

The first 'two-over/two-under' (2O/2U) 2D weave structure assembled from Hg-containing 1D coordination polymer chains†

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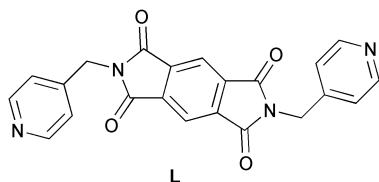
Received (in Columbia, MO) 3rd April 2003, Accepted 21st May 2003

First published as an Advance Article on the web 18th June 2003

Self-assembly of HgI₂ with a semirigid ditopic 'Z' type ligand affords the zigzag chains that interweave into a clothlike 2D network in a 'two-over/two-under' (2O/2U) fashion.

The study of metal–organic coordination polymers is of great current interest not only for their potential applications as functional solid state materials, but also for their intrinsic aesthetic appeal.¹ Great effort has been expended to explore the structural diversity and fascinating topologies of these materials which sometimes are analogs of naturally occurring structures and other times represent entirely new structural architectures.² One intriguing phenomenon contributing to the structural diversity is the occurrence of interpenetrating polymeric networks. Particularly interesting is the concept of 'dimensional expansion' as it relates to interpenetration:^{1b} polymeric assemblies of lower dimensionality can interpenetrate and thereby generate an architecture of an overall higher dimensionality. For example, a frequent occurrence is the 2D → 3D dimensional expansion where many 3D networks have resulted from an inclined interpenetration³ or, in rare cases, by means of a parallel interpenetration⁴ of 2D assemblies.

Entanglement of 1D coordination polymers can also result in a dimensional increase. The best-known examples are 1D ladder networks which, similar to 2D → 3D transformation, may generate 2D networks *via* 1D → 2D parallel interpenetration⁵ or 3D networks *via* 1D → 3D inclined interpenetration.⁶ We previously reported that a terraced stack of coordination polymer ladders with 1/2 offset can be interpenetrated by 1D coordination polymer chains to result in a 3D architecture.⁷ However, dimensional expansion based on only single chain structures is still uncommon. Despite the discovery of a 2D polyrotaxane network threaded by chains containing both rod-like and ring-like components,⁸ woven networks remain rare. Woven networks, however, represent an opportunity for achieving a 1D → 2D dimensional expansion *via* interweaving of chains rather than *via* structural interpenetration. Ciani and co-workers have described a 'warp-and-woof' sheet which represents the first 'one-over/one-under' (1O/1U) interwoven network of 1D coordination polymer strands.⁹ Here we report a 2O/2U interwoven network generated from Hg-containing, zigzag coordination polymer chains.



The ditopic ligand **L**,¹⁰ 2,6-bis(4-pyridinylmethyl)-benzo[1,2-c:4,5-c']dipyrrole-1,3,5,7(2H,6H)-tetrone, contains a

† Electronic supplementary information (ESI) available: One figure showing packing of the interwoven layers in the structure viewed along the *b* direction. See <http://www.rsc.org/suppdata/cc/b3/b303708h/>

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long rigid spacer of three fused rings and two freely-rotating pyridyl arms. It may take on either a *cis*-conformation to act as a 'U' type ligand or a *trans*-conformation to act as a 'Z' type ligand. Reaction of **L** with HgI₂ in a DMF–MeOH mixture resulted in the complex **1**,§ *catena*-poly[HgI₂(**L**)], where single crystals suitable for X-ray diffraction grew on the wall of the tube containing the reaction mixture.¶

As shown in Fig. 1, each ligand coordinates to two Hg(II) ions and each Hg(II) ion is coordinated by two **L** to generate a 1D zigzag chain. The Hg(II) is in a distorted tetrahedral geometry with its coordination sphere completed by two I[−] anions. The two Hg–I distances are virtually equivalent, as are the two Hg–N bond distances. The N–Hg–N angle is dramatically smaller than the I–Hg–I angle, which helps effect the 'weave pattern' (*vide infra*). The two ligands coordinated to the same Hg(II) ion are crystallographically independent, and each possesses a crystallographic inversion center that is situated in the middle of the central benzene ring. As a result, both adopt a distorted 'Z' conformation.

The unusual feature of this material is the zigzag chains of **1** running in perpendicular directions, [1 2 −1] and [1 −2 −1], which enables them to interweave in a 2O/2U fashion to create the cloth-like sheet structure shown in Fig. 2. At each Hg(II) ion,

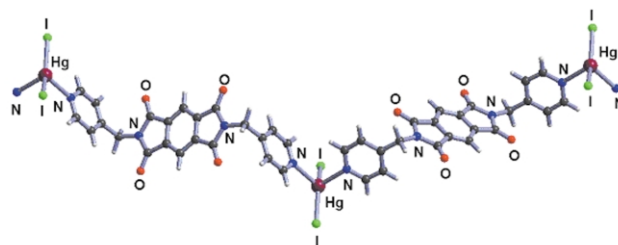


Fig. 1 Molecular structure of **1** showing coordination geometry of Hg(II) ion. Hg–N(3) 2.417(4), Hg–N(1) 2.442, Hg–I(2) 2.6471(4), Hg–I(1) 2.6618(4) Å, N(3)–Hg–N(1) 87.28(13), I(2)–Hg–I(1) 146.795(14)°.

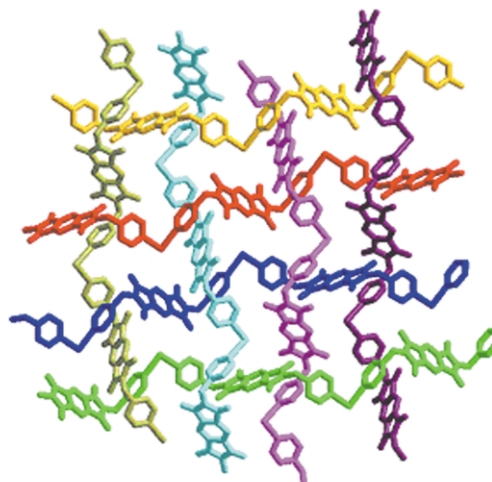


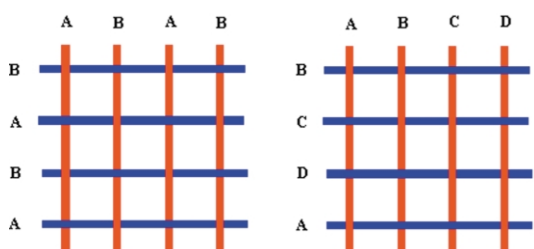
Fig. 2 2O/2U interwoven 2-D network in **1**. The independent chains are distinguished by different colors. Iodine atoms are omitted for clarity.

the two coordinated arms of the ligands pass either both above or both below two other perpendicular 1D chains. A change in orientation from over to under (or vice versa) occurs along the length of these ligands as the two arms of a single ligand point in opposite directions. The most notable feature of this supramolecular entanglement is that each chain is chemically independent but physically interwoven with the perpendicular chains. Thus, in striking contrast with the archetypical interpenetrated network, breaking of chemical bonds is not required to take apart this network structure.

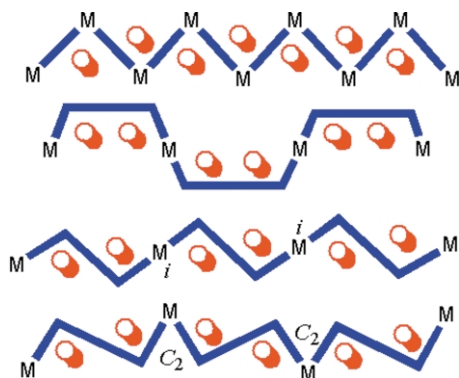
To date, the only interwoven coordination networks that have been discovered are the complexes $\{[\text{Ag}(\text{L}^2)(\mu\text{-PO}_2\text{F}_2)_{0.5}](\text{PF}_6)_{0.5}\}_n$, ($\text{L}^2 = 1\text{-}(\text{isocyanidomethyl})\text{-}1H\text{-benzotriazole}$)¹¹ and $\{[\text{AuI}_2(\mu\text{-bis}(\text{diphenylphosphino})\text{hexane})]\}_n$,¹² which form 2D sheets with a 1O/1U weave pattern. Moreover, in the former case, the interwoven chains are actually connected by the coordinating PO_2F_2^- anion, while in the latter case, the infinite chain structure was formed only *via* weak auriphilic $\text{Au}\cdots\text{Au}$ contacts (3.124(2) Å). The only true 1O/1U 2D weave network assembled from independent 1D coordination polymer chains is the complex $\{[\text{Cu}(2,2'\text{-bipy})(\text{azpy})(\text{H}_2\text{O})](\text{NO}_3)(\text{H}_2\text{O})\}_n$ ⁹ which also contains a zigzag chain composed of a $[\text{Cu}(2,2'\text{-bipy})]^{2+}$ core unit with attached rigid, rod-like azpy ligands.

The topological difference between the 1O/1U and the present 2O/2U weave structure is illustrated in Scheme 1. The former has an ABAB sequence, with two perpendicular sets of two parallel chains as the repeating unit, while the latter has an ABCDABCD sequence, which requires two perpendicular sets of four parallel chains in the repeating unit.

Both rod-like and 'Z' type ligands, among others, can be used to form weave structures, as illustrated in Scheme 2. The zigzag chain formed from rod-like bridging ligands can lead to a simple 1O/1U weave, or potentially a 2O/2U weave for longer ligands. By comparison, the basic weave structure generated from the 'Z' type ligand depends on the local site symmetry of the connectivity between adjacent metal ions: inversion center symmetry results in a weave similar to that obtained from the rod-like ligand, while two-fold (or mirror) symmetry, leads to the formation of, at least, the 2O/2U weave structure. More



Scheme 1 Schematic representation of 1O/1U (left) and 2O/2U (right) clothlike interwoven sheets.



Scheme 2 Schematic of potential weave types utilizing rodlike, 'U' type, and 'Z' type ligands. Red shaded circles represent the perpendicularly running chains and the blue lines represent the ligands.

complicated interwoven networks are possible for both of these cases, but will depend largely on factors such as the overall length of the ligand, the arm-to-spacer length ratio and the width-to-length ratio of the chain unit. In the present case several factors may have contributed to the formation of the 2O/2U weave structure, including the fact that tetrahedral HgI_2N_2 coordination geometry only allows two-fold symmetry, the fact that the small N–Hg–N angle and the short pyridyl arms limit where a chain can fit, and finally the trans orientation of the two pyridyl rings.

In summary, we have isolated what we believe to be the first 2O/2U interwoven 2D network assembled from 1D coordination polymer chains. In contrast to the well known dimensional expansion caused by the interpenetration of 1D ladders^{5,6} and ring-containing chains,⁸ interwoven networks represent another important approach to fabricate multiple-dimensional supramolecular entanglements based on only chain structures. In addition to the weave structure described herein, there are other documented entanglements of 1D chains in three dimensions.¹³ Considering the very large number of potential knit topologies, we expect that more and more chain based supramolecular entanglements will be discovered in the foreseeable future, thereby further increasing the vast structural diversity found for coordination polymers.

Acknowledgement for financial support is made to the ACS-PRF, grant #36822; the NSF grant DMR:0134156; and the NSF/EPSCoR grant #R-02-104.

Notes and references

§ Preparation of **1**: A solution of **L** (6 mg, 0.015 mmol) in 10 mL DMF was slowly mixed with a solution of HgI_2 (6.8 mg, 0.015 mmol) in 5 mL MeOH. The resulting mixture was left standing for several days to give a colorless crystalline product. Yield: 60%. $^1\text{H NMR}$ ($\text{DMSO}-d_6$): δ 8.506 (dd, pyH2), 8.282 (s, benzeneH), 7.349 (dd, pyH3), 4.857 (s, CH_2). TGA: weight loss starting at 190 °C indicates sample decomposition.

¶ Crystal data for **1**: $\text{HgI}_2\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_4$, $M = 852.76$, Monoclinic, space group $P2_1/n$, $a = 11.6675(7)$, $b = 12.2256(7)$, $c = 17.4437(10)$ Å, $\beta = 103.510(1)^\circ$, $U = 2419.4(2)$ Å³, $T = 150$ K, $Z = 4$, 4961 independent reflections measured, final $R1 = 0.0296$ and $wR2 = 0.0599$. CCDC reference number 207401. See <http://www.rsc.org/suppdata/cc/b3/b303708h/> for crystallographic data in .cif or other electronic format.

- S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1461; S. R. Batten, *Cryst. Eng. Comm.*, 2001, **18**, 1; B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117.
- M. J. Zaworotko, *Chem. Commun.*, 2001, 1; M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
- C. B. Aakeroy, A. M. Beatty and D. S. Leinen, *Angew. Chem. Int. Ed.*, 1999, **38**, 1815; M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki and S. Kitagawa, *Chem. Mater.*, 2000, **12**, 1288.
- D. J. Chesnut, A. Kusnetzow, R. Birge and J. Zubietta, *Inorg. Chem.*, 1999, **38**, 5484; L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2000, 1319.
- A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W. S. Li and M. Schroder, *Chem. Commun.*, 1997, 2027.
- M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.
- M. B. Zaman, M. D. Smith and H. C. zur Loye, *Chem. Commun.*, 2001, 2256.
- B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952.
- L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio and S. Rizzato, *Cryst. Eng. Comm.*, 2000, **29**, 1.
- C. A. Hunter, J. K. M. Sanders, G. S. Beddard and S. Evans, *J. Chem. Soc., Chem. Commun.*, 1989, 1765.
- I. Ino, J. C. Zhong, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and Y. Kitamori, *Inorg. Chem.*, 2000, **39**, 4273.
- P. M. VanCalcar, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5231.
- E. A. Axtell, J. H. Liao and M. G. Kanatzidis, *Inorg. Chem.*, 1998, **37**, 5583; L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 1999, **5**, 237.