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A new 2D → 3D network with the coexistence of inclined polycatenation and polythreading constructed by an N-centered tripodal linker

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A new cadmium(II) coordination polymer has been synthesized in a diffusion process by employing the triangular rigid tri(4-pyridylphenyl)amine ligand. The complex crystallizes in the space group *Pbcn* and features a 2D → 3D framework with the coexistence of inclined polycatenation and polythreading.

The rationally designed construction of entangled polymers from multidentate molecular building blocks and metals have attracted extensive attention not only for their structural diversity[1,2] but also for their explosive applications in photochemistry,[3,4] gas adsorption and separation,[5,6] molecular magnetism[7,8] and heterogeneous catalysis.[9,10] Among the coordination networks, an entangled system is an extremely active subject,[11,12] and many fascinating entangled structures such as polycatenation and polythreading have been discussed. Various polythreaded nets have been reported.[13–17] Recently, only a few fascinating structures with the coexistence of interpenetration and polycatenation,[18,19] polycatenation and polythreading,[20] polyrotaxane and polythreading,[21] polyrotaxane and polycatenation[22,23] and polythreading and polyknotting[24] have been described. Therefore, it is still a great challenge for obtaining different types of interpenetrated motifs in one structure.

As far as we know, polycatenation or polythreading is usually constructed from mixed ligands,[25–28] whereas the design of these frameworks with a single ligand is still challenging. Here, we report an unusual 2D → 3D network with the coexistence of polycatenation and polythreading based on an N-centered tripodal linker and a Cd^{II} salt.

The crystal structure of $\{[Cd(Tppa)_2(NO_3)_2]\cdot x\,Solvents\}_n$ **1**[†,‡] is solved in the space group *Pbcn*; the asymmetric unit consists of one Cd^{II} cation (special position), one tri(4-pyridylphenyl)amine (Tppa) moiety and one disorder nitrate anion. As shown in Figure 1, Cd^{II} ions have a distorted octahedral geometry, which is composed of four N atoms from four Tppa at the equatorial plane position

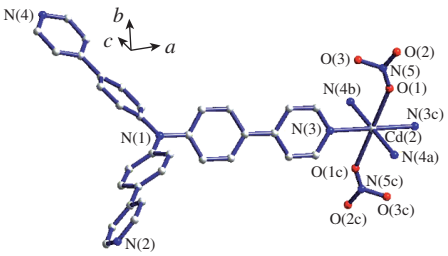

Figure 1 Coordination environment of **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: a = 0.5 + *x*, –0.5 + *y*, 0.5 – *z*; b = 0.5 – *x*, 1.5 – *y*, –0.5 + *z*; c = 1 – *x*, 1 – *y*, –*z*. Selected bond lengths (Å) and angles (°): Cd(2)–N(3) 2.333(3), Cd(2)–O(1) 2.346(6), Cd(2)–N(4a) 2.354(3); N(3)–Cd(2)–N(3c) 180.00(11), N(3)–Cd(2)–O(1c) 83.67(17), N(3)–Cd(2)–O(1) 96.33(17), O(1)–Cd(2)–O(1c) 180.0(3), N(3)–Cd(2)–N(4b) 89.40(11), N(3)–Cd(2)–N(4a) 90.60(11), O(1)–Cd(2)–N(4a) 86.99(17), O(1)–Cd(2)–N(4b) 93.01(17), N(4a)–Cd(2)–N(4b) 180.0(2).

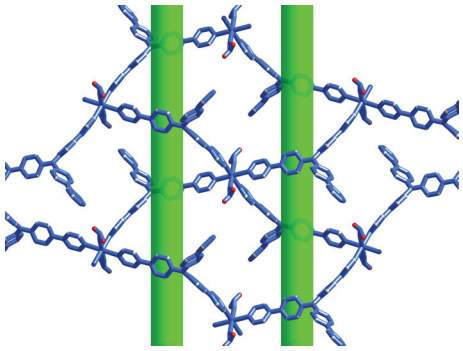

Figure 2 Neighboring Cd^{II} ions linked with Tppa to generate a 2D wave-like sheet with infinitely left-handed and right-handed helical chains.

and two O atoms from two nitrate anions at the equatorial position. The lengths of Cd–N and Cd–O bonds are 2.333(3)–2.345(3) and 2.257 Å, respectively, which are similar to those found in other Cd^{II} complexes. The dihedral angels between phenyl and

† *Synthesis of complex* **1** *(general procedure)*. $CHCl_3$ (6.0 ml) containing Tppa (0.01 mmol) was placed in a tube; then, 6.0 ml of MeOH containing $Cd(NO_3)_2$ (0.02 mmol) was layed at the top. The test tube was sealed and allowed to stand at room temperature. Pale yellow block crystals were collected in a month (yield: ~46% based on a ligand).

‡ *Crystallographic data for* **1**. Crystals of $C_{66}H_{48}C_dN_{10}O_6$ (M = 1189.55) are orthorhombic, space group *Pbcn*, at 273(2) K: a = 29.831(3), b = = 13.3152(16) and c = 18.019(2) Å, V = 7157.2(14) Å^3, Z = 4, d_{calc} = = 1.104 g cm^{-3}, μ(MoKα) = 0.355 mm^{-1}, F(000) = 2440. 8543 reflections were measured and 3871 independent reflections (R_{int} = 0.0650) were used in a further refinement. The refinement converged to wR_2 = 0.2166 and GOF = 1.046 for all independent reflections [R_1 = 0.0650 was calculated against F for 8543 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[29] Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distribution of peaks in the channels of **1** were chemically featureless to refine using conventional discrete-atom models, to resolve these issues, the contribution of the electron density by the remaining solvents was removed by the SQUEEZE routine in PLATON.[30]

CCDC 1024648 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

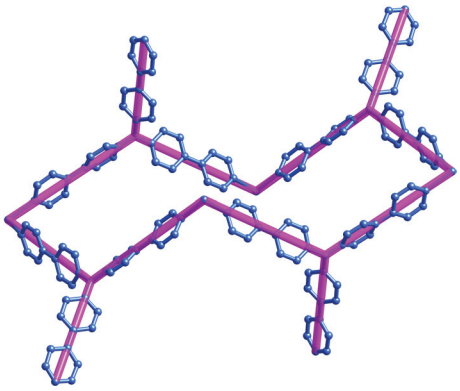

Figure 3 Four Tppa ligands connect four Cd^{II} ions to achieve a 72-membered window.

adjacent pyridyl rings are 24.0(2)°, 11.3(2)° and 20.0(2)°; the angles of N centers to the terminal nitrogen atoms are very close [N(2)···N(1)···N(3), 118.4(6)°; N(2)···N(1)···N(4), 120.5(8)° and N(3)···N(1)···N(4), 119.7(5)°].

In complex **1**, two pyridyl groups of each Tppa connect two Cd^{II} ions, and the third pyridyl group is uncoordinated. Note that a pair of left-handed and right-handed 1D helical channels arranged alternately, and the adjacent Cd(1)···Cd(1) distance is 18.654 Å (Figure 2). These two kinds of helical chains further form a wavelike 2D sheet by sharing the Cd^{II} ions, in which four Tppa ligands connect four Cd^{II} ions to achieve a 72-membered $[Cd_4(Tppa)_4]$ square window exhibiting maximum dimensions of 25.037 × 26.476 Å (two pairs of Cd···Cd distances) (Figure 3).

The packing of sheets generates two sets of sheets oriented toward two directions. The uncoordinated pyridyl groups end-on Tppa dangle above and below the sheet, exhibiting an overall multiarmed sheet (Figure 4). The multiarmed sheets stacked parallel along the *c* directions to form an ABCABC stacked mode, and the dangling uncoordinated pyridyl groups extend into the windows of adjacent sheets; the effective length from an N center to the terminal uncoordinated nitrogen atom is about 8.527 Å (longer than the stacking distance of sheets), which caused the formation of threading. Each window is pierced by two Tppa ligands that belong to two adjacent sheets. Meanwhile, these two sets of sheets catenated each other in a parallel-parallel arrangement to form a 2D → 3D inclined polycatenated network (Figure 5).

In complex **1**, only two N atoms of each Tppa coordinated to Cd^{II}; Tppa acts as a linear linker, and Cd^{II} acts as 4-connector, so the network is 4-connected (4, 4) sheet, the angle between the two sets of inclined sheets is 60.3° (Figure 5). Two polycatenation and polythreading entangled systems observed simultaneously in one complex are unique, although the polycatenation or polythreading is rather common. Also, it is the first example of the construction of a polycatenated and polythreaded framework from a star-like ligand. The entangled mode and the formation of helices benefit not only from the shape of the bridging ligand but also from the large windows.

In summary, an unprecedented 2D → 3D polycatenated and polythreaded framework based on the star-like Tppa ligand has been prepared using $Cd_4(Tppa)_4$ as the loop and the uncoordinated phenylpyridyl arm as a rod.

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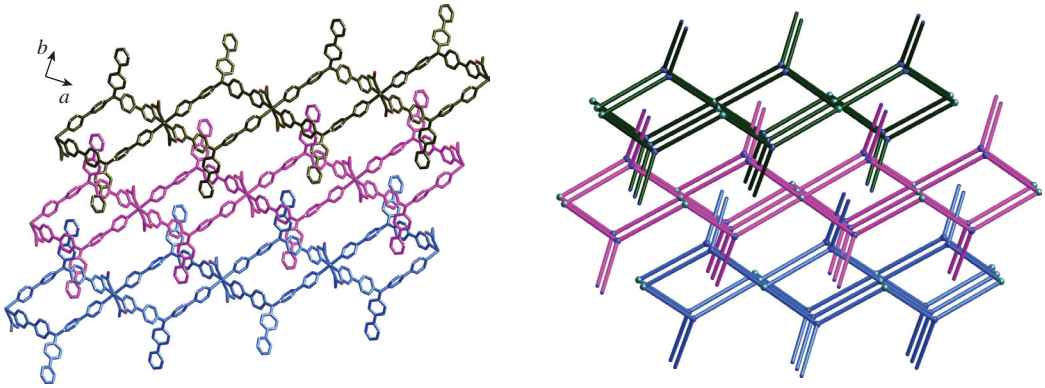

Figure 4 Multiarmed layers stacked parallel in the ABCABC mode, the uncoordinated pyridyl groups extend into the windows of adjacent layers in a mutual relationship, forming a 2D → 3D polythreaded network.

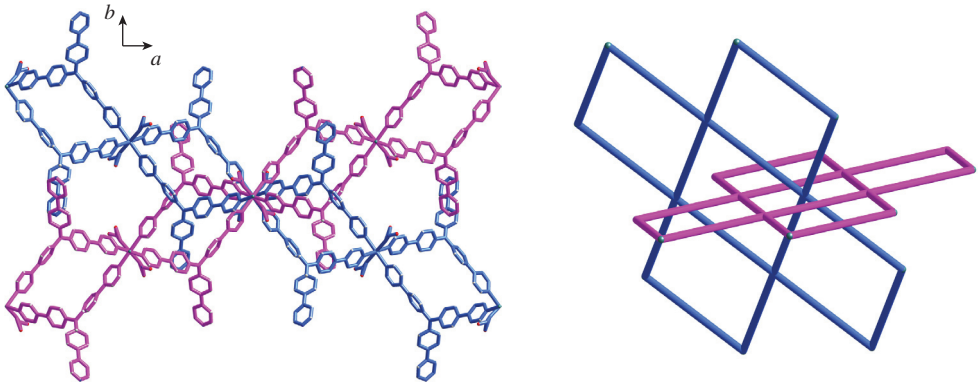

Figure 5 2D → 3D inclined polycatenated network which is formed by two sets of sheets catenated to each other in a parallel-parallel arrangement.

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