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# Coexisting covalent and noncovalent nets: parallel interpenetration of a puckered rectangular coordination polymer and aromatic noncovalent nets

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**[Zn(*m*-isophthalate)(1,2-bis(4-pyridyl)ethane)]$_n$·$x$A (A = benzene, nitrobenzene, toluene, benzaldehyde, dioxane) represent the first examples of parallel interpenetration between noncovalent and metal–organic frameworks.**

Crystal engineering[1] has provided chemists with a useful paradigm for the development of rational approaches to the design of solid-state structures that are based upon self-assembly of metal nodes and multifunctional ligands.[2] However, it has become clear that interpenetration[3] and supramolecular isomerism[4] are common phenomena in coordination polymers and that subtle factors such as choice of solvent and the presence of templates bring an added level of diversity and uncertainty to the outcome of a particular experiment. Batten and Robson[3] have delineated the modes in which coordination polymers can exhibit self-interpenetration and describe such systems in terms of 'nets' (*i.e.* a collection of nodes with some clearly defined connectivity or topology). We[5] recently suggested how topological considerations can be used to explain interpenetration of two very different types of net: 2-D square grids formed from octahedral metal ions coordinated to two linear bifunctional ligands such as 4,4′-bipyridine[6] and planar noncovalent nets comprising organic guest molecules.[7] That the square coordination polymer grids are flat ensures inclined interpenetration between the two types of network. Such 'hybrid' structures might bring with them the intriguing possibility of combining the structural and functional features of two very different types of molecular component.[8]

We report herein several structures† that exhibit the coexistence of coordination polymer and noncovalent nets *via* a parallel interpenetration mode that is possible because the coordination polymer exists as a novel, puckered 2-D grid. We also demonstrate that the absence of a suitable component for the noncovalent nets precludes formation of the 2-D coordination polymer, and rather affords a novel 3-D supramolecular isomer of the coordination polymer. Self-assembly of Zn(II) ions with 1,3-benzenedicarboxylate (bdc) and 1,2-bis(4-pyridyl)ethane (bpeta) in the presence of an appropriately sized guest affords a novel, puckered, rectangular grid structure, [Zn(bdc)(bpeta)]$_n$ **1**. **1** crystallizes from EtOH if benzene (**1a**), nitrobenzene (**1b**), toluene (**1c**), benzaldehyde (**1d**) or 1,4-dioxane (**1e**) are also present. However, if the solvent is changed to pure MeOH, MeOH/naphthalene or $CH_2Cl_2$, a different supramolecular isomer of **1** is formed—a 3-D structure, **2**—which can also be formulated as [Zn(bdc)(bpeta)]$_n$. The covalent network in **1a** is sustained by a tetrahedral Zn(II) ion coordinated to two bdc and two bpeta ligands. Four of these units give rise to a rectangular cavity incorporated in a (4,4)-network in which zinc ion serves as node. The tetrahedral geometry around the zinc ion causes adjacent rectangular cavities to fold with an angle of 99.94° between Zn ions, producing a 'puckered' layer of cavities, as shown in Fig. 1. Adjacent cavities have slightly different environments in that the orientation of the aromatic rings of the bdc units differs: in one (cavity A) the rings are coplanar with the plane of the cavity, while for the next cavity (B) opposite bdc moieties orient up and down with respect to the plane of the cavity. Effective dimensions for the cavities are 4.8 × 13.3 Å (for A) and 6.0 × 13.6 Å (for B). The bpeta ligands contain pyridyl rings that are only slightly twisted (torsion angle 167.7°) and these ligands are bowed when viewed down the Zn···Zn direction. The coordination polymer layers pack close to one another, with metal centres and cavities stacked above one another, when viewed down [1 0 0]. The interlayer separation is 9.672 Å and there are C–H···π and π···π interactions between layers (the C···$\pi_{centroid}$ distance is 3.532 Å and the $\pi_{centroid}\cdots\pi_{centroid}$ distances are 3.611 and 3.705 Å, consistent with distances to be expected for such interactions).

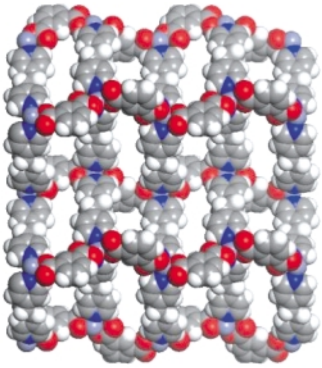

**Fig. 1** Space-filling views of the puckered, rectangular, grid coordination polymer network in **1a**. The puckering of the (4,4)-network can be clearly seen and affords cavities and channels within the plane of the network.

The organic guest molecules in **1a**–**e** form what could be regarded as (6,3)-'puckered brick wall' networks that are sustained by noncovalent interactions (Fig. 2). Fig. 3 illustrates how two of the noncovalent networks engage in parallel interpenetration with the coordination polymers, thereby forming a structure that is similar to the laminated, self-interpenetrated structure exhibited by 1,3,5-benzenetricarboxylic acid and 4,4′-bipyridine.[9]

The critical influence of the solvent and organic components on the self-assembly process is clearly illustrated by the formation of **2**, which exhibits a dramatically different structure that can be described as a pseudo-tetrahedral framework

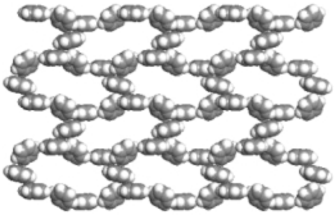

**Fig. 2** A view of the noncovalent nets that are formed by benzene molecules in **1a**.

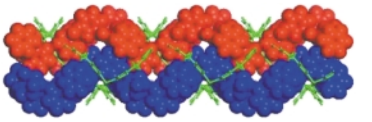

**Fig. 3** An illustration of how two noncovalent networks (illustrated in space-filling mode) generate parallel interpenetration with one puckered rectangular grid (illustrated in stick mode) in **1a**.

because the tetrahedral Zn ions are linked by angular and linear spacer ligands. Zn···Zn separations in **2a** are 9.90 and 13.34 Å; this inequality in spacer length leads to a distortion of the diamondoid network that would otherwise be formed (Fig. 4). The large void generated within the pseudo-diamondoid cage is filled by the mutual interpenetration of three independent networks (Fig. 5). Guest molecules in **2a** occupy cavities between the metal-coordination networks, and are isolated from one another. Each cavity has a volume of 91 Å$^3$, and represents 4.4% of the unit cell volume. Thus the total volume occupied by guest molecules in this structure is only 17.6%.[10]

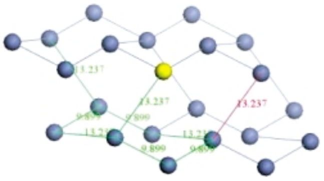

**Fig. 4** The pseudo-diamondoid network in **2a**. The bridging ligands are omitted for clarity.

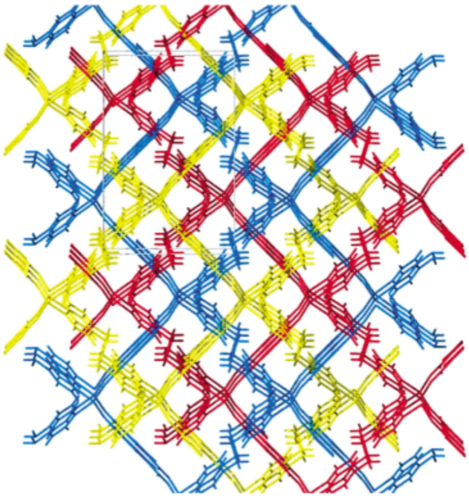

**Fig. 5** An illustration of the three pseudo-diamondoid networks that interpenetrate in **2a**.

The existence of the novel supramolecular isomers **1** and **2** is not in itself surprising. However, that their existence appears to be closely linked to whether or not topologically complementary noncovalent nets can be formed provides insight into how chemists can control such supramolecular isomerism and in the process generate hybrid structures that are based upon very different molecular components.

## Notes and references

† *Synthesis and data:* 2D-[Zn(bdc)(bpeta)]$_n$·$x$(A), **1**(**a**–**e**) and 3D-[Zn(bdc)(bpeta)]$_n$·(solvent), **2**(**a**,**b**), were prepared by dissolving Zn(NO)$_3$·6H$_2$O (typical example: 0.149 g, 0.5 mmol) and 1,3-benzenedicarboxylic acid (0.166 g, 1 mmol) in ethanol and layering this with a solution of 1,2-bis(4-pyridyl)ethane (0.184 g, 1 mmol) in A. Colorless, rod-shaped crystals were formed at the solvent interface. Intensity data for **1a**–**e** and **2a**,**b** were collected at −100 °C on a Bruker SMART-APEX diffractometer using Mo-K$\alpha$ radiation ($\lambda$ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and also for absorption using the SADABS program. Structures were solved using direct methods and refined by full-matrix least squares on $|F|^2$.[11] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 × those of their parent atoms.

**1b**, **1c**, **1d** and **1e** are isostructural with **1a**: they crystallize in $P2_1/n$ with similar cell parameters, they have similar, but not identical, host:guest ratios [for **1a** and **1e** this is 1:2.5, for **1b**–**1d** (which encapsulate slightly larger guests) it is 1:2]; their interlayer separations are in the range 10.244–10.546 Å and they possess cavities with effective dimensions of *ca.* 5 × 13 Å (cavity type A) and *ca.* 5.5 × 14.5 Å (cavity type B). **1b**–**d** have Zn–Zn–Zn angles of 87–89°, while **1e** has an angle of 100.64°, which is closer to that observed in **1a**.

*Crystal data* for **1a**: monoclinic, $P2_1/n$, $a$ = 9.672(1), $b$ = 20.217(2), $c$ = 14.977(2) Å, $\beta$ = 93.545(2)°, $V$ = 2923.2(5) Å$^3$, $Z$ = 4, $D_c$ = 1.384 g cm$^{-3}$, $\mu$ = 0.883 mm$^{-1}$, $F(000)$ = 1268, $2\theta_{\max}$ = 25°. Final residuals (for 377 parameters) were $R_1$ = 0.0406 and $wR_2$ = 0.0764 for 3242 reflections with $I > 2\sigma(I)$, and $R_1$ = 0.0680, $wR_2$ = 0.0817 for all 5077 data. Residual electron density was 0.75 and −0.48 e Å$^{-3}$. [Cell parameters for **1b**: $a$ = 10.546(2), $b$ = 18.400(3), $c$ = 15.209(2) Å, $\beta$ = 90.971(3)°, $V$ = 2950.8(7) Å$^3$. Cell parameters for **1c**: $a$ = 10.243(3), $b$ = 18.317(5), $c$ = 15.391(4) Å, $\beta$ = 91.116(5)°, $V$ = 2887(1) Å$^3$. Cell parameters for **1d**: $a$ = 10.437(2), $b$ = 18.516(4), $c$ = 15.190(3) Å, $\beta$ = 90.119(4)°, $V$ = 2935(1) Å$^3$. Cell parameters for **1e**: $a$ = 10.545(1), $b$ = 20.202(2), $c$ = 14.239(2) Å, $\beta$ = 96.781(2)°, $V$ = 3012.3(6) Å$^3$].

*Crystal data* for **2a**: orthorhombic, $Pnna$, $a$ = 10.020(1), $b$ = 15.195(5), $c$ = 13.689(1) Å, $V$ = 2084.1(4) Å$^3$, $Z$ = 8, $D_c$ = 1.589 g cm$^{-3}$, $\mu$ = 1.466 mm$^{-1}$, $F(000)$ = 1016, $2\theta_{\max}$ = 26°. Final residuals (for 138 parameters) were $R_1$ = 0.0444 and $wR_2$ = 0.1146 for 1934 reflections with $I > 2\sigma(I)$, and $R_1$ = 0.0483, $wR_2$ = 0.1167 for all 2151 data. Residual electron density was 0.72 and −0.58 e Å$^{-3}$. [Cell parameters for **2b**: $a$ = 9.676(3), $b$ = 15.470(5), $c$ = 13.547(5) Å, $V$ = 2028(1) Å$^3$].

High resolution thermogravimetric analysis (TA Instruments TGA 2950) shows a multi-step weight loss between ambient temperature and 200 °C, which can be attributed to the release of guest (for example, **1a**: observed mass loss 33.6%, calc. for 2.5 benzene 32.1%) followed by further thermal decomposition at 300–400 °C, apparently caused by destruction of the coordination polymer.

CCDC 153763–153769. See http://www.rsc.org/suppdata/cc/b1/b102153m/ for crystallographic data in .cif or other electronic format.

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