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Interlocking of molecular rhombi into a 2D polyrotaxane network *via* π–π interactions. Crystal structure of $[Cu_2(bpa)_2(phen)_2(H_2O)]_2 \cdot 2H_2O$ (bpa^{2-} = biphenyl-4,4′-dicarboxylate, phen = 1,10-phenanthroline)

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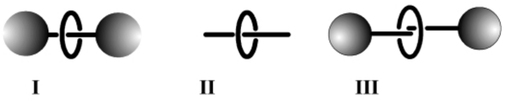
In the solid state, interlocking of the lateral phen ligands at the acute angle sites of the molecular $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$ rhombi *via* aromatic π–π stacking interactions into the cavities of the adjacent rhombi generates laminated polyrotaxanes that are further assembled into a 3D network *via* similar interactions between the phen ligands at the obtuse angle sites.

Coordination polymeric architectures have recently received much attention due to their intriguing potential applications and various structural motifs,[1] in which supramolecular interlocking and intertwining observed in these species are of special interest for chemists.[2] Many interpenetrating networks have been reported, the constituents of which are exclusively coordination polymers.[3] Among these interpenetrating motifs, several rotaxanes (**I**) and pseudorotaxanes (**II**) have been documented in organic and coordination compounds (Scheme 1).[2,3] On the other hand, although a great number of molecular squares have been well investigated,[1,4–6] only one example of molecular squares self-assembled by coordinate bonds into a higher dimensional framework has recently been reported.[6] The assembly of cyclic tetranuclear metal complexes such as molecular squares, rhombi or boxes *via* molecular recognition into multidimensional motifs is therefore an interesting challenge. It is well-known that the structural geometry can be controlled and modulated by selecting the coordination geometry of metal ions and the chemical nature of the terminal and bridging ligands. Usually long ligands will lead to larger voids that may lead to interpenetrated structures.[3b] Moreover, aromatic stacking is an important class of supramolecular forces, which can be used to govern the process of molecular recognition and self-assembly.[7] In our attempt to produce higher dimensional molecular architectures through molecular recognition, we recently chose a long, linear bridging ligand, biphenyl-4,4′-dicarboxylate (bpa^{2-}), a larger aromatic planar chelate, 1,10-phenanthroline (phen), and Cu^{II} ions to construct coordination aggregates that may have larger cavities to accommodate guest molecules and molecular recognition ability. Fortunately, we have now isolated a new neutral molecular rhombus, $[Cu_2(bpa)_2(phen)_2(H_2O)]_2 \cdot 2H_2O$ (**1**), having a large rhombic void, in which the phen ligands display different recognition functions; some penetrate into the rhombic cavities to generate 2D networks and others stack each other to produce a 3D motif in the solid.

Complex **1** was prepared by a simple hydrothermal approach. To a solution of $Cu(NO_3)_2$ (0.2 mmol) and phen (0.2 mmol) in water (10 mL), H_2bpa (0.2 mmol) and Et_3N (0.4 mmol) were added. The mixture was stirred for 20 min in air, then transferred and sealed in a 23-mL Teflon reactor, which was heated at 140 °C for 7 days and cooled to room temperature at a rate of 5 °C h^{-1}. Blue block crystals were obtained in 48% yield.†

Single-crystal X-ray diffraction‡ shows that **1** is a centrosymmetric tetranuclear rhombus (Fig. 1). In the neutral molecule, each $[Cu(phen)]^{2+}$ unit as a corner is bridged by two bpa^{2-} ligands in the monodentate–bidentate mode to form a large open rhombic cavity with the edge and two diagonal distances Cu1···Cu2, Cu1···Cu1A and Cu2···Cu2A at 15.1, 25.1 and 16.8 Å, and the acute angle Cu2···Cu1···Cu2A at 67.4°, respectively, which is larger than a recently documented molecular square with $[Cu(2,2'\text{-bipyridine})]^{2+}$ as corners and 1,2-bis(4-pyridyl)ethane as spacers; also, in the latter, the squares are interconnected by axial chloride bridges into a 3D network.[6] There are two types of coordination environments in **1**. Cu1 at the vertex of the rhombus acute angle is coordinated by a chelate phen (Cu1–N 2.009(3) and 2.023(3) Å), two oxygen atoms from the monodentate ends of two bpa^{2-} (Cu1–O1.945(3) and 1.935(3) Å), and one aqua ligands (Cu1–O1w 2.274(3) Å) at the axial position to furnish a distorted square-pyramidal CuN_2O_2O' (4 + 1) coordination. While Cu2 at the vertex of the rhombus obtuse angle is coordinated by a chelate phen (Cu2–N 2.024(3) and 2.025(3) Å) and four oxygen atoms from the chelate ends of two bpa^{2-} ligands (Cu2–O3 2.279(3), Cu2–O4 2.057(3), Cu2–O7 2.125(3) and Cu2–O8 2.275(4) Å), forming an elongated (4 + 2) octahedron due to the Jahn–Teller effect.

The four phen ligands are extended outward in four directions of the rhombus, which play a very important role in the self-assembly *via* aromatic π–π interaction to form high-dimensional motifs. The two types of corner sites (acute and obtuse angles) of each rhombus display different functions in the self-assembly (Fig. 2). The two lateral phen ligands, each termed as a rod, at the acute angle sites of two centrosymmetrically related rhombi penetrate oppositely into the rhombic cavity of the third



Scheme 1

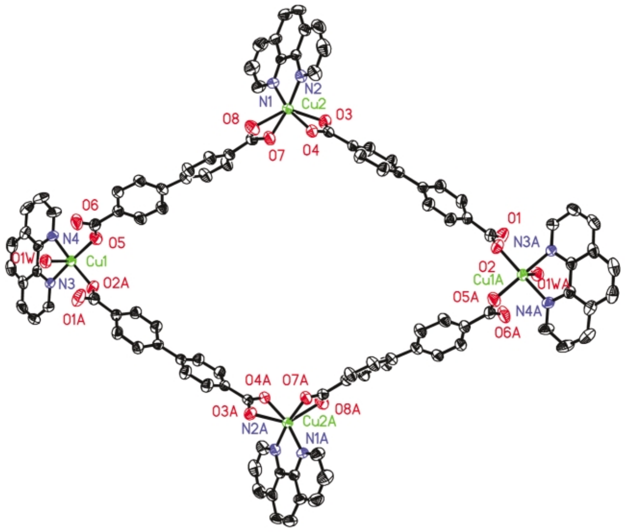


Fig. 1 ORTEP plot of the molecular structure $[Cu(bpa)(phen)]_4$ (**1**) (35% thermal ellipsoids).

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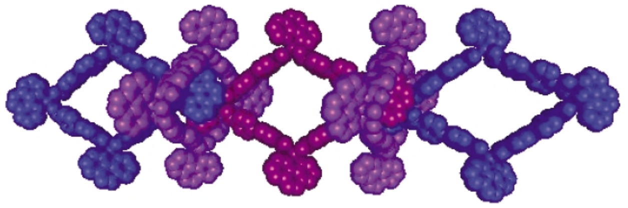

Fig. 2 A space-filling diagram showing the 1D chain formed by interpenetration.

rhombus, termed as a wheel, to generate a molecular node showing a strong aromatic π–π stacking interaction between the two rods (face-to-face and centroid–centroid distances at 3.46 and 3.56 Å, respectively).[8] Adjacent pairs of rhombi are self-assembled in this way into 1D chains along the [011] or [011] directions (Fig. 3). Each pair of the phen rods at the acute angle sites of the wheels of the adjacent, parallel 1D chains meet at the rhombic cavities of the perpendicular 1D chains to produce the same molecular nodes, resulting in 2D networks parallel to the *bc* plane. The origin of this feature is that each rhombus of **1** is multifunctional. Each phen group at the acute angle site acts as a rod, and each rhombic cavity functions as a wheel, while the wheel can also be regarded as a stopper. Therefore, each node can be regarded as a pseudorotaxane, which is unprecendented for the double interpenetration from opposite sides (**III**).[3] On the other hand, if we regard the paired phen rods that strongly stacked within the wheel as a *single* rod, the 2D network can therefore be described as a 2D polyrotaxane formed by interlocking of these rods and wheels. The topology of the 2D polyrotaxane is parallel to that found in a polyrotaxane constructed by 1D coordination polymers, in which the rods are covalent fragments.[9] Examination of the structural details shows that the bpa^{2-} phenyl rings are almost perpendicular to the inserted phen groups (86°), exhibiting edge-to-face C–H$\cdots\pi$ interactions between phen protons and a phenyl ring (C–H$\cdots\pi$ 3.83 or 4.00 Å),[8] as well as a significant hydrogen bond between a phen proton and a carboxy oxygen atom (C51$\cdots$O4 3.284 Å). The driving forces in the formation of the 2D layers may come from the π–π and C–H$\cdots\pi$ interactions, as well as the C–H$\cdots$O hydrogen bonds in the cavity. Finally, it should be noted that these 2D layers further stack into a 3D network *via* aromatic π–π interactions, in which the phen groups at the obtuse angle sites of the rhombi are regularly stacked with each other in an offset fashion with the face–face and centriod–centriod distances at *ca*. 3.59 and 3.91 Å, respectively, also indicating that phen is better for the π–π interaction than 2,2′-bipyridine.[6] To our knowledge, **1** represents the first example of 2D polyrotaxane self-assembled by molecular rhombi into a 3D network *via* supramolecular interactions.

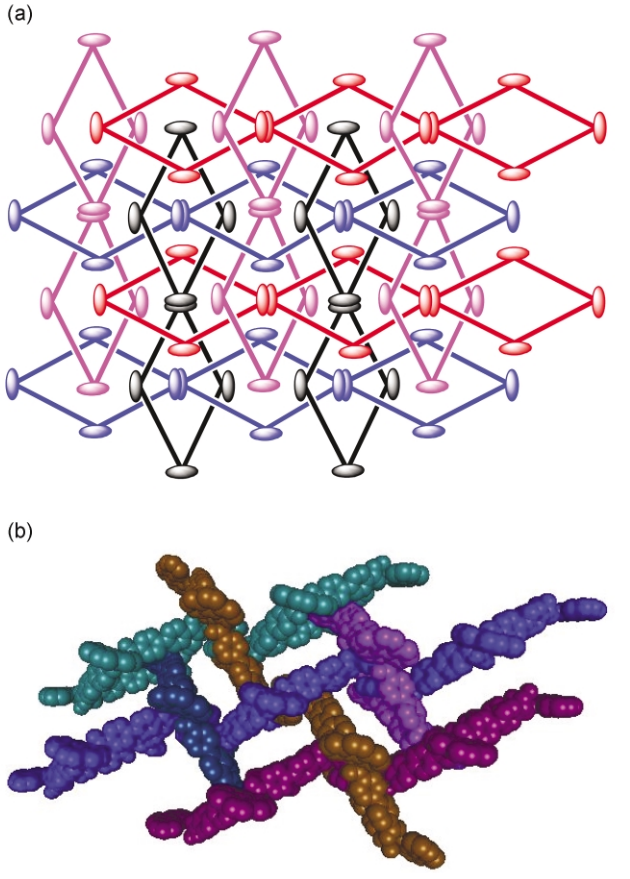

Fig. 3 2D structure of **1**. (a) A schematic presentation with the ellipsoids and solid lines representing the phen ligands and bpa^{2-} ligands, respectively. (b) A space-filling diagram.

In summary, we present an unprecedented polyrotaxane generated by self-assembly based on supramolecular interactions of multi-functional molecular rhombi which have large cavities and lateral aromatic chelate ligands, acting as rods, wheels and stoppers.

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Notes and references

† Anal: Calc. for [Cu(bpa)(phen)]$_4$·2H$_2$O: C, 62.21; H, 3.61; N 5.58. Found: C, 62.17; H, 3.64; N, 6.56%.

‡ *Crystal data* for [Cu(bpa)(phen)]$_4$·H$_2$O: orthorhombic, space group *Pbca*, M_r = 2007.86, a = 23.358(5), b = 15.008(3), c = 25.479(5) Å, V = 8932(3) Å^3, Z = 4, D_c = 1.493 g cm^{-3}. Data collections ($2 \le \theta \le 27°$) were performed at 293 K on a Bruker CCD diffractometer (Mo-Kα, λ = 0.71073 Å). The structures were solved by direct methods and refined with full-matrix least-squares (SHELX-97),[10] giving a final R_1 value of 0.0501 for 614 parameters and wR_2 of 0.1413 for all 9721 reflections. CCDC reference number 184400. See http://www.rsc.org/suppdata/cc/b2/b202716j/ for crystallographic data in CIF or other electronic format.

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