

Topological control in coordination polymers by non-covalent forces

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Reaction of Zn^{2+} salts with the terephthalate dianion results in a herringbone motif coordination polymer; the orientation of the terephthalate spacer ligands and the coordination geometry about the Zn^{2+} ion is crucially dependent on hydrogen bonding to ancillary ligands; replacement of coordinated water with ethylenediamine results in marked changes to the polymer orientation without disruption of the fundamental features of the material.

A key objective in the emerging field of crystal engineering is the control and manipulation of weak interactions in order to tune the properties of the bulk material.^{1–6} Potential applications of such studies include the preparation of new non-linear optical materials, design of porous solids with novel inclusion or reactivity properties (*e.g.* for use in separation science and heterogeneous catalysis, particularly in stereo- or enantio-specific synthesis) and new sensor materials and coatings.^{7–11} The vast majority of current work centres around the controlled assembly of donor and acceptor building blocks (particularly involving hydrogen bond acid–base pairs, *e.g.* nucleobases¹²) in order to generate an entirely ‘supramolecular polymer’, *i.e.* a material held together solely by non-covalent interactions. While such systems can be remarkably robust,¹² such an approach is fundamentally limited by the intrinsic strength of the constituent interactions, which are markedly weaker than covalent or ionic bonds, although our recent work has focussed on the importance of such interactions.^{13–16} With this in mind, we have begun a programme of research aimed at the construction of molecular coordination polymers of low dimensionality in which mechanical strength is imparted by strong coordinate bonds, while admitting scope for weaker, lateral interactions which might enable the material to be tuned in the same way as in more conventional crystal engineered solids. We now report the results of simple, proof of principle studies, which demonstrate how an inherently robust coordination polymeric framework may be manipulated by weak interactions.

In attempting to prepare coordination polymers we were struck by the utility of avoiding the need for counter anions which must *inter alia* disrupt the solid state packing and give rise to additional cation–anion interactions which might be difficult to control.¹⁷ Accordingly we have chosen to examine the reactions of divalent metal cations with the terephthalate dianion, (tph^{2-} , **1**) in the expectation of generating a neutral polymeric material. We chose initially relatively labile Zn^{2+} (as nitrate or acetate salts) in the hope of generating reaction products under thermodynamic control. The structure of zinc acetate itself, $\text{Zn}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$, consists of two essentially bidentate acetate ligands and two water molecules engaging in intra- and intermolecular hydrogen bonding interactions.¹⁸ We reasoned that replacement of acetate with terephthalate would result in an analogous structure consisting of both a polymer chain and ancillary aqua ligands which would exert additional control over the polymer geometry by means of strong hydrogen bonding interactions. Consistent with expectation, an excellent yield of crystalline material of stoichiometry $[\text{Zn}(\text{tph})] \cdot 2\text{H}_2\text{O}$ **2** was deposited within 24 h. This material was characterised by low temperature X-ray crystallography† (100 K) and proved to consist of the desired coordination polymer, Fig. 1. The compound consists of approximately tetrahedral

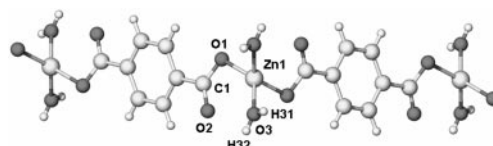


Fig. 1 XSeed²¹ view of the coordination polymer $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-O},\text{O}'\text{-tph})]_\infty$ **2**. Selected bond lengths (Å): Zn(1)–O(1) 2.0049(15), Zn(1)–O(2) 2.5500(16), Zn(1)–O(3) 1.9855(18) Å.

Zn^{2+} centres linked by a herringbone pattern of tph^{2-} spacers aligned approximately along the crystallographic *a/c* diagonal. The *tph* ligands are essentially monodentate with Zn–O(1) 2.0049(15) Å, however the Zn–O(2) distance of 2.5500(16) Å suggests a non-negligible interaction with the uncoordinated oxygen, which may be described as a semi-chelating coordination mode.¹⁹ The two water molecules within the coordination sphere of the metal cation engage in two distinct hydrogen bonded interactions, which, together, are responsible for the conformation of the polymer. In the crystallographic *b* direction, perpendicular to the direction of chain propagation, the metal cations stack precisely on top of one another and are linked in an eight membered hydrogen bonded ring [$\text{R}_2^2(8)$ in graph set notation²⁰] involving the water hydrogen atom H31 attached to O3 and the coordinated oxygen atoms of the *tph* ligand, Fig. 2(a). In addition, lateral hydrogen bonds involving the second unique water hydrogen atom H32 and the uncoordinated terephthalate oxygen atoms link one chain to those adjacent in $\text{R}_2^2(12)$ hydrogen bonded sets, Fig. 2(b). The aryl

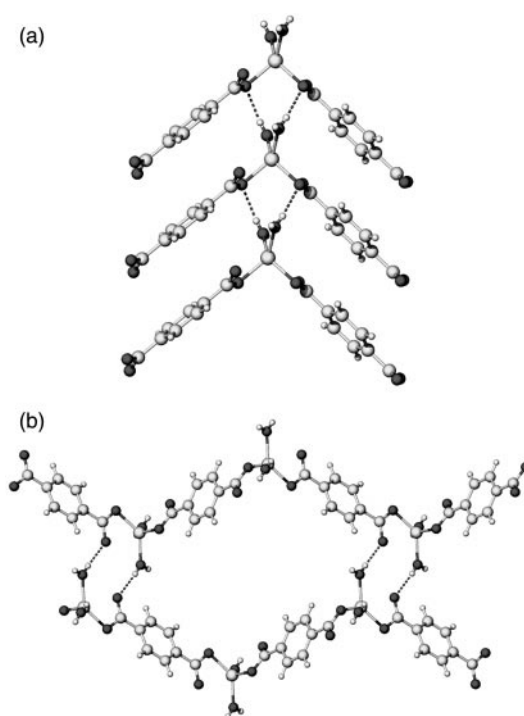


Fig. 2 (a) Stacking of $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-O},\text{O}'\text{-tph})]_\infty$ **2** in the *b* direction via $\text{R}_2^2(8)$ hydrogen bonded sets,²⁰ O...O 2.776(2) Å, (b) lateral $\text{R}_2^2(12)$ motifs which link one polymeric chain to those adjacent, O...O 2.699(3) Å.

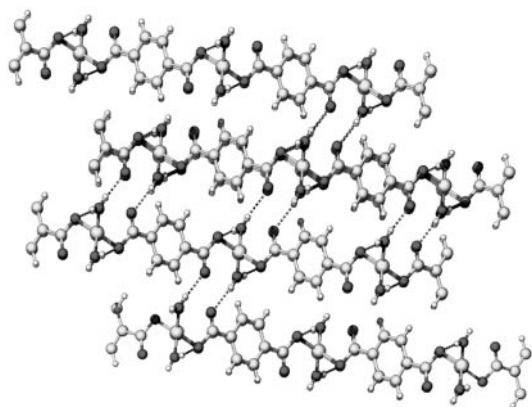


Fig. 3 Crystal packing in **2**.

rings of the tph ligands stack in an offset fashion perpendicular to the *b* direction, *ca.* 3.7 Å apart. The overall crystal packing is shown in Fig. 3.

Clearly the presence of two labile water molecules within the Zn²⁺ coordination sphere, playing only an indirect part in the polymeric chain, suggests that they might be replaced by other ligands with different hydrogen bonding characteristics. This should influence, *via* hydrogen bonding, the geometry of the coordination polymer. Hence we carried out the reaction of Zn²⁺ salts with Na₂tph in the presence of 1 equivalent of ethylenediamine (en). This resulted in the formation of an exactly analogous coordination polymer, [Zn(en)(μ-O,O'-tph)]_∞ **3**, in which the two water molecules have been replaced by a single, chelating en ligand. Fascinatingly, the X-ray crystal structure of this material[†] reveals the same essential features of the coordination geometry and herringbone packing of the polymer observed in **2** despite the greatly different characteristics of the en ancillary ligand. As in **2**, the Zn²⁺ centres stack precisely along the crystallographic *b* direction. However, in **3** there is no possibility of the propagating R₂² (8) hydrogen bonded links because of the steric bulk of the ethylene spacer and this is reflected in the dramatic expansion of the crystallographic *b* axis from 5.00 to 7.25 Å. One of the amine protons on each donor atom is thus unable to take part in any hydrogen bonding. The NH₂ functions are, however, capable of engaging in lateral interactions from one chain to another in the same fashion as **2** to give twelve-membered hydrogen bonded rings, Fig. 4. The most obvious consequence of the reduction in inter-chain connectivity is the dramatic reorientation of the aryl groups of the tph ligands such that in **3** they are approximately parallel with the crystallographic *b* direction, as opposed to perpendicular, as in **2**. This has the curious consequence both of disrupting the π-stacking interactions seen for **2** and changing the coordination mode of the tph ligands from 'semi-chelating', to entirely unidentate, with a non-bonded Zn–O(2) distance of 2.931(3) Å, compared to 2.5500(16) Å in **2** and a shortening of the Zn–O(1) bond length to 1.947(3) Å. Since it is the non-coordinated tph oxygen atom O(2) which is involved as a hydrogen bond acceptor in both cases it is clear that the accommodation of the lateral hydrogen bonds plays a much more significant role in determining the overall structure than factors such as weak interactions of O(2) with the zinc centre and π-stacking.

The key to the future potential of this system clearly lies in the robustness of the one dimensional coordination polymeric

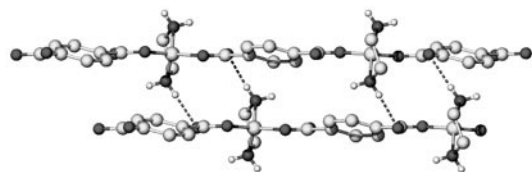


Fig. 4 Lateral R₂² (12) motifs in [Zn(en)(μ-O,O'-tph)]_∞ **3**, N...O 2.984(5) Å (CH hydrogen atoms omitted for clarity). Note the second NH proton does not take part in any hydrogen bonds.

chain and its ability to tolerate other ancillary ligands. In order to explore the phase space of the Zn²⁺–tph²⁻ system a large variety of reactions between these two components were set up with mole ratios of 1 : 1 up to 1 : 4 in a range of solvents and with a range of Zn²⁺ salts. Compound **2** was formed in excellent yield in every case (as determined by solid state IR spectroscopy and measurement of unit cell dimensions) except for one occasion in which the reaction of hydrated zinc acetate with Na₂(tph) in water in a 1 : 1 ratio gave a mixture of **2** and a further product of formula [Zn(H₂O)(tph)]_∞ **4**. Compound **4** is a highly cross-linked polymer involving coordination of all four tph oxygen atoms, each to a different trigonal bipyramidal Zn²⁺ centre (aqua ligand equatorial). The structure is based on a ladder arrangement of puckered eight-membered Zn₂O₄C₂ rings. Thermogravimetric analysis of **2** indicates stepwise loss of the two aqua ligands at 168 and 192 °C, respectively, suggesting the possible conversion of **2** into **4**. Full details of this system will be reported fully in a separate paper.

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Notes and references

[†] *Crystal data*: **2**: C₈H₈O₆Zn, *M* = 265.51, monoclinic, space group *C2/c*, *a* = 14.9503(8), *b* = 5.0031(4), *c* = 12.1617(11) Å, β = 103.647(6)°, *U* = 883.99(12) Å³, *D_c* = 1.995 Mg m⁻³, *Z* = 4, μ = 27.84 cm⁻¹, *T* = 100(2) K, Reflections measured: 8316, unique data: 1010 (*R_{int}* = 0.069), parameters: 78, *R1* [*F*² > 2σ(*F*²)] = 0.0310, *wR2* (all data) = 0.0802.

3: C₁₀H₁₂N₂O₄Zn, *M* = 289.59, monoclinic, space group *P2₁/n*, *a* = 5.6508(11), *b* = 7.2496(14), *c* = 13.179(3) Å, β = 100.468(2)°. *U* = 530.90(18) Å³, *D_c* = 1.812 Mg m⁻³, *Z* = 2, μ = 23.17 cm⁻¹, *T* = 100(2) K, Reflections measured: 2189, unique data: 1212 (*R_{int}* = 0.078), parameters: 87, *R1* [*F*² > 2σ(*F*²)] = 0.0511, *wR2* (all data) = 0.1297.

CCDC 182/1299. See <http://www.rsc.org/suppdata/cc/1999/1563/> for crystallographic data in .cif format.

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