

# Three-Dimensional Zinc(II) and Cadmium(II) Coordination Frameworks with *N,N,N',N'*-Tetrakis(pyridin-4-yl)methanediamine: Structure, Photoluminescence, and Catalysis

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## S Supporting Information

**ABSTRACT:** Coordination polymer networks, i.e.,  $[\text{Zn}(\text{tpmd})(\text{H}_2\text{O})](\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{tpmd})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 4\text{CH}_3\text{OH}$  (**2**), were assembled from  $\text{M}^{\text{II}}(\text{NO}_3)_2$  hydrates ( $\text{M} = \text{Zn}, \text{Cd}$ ) and *N,N,N',N'*-tetrakis(pyridin-4-yl)methanediamine (tpmd) in  $\text{CH}_3\text{OH}$  and characterized. **1** and **2** feature three-dimensional networks formed by coordination of the metal ions to the tpmd ligands. **1** exhibits a strong blue emission at  $\sim 397$  nm, while **2** shows strong emission at  $\sim 361$  nm. **1** is a more efficient catalyst for the transesterification of various esters than **2**.

The self-assembly of functional coordination polymer networks has attracted much attention because of fundamental scientific interest and their potential applications in catalysis, absorption, magnetism, and luminescence.<sup>1</sup> Of these, the self-assembly of compounds that include zinc(II) and cadmium(II) ions and organic ligands has been extensively studied because of their interesting framework structures and luminescent properties.<sup>2</sup> A variety of zinc(II) and cadmium(II) coordination polymers containing aromatic moieties exhibit unique ligand-to-metal charge transfer luminescent properties; these are very dependent upon the geometry of the ligands and counteranions.<sup>3</sup> Furthermore, zinc(II) and cadmium(II) compounds with functional organic ligands can potentially be used in applications such as light-emitting diodes and heterogeneous catalysts.<sup>4</sup> Thus, the rational design of new building blocks for self-assembly is very important. To explore the preparation of bis(4-pyridyl)amine (bpa) derivatives that could be luminescent chromophores, we obtained a new ligand containing methylene and bpa moieties, i.e., *N,N,N',N'*-tetrakis(pyridin-4-yl)methanediamine (tpmd),<sup>5</sup> in which two bpa units are linked by a methylene moiety. Herein, we report three-dimensional (3D) coordination polymer networks, i.e.,  $[\text{Zn}(\text{tpmd})(\text{H}_2\text{O})](\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{tpmd})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 4\text{CH}_3\text{OH}$  (**2**), which were self-assembled in  $\text{CH}_3\text{OH}$  from zinc(II) or cadmium(II) ions and tpmd. These coordination networks feature interesting solid structures, luminescence, and catalytic properties.

The ligand tpmd was obtained as a pale-yellow solid by the treatment of sodium hydride with bpa in  $\text{CH}_2\text{Cl}_2$ .<sup>5</sup> The methylene group is abstracted from  $\text{CH}_2\text{Cl}_2$  by NaH under

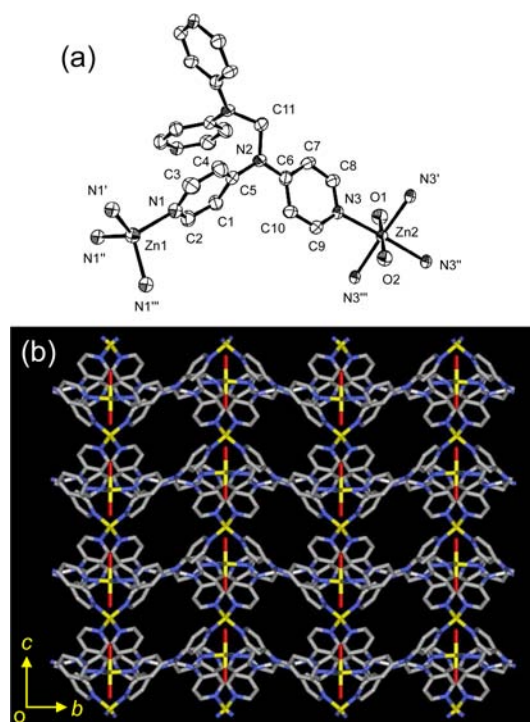
basic conditions. Four pyridine groups that extend outward indicate that the ligand can bind to four individual metal ions to form network structures and lead to  $\pi$ - $\pi$  interactions through the pyridine groups. Coordination polymer networks **1** and **2** were prepared from  $\text{M}^{\text{II}}(\text{NO}_3)_2$  hydrates ( $\text{M} = \text{Zn}$  or  $\text{Cd}$ ) and tpmd ligands in  $\text{CH}_3\text{OH}$  at room temperature.<sup>6</sup> **1** and **2** are slightly soluble in water but insoluble in acetone,  $\text{CH}_3\text{OH}$ , and  $\text{Me}_2\text{SO}$ . Thermogravimetric analysis (TGA) of **1** revealed a weight loss of 20.9% at 100 °C, which corresponds to a loss of eight water molecules per unit formula (Figure S1 in the Supporting Information, SI); no chemical decomposition was observed up to 250 °C. TGA of **2** revealed a weight loss of 28.6% at 75 °C, which corresponds to a loss of all solvent molecules per unit formula (Figure S2 in the SI); no chemical decomposition was observed up to 320 °C. Accordingly, **2** is more thermally stable than **1**.

**1** crystallizes in the tetragonal space group  $P4/ncc$ , and the ORTEP view of **1** is shown in Figure 1a. The asymmetric unit of **1** consists of two crystallographically independent zinc(II) cations: One zinc(II) ion (Zn1) is tetrahedrally coordinated by four pyridyl nitrogen atoms from four different tpmd ligands, while the other zinc(II) ion (Zn2) is octahedrally coordinated by four pyridyl nitrogen atoms from four different tpmd ligands and two water molecules. That is, the coordination numbers of Zn1 and Zn2 are 4 and 6, respectively. The average Zn–N<sub>py</sub> bond distances are 1.997(1) and 2.146(1) Å for Zn1 and Zn2, respectively. The average Zn2–O(water) bond distance is 2.173(3) Å. Each tpmd connects four different zinc(II) ions because all nitrogen atoms of each tpmd ligand are bonded to different zinc(II) ions; this gives rise to a 3D network (Figure 1b). The two bpa moieties of the tpmd ligands are linked by a methylene carbon (C11) at an angle of 110.4(2)°. The shortest Zn...Zn separation is 7.755(1) Å. Calculations using PLATON indicate that 30.7% (1850.5 Å<sup>3</sup>) of the void volume of **1** is occupied by seven water molecules.<sup>7</sup> Guest water molecules and nitrate anions are contained in the cavities; these were located in the X-ray structure and were also evident in the IR spectra and elemental analysis and TGA data.

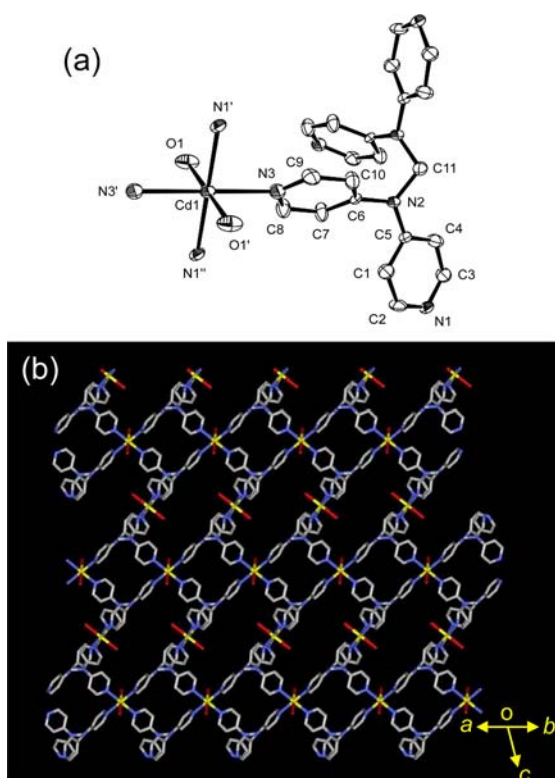
**2** crystallizes in the monoclinic space group  $C2/c$ , and the ORTEP view of **2** is shown in Figure 2a. The tpmd ligand utilizes all of its pyridyl nitrogen atoms to coordinate four cadmium(II)

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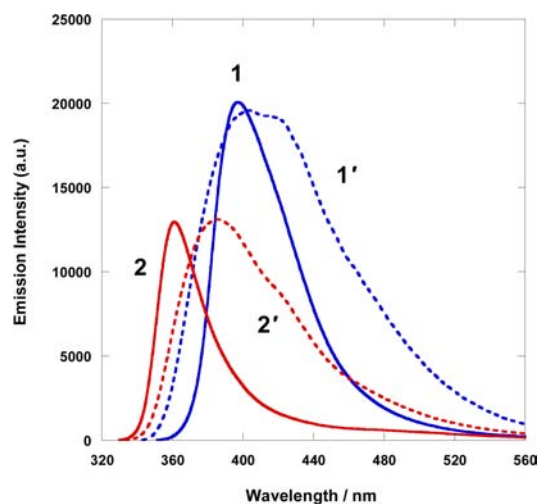
**Figure 1.** (a) ORTEP view of **1**. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms,  $\text{NO}_3^-$ , and solvent are omitted for clarity. (b) Perspective view of **1** showing an extended 3D structure via the coordination of zinc(II) ions and tpmd ligands.



**Figure 2.** (a) ORTEP view of **2**. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms,  $\text{NO}_3^-$ , and solvent are omitted for clarity. (b) Perspective view of **2** showing an extended 3D structure via the coordination of cadmium(II) ions and tpmd ligands.

ions. Each cadmium(II) has a slightly distorted octahedral coordination geometry with four pyridyl nitrogen atoms coordinated in the equatorial plane and two water molecules coordinated at the axial positions. The Cd–N1 and Cd–N3 bond distances are 2.351(5) and 2.348(6) Å, respectively, and the Cd–O1 bond length is 2.323(5) Å. Through the linkage of four tetraconnected tpmd ligands and four tetraconnected cadmium(II) ions, a 3D network structure is formed (Figure 2b). Topologically, one cadmium(II) ion could be viewed as a square-planar tetraconnected node and the two central nitrogen atoms in the tpmd ligand as two trigonal triconnected nodes; this generates an unprecedented 3D bimodal 3,4-connected network. The two bpa groups in the ligands are connected by a methylene carbon at an angle of 109.7(7)°. The shortest Cd...Cd separation is 8.623(1) Å. Calculations using PLATON indicate that 33.8% (1148.7 Å<sup>3</sup>) of the void volume of **2** is occupied by four water and four methanol molecules.<sup>7</sup> The guest solvent molecules and nitrate anions are included in the cavities; these were located in the X-ray structure and also evident in the IR spectra and elemental analysis and TGA data.

The solid-state luminescent properties of **1** and **2** were investigated at room temperature. The fluorescence spectra of **1** and **2** are shown in Figure 3. Upon excitation at  $\lambda_{\text{ex}} = 300$  nm, **1**

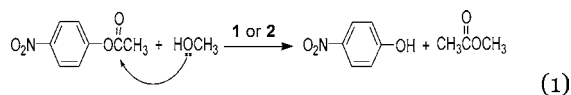


**Figure 3.** Solid-state photoinduced emission spectra of **1** (solid line, blue), dried **1** (**1'**, dashed line, blue), **2** (solid line, red), and dried **2** (**2'**, dashed line, red) at room temperature with  $\lambda_{\text{ex}} = 300$  nm.

displays a strong fluorescent emission band with a maximum at  $\sim 397$  nm, while **2** shows an intense fluorescent signal at 361 nm. The  $\lambda_{\text{max}}$  value of **1** is longer than that of **2**, which can be attributed to the heavy-atom and coordination effects due to the different types and coordination environments of the metal ions.<sup>8</sup> To assess the photoluminescence of desolvated **1** and **2**, they were dried at 110 °C for 3 h. The maximum peak of dried **1** is shifted very slightly and broadened (403 and 420 nm, split). For dried **2**, the maximum peak is red-shifted by  $\sim 25$  nm to 386 nm. The emissions of both compounds undergo a red shift due to desolvation of **1** and **2**. This indicates that the local environments are changed through drying and energy is lost through a nonradiative pathway by contraction due to the coordination effect. The emissive behaviors in **1** and **2** can be mostly attributed to ligand-centered  $\pi \rightarrow \pi^*$  or  $\pi \rightarrow n$  transitions within the aromatic groups of the tpmd ligands.<sup>9</sup>

These compounds are potential candidates for incorporation in luminescent sensors and photoactive materials, e.g., for the detection of aromatic organic molecules.<sup>10</sup> When the dried **1** and **2** solids were exposed to water vapor, the original luminescence spectra were regenerated; this means that the original frameworks of **1** and **2** are fully restored (Figures S3–S5 in the SI).

To assess the catalytic effects of **1** and **2**, we applied them to the transesterification of various esters in CH<sub>3</sub>OH at 50 °C. The reaction of 4-nitrophenyl acetate and methanol in the presence of **1** and **2** quantitatively produced methyl acetate within 2 and 5 h (eq 1), respectively, under neutral conditions (entry 1 of Table S1 in the SI).



The catalytic results indicate that **1** has a higher catalytic activity for ester synthesis by transesterification than **2**. This is attributed to the fact that the second-period transition metals are much less labile, thereby hindering the substitution reaction.<sup>11</sup> Importantly, the transesterification reactivity of zinc-containing **1** is the best among the previously reported catalytic systems with zinc-containing polymeric compounds, to our knowledge.<sup>12a–c</sup> Moreover, **2** is recyclable, although its activity is somewhat reduced after recycling (Table S2 in the SI). The amount of cadmium that leached into the filtrate after two cycles was measured via inductively coupled plasma spectroscopic analysis and determined to be 15 ppm.<sup>12c</sup> The loss of catalyst due to leaching was calculated to be ~2 wt % and thus may be considered negligible. Transesterification reactions of other esters using catalysts **1** and **2** were also carried out, and the results are given in Table S1 in the SI. Various esters were converted to their corresponding products within 2–14 and 5–240 h using **1** and **2**, respectively. On the basis of our present and previous results,<sup>12a–c</sup> we assume that the transesterification reactions occur outside the framework because the results of the transesterification reactions catalyzed by **2** showed a trend similar to those observed using our previously reported homogeneous catalysts.<sup>12a,b</sup> Specifically, **2** did not display any size effects that could possibly occur inside the framework. Therefore, the substrate phenyl acetate substitutes the labile water molecules of the exterior cadmium ions to produce the cadmium–substrate adduct. Then, the methanol nucleophile attacks the carbon atom of the carbonyl moiety of the adduct to produce the methyl phenyl acetate product. These results suggest that **1** and **2** could be used as catalysts for the transesterification of various esters.

In conclusion, two coordination polymer networks, **1** and **2**, with different metal ions were constructed using tpmd. The zinc(II) ions in **1** show octahedral and tetrahedral coordination geometries, while **2** displays only tetrahedral coordination geometries. The topologies of **1** and **2** are 3D network structures. **1** and **2** have strong emission at ~397 and 361 nm, respectively. **1** shows more efficient catalytic activity for the transesterification of various esters than **2** does. Further studies on the mechanism of the catalytic transesterification and luminescence and the fabrication of new coordination networks are ongoing.

## ■ ASSOCIATED CONTENT

### Supporting Information

Details of the synthesis, analytical results, TGA data, luminescence data, transesterification results, PXRD patterns,

structural data, and X-ray crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. W. *Chem. Rev.* **2012**, *112*, 782. (b) Choi, H. S.; Suh, M. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 6865. (c) Halder, G. J.; Kepert, C. J.; Mobaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (d) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (e) Schneider, V.; Demeshko, S.; Dechert, S.; Meyer, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 9274. (f) Seward, C.; Pang, J.; Wang, S. *Eur. J. Inorg. Chem.* **2002**, 1390. (g) Cui, Y.; Xu, H.; Yue, Y.; Guo, Z.; Yu, J.; Chen, Z.; Gao, J.; Yang, Y.; Qian, G.; Chen, B. *J. Am. Chem. Soc.* **2012**, *134*, 3979. (h) Tseng, Y.-H.; Bhattacharya, D.; Lin, S.-M.; Thanasekaran, P.; Wu, J.-Y.; Lee, L.-W.; Sathiyendiran, M.; Ho, M.-L.; Chung, M.-W.; Hsu, K.-C.; Chou, P.-T.; Lu, K.-L. *Inorg. Chem.* **2010**, *49*, 6805.
- (2) (a) Zeng, F.; Ni, J.; Wang, Q.; Ding, Y.; Ng, S. W.; Zhu, W.; Xie, Y. *Cryst. Growth Des.* **2010**, *10*, 1611. (b) Wang, Q.-G.; Xie, Y.-S.; Zeng, F.-H.; Ng, S.-W.; Zhu, W.-H. *Inorg. Chem. Commun.* **2010**, *13*, 929. (c) Bauer, C. A.; Timofeeva, T. V.; Settersten, T. B.; Patterson, B. D.; Liu, V. H.; Simmons, B. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 7136.
- (3) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330.
- (4) (a) Ozdemir, T.; Atilgan, S.; Kutuk, I.; Yildirim, L. T.; Tulek, A.; Bayindir, M.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 2105. (b) Zou, R.-Q.; Sakurai, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542. (c) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. J. *Am. Chem. Soc.* **2005**, *127*, 8940.
- (5) Shin, J. W.; Min, K. S. *Acta Crystallogr.* **2012**, *E68*, o1600.
- (6) See the Supporting Information.
- (7) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- (8) (a) Luo, J.; Li, W. S.; Xu, P.; Zhang, L. Y.; Chen, Z. N. *Inorg. Chem.* **2012**, *51*, 9508. (b) Kunkely, H.; Vogler, A. *Chem. Phys. Lett.* **2003**, *376*, 226.
- (9) (a) Braverman, M. A.; LaDuca, R. L. *Cryst. Growth Des.* **2007**, *7*, 2343. (b) Shyu, E.; Supkowski, R. M.; LaDuca, R. L. *Inorg. Chem.* **2009**, *48*, 2723. (c) Shyu, E.; Supkowski, R. M.; LaDuca, R. L. *Cryst. Growth Des.* **2009**, *9*, 2481. (d) Prabhakar, M.; Zacharias, P. S.; Das, S. K. *Inorg. Chem.* **2005**, *44*, 2585.
- (10) (a) Fang, Q.; Zhu, G.; Xue, M.; Sun, J.; Sun, F.; Qiu, S. *Inorg. Chem.* **2006**, *45*, 3582. (b) Shimizu, M.; Takeda, Y.; Higashi, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3653.
- (11) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
- (12) (a) Kwak, H.; Lee, S. H.; Kim, S. H.; Lee, Y. M.; Lee, E. Y.; Park, B. K.; Kim, E. Y.; Kim, C.; Kim, S.-J.; Kim, Y. *Eur. J. Inorg. Chem.* **2008**, 408. (b) Park, B. K.; Eom, G. H.; Kim, S. H.; Kwak, H.; Yoo, S. M.; Lee, Y. J.; Kim, C.; Kim, S.-J.; Kim, Y. *Polyhedron* **2010**, *29*, 773. (c) Hwang, I. H.; Bae, J. M.; Kim, W.-S.; Jo, Y. D.; Kim, C.; Kim, Y.; Kim, S.-J.; Huh, S. *Dalton Trans.* **2012**, *41*, 12759. (d) Samanta, D.; Mukherjee, S.; Patil, Y. P.; Mukherjee, P. S. *Chem.—Eur. J.* **2012**, *18*, 12322.