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ARTICLE TYPE

Supramolecular materials with robust and tunable channels constructed from tin(IV)porphyrin phenolates†

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Three robust molecular porous materials (MPMs) constructed from Sn(IV)TTP(bisphenolates) were reported. They all possess 1D hourglass-shaped channels within their crystal structures. Functionalisation of the channel lining through judicial choice of substituted phenol was demonstrated, which also allowed for a change the pore diameter. TGA investigations revealed these novel supramolecular systems are thermally stable over 550K.

Porous materials have aroused wide interest amongst scientists in the past decade because of their various applications in catalysis,[1-3] guest exchange,[4] gas adsorption,[5-8] drug delivery and release,[9, 10] and sensing.[11] As defined by the interactions between each building block, they can be classified as either bonded (including coordination bonds) frameworks or non-bonded networks. Bonded frameworks such as zeolites and clays, carbonaceous derivatives,[12-14] metal–organic frameworks,[15-19] mesoporous metal oxides,[20-22] porous organosilicas,[23, 24] and organic polymers[25, 26] have been comprehensively studied due to their rigidity, structural and thermal stability, as well as storage capacity and selectivity. In comparison, the study of molecular materials with extended structures that are defined by much weaker non-covalent forces is still in its early stage and need to be explored.[27, 28] Molecular materials with purely non-covalent interactions tend to pack as close to one another as possible in order to maximise attractive intermolecular contacts. In cases where host-guest design elements are used to construct non-bonded porous materials, the majority of hosts are known to collapse into a dense form once the stabilizing guest template is removed; only a few examples exist in a permanent porous polymorph.[29-31]

Porphyrins and related molecules play essential roles in the critical reactions within photosynthetic systems. These elegant processes are associated with the precise assemblies of porphyrin molecules have attracted many scientists as the formation of structures containing multiple porphyrin molecules using self-assembly processes is an attractive research target.[32-34],. A wide variety of intricate structures can be obtained through self-assembly thanks to the molecular design flexibility of porphyrins, since they can be easily modified with relatively little synthetic effort. Tin(IV) porphyrins have been extensively studied in biomedical and photocatalytic applications, including splitting of water for the production of hydrogen.[35-37] Due to the oxophilic nature of the Sn(IV) center, the complexes with carboxylate, alkoxide and phenoxide axial anions are readily prepared and tractable, making them ideal building blocks for the construction of elegant and elaborate supramolecular arrays.[38-41]

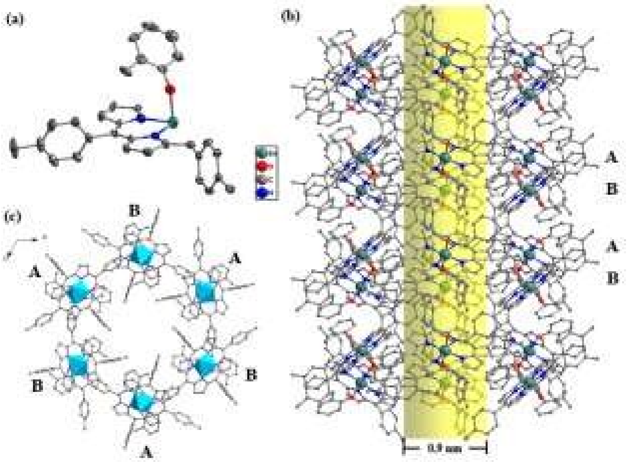

Fig. 1 (a) View of asymmetry unit in **MPM-1** with the ellipsoids drawn at the 30% probability level, hydrogen atoms and solvent molecules were omitted for clarity; (b) Side view of the nano channel of **MPM-1** showing ABAB packing fashion; (c) A perspective view down the crystallographic *c*-axis of **MPM-1** showing intersecting arrangement between adjacent layers and the pore that leads to the 1D channel.

We previously reported two Sn(IV)porphyrin phenolate compounds that form one dimensional infinite channels running through the framework,[39] as well as the use of such systems to study the interactions and orientations of water molecules in a single chain formation.[42] However, the scope of the self-assembly of Sn(IV)porphyrin phenolate units to form supramolecular porous structures has never been systematically studied.

Herein, we report three novel molecular porous materials (MPMs) constructed from Sn(IV)porphyrin phenolates: *di-2-methyl*-phenoxy(5,10,15,20-tetra-*p*-tolyl-porphyrinato)tin(IV) **1**; *di-2,5-dimethyl*-phenoxy(5,10,15,20-tetra-*p*-tolyl-porphyrinato) tin(IV) **2**; *di-3,5-dimethyl*-phenoxy(5,10,15,20-tetra-*p*-tolyl-porphyrinato)tin(IV) **3**. Investigation of the crystal structures of **MPMs 1-3** reveals not only a tolerance to large and dissymmetric phenolates, but that modulation of the channel functionalisation can be realised via substitution on the axial phenolic rings. TGA investigation of these materials indicates they exhibit excellent thermal stabilities in comparison with other molecular inclusion

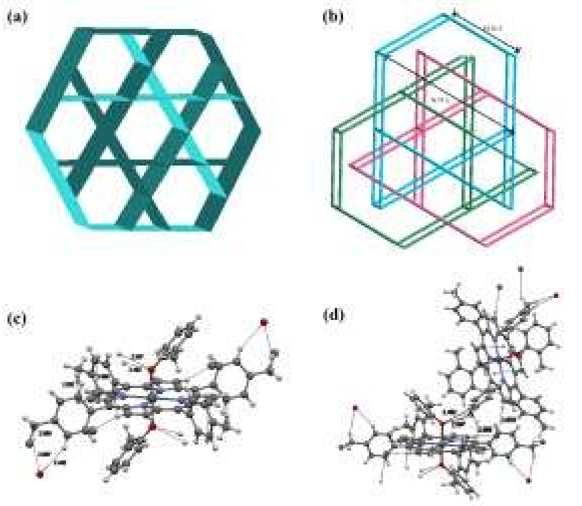

Fig. 2 (a) Schematic representation of supramolecular kagomé lattice net in **MPM-1**; (b) Three-fold interpenetrating kagomé lattice net was shown in different colour; (c) Observed short contacts in **MPM-1**, non-classical hydrogen bonding and weak interactions are shown as black dashed lines; (d) Stereo connection of two neighbouring MPM-1 molecules by non-classical hydrogen bonding and weak interactions.

compounds, which shows this series of MPMs may serve as new candidates for guest exchange or in small molecule capture applications.

Sn(IV)TPP(OH)$_2$ was prepared by using a well-established procedures.[43-45] Sn(IV)TTP(bisphenolates) **1-3** were achieved by reacting Sn(IV)TTP(OH)$_2$ with the corresponding phenol in a 1:2 ratio in dichloromethane at room temperature for two days [see ESI]. Purple needle-shaped crystals of compounds **1-3** were collected by slow diffusion of hexane into a concentrated dichloromethane solution and their purity were examined by ^{1}H NMR, IR characterisation (Fig. S2, in the ESI). The Sn(IV)TTP(bisphenolates) **1-3** are insoluble in water and common organic solvents such as benzene and hexane.

MPMs 1-3 are conformational analogues, here we take **MPM-1** as an example to illustrate their crystal structures. **MPM-1** crystallises in the space group *R*-3. The asymmetric unit of **1** comprises half Sn(IV)TTP(bisphenolates) monomer and two water molecules (Fig 1a. water molecules were omitted for clarity). The Sn(IV) center adopts octahedral geometry completed by the four inner peripheral nitrogens of the porphyrin ligand and axially via the two phenolic oxygens with Sn-N distance of 2.118(6) Å and 2.091(2) Å, Sn-O distance of 2.0456 Å. The phenolate groups lies in an anti-orientation with respect to each other. A view down crystallographic *a* axis shows that every three discrete units stacking on the other three from an adjacent layer in an alternating ABAB fashion. Six molecules from every two layers intersect with each other forming a hexagonal pattern (Fig. 1b and c). The supramolecular net presents a threefold interpenetrating kagomé lattice (Fig. 2a).[46] Further inspection reveals each framework constitutes a trigonal-hexagonal array in the *ab* plane which gives rises to an extremely large diameter of 36.53 Å with each edge of the regular hexagon being 18.26 Å long. Each hexagon is offset to the next two in a regular fashion, giving rise to hourglass-shaped channels best described as 120° for every 3.4 Å (Fig. 2b). These channels are lined with methyl groups from both the phenolic and peripheral aromatic rings of **1**.

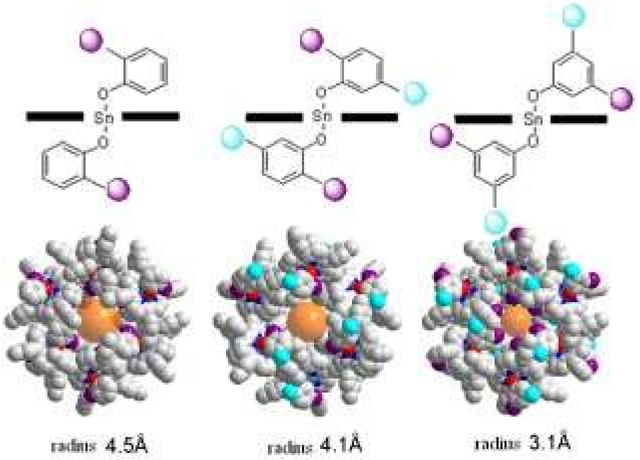

Fig. 3 Space-filling mode of **MPMs 1-3** down the crystallographic *c* axis featuring one-dimensional channels with radium from 4.5 Å to 3.1 Å (orange spheres), phenolic methyl groups lining the channel are coloured in purple (hydrogen atoms were omitted for clarity).

Like other reported supramolecular kagomé lattice nets, [29] small trigonal channels that lie parallel to the *c* axis were observed in **MPM-1**, however they are fully occupied by the large porphyrin molecules. The 3D supramolecular network appears to be maintained and stabilised by non-classical but significant hydrogen bonding and weak interactions. As can be seen from Fig. 2c and d, each MPM-1 single molecule has four main short contacts with adjacent molecules that help it extend into a three dimensional supramolecular network. The interactions between O1-H11 (with a distance of 2.492(2) Å) and O1-H21A (with a distance of 2.597(3) Å) play a crucial role in stabilising the whole network. The robustness of the supramolecular network was further enhanced by weak stacking interactions with C17-H17$\cdots$C13 distance of 2.832(4) Å and C21-H21$\cdots\pi$ distance of 2.868(8) Å.

The diameter of the effective pore size in **MPMs 2-3** was reduced from 9Å to 6.2 Å as a result of the added methyl group to the axially linked phenolic ring. Surprisingly, the whole supramolecular network is maintained and is tolerant to the added steric bulk of the additional methyl groups and their orientations. It also appears the channel property is greatly improved in **MPM-3** as the axial methyl groups line the channel compared to **MPM 1-2**, of which phenolic methyl groups are half-hidden in the channel (Fig. 3). This indicates that future designs should likely have a 1, 3-substitution pattern.

In **MPMs 1-3**, a large region of disordered solvent molecules was entrapped in the unit cell, which could not be assigned as discrete atomic sites by sc-XRD. We employed PLATON/SQUEEZE[47, 48] to remove the scattering from the highly disordered solvent molecules in **MPMs 1-3**. The resulting new files were used to further refine their crystal structure.

Thermal gravimetric analyses (TGA) of **MPMs 1-3** revealed that the guest solvent molecules can be released upon heating from 80 °C to 225 °C (Fig. 4). Weight loss at 80- 150°C for **MPM-2** and at 80- 190°C for **MPM-1** provided evidence for the loss of included solvent from the honeycomb-like materials. In **MPM-3**, the remove of solvent took two steps to finish (80- 148°C; 148- 225°C) which suggests that two kinds of solvents existed inside the 1D channel. At higher temperatures, weight loss of **MPMs 2-3** are quite similar, 5.4 % and 6.0% weight loss from 300°C corresponds to four methyl groups per Sn(IV)TTP(bisphenolates) unit (calculated: 5.8% and 6.1%). The whole network began to collapse gradually after they lose the methyl groups from 330°C. While, no obvious weight loss was observed from 190 to 350°C for **MPM-1**, after which the desolvated framework began to decompose. The exceptional high thermal stability of compound **MPM-1** may be caused by non-classical hydrogen bonding and week interactions within the framework. Despite the decomposition, each MPM shows surprising thermal stability for application.

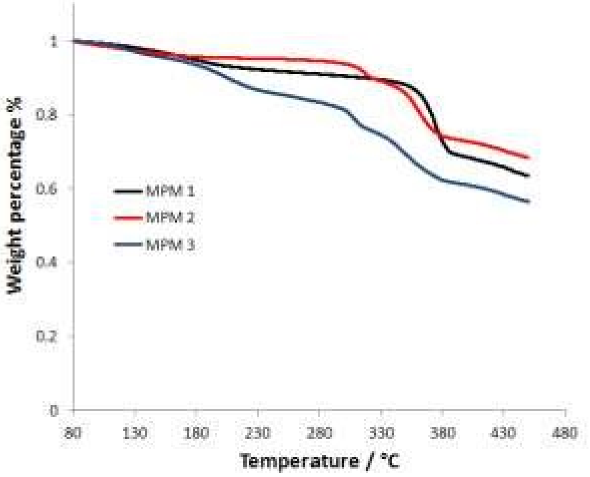

Fig. 4 TGA curves of **MPM-1** (black), **2** (red) and **3** (deep blue)

Conclusions

To conclude, we have designed and synthesised molecular porous materials **MPMs 1-3** with extrinsically 1D channels based on the interactions of Sn(IV)porphyrin phenolates. The channel properties can be diversified through axial ligand substitution. XRD, NMR, IR and TGA measurements on **MPMs 1-3** were investigated, which shows they exhibit excellent thermal stability and exceptional solvent (water and common organic solvents) stability as well. Coupled with the good stability and fine tunability, Sn(IV)porphyrin phenolates may be able to serve as a prominent nano-material for practical applications. Further investigation of these Sn(IV)porphyrin phenolates are ongoing.

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Notes and references

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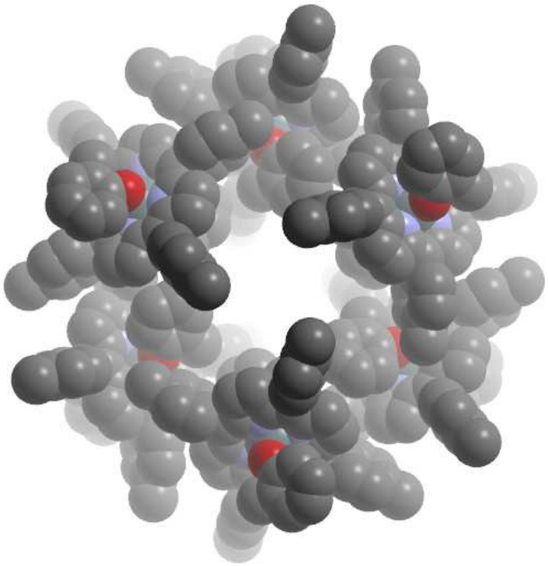
† Crystal data for Sn(IV)TTP(*o*-cresol)$_2$: $SnC_{62}H_{50}N_4O_2$, M = 1001.75, $a = b$ = 36.528(2), c = 10.5054(1) Å, purple acicular, trigonal R-3, V = 12139.0(2) Å^3, ρ = 1.233 g/cm^3, F(000) = 4644, T = 123 K, λ = 0.71073 Å, Z = 9, R_1 [$I>2\sigma(I)$] = 0.0606, wR_2 = 0.1890, GOF = 0.893. Crystal data for Sn(IV)TTP(*2,5*-methyl)$_2$: $SnC_{64}H_{54}N_4O_2$, M = 1029.82, $a = b$ = 37.419(5), c = 10.7471(1) Å, purple acicular, trigonal R-3, V = 13032(4) Å^3, ρ = 1.181 g/cm^3, F(000) = 4788, T = 123 K, λ = 0.71073 Å, Z = 9, R_1 [$I>2\sigma(I)$] = 0.0562, wR_2 = 0.2089, GOF = 0.967. Crystal data for Sn(IV)TTP(*3,5*-methyl)$_2$: $SnC_{64}H_{54}N_4O_2$, M = 1029.82, $a = b$ = 37.361(5), c = 10.403(2) Å, purple acicular, trigonal R-3, V = 12576 (5) Å^3, ρ = 1.224 g/cm^3, F(000) = 4788, T = 123 K, λ = 0.71073 Å, Z = 9, R_1 [$I>2\sigma(I)$] = 0.0720, wR_2 = 0.2394, GOF = 0.927.

Crystallographic data (including structure factors) for Sn(IV)TTP(*o*-cresol)$_2$, Sn(IV)TTP(*2,5*-dimethyl)$_2$, Sn(IV)TTP(*3,5*-dimethyl)$_2$, have been deposited at the Cambridge Crystallographic Data Center as supplementary publication CCDC reference no. 921008-921009 and 921011. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

Reference

1. C. Peregoa and R. Millinib, *Chem.Soc.Rev.*, 2013, **42**, 3956--3976.
2. Urbano Dı´az, B. D and A. Corma, *Chem. Soc. Rev.*, 2013, **42**, 4083-4097.
3. J. Y. Lee, O. K. Farha and J. Roberts, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
4. S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109–119.
5. L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294-1314.
6. J. R. Li, R. J. Kuppler and Z. H. C, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
7. D.M. D. Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058-6082.
8. N. L. Rosi, J. Eckert and M. Eddaoudi, *Science*, 2003, **300**, 1127-1129.
9. D. Tarn, C. E. Ashley and M. Xue, *Acc. Chem. Res.*, 2013, **46**, 792-801.
10. M. Colilla, B. González and M.V. Regí, *Biomater. Sci.*, 2013, **1**, 114-134.
11. C. Coll, A. Bernardos and R. M. Manez, *Acc. Chem. Res.*, 2013, **46**, 339-349.
12. B. Allen, *Nature Mater.*, 2003, **2**, 438-440.
13. S. J. Zhang, T. Shao and H. S. Kose, *Environ. Sci. Technol.*, 2010, **44**, 6377–6383.
14. M. L. Pinto and J. Pires, *Microporous and Mesoporous Materials*, 2012, **151**, 403-410.
15. M. Eddaoudi, J. Kim and N. Rosi, *Science*, 2002, **295**, 469-472.
16. S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276–288.
17. M. D. Allendorf, C. A. Bauer and R. K. Bhakta, *Chem. Soc. Rev.*, 2009, **38**, 1330–1352.
18. A. U. Czaja, N. Trukhanb and M. l. U, *Chem. Soc. Rev.*, 2009, **38**, 1284–1293.
19. M. Kurmoo, *Chem.Soc.Rev.*, 2009, **38**, 1353–1379.
20. J. L. Blin, A. Leonard and Z. Y. Yuan, *Angew. Chem. Int. Ed.*, 2003, **42**, 2872 – 2875.
21. Y. Ren, Z. Ma and P. G. Bruce, *Chem. Soc. Rev.*, 2012, **41**, 4909–4927.
22. P. Yang, D. Y. Zhao and D. I. Margolese, *Nature*, 1998, **139**, 152-155.
23. M. C. Burleigh, M. A. Markowitz and M. S. Spector, *Langmuir*, 2001, **17**, 7923-7928.

24. S. Ungureanu, M. Birot and G. Laurent, *Chem. Mater.*, 2007, **19**, 5786-5796.
25. J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.* , 1998, **120**, 11864-11873.
26. A. P. Cote, A. I. Benin and N. W. Ockwig, *Science*, 2005, **310**, 1166-1170.
27. J. Tian, P. K. Thallapally and B. P. McGrail, *CrystEngComm*,, 2012, **14**, 1909–1919.
28. N. B. McKeown, *J. Mater. Chem.*, 2010, **20**, 10588-10597.
29. A. I. Cooper, *Angew. Chem. Int. Ed.* , 2012, **51**, 7892 – 7894.
30. X. Z. Luo, X. J. Jia and J. H. Deng, *J. Am. Chem. Soc.*, 2013.
31. P. S. Nugent, V. L. Rhodus and T. Pham, *J. Am. Chem. Soc.*, 2013, **135**, 10950-10953.
32. R. Bonnett, *Chem. Soc. Rev.* , 1995, **24**, 19-33.
33. T. Hasobe, *J. Phys. Chem. Lett.*, 2013, **4**, 1771−1780.
34. A. D’Urso, M. E. Fragala and R. Purrello, *Chem. Commun.*, 2013, **49**, 4441.
35. S. Nimr and E. Keinan, *J. Am. Chem. Soc.*, 1999, **121**, 8978-8982.
36. W. Kim, J. Park and H. J. Jo, *J. Phys. Chem. C*, 2008, **112**, 491-499.
37. S. Tangestaninejad and V. Mirkhani., *Syn. Commun.*, 1999, **29**, 2079-2083.
38. D. P. Arnold and J. Blok, *Coord. Chem. Rev.* 2004, **248**, 299-319.
39. G. D. Fallon, M. A.-P. Lee and S. J. Langford, *Org. Lett.*, 2002, **4**, 1895-1898.
40. S. J. L. Gary D. Fallon, Marcia A.-P. Lee, Emmanuel Lygris, *Inorg. Chem. Commun.*, 2002, **5**, 715-718.
41. M. J. L. Steven J. Langford , Jens Beckmann, *Inorg. Chem. Commun.* 2005, **8**, 920–923.
42. S. J. Langford and C. P. Woodward, *CrystEngComm*,, 2007, **9**, 218–221.
43. D. P. Arnold, *Polyhedron*, 1986, **5**, 1957-1963.
44. D. P. Arnold, *J. Chem. Educ.* , 1988, **65**, 1111-1112.
45. S. J. Langford, M. A.-P. Lee and K. J. Macfarlane, *J. Incl. Phenom. and Macrocyc. Chem.*, 2001, **41**, 135-139.
46. B. Moulton, J. J. Lu and R. Hajndl, *Angew. Chem. Int. Ed.*, 2002, **41**, 2821-2824.
47. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.
48. A. L. Spek, *Acta Cryst. Section D Biological Crystallography*, 2009, **65**, 148-155.



A new series of highly stable supramolecular porous materials (SPMs) have been developed using porphyrin bisphenolates as the building blocks. Self-assembly optimization investigations carried out during crystalisation has helped to improve and control the stereo-stacking within the arrays and ultimately the functionalisation of the SPM inner surface. Ultimately, we have identified ways to systematically tune the pore lining by substituting different groups on phenolic ring, which also allows pore size modulation with diameters ranging from 9.0-6.2 Å. Their structures were confirmed by single crystal X-ray Diffraction and TGA investigations revealed these SPMs possess exceptional thermal stability.