

From arm-shaped layers to a new type of polythreaded array: a two fold interpenetrated three-dimensional network with a rutile topology†

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The self-assembly based on 2D motifs with side arms leads to the formation of a new type of polythreaded network which exhibits a 2-fold interpenetrated 3D array if H-bonds are taken into account.

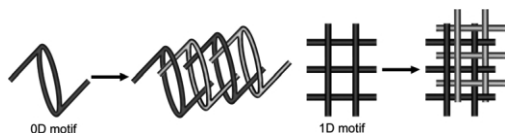
Entangled systems, which are common in biology as seen in catenanes, rotaxanes, and molecular knots, have been attracting considerable interest, not only because of their intriguing topological structures but also due to their interesting properties and potential applications. Interpenetrating nets, being an important subject in the area of entanglement, have provided a long-standing fascination for chemists, and many beautiful structures have been constructed^{1,2} and well discussed in comprehensive reviews by Batten and Robson.³ Besides the common types of interpenetrating networks, particular attention has recently been turning to a burgeoning family described as polythreaded coordination networks, which can be considered as periodic analogues of the molecular rotaxanes or pseudo-rotaxanes. Furthermore, interest in these compounds is increasingly heightened by their potential applications ranging from drug delivery vehicles to sensor devices.⁴ Some elegant examples belonging to this family have been recently designed.⁵ However, polythreading with finite components is still rare, as evidenced in a recent review by Ciani and coworkers.⁶ Only a few fascinating examples up to now, to the best of our knowledge, have been characterized, all constructed from 0D or 1D motifs with side arms (Scheme 1),⁷ exhibiting 0D → 1D,^{7a} 0D → 2D,^{7b} 1D → 2D,^{7c} and 1D → 3D^{7d} polythreaded array. Higher dimensional motifs in this facet remain unexplored and, therefore, much work is still necessary to enrich and develop this branch.

Taking inspiration from previous work, our synthetic strategy is to build up a higher dimensional motif with rigid linear ligands as threading components in an attempt to gain a new polythreaded array. At first, construction of 2D motifs appeared to be a simple extension of the work on 1D motifs, but it turned out to be a challenging goal. Fortunately, by trial and error we have now isolated a new compound, [Zn(HBTC)(4,4'-bpy)]_n (**1**) (BTC = 1,2,4-benzenetricarboxylate; 4,4'-bpy = 4,4'-bipyridyl), consisting of 2D motifs with dangling lateral arms suitable to give threading, according to the aforementioned idea. This species has several unusual features: (i) considering only the coordinative bonds, it represents a new (2D → 3D) polythreaded array, (ii) it is the first time that dinuclear metal species have been introduced into a polythreaded system with finite components and (iii) when considering the strong hydrogen bonds between layers, the overall

resulting network is a 2-fold interpenetrated architecture with a rutile topology.

Compound **1** was prepared by hydrothermal reaction of Zn(NO₃)₂·6H₂O, BTC, 4,4'-bpy, triethylamine and H₂O in a molar ratio of 1 : 1.2 : 1 : 1 : 1110 at 160 °C for 5 days.† Single-crystal X-ray diffraction‡ reveals that, unlike the reported non-entangled species of the BTC ligand,⁸ **1** is an extended 3D threaded network involving 2D coordination frameworks of (4,4) topology. In these layers each Zn(II) atom is coordinated by four oxygen atoms of four BTC ligands and one nitrogen atom of a bpy ligand to give a square-pyramidal geometry (Fig. 1). Two Zn(II) atoms, related by a twofold axis, are bridged by two pairs of BTC carboxylate ends into a dinuclear unit with a Zn(1)···Zn(1A) distance of 2.9779(13) Å. Three factors can be envisaged to play a role in the generation of mutual polythreading in **1**: (i) the presence within the 2D motif of very large rhombic windows (with dimensions of 10.86 × 10.86 Å) built up by eight Zn atoms and four BTC ligands, (ii) the dangling bpy groups, occupying the axial position of each Zn atom, are just like open arms nearly perpendicularly protruding from both sides of the sheets and (iii) all the layers are stacked parallel and arranged in a staggered fashion, with a distance of 8.1 Å, while the effective length of each lateral arm is ca. 10.5 Å (from the baricentre of the node to the uncoordinated N atom), thus providing, obviously, the possibility for the ultimate realization of threading. Under this premise, the bpy lateral arms of each layer are threaded into the rhombic voids of the adjacent layers, in a mutual relationship. Each rhombic window is therefore penetrated by two bpy molecules that belong to two different sheets, one entering from one side and the other from the opposite one, as shown in Fig. 2. This results in a novel 3D polythreaded array (2D → 3D), originating from the entanglement of three adjacent polymeric units at a time. To our knowledge, described here is the first polythreaded species involving finite components built up exclusively from 2D motifs. Interestingly, if we regard each rhombic window as a wheel and the paired bpy groups within the windows as a *single rod*, the nature of the entanglement in **1** can be described as poly-pseudo-rotaxane.

Whilst exploring the acting forces that stabilize the whole entanglement, we found that there exists strong hydrogen bonding interactions between the N atoms of bpy from one layer and the uncoordinated carboxyl oxygen atoms from the second nearest neighbouring layer, whose length is 2.644(10) Å, which make a



Scheme 1



Fig. 1 The structure of a single 2D motif showing the dangling arms.

† Electronic Supplementary Information (ESI) available: details of the synthesis and solid state emission spectra of **1**. See <http://www.rsc.org/suppdata/cc/b4/b405016a/>

great contribution to the structural stabilization. The most interesting feature is that when these hydrogen bonds are taken into account, the resulting structure displays a 2-fold interpenetrated 3D structure of rutile topology.⁹ All the (4,4) 2D layers stack on top of each other with an ABAB sequence in the $[-1\ 0\ 1]$ direction. The bpy ligands of the A layers penetrate the B ones to connect the next A layers *via* H-bonds, thus forming a binodal net with 6-coordinated (Zn dimer) and 3-coordinated (Y-shaped ligand) (see ESI[†]) centers, with a stoichiometry of 1 : 1 as in rutile. Finally, the two nets of the 2-fold interpenetrating 3D array originate respectively from layers of type A only or type B only (Fig. 3). To our knowledge, few examples of coordination networks with 2-fold rutile topology have been previously reported.¹⁰

In the solid state **1** exhibits an intense emission at 426 nm in the blue region ($\lambda_{\text{ex}} = 353$ nm), a blue shift compared with $[\text{Zn}_3(\text{BTC})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n$,^{8a} which may be due to the influences of the extent of deprotonation of the BTC ligand and the second ligand used. According to the literature,¹¹ it may be assigned to ligand to metal charge transfer (LMCT). This observation suggests that compound **1** may be an excellent candidate for potential photoactive materials.

In conclusion, we have prepared and characterized a new member of the class of polythreaded compounds previously

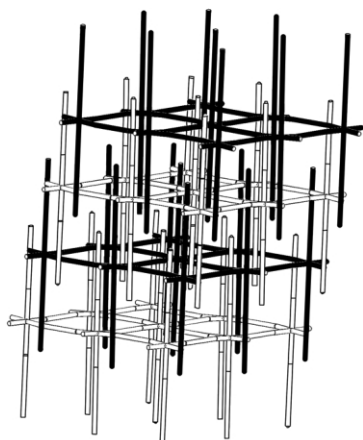


Fig. 2 Schematic illustration of the mutual polythreading of the 2D sheets in **1**.

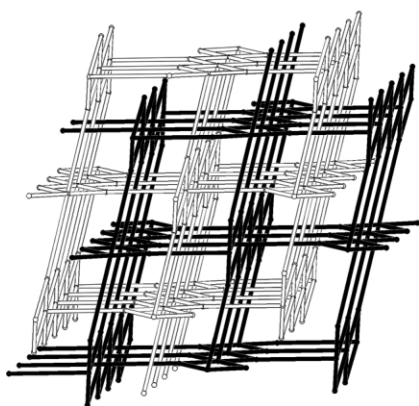


Fig. 3 A schematic view of the self-penetrating network. Highlighted are two interpenetrating motifs with rutile topology.

obtained only from low-dimensional (0D or 1D) motifs, whereas **1** is constructed from a higher dimensional (2D) motif.

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Notes and references

† Crystal data for **1**: $\text{C}_{19}\text{H}_{12}\text{N}_2\text{ZnO}_6$, $M = 429.68$, monoclinic, $a = 9.869(2)$, $b = 16.781(3)$, $c = 11.299(2)$ Å, $\beta = 100.02(3)^\circ$, $U = 1842.8(6)$ Å³, $T = 293$ K, space group $P2(1)/n$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.372$ mm⁻¹, 7284 reflections measured, 4122 unique ($R_{\text{int}} = 0.0541$) which were used in all calculations. $R1 = 0.0658$ and $wR2 = 0.1148$ for $I > 2(I)$. CCDC 233352. See <http://www.rsc.org/suppdata/cc/b4/b405016a/> for crystallographic data in .cif format.

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