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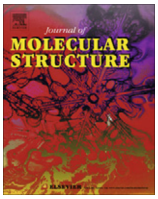

Luminescent cadmium phenylenedipropionate coordination polymers with long-spanning dipyridine ligands

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ABSTRACT

Hydrothermal synthesis has generated oxoanion-free divalent cadmium 1,4-phenylenedipropionate (phdp) coordination polymers containing either bis(4-pyridylmethyl)piperazine (bpmp) or bis(4-pyridylformyl)piperazine (bpfp) ligands. The coordination environment at cadmium appears to dictate the overall dimensionality of the resulting coordination polymer crystal structure. $\{[Cd(phdp)(bpfp)(H_2O)]\cdot 4H_2O\}_n$ (**1**) possesses pentagonal bipyramidal coordination at cadmium with *trans* pyridyl donors and displays a simple 2-D (4,4) grid network. $\{[Cd(phdp)(bpmp)]\cdot 5H_2O\}_n$ (**2**) exhibits distorted octahedral coordination with *cis* pyridyl donors, resulting in a 3-D 3-fold interpenetrated diamondoid network. Both **1** and **2** show visible-light luminescence upon ultraviolet excitation, with the emission maximum depending on the nature of the dipyridyl coligand.

1. Introduction

Coordination polymer design and characterization remains under intensive investigation because of the potentially industrially important applications of these phases [1], including gas storage [2], adsorption and separation [3], ion exchange [4], catalysis [5], fluorescence and sensing [6], and second harmonic generation [7]. Aromatic dicarboxylates such as terephthalate [8] or isophthalate [9] have proven very advantageous for the construction of divalent metal coordination polymers. These ligands provide both the structural rigidity and charge balance important for the self-assembly of crystalline extended networks. Metal coordination environment and carboxylate group binding mode can be tailored to provide access to a host of possible framework topologies [10]. For divalent zinc- and cadmium-containing coordination polymers, the absence of crystal field stabilization in the d^{10} electronic configuration allows the specific coordination environment to respond sensitively to the geometric and steric requirements of the dicarboxylate ligands [11].

Expansion of the scope of coordination polymer topologies has been made possible by the use of more conformationally flexible phenylenediacetate (phda) ligands [12–16]. A recently published family of divalent cobalt coordination polymers with phda and long-spanning bis(4-pyridylmethyl)piperazine (bpmp, Scheme 1) ligands reveals an important topological dependence imparted by the carboxylate pendant arm disposition [15]. $\{[Co(1,4\text{-}phda)(4\text{-}bpmp)(H_2O)_2]\cdot 2H_2O\}_n$ exhibits a very common 4-connected 2-D grid topology, while its *ortho*-acetate analog $\{[Co(1,2\text{-}phda)(4\text{-}bpmp)_{1.5}(H_2O)](H_24\text{-}bpmp)_{0.5}(ClO_4)\cdot 12H_2O\}_n$ possesses a unique 5-connected layered framework with an Archimedean topology based on rectangular and triangular circuits. Topological variances are also seen across a series of cadmium phda coordination polymers containing the seldom used [16–19] neutral tethering ligand bis(4-pyridylformyl)piperazine (bpfp, Scheme 1), structurally similar to bpmp, but possessing hydrogen bonding accepting ability at its two amide groups. $[Cd(1,2\text{-}Hphda)_2(bpfp)]_n$ shows 2-D polymeric layers with embedded cadmium carboxylate ribbon motifs, $\{[Cd(1,3\text{-}phda)(bpfp)(H_2O)]_2\}_n$ has 2-fold parallel interpenetrated (4,4) grids, and $\{[Cd(1,4\text{-}phda)(bpfp)(H_2O)]\}_n$ manifests acentric 1-D chains with an uncommon 4-connected 3^34^25 topology [16].

In this follow-up contribution we present the results of our attempts to prepare analogous phases with the longer and more conformationally flexible 1,4-phenylenedipropionate (phdp, Scheme 1) ligand, with the synthesis and single-crystal X-ray structures of the $\{[Cd(phdp)(bpfp)(H_2O)]\cdot 4H_2O\}_n$ (**1**) and $\{[Cd(phdp)(bpmp)]\cdot 5H_2O\}_n$ (**2**). The coordination environment at cadmium appears to dictate the overall dimensionality of the resulting coordination polymer crystal structure in this system, resulting in a switch from a 2-D network in **1** to a 3-D framework in **2**. Luminescent properties of these new materials are also reported herein.

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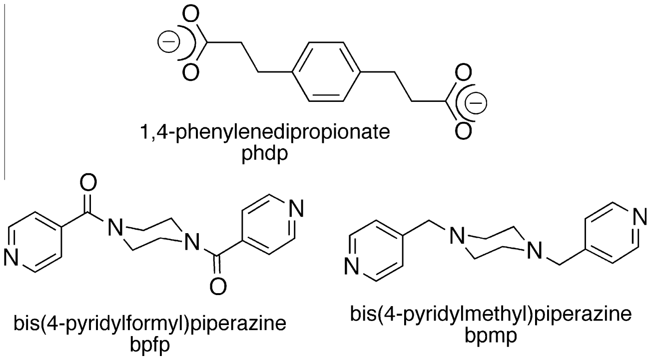

Scheme 1. Ligands used in this study.

2. Experimental

2.1. General considerations

Cadmium salts and 1,4-phenylenedipropionic acid were obtained commercially from Aldrich. Bis(4-pyridylformyl)piperazine (bpfp) [17] and bis(4-pyridylmethyl)piperazine (bpmp) [20] were prepared via modification of published procedures. Pyridine was refluxed with CaH_2 under flowing N_2 and distilled immediately prior to use. Water was deionized above 3 MΩ cm in-house. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were recorded on powdered samples on a Perkin Elmer Spectrum One instrument. 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 ultraviolet-transparent epoxy adhesive.

2.2. Preparation of $\{[Cd(phdp)(bpfp)(H_2O)]\cdot 4H_2O\}_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (30 mg, 0.097 mmol), bpfp (29 mg, 0.097 mmol), 1,4-phenylenedipropionic acid (22 mg, 0.097 mmol), 1 mL of 1.0 M NaOH, and 5 mL deionized water were placed into a 15 mL screw-cap vial. The vial was sealed and heated in an oil bath at 90 °C for 48 h, and then cooled slowly to 25 °C. Colorless blocks of **1** (27 mg, 39% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{28}H_{38}CdN_4O_{11}$ **1**: C, 46.77; H, 5.33; N, 7.79% Found: C, 46.11; H, 4.97; N, 7.29%. IR (cm^{-1}): 3300 (w, br), 2995 (m), 1638 (s), 1603 (s), 1557 (m), 1471 (m), 1439 (m), 1417 (w), 1366 (m), 1324 (w), 1286 (s), 1262 (s), 1218 (m), 1164 (m), 1130 (w), 1079 (w), 1052 (m), 1026 (m), 1005 (s), 965 (m), 906 (m), 872 (m), 831 (w), 759 (w), 670 (w).

2.3. Preparation of $\{[Cd(phdp)(bpmp)]\cdot 5H_2O\}_n$ (**2**)

$CdCl_2\cdot 6H_2O$ (52 mg, 0.18 mmol), bpmp (99 mg, 0.37 mmol), 1,4-phenylenedipropionic acid (44 mg, 0.18 mmol), and 5 mL deionized water were placed into a 15 mL screw-cap vial. The vial was sealed and heated in an oil bath at 80 °C for 72 h, and then cooled slowly to 25 °C. Colorless blocks of **2** (45 mg, 36% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{28}H_{42}CdN_4O_9$ **2**: C, 48.66; H, 6.13; N, 8.11% Found: C, 48.34; H, 5.72; N, 7.90%. IR (cm^{-1}): 3245 (w, br), 2844 (w), 1638 (w), 1617 (w), 1539 (s), 1430 (s), 1408 (s), 1359 (m), 1339 (m), 1309 (w), 1270 (w), 1229 (w), 1145 (w), 1120 (w), 1069 (w), 1021 (w), 1010 (w), 956 (w), 941 (w), 892 (w), 854 (m), 838 (m), 802 (s), 705 (s).

3. X-ray crystallography

Single-crystal diffraction data for **1** and **2** were collected using a Bruker-AXS Apex2 CCD instrument. Diffraction data was acquired using graphite–monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were integrated with SAINT [21]. Lorentz and polarization effect and empirical 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 with anisotropic thermal parameters. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined with isotropic thermal parameters using a riding model. Hydrogen atoms bound to water molecules were located by Fourier difference map and restrained at fixed positions. The crystal of **1** was non-merohedrally twinned, and the twin law was obtained using CELLNOW [24]. Only reflections from the major twin component were used during refinement. Although some data completeness was lost because of the use of the twinning routine, refinement statistics for **1** were amply satisfactory. Relevant crystallographic data for **1** and **2** are listed in Table 1.

4. Results and discussion

4.1. Synthesis and spectral characterization

Hydrothermal reaction of a cadmium salt, 1,4-phenylenedipropionic acid, and the requisite dipyridine ligand generated crystalline samples of **1** and **2**. Their infrared spectra were consistent with their single crystal structures. A strong band at 1638 cm^{-1}

Table 1
Crystal and structure refinement data for **1** and **2**.

Compound	1	2
Empirical formula	$C_{28}H_{38}CdN_4O_{11}$	$C_{28}H_{42}CdN_4O_9$
Formula weight	719.02	691.05
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.430(4)	11.3356(15)
b (Å)	11.398(3)	12.1513(16)
c (Å)	15.385(4)	12.8611(17)
α (°)	75.768(4)	87.543(1)
β (°)	82.849(4)	68.761(1)
γ (°)	73.921(4)	71.799(1)
V (Å^3)	1537.5(9)	1563.6(4)
Z	2	2
D_{calc} (g cm^{-3})	1.553	1.468
μ (mm^{-1})	0.776	0.755
Min./max. trans.	0.8244/0.9321	0.6664/0.7452
hkl ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 18$	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 15$
Total reflections	39,929	23,290
Unique reflections	5537	5744
R(int)	0.0653	0.0285
Parameters/restraints	430/12	409/15
R_1 (all data)[a]	0.0598	0.0270
R_1 ($I > 2\sigma(I)$)[a]	0.0498	0.0246
wR_2 (all data)[b]	0.1291	0.0603
wR_2 ($I > 2\sigma(I)$)[b]	0.1252	0.0587
Max./min. residual (e^-/Å^3)	1.210/−1.285	1.213/−0.750
G.O.F.	1.206	1.032

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$.