



# Substituent effects in 4-connected zinc isophthalate coordination polymers with a pyridylnicotinamide ligand: From dimer-based layers to ribbons with embedded infinite water molecule chains



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## ABSTRACT

The dimensionality and structure of divalent zinc coordination polymers containing the dipyrindylamide ligand 3-pyridylnicotinamide (3-pna) can be adjusted by varying the 5-position substituent on an isophthalate moiety. Two new coordination polymer solids were obtained by hydrothermal self-assembly and structurally characterized via single-crystal X-ray diffraction. Using the unsubstituted isophthalate (ip) ligand,  $[\text{Zn}(\text{ip})(3\text{-pna})]_n$  (**1**) was obtained. This material exhibits  $\{\text{Zn}_2(\text{OCO})_2\}$  dimer-based  $[\text{Zn}(\text{ip})]_n$  chains linked into  $(4^26)(4^26^78)$  3,5L2 topology layers by *anti* conformation 3-pna ligands. By employing 5-methylisophthalate (mip), the coordination polymer  $[\{\text{Zn}(\text{mip})(3\text{-pna})\} \cdot 2\text{H}_2\text{O}]_n$  (**2**) was obtained; these feature *syn* conformation 3-pna ligands. Compound **2** shows a rarely encountered 4-connected 1-D ribbon motif with  $3^34^25$  topology, encapsulating infinite single-file water molecule chains within incipient tubular channels. Thermal and luminescent properties of these materials are also discussed.

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## 1. Introduction

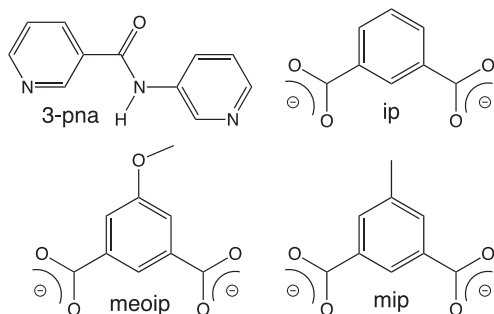
Recent efforts in the design and structural characterization of crystalline metal–organic coordination polymers have been mostly aimed at applications in hydrogen storage [1], carbon dioxide sequestration [2], molecular separations [3], heterogeneous catalysis [4], and luminescent sensing of guest molecules [5]. In the case of materials containing closed-shell divalent zinc ions, the lack of crystal field stabilization results in varied and unpredictable coordination geometry preferences, and an open spectral window for the exploitation of visible light-based emissive properties [6]. The wide scope of possible anionic dicarboxylate and neutral dipyrindyl ligands has produced myriad structural topologies in zinc coordination polymer systems [7]. Some coordination polymers, by means of supramolecular interactions, can produce unique container environments for the trapping of hydrogen bonded water molecule clusters, chains, tapes, or layers [8].

The aromatic *meta*-dicarboxylate isophthalate (ip, Scheme 1) ligand has proven beneficial for the construction of divalent zinc coordination polymers in tandem with dipyrindyl-type coligands that can play a key structure-directing role [9–14]. Using the

rigid-rod tethering ligand 4,4'-bipyridine (bpy), the 2-D (4,4) grid compound  $\{[\text{Zn}(\text{ip})(\text{bpy})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}\}_n$  was obtained [9]. Higher levels of interpenetration within 3-D zinc isophthalate phases is seen with longer dipyrindyl coligands. The relatively short-spanning ligand 1,2-bis(4-pyridyl)ethane (dpe) afforded a three-fold interpenetrated system of rare 3-D 6<sup>58</sup> **dmp** nets in  $\{[\text{Zn}(\text{ip})(\text{dpe})\text{-solvent}]_n\}$  [10]; the even longer-spanning bis(4-pyridylmethyl)piperazine (bpmp) ligand generated a five-fold interpenetrated 6<sup>6</sup> **dia** network in  $\{[\text{Zn}(\text{ip})(\text{bpmp})] \cdot \text{H}_2\text{O}\}_n$  [11]. Inclusion of a 5-position substituent within the parent isophthalate can dramatically affect the resulting coordination polymer topology by altering the steric and supramolecular environment during self-assembly.  $[\text{Zn}(\text{mip})(\text{dpe})]_n$  (mip = 5-methylisophthalate, Scheme 1) shows a similar three-fold interpenetrated system of 6<sup>58</sup> 3-D networks to its unsubstituted analog, but with a more traditional **cds** topology [12]. Extension of the tether by one methylene unit resulted in a four-fold interpenetrated 6<sup>6</sup> **dia** net in  $[\text{Zn}(\text{mip})(\text{dpp})]_n$  (dpp = 1,3-bis(4-pyridyl)propane) [12]. A sterically bulkier alkylether substituent in 5-methoxyisophthalate (meoip, Scheme 1) resulted in stacked 2-D (4,4) grids in both  $\{[\text{Zn}(\text{meoip})(\text{bpmp})] \cdot 8\text{H}_2\text{O}\}_n$  [13] and  $\{[\text{Zn}(\text{meoip})(\text{bpy})] \cdot (0.5\text{DMF} \cdot 0.5\text{MeOH})\}_n$  [14]. By forming solid solutions with an isostructural 5-nitroisophthalate compound, the latter phase can absorb CO<sub>2</sub> selectively from a CH<sub>4</sub>/CO<sub>2</sub> gaseous mixture [14].

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Scheme 1. Ligands discussed in this article.

In comparison to the nearly ubiquitous rigid-rod bpy ligand [15], the kinked dipyridylamide 3-pyridylnicotinamide (3-pna, Scheme 1) has been employed far less frequently as a coligand for the construction of zinc coordination polymers [16]. This ligand has the ability to adopt different nitrogen donor dispositions, with possible *syn*, *anti*, or intermediate skewed conformations (Scheme 2), resulting in different metal–metal contact distances. Additionally, the internal amide functional groups of 3-pna can provide both hydrogen bonding donor and acceptor groups, potentially helpful in facilitating structure direction or serving as points of contact for the stabilization of water molecule aggregations. In this contribution we report the successful synthesis, structural characterization, and preliminary physical property measurements of two new crystalline coordination polymers:  $[Zn(ip)(3-pna)]_n$  (**1**) and  $\{[Zn(mip)(3-pna)] \cdot 2H_2O\}_n$  (**2**).

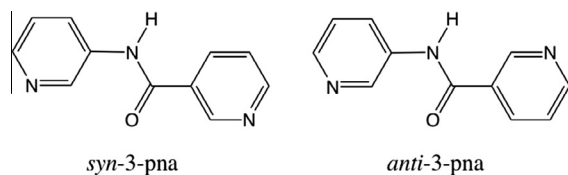
## 2. Experimental

### 2.1. General considerations

Zinc salts and dicarboxylic acids were purchased commercially. The dipyridylamide ligand was prepared using a published procedure [17]. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Thermogravimetric analysis was performed on a TA Instruments high-resolution Q50 thermal analyzer under flowing N<sub>2</sub>. 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 $[Zn(ip)(3-pna)]_n$ (**1**)

Zn(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (110 mg, 0.37 mmol), isophthalic acid (62 mg, 0.37 mmol) and 3-pna (74 mg, 0.37 mmol) were placed into 10 mL distilled H<sub>2</sub>O and 0.5 mL of 1 M NaOH in a 23 mL Teflon-lined digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 72 h, and then cooled slowly to 25 °C. Colorless blocks of **1** (70 mg, 44% yield based on Zn) were isolated after washing



Scheme 2. Conformations of 3-pna.

with distilled water and acetone, and drying in air. *Anal. Calc.* for C<sub>19</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>Zn **1**: C, 53.23; H, 3.06; N, 9.80. Found: C, 53.32; H, 3.01; N, 9.66%. IR (cm<sup>-1</sup>): 3088 (w), 3068 (w), 1682 (m), 1612 (m), 1585 (m), 1549 (m), 1487 (m), 1472 (m), 1443 (m), 1428 (m), 1392 (s), 1332 (m), 1302 (m), 1273 (m), 1233 (m), 1197 (m), 1130 (w), 1118 (w), 1099 (w), 1081 (w), 1057 (w), 1044 (w), 1031 (m), 964 (w), 946 (w), 927 (w), 899 (m), 849 (w), 826 (m), 801 (m), 748 (s), 717 (s), 700 (s), 691 (m), 659 (m).

### 2.3. Preparation of $\{[Zn(mip)(3-pna)] \cdot 2H_2O\}_n$ (**2**)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (110 mg, 0.37 mmol), 3-pna (74 mg, 0.37 mmol), and 5-methylisophthalic acid (66 mg, 0.37 mmol) were mixed with 10 mL of distilled H<sub>2</sub>O and 0.5 mL of 1 M NaOH in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated at 120 °C for 20 h, and then was cooled slowly to 25 °C. Colorless blocks of **2** (93 mg, 57% yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal. Calc.* for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>7</sub>Zn **2**: C, 50.17; H, 4.00; N, 8.78. Found: C, 50.92; H, 3.82; N, 8.74%. IR (cm<sup>-1</sup>): 3250 (w), 3078 (w), 2437 (w), 1693 (m), 1674 (m), 1618 (m), 1607 (m), 1557 (s), 1486 (m), 1421 (m), 1338 (s), 1312 (m), 1298 (m), 1247 (m), 1210 (m), 1129 (m), 1109 (m), 1054 (m), 918 (m), 899 (m), 852 (m), 829 (m), 807 (m), 770 (s), 759 (m), 724 (s), 690 (s), 654 (s).

## 3. X-ray crystallography

Single crystal X-ray diffraction was performed on single crystals of **1** and **2** with a Bruker-AXS ApexII CCD instrument at 173 K. Diffraction data was acquired using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data was integrated via SAINT [18]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS (**1**) [19] or TWINABS (**2**) [20]. The structures were solved using direct methods and refined on F<sup>2</sup> using SHELXTL [21]. 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. The hydrogen atoms bound to the amide nitrogen atoms, and water molecules where possible, were found via Fourier difference maps. These were then restrained at fixed positions and refined isotropically. The crystal of **2** was non-merohedrally twinned; their twin laws were found using CELL NOW [22]. Only the reflections from the major twin component were used in the solution and refinement for **2**. Positional disorder within the amide moieties of the 3-pna ligands in **2** was modeled using partial occupancies. Some distended thermal ellipsoids in the pyridine rings in the 3-pna ligands in **2** are indicative of a level of unresolved disorder that could not be successfully modeled with partial occupancies. Relevant crystallographic data for **1–2** is listed in Table 1.

## 4. Results and discussion

### 4.1. Synthesis and infrared spectra

Compounds **1** and **2** were prepared by hydrothermal reaction of zinc nitrate with the requisite isophthalic acid and 3-pna in the presence of aqueous base. Their infrared spectra were consistent with structural components determined by single-crystal X-ray diffraction. Intense, slightly broadened asymmetric and symmetric C–O stretching bands were observed at 1549 and 1391 cm<sup>-1</sup> in **1**, and 1557 and 1338 cm<sup>-1</sup> in **2**. Sharper bands in the range of ~1610 cm<sup>-1</sup> to ~1300 cm<sup>-1</sup> were attributed to stretching modes of pyridyl rings of nitrogen base ligands and the aromatic rings of the isophthalate ligands [23]. Features corresponding to C–H

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