, CDCl₃, 300 K) δ = -1.29 (s, 6 H, phenol-methyl group), 1.06 (d, *J* = 1.2 Hz, 1 H, ArH), 1.08 (d, *J* = 1.6 Hz, 1 H, ArH), 2.74 (s, 12 H, *meso*-ArCH₃), 5.41 (m, *J* = 6.4 Hz, 2 H, ArH), 5.54 (m, *J* = 6.4 Hz, 2 H, ArH), 5.59 (m, *J* = 6.0 Hz, 2 H, ArH), 7.59 (d, *J* = 8.0 Hz, 8 H, *meso*-ArH), 8.04 (d, *J* = 8.0 Hz, 8 H, *meso*-ArH), 9.091 (s, 8 H, *β*-pyrrolic H).

Synthesize for Sn(IV)tTTP(2,5-dimethylphenolate)₂ 2

Dihydroxo(5,10,15,20-tetra-*p*-tolyl-porphyrinato) tin(IV) (82.2 mg, 0.1 mmol) was added to 2 equivalents of 2,5-dimethyl-phenol (24.4 mg, 0.2 mmol) in base washed CHCl₃ and the solution was left to stir at room temperature for 2 days, monitored for completion by taking aliquots for NMR analysis. M.p. >300°C. ¹H NMR (400 MHz, CDCl₃, 300 K) δ = -1.32 (s, 6H, phenol-methyl group), 0.82 (s, 2H, phenol H), 1.27 (s, 6H, phenol-methyl group), 2.73 (s, 12H, *meso*-ArCH₃), 5.42 (s, 4H, phenol H), 7.69 (d, *J* = 8.0 Hz, 8H, *meso*-ArH), 8.04 (d, *J* = 8.0 Hz, 8H, *meso*-ArH), 9.08 (s, 8H, β -pyrrolic H).

Synthesize for Sn(IV)tTTP(3,5-dimethylphenolate)₂ 3

Dihydroxo(5,10,15,20-tetra-*p*-tolyl-porphyrinato) tin(IV) (82.2 mg, 0.1 mmol) was added to 2 equivalents of 3,5-dimethyl-phenol (24.4 mg, 0.2 mmol) in base washed CHCl₃ and the solution was left to stir at room temperature for 2 days, monitored for completion by taking aliquots for NMR analysis.. M.p. >350°C. ¹H NMR (400 MHz, CDCl₃, 300 K) $\delta = 1.26$ (s, 12H, phenol-methyl group), 0.87 (d, J = 7.6 Hz, 2H, phenol H), 1.43 (s, 2H, phenol H), 2.73 (s, 12H, *meso*-ArCH₃), 5.42 (s, 2H, phenol H), 7.60 (d, J = 7.6 Hz, 8H, *meso*-ArH), 8.08 (d, J = 6.6 Hz, 8H, *meso*-ArH), 9.05 (s, 8H, β -pyrrolic H).

NMR spectrum





Fig. S1. NMR spectrum of MPM1-3.

Crystallography studies

X-ray crystal diffraction patterns are determined using an Enraf Nonius FR 590 Kappa CCD diffractometer or a Brüker Kappa Apex II diffractometer with graphite-monochromated Mo *K*α radiation at 123K unless otherwise stated. Indexing was performed using APEX2.¹ Data integration and reduction were completed using SaintPlus 6.01.² Absorption correction was performed by the multi-scan method implemented in SADABS.³ The space group was determined using XPREP implemented in APEX2.1 The structure was solved with SHELXS-97⁵⁻⁷ (direct methods) with the graphical interface X-Seed v2.0,⁸ and refined on F2(nonlinear least-squares method) with SHELXL-97 contained in APEX2,WinGX v1.70.01,⁴⁻⁷ and OLEX2 v1.1.5⁹ program packages. All non-hydrogen atoms were refined anisotropically.

Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. 921008-921009 and 921011. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or <u>http://www.ccdc.cam.ac.uk</u>).

Table 1. Single-Crystal X-ray Data for compounds MPM 1-3

compound	MPM-1	MPM-2	MPM-3
formula	$C_{62}H_{50}N_4O_2Sn$	$\mathrm{C}_{64}\mathrm{H}_{64}\mathrm{N}_4\mathrm{O}_2\mathrm{Sn}$	$C_{64}H_{54}N_4O_2Sn$

Т,К	123	123	123
Fw	1001.77	1029.82	1029.80
Lattice	Trigonal	Trigonal	Trigonal
<i>a</i> , Å	36.528(2)	37.419(5)	37.361(5)
<i>b</i> , Å	36.528(2)	37.419(5)	37.361(5)
<i>c</i> , Å	10.5054(10)	10.7471(11)	10.403(2)
V, Å ³	12139.0(2)	13032(3)	12575(4)
space group	<i>R</i> -3	<i>R</i> -3	<i>R</i> -3
Ζ	9	9	9
$Dc/g \text{ cm}^{-3}$	1.233	1.191	1.224
<i>F</i> (000)	4644.0	4788	4788
R_1^a values [$I > 2\sigma(I)$]	0.0606	0.0562	0.0720
wR_2^{b} (all data)	0.1890	0.2029	0.2394
GOF	0.893	0.967	0.927

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}wR_{2} = |\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})| / \Sigma |w(F_{o})^{2}|^{1/2}$

Hydrogen bonding interactions within MPM 1-3



Fig. S1 View of non-classical hydrogen bonding and weak interactions in **MPM 1-3**, shown as red dashed lines

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