

Research paper

Control of topology in luminescent nitrobenzene-detecting cadmium camphorate polymers via hydrogen-bonding capable dipyridyl ligands

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ABSTRACT

Hydrothermal reaction of cadmium nitrate, *D*-camphoric acid (*D*-camH₂), and a hydrogen-bonding capable dipyridyl ligand resulted in coordination polymers whose dimensionalities and topologies depend critically on the pyridyl nitrogen donor disposition and tether length. The four new phases were characterized by single crystal X-ray diffraction; racemization of the camphorate ligands was observed in three cases. {[Cd(*DL*-cam)(hdin)]_n (**1**, hdin = *N,N'*-(hexane-1,6-diyl)diisonicotinamide) shows a 2D sawtooth (4,4) grid structure. [Cd₂(*D*-cam)₂(3-bpmp)(H₂O)₂]_n (**2**, 3-bpmp = bis(3-pyridylmethyl)piperazine) displays a 1D ladder coordination polymer structure with [Cd(*D*-cam)(H₂O)]_n uprights pillared by 3-bpmp rungs. The minor product [Cd₂(*DL*-cam)₂(3-bpmp)]_n (**3**) manifests a {Cd₂O₂} dimer-based 6-connected 3D 4¹²6³ **pcu** topology. [Cd₂(*DL*-cam)₂(4-bpmp)]_n (**4**, 4-bpmp = bis(4-pyridylmethyl)piperazine) also displays a dimer-based 6-connected 3D net, but with a 4⁴6¹⁰8 **mab** self-penetrated net due to cross-pillaring of the pyridyl ligands. Thermal and luminescent properties of were investigated; compounds **2** and **4** showed very good ability to detect nitrobenzene in ethanol suspension via luminescence quenching.

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1. Introduction

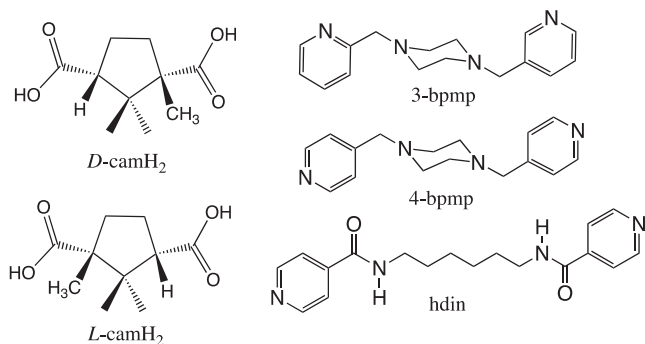
The synthesis, structural characterization, and physical and chemical property investigations of divalent metal coordination polymers remains an extremely fertile area of basic research in inorganic chemistry. This genre of crystalline solids has been shown to have applications in hydrogen storage [1], shape selective separation [2], ion exchange [3], heterogeneous catalysis [4], non-linear optics [5], explosives residue detection [6], drug delivery [7], and dye degradation [8]. By employing chiral ligands, the resulting coordination polymers have shown utility for enantioselective heterogeneous catalysis or separations [9]. Lin *et al.* reported a twofold interpenetrated cadmium coordination polymer formed from a chiral dipyridyl linker, that after post-synthetic modification with titanium isopropoxide, catalyzes the generation of chiral secondary alcohols from aromatic aldehydes [9a]. Rosseinsky *et al.* utilized *L*-aspartic acid to form the 3D chiral phase [Ni₂(*L*-aspartate)₂(bpy)]_n (bpy = 4,4'-bipyridine), which can perform separations of aliphatic diol enantiomers [9b].

The commercially available and inexpensive *D*-camphoric acid (*D*-camH₂, Scheme 1), obtained from the oxidation of naturally occurring camphor, has proven to be a most useful agent for

inducing chirality in divalent metal coordination polymers [10–13]. Bu *et al.* have reported the isolation and structural characterization of three different 3-D cadmium *D*-camphorate phases by varying the synthesis temperature in the absence any dipyridyl-type coligands [10]. Control of dimensionality has been reported by changing the divalent metal ion in the presence of the flexible coligand 1,3-di-4-pyridylpropane (dpp). [Ni(*D*-cam)(dpp)]_n displayed an uncommon chiral bilayer structure with 4²6³8 topology, while the cobalt derivative {[Co(*D*-cam)(dpp)]·H₂O}_n manifested a three-fold interpenetrated diamondoid net [11]. {[Cd(*D*-cam)(dpp)]·2H₂O}_n has an isostructural diamondoid topology as {[Co(*D*-cam)(dpp)]·H₂O}_n, but unlike it, undergoes a single crystal-to-single crystal structural shift upon thermal treatment due to subtle alterations in its helical subunits [12]. Using longer hydrogen-bonding capable dipyridylamide ligands with enhanced conformational flexibility afforded cobalt and cadmium camphorate coordination complexes with a wide diversity of structures and topologies [13]. {[Co₂(*DL*-cam)₂(bdn)]·2H₂O}_n (bdn = *N,N'*-(butane-1,4-diyl)dinicotinamide) possesses a {Co₂(OCO)₄} paddle-wheel dimer-based 6-connected 4¹²6³ **pcu** network. Its cadmium analog {[Cd₂(*D*-cam)₂(bdn)₂]·5H₂O}_n also shows a dimer-based structure but with an 8-connected 4²⁴6⁴ **bcu** network predicated on its larger metal ion radius. {[Co₂(*D*-cam)₂(pdn)]·2H₂O}_n (pdn = *N,N'*-(propane-1,3-diyl)dinicotinamide) displays a rarer self-penetrated 4⁴6⁸10 **mab** network in contrast to its bdn analog, with

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Scheme 1. The ligands used in this study.

retention of chirality. $\{[Cd_2(D\text{-cam})_2(\text{pdn})]\cdot H_2O\}_n$ also manifests a dimer-based structure with a unique 3,7-connected 3D network with $(3.5^2)(3^2 4^4 5^6 6^8 7)$ topology. $\{[Co_2(DL\text{-cam})_2(\text{pedn})]\cdot 2H_2O\}_n$ ($\text{pedn} = N,N'$ -(pentane-1,5-diyl)diisonicotinamide) shows a ligand-disordered structure consisting of discrete slabs of a 3D **pcu** network with some interleaved **hxl** (3,6) layers at random intervals [13].

In this study we have aimed to expand the scope of chiral cadmium *D*-camphorate coordination polymers by employing various hydrogen-bonding capable dipyriddy ligands with significant conformational degrees of freedom within their central regions, such as *N,N'*-(hexane-1,6-diyl)diisonicotinamide (hdn, Scheme 1), bis(3-pyridylmethyl)piperazine (3-bpmp, Scheme 1), and bis(4-pyridylmethyl)piperazine (4-bpmp, Scheme 1). While hdn has not been often used in coordination polymer chemistry to this point [14], the 3-bpmp and 4-bpmp ligands have successfully been employed to construct coordination polymers with diverse and often striking topologies [15–18]. $[Cd(\text{oba})(\text{hdn})]_n$ ($\text{oba} = \text{oxybisbenzoate}$) manifests a unique 4,6-connected 3D self-penetrated network with $\{4^2 6^2 7^2\}(4^2 6^8 7^2 8^3)$ topology, while $[Co_2(\text{oba})_2(\text{hdn})]_n$ exhibits a dimer-based 6-connected 3-fold interpenetrated **jsm** net with $5^{10} 6^4 8$ topology [14]. $[Co_3(\text{oba})_3(4\text{-bpmp})_2]_n$ showed a chiral 3D self-catenated structure with a unique 8-connected $4^4 5^{17} 6^7$ topology [15]. $\{[Zn_2(\text{Hpyro})_2(H_2O)_2(H_2\text{-}3\text{-bpmp})]\cdot H_2O\}_n$ ($\text{pyro} = \text{pyromellitate}$) possessed a rare 4,5-connected net with $(4^4 6^2)(4^4 6^6)$ **tcs** topology, while $\{[Zn_2(\text{Hpyro})_2(H_2\text{-}4\text{-bpmp})]\cdot 4H_2O\}_n$ showed a 3,4-connected binodal net with $(4.8^2)(4.8^2 10^3)$ self-penetrated topology [16]. We herein report the synthesis, single-crystal structures, thermal and luminescent properties, nitrobenzene detection capability of three new coordination polymers $[Cd(DL\text{-cam})(\text{hdn})]_n$ (**1**), $[Cd_2(D\text{-cam})_2(3\text{-bpmp})(H_2O)_2]_n$ (**2**), and $[Cd_2(DL\text{-cam})_2(4\text{-bpmp})]_n$ (**4**). We also report the single-crystal structure of the minor product $[Cd_2(DL\text{-cam})_2(3\text{-bpmp})]_n$ (**3**), which formed concomitantly during the synthesis of **2** but could not be isolated in phase-pure fashion.

2. Experimental section

2.1. General considerations

Cadmium nitrate and *D*-camphoric acid were commercially obtained. *N,N'*-(hexane-1,6-diyl)diisonicotinamide (hdn) was prepared by condensation of 1,6-hexanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine. The reaction mixture was quenched with water, and then the product was isolated via CH_2Cl_2 extraction and removal of solvent *in vacuo* [19]. The 3-bpmp and 4-bpmp ligands were prepared by literature procedures [20,21]. Water was deionized above $3M\Omega\text{-cm}$ in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. Thermogravimetric

analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ up to 600°C . 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 ultraviolet-transparent epoxy adhesive.

2.2. Preparation of $[Cd(D\text{-cam})(\text{hdn})]_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (113 mg, 0.37 mmol), *D*-camphoric acid (73 mg, 0.37 mmol), hdn (119 mg, 0.37 mmol), and 0.75 mL of a 1.0 M NaOH solution were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120°C for 48 h, and then was cooled slowly to 25°C . Colorless crystals of **1** (26 mg, 11% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal. Calc.* for $C_{28}H_{36}CdN_4O_6$ **1**: C, 52.79; H, 5.70; N, 8.80% Found: C, 52.84; H, 5.61; N, 8.69%. IR (cm^{-1}): 2962 (w), 1674(w), 1576(s), 1403(s), 1323(w), 1098(m), 1013(m), 801 (m), 698(m).

2.3. Preparation of $[Cd_2(D\text{-cam})_2(3\text{-bpmp})(H_2O)_2]_n$ (**2**) and $[Cd_2(DL\text{-cam})_2(3\text{-bpmp})]_n$ (**3**)

$Cd(NO_3)_2\cdot 4H_2O$ (226 mg, 0.73 mmol), *D*-camphoric acid (146 mg, 0.73 mmol), 3-bpmp (98 mg, 0.37 mmol), and 1.5 mL of a 1.0 M NaOH solution were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120°C for 48 h, and then was cooled slowly to 25°C . Colorless crystals of **2** (80 mg, 47% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. A few large block crystals of **3** were removed by manual separation. Running the reaction at 100°C resulted in phase-pure samples of **2**. *Anal. Calc.* for $C_{36}H_{48}Cd_2N_4O_8$ **2**: C, 48.60; H, 5.44; N, 6.30% Found: C, 48.68; H, 4.82; N, 6.19%. IR (cm^{-1}): 3000 (w, br), 1530(s), 1481(w), 1458(w), 1425(w), 1398 (m), 1366(m), 1305(w), 1291(w), 1121(w), 1060(w), 997(w), 924 (w), 835(m), 793(s), 758(m), 704(s).

2.4. Preparation of $[Cd_2(DL\text{-cam})_2(4\text{-bpmp})]_n$ (**4**)

$Cd(NO_3)_2\cdot 4H_2O$ (113 mg, 0.37 mmol), *D*-camphoric acid (73 mg, 0.37 mmol), 4-bpmp (98 mg, 0.37 mmol), and 0.75 mL of a 1.0 M NaOH solution were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120°C for 48 h, and then was cooled slowly to 25°C . Straw-colored crystals of **4** (46 mg, 28% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal. Calc.* for $C_{36}H_{48}Cd_2N_4O_8$ **4**: C, 48.60; H, 5.44; N, 6.30% Found: C, 48.76; H, 5.41; N, 6.34%. IR (cm^{-1}): 2961(w), 1578(s), 1396(s), 1363(m), 1326(m), 1093(m), 1013(m), 842(m), 801(s), 782(m), 698(m).

2.5. Nitrobenzene detection studies

Suspensions of 5 mg finely ground samples of coordination polymers **1**, **2**, and **4** were made in 5 mL ethanol in volumetric flasks, with immersion in an ultrasonic bath for 60 s to ensure an even dispersion. The fluorescence spectra in suspension were recorded with an excitation wavelength of 270 nm. Aliquots of a stock solution of nitrobenzene (1×10^{-4} M) in dimethyl sulfoxide were added sequentially to the ethanol suspensions of the coordination polymers in quartz cuvettes with sonication for 30 s after each addition. The emission spectra were then measured after each aliquot of analyte solution.

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