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Simple layered or complex self-penetrated networks in cadmium homophthalate coordination polymers containing 1,3-bis(4-pyridyl)propane

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ABSTRACT

Hydrothermal reaction of cadmium salts with homophthalic acid (H₂hmph) and 1,3-bis(4-pyridyl)propane (dpp) afforded coordination polymers whose topologies are determined by the absence or presence of any unligated counteranions. $[Cd(hmph)(dpp)]_n$ (1) has a zig-zag (4,4) layer topology with simple *AAA* stacking. ${[Cd_6(hmph)_4(dpp)_{11}(H_2O)_4]}$ (ClO₄)₄·4H₂O}_{*n*} (2) has a complicated, unprecedented tetranodal self-penetrated cationic three-dimensional net built from the linkage of 5-fold interpenetrated 3-connected 4.14² cds-a topology $[Cd_6(H_2O)_4(dpp)_{11}]_n^{12n+}$ subnets by bridging and exotridentate hmph ligands. Luminescent properties of these materials are also discussed.

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1. Introduction

Investigations into crystalline metal-organic aromatic dicarboxylate solids remain intensely active because of their significant potential as gas storage substrates [1], selective small-molecule absorbents [2], ion-exchange substrates [3], heterogeneous catalysts [4], and in optical devices [5]. The architectural appeal of the underlying molecular topologies also drives basic research in this area [6]. Divalent transition metal cations have a variety of coordination geometry preferences, which in turn can influence the binding and bridging modes of the aromatic carboxylate functional groups [7]. Even with an identical ligand set, judicious alteration of precursor [8] or synthesis temperature [9] or pH [10] can instill significant structural diversity, because of changing supramolecular conditions during self-assembly. Sensitivity to supramolecular environment is especially prevalent in coordination polymers based on closed-shell d^{10} ions such as divalent zinc or cadmium [11], which lack any crystal field driven geometric preferences. The presence of occluded counteranions can alter the overall structural framework of crystalline coordination polymers with similar ligand sets, through the imposition of a different supramolecular environment [12].

Interpenetration of distinct coordination polymer networks is a quite commonly encountered phenomenon [13]. In contrast, self-penetrated networks, which possesses tethering ligands that pen-

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etrate through the shortest circuits between metal atom or multiexodentate ligand nodes, are far more rarely observed in these systems [14–20]. Recent research has uncovered a few approaches that can generate self-penetrated networks, although their deliberate design remains an elusive goal. High nodal connectivity can provide multiple points of connection that can establish both simple and complicated self-penetrated networks, for example in the 6-connected 4⁸6⁶8 **rob** network in {[Cu₂(glutarate)₂(4,4'-bipyridine)] $3H_2O_{n}$ [14] and the cluster-based 8-connected $4^{24}5.6^3$ ilc network seen in $[Zn_5(\mu_3-OH)_2(terephthalate)_4(1,10-phenanthro \lim_{n \to \infty} [15]$. Self-penetrated coordination polymer networks can also be built up through the direct pillaring of a system of interpenetrated 3-D subnets. For instance, {[Cd(pht)(4,4'-dipyridylamine) (H_2O)]·4H₂O}_n has a unique 4-connected 3-D self-penetrated 7⁴8² yyz net formed from the phthalate linkage of 3-fold interpenetrated 12³ twt networks [16]. Conformationally flexible tethering ligands have proven useful in the construction of intriguing selfpenetrated networks, including that in the layered coordination polymer { $[Cu(N,N'-bis(4-pyridyl)suberamide)_2 (H_2O)_2](SO_4) \cdot H_2O \cdot$ $2EtOH_{n}$, whose very long tethering dipyridyl ligands intertwine with each other within the grid apertures [17].

In this contribution, we outline our investigations into a cadmium homophthalate (hmph) coordination polymer system with the very flexible 1,3-bis(4-pyridyl)propane (dpp) dipodal nitrogen-base ligand. Herein we discuss the synthesis, crystal structures, and luminescent properties of $[Cd(hmph)(dpp)]_n$ (1) and ${[Cd_6(hmph)_4(dpp)_{11}(H_2O)_4](ClO_4)_4 \cdot 4H_2O}_n$ (2), with the latter manifesting a complicated multi-nodal self-penetrated net based on the interlocking of rarely encountered 3-connected



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| Table 1 | | |
|---------------------------------------|-----|------|
| Crystal and structure refinement data | for | 1-2. |

| Data | 1 | 2 |
|--|--|--|
| Empirical formula | C ₂₂ H ₂₀ CdN ₂ O ₄ | $C_{179}H_{194}Cl_4Cd_6N_{22}O_{40}$ |
| Formula weight | 488.80 | 4109.77 |
| Crystal system | monoclinic | monoclinic |
| Space group ^a | $P2_1/c$ | C2/c |
| a (Å) | 10.8890(6) | 54.473(6) |
| b (Å) | 13.5368(8) | 11.9715(13) |
| <i>c</i> (Å) | 14.2736(8) | 27.928(3) |
| β (°) | 107.320(1) | 100.890(1) |
| V (Å ³) | 2008.6(2) | 17 885(3) |
| Ζ | 4 | 4 |
| D_{calc} (g cm ⁻³) | 1.616 | 1.524 |
| μ (mm ⁻¹) | 1.118 | 0.843 |
| Minimum/maximum transmission | 0.7455/0.8538 | 0.8169/0.9167 |
| hkl ranges | $-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 14$, $-17 \leqslant l \leqslant 17$ | $-65 \leqslant h \leqslant 65, -14 \leqslant k \leqslant 14, -33 \leqslant l \leqslant 33$ |
| Total reflections | 12 245 | 127 108 |
| Unique reflections | 3683 | 16 417 |
| R _{int} | 0.0196 | 0.1176 |
| Parameters/restraints | 262/0 | 1191/9 |
| R_1^a (all data) | 0.0310 | 0.1080 |
| $R_1^a [I > 2\sigma(I)]$ | 0.0279 | 0.0513 |
| wR_2^{b} (all data) | 0.0740 | 0.1235 |
| $wR_2^b [I > 2\sigma(I)]$ | 0.0717 | 0.0995 |
| Maximum/minimum residual (e Å ³) | 1.060/-0.502 | 0.837/-0.724 |
| Goodness-of-fit (GOF) on F^2 | 1.058 | 1.027 |

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[wF_0^2]^2\}^{1/2}.$



Fig. 1. Coordination environment of 1. The numbering scheme is the same as in Table 2.

interpenetrated networks. Oxoanion occlusion, coordination geometry preferences, and ligand conformational flexibility play a crucial cooperative structure-directing role in this system.

2. Experimental

2.1. General considerations

Cadmium salts and homophthalic acid were obtained from Aldrich. 1,3-bis(4-Pyridyl)propane was purchased from TCI America. Water was deionized above 3 M Ω -cm in-house. IR spectra were recorded on a Perkin–Elmer Spectrum One DRIFT instrument on powdered samples. Elemental analysis was carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. The luminescence spectra were obtained with a Hitachi F-4500 Fluorescence Spectrometer on solid crystalline samples anchored to quartz microscope slides with Rexon Corporation RX-22P ultraviolettransparent epoxy adhesive.

2.2. Preparation of $[Cd(hmph)(dpp)]_n$ (1)

 $CdSO_4 \cdot 8H_2O$ (64 mg, 0.18 mmol), dpp (73 mg, 0.37 mmol) and homophthalic acid (32 mg, 0.18 mmol) were placed into 5 mL distilled H₂O in a 15 mL screw-cap vial. The vial was sealed as tightly

| Table 2 |
|--|
| Selected bond distance (Å) and angle (°) data for 1 . |

| Cd1-04 ^{#1} | 2.248(3) | N1-Cd1-N2 ^{#2} | 88.05(8) |
|--|------------|--|------------|
| Cd1-N1 | 2.294(2) | 02-Cd1-N2 ^{#2} | 88.34(9) |
| Cd1-02 | 2.295(2) | 04 ^{#1} -Cd1-01 | 96.50(8) |
| Cd1-N2 ^{#2} | 2.307(2) | N1-Cd1-O1 | 89.29(8) |
| Cd1-01 | 2.412(2) | 02-Cd1-01 | 54.25(7) |
| Cd1-03 ^{#1} | 2.457(2) | N2 ^{#2} -Cd1-O1 | 127.11(8) |
| | | 04 ^{#1} -Cd1-03 ^{#1} | 54.65(7) |
| 04 ^{#1} -Cd1-N1 | 120.35(10) | N1-Cd1-O3 ^{#1} | 93.33(8) |
| 04 ^{#1} -Cd1-02 | 100.79(12) | 02-Cd1-03 ^{#1} | 137.47(10) |
| N1-Cd1-O2 | 128.50(10) | N2 ^{#2} -Cd1-O3 ^{#1} | 85.45(8) |
| 04 ^{#1} -Cd1-N2 ^{#2} | 129.39(8) | 01-Cd1-03 ^{#1} | 147.42(8) |
| | | | |

Symmetry equivalent positions: #1 x, -y + 1/2, z + 1/2; #2 -x + 2, y + 1/2, -z + 1/2.

as possible by hand and heated at 80 °C in an oil bath for 48 h. It was then withdrawn from the oil bath and allowed to air cool to 25 °C. Colorless blocks of **1** (49 mg, 56% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{22}H_{20}CdN_2O_4$ **1**: C, 54.06; H, 4.12; N, 5.73. Found: C, 53.87; H, 3.87; N, 5.39%. IR (cm⁻¹): 3253 w, 3058 w, 2924 w, 2871 w, 1699 w, 1611 w, 1563 s, 1503 w, 1467 w, 1449 w, 1426 w, 1396 s, 1273 w, 1224 s, 1170 w, 1149 w, 1084 w, 1067 w, 1016 s, 940 w, 847 w, 818 w, 806 w, 747 w, 712 w, 712 w, 672 w.

2.3. Preparation of $\{ [Cd_6(hmph)_4(dpp)_{11}(H_2O)_4](ClO_4)_4 \cdot 4H_2O \}_n$ (2)

The procedure for the synthesis of **1** was followed, with the exception of the use of $Cd(ClO_4)_2 \cdot 6H_2O$ (75 mg, 0.18 mmol) as the metal salt. Colorless blocks of **2** (49 mg, 40% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{179}H_{194}Cl_4Cd_6N_{22}O_{40}$ **2**: C, 52.49; H, 4.43; N, 7.52. Found: C, 52.76; H, 4.10; N, 7.73%. IR (cm⁻¹): 3220 w br, 3063 w, 2940 w, 2862 w, 1606 m, 1586 w, 1571 m, 1550 s, 1502 w, 1425 m, 1385 s, 1297 w, 1224 m, 1084 vs, 1064 s, 1013 m, 942 w, 930 w, 865 w, 845 w, 815 m, 804 m, 791 w, 767 w, 735 m, 724 m, 683 w, 665 w.

3. X-ray crystallography

Single crystal reflection data for **1–2** were collected at 173 K using a Bruker-AXS Apex II CCD instrument. Reflection data was acquired using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data was integrated via SAINT [21]. Lorentz

and polarization effect and absorption corrections were applied with sADABS [22]. The structures were solved using direct methods and refined on F^2 using SHELXTL [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. Where possible, hydrogen atoms belonging to water molecules were found by Fourier difference map and refined with isotropic thermal displacement parameters. Disorder within the perchlorate ions of **2** was modeled successfully using partial occupancies. Relevant crystallographic data for **1–2** are listed in Table 1.

4. Results and discussion

4.1. Synthesis and spectral characterization

Compounds **1–2** were prepared by the hydrothermal reaction of the appropriate cadmium salt, homophthalic acid, and dpp. The infrared spectra of all of the compounds were consistent with their crystal structures. Weak, highly broadened features above ~3200 cm⁻¹ in the spectrum of **2** indicate the presence of the bound and/or unligated water molecules. Bands between 2800 and 3100 cm⁻¹ in both spectra represent C–H stretching modes. Asymmetric and symmetric C–O stretching modes of the hmph ligands are present as broadened, strong bands at 1563 and 1396 cm⁻¹ (**1**), and 1550 and 1385 cm⁻¹ (**2**). Medium intensity bands in the range of ~1600 to ~1200 cm⁻¹ are caused by stretching modes of the pyridyl rings of the dpp ligands and the aromatic rings of the hmph ligands [24]. Unligated perchlorate ions in **2** are marked by the very strong band at 1084 cm⁻¹. Spectral features



Fig. 2. (a) $[Cd(hmph)]_n$ chain motif in **1**. (b) $[Cd(hmph)(dpp)]_n$ (4,4) grid layer in **1**.

corresponding to aromatic ring puckering were observed in the region between 600 and 820 cm⁻¹.

4.2. Structural description of $[Cd(hmph)(dpp)]_n$ (1)

Compound **1** contains a small asymmetric unit containing one cadmium atom, one hmph ligand, and one dpp ligand (Fig. 1), with a { CdN_2O_4 } distorted octahedral coordination environment. Chelating carboxylate groups from two hmph ligands fill axial and equatorial coordination sites, while the two remaining *cis* positions are occupied by dpp pyridyl donors. Bond lengths and angles within the coordination sphere are given in Table 2.

The hmph ligands connect cadmium atoms into $[Cd(hmph)]_n$ chain motifs (Fig. 2a), with a bis(chelating) μ_2 - κ^4 -O,O':O'',O''' binding mode. Along the chains, the Cd···Cd internuclear through-ligand distance is 7.141 Å. Individual $[Cd(hmph)]_n$ chains are strutted by *anti–anti* conformation dpp tethers (torsion angles = 175.6° and 178.2°) into $[Cd(hmph)(dpp)]_n$ coordination polymer 4-connected (4,4) grid layers (Fig. 2b). The through-ligand Cd···Cd distance across the splayed open dpp tethers is 13.663 Å. Because of the *cis* orientation of the pyridyl donors at each cadmium atom, a sawtooth grid morphology is adopted. The peak-to-peak "wavelength" of the grid pattern is 13.537 Å. Two subtly different types of grid window are evident in the layers in **1**, brack-eted by "concave" and "convex" pairs of dpp ligands, with Cd···Cd through-space distances of 14.72 × 16.08 or 14.50 × 16.28 Å.

Adjacent $[Cd(hmph)(dpp)]_n$ coordination polymer layers stack along the *a* crystal direction, with hmph phenyl rings interdigitating from above and below into apertures within a single grid (Fig. S1). Crystal packing forces and non-classical C-H···O interactions (C···O distance = 3.167(4) Å) between dpp trimethylene tethers and hmph carboxylate groups provide the supramolecular impetus for the layer aggregation. The rectangular grid structure of **1** differs from that of the few reported cadmium homophthalate coordination polymers. {[Cd(hmph)(4,4'-dipyridylamine)]·H₂O}_n possesses interdigitated herringbone (6,3) grid layers with an *ABAB* stacking pattern [25], while [Cd(hmph)(1,10-phenanthroline)]_n and [Cd(hmph)(2,2'-bipyridine)]_n are simple 1-D chain polymers [26].

4.3. Structural description of ${[Cd_6(hmph)_4(dpp)_{11}(H_2O)_4](ClO_4)_4 \cdot 4H_2O]_n}$ (2)

The very large asymmetric unit of compound **2** contains three divalent cadmium atoms, two hmph ligands, five full dpp ligands, another dpp ligand whose central methylene carbon atom is sited on a crystallographic 2-fold rotation axis, two aqua ligands, two unligated perchlorate anions, and two water molecules of crystallization (Fig. 3). To aid in the discussion of this complex structure, crystallographically distinct hmph and dpp ligands are named as follows: hmph-A, O1-O4; hmph-B, O5-O8; dpp-A, N1-N2; dpp-B, N3, situated across the 2-fold axis; dpp-C, N5-N6; dpp-D, N7-N8; dpp-E, N9-N10; dpp-F, N11-N12. The first cadmium atom (Cd1) has a nearly ideal {CdN₄O₂} octahedral coordination environment, with oxygen donor atoms from acetate carboxylates of hmph-A and hmph-B in trans axial positions. In the equatorial positions at Cd1 are pyridyl nitrogen donor atoms from dpp-A, dpp-C, dpp-D, and dpp-E. Both Cd2 and Cd3 have distorted {CdN₃O₃} octahedral coordination geometries. Nitrogen donors from dpp-B and dpp-D are located in the axial positions at Cd2,



Fig. 3. Coordination environments of 2. The numbering scheme is the same as in Table 3.

| Table 3 | | | | | | | |
|------------------------|-----|-------|-------|-----|------|-----|---|
| Selected bond distance | (Å) |) and | angle | (°) | data | for | 2 |

| Cd1-07 | 2.281(4) | N9-Cd1-N6 ^{#3} | 170.14(17) |
|--|------------|--|------------|
| Cd1-03 | 2.312(4) | N2-Cd1-N6 ^{#3} | 86.46(16) |
| Cd1-N8 ^{#1} | 2.339(5) | 01-Cd2-06#4 | 171.56(16) |
| Cd1-N9 | 2.348(5) | 01-Cd2-N3 | 87.62(16) |
| Cd1-N2 ^{#2} | 2.386(5) | 06#4-Cd2-N3 | 87.74(16) |
| Cd1-N6 ^{#3} | 2.391(4) | 01-Cd2-N7 | 100.28(17) |
| Cd2-01 | 2.239(4) | 06 ^{#4} -Cd2-N7 | 83.88(17) |
| Cd2-06 ^{#4} | 2.318(4) | N3-Cd2-N7 | 171.00(18) |
| Cd2-N3 | 2.381(5) | 01-Cd2-N5 | 87.49(17) |
| Cd2-N7 | 2.402(5) | 06#4-Cd2-N5 | 85.08(16) |
| Cd2-N5 | 2.408(5) | N3-Cd2-N5 | 84.88(17) |
| Cd2-05#4 | 2.429(4) | N7-Cd2-N5 | 91.11(17) |
| Cd3-04 | 2.262(4) | 01-Cd2-05 ^{#4} | 132.05(17) |
| Cd3-09 | 2.280(4) | 06 ^{#4} -Cd2-05 ^{#4} | 55.22(15) |
| Cd3-N1 | 2.344(5) | N3-Cd2-O5 ^{#4} | 92.26(16) |
| Cd3-N11 | 2.346(5) | N7-Cd2-O5 ^{#4} | 85.67(15) |
| Cd3-N12 ^{#5} | 2.365(5) | N5-Cd2-O5#4 | 140.29(16) |
| Cd3-010 | 2.371(4) | 04-Cd3-09 | 89.93(15) |
| | | 04-Cd3-N1 | 96.63(16) |
| 07-Cd1-03 | 172.95(14) | 09-Cd3-N1 | 91.31(19) |
| 07-Cd1-N8 ^{#1} | 90.36(16) | 04-Cd3-N11 | 89.56(15) |
| O3-Cd1-N8 ^{#1} | 96.68(16) | 09-Cd3-N11 | 174.90(18) |
| 07-Cd1-N9 | 88.07(15) | N1-Cd3-N11 | 93.79(17) |
| O3-Cd1-N9 | 91.43(15) | O4-Cd3-N12 ^{#5} | 94.64(16) |
| N8 ^{#1} -Cd1-N9 | 96.65(18) | O9-Cd3-N12 ^{#5} | 92.22(19) |
| 07-Cd1-N2 ^{#2} | 84.03(15) | N1-Cd3-N12 ^{#5} | 168.20(17) |
| 03-Cd1-N2 ^{#2} | 88.93(15) | N11-Cd3-N12 ^{#5} | 82.77(18) |
| N8 ^{#1} -Cd1-N2 ^{#2} | 174.14(17) | 04-Cd3-010 | 174.21(15) |
| N9-Cd1-N2 ^{#2} | 84.89(16) | 09-Cd3-010 | 84.28(15) |
| 07-Cd1-N6 ^{#3} | 95.72(15) | N1-Cd3-O10 | 83.65(16) |
| O3-Cd1-N6 ^{#3} | 83.69(15) | N11-Cd3-O10 | 96.19(15) |
| N8 ^{#1} -Cd1-N6 ^{#3} | 92.43(17) | N12 ^{#5} -Cd3-O10 | 85.50(16) |
| | | | |

Symmetry equivalent positions: #1 x, -y + 2, z + 1/2; #2 x, -y + 1, z - 1/2; #3 -x, y + 1, -z + 1/2; #4 x, y - 1, z; #5 -x + 1/2, -y + 3/2, -z + 1.

with the equatorial plane filled by a donor from dpp-C, an oxygen atom from a monodentate carboxylate group from hmph-A, and a chelating carboxylate from hmph-B. At Cd3, axial sites are taken up by nitrogen donors from dpp-A and dpp-F, while an oxygen atom from a hmph-A acetate group, two aqua ligands, and a pyridyl donor from another dpp-F ligand are located in the equatorial positions. At both Cd2 and Cd3, the nitrogen donors lie in a meridional orientation. Bond lengths and angles within the various coordination environments in **2** are listed in Table 3.

With the exception of dpp-E, which binds to Cd1 as a pendant monodentate ligand with a curled gauche-anti conformation (torsion angles = $59.5^{\circ}/168.4^{\circ}$), all other dpp ligands in **2** serve as dipodal tethers, linking cadmium atoms into complicated $[Cd_6(H_2O)_4(dpp)_{11}]_n^{12n+}$ subnets, which are 5-fold interpenetrated (Fig. S2). The anti-anti conformation dpp-A ligands (torsion angles = 172.5°/174.3°) join Cd1 and Cd3 with a metal-metal internuclear distance of 12.839 Å. while *anti–anti* conformation dpp-D ligands (torsion angles = $177.3^{\circ}/174.7^{\circ}$) connect Cd1 and Cd2 atoms at an inter-nuclear distance of 13.174 Å. Cd1 and Cd2 atoms are also connected by twisted gauche-anti conformation dpp-C ligands (torsion angles = $72.0^{\circ}/178.2^{\circ}$), at a slightly shorter internuclear distance of 12.742 Å. Neighboring Cd3 atoms are linked by pairs of gauche-anti conformation dpp-F ligands (torsion angles = $40.9^{\circ}/175.3^{\circ}$), which provide a Cd···Cd distance of 12.646 Å. Pairs of Cd2 atoms are further conjoined by gauchegauche dpp-B ligands, whose torsion angles are restricted by crystallographic symmetry to be identical (47.7°). Among all the dpp-bridged contacts in 2, these latter interactions are the shortest (9.117 Å) due to the very curled dpp-B conformation. The resulting $[Cd_6(H_2O)_4(dpp)_{11}]_n^{12n+}$ subnet has prodigious incipient voids, measuring $\sim 51 \text{ Å} \times 57 \text{ Å}$ from closest Cd···Cd contacts, which allow the mutual 5-fold interpenetration of identical subnets.

In order to understand the underlying topology of these cationic nets, the Cd1 atoms are considered 3-connected nodes, linked by dpp ligands to one Cd3 atom and two Cd2 atoms, and the Cd2 atoms are also treated as 3-connected nodes, linked by dpp ligands to two Cd1 atoms and another Cd2 atom. Each Cd3 atom is only 2-connected, joined by a single tether (dpp-A)



to Cd1 atom, and by a pair of dpp-F ligands to one other Cd3 atom. Therefore the Cd3 atoms should just be considered linkers, instead of connecting nodes, within the $[Cd_6(H_2O)_4(dpp)_{11}]_n^{12n+}$ subnet. From this perspective, the resulting 3-connected binodal net has a 4.14^2 **cds-a** topology (Fig. 4), with a Vertex symbol of $[4.14_4, 14_4][4.14_8, 14_8]$ as calculated by TOPOS [27]. The same 4.14^2 point symbol can be invoked for the 5-fold interpenetrated

3-connected phase {[Ag₆Cl(3-amino-1,2,4-triazolate)₄]OH·6H₂O}_n [28], which is based on face-sharing Ag₈(μ_8 -Cl) cluster nodes, but its **dia-f** net is uninodal and has a Vertex symbol of [4.14₁₂.14₁₂]. To date, there are only two known examples of the 3-connected **cds-a** net in chemical systems, [Cu₂Co(1,3,5-tris(pyrazol-l-ylmethyl)benzene)₂Cl₆(H₂O)₃]_n [29] and [Mn(ethylenediamine)₂Ga₂S₄]_n [30]. Neither of these cases exhibit any



Fig. 5. $[Cd_3(hmph)_2(H_2O)_2]_n$ chain motif in **2**.



Fig. 6. {[Cd₆(hmph)₄(dpp)₁₁(H₂O)₄](ClO₄)₄·4H₂O)_n 3-D network in 2. Perchlorate ions and water molecules occupy the extra-framework space.



Fig. 7. Schematic perspective of the 3,3,5,5-connected tetranodal self-penetrated net in **2**. The blue, purple, and magenta spheres represent Cd1, Cd2, and Cd3 atom nodes, respectively. The black spheres represent the hmph-A 3-connected ligand nodes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Table 4

| D−H···A | $d(H \cdot \cdot \cdot A)$ | ∠DHA | $d(D \cdots A)$ | Symmetry transformation for A |
|--------------------|----------------------------|--------|-----------------|-------------------------------|
| 01W-H1WA · · · 012 | 2.09(2) | 174(3) | 2.931(9) | -x + 1/2, -y + 1/2, -z + 1 |
| 01W–H1WB· · · 011 | 2.11 | 179.7 | 2.955(10) | |
| 09–H9A···02 | 1.94(3) | 162(6) | 2.767(6) | |
| O9–H9B· · · O8 | 1.97(4) | 147(6) | 2.720(6) | x, y - 1, z |
| 010-H10G···01W | 1.89(2) | 167(5) | 2.731(6) | |
| 010-H10H···08 | 1.89(2) | 163(5) | 2.716(6) | x, y - 1, z |

| Hydrogen bo | nding distance | (Å) and angle | (°) data for 2 . |
|-------------|----------------|---------------|-------------------------|

interpenetration, so the 5-fold interpenetration of **cds-a** subnets in **2** is unprecedented.

The 5-fold interpenetrated $[Cd_6(H_2O)_4(dpp)_{11}]_n^{12n+}$ subnets are then conjoined into a $[Cd_6(hmph)_4(H_2O)_4(dpp)_{11}]_n^{4n+}$ lattice by exotridentate hmph-A ligands with a μ_3 - κ^3 -O:O':O" binding mode and by hmph-B ligands with a chelating/monodentate μ_2 - κ^3 -O,O':O" binding mode. The hmph-A ligands connect Cd1, Cd2, and Cd3 atoms, with their acetate arms bridging Cd1 and Cd3 atoms, and their short carboxylate arms binding to Cd2 atoms in a monodentate fashion. Meanwhile the hmph-B ligands chelate via their acetate carboxylate groups to Cd2 atoms, while their short carboxylate arms act as monodentate donors to Cd1 atoms. The hmph ligands and cadmium atoms within the net of **2** form $[Cd_3(hmph)_2(H_2O)_2]_n$ chain motifs (Fig. 5). A self-penetrated network is therefore formed the covalent linkage of separate interpenetrated $[Cd_6(H_2O)_4$ $(dpp)_{11}]_n^{12n+}$ subnets through the hmph ligands (Fig. 6).

Topological analysis of this complicated $[Cd_6(hmph)_4 (H_2O)_4(dpp)_{11}]_n^{4n+}$ net was undertaken by treating the exotridentate hmph-A ligands as 3-connected nodes and the exobidentate hmph-B as simple linkers. In turn, the Cd1 atoms and Cd2 atoms now become 5-connected nodes because of a new connection to an hmph-A node and linkage through hmph-B. Instead of acting as linkers, Cd3 atoms now serve as 3-connected nodes because of the additional connection to an hmph-A ligand node. A schematic view of the resulting 3,3,5,5-connected tetranodal net is shown in Fig. 7 with dpp connections in blue and hmph connections in red. The Schläfli symbol for this self-penetrated network is $(7^{2}9)(7.10^{2})(3.4.5.7^{3}.8^{2}.9.10)(3^{2}4^{2}5.6.7^{3}8)$, with the individual symbols referring to the hmph-A, Cd3, Cd1, and Cd2 nodes, respectively. All dpp ligands with the exception of dpp-E and the monodentate dpp-B engage in self-penetration through shortest 8-membered, 9-membered, and 10-membered circuits within the network of 2. In one of the self-penetration mechanisms, the dpp-C ligands linking Cd1 and Cd2 atoms from two different 8-membered circuits penetrate through a third 8-membered circuit, while all three circuits are joined through hmph-B linkers. A close-up view of the mutual self-penetration of the 8-membered circuits is shown in Fig. S3. Full details of the topological analysis can be found in the Supplementary information.

Unligated perchlorate counteranions and water molecules occupy the tight solvent-accessible extra-framework space within the self-penetrated net, which comprises 13.2% of the unit cell volume according to PLATON [31]. Supramolecular aggregations of perchlorate ion pairs through water molecule dimers, or pairs of isolated water molecules, are formed via hydrogen bonding (Table 4).

4.4. Luminescent properties

Irradiation of crystalline samples of complexes **1** and **2** with ultraviolet light ($\lambda_{ex} = 375 \text{ nm}$) caused moderately intense blueviolet visible light emission with λ_{max} values of 449 and 443 nm, respectively (Fig. 8). These emission maxima correspond closely to those produced by the free homophthalic acid (445 nm) or dpp ligands (460 nm) under the same excitation wavelength. Thus,



Fig. 8. Emission spectra of 1 and 2.

by comparison with other d^{10} metal coordination polymers with aromatic ligands [32], the emissive behavior of **1** and **2** plausibly arises from ligand-centered π - π^* or π -n molecular orbital electronic transitions within the pyridyl rings of the dpp ligands and/ or the phenyl rings of the hmph ligands. The similarity in the emission profiles is likely caused by the presence of the same aromatic ligands, despite some differences in carboxylate binding mode.

5. Conclusions

Oxoanion occlusion in luminescent cadmium homophthalate coordination polymers with flexible dipyridylpropane coligands results in a switch from a layered grid network to a complicated self-penetrated framework. The conformational flexibility of the dpp trimethylene tethers allows self-assembly of cationic subnets with very large apertures in **2**, generating a simple 3-connected 5-fold interpenetrated **cds-a** network. Self-penetration is then achieved in **2** via bridging and exotridentate dicarboxylate ligands. The self-penetrated network of **2** shows pillaring of interpenetrated subnets and conformationally flexible ligands, two features in common with other reported self-penetrated networks. Although some approaches towards self-penetrated networks have been identified, their deliberate design is as yet an unrealized goal.

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Appendix A. Supplementary material

CCDC 811778 and 811777 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.029.

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