Unprecedented 3D entanglement of 1D zigzag coordination polymers leading to a robust microporous framework†

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Received (in Cambridge, UK) 13th September 2006, Accepted 18th October 2006
First published as an Advance Article on the web 3rd November 2006
DOI: 10.1039/b613295b

One-dimensional zigzag coordination chains in four different directions are hierarchically entangled to generate an unprecedented 3D interwoven framework, which exhibits permanent porosity and guest selectivity.

The research activities concerning coordination polymers are expanding rapidly, not only for the pragmatic perspective to obtain new functional materials, but also for the fundamental interest to reveal the intriguing structural diversity and assembling processes of these materials.[1] Supramolecular entanglements have contributed much to the structural diversity.[2] Particular attention has been devoted to the entanglements of polymeric coordination motifs that contain ring moieties, through which the motifs are entangled by polycatenating, polythreading or polyknotting. The resulting networks can be interpenetrated—the network cannot be disentangled without breaking chemical bonds—or non-interpenetrated, and a plethora of these networks have been obtained based on 1D (ladders and other ring-containing chains), 2D and 3D motifs, as reviewed by Batten, Robson, and Ciani.[2] On the other hand, the intertwining of 1D single chains, without the participation of ring moieties, represents a different class of entanglements, which have aroused increasing interest recently.[2a] Such structures, in contrast with the interpenetrated structures, can be disentangled by slipping off the chains without breaking bonds. However, such species are still rare, and the construction of new entangled networks from single coordination chains is still a great challenge, due to the fact that single chains usually tend to be packed separately in space without entanglements. It is noted that the known entanglements of single coordination chains depend strongly upon the shape and the propagating direction of the chains. For helical chains, only parallel entanglements have been reported, and the resulting assemblies have been 1D multiple helices or interwoven braids,[3,4] if the entangling chains propagate along the same axis, and interlocked 3D architectures,[5] if the entangling chains propagate along different axes. For linear chains, only the packing of three or more sets of chains propagating in different and non-coplanar directions can lead to entanglements, and three isotopological examples built of three sets of chains have been described.[6] For zigzag chains, only two examples of 2D entanglements have been reported, where the zigzag chains in two different directions are interwoven into warp-and-woof sheets.[7]

Entanglements can also contribute to the functions of the frameworks. For porous coordination polymers, which have been extensively pursued for their potential applications,[1c–h] entanglement is usually regarded as undesirable, but it can enhance the robustness of the networks. Thus, several robust 3D interpenetrated but porous frameworks have been synthesized.[8] For 1D chains, it can be expected that 3D entanglements can significantly enhance the robustness of the chain packing, as exemplified recently by the robust porous materials constructed from entangled linear chains[6b,c] and from interlocked quintuple helices.[5a] Here we report how the zigzag coordination chains in four different directions are entangled *via* π–π interactions to generate an unprecedented 3D interwoven framework, $[Zn(phen)(L)]_n$ (**1**, phen = 1,10-phenathroline, H_2L = trans-stilbene-4,4′-dicarboxylic acid), which exhibits permanent microporosity and guest selectivity.

The material was initially obtained as **1**·DMSO by the solvothermal reaction of $Zn(OAc)_2$, H_2L and phen with a molar ratio of 1 : 1 : 1 in DMSO‡ and characterized by single crystal X-ray analysis.§ The Zn ion is located in a highly distorted octahedral environment and ligated by a chelate phen ligand and two chelate carboxylato groups from two equivalent L ligands, with a 2-fold axis passing Zn and bisecting the phen ligand. The carboxylato group adopts a highly asymmetric chelate mode, as evidenced by the Zn–O distances (1.937 and 2.699 Å). The L ligands, each having an inversion center at the midpoint of the central C=C bond, serve as quasi-linear linkers between Zn ions to generate infinite 1D zigzag chains. Interestingly, the chains in the crystal lattice are arranged around the crystallographic 4-fold axes in the [001] direction (Fig. 1A), and propagate along four non-coplanar directions ([111], [−1−11], [1−11] and [−111]). This unusual arrangement enables the chains to interweave in a complicated fashion (Fig. 1B), generating a 3D framework with open channels in the [001] direction (see below, and ESI, Fig. S1†).

The complicated entanglement can be made clear by topological analyses. The chains along [1−11] and [−111] are interwoven like the warps and woofs in cloth to give 2D sheets parallel to the (110) planes (Fig. 1C). A second set of sheets with the same warp-and-woof pattern are formed along the (1−10) planes from the chains along [111] and [−1−11]. The two sets of 2D sheets, perpendicular to each other, are further interlocked to generate the 3D entangled

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† Electronic supplementary information (ESI) available: Additional structural diagram, thermogravimetric plots, IR spectra, and XRD patterns for the materials. See DOI: 10.1039/b613295b

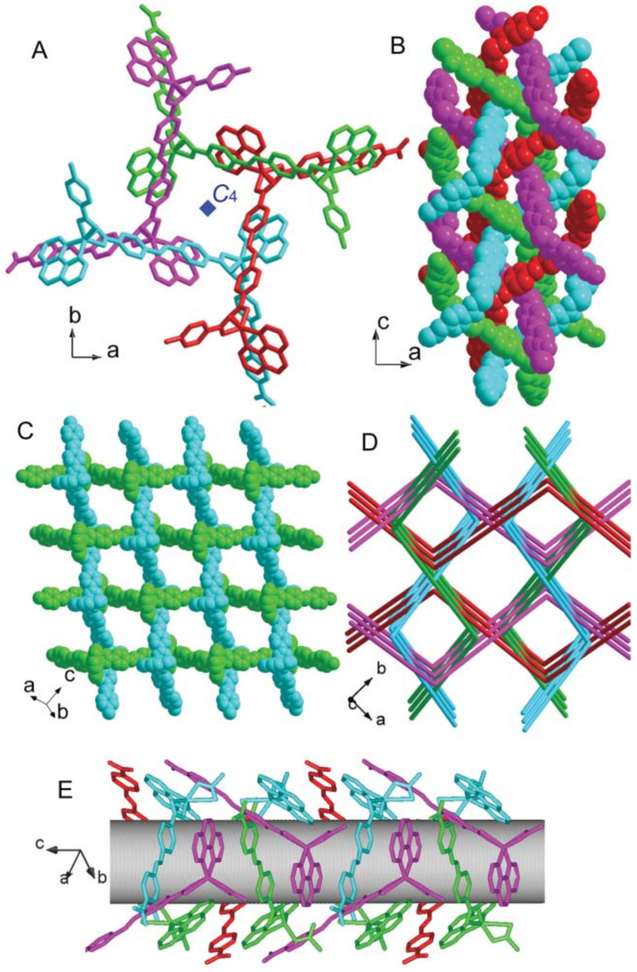

Fig. 1 Views showing four 1D zigzag chains arranged around a 4-fold axis (A), the entanglement of the chains (B), the 2D warp-and-woof weave sheet (C), the 3D entanglement of the 2D sheets (D), and the π–π stacking interactions around a channel (E). The colours are used to distinguish the chains of different propagating directions.

framework (Fig. 1D). Topologically, the interlocking fashion of the interwoven sheets strongly resembles the well-documented 2D → 3D inclined interpenetration of (4,4) coordination sheets.[2b,c] However, no real interpenetration has occurred here, because the structure can be disentangled by slipping off the chains, without breaking any chemical bonds.

The structure of **1**·DMSO is unprecedented, and represents the first 3D entangled framework assembled from 1D chains in four different directions. It may be called a "*hierarchical entanglement*", because it bears both the 2D warp-and-woof interwoven feature arising from 1D zigzag chains[7] and the 2D → 3D interlocking feature resembling the inclined interpenetration of 2D nets.[2b,c] A peculiar feature of the structure is that you have to slip off at least two sets of chains, one from the (110) sheet set and one from the (1−10) sheet set, to fully disentangle the structure. If only the chains that belong to the same set of sheets are slipped off, the 2D warp-and-woof entanglement is retained.

A remarkable consequence of the 3D entanglement in **1**·DMSO is the formation of 1D channels (Fig. 1D and E), which extend along the 4-fold axes and have dimensions of *ca.* 5 Å × 5 Å. The channels are occupied by DMSO molecules with symmetry-imposed disorder in the methyl groups, and PLATON calculations[9] show that the guest-accessible volume comprises 18.6% of the crystal volume. The porous framework is sustained by extensive interchain π–π interactions, which operate between the phen and benzene rings with the face-to-face distance being about 3.49 Å. As shown in Fig. 1A, the four chains around each 4-fold axis are stuck together by four π–π interactions to form a cyclic building unit for the channels. It is worth noting that all the aromatic rings in the structure are involved in π–π interactions. Thus, in the walls of the channels, the phen and stilbene groups are alternately aligned along the *c* direction, and each group interacts with two different ones to form infinite π–π stacking arrays (Fig. 1E).

Several factors may be distinguished as being of great importance for the 3D entanglement. The zigzag shape of the coordination chains is obviously essential for the formation of the 2D interwoven motif. The shape is mainly dictated by the coordination geometries of the metal center and the ligands, and particularly, the phen ligand serves as a "geometry regulator" to facilitate the zigzag shape. The aromatic groups in the ligands play fundamental roles in the 3D entanglement of the chains. The aromatic groups serve as the recognition sites for π–π stacking interactions, which are the main forces that organize the chains in position and stabilize the 3D entanglement. Furthermore, the length of the L ligand and the zigzag shape of the chains are important for the π–π interactions to operate throughout the whole structure. Finally, the reaction conditions, especially the use of DMSO as solvent, are very important in generating the structure.¶

Thermogravimetric analysis (TGA) showed that **1**·DMSO loses the guest molecules at 60–150 °C, and the remaining material (**1**) is stable up to 350 °C (see ESI, Fig. S2†). Although the single crystal nature is not retained upon evacuation, powder X-ray diffraction (PXRD) studies suggested that the entangled porous framework remains intact in **1**: the PXRD pattern of **1** is similar to that of **1**·DMSO (Fig. 2) with slight shifts in peak positions, and unit cell refinement by the CELREF program suggested a contraction of *ca.* 4% in cell volume.[10] The permanent microporosity of **1** is confirmed by N_2 gas sorption studies, which revealed a reversible type I isotherm with a Langmuir surface area of 303 m^2 g^{-1} and

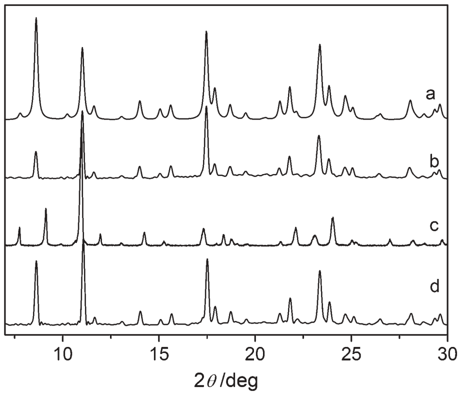

Fig. 2 XRPD patterns: (a) calculated from the X-ray single-crystal data of **1**·DMSO; (b) for as-synthesized **1**·DMSO; (c) for **1** (evacuated at 120 °C under vacuum for 24 h); (d) for **1**·DMSO obtained by immersing **1** in liquid DMSO for 10 h.

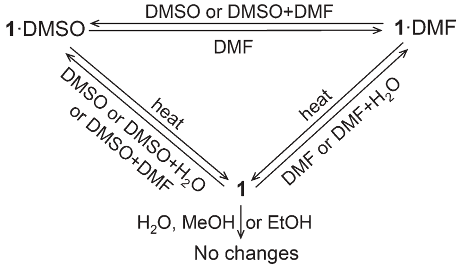

Fig. 3 A summary of the reversible guest inclusion and exchange properties of the materials. Guest adsorption and exchange: immersing the appropriate samples in liquid solvents for 10 h at room temperature. Evacuation: heating the samples at 120 °C under vacuum for 10 h. In the cases of solvent mixtures, a 1 : 1 ratio (v/v) was used.

an estimated pore volume of 0.12 $cm^3 g^{-1}$. The original material, **1**·DMSO, can be recovered by soaking **1** in liquid DMSO (Fig. 3d). The reversible adsorption–desorption of DMSO is also supported by the presence/absence of the IR band at 1030 cm^{-1}, which is attributable to the ν(S=O) absorption (see ESI, Fig. S3†). The guest inclusion and exchange properties of **1** have been investigated by means of PXRD, IR and TGA measurements (see ESI†), and a summary of the results is illustrated in Fig. 3, from which the following remarks can be concluded. (i) The material exhibits selectivity in guest inclusion: it can reversibly adsorb DMF and DMSO, without appreciable adsorptions for water, methanol and ethanol. (ii) The DMSO and DMF guests in the materials are exchangeable. (iii) The porous framework has a preference of DMSO over DMF, because the materials absorb DMSO selectively from the mixture of DMSO and DMF. Finally, the materials exhibit consistent PXRD patterns after ten cycles of DMSO absorption–desorption, suggesting a resistance to fatigue.

In summary, we have illustrated here how the 1D zigzag chains in four different directions are hierarchically entangled to generate an unprecedented 3D interwoven framework, which exhibits permanent porosity and guest selectivity. Considering the very large number of available building blocks and possible assembling topologies, it can be expected that more and more multidimensional entanglements of 1D coordination polymers will be discovered in the near future. Studies along this line will not only increase our knowledge of these intriguing architectures, but also lead to new functional materials.

This work is supported by NSFC (20571026 and 20490210), MOE (NCET-05-0425), and "Shuguang" Project of Shanghai (04SG28).

Notes and references

‡ Synthesis of **1**·DMSO: A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.066 g, 0.30 mmol), H_2L (0.080 g, 0.30 mmol) and phen (0.060 g, 0.30 mmol) in DMSO (8 mL) was stirred for 10 min, and then heated in a Teflon-lined autoclave at 110 °C for 4 days. After cooling to room temperature slowly, block colorless crystals of **1** were obtained and collected by filtration. Yield, 70%. Anal. calcd (%) for $C_{30}H_{24}N_2O_5ZnS$: C 61.22, H 4.11, N 4.76%. Found: C 61.53, H 4.42, N 5.05%. The product is stable in air and insoluble in water and common organic solvents.

§ Crystal data for **1**·DMSO: $C_{30}H_{24}N_2O_5ZnS$, Mr = 589.94, tetragonal, space group $P4/ncc$, a = 16.0428(8) Å, c = 20.4985(8) Å, V = 5275.7(4) $Å^3$, Z = 8, μ(Mo Kα) = 1.054 mm^{-1}, ρ_{calcd} = 1.485 g cm^{-3}, T = 293 K, S = 0.962, $R1$ = 0.0514 for 1055 observed reflections with $I > 2\sigma(I)$, and w$R2$ = 0.1482 for 2323 independent reflections. Intensity data were collected on a Nonius KappaCCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). CCDC 620559. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613295b

¶ While preparing this paper, a different structure (**2**) having the same composition as **1** has been reported.[11] Compound **2** consists of Zn(phen)(L) zigzag chains similar to those in **1**. However, no chain entanglement occurs in **2**: the chains propagating in only two directions are arranged on separate layers, and the 3D structure is sustained by C–H···π interactions. Compound **2** was synthesized by a hydrothermal reaction in the presence of triethylamine. The differences suggest that DMSO may act as a template for the microporous framework in **1**, and demonstrate the great challenge of constructing entangled structures from chains.

1 (*a*) M. J. Zaworotko, *Chem. Commun.*, 2001, 1; (*b*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*c*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*d*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*e*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (*f*) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176; (*g*) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (*h*) C. J. Kepert, *Chem. Commun.*, 2006, 695; (*i*) L. Brammer, *Chem. Soc. Rev.*, 2004, **33**, 476; (*j*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*k*) N. R. Champness, *Dalton Trans.*, 2006, 877.

2 (*a*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (*b*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*c*) S. R. Batten, *CrystEngComm*, 2001, **3**, 67; (*d*) L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269; (*e*) V. A. Blatov, L. Carlucci and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378; (*f*) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *J. Solid State Chem.*, 2005, **178**, 2452.

3 (*a*) I. G. Dance, L. J. Fitzpatrick, A. D. Rae and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, 3785; (*b*) J. W. Lee, E. A. Kim, Y. J. Kim, Y.-A. Lee, Y. Pak and O. S. Jung, *Inorg. Chem.*, 2005, **44**, 3151; (*c*) L. Carlucci, G. Ciani, D. W. v. Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812; (*d*) A. Erxleben, *Inorg. Chem.*, 2001, **40**, 2928; (*e*) O. Mamula, A. Zelewsky, T. Bark and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 2945; (*f*) X.-M. Chen and G. F. Liu, *Chem.–Eur. J.*, 2002, **8**, 4811; (*g*) H.-F. Zhu, W. Zhao, T. Okamura, B.-L. Fei, W.-Y. Sun and N. Ueyama, *New J. Chem.*, 2002, **26**, 1277.

4 (*a*) S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586; (*b*) P. Grosshans, A. Jouaiti, V. Bulach, J.-M. Planeix, M. W. Hosseini and J.-F. Nicoud, *Chem. Commun.*, 2003, 1336; (*c*) Y. Cui, H. L. Ngo and W.-B. Lin, *Chem. Commun.*, 2003, 1388; (*d*) X.-J. Luan, Y.-Y. Wang, D.-S. Li, P. Liu, H.-M. Hu, Q.-Z. Shi and S.-M. Peng, *Angew. Chem., Int. Ed.*, 2005, **44**, 3864; (*e*) X.-J. Luan, X.-H. Cai, Y.-Y. Wang, D.-S. Li, C.-J. Wang, P. Liu, H.-M. Hu, Q.-Z. Shi and S.-M. Peng, *Chem.–Eur. J.*, 2006, **12**, 6281.

5 (*a*) Y. Cui, S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 6014; (*b*) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036.

6 (*a*) L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem.–Eur. J.*, 1999, **5**, 237; (*b*) E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798; (*c*) H. R. Moon, J. H. Kim and M. P. Suh, *Angew. Chem., Int. Ed.*, 2005, **44**, 1261.

7 (*a*) L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2000, **29**, 1; (*b*) 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.

8 (*a*) T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 4843; (*b*) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (*c*) R. Kitaura, K. Seki, G. Akiyama and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2003, **42**, 428.

9 A. L. Spek, *PLATON*, Version 1.62, University of Utrecht, 1999.

10 (*a*) J. Laugier and B. Bochu, *LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments*, Institut National Polytechnique de, Grenoble; (*b*) The cell refinement based on the tetragonal system leads to a = 16.235(8) Å, c = 19.174(1) Å, and V = 5054(2) $Å^3$.

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