

Self-assembly

Interlocked and Interdigitated Architectures from Self-Assembly of Long Flexible Ligands and Cadmium Salts**

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The current interest in the crystal engineering of coordination polymer frameworks not only stems from their potential applications in microelectronics, nonlinear optics, porous materials, and catalysis, but also from their intriguing variety of architectures and topologies.^[1,2] Up to now, a variety of

appealing interpenetrated nets, in which only internal connections are broken to separate individual nets, have been reported and reviewed by Batten and Robson.^[3] In contrast, other types of entangled architectures that have recently been described—such as infinite multiple helices,^[4] two-dimensional clothlike warp-and-weft sheet structures,^[5] interdigitated structures in a gearlike (or tongue-and-groove) fashion,^[6] and polythreaded structures with poly-pseudo-rotaxanes^[7]—can, in principle, be disentangled without breaking links. Moreover, these entangled nets can lead to synthetic supramolecular arrays with potential applications in asymmetric catalysis, drug-delivery vehicles, and sensor devices.

Unfortunately, these species are still rare, as evidenced in a recent review by Ciani and co-workers,^[8] and therefore the exploration of new synthetic routes to this class of supramolecular architectures is one of the most challenging issues in current synthetic chemistry. On the other hand, it is well-known that product topology can often be controlled and modulated by selecting the coordination geometry of the metal ions and the chemical nature of the organic ligands. Usually, long ligands will lead to larger voids that may result in interpenetrated structures,^[3] the most outstanding example of which is 1,2-bis(4-pyridyl)ethane (bpe). With this ligand, many beautiful interpenetrated networks of ingenious design have been constructed, ranging from interpenetrating 1D ladders to 3D nets.^[9]

However, these results do not mean that other types of entangled structures cannot be formed in the presence of long flexible ligands. If another configurational ligand is introduced, it may be possible to gain noninterpenetrating nets by combining different precursors. In this regard, for our synthetic strategy we choose an analogy of bpe, biphenylthene-4,4'-dicarboxylic acid (bpea), whose coordination chemistry, to the best of our knowledge, has not been previously investigated. Due to the replacement of two pyridyl groups by aromatic carboxy groups, bpea will be more flexible than bpe. Therefore, to avoid interpenetration the heterocyclic aromatic ligand 1,10-phenanthroline (phen) was introduced based on the following considerations: 1) The steric hindrance at the metal center will be increased when the bulky aromatic ligand binds to the metal ion; this reduces the dimension of the net formed. Lower dimensional nets are usually less likely to interpenetrate because there are more possible ways to maximize the packing efficiency.^[10] 2) Chelating bipyridyl-like ligands may provide recognition sites for π - π stacking interactions to form interesting supramolecular structures. 3) The conjugated π systems containing (hetero)aromatic rings are currently of interest in the development of fluorescent materials and use as model compounds for electroluminescence and optical switching devices.^[11]

Due to the low solubility of the ligands, we adopted hydrothermal techniques and successfully synthesized three noninterpenetrating species. The first complex [Cd(bpea)(phen)₂] (**1**) exhibits a remarkable assembly of ninefold interlocked homochiral helices that are built from achiral components. [Cd₂(bpea)(pt)(phen)₂][Cd(pt)(phen)]·2H₂O (**2**, pt = phthalate) contains neutral 2D puckered sheets that are interdigitated by neutral 1D zigzag chains. The final compound [Cd₃(bpea)(phen)₃(OH)₃(H₂O)]·0.5bpea·4H₂O (**3**)

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[**] This work was financially supported by the National Natural Science Foundation of China (No. 20371011).

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has unprecedented hexanuclear cadmium clusters that show a 3D supramolecular host–guest network.

X-ray crystallography^[12] shows that **1** has a 3D chiral framework assembled by nine interlocking nanotubes. Complex **1** crystallizes in the chiral space group $P4_1(3)$, with one Cd atom, one bpea ligand, and two phen ligands in the asymmetric unit. The Cd center is coordinated by four nitrogen atoms from two chelating phen ligands (mean Cd–N 2.477(3) Å) and two oxygen atoms from two monodentate carboxylate ends of two bpea ligands (mean Cd–O 2.259(3) Å) to furnish a distorted octahedral geometry. The $[\text{Cd}(\text{phen})_2]^{2+}$ molecular corners are bridged by long linear spacers to form an infinite helical chain running along the c axis (Figure 1a). The left-handed helix is generated around

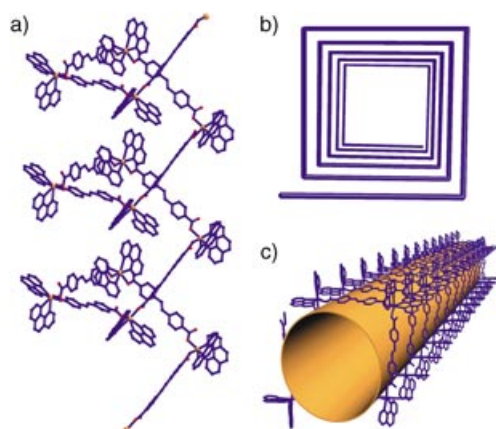


Figure 1. Crystal structure of **1**. a) View of the left-handed 4_1 helical chain. b) Schematic view of the helical chain. c) Perspective view of a chiral nanotube with an opening of about 1.8×1.8 nm.

the crystallographic 4_1 axis with a pitch of 24.46 Å. Notably, each pair of nearly perpendicular phen ligands bonded to the Cd atom point away from the helical axis; this steric orientation leads to the generation of a tetragonal nanotube with an opening of about 1.8×1.8 nm (Figure 1b,c).

The most fascinating structural feature of **1** is that each helical chain is chemically independent but physically interwoven with the same independent chains in all directions, whose unique entangled fashion can be described stepwise. First of all, four identical helices interweave the central one along the a and b axes with an extent of intercalation of about 0.72 nm. Another four helices further interlock the central one along the $[a,b]$, $[-a,-b]$, $[a,-b]$, and $[-a,b]$ directions with an extent of intercalation of about 0.24 nm. Thus, each helical chain is interlocked by eight equivalent polymeric units to give a periodically ordered interlocked architecture (Figure 2). The resulting 3D chiral network can therefore be described as an infinite interlocked array originating from ninefold interwoven homochiral helices. The framework is stabilized by strong π – π stacking interactions between the interwoven aryl groups: Parallel stacking with face-to-face distances of 3.350 Å between phen ligands and 3.400 Å between phen and bpea ligands. In contrast to the inter-



Figure 2. A schematic illustration of the ninefold interlocked homochiral helices of **1**.

penetrated network, the individual chains can “ideally” be separated without breaking links.

For typical interpenetrating systems, the world record is held by a tenfold interpenetrated diamondoid net exclusively based on coordinative bonds.^[13] Among the new structures showing entanglement, a rather remarkable example was reported by Lin and co-workers in which the 3D chiral framework results from the assembly of quintuple interwoven helices built from axially chiral bityridines.^[14] Therefore, to our knowledge, the ninefold interlocking homochiral helices constructed from achiral components in **1** represents the highest degree of entanglement known in a noninterpenetrating system.

The structure determination of **2** shows the presence of two crystallographically independent polymer motifs in the same crystal. One motif is a 1D zigzag chain constructed from mononuclear Cd atoms, pt, and phen (Figure 3a). The Cd center has a distorted octahedral coordination environment containing two nitrogen atoms of a chelating phen ligand (Cd–N 2.278(5) Å) and four oxygen atoms of two chelating carboxylate ends of two pt ligands (Cd–O 2.332(5) Å). The dangling phen groups are perpendicular to the propagation direction of the chain and bristle out in opposite directions. This arrangement paves the way for interdigitation.

The other polymer motif of **2** is a 2D puckered sheet of (4,4) topology built up from dinuclear Cd units with three types of ligands, that is, pt, bpea, and phen (Figure 3b). Although a few polymer frames with two kinds of aromatic ligands have been reported,^[15] there are no examples in which more than two different aromatic ligands are incorporated into a metal–organic polymer network. In contrast to the Cd atom in the first motif, the Cd center in the second motif adopts a seven-coordinate geometry made up of two nitrogen atoms of a chelating phen ligand (Cd–N 2.351(5) Å) and five oxygen atoms from one chelating bpea and two pt ligands (Cd–O 2.425(4) Å). Two crystallographically equivalent Cd atoms are bridged by two μ_3 -oxygen atoms to generate a dinuclear unit $[\text{Cd}\cdots\text{Cd}(\text{A})\ 3.693(9)\ \text{\AA}]$. Four such dinuclear

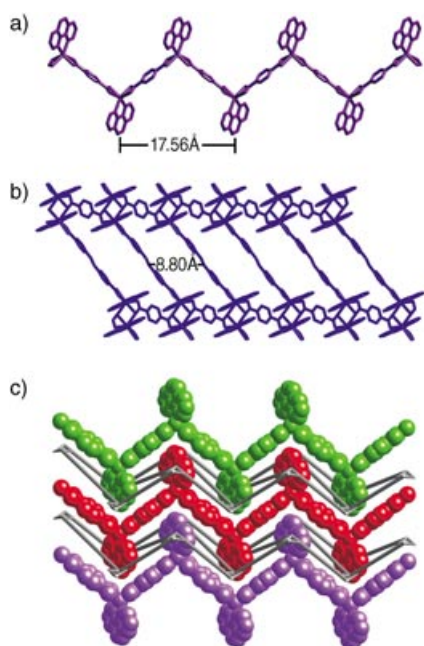


Figure 3. Crystal structure of **2**. a) View of the zigzag chain. b) View of the puckered sheet. c) View of the entanglement of the 1D chains and 2D sheets in the ABAB mode. The interdigitation of the phen groups is clearly visible.

units are alternately linked by pt and bpea ligands to form a long and narrow window, which provides a snug habitat for dangling phen groups of the 1D chain.

The unexpected aspect of **2** is how structurally divergent the two motifs are rationally combined together. The width of a window within a puckered sheet, dictated by the shortest carbon–carbon separation between two opposite bpea ligands, is about 8.80 Å, while the period of a zigzag chain is about 17.56 Å. This allows every other window of a sheet to be penetrated by one side of the phen groups of the 1D chains above the layer. The remaining windows are penetrated in the same way by the phen groups below the layer. Thus, each sheet is simultaneously interdigitated by chains located above and below. The two different structural motifs alternate in the crystals, stacking with a sequence ABAB to form a beautiful 3D array (Figure 3c).

The coexistence of different structural motifs in the same crystal is rather rare.^[16] Among the few examples of interdigitation—almost all with identical motifs, generally a 2D sheet^[6a–d]—only one involves two different polymer motifs, namely, $[\text{Zn}_{2.5}(\text{L})(\mu_3\text{-OH})](\text{H}_2\text{O})_5$ ($\text{L} = 3\text{-}[[4\text{-(4-pyridylethenyl)phenyl]ethenyl}]benzoate$).^[6e] In this structure the 1D and 2D motifs are both constructed from the L ligand. Therefore, compound **2**, in which the 1D and 2D motifs are constructed from different components (1D: pt and phen; 2D: pt, phen, and bpea) represents a new example of interdigitation: there has now been a progression from one motif with a single ligand, to different motifs with a single ligand, to finally different motifs with diverse ligands.

The structure of **3** consists of positive 1D pseudo-molecular ladders and negative bpea^{2-} ions. As shown in Figure 4a, the 1D ladder contains unprecedented hexanuclear

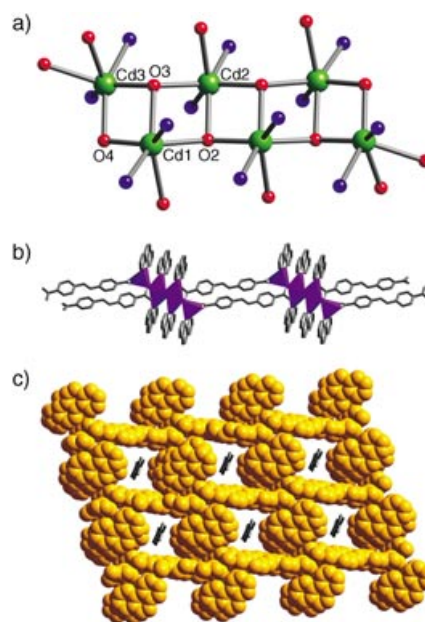


Figure 4. Crystal structure of **3**. a) View of the ladderlike hexanuclear cadmium cluster. b) View of the 1D ladder highlighting the hexanuclear metal clusters as rungs. c) View of the supramolecular host–guest network in which the location of the guest bpea^{2-} ions in the parallelogram channels is created by stacking of the ladders.

cadmium clusters in which three crystallographically independent cadmium(II) atoms exhibit three different coordination environments. In addition to a chelating phen ligand, Cd1 is coordinated by a monodentate bpea ligand and three μ_3 -OH groups, Cd2 is coordinated by one aqua ligand and three μ_3 -OH groups, and Cd3 is coordinated by a chelating bpea ligand and two μ_3 -OH groups. Each μ_3 -OH group interlinks three Cd atoms in a trigonal shape ($\text{Cd}\cdots\text{Cd}$ 3.511(6)–3.909(7) Å) to give an edge-sharing hexanuclear cadmium cluster. While a few $[\text{Cd}_3(\mu_3\text{-OH})]^{5+}$ cores^[17] and octanuclear cadmium clusters^[18] have been reported, such a hexanuclear ladderlike metal core featuring cadmium–hydroxy clusters has never been shown before. Neighboring hexanuclear cadmium clusters are linked by two linear bpea spacers, thus producing a new type of pseudo-molecular ladder in which the hexanuclear cadmium clusters act as inner rungs (Figure 4b). The phen ligands are orientated away from the ladder and play an important role in subsequent packing into a three-dimensional network.

Interestingly, adjacent ladders in **3** are interdigitated in a zipper fashion to form 2D layers with significant C–H $\cdots\pi$ interactions between the aromatic rings of different ladders; the edge-to-face separation is about 3.70 Å. These layers are further packed into a 3D network featuring 1D parallelogram-shaped cationic channels (8.91×9.97 Å) under the direction of strong π – π stacking interactions between the phen groups; the face-to-face distance is about 3.414 Å. Completely deprotonated bpea guests reside in the channels and are hydrogen-bonded to the aqua ligands of the ladders ($\text{O}\cdots\text{O}$ 2.659(9) Å, Figure 4c). Therefore, the architecture of **3** can be best described as a 3D supramolecular host–guest network.

Compounds **1–3** have much in common: All are Cd(bpea)(phen) derivatives and contain 1D chain motifs in their crystal structures. This could be related to the fact that chelating ligands such as phen serve a “passive” role by occupying coordination sites on the metal centers and providing steric constraints, thus preventing spatial extension of the skeleton to higher dimensions. Similar behavior has been observed before.^[19] Despite the similarities among **1–3**, the three types of chains (helical, zigzag, and ladderlike) fulfill different functions in crystal packing. Although some possible factors have been discussed here, we are unable to propose definite reasons as to why each compound adopts a different strategy.

To examine the contribution of d¹⁰ metal polynuclear clusters to the photoluminescent properties of these systems, the luminescence of **3** was investigated. While the free H₂bpea ligand displays weak luminescence in the solid state at room temperature (see Figure S1 in the Supporting Information), compound **3** exhibits an intense blue radiation emission maximum at $\lambda \approx 489$ nm upon excitation at $\lambda = 386$ nm (Figure 5). The enhancement of luminescence may be attrib-

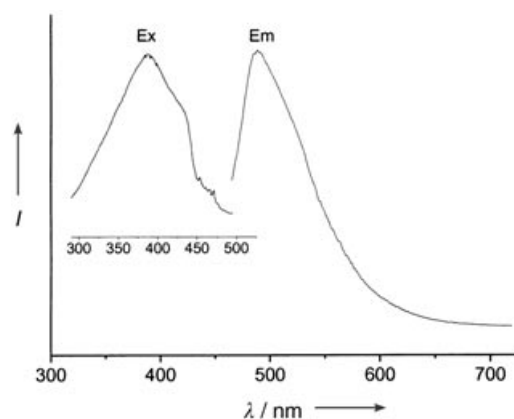


Figure 5. Photoluminescent spectra of **3** in the solid state at room temperature. Ex = excitation, Em = emission.

uted to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.^[20] As with other metal-hydroxy clusters,^[18b,21] the lifetime of **3** is about 14 ns, which is significantly longer than for systems without metal-hydroxy clusters. This fact may be ascribed to the presence of the metal clusters, since the μ_3 -OH ligand may tighten the whole skeleton, resulting in much weaker vibrations.

In conclusion, we have presented a rational synthetic strategy that successfully provided three coordination polymers by combining a long flexible ligand and a bulky heterocyclic aromatic ligand, which show different packing modes. Although the final polymeric architectures are impossible to predict with our present state of knowledge, the strategy represents a potential approach for the design of noninterpenetrating structures with long flexible ligands. In addition to the well-known interpenetrated frameworks, these new types of supramolecular entangled networks

represent another important branch in the realm of entanglement and open interesting perspectives in the study of these materials.

Experimental Section

1: A mixture of Cd(NO₃)₂·4H₂O (154 mg, 0.5 mmol), H₂bpea (134 mg, 0.5 mmol), phen (198 mg, 1 mmol), and water (10 mL) was placed in a 23-ml Teflon reactor and kept under autogenous pressure at 140 °C for 5 d. Then the mixture was cooled to room temperature at a rate of 10 °C h⁻¹, and colorless crystals of **1** were obtained (yield: 192 mg, 52% based on Cd). C, H, N analysis calcd (%) for C₄₀H₂₆CdN₄O₄: C 65.00, H 3.55, N 7.58; found: C 64.65, H 3.27, N, 7.81.

2: A mixture of Cd(NO₃)₂·4H₂O (460 mg, 1.5 mmol), H₂bpea (134 mg, 0.5 mmol), phen (300 mg, 1.5 mmol), H₂pt (250 mg, 1.5 mmol), and water (10 mL) was placed in a 23-ml Teflon reactor and kept under autogenous pressure at 160 °C for 5 d. Then the mixture was cooled to room temperature at a rate of 10 °C h⁻¹, and light-yellow crystals of **2** were obtained (yield: 140 mg, 56% based on Cd). C, H, N analysis calcd (%) for C₆₈H₄₆Cd₃N₆O₁₄: C 54.10, H 3.07, N 5.57; found: C 53.84, H 2.77, N, 5.75.

3: A mixture of Cd(NO₃)₂·4H₂O (308 mg, 1 mmol), H₂bpea (134 mg, 0.5 mmol), phen (300 mg, 1.5 mmol), and water (10 mL) was placed in a 23-ml Teflon reactor and kept under autogenous pressure at 180 °C for 3 d. Then the mixture was cooled to room temperature at a rate of 10 °C h⁻¹, and colorless crystals of **3** were obtained (yield: 302 mg, 64% based on Cd). C, H, N analysis calcd (%) for C₆₀H₅₂Cd₃N₆O₁₄: C 50.80, H 3.70, N 5.93; found: C 50.45, H 3.44, N, 6.38.

Received: May 24, 2004

Keywords: cadmium · hydrothermal synthesis · luminescence · polymers · supramolecular chemistry

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- [12] Crystal data for **1** ($\text{C}_{40}\text{H}_{26}\text{CdN}_4\text{O}_4$): $M_r = 739.05$, tetragonal, space group $P4(3)$, $a = b = 11.1568(16)$, $c = 24.461(5)$ Å, $V = 3044.7(9)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.612$ mg m⁻³, Flack parameter = 0.028(16), final $R1 = 0.0267$ for 6819 independent reflections [$I > 2\sigma(I)$]. Crystal data for **2** ($\text{C}_{68}\text{H}_{46}\text{Cd}_3\text{N}_6\text{O}_{14}$): $M_r = 1508.31$, monoclinic, space group $P2_1/c$, $a = 16.776(3)$, $b = 10.141(2)$, $c = 17.559(4)$ Å, $\beta = 97.11(3)^\circ$, $V = 2964.2(10)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.690$ mg m⁻³, final $R1 = 0.0670$ for 6666 independent reflections [$I > 2\sigma(I)$]. Crystal data for **3** ($\text{C}_{60}\text{H}_{52}\text{Cd}_3\text{N}_6\text{O}_{14}$): $M_r = 1418.28$, triclinic, space group $P\bar{1}$, $a = 13.214(3)$, $b = 13.661(3)$, $c = 16.964(3)$ Å, $\alpha = 113.03(3)^\circ$, $\beta = 92.53(3)^\circ$, $\gamma = 90.27(3)^\circ$, $V = 2814.6(10)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.673$ mg m⁻³, final $R1 = 0.0613$ for 12603 independent reflections [$I > 2\sigma(I)$]. The data were collected at 298(2) K on a Rigaku R-Axis RAPID IP diffractometer with $\text{MoK}\alpha$ monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined using Fourier techniques. CCDC 239159–239161 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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