

两个基于半刚性双甲基苯并咪唑配体的螺旋型镉配位聚合物

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摘要: 以 1,4-双(2-甲基苯并咪唑-1-亚甲基)苯(bmb)为主配体与 $\text{Cd}(\text{NO}_3)_2$ 反应, 通过改变辅助双羧酸配体 2 个羧基间的连接基团, 得到了 2 个配位聚合物 $[\text{Cd}(\text{bmb})(\text{tba}) \cdot \text{DMF}]_n$ (**1**) 和 $[\text{Cd}(\text{bmb})(\text{ada})]_n$ (**2**) (H_2tba =5-叔丁基间苯二甲酸, H_2ada =1,3-金刚烷二乙酸)。结构分析表明聚合物 **1** 显示二维三明治结构, 带有交替的左手和右手螺旋链。聚合物 **2** 也显示了二维三明治结构, 带有 *meso*-螺旋和微孔。聚合物 **1** 和 **2** 都显示了强的荧光发射和高的热稳定性。

关键词: 螺旋; 镉; 荧光; 热稳定性

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Two Helical Cadmium Coordination Polymers Based on Semi-rigid Bis(methylbenzimidazole) Ligand

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Abstract: By varying the spacers between two carboxyl of dicarboxylic acid co-ligands, the reaction between ligand bmb ((bmb=1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene) and $\text{Cd}(\text{NO}_3)_2$ gave two coordination polymers, $[\text{Cd}(\text{bmb})(\text{tba}) \cdot \text{DMF}]_n$ (**1**) and $[\text{Cd}(\text{bmb})(\text{ada})]_n$ (**2**) (H_2tba =5-*tert*-butylisophthalic acid, H_2ada =1,3-adamantanediacyetic acid). Structural analyses reveal that polymer **1** shows a 2D sandwich structure with alternate left- and right-handed helices. Polymer **2** also exhibits a 2D sandwich structure but with *meso*-helix and micropore. In addition, polymers **1** and **2** show intense fluorescence emissions and high thermostability. CCDC: 1474502, **1**; 1474503, **2**.

Keywords: helix; cadmium; photoluminescence; thermostability

Helical structures, as the foundation of the genetic code, have attracted intense interest in field of metal-organic frameworks (MOFs) not only for their ubiquitous appearance in nature, a typical example being the DNA molecule, but also for their practical implications in multidisciplinary areas, such as biomimetic chemistry, optical devices, asymmetric catalysis chemistry, and structural biology^[1-5]. Until now, there

are many reports about single-, double-, triple-, and even multiple-stranded helices as well as circular and cylindrical helices^[6-9]. In contrast, the series reports about single-, double-, triple- or more flexures helix are extremely infrequent^[10-13]. The reason may be that it is quite difficult to control the formation of two or more flexures in single-stranded helix. To get such series of helices, the crucial step is to choose

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multifunctional organic ligands containing appropriate coordination sites and spacers with specific positional orientation^[14-15]. According to our previous studies^[16-17], 1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene (bmb) is an excellent semi-rigid N-heterocyclic ligand with an “arm-spacer-arm” type structural feature, which may generate flexures and favor to form helical motifs. Bmb comprises two flexible methylbenzimidazol pendants as arms attached to a rigid aromatic core as a spacer via freely rotatable methylene (-CH₂-) hinges. It is quite different from highly rigid and completely flexible ligands. The rigid components of bmb could take on distinctive conformations to enhance the structural variation, while the restricted flexibility of the ligand would provide limited modes subjected to subtle influences in the assembly of target coordination structures. In view of the characters, bmb has the potential to produce unique *n*-flexure helical motifs.

On the other hand, it is well known that dicarboxylate organic groups are excellent structural constructors^[18]. In view of the development of synthetic strategy, it will be valuable to introduce the dicarboxylates with different spacers into the *meso*-helices synthetic process based on N-donor ligand bmb, which can result in greater tunability of the helical features and build much more complicated and fascinating MOFs.

Based on the above considerations, by introducing two dicarboxylate co-ligands with different spacer into the Cd(II)-bmb synthesis system, fascinating helical coordination polymers, namely {[Cd(bmb)(tba)]·DMF}_n (**1**) and [Cd(bmb)(ada)]_n (**2**) were synthesized under similar hydrothermal conditions. A systematically structural comparison of polymers **1** and **2** indicates that the conformation of bmb plays an important role in the conformation of helix from single- to two-flexures helices. In addition, the thermal stabilities and photoluminescence properties of **1**~**2** in the solid state have also been investigated.

1 Experimental

1.1 Materials and methods

All chemicals and reagents were used as received

from commercial sources without further purification except for bmb, which was synthesized according to the literature^[19]. All reactions were carried out under hydrothermal conditions. Elemental analyses (C, H, N) were determined with a Elementar Vario EL III elemental analyzer; IR spectra were recorded as KBr pellets on a Bruker EQUINOX55 spectrophotometer in the 4 000~400 cm⁻¹ region. Powder X-ray diffractions (XRD) were made under a Rigaku D/Max-2500 PCT with Cu K α radiation (λ =0.154 2 nm), using an operating voltage of 45 kV and an operating current of 40 mA at room temperature in the 2θ range between 5° and 50°. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TAG-7 instrument with a heating rate of 10 °C·min⁻¹ in air. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

1.2 Synthesis of {[Cd(bmb)(tba)]·DMF}_n (**1**)

A mixture of Cd(NO₃)·4H₂O (61.7 mg, 0.2 mmol), bmb (0.2 mmol, 73.2 mg), H₂tba (0.2 mmol, 24.4 mg), NaOH (0.4 mmol, 16 mg), DMF (3 mL) and deionized water (7 mL) was sealed in a sealed Teflon-lined stainless steel vessel (25 mL) at 150 °C for 5 days. After being cooled to room temperature, crystals of **1** were collected by filtration. Yield: 48% based on Cd. Anal. Calcd. for C₃₉H₄₁CdN₅O₅ (%): C, 60.66; H, 5.35; N, 9.07. Found (%): C, 60.71; H, 5.40; N, 9.10. IR (KBr, cm⁻¹): 2 957(s), 1 705(w), 1 655(m), 1 619(m), 1 562 (s), 1 514 (m), 1 462 (m), 1 408 (s), 1 349(m), 1 265(m), 1 163(w), 1 017(w), 876(m), 792(s), 743(s), 672(m), 618(m), 524(m), 470(m).

1.3 Synthesis of [Cd(bmb)(ada)]_n (**2**)

The same synthetic method as that for **1** was used except that H₂tba was replaced by H₂ada (0.2 mmol, 50.4 mg). Yield: 43% based on Cd. Anal. Calcd. for C₃₈H₄₀N₄O₄Cd (%): C, 62.59; H, 5.53; N, 7.68. Found(%): C, 64.52; H, 5.49; N, 7.65. IR (KBr, cm⁻¹): 3 438(s), 2 907(m), 2 842(m), 1 617(w), 1 546 (s), 1 452(m), 1 406(s), 1 337(m), 1 289(m), 1 249(m), 1 216(w), 1 158(m), 975(m), 948(m), 755(s), 665(m), 613(w), 549(w), 587(w), 459(m).

1.4 Crystal structural determination

The data of the two polymers were collected on a

Rigaku Saturn 724 CCD diffractometer (Mo $K\alpha$, $\lambda = 0.071\ 073\ \text{nm}$) at temperature of $(20 \pm 1)^\circ\text{C}$. Absorption corrections were applied by using multi-scan program. The data were 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^[20]. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystal data and structural refinement parameters for **1**~**2** are summarized in Table 1.

CCDC: 1474502, **1**; 1474503, **2**.

Table 1 Crystal data and structure refinement details for polymers **1**~**2**

Polymer	1	2
Formula	$\text{C}_{39}\text{H}_{41}\text{N}_5\text{O}_5\text{Cd}$	$\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_4\text{Cd}$
Formula weight	772.18	671.04
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.176 6(2)	0.932 37(19)
b / nm	1.818 4(4)	1.047 9(2)
c / nm	1.738 6(4)	1.796 1(5)
$\beta / (^\circ)$	108.80(3)	108.80(3)
V / nm^3	3.521 3(14)	1.661 2(7)
Z	4	2
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.457	1.458
μ / mm^{-1}	0.672	0.704
$F(000)$	1 592	752
GOF on F^2	1.072	1.094
$R_1 [I > 2\sigma(I)]^a$	0.044 3	0.049 2
$wR_2 (\text{all data})^b$	0.095 7	0.128 6

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

2 Results and discussion

2.1 Structure description of $[\{\text{Cd}(\text{bmb})(\text{tba})\} \cdot \text{DMF}]_n$ (**1**)

Single X-ray diffraction analysis reveals that **1** features a 2D sandwich structure. As shown in Fig. 1a, the asymmetric unit contains one crystallographically independent Cd(II) ions, one bmb, one completely deprotonated tba^{2-} and one free DMF molecule. The center Cd(II) ions are defined in distorted tetragonal pyramid coordination environment supplied by

three carboxylate oxygen atoms from two symmetry-related tba^{2-} anions and two nitrogen atoms from bmb. Both Cd-O and Cd-N bond lengths are fall into the normal range^[21-22].

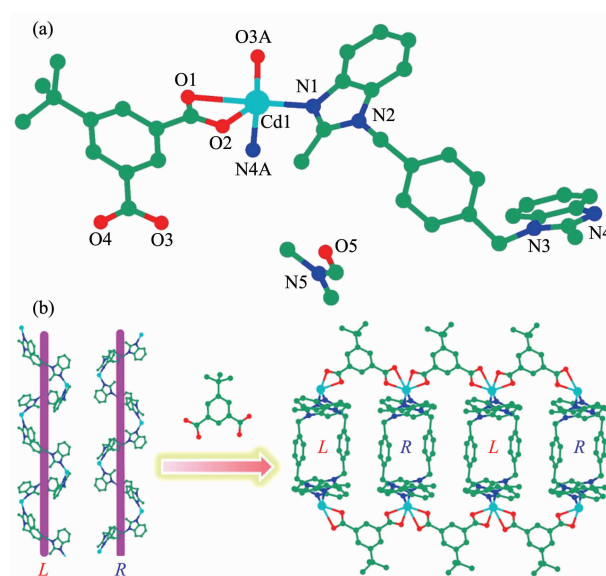


Fig.1 (a) Coordination environment of Cd(II) ion with hydrogen atoms omitted for clarity; (b) 2D sandwich structure of **1** with alternate left- and right-handed helices

Bmb adopts asymmetric *cis*-conformation with the dihedral angle between two methylbenzimidazole rings being $33.0(1)^\circ$ and the $\text{N}_{\text{donor}} \cdots \text{N}-\text{C}_{\text{sp}^3} \cdots \text{C}_{\text{sp}^3}$ torsion angles being $102.4(7)^\circ$ and $114.2(7)^\circ$. Bmb link with Cd(II) ions to form the left- and right-handed helices (Fig.1b) with large quadrilateral microchannels. Both the helical pitches are $1.82(0)\ \text{nm}$ corresponding to the length of c axis. One carboxyl of tba^{2-} adopts $\mu_1\text{-}\eta^1\text{:}\eta^0$ and the other adopts $\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination fashions. The tba^{2-} ligands connect the left- and right-handed helices alternately to form a 2D sandwich architecture. The Cd/bmb helix chains locate in middle as intermediate sandwich material and the tba^{2-} locate in the top and bottom.

2.2 Structure description of $[\text{Cd}(\text{bmb})(\text{ada})]_n$ (**2**)

When H_2ada with adamantane spacer instead of H_2tba is introduced into the synthetic procedure, a similar 2D sandwich structure with rare *meso*-helix was obtained. As shown in Fig.2a, the asymmetric unit of **2** contains one crystallographically independent

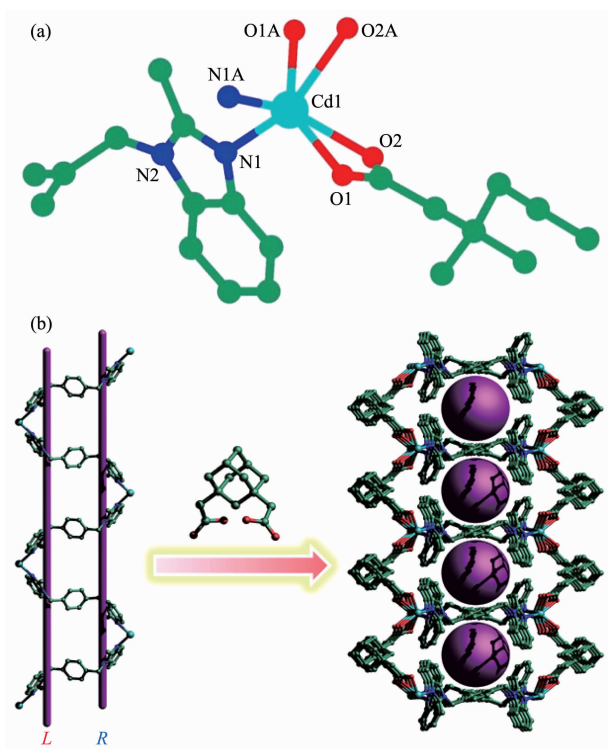


Fig.2 (a) Coordination environment of Cd(II) ion with hydrogen atoms omitted for clarity; (b) 2D sandwich structure of **2** with *meso*-helix and micropore

Cd(II) ions, one bmb and one ada⁻ anion. The coordination environment around the Cd(II) center is best portrayed as a distorted octahedral geometry, and the equatorial plane comprises of three carboxylate oxygen atoms (O1, O2 and O1A) from two symmetry-related ada²⁻ anions and one nitrogen atoms from bmb (N1A). One carboxylate oxygen atom from ada²⁻ anion (O2A) and one nitrogen atoms from bmb (N1) occupy the apical site. The Cd-O/N bond lengths are in the normal range^[21-22].

Bmb adopts symmetric *trans*-conformation with the $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angles being 111.0(9)°. As shown in Fig.2b, Bmb are linked by Cd(II) ions to form a rare *meso*-helix motif with two flexures in single-stranded helix. The helical pitches are 1.80(0) nm corresponding to the length of *c* axis. Two carboxyl groups of ada²⁻ adopt $\mu_2-\eta^1:\eta^1$ coordination pattern coordinating with Cd(II) as linking. As a result, the Cd/bmb *meso*-helix chains are linked to form a 2D sandwich structure. The Cd/bmb *meso*-helix act as

cores and the ada²⁻ locate in the top and bottom as adorn. Interestingly, polymer **2** exhibits a micropore structure.

2.3 Effect of semi-rigid bis(methylbenzimidazole) ligand

Due to the semi-rigid character, bmb can show stable *cis/trans*-conformation and symmetric (with the same $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angles of two methylbenzimidazol arms)/asymmetric (with different $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angles of two methylbenzimidazol arms) conformations. From the structural descriptions above, the spacer of carboxylate co-ligands have important effects on the spatial structure of bmb, which further effect on the ultimate frameworks. From polymers **1** to **2**, the spacer of carboxylate co-ligands change from tert-butyl benzene to adamantane. Both the conformation and symmetry of bmb are changed. So, **1** exhibits common helix and **2** shows rare *meso*-helix. Apparently, these analyses above forcefully demonstrate that the change of spacer and the freely conformational bmb play essential roles in determining the architecture of the final products.

2.4 XRD patterns and thermal analyses

In order to confirm the phase purity of polymer **1-2**, the PXRD patterns were recorded for **1-2**, and they were comparable to the corresponding simulated ones calculated from the single-crystal diffraction data (Fig.3), indicating a pure phase of each bulky sample. Thermal gravimetric analysis (TGA) was used to evaluate the framework stability. As shown in Fig.4, **1** shows a weight loss of 9.44% in the range of 217~290 °C corresponding to the loss of free DMF molecule (Calcd. 9.47%). Such high temperature probably results from the presence of hydrogen-bonding (C-H \cdots O 0.340 8(6) nm) between the DMF and ligand bmb. Then a plateau region follows. The overall framework starts to decompose at about 380 °C. At 546 °C, a CdO residue of 16.91% (Calcd. 16.63%) is obtained. No obvious weight loss is observed for anhydrous polymer **2** until the decomposition of the framework occurs at 390 °C. At 607 °C, a CdO residue of 18.24% (Calcd. 17.61%) is obtained.

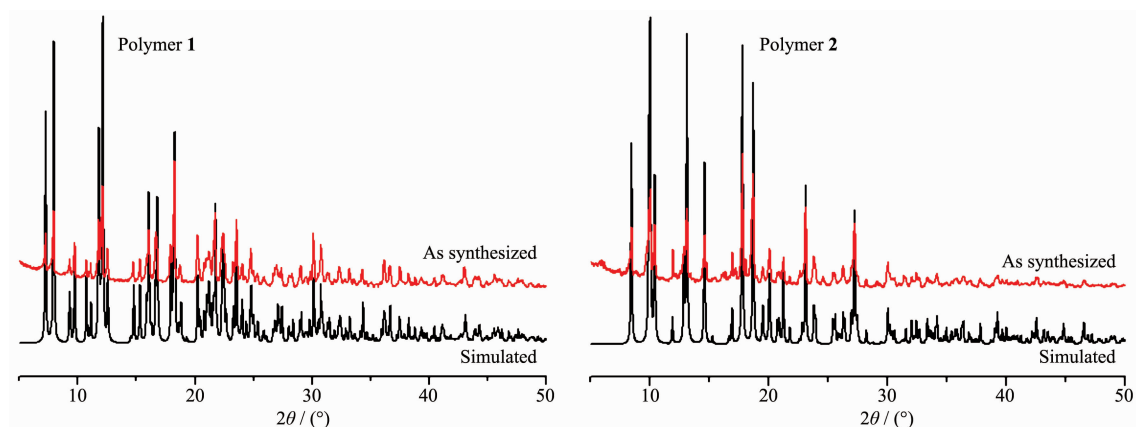


Fig.3 PXRD patterns of polymers 1~2

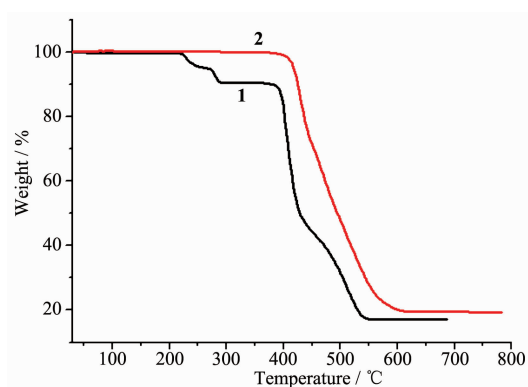


Fig.4 TGA curves of polymers 1~2

2.5 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 photochemistry^[23-26]. Hence, the solid state photoluminescence properties of Cd(II) polymers **1~2**, together with the free bmb ligand and dicarboxylic acid co-ligands were investigated at room temperature (Fig.5) under the same experimental conditions. The free ligands bmb and H₂tba show intense emissions bands at 309 nm (λ_{ex} =293 nm) and 330 nm (λ_{ex} =305 nm), respectively. The non-conjugated organic linker H₂ada has no emissions band. Obviously, the fluorescent emissions bands of **1** (λ_{em} =308 nm, λ_{ex} =292 nm) can be attributed to the intraligand charge transitions of bmb and H₂tba due to their similar emission bands. Polymer **2** exhibits an intense emission at 305 nm (λ_{ex} =305 nm), which also can be attributed to the intraligand charge transitions of bmb. The small blue-shifted peak of **1** and **2** are probably

caused by the coordination of aromatic carboxylic acid to the metal centers.

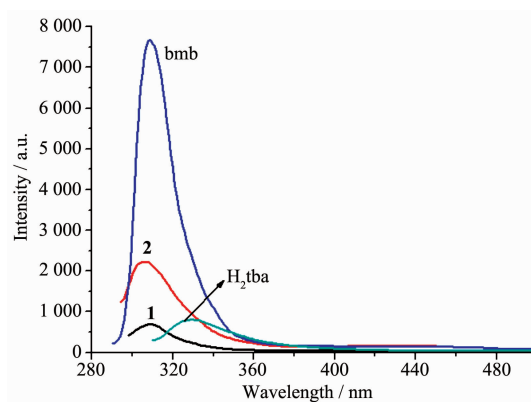


Fig.5 Solid-state photoluminescent spectra of polymers 1~2 and free ligands

3 Conclusions

In summary, two fluorescent polymers with different dicarboxylic acid co-ligands have been obtained under the same experimental conditions. The investigation indicates that the spacers of dicarboxylic acid co-ligands have important influences in the conformation of bmb, which lead to diverse helices from common single-helix to *meso*-helix.

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