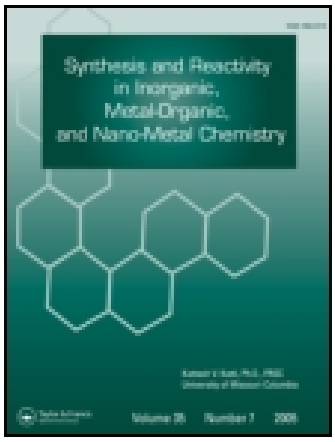

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A Novel 2D Tubular Polymer Based on Flexible Bis-Methylbenzimidazole Ligand

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A novel metal-organic polymer [Cd(bmb)(p-bdc)]$_n$ (1) (bmb = (1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene); p-H_2bdc = p-benzenedicarboxylic acid) has been hydrothermally synthesized and structural characterized. Crystal data: 1, monoclinic, space group *C*2/*c*, $a = 22.786(5)$ Å, $b = 15.712(3)$ Å, $c = 18.305(4)$ Å, $\beta = 18.305(4)°$, $Z = 4$. Polymer 1 exhibits a 2D puckered layer structure with two different elongated tubular channels. In addition, the thermal stability, PXRD pattern, and photoluminescence properties of 1 in the solid state have also been investigated.

Keywords flexible, photoluminescence, tubular channel

INTRODUCTION

During the past decades, intense interest has been focused on the design and synthesis functional metal-organic frameworks (MOFs) owing to their variety of intriguing topologies[1] and potential applications in the areas of anion/guest exchange,[2] catalysis,[3] magnetism,[4] luminescence,[5] and gas storage.[6] Up to now, many researches demonstrate that using mixed organic ligands, especially the mixed polycarboxylate and N-containing ones, with more tunable factors, are good strategies for the construction of novel MOFs.[7] However, unfortunately, it is difficult to get their mixed-ligand complexes for some excellent candidate ligands, such as 1,4-bis(benzimidazol-1-ylmethyl) benzene (bbb).[8] So, it is very necessay to make some modifictions of such ligands and enhance their cooperative coordination abilities with organic carboxylic acids. With this understanding, we introduce substituent methyl to the 2-position of benzimidazole ring, which would greatly enhance the donated-electrons ability of the ligand. We anticipate that the novel ligand 1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene (bmb) would have good cooperative coordination abilities with polycarboxylate. In addition, bmb with a rigid spacer of phenyl ring and two freely rotating methylbenzimidazol arms can freely rotate to form diverse conformations and meet the requirement of coordination geometries of metal ions.[9] In view of the characters, bmb has the potential to produce unique structural motifs with beautiful channels or cavities.

In this work, by introducing p-benzenedicarboxylic acid into the Cd(II)-bmb hydrothermal synthesis process, a 2D polymer [Cd(bmb)(p-bdc)]$_n$ (**1**) with different tubular channels was obtained. Thermal analysis indicates that polymer **1** is stabile up to 324°C. Moreover, an intense fluorescent emission bond is obtained at 441 nm for **1**.

EXPERIMENTAL

Materials and Physical Measurements

All reagents and solvents were commercially available except for bmb, which was synthesized according to the literature.[10] The FT-IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Bruker Tensor 27 spectrophotometer (Germany). Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer (USA). PXRD patterns were recorded using Cu Kα1 radiation on a PANalytical X'Pert PRO diffractometer (USA). Thermal analyses were performed on a Netzsch STA 449C thermal analyzer (Germany) from room temperature at a heating rate of 10°C min^{-1} in air. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-4500 Fluorescence Spectrophotometer (Japan). The excitation slit and the emission slit were 2.5 nm.

Synthesis of [Cd(bmb)(p-bdc)]$_n$ (1)

A mixture of $Cd(NO_3)\cdot 4H_2O$ (61.7 mg,0.2mmol), p-H_2bdc (33.2 mg, 0.2 mmol), NaOH (8.0 mg, 0.2 mmol), and bmb (36.6 mg, 0.1 mmol) in 10 mL distilled H_2O was sealed in a 25 mL Teflon-lined stainless steel container and heated at 160°C for 4 days. After the mixture cooled to room temperature at a rate of 5°C/h, colorless block crystals of **1** were obtained with a

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TABLE 1
Crystallographic data for **1**[a]

	1
Formula	$C_{32}H_{26}CdN_4O_4$
Formula mass	642.97
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	22.786(5)
b (Å)	15.712(3)
c (Å)	18.305(4)
α (°)	90
β (°)	119.13(3)
γ (°)	90
V (Å^3)	5724(12)
Z	4
D_{calcd}.(g·cm^{-3})	1.492
μ (mm^{-1})	0.807
F(000)	2608.0
θ (°)	1.65–25.00
Data / restraints / parameters	5040 / 0 / 372
GOF	1.088
R_1 (I >2sigma(I))	0.0352
wR_2 (I >2sigma(I))	0.0839

[a]$R_1 = \sum \| F_0 | - | F_c \| / \sum | F_0 |$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

yield of 25% (based on Cd). Anal. Calcd. For $C_{32}H_{26}N_4O_4Cd$ (%): C, 59.77; H, 4.08; N, 8.71. Found: C, 59.59; H, 3.92; N, 8.57. IR (KBr, cm^{-1}): 3440(m), 2924(w), 2853(w), 1562(s), 1509(m), 1475(w), 1456(m), 1382(s), 1290(m), 1258(w), 1223(w), 1159(w), 1015(m), 991(w), 8369s), 751(s), 739(m), 527(m), 474(w), 431(w).

Crystallographic Data Collection and Structure Determination

The data of polymer **1** was collected on a Rigaku Saturn 724 CCD diffractometer (Japan) (Mo-$K\alpha$, $\lambda = 0.71073$ Å) at temperature of 20 ± 1°C. Absorption corrections were applied by using multiscan program. The data was corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package (Germany).[11] The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for **1** is summarized in Table 1. Selected bond lengths and bond angles of **1** are listed in Table 2.

RESULTS AND DISCUSSION

Crystal Structure of [Cd(bmb)(p-bdc)]$_n$ (1)

Single-crystal X-ray analysis reveals that polymer **1** crystallizes in the monoclinic C2/c space group, which consists of two half bmb, one p-bdc^{2-}, and one Cd(II) ion in the asymmetric unit. As shown in Figure 1, the center Cd(II) ion is six-coordinated in a badly distorted octahedral geometry, ligated by four oxygen atoms (O1, O2, O3, and O4) from two symmetry-related p-bdc^{2-} and two nitrogen atoms (N1, N4) from two distinct bmb. The Cd-O bond lengths vary from 2.242(2) to 2.572(2) Å, while the Cd-N bond lengths are 2.247(2) and 2.344(2) Å, which are in the normal range.[12] The p-bdc^{2-}anion with bi-chelate mode bridges adjacent Cd(II) ions to form a common zigzag chain, which is further linked by bmb to generate a 2D puckered network (Figure 2). Interestingly, viewing from the *c*-axis, the 2D layer shows two kinds of tubular channel, elongated into different directions (Figure 3). Further investigation indicates that it is due to the various conformations of bmb. In **1**, bmb exhibits two different *cis*-conformations. One adopts a $N_{donor}\cdots N\text{-}C_{sp3}\cdots C_{sp3}$ torsion angle of 73.45° and neighboring Cd/p-bdc zigzag chains are associated together by this type of

TABLE 2
Selected bond lengths (Å) and angles (°) for **1**

Cd(1)-O(2)	2.240(2)	Cd(1)-N(4)	2.247(2)
Cd(1)-O(3)#4	2.288(2)	Cd(1)-N(1)	2.344(3)
Cd(1)-O(4)#4	2.386(2)	Cd(1)-O(1)	2.572(2)
O(2)-Cd(1)-N(4)	104.99(8)	N(1)-Cd(1)-O(4)#4	113.84(10)
O(2)-Cd(1)-O(3)#4	104.18(9)	O(2)-Cd(1)-O(1)	54.05(8)
N(4)-Cd(1)-O(3)#4	147.93(9)	N(4)-Cd(1)-O(1)	98.07(9)
O(2)-Cd(1)-N(1)	95.35(9)	O(3)#4-Cd(1)-O(1)	88.41(9)
N(4)-Cd(1)-N(1)	94.32(9)	N(1)-Cd(1)-O(1)	149.05(8)
O(3)#4-Cd(1)-N(1)	95.96(9)	O(4)#4-Cd(1)-O(1)	93.92(9)
O(2)-Cd(1)-O(4)#4	144.87(10)	O(3)#4-Cd(1)-O(4)#4	55.73(9)
N(4)-Cd(1)-O(4)#4	92.37(9)		

Symmetry transformations used to generate equivalent atoms: #1 −x, y, −z + 1/2, #4 x, −y + 1, z − 1/2.

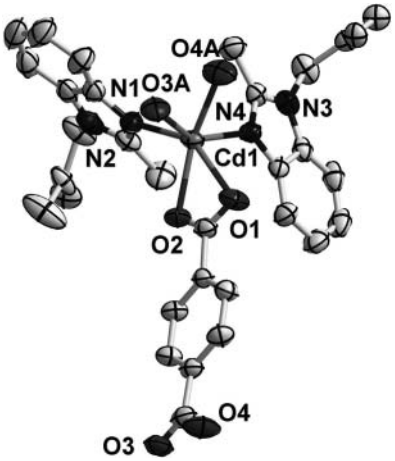

FIG. 1. The asymmetric unit of **1** with hydrogen atoms omitted for clarity. (thermal ellipsoids at 50% probability level). Symmetry codes: A x, $1-y$, $-0.5+z$.

bmb facing opposite directions alternatively to form the horizontally elongated tubular channel. By the same connection way, the other type of bmb with a bigger $N_{donor}\cdots N\text{-}C_{sp3}\cdots C_{sp3}$ torsion angle of 81.96° forms the vertically elongated tubular channel.

XRD patterns and thermal analyses

In order to confirm the phase purity of polymer **1**, the PXRD pattern was recorded for **1**, and it was comparable to the corresponding simulated one calculated from the single-crystal diffraction data (Figure 4), indicating a pure phase of bulky sample.

The thermal stability of **1** was also estimated. As shown in Figure 5, no obvious weight loss is observed for anhydrous polymer **1** until the decomposition of the framework occurs at 324°C. The sharp weight loss (26.38%) attributes to the combustion of p-bdc^{2-} (calcd.: 25.51%) accompanied by the initial breakdown of the organic moieties ranging from 324°C to 360°C. Then bmb starts to loss until 580°C. The final products CdO (20.70%, calcd.: 19.97%) are obtained.

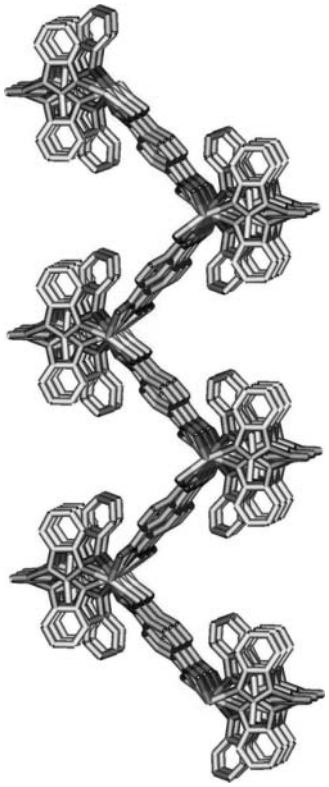

FIG. 2. The 1D Cd/p-bdc^{2-} zigzag chains are linked by bmb to generate a 2D puckered network.

Photoluminescence properties

Coordination polymers with d^{10} metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and

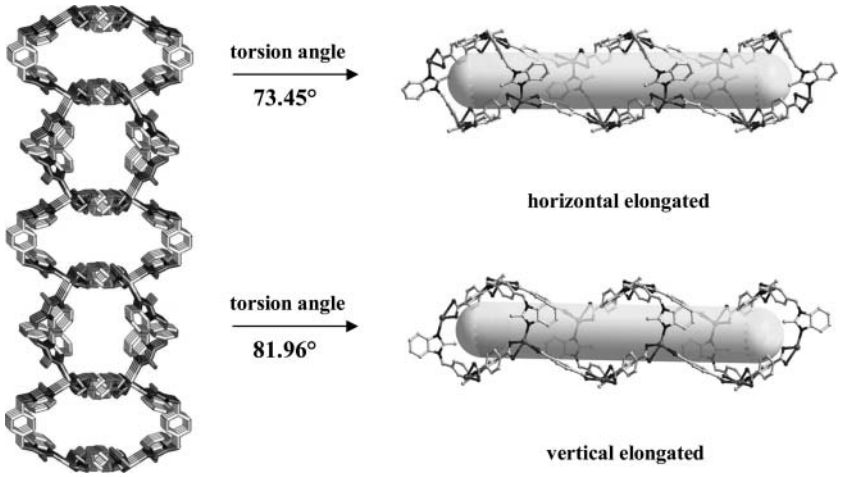

FIG. 3. Viewing from the c-axis, the 2D layer of **1** shows two kinds of tubular channel, elongated into different directions.

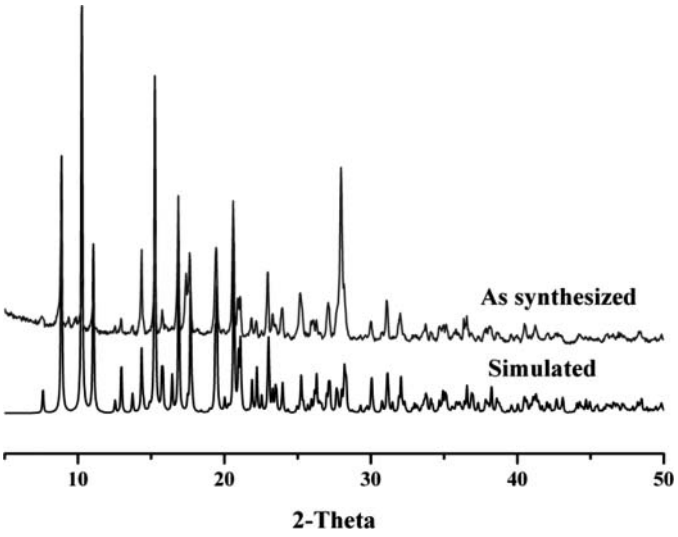

FIG. 4. Experimental and simulated PXRD patterns of polymer **1**.

photochemistry.[13] Hence, the solid-state photoluminescence properties of Cd(II) polymer **1**, together with the free bmb ligand and p-H_2bdc, were investigated at room temperature. As shown in Figure 6, polymer **1,** free ligands p-H_2bdc and bmb show intense emission bands at 441 nm ($\lambda_{ex} = 336$ nm), 383 nm ($\lambda_{ex} = 314$ nm), and 309 nm ($\lambda_{ex} = 293$ nm), respectively. Obviously, the emission band of **1** is likely to that of p-H_2bdc, but with a large red-shift more than 100 nm. So, such broad band of **1** may be tentatively assigned to ligand(p-H_2bdc)-to-metal charge transfer (LMCT) as reported for other d^{10} metal polymers.[14] In addition, further investigation indicates that the fluorescent intensity of **1** decrease compared with the corresponding ligands p-H_2bdc. It may be attributed to ligand coordination to the metal center, which reduce the rigidity of the ligand, and enhance the loss of energy by radiationless decay.[15]

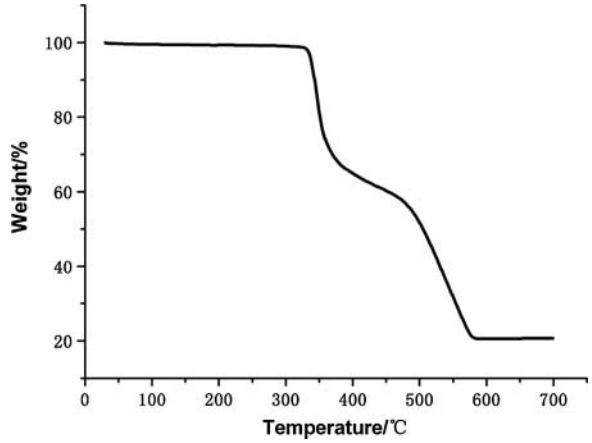

FIG. 5. TGA curve of polymer **1**.

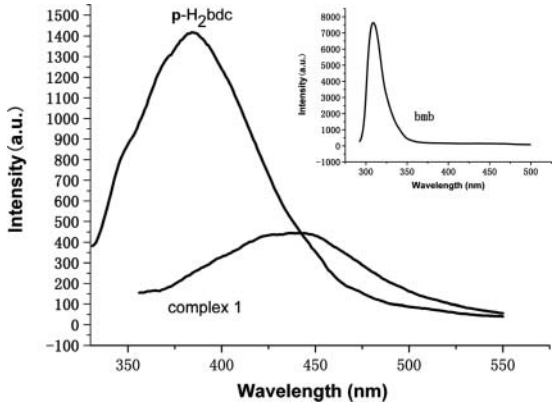

FIG. 6. Photoluminescence of free ligands and polymer **1**.

CONCLUSION

In summary, a 2D fluorescent polymer $[Cd(bmb)(p\text{-}bdc)]_n$ (**1**) has been synthesized under the hydrothermal reaction condition. In **1**, flexible bmb shows two kinds of *cis*-conformations with different $N_{donor}\cdots N\text{-}C_{sp3}\cdots C_{sp3}$ torsion angles, which lead to the formation of two different elongated tubular channels. Photoluminescence investigation reveals that a large red-shift more than 100 nm of **1** takes place, compared with p-benzenedicarboxylic acid, and it can be assigned to LMCT.

SUPPLEMENTARY MATERIALS

Complete crystallographic data has been deposited with the Cambridge Crystallographic Data Center, CCDC No.818125 for polymer **1**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk. www: http://www.ccdc. cam.ac.uk).

REFERENCES

1. (a) Moulton, B.; Zaworotko, M. From molecules to crystal engineering: supramolecular isomerism and polymorphism in network solids. *J. Chem. Rev.* **2001**, *101*, 1629–1658; (b) Batten, S.R.; Robson, R. Interpenetrating nets: ordered, periodic entanglement. *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.
2. Davis, A.V.; Fiedler, D.; Seeber, G.; Zahl, A.; Eldik, R.; Raymond, K.N. Guest exchange dynamics in an M_4L_6 tetrahedral host. *J. Am. Chem. Soc.* **2006**, *128*, 1324–1333.
3. Ma, L.; Abney, C.; Lin, W. Enantioselective catalysis with homochiral metal-organic frameworksw. *Chem. Soc. Rev.* **2009**, *38*, 1248–1256.
4. Wang, Z.M.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. $Mn_3(HCOO)_6$: a 3D porous magnet of diamond framework with nodes of Mn-centered $MnMn_4$ tetrahedron and guest-modulated ordering temperature. *Chem. Commun.* **2004**, *4*, 416–417.
5. Zheng, X.; Sun, C.; Lu, S.; Liao, F.; Gao, S.; Jin, L. New porous lanthanide-organic frameworks: synthesis, characterization, and properties of lanthanide 2,6-naphthalenedicarboxylates. *Eur. J.* Inorg. Chem. **2004**, 3262–3268.
6. (a) Zhang, Y.-J.; Liu, T.; Kanegawa, S.; Sato, O. Interconversion between a nonporous nanocluster and a microporous coordination polymer showing selective gas adsorption. *J. Am. Chem. Soc.* **2010**, *1329*, 912–913; (b) Demessence, A.; Long, J.R. Selective gas adsorption in the flexible

metal-organic frameworks Cu(BDTri)L (L = DMF, DEF). *Chem. Eur. J.* **2010**, *16*, 5902–5908.
7. Ren, C.; Hou, L.; Liu, B.; Yang, G.-P.; Y.-Y. Wang, Shi, Q.-Z. Distinct structures of coordination polymers incorporating flexible triazole-based ligand: topological diversities, crystal structures and property studies. *Dalton Trans.* **2011**, *40*, 793–804.
8. Chen, J.-Q.; Cai, Y.-P.; Fang, H.-C.; Zhou, Z.-Y.; Zhan, X.-L.; Zhao, G.; Zhang, Z. Construction of three-dimensional metal-organic frameworks with helical character through coordinative and supramolecular interactions. *Cryst. Growth Des.* **2009**, *9*, 1605–1613.
9. Lin, J.-D.; Cheng, J.-W.; Du, S.-W. Five d^{10} 3D metal-organic frameworks constructed from aromatic polycarboxylate acids and flexible imidazole-based ligands. *Cryst. Growth Des.* **2008**, *8*, 3345–3353.
10. Aakeröy, C.B.; Desper, J.; Leonard, B.; Urbina, J.F. Toward high-yielding supramolecular synthesis: directed assembly of ditopic imidazoles/benzimidazoles and dicarboxylic acids into cocrystals via selective O-H···N hydrogen bonds. *Cryst. Growth Des.* **2005**, *5*, 865–873.
11. Sheldrick, G.M. *SHELXL-97, Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Germany, **1997**.
12. He, Q.-F.; Li, D.-S.; Zhao, J.; Ke, X.-J.; Li, C.; Mou, Y.-Q. Positional isomeric effect of phenylenediacetate on the construction of mixed-ligand Cd^{II} coordination frameworks. *Inorg.Chem. Commun.* **2011**, *14*, 578–583.
13. Yue, J.-M.; Wang, W.-J.; Fu, W.-Z.; Han, X.-N.; Zhang, Z.-H.; Wang, L.-F.; Niu, Y.-Y. Syntheses, crystal structures, and fluorescent properties of two cation-induced complexes: [(CdI_4)(BPHX)] and [(Ag_2I_4)(BPHX)]. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2011**, *41*, 100–106.
14. Zheng, S.-L.; Yang, J.-H.; Yu, X.-L.; Chen, X.-M.; Wong, W.-T. Syntheses, structures, photoluminescence, and theoretical studies of d^{10} metal complexes of 2,2′-dihydroxy-[1,1′]binaphthalenyl-3,3′-dicarboxylate. *Inorg. Chem.* **2004**, *43*, 830–838.
15. Sun, D.; Zhang, N.; Huang, R.-B.; Zheng, L.-S. Series of Ag(I) coordination complexes derived from aminopyrimidyl ligands and dicarboxylates: syntheses, crystal structures, and properties. *Cryst. Growth Des.* **2010**, *10*, 5031–5033.