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Organic/inorganic supramolecular channel frameworks containing a photosensitive azobenzene molecule as an included guest

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Two independent channel frameworks are occupied by photoactive *E*-azobenzene in an unprecedented one-dimensional zigzag motif and thus form virtual three-dimensional supramolecular host–guest networks.

Several novel coordination polymer networks have been shown to form porous materials whose host frameworks can withstand the removal and/or addition of guest molecules.[1,2] Special interest centres on the design of crystalline host–guest materials containing a cavity including ligand-bridged metallocycles (squares,[2–4] rectangles,[5] triangles,[6] hexagons,[7] *etc*.) as nanoscale hosts in technological applications in the area of chemical recognition and sensing. Among these metallocycles, square-grid and rectangular-grid type architectures are promising because of their predictable pore sizes and selective inclusion of guest molecules. Initially these grids were reported in metal complexes of 4,4′-bipyridine with open and interpenetrating networks.[8] The length, linear or nonlinear geometries, and conformationally rigid or nonrigid molecular skeletons of 4,4′-bipyridine can also be controlled by interconnecting spacers between the pyridyl donors.[9–11] The conjugated π-systems containing ethinylene units and/or (hetero)aromatic ring spacers are currently of interest in developing fluorescent materials and are used as model compounds for electroluminescence and optical switching devices.[12] This inspired the development of the 1,4-bis(*x*-pyridyl)butadiyne ligands; x = 2 (**L1**), 3 (**L2**), 4 (**L3**).[13] The specific local geometry, the different orientations of N-donors and the linear conformation of the spacer moiety (–C≡C–C≡C–) in these ligands have been quite useful in the construction of unusual building blocks for use in assembling a large variety of new coordination polymers. Our goal in this paper is to highlight some guest species with photo and catalytic activities in developing new approaches towards large pore framework architectures. To realize this goal, we wish to exploit photosensititive guests such as anthracene, azobenzene, quinizarin, methylviologen, pyrene, perylene, *p*-nitroaniline *etc.* in different channel frameworks based on dipyridyl ligands and copper nitrate salts.

Two independent organic–inorganic polymeric templates and guests have been obtained in the crystal lattice, depending on the geometry and orientations of nitrogen atoms of the ligands and the solvent system.[14] These template frameworks have been isolated by direct reactions carried out using ligand (**L2** and **L3**) and copper(II) nitrate in a stoichiometric ratio of 1 : 1, that is, a three-dimensional (3D) channel like network [Cu(**L2**)(NO$_3$)$_2$(H$_2$O)$_2$·AZO]$_n$ (**1**, AZO = azobenzene) from mixed solvent systems involving methylene chloride and methanol, and a two-dimensional interpenetrating square network [Cu(**L2**)$_2$(NO$_3$)$_2$·AZO]$_n$ (**2**) from methanol solution. In this communication, we have focused our investigation on the azobenzene guest species[15] and describe the synthesis,‡ X-ray single-crystal structures,§ and thermal stabilities¶ of the copper compounds.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and generates a pseudooctahedral coordination environment around the copper centers. The framework of **1** initially possesses an infinite 1D zigzag chain architecture consisting of alternating *cis* [N(2)–Cu–N(2)* = 93.8°] and *trans* [N(6)–Cu–N(6)* = 179.9°] orientations of the metal and pyridine rings of the ligands, **L2** (Fig. 1a). Two such zigzag chains are combined with two different hydrogen bonded interactions: (i) water and nitrate ions [O(3)–H(6)···O(1) = 1.978 Å]; (ii) oxygens of nitrate ions [O(7)···O(8) = 3.075 Å] resulting in 2D rectangular type channel frameworks (Fig. 1b). Moreover, *E*-AZO isomers are packed next to one another with the nearest C–H···C distances of 3.138 Å between the benzene rings, and an additional infinite 1D zigzag chain is formed along the crystallographic *a*-axis. These chains are aligned parallel to each other as they snake through the channels of the main framework (Fig. 2). Thus virtual host–guest structural motifs combine to form the distinct 3D-templated framework of **1** (Fig. 1c).

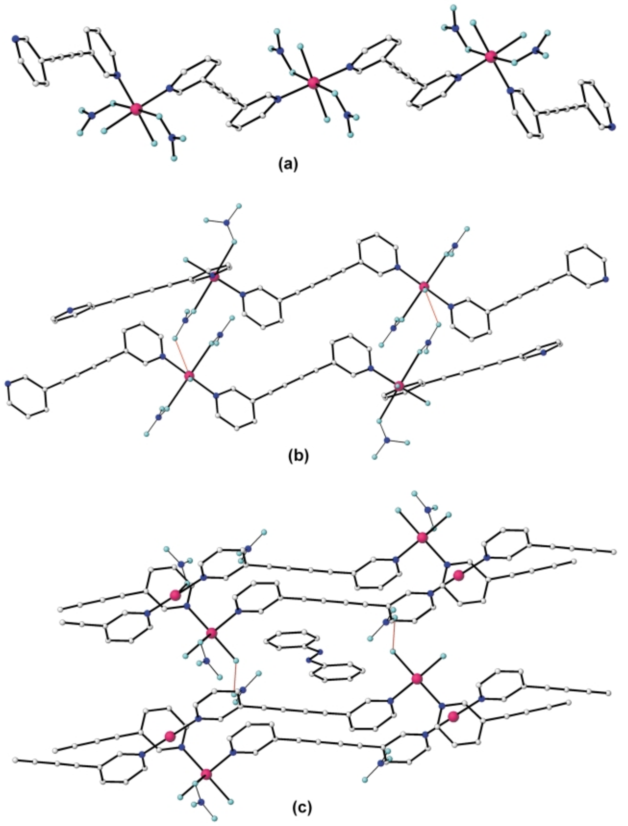

Fig. 1 Stepwise representation of the construction of channel framework **1**: (a) 1D zigzag chain depicting the coordination environment around the Cu(II) center; (b) red lines showing the hydrogen bond linkage (oxygens of water and nitrate ions) between two neighbouring chains. (c) *E*-AZO shown in the channel forming a 1D structural motif.

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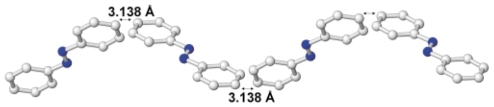

Fig. 2 View of a single zigzag chain of *E*-AZO in **1**. Weak interlayer interactions are shown as dotted lines.

In the second framework, four crystallographically equivalent ligands of **L3** are situated in a square planar fashion around the copper center [Cu–N(1) = 2.024(2) and Cu–N(3) = 2.030(2) Å]; two crystallographically equivalent nitrate ions (Cu–O(1) = 2.112(2) Å) occupy the axial positions. The template of compound **2** consists of 2D square-grid type layers with inner square cavity dimensions of 16.17 × 16.17 Å^2.[10] The square grid layers are flat, and crystallographically equivalent sets interpenetrate at an angle of 60.4° to one another. Though the interpenetration severely reduces the porosity, the intersection of grids formed from such a long ligand is still capable of giving rise to large continuous channels that can be filled by organic molecules. In **2**, the zigzag channels are occupied by *E*-AZO, located approximately in the middle of the channel. Fig. 3 shows a view down the channel direction (the *c*-axis) exhibiting the beautiful pattern of rhombic shaped channels and also the AZO molecules residing therein.

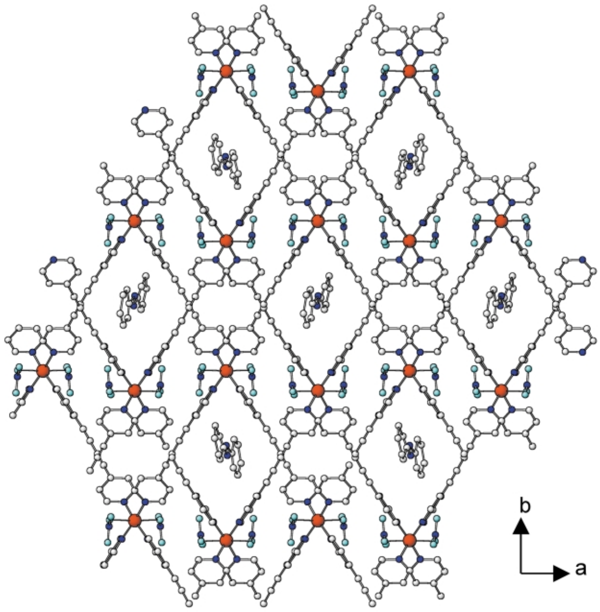

Fig. 3 View down the *c*-axis of the interpenetrating square-grid structure of **2** showing the rhombic channels occupied by photosensitive guest *E*-AZO.

The thermal decomposition behaviour of compound **1** is different to that of **2**, which is reasonable since they possess two different polymeric motifs. The TGA showed that the frameworks of **1** and **2** are thermally stable up to 210 and 170 °C, respectively.

This study again demonstrates the utility of a long ligand as a precursor for constructing porous framework structures. We expect this approach to be valuable for the construction of many new and interesting photoactive coordination polymers, and studies towards the preparation, as well as properties, of template frameworks containing a number of photoactive guests are underway.

Notes and references

‡ Compound **1**: A solution of $Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol) in methanol (5 mL) was allowed to diffuse slowly into a methylene chloride (5 mL) solution of **L2** (20.1 mg, 0.1 mmol) and azobenzene (20 mg). Greenish blue single crystals formed, together with unidentified products, in this mixture after 2 days. The yield was 48% based on copper nitrate. IR (KBr, cm^{-1}): 2224 (w), 2185 (w), 1599 (m), 1511 (s), 1479 (s), 1416 (s), 1384 (w), 1281 (w), 1194 (s), 1127 (m), 1063 (m), 1003 (s), 805 (s), 680 (s). Compound **2**: A blue solution of $Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol) in methanol (3 mL) was carefully layered onto a methanol (3 ml) solution of **L3** (20.2 mg, 0.1 mmol) and azobenzene (21 mg). After five days, green crystals of **2** grew at the interface of the two layers and also at the top of the mixture. The yield was 52% based on copper nitrate. IR (KBr, cm^{-1}): 2206 (w), 2162 (w), 1608 (s), 1587 (s), 1492 (m), 1426 (w), 1285 (w), 1201 (m), 1070 (s), 1027 (m), 829 (m).

§ *Crystal data* for **1**: $C_{20}H_{17}N_5O_8Cu$, M = 518.93, monoclinic, space group $P2_1/n$; a = 15.687(1), b = 7.842(1), c = 17.256(1) Å, β = 90.41(1)°, V = 2122.7(2) Å^3, T = 173(2) K, Z = 4, D_c = 1.624 g cm^{-3}, μ(Mo-Kα) = 1.089 mm^{-1}, 5509 reflection measured, 4177 unique (R_{int} = 0.065), R = 0.0392, R_w = 0.0892 [data $I > 2\sigma(I)$]. *Crystal data* for **2**: $C_{30.88}H_{18.4}N_{6.48}O_6Cu$, M = 639.74, orthorhombic, space group $C222_1$; a = 14.036(1), b = 22.980(1), c = 9.033(1) Å, V = 2913.6 (5) Å^3, T = 173(2) K, Z = 4, D_c = 1.458 g cm^{-3}, μ(Mo-Kα) = 0.806 mm^{-1}, 3776 reflection measured, 3468 unique (R_{int} = 0.035), R = 0.042, R_w = 0.112 [data $I > 2\sigma(I)$]. Both structures were solved using direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.[16] CCDC reference numbers 181463 and 181464. See http://www.rsc.org/suppdata/cc/b2/b204315g/ for crystallographic data in CIF or other electronic format.

¶ Thermogravimetric analysis was performed on **1** (4.25 mg) and **2** (5.18 mg) by heating the compounds from 27 to 800 °C under flowing nitrogen.

1. F. M. Tabellion, S. R. Seidel, A. M. Arif and P. S. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11982; H. Li, C. E. Davis, T. L. Groy, D. G. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186; G. M. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792.
2. K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843.
3. P. S. Stang and D. H. Cao, *J. Am. Chem. Soc.*, 1994, **116**, 4981; S-i. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.
4. M. J. Zaworotko, *Chem. Commun.*, 2001, 1 and references cited therein; M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725.
5. L. R. MacGillivary, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676; K. D. Benkstein, J. T. Hupp and C. L. Stern, *J. Am. Chem. Soc.*, 1998, **120**, 12982; K. Biradha and M. Fujita, *Chem. Commun.*, 2001, 15.
6. R.-D. Schnebeck, L. Randaccio, E. Zangrando and B. Lippert, *Angew. Chem., Int. Ed.*, 1998, **37**, 119.
7. P. J. Stang, N. E. Persky and J. Manna, *J. Am. Chem. Soc.*, 1997, **119**, 4777; J. R. Hall, S. J. Loeb, G. K. H. Shimizu and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 1998, **37**, 121.
8. Relevant articles on 4,4′-bypyridine-based crystalline networks: for polymeric chain architectures see: Y. S. Zhang, G. D. Enright, S. R. Breeze and S. N. Wang, *New J. Chem.*, 1999, **23**, 625; for ladder architectures see: P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779; O. M. Yaghi, H. L. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**, 4292: for square grid architectures see: M. Fujita, Y. J. Kwon, S. Washizy and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151: for diamondoid architectures see: L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325.
9. M. L. Hernandez, M. G. Barandika, M. K. Urtiaga, R. Cortes, L. Lezama and M. I. Arriortua, *J. Chem. Soc., Dalton Trans.*, 2000, 79; Y.-B. Dong, R. C. Layland, N. G. Pschirer, M. D. Smith, U. H. F. Bunz and H.-C. zur Loye, *Inorg. Chem.*, 1999, **38**, 3056.
10. M. B. Zaman, M. D. Smith and H.-C. zur Loye, *Chem. Mater.*, 2001, **13**, 3534.
11. A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schroder, *Chem. Commun.*, 1997, 2027; M. Maekawa, H. Konaka, Y. Suenaga, T. Kuroda-Sowa and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 2000, 4161; M. Maekawa, K. Sugimoto, T. Kuroda-Sowa, Y. Suenaga and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 1999, 4357.
12. Synthesis and photophysical behaviour of some model compounds containing acetylene moieties. See U.-W. Grummt, E. Birckner, E. Klemm, D. A. M. Egbe and B. Heise, *J. Phys. Org. Chem.*, 2000, **13**, 112.
13. L. D. Ciana and A. Haim, *J. Heterocycl. Chem.*, 1984, **21**, 607.
14. M. B. Zaman, M. Tomura and Y. Yamashita, *Org. Lett.*, 2000, **2**, 273; M. B. Zaman, M. D. Smith, D. M. Ciurtin and H.-C. zur Loye, *Inorg. Chem.*, 2002, **41**, in press.
15. Azobenzene is very fast for photoisomerization reaction and often considered as a prototype molecular switch. See J-I. Anzai and T. Osa, *Tetrahedron*, 1994, **50**, 4039; P. Cudic, J.-P. Vigneron, J.-M. Lehn, M. Cesario and T. Prange, *Eur. J. Org. Chem.*, 1999, 2479 and references cited therein.
16. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1993, **49**, C467.