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Passing it up the ranks: Hierarchical ion-size dependent supramolecular response in 1D coordination polymers

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Debobroto Sensharma,^a Paul Wix,^a Amal Cherian Kathalikkattil^a and Wolfgang Schmitt^a

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The synthesis and structural characterisations of four 1D coordination polymers based on the 1,3,5-tris(4-carboxyphenyl)benzene (H₃btb) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (2-tpt) ligands are reported: [M^{II}(Hbtb)(2-tpt)]·xDMF, M = Zn (1), Ni (2), Mn (3) and Cd (4). The tridentate chelating mode of the 2-tpt ligand hinders the formation of polynuclear assemblies, leading to the recurrence of structurally related 1D motifs in all four compounds. Two distinct packing arrangements are obtained for the 1D motifs demonstrating how variable radii and coordination environments influence supramolecular interactions throughout the structures. Further, the nature of the metal ion influences respective orientations of interacting groups in the structures, illustrating the importance of ligand flexibility in coordination polymer design.

After Bailar's analogy between organic polymers and coordination polymers in 1964, research activities encompassing the synthesis, characterisation, and use of coordination polymers have grown exponentially.^{1,2} Extended metal-ligand assemblies such as coordination networks, coordination polymers and metal-organic frameworks have become desired synthetic targets as these materials have proven utility in catalysis, sensing, gas storage, and drug delivery, among other areas.^{3–10} One-dimensional coordination polymers (1D CPs), which extend only lengthwise, are topologically the simplest class of these materials and are of interest due to their electronic, magnetic, optic and catalytic properties.^{11–14}

From a supramolecular point of view, 1D CPs offer a platform in which both, bonding and non-bonding interactions play a key role in influencing connectivity in their respective dimensions, and therefore the functions of the materials.^{15,16} 1D chains may consist of straight, zigzag, or more intricate

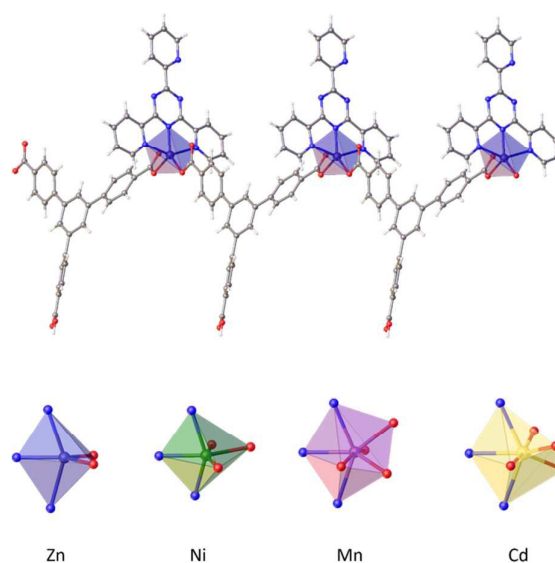


Fig. 1 The 1D polymer chain motif in **1** (above). Two Hbtb ligands are bound to each metal centre along with one 2-tpt ligand. Hydrogen atoms are omitted for clarity. Given below are the coordination environments observed in compounds **1–4** which adopt structurally similar 1-D chain motifs. Steric hindrance in **3** (Mn) and **4** (Cd) leads to the tilting of the carboxylate groups out of the horizontal plane present in **1** (Zn) and **2** (Ni).

ladder or ribbon conformations.^{12,17} The overall crystal structures are determined by the non-bonding interactions between individual chains, commonly involving H-bonding or π - π stacking interactions.^{18–20} Various interwoven structural motifs and entanglements between chains can be promoted by these interactions, and dynamic changes in these arrangements can be engineered.²¹

^a School of Chemistry & CRANN Institute, University of Dublin, Trinity College, Dublin 2, Ireland. E-mail: schmittw@tcd.ie; Fax: +353-1-6712826; Tel: +353-1-8963495.

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1,3,5-Tris(4-carboxyphenyl)benzene (H_3btb) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (2-tpt) are examples of typical tritopic ligands used in coordination chemistry.^{22,23} The H_3btb ligand has previously been combined with N-donors, and 2-tpt with carboxylate ligands, to yield a number of extended mixed-ligand materials.^{24,25} The combination of these ligands presents attractive synthetic possibilities due to the availability of N- and O-donor functionalities, as well as extensive π -conjugation. These features confer stability and functionality to the resulting coordination polymers, and can result in synergistic structure directing effects.^{26–29} The availability of the chelating 2,2':6',2''-terpyridine-type coordination mode by the 2-tpt ligand allows the conception of a polymer in which three coordinative positions on the metal centre are occupied by N-donor atoms. This impairs the formation of oligonuclear secondary building units (SBUs) and leads to structures based on mononuclear metal centres.³⁰ In this scenario, the variability between metal centres in terms of SBU formation becomes greatly reduced, potentially giving rise to systems in which a variety of metal centres could be applied for the formation of structurally related coordination polymers.

In this communication, we report the synthesis, X-ray crystal structures, and physicochemical characterisations of four one-dimensional coordination polymers based on M(II) centres with varying ionic radii, and the combination of H_3btb and 2-tpt ligands. The diversity of packing modes and differences in weak interactions are understood by examining essential changes in the coordination environments of each 1D polymer. We elucidate the underlying structural flexibility of the polymer motif that allows various coordination geometries around the M(II) centres to result in the same 1D polymer, as well as the consequences of this accommodation for the organisation of 1D chains relative to each other in the 3D crystal structure, mediated by various π - π and H-bonding interactions between ligand moieties.

A variety of differently sized M(II) centres – Mn(II), Ni(II), Zn(II), and Cd(II) – were combined as chloride or nitrate salts with btb and 2-tpt in N,N-dimethylformamide. The initially formed slurry was clarified simply by agitation at room temperature. On heating the solutions for 4 days at 100°C, single crystals of the four compounds were obtained. Single crystal X-ray diffraction studies were carried out on all four compounds: $[Zn(H_3btb)(2-tpt)] \cdot DMF$ (**1**), $[Ni(H_3btb)(2-tpt)] \cdot 0.7DMF$ (**2**), $[Mn(H_3btb)(2-tpt)] \cdot 1.25DMF$ (**3**) and $[Cd(H_3btb)(2-tpt)] \cdot DMF$ (**4**). All four compounds consist of infinite one-dimensional coordination polymer chains (Figure 1). Each metal centre is bound to two H_3btb ligands *via* the carboxylate groups, as well as one 2-tpt ligand. Two carboxylate groups of each H_3btb ligand bind to a metal centre, leaving one protonated carboxylic acid group unbound and pendant in the structure. The 2-tpt ligand, in which one pyridine ring remains uncoordinated acts as a capping group for the metal centres. Together the two ligands give rise to 1D polymeric chains with

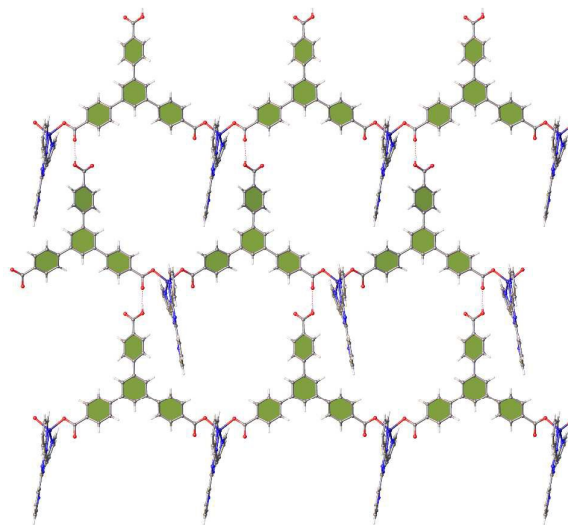


Fig. 2 The H-bonded 2D honeycomb structure present in all four compounds. Here shown for $[Zn(H_3btb)(2-tpt)] \cdot 2DMF$ (**1**). View in the direction of the crystallographic *c*-axis.

both uncoordinated N- and O- donors. All structures build out honeycomb-like 2D networks which are facilitated by hydrogen bonds between the protonated moiety of the H_3btb ligand and the carboxylate group of a deprotonated H_3btb arm (Figure 2). Stabilised by numerous π - π interactions, these layers are stacked on top of each other adopting various accommodating stacking motifs, which we show to be determined by the size of the metal ion.

In $[Zn(H_3btb)(2-tpt)] \cdot DMF$ (**1**) the carboxylate groups of the H_3btb ligands are bound to the Zn(II) centres in a *syn*-monodentate fashion. This creates a slightly distorted trigonal bipyramidal Zn(II) coordination environment in which two nitrogen donor atoms from the 2-tpt ligand are located in the axial positions. The M-O distances are the shortest in the reported series with 1.948(3) Å and 1.963(3) Å. With increasing ionic radii (Zn < Ni < Mn < Cd; see Table 1) the coordination number increases from 5 to 7 and the binding mode of the carboxylate functionality changes from mono-dentate to bidentate. Structural disorder leads to some variation in the denticity of **2**, **3**, and **4**. While the oxygen donors reside in the equatorial planes for **1** and **2**, steric effects lead to the rotation of the carboxylate functionalities relative to each other and hence, move out of the plane for **3** and **4** as shown in Figure 1. This effect promotes a distorted octahedral Ni(II) coordination geometry in **2** and distorted capped octahedral Mn(II) or capped trigonal prismatic Cd(II) coordination environments in **3** and **4**, respectively, as determined by geometrical analysis with the program SHAPE V2.1. (Figure 1, Table S3).³¹

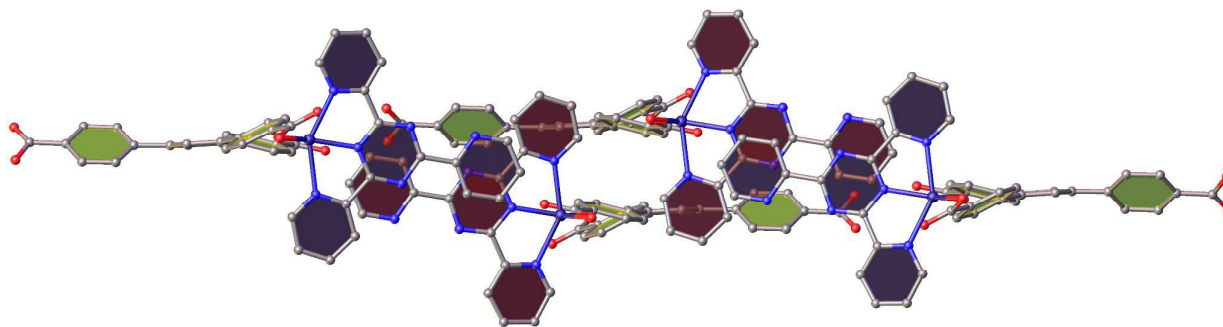


Fig. 3 Stacking of the 2-tpt ligand viewed in the direction of the crystallographic *b*-axis of compound **1**.

The packing is stabilised by numerous π - π interactions between the Hbtb ligands. For the compounds containing the smaller metal ions, **1** (Zn(II)) and **2** (Ni(II)), two different stacking modes occur in the crystal structures, *type 1* and *type 2* (Figure 4). *Type 1* stacking is facilitated by two Hbtb ligands that are rotated 180° to each other and engage in π - π interactions with the central and the peripheral benzene rings. For *type 2* stacking the Hbtb ligands are rotated 180° to each other and overlap with two peripheral benzene rings. Further, in **1** and **2**, the Hbtb ligands are stacked in a 1-2-1-2 fashion adopting alternating *type 1* and *type 2* stacking sequences throughout the structure. *Type 2* stacking is additionally stabilised through π - π interactions of the 2-tpt ligands which facilitate perpendicular arrangements to the Hbtb-based sheets (Figure 3). The absence of crystalline products when 2,2',6',2''-terpyridine was used in place of 2-tpt under identical conditions indicates the importance of the pendant pyridyl aromatic system and consequent stacking interactions for the overall formation of the compounds. Contrarily, *type 1* stacking does not involve such stabilising interactions of the 2-tpt ligands.

Generally, the strength of π - π interactions is perceived to be dependent on the angle between the two π -systems and correlates with the inter-plane distance.^{32,33} Misalignments, tilting effects and consequent increased inter-plane distances hamper π - π interactions and thus they become less favourable within a supramolecular arrangement. Aromatic carboxylate ligands possess a conjugated π -system which aligns the aromatic rings with the carboxylate group. The benzene rings of the ligand itself are naturally non-coplanar with respect to each other because of the steric repulsion from hydrogen atoms on adjacent rings. Usually, angles of around 35°-45° between benzene rings in biphenyl-type pairs are found in the

literature.³⁴

In **1** and **2**, in which the carboxylate ligand is bound in a monodentate fashion, this angle is consistent with the literature values as the free oxygen atom facilitates the facile rotation of the benzoate group to accommodate this preferred

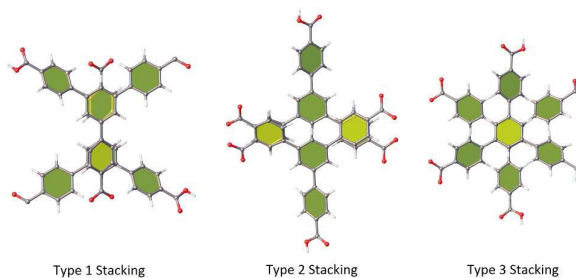


Fig. 4 Different stacking modes present in the crystal structures. *Type 3* stacking only occurs in **3** and **4**.

geometry. Only in the case of the larger M(II) ions, Mn (**3**) and Cd (**4**), the bidentate binding mode and subsequent steric repulsion of the oxygen atoms lead to an increase of the angle between the two carboxylate groups bound to the same metal ion from 41° up to 69° (Figure 1). In this way the modified coordination environment of the metal ions extends to the aromatic system of the ligand and influences the relative orientations of the phenyl rings, leading to less favourable π - π interactions between the 2D sheets. Centroid-centroid distances and interplanar angles between phenyl rings in the case of *type 2* stacking increase from 3.6 Å and 14.8° in **1** to 5.0 Å and 46.4° (outside the range of conventional π - π interactions) in **3** as a result of the steric repulsion from

Table 1. Comparison of different structural features in **1-4**. (compare also ESI, Table S3 for further details).

	1 – Zn	2 – Ni	3 – Mn	4 – Cd
COORDINATION	5	5/6	6/7	6/7
DENTICITY	Mono/mono	Mono/bi	Mono/bi	Mono/bi
IONIC RADII (Å)	0.68	0.69	0.90	1.03
STACKING PATTERN	1-2-1-2	1-2-1-2	1-2-1-3	1-2-1-3
M-O DISTANCES (Å)	1.94	1.95	2.17 – 2.41	2.14 – 2.56
SHAPE ANALYSIS	Square pyramidal	Octahedral	Capped octahedral	Capped trigonal prismatic

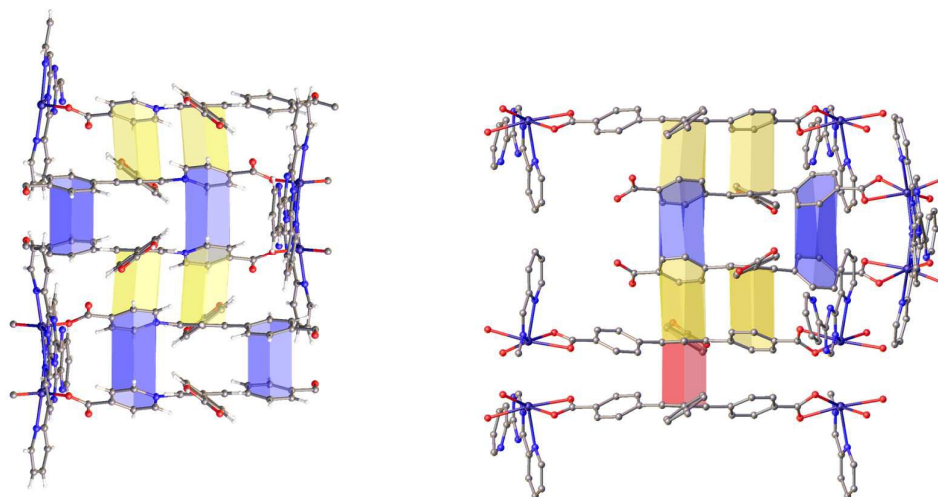


Fig. 5 Left: Packing representations in **1** with view in the [101]-direction showing the 1-2-1-2 stacking pattern; Right: Packing representations in **3** with view in the direction of the crystallographic *b*-axis showing the 1-2-1-3 stacking pattern.

the coordination environment. While *type 1* and *type 2* stacking modes are observed in **3** and **4**, reduced favourability for stabilising π - π interactions forces the structures to accommodate a third, new stacking motif that governs the packing of the 2D sheets. This *type 3* stacking motif is facilitated by two Hbtb ligands that are rotated 180° to each other around the perpendicular axis of the central benzene ring (Figure 4). Consequently, the honeycomb type sheets in **3** and **4** stack in 1-2-1-3 fashion instead of 1-2-1-2. Thus, this flexibility in packing enables the system to accommodate various metal ions with large ionic radii difference (Figure 5).

The challenge posed by unfavourable steric effects due to ion size in the 1D polymeric structure is overcome by rearrangements in the three dimensional packing illustrating a hierarchical supramolecular response to a local modification created at the metal centre.

Hirshfeld surface analyses were carried out in order to gain a better understanding of the nature of these interactions.^{35,36} Decomposed fingerprints for percent values corresponding to C-C and C-H interactions were used as an indicator of the prevalence of the π - π interactions and the π -system overlap. Tilting of the benzene rings results in more C-H and less C-C contribution and therefore raises the C-H/C-C ratio, as stacking phenyl rings become more misaligned. The analysis highlights that this ratio correlates with the ion size of the transition metal. One notices a clear effect on the ratios, increasing from 3.9 for the smallest to 6.1 for the largest metal ion in the series. (ESI, Table S3).

In addition, Hirshfeld surface analysis also confirms the role of the pendant protonated carboxylic acid moiety in forming short H-bonding interactions with oxygen atoms from deprotonated carboxylate groups, resulting in 2D honeycomb-like motifs in all four compounds. The constitutional DMF solvent molecules do not play any apparent structural role in

1-4, which is an explanation as to why they are heavily disordered.

Whilst **2** forms in low yield, bulk characterisations for **1**, **3**, and **4** were carried out. Phase-purity of the as-synthesised crystalline materials was ascertained by powder X-ray diffraction studies, elemental analysis (ESI) and FTIR spectroscopy. The thermal stability of the compounds was evaluated by thermogravimetric analysis, revealing stability up to 370 °C upon which the organic ligands undergo degradation. A preceding step corresponding to the loss of trapped DMF molecules at 120 °C is observed for all investigated compounds. The relative high temperature of solvent loss agrees well with the observation that in both kinds of packing arrangement, disordered DMF molecules are contained in inaccessible voids. Therefore, solvent loss can only occur with a related structural degradation.

In conclusion, we report the synthesis of a number of one-dimensional transition metal coordination polymers based on a mixed ligand strategy. The Hbtb ligand is used to provide linear extension, while the 2-tpt ligand chelates the metal centres, providing a valuable synthetic handle over SBU formation. The versatility of the synthetic strategy is demonstrated by the characterisation of four, structurally closely-related polymers formed by different metal centres, namely Cd(II), Zn(II), Mn(II), and Ni(II), and the analysis of their single crystal X-ray structures. These coordination polymers are formed despite large differences in the size and coordination environments of the metal centres used. We show how these differences are accommodated in the versatile 1D motif, but re-emerge in the 3D structure by re-organising the supramolecular interactions between individual 1D chains, resulting in divergent packing arrangements and exemplifying several key concepts in the engineering of crystalline coordination polymer frameworks. In future we aim to extend to our findings to structurally modified carboxylate

and pyridyl ligands. The concept may provide a valuable a synthetic platform for the preparation of polymers that facilitate some control over optical, electronic or magnetic properties. Such advances towards the synthesis of 1-D polymers may impact on diverse areas of application, e.g. sensing or catalysis.

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Conflicts of interest

There are no conflicts to declare.

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