

# Effect of metal coordination environment on topology of coordination polymers containing 2,5-thiophenedicarboxylate and long-spanning dipyridine ligands



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## ABSTRACT

Hydrothermal reaction of a metal nitrate, 2,5-thiophenedicarboxylic acid (H<sub>2</sub>tpdc), and bis(4-pyridylmethyl)piperazine (4-bpmp) afforded a series of crystalline coordination polymers with different dimensionality and topology depending on the metal coordination geometry. These materials were characterized by single-crystal X-ray diffraction. [Cu(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**1**), with square pyramidal coordination, shows parallel stacked (4,4) grid motifs. {[Co(tpdc)(4-bpmp)<sub>1.5</sub>(H<sub>2</sub>O)<sub>2</sub>·4H<sub>2</sub>O]<sub>n</sub> (**2**) exhibits graphitic (6,3) honeycomb layer motifs and octahedral coordination at the metal. {[Cd(tpdc)(4-bpmp)(H<sub>2</sub>O)]·H<sub>2</sub>O]<sub>n</sub> (**3**) shows pentagonal bipyramidal geometry and manifests (4,4) grid layers as in **1**, but with 2D + 2D → 3D parallel entanglement. [Zn(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**4**), which has distorted “5 + 1” octahedral coordination at zinc, displays an acentric 6<sup>6</sup> 3-D diamondoid topology. Luminescent properties of **3** and **4** are presented, along with thermal analyses.

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## 1. Introduction

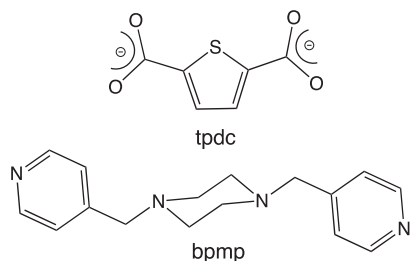
Research into the synthesis and characterization of divalent metal coordination polymers remains a fertile avenue of scientific discovery in large part due to their increasing utility in gas storage [1], shape-selective molecular separations [2], ion exchange [3], heterogeneous catalysis for industrially relevant organic transformations [4], and sensor devices for detection of explosives residues [5]. A popular choice for the necessary anionic component in these materials is the easily accessible and inexpensive isophthalate (ip) ligand. Here, the rigid aromatic backbone and multiple possible binding modes of the *meta*-disposed carboxylate arms can install a wide scope of structural diversity, especially when employed with a second neutral dipyridyl ligand. Using the rigid-rod ligand 4,4'-bipyridine (bpy), which has been termed “the C–C bond of crystal engineering” [6], Guo prepared the strongly fluorescent (4,4) grid material [Zn(ip)(4,4'-bpy)(H<sub>2</sub>O)]·1.5H<sub>2</sub>O]<sub>n</sub> [7], which exhibited trigonal bipyramidal coordination at zinc. Two supramolecular isomers with formulation {[Zn(ip)(bpe)]·solvent]<sub>n</sub> could be obtained by utilizing the longer 1,2-bis(4-pyridyl)ethane (bpe), depending on the solvent system used in the synthesis [8]. One phase showed a (4,4) grid topology just like its 4,4'-bpy analog,

while the other manifested a rare non-diamondoid 6<sup>5</sup>8 **dmp** 4-connected net. Use of longer dipyridyl ligands such as bis(4-pyridylmethyl)piperazine (4-bpmp, Scheme 1) resulted in topologies different from those using shorter dipyridyl coligands [9]. The isostructural phases {[Cd(ip)(4-bpmp)]·H<sub>2</sub>O]<sub>n</sub> and {[Co(ip)(4-bpmp)]·H<sub>2</sub>O]<sub>n</sub> both displayed dimer-based (3,6) triangular layer topologies, while {[Zn(ip)(4-bpmp)]·H<sub>2</sub>O]<sub>n</sub> manifested a centrosymmetric fivefold interpenetrated 6<sup>6</sup> **dia** diamondoid topology. {[Cu(ip)(4-bpmp)(H<sub>2</sub>O)]·5H<sub>2</sub>O]<sub>n</sub> displays acentric (4,4) rectangular grids that stack in an ABCD repeat pattern [10].

The aromatic ligand 2,5-thiophenedicarboxylate (tpdc, Scheme 1) is similar to isophthalate but the five-membered thiophene ring orients the carboxylate groups ~152° apart [11], as opposed to the 120° disposition in isophthalate. As a result of the geometric difference in the angle subtended between the carboxylate groups, dual ligand coordination polymers containing tpdc ligands can sometimes show different topologies or dimensionalities than their isophthalate analogs. For example, [Co(ip)(4,4'-bpy)]<sub>n</sub> shows a decorated (4,4) grid structure built from pillared [Co(ip)]<sub>n</sub> dimer-based chains [12], while [Co(tpdc)(4,4'-bpy)]<sub>n</sub> manifests a twofold interpenetrated **pcu** net built from pillaring of 2-D [Co(tpdc)]<sub>n</sub> layer motifs [13]. In some other cases, the isophthalate and tpdc coordination polymer congeners present the same structural topology. For instance, {[Cu(ip)(dpa)]·0.5H<sub>2</sub>O]<sub>n</sub> (dpa = 4,4'-dipyridylamine) and [Cu(tpdc)(dpa)]<sub>n</sub> are largely isostructural, with both showing {Cu<sub>2</sub>(OCO)<sub>2</sub>} dimer-based copper

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Scheme 1. Ligands used in this study.

dicarboxylate chain motifs, linked into non-interpenetrated 4-connected 6<sup>5</sup>8 **cds** net by the kinked dpa tethers [14]. Despite possessing the same overall topology as the isophthalate compound, slight differences in the bridging distances and angles within the dimer units in the tpdc derivative caused slightly weaker antiferromagnetic coupling. Thus, it is not possible to predict *a priori* whether or not related isophthalate or 2,5-thiophenedicarboxylate coordination polymers will display the same or different structural topologies.

We thus sought to prepare a series of divalent metal 2,5-thiophenedicarboxylate coordination polymers containing the long-spanning and hydrogen-bonding capable 4-bpmp ligand in order to compare their structures with our previously reported set of divalent metal 4-bpmp isophthalates [9]. Herein we report the synthesis, structural characterization, and preliminary physical property studies of [Cu(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**1**), {[Co(tpdc)(4-bpmp)<sub>1.5</sub>(H<sub>2</sub>O)<sub>2</sub>]}<sub>n</sub>·4H<sub>2</sub>O (**2**), {[Cd(tpdc)(4-bpmp)(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> (**3**), and [Zn(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**4**).

## 2. Experimental

### 2.1. General considerations

Metal nitrates and 2,5-thiophenedicarboxylic acid were commercially obtained. Bis(4-pyridylmethyl)piperazine was prepared according to a literature procedure [15]. 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. 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.

### 2.2. Preparation of [Cu(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**1**)

Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (69 mg, 0.30 mmol), 2,5-thiophenedicarboxylic acid (64 mg, 0.37 mmol), and 4-bpmp (99 mg, 0.37 mmol) were mixed with 10 mL of distilled H<sub>2</sub>O and 0.9 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 100 °C for 1 d, and then was cooled slowly to 25 °C. Blue blocks of **1** (83 mg, 53% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air.

*Anal.* Calc. for C<sub>22</sub>H<sub>24</sub>CuN<sub>4</sub>O<sub>5</sub>S **1**: C, 50.81; H, 4.65; N, 10.77. Found: C, 49.83; H, 4.43; N, 10.35%. IR (cm<sup>-1</sup>): 3242(w), 2952(w), 2818(w), 2775(w), 1660(w), 1615(w), 1583(m), 1520(m), 1457(w), 1424(w), 1396(w), 1357(s), 1340(s), 1294(m), 1265(m), 1224(w), 1159(w), 1142(w), 1125(w), 1104(w), 1055(w), 1029(m), 1008(w), 995(w), 973(w), 932(w), 864(w), 853(m), 835(w), 795(s), 780(s), 751(w), 739(w), 719(w), 680(w), 667(w).

### 2.3. Preparation of {[Co(tpdc)(4-bpmp)<sub>1.5</sub>(H<sub>2</sub>O)<sub>2</sub>]}<sub>n</sub>·4H<sub>2</sub>O (**2**)

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (34 mg, 0.12 mmol), 2,5-thiophenedicarboxylic acid (32 mg, 0.19 mmol), and 4-bpmp (50 mg, 0.19 mmol) were mixed with 5 mL of distilled H<sub>2</sub>O and 0.45 mL of 1 M NaOH in a 15 mL glass vial. The vial was sealed and heated in an oil bath at 80 °C for 4 d, and then was cooled slowly to 25 °C. Orange blocks of **2** (50 mg, 58% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C<sub>30</sub>H<sub>44</sub>CoN<sub>6</sub>O<sub>10</sub>S **2**: C, 48.71; H, 6.00; N, 11.36. Found: C, 48.11; H, 6.05; N, 10.88%. IR (cm<sup>-1</sup>): 3161(w), 2942(w), 2811(w), 2164(w), 1614(m), 1573(m), 1531(m), 1456(w), 1423(w), 1362(s), 1351(s), 1323(m), 1300(m), 1267(w), 1228(w), 1213(w), 1160(w), 1134(w), 1108(w), 1061(w), 1010(m), 932(w), 839(m), 798(s), 775(s), 758(s), 728(m), 669(m).

### 2.4. Preparation of {[Cd(tpdc)(4-bpmp)(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> (**3**)

Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (88 mg, 0.29 mmol), 2,5-thiophenedicarboxylic acid (64 mg, 0.37 mmol), and 4-bpmp (99 mg, 0.37 mmol) were mixed with 10 mL of distilled H<sub>2</sub>O and 0.9 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 blocks of **3** (83 mg, 49% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C<sub>22</sub>H<sub>26</sub>CdN<sub>4</sub>O<sub>6</sub>S **3**: C, 45.02; H, 4.47; N, 9.55. Found: C, 44.89; H, 4.27; N, 9.46%. IR (cm<sup>-1</sup>): 3175(w), 2949(w), 1613(w), 1558(m), 1526(m), 1458(w), 1447(w), 1426(w), 1373(m), 1317(w), 1294(w), 1271(w), 1247(w), 1221(w), 1169(w), 1133(w), 1065(w), 1031(w), 1012(w), 1003(w), 935(w), 921(w), 859(w), 844(w), 823(m), 794(m), 768(s), 688(w).

### 2.5. Preparation of [Zn(tpdc)(4-bpmp)(H<sub>2</sub>O)]<sub>n</sub> (**4**)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (35 mg, 0.12 mmol), 2,5-thiophenedicarboxylic acid (32 mg, 0.19 mmol), and 4-bpmp (50 mg, 0.19 mmol) were mixed with 5 mL of distilled H<sub>2</sub>O and 0.45 mL of 1 M NaOH in a 15 mL glass vial. The vial was sealed and heated in an oil bath at 80 °C for 4 d, and then was cooled slowly to 25 °C. Colorless blocks of **4** (29 mg, 46% yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C<sub>22</sub>H<sub>24</sub>N<sub>4</sub>O<sub>5</sub>SZn **4**: C, 50.62; H, 4.63; N, 10.73. Found: C, 50.45; H, 4.23; N, 10.70%. IR (cm<sup>-1</sup>): 3322(w), 2945(w), 2878(w), 2815(w), 2771(w), 1614(w), 1600(w), 1557(m), 1526(m), 1500(m), 1455(w), 1419(m), 1397(m), 1370(s), 1350(m), 1335(m), 1321(m), 1297(s), 1263(m), 1225(w), 1213(w), 1199(w), 1161(w), 1146(m), 1127(m), 1101(w), 1068(w), 1033(w), 1011(m), 999(w), 936(w), 927(w), 890(w), 837(m), 852(m), 824(m), 796(s), 780(s), 739(w), 729(w), 684(w), 670(w), 653(w).

## 3. X-ray crystallography

Reflection data for **1–4** were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were processed via SAINT [16], and subjected for Lorentz and polarization effect and absorption corrections using SADABS [17]. The structures were solved using direct methods with the XS subroutine of SHELXTL [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon or oxygen were placed in calculated positions and refined isotropically with a riding model. Crystallographic details for **1–4** are given in Table 1.

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