

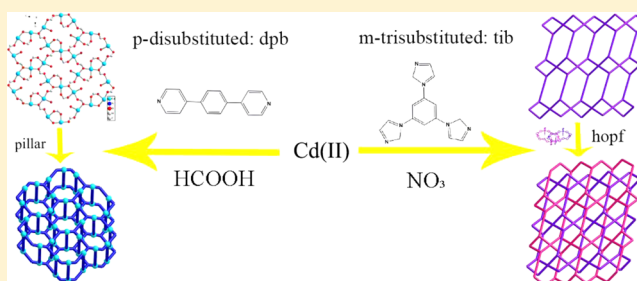
Cadmium–Organic Coordination Polymers Based on N-Donor Ligands and Small Anions: Syntheses, Crystal Structures, and Photoluminescent Properties

Jie Guo, Di Sun, Liangliang Zhang, Qiao Yang, Xiaoliang Zhao, and Daofeng Sun*

Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China

S Supporting Information

ABSTRACT: By using two types of arene core-based rigid N-containing ligands, we have solvothermally synthesized two cadmium metal–organic coordination polymers, $\{[\text{Cd}_6(\text{dpb})_6(\text{HCOO})_8(\text{H}_2\text{O})_4] \cdot 4\text{NO}_3 \cdot 4\text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Cd}_4(\text{tib})_4(\text{H}_2\text{O})_4(\text{NO}_3)_6] \cdot 2\text{NO}_3\}_n$ (**2**) (dpb = 1,4-bis-(4-pyridyl)-benzene, tib = 1,3,5-tris(1-imidazolyl)benzene), and characterized them. The coordinated small anions HCOO^- and NO_3^- play important roles in the formation of **1** and **2**. In **1**, the coordinated formate ligand from in situ hydrolysis of DMF binds metal centers to generate a rigid 2D metal–formate honeycomb layer, which is further connected by dpb ligands to generate a 3D pillar–layer complex. Complex **2** possesses a 2-fold interpenetrating 2D framework with an extremely rare (3,4) connected topology. Photochemical properties of these new complexes have been studied.



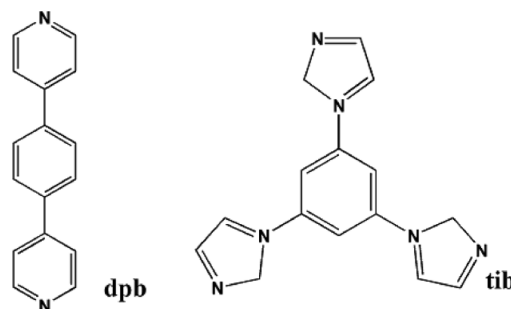
INTRODUCTION

The rational design and synthesis of novel metal–organic coordination polymers (MOPs) are currently of significant interest, not only due to their potential applications such as optoelectronic devices and microporous materials for catalysis and shape- and size-selective separations but also because of their enormous variety of interesting molecular architectures and topologies.¹ So far, the rapid growth of coordination chemistry and crystal engineering, has led to new and more complex types of topology being discovered, such as one-dimensional chains (helical chains, ladder, zigzag chain), two-dimensional sheets (4^4 -sq1, 6^3 -hcb, and $3^2 \cdot 6^2 \cdot 7^2$ -kgm nets), and three-dimensional structures (diamondoid, corundunoid, and chiral adamantoid network).² However, an accurate prediction of the overall crystal structure currently is almost impossible since many factors, such as the geometries of the ligand and metal ion and the reaction conditions, influence the final structure of a product.³ Accordingly, the main rational synthetic strategy has been focused on the use of a suitable organic ligand with certain features, such as flexibility, appropriate angles, and versatile binding modes, where the network topology can be controlled and modified by changing the chemical structure of the organic ligand.⁴ Bipyridine-type and imidazole-type ligands with N donors are convenient linkers to connect metal ions, and a series of one-, two-, and three-dimensional coordination architectures have been generated with them.⁵

As is known, some small anions such as formate and nitrate may play important roles in the formation of coordination polymers. Sometimes, this type of small anion can be considered as primary ligand, whereas other carboxylate- or

pyridine-based ligands act as secondary ligands. In this paper, we report two novel metal–organic coordination polymers, $\{[\text{Cd}_6(\text{dpb})_6(\text{HCOO})_8(\text{H}_2\text{O})_4] \cdot 4\text{NO}_3 \cdot 4\text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Cd}_4(\text{tib})_4(\text{H}_2\text{O})_4(\text{NO}_3)_6] \cdot 2\text{NO}_3\}_n$ (**2**) (dpb = 1,4-bis-(4-pyridyl)-benzene, tib = 1,3,5-tris(1-imidazolyl)benzene), based on small anions and arene core-based rigid N-containing ligands (Scheme 1). Complex **1** is based on a rigid 2D honeycomb layer involving formate ligands as the small bridging ligand, which is generated in situ from the hydrolysis of DMF. The linear dpb ligands as the pillars further connect the 2D layer to give a 3D structure with hexagonal cavities. In complex **2**, ligand tib as u_3 -bridging ligand combined with

Scheme 1. N-Containing Ligands Involved in This Work



Received: August 9, 2012

Revised: September 16, 2012

Published: September 19, 2012

octahedral Cd(II) ions produce 2D layers with an extremely rare (3,4) network that are interpenetrated in parallel fashion.

EXPERIMENTAL SECTION

Materials and General Methods. All the starting materials used were commercially available and used without further purification. Powder X-ray diffraction measurements were finished with a Bruker AXS D8 Advance to check the phase purity. Elemental analyses (for C, H, and N) were carried out on a PerkinElmer 240 elemental analyzer. The FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Bruker VERTEX-70 spectrometer using the KBr pellet method. Thermogravimetric analysis (TGA) experiments were performed using a PerkinElmer TGA 7 instrument (heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$; nitrogen stream). Photoluminescence spectra were measured on a F-280 fluorescence spectrophotometer (slit width = 5 nm; sensitivity, high).

Preparation of Complexes 1 and 2. $\{[\text{Cd}_6(\text{dpb})_6(\text{HCOO})_8(\text{H}_2\text{O})_4]\cdot 4\text{NO}_3\cdot 4\text{H}_2\text{O}\}_n$ (**1**). A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.016 mmol, 5 mg) and dpb (0.01 mmol, 3 mg) were dissolved in DMF/EtOH/ H_2O (1/1/1, v/v/v, 1 mL). Then the solution was sealed in a pressure-resistant glass tube, slowly heated to 90 $^{\circ}\text{C}$ from room temperature in 300 min, kept at 90 $^{\circ}\text{C}$ for 3000 min, and then slowly cooled to 30 $^{\circ}\text{C}$ in 600 min. The colorless rod crystals were collected and dried in the air. Yield: ca. 36% based on Cd. Elemental Anal. Calcd. for $\text{C}_{104}\text{H}_{120}\text{Cd}_6\text{N}_{16}\text{O}_{36}$: C 44.01, H 4.45, N 7.84%. Found: C 43.93, H 4.25, N 7.88%. Selected IR peaks (cm^{-1}): 3422(w), 1608(s), 1486(w), 1425(w), 1384(s), 1357(s), 1335(m), 1224(m), 1008(w), 797 (s), 737 (s), 579(m).

$\{[\text{Cd}_4(\text{tib})_4(\text{H}_2\text{O})_4(\text{NO}_3)_6]\cdot 2\text{NO}_3\}_n$ (**2**). A similar procedure as for the preparation of **1** was applied except that the N-containing ligand was replaced by tib. Colorless crystals of **2** were obtained in 39% yield based on Cd. Elemental Anal. Calcd. for $\text{C}_{60}\text{H}_{52}\text{Cd}_4\text{N}_{32}\text{O}_{28}$: C 34.30, H 2.64, N 21.18%. Found: C 34.04, H 2.47, N 21.14%. Selected IR peaks (cm^{-1}): 3426(w), 3113(w), 1620(s), 1511(s), 1384(s), 1256(s), 1142(m), 1075(s), 1013(w), 932(w), 877(w), 861(m), 837(m), 750(m), 684(m), 650(s).

X-ray Crystallography. Diffraction data for compounds **1** and **2** were collected with a Bruker APEX II CCD single-crystal X-ray diffractometer with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) source at 25 $^{\circ}\text{C}$. All absorption corrections were applied using the multiscan program SADABS.⁶ In both cases, the highest possible space group was chosen. All structures were solved by direct methods using the SHELXS-97⁷ program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL-97.⁸ All non-hydrogen atoms in the two structures were refined on F^2 with anisotropic displacement parameters. Crystallographic data and experimental details for structural analyses for **1** and **2** are summarized in Table S1 (Supporting Information), and selected bond lengths and bond angles are listed in Table S2 (Supporting Information).

RESULT AND DISCUSSION

Synthesis and General Characterization. All crystallizations of complexes **1** and **2** were obtained in the same reaction condition by hydro/solvothermal technology, which has been proven to be an effective and powerful method for the self-assembly of metal–organic frameworks.⁹ It is worth noting that under high pressure and temperature, DMF can hydrolyze to form formate ion.¹⁰ In this work, we selected DMF/EtOH/ H_2O (1/1/1, v/v/v) as solvent. Then, formate ligands in complex **1** are generated in situ from the hydrolysis of DMF.

Complexes **1** and **2** were characterized via X-ray powder diffraction (XRPD) at room temperature. As shown in the Figure S1 (Supporting Information), all the XRPD patterns measured for the as-synthesized samples were in good agreement with the XRPD patterns simulated from the respective single-crystal X-ray data using the Mercury 1.4 program, demonstrating the phase purity of the product. The

dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

Structure Descriptions. $\{[\text{Cd}_6(\text{dpb})_6(\text{HCOO})_8(\text{H}_2\text{O})_4]\cdot 4\text{NO}_3\cdot 4\text{H}_2\text{O}\}_n$ (**1**). X-ray single crystal structure analysis reveals that complex **1** is a pillar–layer complex, crystallizes in monoclinic $P2_1/n$ space group with an asymmetric unit contains one and a half Cd ions, one and a half dpb ligands, two coordinated formate molecules, one coordinated water molecule, one uncoordinated water molecule, and one nitrate ion. There are one and a half crystallographically independent cadmium ions (Cd1 and Cd2). Figure 1a illustrates the

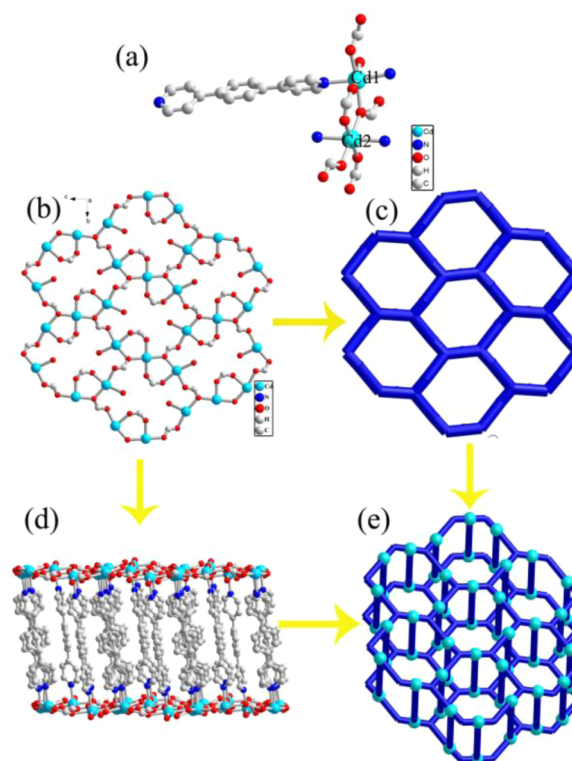


Figure 1. (a) The coordination environment of Cd(II) ions in **1** (hydrogen atoms omitted for clarity). (b) Ball-and-stick view of metal–formate 2D layer composed of hexagonal rings. (c) Honeycomb lattice for the title 2D layer. (d) Ball-and-stick view of 3D network. (e) 3D pillar–layer architecture of **1**. Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, y + 1/2, -z + 3/2$; (iii) $-x + 2, -y, -z + 2$; (iv) $x + 1, y, z$; (v) $-x + 2, y - 1/2, -z + 3/2$; (vi) $-x + 3, -y, -z + 2$.

coordination environments of the two Cd(II) ions. Cd1 is hexacoordinated in a distorted octahedral fashion, which is coordinated by three oxygen atoms from three formate ions and one oxygen atom from one water molecule with Cd–O distances of 2.09–2.16 Å, and the axial positions are occupied by two N atoms from two coordinated dpb ligands with an average Cd–N distance of 2.12 Å. The coordination bond lengths and angles around the Cd(II) ion are in good agreement with those typically observed (Table S2, Supporting Information).¹¹ Cd2 is similar to Cd1 and is hexacoordinated by four oxygen atoms from four different formate ligands and two N atoms from two dpb ligands, forming an octahedral coordination environment. As shown in Figure 1b, there are two types of formate ligands with different coordination modes: (a) one acts in bidentate bridging mode to link two cadmium ions; (b) the other one links three cadmium ions in a tridentate bridging mode. Apparently, in contrast with other small

multitopic ligands such as cyanide and azide, the formate anion has been observed to exhibit a large variety of bridging modes.¹²

Thus, Cd1 and Cd2 ions are connected by formate ligands to generate a 2D sheet structure that is composed of hexagonal rings, schematically represented in Figure 1b. The shortest Cd...Cd distance in the 2D layer is 4.608 Å. If the formate ligands with tridentate bridging mode are viewed as three-connected linkers, then the topological architecture type of the 2D layer is honeycomb (Figure 1c). As far as we know, this is the first example of a metal–formate honeycomb layer. The planar 2D honeycomb layers are further connected by the long dpb ligands to result in the formation of a 3D cationic framework, $[Cd_6(dpb)_6(HCOO)_8(H_2O)_4]_n$ (Figure 1d,e). In addition, as shown in Figure 2a, a hexagonal cavity exists in the

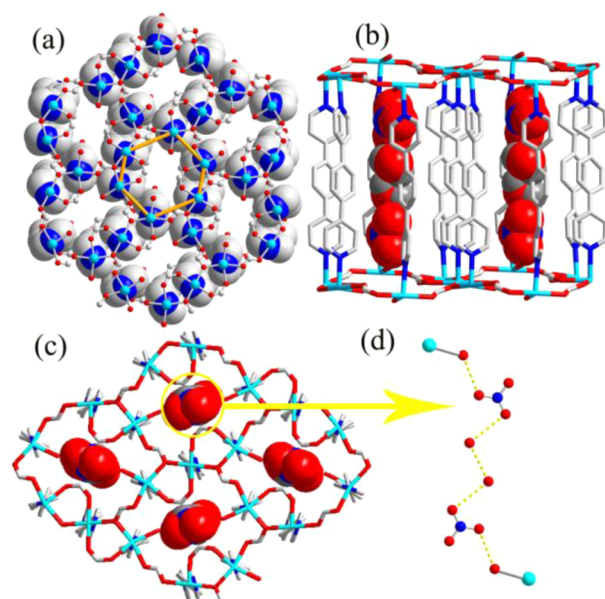


Figure 2. (a) Irregular cavity built from the hexagonal ring pillared by dpb ligand. (b, c) Inhabiting water molecules and nitrate ions in the channel along different directions. (d) The water molecules and nitrate ions of each cavity. Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, y + 1/2, -z + 3/2$; (iii) $-x + 2, -y, -z + 2$; (iv) $x + 1, y, z$; (v) $-x + 2, y - 1/2, -z + 3/2$; (vi) $-x + 3, -y, -z + 2$.

3D cationic framework. Unfortunately, the void space of the cavity is occupied in the crystal by water molecules and free nitrate ions, which break the porosity (Figure 2b,c). The water molecules and nitrate ions in each cavity (Figure 2d) of the framework show interesting characteristics. The distances between the neighboring oxygens in the monomers that form hydrogen bonds are O5–O6 2.765, O8–O9 2.944, and O9–O9a 2.745 Å. The solvent-accessible volume after the removal of uncoordinated solvents is 15.0%, obtained through an analysis using the PLATON software.

In complex **1**, we use dpb ligand as a linear ligand to coordinate with Cd(II) ions, providing a 3D pillar–layer framework with hexagonal cavities. However, if the ligand is replaced by the tripodal ligand, what kind of structure will result?

$\{[Cd_4(tib)_4(HCOO)_2(H_2O)_4(NO_3)_4] \cdot 2NO_3\}_n$ (**2**). Fortunately, when we used tib as the tripodal ligand to assemble with the Cd ions, complex **2** was obtained in good yield. Single-crystal X-ray diffraction study reveals that **2** contains a 2D interdigitated

architecture and crystallizes in the monoclinic $C2/c$ space group. The asymmetric unit consists of two halves of Cd ions, one tib ligand, one and half coordinated nitrate ions, one coordinated water molecule, and half of an uncoordinated nitrate ion. As shown in Figure 3a, both Cd1 and Cd2 centers

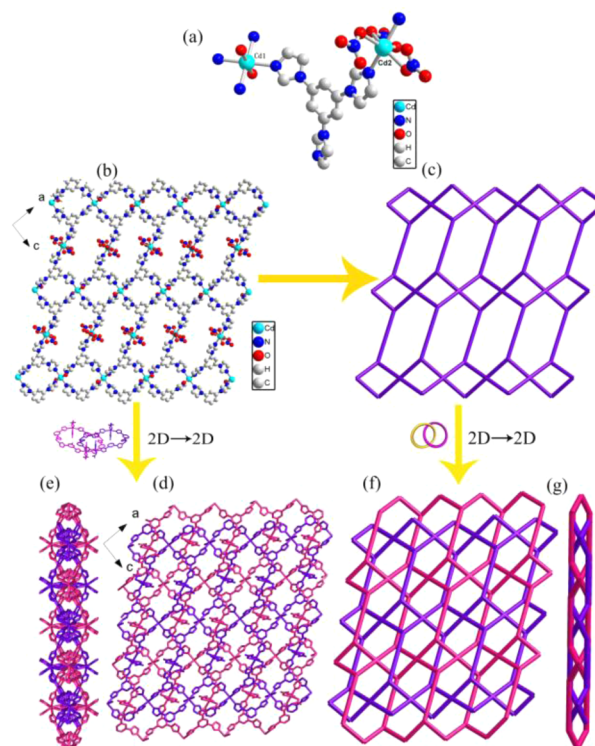


Figure 3. (a) The coordination environment of Cd(II) ions in **2** (hydrogen atoms omitted for clarity). (b) Ball-and-stick view of 2D layer composed of hexagonal rings. (c) View of the single (3,4) net. (d, e) stick views of the parallel 2-fold interpenetrating nets along the b -axis and c -axis. (f, g) top view and side view of 2-fold parallel interwoven (3,4) nets along b -axis and c -axis. Symmetry codes: (i) $-x + 1/2, -y + 1/2, -z$; (ii) $x + 1/2, -y + 1/2, z + 1/2$; (iii) $-x, y, -z - 1/2$; (iv) $-x - 1, y, -z + 1/2$; (v) $-x, y, -z + 1/2$.

adopt slightly distorted octahedral geometries. The Cd1 center is coordinated by four nitrogen atoms of imidazole from four different tib ligands (Cd–N 2.275(4)–2.338(4) Å) with the coordination angles are varying from $87.50(15)^\circ$ to $180.0(2)^\circ$ and two oxygen atoms of H_2O molecules (Cd–O 2.413(4) Å); while the Cd2 center is coordinated by two nitrogen atoms from two tib ligands (Cd–N 2.273(4) Å) and four oxygen atoms from three nitrate ions (Cd–O 2.345(4)–2.499(5) Å). The coordination modes of nitrate ions in **2** are bidentate chelating and monodentate bridging coordination modes. Different with some complexes based on tib reported by Sun et al.,^{13,14} in which each tib ligand coordinates to metal ions with two imidazole groups, in complex **2**, the third imidazole group of the tib ligand also participates in the coordination. In other words, the tib ligand in **2** acts as a three-connected ligand, which is similar to the previously reported complex $[Ag(tib)]ClO_4$ obtained by reaction of $[Ag(Py)_2]ClO_4$ with tib ligand.¹⁴ The three imidazole ring planes of tib ligand in **2** are not parallel to the central benzene ring at the dihedral angles of 21.54° , 35.4° , and 31.08° .

Three Cd atoms in **2** are bridged by one tib ligand into a 2D network structure with two kinds of windows along the b -axis

(Figure 3b). In order to separate the two different windows distinctly, they are named A and B. In A, two Cd1 atoms and two molecules of ligand tib form a 20-membered macrocyclic ring with a Cd...Cd distance of 10.314 Å, while four tib ligands, each using two arms, link four Cd atoms form a 40-membered macrocyclic ring in B.

In **2**, if tib can be considered as a μ_3 -bridge connector, Cd2 centers can be regarded as four-connected nodes. Thus a structural feature in **2** can be represented as a (3,4)-connected 2-nodal net, and windows A and B can be simplified as two types of macrometallacyclic arrays (quadrilateral grid and hexagonal ring), as shown in Figure 3c. The quadrilateral grids form a line through a common vertex and hexagonal rings are linked by sharing an edge, then the two types of arrays are arranged alternately. Therefore, the short Schläfli vertex notation of the net can be represented as indicated $\{4.6^2\}_2\{4^2.6^2.8^2\}$ by TOPOS software.¹⁵ As we know, the most common topologies of 2D coordination networks are square lattice,¹⁶ honeycomb,¹⁷ hexagonal lattice,¹⁸ kagomé dual,¹⁹ kagomé,²⁰ and so on. Nevertheless, coordination polymers having the topology of **2** are extremely rare.

In contrast to the frequent occurrence of network interpenetrating in coordination polymers with (6,3) and (4,4) topology,²¹ the interpenetration of $\{4.6^2\}_2\{4^2.6^2.8^2\}$ networks are not reported yet. It is well-known that when coordination polymeric complexes with large holes, the structures usually interpenetrate in order to satisfy close-packing.²² In this case, the hexagonal ring is sufficiently large and quite corrugated, which allows the other layer to interpenetrate it through Hopf links, still making an infinite 2D network structure (Figures 2d–g). These interlocked double sheets (pink and purple) are packed in a parallel fashion.

Structural Diversities. As far as compounds **1** and **2** are concerned, the same metal ions but different ligands combination are used. From the structural descriptions above, it can be seen that the N-donor ligands are also critical factors in the construction of various structures. In this work, two kinds of the arene core-based rigid N-containing ligands, namely, dpb and tib, to observe their effect on the assembly of the coordination compounds. Compared with dpb, which is a linear bidentate bipyridine-type ligand, tib is a tripodal tridentate imidazole-type ligand. Ligand dpb acting as pillar in **1** leads to a highly unusual 2D sheet structure, which makes it show a 3D pillar-layered framework. However, as a tripodal rigid ligand, tib connected 2D layers to form a 3D structure is unrealistic. For **2**, cadmium complex exhibits 2D (3,4) grids with mononuclear cadmium as node on the control of the tib ligand. Apparently, these analyses above forcefully demonstrate that the selection of organic ligands can mediate or even satisfy the coordination needs of the metal center and further generate more meaningful architectures.

Thermal Analysis. The thermogravimetric (TG) analyses of the title compound **1** and **2** under N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ were investigated in the temperature range of 30–600 $^\circ\text{C}$ and the TG curves are shown in Figure S3, Supporting Information. The TGA curve of **1** displays a weight loss of 67.3% at 30–349 $^\circ\text{C}$, which corresponds to the loss of lattice water molecules and nitrate anion and coordinated water and dpb ligands. Then, the metal-formate layer is decomposed starting at 500 $^\circ\text{C}$. The TGA curve of complex **2** shows a first weight loss of 3.543% at 90–130 $^\circ\text{C}$, corresponding to the loss of coordinated water molecules. The dehydrated framework is stable to 405 $^\circ\text{C}$, and

then the framework begins to collapse, accompanying the release of organic ligands.

Photoluminescence Properties. The photoluminescence spectra of the free ligands and complexes **1** and **2** were investigated at room temperature, as depicted in Figure 4. The

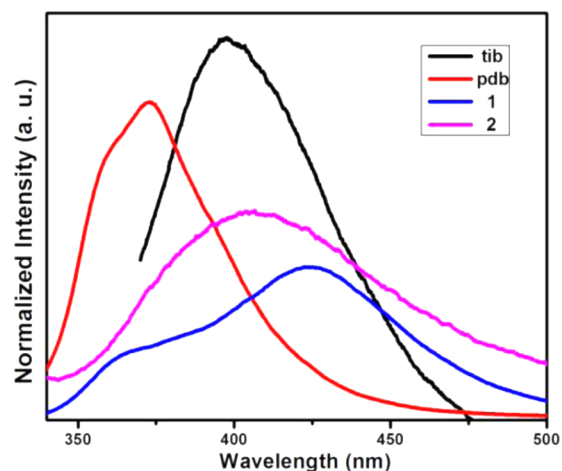


Figure 4. Photoluminescences of free ligands and complexes **1** and **2**.

free ligands dpb and tib display photoluminescence with emission maxima at 372 and 397.4 nm upon 300 nm excitation, respectively. It can be assumed that these peaks derive from the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. The emission spectra for Cd(II)-containing compounds exhibit emission peaks at 424 nm for **1** ($\lambda_{\text{ex}} = 300$ nm), and 407 nm for **2** ($\lambda_{\text{ex}} = 330$ nm), respectively. These emissions are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer, because the Cd(II) ion is difficult to oxidize or to reduce due to its d^{10} electronic configuration.²³ Thus, the photoluminescence can be assigned to intraligand (IL) and ligand-to-ligand charge transfer (LLCT) emissions. Compared with the dpb ligand, a red shift of 52 nm for **1** is observed, which is considered to originate from the influence of the coordination of the ligand to the metal centers.²⁴

CONCLUSIONS

In conclusion, two novel cadmium coordination polymers (**1** and **2**) based on small anions and N-containing ligands have been synthesized and characterized, and complex **2** possesses a rare example of topology systems. They show diverse structures and dimensionalities by changing from a three-dimensional pillar-layer complex to 2D \rightarrow 2D parallel interpenetrated structure. The changes of structure result from the different bridging abilities of small anions and structures of the arene core-based rigid N-containing ligands, as well as the adaptable coordination spheres of Cd(II). In addition, such complexes display modest thermal stability and strong solid-state fluorescent emission.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, tables of crystal data and bond distances and angles, powder X-ray diffraction (PXRD) patterns, TGA, and IR spectra for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dfsun@sdu.edu.cn. Fax: +86-531-88364218.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSFC (Grant No. 90922014), the Shandong Natural Science Fund for Distinguished Young Scholars (Grant JQ201003), the NSF of Shandong Province (Grant BS2009L007), and Independent Innovation Foundation of Shandong University (Grants 2010JQ011 and 2011GN030).

REFERENCES

- (1) (a) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. (b) Zhang, J.-P.; Chen, X.-M. *J. Am. Chem. Soc.* **2009**, *131*, 5516. (c) Inoue, K.; Imai, H.; Ghalsasi, P. S.; Kikuchi, K.; Ohba, M.; Okawa, H.; Yakhmi, J. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 4242. (d) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103. (e) Robson, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (f) Zaworotko, M. J.; Moulton, B. *Chem. Rev.* **2001**, *101*, 1629. (g) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (h) Rowsell, J. L. C.; Yaghi, O. M.; Chen, B. L.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4647. (i) Hou, L.; Lin, Y.-Y.; Chen, X.-M. *Inorg. Chem.* **2008**, *47*, 1346. (j) Dybtsev, D. N.; Nu zhdin, A. L.; Chun, H.; Brylia kov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 916. (k) Yuan, D. Q.; Zhao, D.; Sun, D. F.; Zhou, H. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357. (l) Sun, D. F.; Ma, S. Q.; Ke, Y. X.; Collins, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (m) Moulton, B.; Zaworotko, M. J. *Chem Rev* **2001**, *101*, 1629.
- (2) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Li, X.-J.; Jiang, F.-L.; Wu, M.-Y.; Zhang, S.-Q.; Zhou, Y.-F.; Hong, M.-C. *Inorg. Chem.* **2012**, *51*, 4116. (c) Zhang, Z.-M.; Yao, S.; Li, Y.-G.; Lu, Y.; Su, Z.-M.; Wang, E.-B. *J. Am. Chem. Soc.* **2009**, *131*, 14600. (d) Cui, Y.; Lee, L. J.; Lin, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 6014. (e) Wang, R. H.; Han, L.; Xu, L. J.; Gong, Y. Q.; Yuan, D. Q.; Hong, M. C. *J. Mol. Struct.* **2004**, *694*, 79. (f) Qi, Y.; Che, Y.-X.; Batten, S. R.; Zheng, J.-M. *CrystEngComm* **2008**, *10*, 1027. (g) Sun, D.; Luo, G. G.; Xu, Q. J.; Zhang, N.; Jin, Y. C.; Zhao, H. X.; Lin, L. R.; Huang, R. B.; Zheng, L. S. *Inorg. Chem. Commun.* **2009**, *12*, 782. (h) Zhang, J.; Chen, Y.-B.; Chen, S.-M.; Li, Z.-J.; Cheng, J.-K.; Yao, Y.-G. *Inorg. Chem.* **2006**, *45*, 3161. (i) Sun, D.; Zhang, N.; Huang, R. B.; Zheng, L. S. *Cryst. Growth Des.* **2010**, *10*, 3699. (g) Jiang, J. J.; Li, X. P.; Zhang, X. L.; Kang, B. S.; Su, C. Y. *CrystEngComm* **2005**, *7*, 603. (k) Cui, P.; Wu, J.; Zhao, X.; Sun, D.; Zhang, L.; Guo, J.; Sun, D. *Cryst. Growth Des.* **2011**, *11*, 5182. (l) Du, m.; Bu, X. H.; Guo, Y. M.; Liu, H. *Inorg. Chem.* **2002**, *41*, 4904. (m) Sudik, A. C.; Cote, A. P.; Yagh, O. M. *Nature* **1999**, *402*, 276. (n) Sun, D.; Collins, D. J.; Ke, Y.; Zuo, J. L.; Zhou, H. C. *Chem.—Eur. J.* **2006**, *12*, 3768.
- (3) (a) Lang, J. P.; Xu, Q. F.; Yuan, R. X.; Abrahams, B. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4741. (b) Chiang, L. M.; Yeh, C. W.; Chan, Z. K.; Wang, K. M.; Chou, Y. C.; Chen, J. D.; Wang, J. C.; Lai, J. Y. *Cryst. Growth Des.* **2008**, *8*, 470. (c) Rispens, M. T.; Meetsma, A.; Rittberger, R.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Chem. Commun.* **2003**, *5*, 2116. (d) Chen, Y.; Li, H. X.; Liu, D.; Liu, L.; Li, N. Y.; Ye, H. Y.; Zhang, Y.; Lang, J. P. *Cryst. Growth Des.* **2008**, *8*, 3810. (e) Lan, Y.-Q.; Li, S.-L.; Wang, X.-L.; Shao, K.-Z.; Su, Z.-M.; Wang, E.-B. *Inorg. Chem.* **2008**, *47*, 529. (f) Stover, A. K.; Gutnick, J. R.; Sarjeant, A. N.; Norquist, A. J. *Inorg. Chem.* **2007**, *46*, 4389.
- (4) (a) Peng, R.; Li, D.; Wu, T.; Zhou, X. P.; Ng, S. W. *Inorg. Chem.* **2006**, *45*, 4035. (b) Zhang, Z. H.; Okamura, T.; Hasegawa, Y.; Kawaguchi, H.; Kong, L. Y. *Inorg. Chem.* **2005**, *44*, 6219. (c) Dong, Y. B.; Jiang, Y. Y.; Li, J.; Ma, J. P.; Liu, f. L.; Tang, B.; Huang, R. Q.; Britten, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 4520. (d) Ma, Y.; Cheng, A. L.; Gao, E. Q. *Cryst. Growth Des.* **2010**, *10*, 2832. (e) Ma, L. Q.; Jin, A.; Xie, Z. G.; Lin, W. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9905.
- (5) (a) Fan, J.; Gan, L.; Kawaguchi, H.; Sun, W.-Y.; Yu, K.-B.; Tang, W.-X. *Chem.—Eur. J.* **2003**, *9*, 3965. (b) Chen, S.-S.; Zhao, Y.; Fan, J.; Okamura, T.; Bai, Z.-S.; Chen, Z.-H.; Sun, W.-Y. *CrystEngComm* **2012**, *14*, 3564. (c) Gardner, G. B.; Ventakaraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792. (d) Takaoka, K.; Kawano, M.; Hozumi, T.; Ohkoshi, S.; Fujita, M. *Inorg. Chem.* **2006**, *45*, 3976. (e) Osuga, T.; Murase, T.; Ono, K.; Yamauchi, Y.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 15553. (f) Zhang, L.-P.; Ma, J.-F.; Pang, Y.-Y.; Ma, J.-C.; Yang, J. *CrystEngComm* **2010**, *12*, 4433.
- (6) Sheldrick, G. M. SADABS; University of Göttingen: Germany, 1996.
- (7) Sheldrick, G. M. SHELXS-97, Program for X-ray Crystal Structure Determination, University of Göttingen: Germany, 1997.
- (8) Sheldrick, G. M. SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen: Germany, 1997.
- (9) (a) Gutschke, S. O. H.; Molinier, M.; Powell, A. K.; Winpenny, R. E. P.; Wood, P. T. *Chem. Commun.* **1996**, *7*, 823–824. (b) Wang, Z.; Tanabe, K. K.; Cohen, S. M. *Inorg. Chem.* **2008**, *48*, 296–306.
- (10) (a) Dai, F.; Cui, P.; Ye, F.; Sun, D. *Cryst. Growth Des.* **2010**, *10*, 1474. (b) Xie, L. H.; Liu, S. X.; Gao, B.; Zhang, C. D.; Sun, C. Y.; Li, D. H.; Su, Z. M. *Chem. Commun.* **2005**, 2402. (c) Chen, W.; Wang, J.-Y.; Chen, C.; Yue, Q.; Yuan, H.-M.; Chen, J.-S.; Wang, S.-N. *Inorg. Chem.* **2003**, *42*, 944.
- (11) (a) Li, B.; Peng, Y.; Li, B.; Zhang, Y. *Chem. Commun.* **2005**, 2333. (b) Cheng, J.-Y.; Dong, Y.-B.; Huang, R.-Q.; Smith, M. D. *Inorg. Chim. Acta* **2005**, *358*, 891. (c) Wang, R.; Han, L.; Jiang, F.; Zhou, Y.; Yuan, D.; Hong, M. *Cryst. Growth. Des.* **2005**, *5*, 129. (d) Evans, O. R.; Lin, W. *Inorg. Chem.* **2000**, *39*, 2189.
- (12) (a) Kaneko, W.; Kitagawa, S.; Ohba, M. *J. Am. Chem. Soc.* **2007**, *129*, 248. (b) Inoue, K.; Kikuchi, K.; Ohba, M.; Ohkawa, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4810. (c) Liu, T. F.; Fu, D.; Gao, S.; Zhang, Y. Z.; Sun, H. L.; Su, G.; Liu, Y. J. *J. Am. Chem. Soc.* **2003**, *125*, 13976. (d) Zhang, X.-M.; Wang, Y.-Q.; Song, Y.; Gao, E.-Q. *Inorg. Chem.* **2011**, *50*, 7284.
- (13) (a) Zhao, W.; Fan, J.; Okamura, T.; Sun, W.-Y.; Ueyama, N. *Microporous Mesoporous Mater.* **2005**, *78*, 265. (b) Fan, J.; Gan, L.; Kawaguchi, H.; Sun, W.-Y.; Yu, K.-B.; Tang, W.-X. *Chem.—Eur. J.* **2003**, *9*, 3965.
- (14) Fan, J.; Sun, W.-Y.; Kawaguchi, H.; Ueyama, N. *Inorg. Chem.* **2003**, *42*, 3168.
- (15) Blatov, V. A. *IUCr CompComm Newsl.* **2006**, *7*, 4. See also <http://www.topos.ssu.samara.ru>.
- (16) (a) Thirumurugan, A.; Li, W.; Cheetham, A. K. *Dalton Trans.* **2012**, *14*, 4126. (b) Sun, D.; Zhang, N.; Huang, R.-B.; Zheng, L.-S. *Cryst. Growth Des.* **2010**, *10*, 3699. (c) Liu, X.-M.; Lin, R.-B.; Zhang, J.-P.; Chen, X.-M. *Inorg. Chem.* **2012**, *51*, 5686. (d) Yang, G.; Duan, P.-C.; Shi, K.-G.; Raptis, R. G. *Cryst. Growth Des.* **2012**, *12*, 1882.
- (17) (a) Chen, M.; Lu, Y.; Fan, J.; Lv, G.-C.; Zhao, Y.; Zhang, Y.; Sun, W.-Y. *CrystEngComm* **2012**, *14*, 2015. (b) Yaghi, O. M.; Li, G. *Angew. Chem.* **1995**, *107*, 232; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. (c) Jiang, T.; Zhang, X.-M. *Cryst. Growth Des.* **2008**, *8*, 3077. (d) Chen, S.-S.; Chen, Z.-H.; Fan, J.; Okamura, T.; Bai, Z.-S.; Lv, M.-F.; Sun, W.-Y. *Cryst. Growth Des.* **2012**, *12*, 2315. (e) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.
- (18) (a) Pan, Z.; Xu, J.; Zheng, H.; Huang, K.; Li, Y.; Guo, Z.; Batten, S. R. *Inorg. Chem.* **2009**, *48*, 5772. (b) Gould, J. A.; Bacsa, J.; Park, H.; Claridge, J. B.; Fogg, A. M.; Ramanathan, V.; Warren, J. E.; Rosseinsky, M. J. *Cryst. Growth Des.* **2010**, *10*, 2977. (c) Chen, H.; Xiao, D.; He, J.; Li, Z.; Zhang, G.; Sun, D.; Yuan, R.; Wang, E.; Luo, Q.-L. *CrystEngComm* **2011**, *13*, 4988. (d) Zhang, X.; Huang, Y.-Y.; Cheng, J.-K.; Yao, Y.-G.; Zhang, J.; Wang, F. *CrystEngComm* **2012**, *14*, 4843.
- (19) (a) Zhong, D.-C.; Lu, W.-G.; Jiang, L.; Jiang, X.-L.; Lu, T.-B. *Cryst. Growth Des.* **2010**, *10*, 739. (b) Liu, S.-J.; Xue, L.; Hu, T.-L.; Bu, X.-H. *Dalton Trans.* **2012**, *41*, 6813. (c) Fujita, W.; Awaga, K.; Yokoyama, T. *Inorg. Chem.* **1997**, *36*, 196. (d) Cao, X.-Y.; Zhang, J.; Li, Z.-J.; Cheng, J.-K.; Yao, Y.-G. *CrystEngComm* **2007**, *9*, 806.
- (20) (a) Eubank, J. F.; Wojtas, L.; Hight, M. R.; Bousquet, T.; Kravtsov, V. C.; Eddaoudi, M. *J. Am. Chem. Soc.* **2011**, *133*, 17532.

(b) Perry, J. J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2004**, 2534. (c) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. *Inorg. Chem.* **2003**, *42*, 5459. (d) Li, Y. L.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 7266.

(21) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Batten, S. R.; Hoskins, B. F.; Robson, R. *New J. Chem.* **1998**, 173. (c) Sun, Q.; Wang, Y.-Q.; Cheng, A.-L.; Wang, K.; Gao, E.-Q. *Cryst. Growth Des.* **2012**, *12*, 2234. (d) Chen, L.; Tan, K.; Lan, Y.-Q.; Li, S.-L.; Shao, K.-Z.; Su, Z.-M. *Chem. Commun.* **2012**, *42*, 5919. (e) Zhang, X. L.; Guo, C. P.; Yang, Q. Y.; Wang, W.; Liu, W. S.; Kang, B. S.; Su, C. Y. *Chem. Commun.* **2007**, 4242.

(22) (a) Bureekaew, S.; Sato, H.; Matsuda, R.; Kubota, Y.; Hirose, R.; Kim, J.; Kato, K.; Takata, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7660. (b) Nattinen, K. I.; Rissanen, K. *Inorg. Chem.* **2003**, *42*, 5126. (c) Zhang, J.; Wojtas, L.; Larsen, R. W.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 17040. (d) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2010**, *1*, 695. (e) Xu, B.; Lv, J.; Cao, R. *Cryst. Growth Des.* **2009**, *9*, 3003.

(23) Ji, C.-C.; Qin, L.; Li, Y.-Z.; Guo, Z.-J.; Zheng, H.-G. *Cryst. Growth Des.* **2011**, *11*, 480.

(24) (a) Wen, L.; Lu, Z.; Lin, J.; Tian, Z.; Zhu, H.; Meng, Q. *Cryst. Growth Des.* **2007**, *7*, 93. (b) Lin, J.-G.; Zang, S.-Q.; Tian, Z.-F.; Li, Y.-Z.; Xu, Y.-Y.; Zhu, H.-Z.; Meng, Q.-J. *CrystEngComm* **2007**, *9*, 915. (c) Wen, L.; Li, Y.; Lu, Z.; Lin, J.; Duan, C.; Meng, Q. *Cryst. Growth Des.* **2006**, *6*, 530. (d) Zhao, X.; Wang, X.; Sun, D.; Sun, D. *Cryst. Growth Des.* **2012**, *12*, 2736.