Solvent-free porous framework resulted from 3D entanglement of 1D zigzag coordination polymer†

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A solvent-free porous metal organic framework is constructed by the 3D entanglement of 1D zigzag coordination polymeric chains. The role of solvents and the effect of reaction conditions on such unique entanglement are addressed.

Porous coordination polymers (PCPs) or metal organic frameworks (MOFs) have now become a fascinating class of materials[1] from both the fundamental and application point of view.[2] The very interesting topologies of the frameworks inspire the creative minds of the researchers to enrich the field with new materials of versatile topologies. These materials serve various potential applications including gas storage,[3] separation,[4] ion exchange,[5] catalysis[6] and drug delivery.[7] The self-assembly of metal-ion centers bridged through multi-dentate ligands often reveals extended polymeric networks with void spaces that are ideally suited for such applications. However, the available free volume is often occupied by solvent and/or guest molecules, which must be exchanged in order to exploit the porous features of these materials. The desolvated MOFs may or may not retain the crystallinity, leave alone the single crystal nature of the material.[2a–c,8] Hence, only a few examples are known in the literature for solvent-free single crystals which have been obtained after the removal of the solvents from solvent-filled MOFs. Thus designing a PCP without any solvent molecule in its pores has proven to be a continuous challenge, as '*nature abhors void space*'. Interpenetration often occurs during the propagation of the network to obstruct the formation of the void space in the materials.[9] Using chelating ligands along with the spacers is a well-known strategy to stop the interpenetration to take place but it often reduces the dimensionality of the frameworks. Although the sorption properties of 2- and 3-periodic frameworks have been extensively studied, the use of one periodic framework materials for this purpose is scarce,[10] as single chains tend to pack separately and fail to form porous channels. Despite forming porous channels completely filled with solvent molecules, the frameworks collapse upon removal of the solvent, thus devoid of any gas/solvent exchange application. The formation of porous channels in 1D zigzag coordination polymer is only possible when three or more single chains propagate in different and non-coplanar directions to undergo rare 3D entanglements. 'Warp-and-woof' like interwoven molecular fabric structures are known to form *via* the 2D entanglement of 1D coordination polymeric strands.[11] Entanglement *via* H-bonding, extensive interchain π–π stacking and C–H···π interactions often enhances the robustness of the networks upon guest removal.[12–14]

Recently, Gao and co-workers have documented the first example of '*hierarchical entanglement*' of 1D zigzag chain that resulted in a robust microporous framework.[13] The 1D zigzag coordination chains of **1**·DMSO (**1** = [Zn(phen)(SDC)]$_n$, where phen = 1,10-phenanthroline, H$_2$SDC = *trans*-4,4′-stilbenedicarboxylic acid) were found to propagate in four different directions to undergo 3D entanglement *via* π–π interactions. Accordingly, this led to the formation of a rare 3D interwoven framework. Wang and co-workers reported 1D zigzag chains of same composition, synthesized by hydrothermal method, with a different structure where the zigzag chains propagate in two non-coplanar directions that resulted in three-dimensional polycatenated network.[14] The authors who reported **1**·DMSO[13] had anticipated that DMSO might have played the role of a template in that reaction condition to result such unique 3D entanglement that resulted in a microporous framework. It is well known that experimental conditions influence the nature of overall topology. Hence, we have revisited the system to investigate the role of DMSO in this 3D-entanglement.

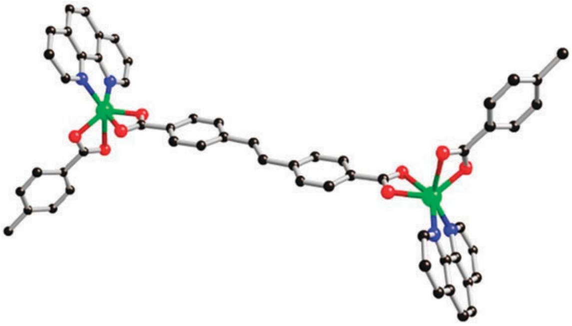

Fig. 1 A fragment of the 1D zigzag coordination chain in **2**.

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We have successfully synthesized‡ $[Zn(phen)(SDC)]_n$, **2**, the same 1D zigzag chains (Fig. 1) with the same connectivity and entanglement as in **1** but from a different reaction condition without any lattice solvent molecule. The structure was refined in the tetragonal space group§ $P4/ncc$ where the Zn(II) ion occupies a distorted octahedral centre and coordinated by a chelating phen ligand and two chelating carboxylate groups from two different SDC ligands. The SDC ligand lies about an inversion centre and a 2-fold axis passes through Zn(II) bisecting phen. The chelate modes of SDCs are highly asymmetric with unequal Zn···O distances 1.960(4) and 2.598(4) Å. The coordination geometry around Zn can be described as a distorted trigonal prism where the corner angle is 118.2°.

The zigzag chains of the coordination polymer propagate in four different non-coplanar directions around the crystallographic four-fold axes in the [001] direction to generate an interwoven framework (see ESI†). The chains are entangled *via* strong π–π interactions between the aromatic rings of the phen and SDC ligands that lead to the formation of a robust microporous framework. The total potential solvent area volume is 797.4 $Å^3$ (15.8% per unit cell volume), as calculated by PLATON.[15] The void channels of diameter 6 Å (distance between the centers of the diagonal hydrogen atoms in the channel) that are readily available to host gases or solvents (Fig. 2) are passing through the [001] direction. The absence of solvent or guest molecules in **2** was also confirmed by thermogravimetry which shows no weight loss from room temperature up to 350 °C. A quick comparison between the structures of **1**·DMSO and **2** reveals that the diameter of the channel is reduced from 6.304 to 6.056 Å while the Zn–O1 distance increased from 1.939(3) to 1.960(4) Å upon removal of the solvent. Since the data collections for the two structures were done at two different temperatures (293 and 223 K respectively) these differences may not mean much.

When the sample **2** was immersed in DMSO for 3 days, one equivalent of the solvent was sorbed into the channels that was measured by thermogravimetric analysis. The PXRD pattern after DMSO sorption of the samples exactly matches with the simulated pattern for **1**·DMSO (Fig. 3). Although the attempt to observe the process *via* single-crystal to single-crystal failed, the conversion from **2** to **1**·DMSO was found to be complete and reversible. The observed cell data¶ after 12 h immersion of the sample **2** in DMSO clearly indicate the contraction of *a* and *b* values and the expansion of *c* value. When the sample **2** was immersed in DMF, 0.5 equivalent DMF was found to be sorbed in after 4 days as indicated by the TGA experiment (see ESI†). Xylene is bulkier than toluene but the data shows higher uptakes for xylene (any noticeable changes in the PXRDs). The hydrophobic channels in **2** were also found to sorb small guest molecules like 1.8 equivalent of cyclohexane, 1.8 equivalent of benzene, 2.3 equivalent of toluene and 3.5 equivalent of xylene upon immersing the sample in respective solvents, as estimated by TGA experiment (see ESI†). However, **2** was found not to sorb any water, methanol and ethanol molecules in its channels. This could be due to the hydrophobic nature of the channels, or the solvent molecules trapped initially may have escaped rapidly when the crystals were taken out of the mother liquor.

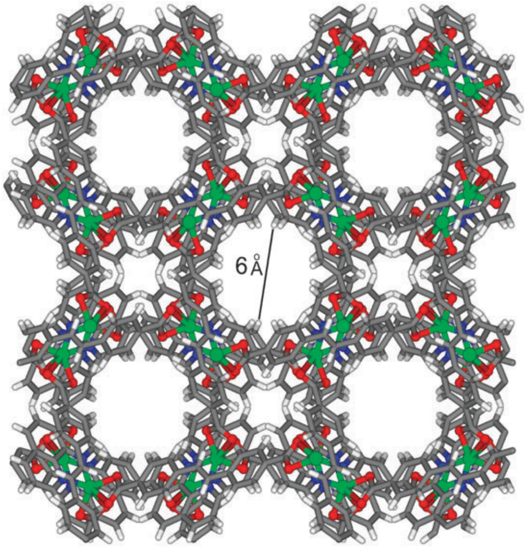

Fig. 2 Solvent-free porous channels along the [001] direction.

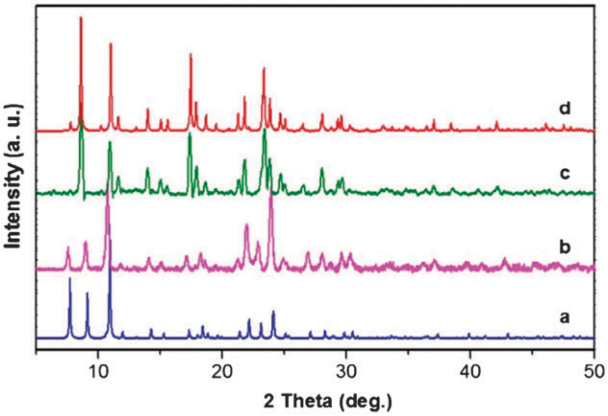

Fig. 3 PXRD patterns: (a) simulated pattern for **2**; (b) observed pattern for as-synthesized sample **2**; (c) for **2**·DMSO after **2** was immersed in DMSO for 3 days; (d) simulated pattern for **1**·DMSO.[13a]

The presence of narrow open channels in **2** prompted us to evaluate its potential gas sorption properties. The solvent-free as-synthesized compound was initially evacuated at room temperature for 24 h and subsequently heated to 100 °C for 8 h. The permanent microporosity of **2** was confirmed from the argon type I adsorption isotherm which revealed an apparent BET and Langmuir surface areas of 220 and 349 $m^2\ g^{-1}$, respectively (see ESI†). The estimated experimental pore volume was determined to be 0.10 $cm^3\ g^{-1}$, as obtained using the Dubinin–Radushkevich (D–R) equation. The hydrogen capacity at 77 K (0.49 wt%) is low (Fig. 4); however, this creates a new landmark for the sorption studies on the 1D zigzag coordination polymers. The creation of solvent free porous channels by a complicated 3D entanglement of single zigzag chains is unique.

Interestingly, the isosteric heat of adsorption has an estimated value of 7.0 kJ mol^{-1} at the lowest coverage and remains constant until approximately 0.2 wt% (see ESI†). This observation can be explained by the presence of narrow pores which promote stronger adsorbate–adsorbent interactions because

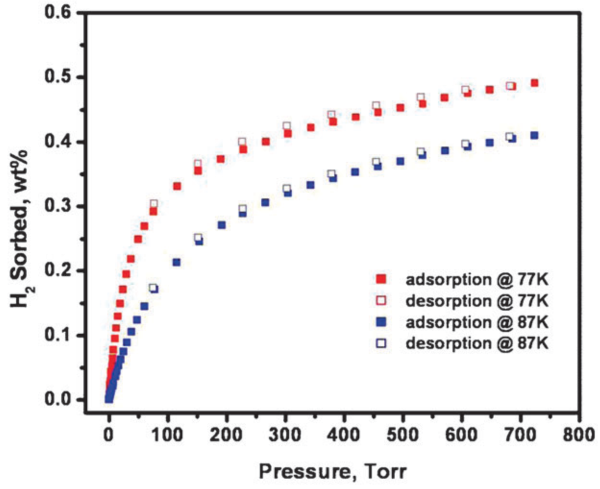

Fig. 4 H_2 adsorption isotherm at 77 and 87 K.

the adsorption potentials of neighboring walls overlap. On the other hand, at higher loadings these sites are occupied and weaker adsorbate–adsorbate interactions are predominate, hence the slight decrease in the isosteric heat of adsorption.

In another experiment, equivalent amount of reactants were mixed and stirred in a mixture of solvents water, ethanol and methanol for an hour at room temperature.‖ The resulting product (here we denote **3**) has the same structure as **2**, as was evidenced by PXRD patterns (see ESI†). When the same reactants are mixed and stirred in DMSO at room temperature, the PXRD pattern of the resulting compound matches with **1**·DMSO (see ESI†). These observations conclude that the 3D entanglement that leads to microporosity in the aforementioned system can be achieved simply by mixing the reactants in stoichiometric amounts. We anticipate that neither the reaction condition (temperature and pressure in solvothermal method) nor the solvent played any template effect for the entanglement. It might be the Nature's selection for this particular system as none other 1D zigzag coordination polymer obtained from SDC shows this property.[16]

The results presented herein raise two important and interesting questions: (1) is it possible to synthesize solvent-free PCPs in general or is this observation an isolated special case? (2) Is there any restriction to the pore size that can still exist without guest molecule? Research is in progress towards understanding these issues in the formation of solvent-free PCPs. In conclusion, we have presented a very unique 1D zigzag coordination polymer with solvent-free porous channels for the first time, constructed by 3D entanglement and stabilized by interchain π–π stacking interactions. The solvent and gas sorption properties are thus discussed.

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Notes and references

‡ Synthesis of **2**: triethyl amine salt of H_2SDC (0.0134 g, 0.05 mmol) in ethanol was carefully layered over 1 : 1 mixture of $Zn(NO_3)_2$ (0.0149 g, 0.05 mmol in 0.5 ml H_2O) and 1,10-phenanthroline monohydrate (0.0099 g, 0.05 mmol, 0.5 ml MeOH) using methanol as buffer layer in a long test tube. Octahedral shaped, colourless single crystals were obtained after 2 days and were used for X-ray diffraction analysis. Yield 0.02 g, 78%. Analysis found: C, 65.58; H, 3.48; N, 5.69, $C_{56}H_{36}N_4O_8Zn_2$ requires: C, 65.70; H, 3.54; N, 5.47%.

§ Crystal data for **2** at 223 K: $C_{28}H_{18}N_2O_4Zn$, M = 511.83, tetragonal, space group $P4/ncc$, a = 16.1598(4), c = 19.3303(11) Å, V = 5047.9(3) Å^3, Z = 8, D_{calc} = 1.347 g cm^{-3}, μ = 1.008 mm^{-1}, GOF = 1.047, Final R_1 = 0.0784, wR_2 = 0.2385 [for 2221 data $I > 2\sigma(I)$].

¶ The observed cell data after 12 h immersion of **2** into DMSO (incomplete conversion) were as: a = 16.129, c = 19.547 Å, and V = 5085.2 Å^3. The contraction in a and b but the expansion in c and V clearly indicate that **2** slowly converted to **1**·DMSO.

‖ Synthesis of **3**: H_2SDC (0.268 g, 1 mmol) was dissolved in 8 ml water with the addition of triethyl amine and then was mixed with a mixture of $Zn(NO_3)_2$ (0.298 g, 1 mmol in 12 ml ethanol) and 1,10-phenanthroline (0.198 g, 1 mmol in 12 ml methanol). The resulting mixture was stirred for an hour and then the white powder was collected by filtration and dried. The structure was determined by comparing PXRD patterns with **2**.

1 K. Biradha, A. Ramanan and J. J. Vittal, *Cryst. Growth Des.*, 2009, **9**, 2969.

2 Some reviews: (*a*) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; (*b*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*c*) S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490; (*d*) J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; (*e*) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**, 401.

3 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*b*) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (*c*) H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem.–Eur. J.*, 2005, **11**, 3521; (*d*) L. Ma, D. J. Mihalcik and W. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 4610; (*e*) M. Dincă and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766; (*f*) A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson and R. E. Morris, *J. Am. Chem. Soc.*, 2008, **130**, 10440; (*g*) J. Luo, H. Xu, Y. Liu, Y. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Ma and H.-C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 9626; (*h*) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (*i*) J. Moellmer, E. B. Celer, R. Luebke, A. J. Cairns, R. Staudt, M. Eddaoudi and M. Thommes, *Microporous Mesoporous Mater.*, 2010, **129**, 345; (*j*) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833.

4 (*a*) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 32; (*b*) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106.

5 (*a*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (*b*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (*c*) F. Nouar, J. Eckert, J. F. Eubank, P. Forster and M. Eddaoudi, *J. Am. Chem. Soc.*, 2009, **131**, 2864; (*d*) T. K. Maji, R. Matsuda and S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142.

6 (*a*) J. S. Seo, D.-M. Whang, H.-Y. Lee, S. I. Jun, J.-H. Oh, Y.-J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (*b*) T. Sawaki and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 4793; (*c*) M. Fujita, Y.-J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*d*) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.

7 (*a*) P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774; (*b*) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and G. Ruxandra, *Nat. Mater.*, 2010, **9**, 172; (*c*) A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson and R. E. Morris, *J. Am. Chem. Soc.*, 2008, **130**, 10440.

8 (*a*) T. Min, B. Zheng, J. Bai, R. Sun, Y. Li and Z. Zhang, *CrystEngComm*, 2010, **12**, 70; (*b*) R. Sun, S. Wang, H. Xing, J. Bai, Y. Li, Y. Pan and X. You, *Inorg. Chem.*, 2007, **46**, 8451;

(*c*) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607.

9 (*a*) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Am. Chem. Soc.*, 2007, **129**, 7136; (*b*) O. M. Yaghi, *Nat. Mater.*, 2007, **6**, 92; (*c*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

10 (*a*) E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798; (*b*) H. R. Moon, J. H. Kim and M. P. Suh, *Angew. Chem., Int. Ed.*, 2005, **44**, 1261; (*c*) C.-D. Wu and W. Lin, *Dalton Trans.*, 2006, 4563; (*d*) S. Takamizawa, E.-I. Nakata, H. Yokoyama, K. Mochizuki and W. Mori, *Angew. Chem., Int. Ed.*, 2003, **42**, 4331; (*e*) S. Hu, K.-H. He, M.-H. Zeng, H.-H. Zou and Y.-M. Jiang, *Inorg. Chem.*, 2008, **47**, 5218; (*f*) G. Li, C. Zhu, X. Xi and Y. Cui, *Chem. Commun.*, 2009, 2118; (*g*) S. Noro, D. Tanaka, H. Sakamoto, S. Shimomura, S. Kitagawa, S. Takeda, K. Uemura, H. Kita, T. Akutagawa and T. Nakamura, *Chem. Mater.*, 2009, **21**, 3346.

11 (*a*) A. M. P. Peedikakkal and J. J. Vittal, *Cryst. Growth Des.*, 2008, **8**, 375; (*b*) L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2000, **2**, 154; (*c*) Y.-H. Li, C.-Y. Su, A. M. Goforth, K. D. Shimizu, K. D. Gray, M. D. Smith and H.-C. zur Loye, *Chem. Commun.*, 2003, 1630.

12 (*a*) L. Han and Y. Zhou, *Inorg. Chem. Commun.*, 2008, **11**, 385; (*b*) H.-D. Guo, D.-F. Qiu, X.-M. Guo, G.-L. Zheng, X. Wang, S. Dang and H.-J. Zhang, *CrystEngComm*, 2009, **11**, 2425.

13 (*a*) A.-L. Cheng, N. Liu, Y.-F. Yue, Y.-W. Jiang, E.-Q. Gao, C.-H. Yanb and M.-Y. He, *Chem. Commun.*, 2007, 407; (*b*) A.-L. Cheng, Y. Ma, J.-Y. Zhang and E.-Q. Gao, *Dalton Trans.*, 2008, 1993.

14 X.-L. Wang, C. Qin, E.-B. Wang and L. Xu, *Cryst. Growth Des.*, 2006, **6**, 2061.

15 A. L. Spek, *PLATON, a multipurpose crystallographic tool*, University of Utrecht, Utrecht, The Netherlands, 2003.

16 (*a*) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036; (*b*) Y. Ma, A.-L. Cheng, J.-Y. Zhang, Q. Yue and E.-Q. Gao, *Cryst. Growth Des.*, 2009, **9**, 867; (*c*) H.-Y. Wang, S. Gao, L.-H. Huo and J.-G. Zhao, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m3395.