

Substituent-induced effects on dimensionality in cadmium isophthalate coordination polymers containing 3-pyridylisonicotinamide



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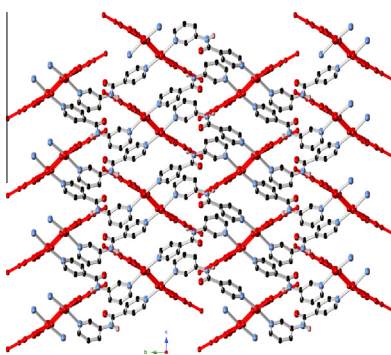
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HIGHLIGHTS

- Cadmium 5-substituted isophthalate coordination polymers.
- Hydrogen-bonding capable 3-pyridylisonicotinamide (3-pina) coligands.
- Dimensionality depends greatly on nature of isophthalate substituent.
- 1D chains with hydroxy and methoxy substituents, 3D net with methyl.
- Slightly different emission maxima on ultraviolet excitation.

GRAPHICAL ABSTRACT

Hydrothermal treatment of cadmium nitrate, a 5-substituted isophthalic acid, and 3-pyridylisonicotinamide (3-pina) resulted in three luminescent coordination polymers whose dimensionality depends greatly on the substituent. $[\text{Cd}(\text{mip})(3\text{-pina})]_n$ (pictured, mip = 5-methylisophthalate) has dimer-bearing $[\text{Cd}(\text{mip})]_n$ 1-D chains linked by 3-pina ligands into a non-interpenetrated **pcu** network.



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ABSTRACT

Hydrothermal treatment of cadmium nitrate, a 5-substituted isophthalic acid, and 3-pyridylisonicotinamide (3-pina) resulted in three coordination polymers whose dimensionality depended critically on the nature of the aromatic ring substituent. These three new phases were characterized by single crystal X-ray diffraction. $\{[\text{Cd}(\text{hip})(3\text{-pina})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**1**, hip = 5-hydroxyisophthalate) and $\{[\text{Cd}(\text{meoip})(3\text{-pina})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**, meoip = 5-methoxyisophthalate) both manifest simple 1-D chain structures with pendant 3-pina ligands. $[\text{Cd}(\text{mip})(3\text{-pina})]_n$ (**3**, mip = 5-methylisophthalate) possesses $[\text{Cd}(\text{mip})]_n$ 1-D chains featuring $\{\text{Cd}_2(\text{OCO})_2\}$ dimeric units, linked by tethering 3-pina ligands into a non-interpenetrated 3-D 6-connected $4^{12}6^3$ **pcu** network. Luminescent behavior in all cases is attributed to intra-ligand molecular orbital transitions.

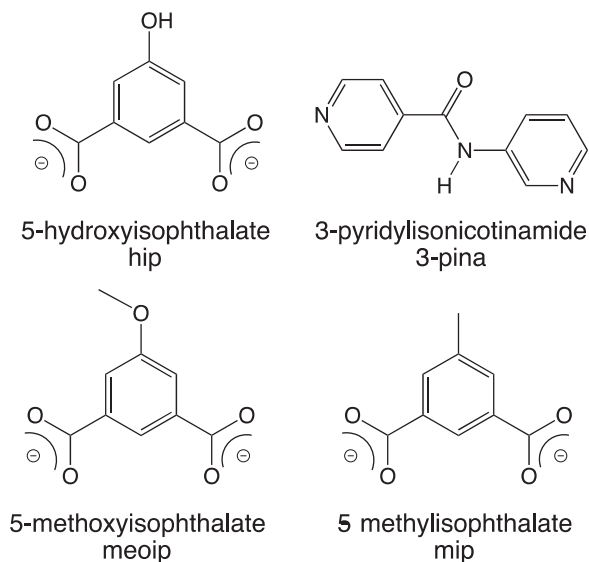
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Introduction

Basic research interest in the synthesis and characterization of divalent metal coordination polymers remains intense due to their ability to serve as hydrogen storage substrates [1], selective

adsorbents [2], drug-delivery agents [3], heterogeneous catalysts [4], and even as sensors for detection of explosives traces via changes in luminescent properties [5]. Coordination polymers with potentially useful optical properties tend to be based on the closed shell divalent zinc or cadmium ions, as there are no allowed visible-light absorbing *d-d* electronic transitions. Aromatic dicarboxylates have to proven to be exceptionally advantageous ligands for

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Scheme 1. Ligands used in this study.

the formation of cadmium-bearing coordination polymers [6]. Their varying oxygen donor dispositions and binding modes can instill a near infinite variety of possible structural topologies, especially when coupled with the lack of geometric preferences at the metal in the absence of any crystal field stabilization. In addition, this type of ligand can provide the thermally robust scaffolding and structural integrity necessary for maintaining open frameworks upon desolvation [7].

Employing 5-substituted isophthalate ligands and a flexible neutral dipyrindyl tethering ligand has resulted in preparation of cadmium coordination polymers with divergent topologies [8–13]. Reports of dual-ligand coordination polymers based on the hydrogen-bonding capable 5-hydroxyisophthalate (hip, Scheme 1) can illustrate this trend. $[\text{Cd}(\text{hip})(\text{dpe})_{1.5}]_n$ (dpe = 1,2-di(4-pyridyl)ethane) exhibits a 5-connected 2-D slab structure with 2D + 2D → 3D parallel interpenetration, and undergoes intense yellow light emission upon ultraviolet excitation [8]. Use of the longer and more flexible 1,3-di(4-pyridyl)propane ligand (dpp) resulted in an increase in dimensionality, affording a 2-fold interpenetrated 3D diamondoid net in $[\{\text{Cd}(\text{hip})(\text{dpp})(\text{H}_2\text{O})\} \cdot 2\text{H}_2\text{O}]_n$ [9]. Utilizing different 5-substituted isophthalate ligands with either enhanced steric bulk or poorer hydrogen bonding capability altered coordination polymer topology in some, but not all cases. $[\{\text{Cd}(\text{meoip})(\text{dpp})\} \cdot \text{H}_2\text{O}]_n$ (meoip = 5-methoxyisophthalate, Scheme 1) shows a layered topology in which the dpp ligands pillar 1-D $[\text{Cd}(\text{meoip})]_n$ ribbons, which contain embedded *anti-syn* $\{\text{Cd}_2(\text{OCO})_2\}$ dimeric clusters [10]. Higher temperature regimes during synthesis generated $[\{\text{Cd}(\text{meoip})(\text{dpp})(\text{H}_2\text{O})\} \cdot \text{H}_2\text{O}]_n$, which possesses a 2-fold interpenetrated diamondoid net, identical to its dpe analog [11]. $[\text{Cd}(\text{mip})(\text{dpp})]_n$ (mip = 5-methylisophthalate, Scheme 1) also manifests a 3-D diamondoid net, but now with 4-fold interpenetration [12]. A lower temperature polymorph $[\{\text{Cd}(\text{mip})(\text{dpp})(\text{H}_2\text{O})\} \cdot 0.33\text{H}_2\text{O}]_n$ has a common, simple (4,4) rhomboid grid topology [13].

In comparison to coordination polymers containing the more commonly employed flexible ditopic ligands dpe or dpp, there are fewer reports of related phases containing the easily prepared dipyrindylamide 3-pyridylisonicotinamide (3-pina, Scheme 1) [14–17]. The geometric requirements instilled by the kinked but rigid pyridyl donor disposition of 3-pina are expected to produce different coordination polymer topologies. Additionally, the central

amide functional group of 3-pina can act as both hydrogen bonding donor and acceptor points of contact, accessing potential structure-directing supramolecular interactions not feasible for bpy and dpe.

$[\text{Cd}_2(\text{pht})_2(3\text{-pina})(\text{H}_2\text{O})]_n$ (pht = phthalate) exhibits tetranuclear clusters linked into $[\text{Cd}_4(\text{pht})_4(\text{H}_2\text{O})_2]_n$ ribbon motifs, further tethered into a non-interpenetrated 3-D $4^{12}6^3$ **pcu** net by ditopic 3-pina ligands [14]. Recently we were able to exploit parent and substituted isophthalate ligands to prepare a series of copper coordination polymers containing 3-pina. $\{\{\text{Cu}(\text{iph})(3\text{-pina})\} \cdot \text{H}_2\text{O}\}_n$ (iph = isophthalate) exhibits $\{\text{Cu}_2(\text{OCO})_2\}$ dimeric units connected into $[\text{Cu}_2(\text{iph})_2]_n$ ribbons, further pillared by 3-pina ligands into a non-interpenetrated 3-D 6^58 **cds** network. Both $[\text{Cu}(\text{mip})(3\text{-pina})]_n$ and $[\text{Cu}(\text{meoip})(3\text{-pina})]_n$ show isostructural dimer-based $4^{12}6^3$ **pcu** networks in contrast. A multi-phase mixture of the 2-D interdigitated layered phase $[\{\text{Cu}_2(\text{hip})_2(3\text{-pina})_4\} \cdot 9.5\text{H}_2\text{O}]_n$, which possesses monodentate 3-pina ligands, and the $4^{12}6^3$ **pcu** phase $[\text{Cu}(\text{hip})(3\text{-pina})]_n$, was obtained when the H_2hip precursor was employed in synthesis [15].

We therefore attempted to extend this previous work into the preparation of a series of divalent cadmium coordination polymers containing both an isophthalate ligand and 3-pina. While unfortunately we were unable to prepare a parent iph derivative, we were able to isolate new phases containing the substituted congeners hip, meoip, and mip. In this contribution we report the single-crystal structures, topology, thermal properties, and fluorescent behavior of three new phases, whose topology depends critically on the nature of the aromatic substituent: $\{\{\text{Cd}(\text{hip})(3\text{-pina})(\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{\{\text{Cd}(\text{meoip})(3\text{-pina})(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O}\}_n$ (**2**), and $[\text{Cd}(\text{mip})(3\text{-pina})]_n$ (**3**).

Experimental section

General considerations

Cadmium nitrate and the substituted isophthalic acids were commercially obtained. Condensation of 3-aminopyridine and isonicotinoyl chloride hydrochloride in dry pyridine was used to prepare 3-pyridylisonicotinamide (3-pina), which was isolated via CH_2Cl_2 extraction, rotary evaporation, and recrystallization from water [18]. Water was deionized above 3 MΩ cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT 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. Thermogravimetric analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

Preparation of $[\{\text{Cd}(\text{hip})(3\text{-pina})(\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}]_n$ (**1**)

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (86 mg, 0.28 mmol), 3-pina (55 mg, 0.28 mmol), and 5-hydroxyisophthalic acid (51 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O and 1.0 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 2 d, and then was cooled slowly to 25 °C. Colorless crystals of **1** (114 mg, 72% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $\text{C}_{19}\text{H}_{21}\text{CdN}_3\text{O}_{10}$ **1**: C, 40.48; H, 3.75; N, 7.45% Found: C, 40.09; H, 3.35; N, 7.26%. IR (cm^{-1}): 3276 (m), 1686 (m), 1487 (m), 1544 (s), 1376 (s), 1333 (m), 1302 (m), 1272 (m), 1219 (w), 1127 (w), 1065 (w), 981 (w), 1003 (w), 903 (w), 775 (m), 693 (m).

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