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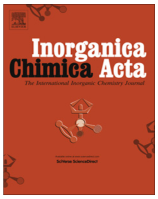

Dipyridylamide isomer influenced dimensionality in luminescent cadmium phthalate coordination polymers with similar tetranuclear clusters and ribbon motifs

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ABSTRACT

Hydrothermal reaction of cadmium nitrate, potassium hydrogen phthalate (KHphth), and either 4-pyridylnicotinamide (4-pna) or 3-pyridylisonicotinamide (3-pina) afforded two new luminescent coordination polymers with similar structural components but different dimensionality. $\{[Cd_2(phth)_2(4\text{-}pna)(H_2O)]\cdot 0.25H_2O\}_n$ (**1**, phth = phthalate) manifests $[Cd_4(phth)_4(H_2O)_2]$ ribbons based on tetranuclear clusters, connected to two others by pairs of tethering 4-pna ligands to afford 4-connected 2D (4,4) layers. $[Cd_2(phth)_2(3\text{-}pina)(H_2O)]_n$ (**2**) has similar tetranuclear clusters and $[Cd_4(phth)_4(H_2O)_2]$ ribbons, which are linked to four others by 3-pina tethers to construct a 6-connected 3D $4^{12}6^3$ **pcu** network. Subtle differences in phth binding and bridging mode, along with changes in coordination environment, serve to influence the dimensionality of the resulting coordination polymer. Thermal decomposition behavior is also discussed.

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1. Introduction

Because of their potential uses as gas storage substrates [1], molecular absorbents [2], ion-exchange materials [3], heterogeneous catalysts [4], and optical materials [5], the exploratory synthesis and structural characterization of crystalline coordination polymer solids remains a very active research focus. The often aesthetic appeal of their underlying grids or networks certainly provides a significant impetus for further investigations [6]. For two reasons, divalent zinc and cadmium ions are among the most commonly employed metal nodes in the design of coordination polymer solids; both arise from their stable d^{10} closed-shell electronic configuration. The resultant absence of any ligand field stabilization energy results in flexible coordination environments that can respond to the requirements imposed by donor disposition and steric bulk within the organic ligands, thus these effects play a predominant structure directing role. Also, an open spectral window for optical properties such as fluorescence or second harmonic generation [7] arises from the impossibility of any allowed *d–d* transitions.

Cadmium phthalate (phth) coordination polymers show an especially rich topological chemistry depending on the nature of any included dipodal nitrogen-base coligand (Scheme 1) [8–14]. Tethering ligands such as 4,4′-bipyridine (bpy) [8], 4,4′-dipyridylamine (dpa) [9], bis(4-pyridylmethyl)piperazine (bpmp) [10], bis(4-pyridylformyl)piperazine (bpfp) [11], and 1,4-bis(1,2,4-triazol-1-yl)butane (btb) [12] can instill tremendous differences in the resulting coordination polymer dimensionality and topology. For example, with the simple rigid-rod bpy tether, $[Cd(Hphth)_2(bpy)]_n$ could be synthesized; it has a simple yet self-penetrated 6-connected 3D network with $5^{10}6^47$ topology [8a]. The kinked and hydrogen-bonding capable dipyridyl ligand dpa afforded $\{[Cd(phth)(dpa)(H_2O)]\cdot 4H_2O\}_n$, which manifests a striking self-penetrated 7^48^2 **yyz** 4-connected topology built from the junction of three chiral self-penetrated (12,3) regular networks [9a]. Longer tethering ligands have allowed access to more complex unprecedented multi-nodal topologies, with $\{[Cd_2(phth)_2(bpfp)(H_2O)_2]_n$ displaying a very uncommon 4,5-connected binodal **tcs** topology [11] and $\{[Cd_2(phth)(btb)(H_2O)_3]\cdot 4.5(H_2O)\}_n$ showing layers with a complicated trinodal lattice [12]. Extension of the carboxylate arms can results in adjustments in coordination polymer topology [15,16].

Hundreds of coordination polymers have been prepared using the “C–C bond of crystal engineering”, the rigid-rod 4,4′-bpy ligand, which lacks any hydrogen bonding facility [17]. Scores more have been synthesized using the related, kinked, hydrogen-bonding donation capable dpa ligand [9d]. Nevertheless, there are rather few reports of coordination polymers containing any of the four simple isomeric dipyridylamide ligands 3-pyridylisonicotinamide (3-pina), 3-pyridylnicotinamide (3-pna), 4-pyridylisonicotinamide

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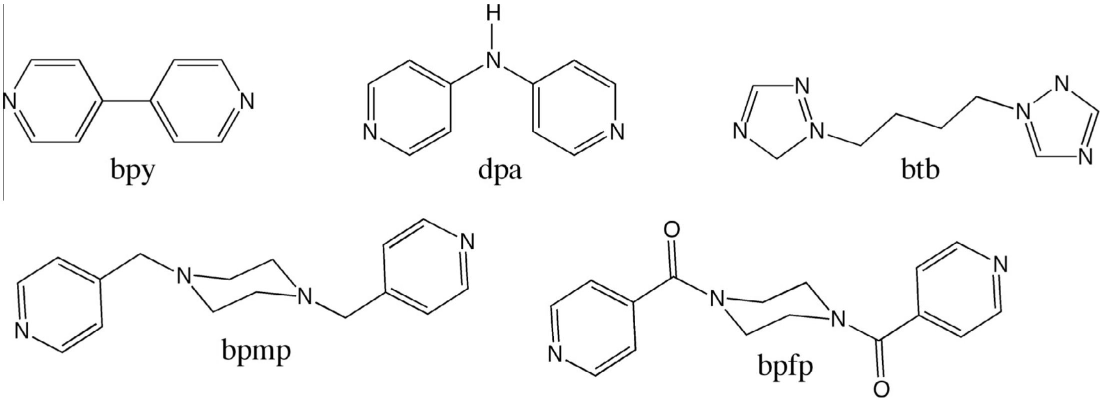
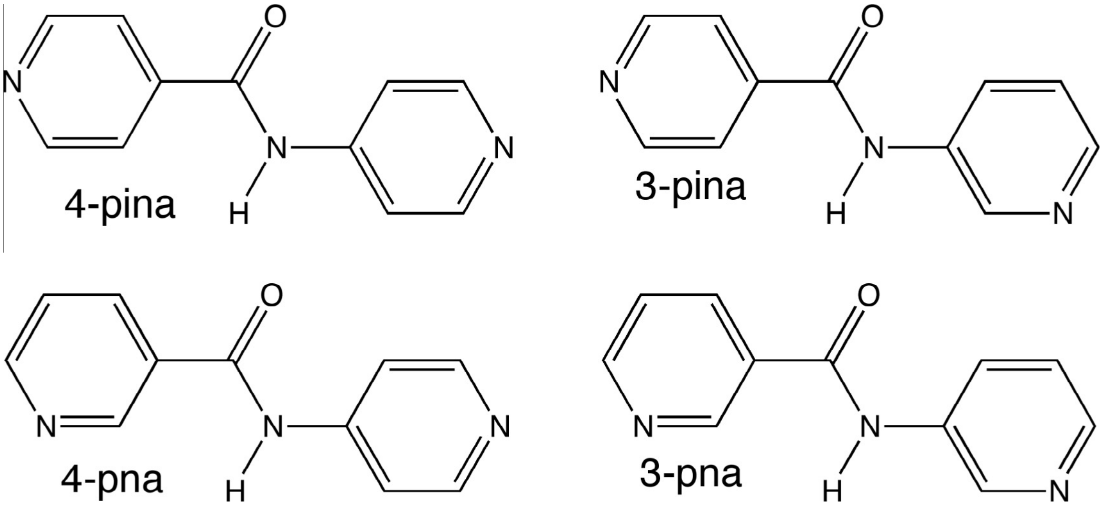


Scheme 1. Tethering dipyridyl ligands used in prior studies.



Scheme 2. Dipyridylamide isomers.

(4-pina), or 4-pyridylnicotinamide (4-pna) (Scheme 2) [18–20]. In the three published systematic surveys of divalent metal dicarboxylate coordination polymers utilizing one or more of these ligands, aliphatic dicarboxylates such as maleate [18c], fumarate [19], or adipate [20] were employed. In nearly all of these cases, the central amide moiety of the dipyridylamide ligands served dual hydrogen bonding roles as both a donor and an acceptor.

We thus sought to extend the use of these ligands into a divalent metal aromatic dicarboxylate system for the first time, and to expand the scope of known cadmium phthalate dual-ligand coordination polymers. Herein we report the synthesis, structural characterization, and thermal and luminescent properties of $\{[Cd_2(phth)_2(4\text{-pna})(H_2O)]\cdot 0.25H_2O\}_n$ (**1**) and $[Cd_2(phth)_2(3\text{-pina})(H_2O)]_n$ (**2**), which are the first divalent metal phthalate coordination polymers to contain any of these dipyridylamide isomers. While the two new cadmium phthalate phases share some important structural features, their overall topology and dimensionality are influenced very substantially by the geometric disposition of the nitrogen donors within the dipyridylamide ligands.

2. Experimental

2.1. General considerations

Cadmium nitrate and potassium hydrogen phthalate were commercially obtained. Condensation of 4-aminopyridine and nicotinoyl chloride hydrochloride in pyridine afforded crystalline 4-pyridylnicotinamide (4-pna) after quenching with water, extracting with chloroform, removal of solvent *in vacuo*, and recrystallization from water [21]. A similar condensation of 3-aminopyridine and isonicotinoyl chloride hydrochloride produced 3-pyridylisonicotinamide (3-pina) after an identical workup regimen. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using 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 $\{[Cd_2(phth)_2(4\text{-pna})(H_2O)]\cdot 0.25H_2O\}_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (171 mg, 0.55 mmol), 4-pna (55 mg, 0.28 mmol), and potassium hydrogen phthalate (92 mg, 0.55 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 72 h, and then was cooled slowly to 25 °C. Colorless needles of **1** (180 mg, 85% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $C_{27}H_{19}Cd_2N_3O_{10}\cdot 0.25H_2O$ **1**: C, 42.10; H, 2.49; N, 5.45. Found: C, 42.82; H, 2.27; N, 5.47%. IR (cm^{-1}): 3265 (w, br), 1691 (w), 1595 (m), 1571 (m), 1531 (s), 1507 (s), 1493 (s), 1481 (m), 1450 (m), 1389 (s), 1333 (m), 1297 (m), 1281 (m), 1211

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