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杂金属杯[4]配位聚合物的合成与表征

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摘要: 合成了 4 个杂金属杯[4]配位聚合物{[Cd(L)(tpa)]·3H_2O}$_n$ (**1**), {[Zn_2($L)_2$($tpa)_2$]·3H_2O}$_n$ (**2**), {[Co(L)(oba)]·2DMA·0.5H_2O}$_n$ (**3**)和{[Zn(L)(oba)]·DMA}$_n$ (**4**)(L=2-(1*H*-咪唑基-甲基)-6-(3-(1*H*-咪唑基-甲基)-5-叔丁基-2-羟基)苄基-4-叔丁基苯酚,H_2tpa=对苯二甲酸,H_2oba=4,4′-二苯醚二甲酸),并通过元素分析、热重、红外光谱、固态紫外、单晶 X 射线衍射和粉末 X 射线衍射对其进行了表征。单晶结构分析表明晶体 **1** 是单斜晶系,$P2_1/n$ 空间群, 而晶体 **2**,**3** 和 **4** 均为三斜晶系,$P\bar{1}$ 空间群。 化合物 **1**,**2**,**3** 和 **4** 是由 0 维[M($N_4O_2C_{29}H_{36}$)](M=Zn,Co,Cd)的杂金属杯[4]与配体对苯二甲酸和 4,4′-二苯醚二甲酸形成的一维配位聚合物。

关键词: 金属杯芳烃; 配位聚合物; 水热合成
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Syntheses and Characterization of Metal Hybrid Calix[4]arene Coordination Polymers

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Abstract: Four metal hybrid calix[4]arene coordination polymers: {[Cd(L)(tpa)]·3H_2O}$_n$ (**1**), {[Zn_2($L)_2$($tpa)_2$]·3H_2O}$_n$ (**2**), {[Co(L)(oba)]·2DMA·0.5H_2O}$_n$ (**3**) and {[Zn(L)(oba)]·DMA}$_n$ (**4**) (L=2-((1*H*-imidazol-1-yl)methyl)-6-(3-((1*H*-imidazol-1-yl)methyl)-5-*tert*-butyl-2-hydroxybenzyl)-4-*tert*-butylphenol, H_2tpa=terephthalic acid, H_2oba=4,4′-oxybisbenzoic acid) have been successfully synthesized and characterized by elemental analysis, thermogravimetry, IR, the solid-sate UV-Vis spectra, single-crystal X-ray diffraction and PXRD. The single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic system, space group $P2_1/n$ while complexes **2**, **3** and **4** crystallize in the triclinic, space group $P\bar{1}$. Complexes **1**, **2**, **3** and **4** are one-dimensional coordination polymers, which are formed through 0D [M($N_4O_2C_{29}H_{36}$)] (M=Zn, Co, Cd) metal hybrid calix[4]arene bridged H_2tpa and H_2oba ligands. CCDC: 1028976, **1**; 1028977, **2**; 1028978, **3**; 1028979, **4**.

Keywords: metal calixarene; coordination polymers; hydrothermal synthesis

0 Introduction

Coordination polymers have drawn much attention over the past decades, not only for their fascinating structures, but also for their underlying application in sensors [1-2], catalysis [3-6], magnetism [7-9], adsorption [10-12] and luminescence[13-15]. Therefore, further synthetic coordination polymers with specific structure and function have very important meaning and value. As we all know, ligands including imidazole rings play an important role in the process of synthesis of coordination polymers. The nitrogen atoms of imidazole

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rings are used to coordinate with a series of transition metals forming different coordination polymers [16-18]. Moreover, the OH groups are widely employed in construction of coordination polymers, because they can further coordinate with metal ions and form hydrogen bonds[19-20]. It has been reported that ligands of calix [4]arene containing imidazole rings and OH groups were applied to fluorescent sensor, biologically active and catalysts, *etc*[21-22], but metal hybrid calix[4] arene has scarcely been reported[23-24].

So, we have designed and prepared a bidentate imidazole ligand 2-((1*H*-imidazol-1-yl)methyl)-6-(3-((1*H*-imidazol-1-yl)methyl)-5-*tert*-butyl-2-hydroxylbenzyl)-4-*tert*-butylphenol (L). Then four coordination polymers, namely $\{[Cd(L)(tpa)]\cdot 3H_2O\}_n$ (**1**), $\{[Zn_2(L)_2(tpa)_2]\cdot 3H_2O\}_n$ (**2**), $\{[Co(L)(oba)]\cdot 2DMA\cdot 0.5H_2O\}_n$ (**3**) and $\{[Zn(L)(oba)]\cdot DMA\}_n$ (**4**) containing dicarboxylates and metal hybrid calix [4]arene, have been synthesized by hydrothermal synthesis.

1 Experimental

1.1 Reagents and physical measurements

All solvents were purified by standard procedures. All the reagents for synthesis and analyses were of analytical grade and without further purification. Elemental analyses were determined with a Perkin-Elmer 240 elemental analyzer. Thermal analysis were performed on a Netzsch STA 449 F3 from room temperature to 800 ℃ with a heating rate of 20 ℃·min^{-1} under N_2 atmosphere. IR spectra (KBr pellets) were measured on a Nicolet 6700 in the range of 4 000~400 cm^{-1}. The solid-state UV-Vis spectra were obtained on a Shimadzu UV3600 by using $BaSO_4$ as a standard. Powder X-ray diffraction were collected with a Rigaku D/max-3B diffractometer using Cu $K\alpha$ radiation (λ=0.154 06 nm, 40 kV, 30 mA, 2θ=5°~80°). Mass spectrum was measured on Bruker microTOF-Q Ⅱ electrospray ionization instrument and NMR (^{1}H and ^{13}C) were acquired by a Bruker SF-400 spectrometer.

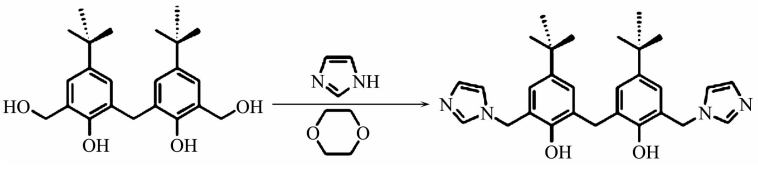
1.2 Synthesis of the ligand L

The synthetic method of ligand L was shown in Scheme 1. 2-(5-*tert*-butyl-2-hydroxy-3-(hydroxymethyl) benzyl)-4-*tert*-butyl-6 (hydroxymethyl)phenol (1.0 g, 3 mmol), imidazole (0.4 g, 6 mmol), 1,4-dioxane(10 mL) were added to a 50 mL round-bottom flask. The mixture was refluxed for 24 h after stirred 8 h, and then the solvent was evaporated. Pure white ligand L was obtained on a silica-gel column with dichloromethane and petroleum as eluent. Yield: 50%. m.p. 123~125 ℃. Anal. Calcd. for $C_{29}H_{36}N_4O_2$(%): C, 73.68; H, 7.68; N, 11.86; Found(%): C, 73.65; H, 7.72; N, 11.89. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12~1.13 (d, 18H), 3.90 (s, 2H), 5.13 (s, 4H), 6.86(s, 2H), 6.95~6.96 (d, 2H), 6.98~6.99 (d, 2H), 7.14 (s, 2H), 7.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.52, 33.02, 34.04, 47.69, 119.50, 123.59, 125.16, 127.53, 127.95, 129.72, 137.09, 143.35, 150.58. ESI-MS: m/z=473.294 2 $[M+H]^+$.

1.3 Preparation of the complexes

Complex **1**: A mixture of ligand L (13 mg, 0.03 mmol), H_2tpa (10 mg, 0.06 mmol) and $Cd(NO_3)_2\cdot 4H_2O$ (15 mg, 0.05 mmol) were dissolved in 5 mL of DMF/H_2O (3:2, *V*/*V*) in a 10 mL Teflon-lined stainless steel reactor and then heated to 160 ℃ for 96 h. The colorless block crystals were collected. Yield: 58.3%. Anal. Calcd. for $C_{37}H_{46}CdN_4O_9$(%): C, 55.33; H, 5.77; N, 6.98. Found(%): C, 55.16; H, 5.77; N, 6.85. IR(cm^{-1}): 3 839(w), 3 714(w), 3 442(s), 2 958(m), 1 557(w), 1 516(w), 1 485(w), 1 390(m), 1 293(w), 1 232(w), 1 087(w), 841(w), 748(m).

Complex **2**: The preparation of **2** was similar to that of **1** except that $Zn(NO_3)_2\cdot 6H_2O$ (15 mg, 0.05 mmol) was used instead of $Cd(NO_3)_2\cdot 4H_2O$. The colorless crystals were collected. Yield: 50.6%. Anal. Calcd. for $C_{74}H_{86}N_8O_{15}Zn_2$(%): C, 60.90; H, 5.90; N, 7.68. Found (%): C, 60.95; H, 5.93; N, 7.69.IR (cm^{-1}): 3 439(s),



Scheme 1 Synthetic process of L

2 958(m), 1 618(m), 1 524(w), 1 482(w), 1 386(m), 1 296(w), 1 092(m), 952(w), 825(m), 749(m), 658(w).

Complex **3**: A mixture of ligand L (23 mg, 0.05 mmol), H_2oba (25.8 mg, 0.1 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (33.2 mg, 0.11 mmol) in 13 mL of DMA/H_2O (8:5, *V*/*V*) was sealed in a 20 mL Teflon-lined stainless steel reactor and then heated to 160 ℃ for 96 h. After cooled to room temperature, the red rod crystals were collected. Yield: 30.6%. Anal. Calcd. for $C_{51}H_{63}CoN_6O_{9.5}$ (%): C, 63.03; H, 6.49; N, 8.65. Found (%): C, 63.34; H, 6.01; N, 7.85.IR(cm^{-1}): 3 420(w), 3 134(w), 2 958 (m), 1 599(s), 1 553(w), 1 389(s), 1 296(w), 1 238(s), 1 160(m), 1 090(m), 877(m), 782(m), 658(m).

Complex **4**: The preparation of **4** was similar to that of **3** except that $Zn(NO_3)_2\cdot 6H_2O$(36.3 mg, 0.12 mmol) was used instead of $Co(NO_3)_2\cdot 4H_2O$. The colorless block crystals were collected. Yield: 60.7% . Anal. Calcd. for $C_{47}H_{53}N_5O_8Zn$(%): C, 63.99; H, 6.01; N, 7.94. Found(%): C, 62.76; H, 6.17; N,7.79. IR(cm^{-1}): 3 422 (w), 3 134(w), 2 958(m), 1 601(s), 1 563(w), 1 525(w), 1 490(w), 1 383(s), 1 283(s),877(w), 782(w), 656(w).

1.4 Crystal structure determination

The crystal data of **1**, **2**, **3** and **4** were collected with a Bruker SMART APEX-Ⅱ CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation (λ = 0.071 073 nm) at room temperature (Table 1). The structures of four coordination polymers were solved by direct methods and refined with the full-matrix least-squares procedures on F^2 using the SHELXS-97[25] and SHELXL-97 programs[26], respectively. All hydrogen atoms were placed at idealized positions except for water H atoms, which were directly found from Fourier map. The selected bond lengths and angles for complexes **1**, **2**, **3** and **4** are summarized in Table 2.

CCDC: 1028976, **1**; 1028977, **2**; 1028978, **3**; 1028979, **4**.

2 Results and discussion

2.1 Crystal structures of 1, 2

As shown in Fig.1a, the Cd (Ⅱ) center is octahedral coordinated by two nitrogen atoms from L ligand and four oxygen atoms from two tpa^{2-}. The asymmetric

Table 1　Crystal data and structure refinement data for complexes 1, 2, 3 and 4

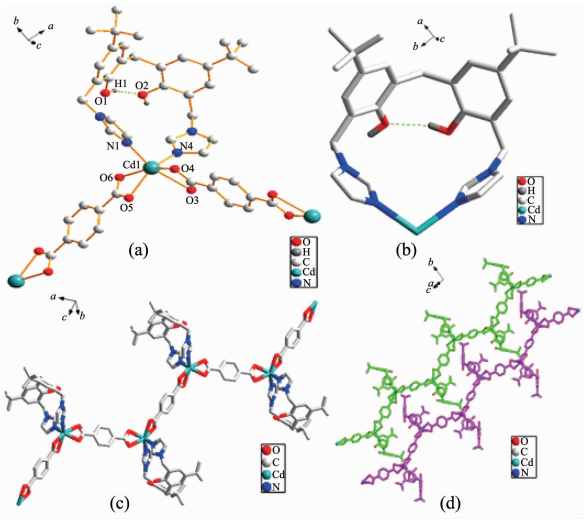
Complex	1	2	3	4
Empirical formula	$C_{37}H_{46}CdN_4O_9$	$C_{74}H_{86}N_8O_{15}Zn_2$	$C_{51}H_{63}CoN_6O_{9.5}$	$C_{47}H_{53}N_5O_8Zn$
Formula weight	803.18	1 458.20	971.00	881.31
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / nm	1.277 8(3)	1.231 2(4)	1.365 8(11)	1.382 79(16)
b / nm	2.207 7(5)	1.582 5(5)	1.471 1(12)	1.469 29(16)
c / nm	1.530 5(3)	2.148 0(7)	1.541(2)	1.537 25(17)
α / (°)	90.00	87.699(7)	102.23(2)	101.733(2)
β / (°)	92.336(4)	88.897(7)	110.84(2)	111.624(2)
γ / (°)	90.00	88.270(7)	109.166(15)	109.123(2)
V / nm^3	4.313 8(16)	4.179(2)	2.538(5)	2.549 7(5)
D_c / ($g\cdot cm^{-3}$)	1.237	1.154	1.271	1.148
μ / mm^{-1}	0.557	0.635	0.399	0.533
F(000)	1 664	1 520	1 028	928
Reflections collected	7 557	16 108	8 759	8 844
Independent reflections	6 318 (R_{int}=0.028 8)	5 979 (R_{int}=0.067 4)	4 269 (R_{int}=0.043 7)	6 344 (R_{int}=0.023 1)
GOF on F^2	1.077	1.024	1.087	1.063
R_1[a] [$I>2\sigma(I)$]	0.032 0	0.094 1	0.086 8	0.052 4
wR_2[b] [$I>2\sigma(I)$]	0.089 1	0.176 4	0.227 1	0.141 2

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

Table 2 Selected bond lengths (nm) and angles (°) for complexes 1, 2, 3 and 4

			1		
Cd1-N1	0.223 9(4)	O5-Cd1	0.229 3(3)	O6-Cd1	0.242 2(3)
O4-Cd1	0.228 0(3)	C32-C33^{i}	0.384(6)	Cd1-N4	0.223 5(4)
C37-C36^{ii}	0.138 0(6)				
C33^{i}-C32-H32	119.7	N4-Cd1-N1	104.05(13)	O4-Cd1-O5	104.96(13)
N1-Cd1-O6	93.31(13)	O5-Cd1-O3	85.13(11)	O6-Cd1-O3	121.42(12)
			2		
Zn1-O4	0.195 0(5)	Zn1-N3	0.201 0(7)	Zn1-O5	0.196 4(5)
Zn1-N1	0.200 8(6)	Zn2-N5	0.199 7(6)	Zn2-N7	0.200 6(7)
O4-Zn1-O5	113.4(2)	O4-Zn1-N1	115.3(2)	N1-Zn1-N3	107.6(2)
O11-Zn2-N7	115.4(2)	O9-Zn2-N7	107.3(3)	N5-Zn2-N7	109.8(3)
			3		
Co1-N3	0.202 0(5)	Co1-N1	0.203 8(5)	O2-Co1	0.200 0(4)
O4-Co1	0.198 5(4)				
O2-Co1-O4	111.35(17)	O2-Co1-N1	123.85(17)	O4-Co1-N1	105.70(18)
N3-Co1-N1	108.16(19)				
			4		
Zn1-O6	0.196 5(2)	Zn1-O4	0.197 5(2)	Zn1-N1	0.202 0(2)
Zn1-N4	0.203 2(3)				
O6-Zn1-O4	114.00(9)	O6-Zn1-N1	96.89(10)	N1-Zn1-N4	109.39(10)
O4-Zn1-N4	119.11(10)	O4-Zn1-N1	107.62(10)	O6-Zn1-N4	107.50(10)

Symmetry codes: ^{i} $-x$, $-y$, $2-z$; ^{ii} $-1-x$, $-y$, $1-z$ for **1**



Some hydrogen atoms are omitted for clarity, all solvent molecules are omitted for clarity

Fig.1 (a) Coordination environment of Cd (Ⅱ) ions in **1**; (b) Cd (Ⅱ) hybrid calix[4]arene; (c) Schematic view of a chain of **1**; (d) View of two neighbouring chains of **1**

unit contains one Cd(Ⅱ) ion, one L ligand, one tpa^{2-} and three water molecules. The L ligand coordinates one Cd (Ⅱ) ion to construct 0 D metal hybrid calix[4] arene which is cone conformation and has a cavity containing a stronger O1 –H1 ⋯ O2 hydrogen bond (0.194 64(21) nm) (Fig.1b). A μ_2-coordinated tpa^{2-} ion connected two adjacent Cd(Ⅱ) ions of metal hybrid calix[4]arene forming a *trans*-configuration zigzag structure. Neighboring zigzag structures were further connected by tpa^{2-} ions to form infinite *trans*-configuration chains through weak interchain C –H ⋯ π interactions (distance of C–H⋯Cg 0.303 97(6)~0.368 33(6) nm) between H_2tpa and hydrogen atoms of C_{14}, C_2, C_3 (Fig.1c and Fig.1d).

Because the structure of complex **2** (Fig.2) is similar to complex **1**, complex **2** will not be discussed in detail.

2.2 Crystal structures of 3, 4

Complexes **3** and **4** are isostructural, hence, only

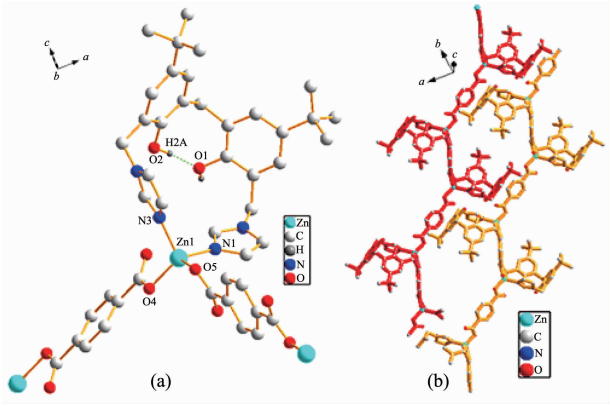
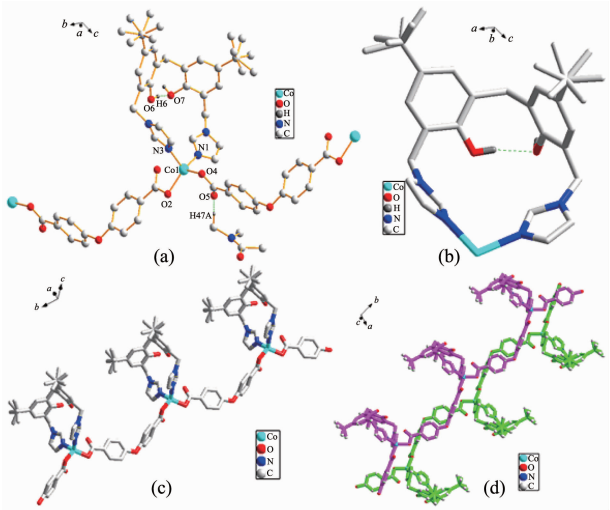


Fig.2　(a) Structure of **2**; (b) Schematic representation of two adjacent chains of **2**

the structure of **3** is discussed here. There are one Co(Ⅱ) ion, one L ligand and one oba^{2-}, two DMA molecules and half of lattice water in the asymmetric unit of **3**. The Co(Ⅱ) cation is four-coordinated by two oxygen atoms from two oba^{2-} and two nitrogen atoms from L ligand. C25/C25A, C26/C26A, C27/C27A, C36/C36A, C37/C37A and C38/C38A in complex **3** are disordered. Moreover, intramolecular O–H⋯O (O6–H6⋯O7) and intermolecular C–H⋯O (C47–H47A⋯O5) can be discovered (Fig.3a). Similar to complex **1**, complex **3** contains a Co(Ⅱ) metal hybrid calix[4]arene including the cavity with a hydrogen bond (O6–H6⋯O7 0.186 06(66) nm) (Fig.3b).



Some hydrogen atoms and solvent molecules are omitted for clarity

Fig.3　(a) View of the coordination environment of Co(Ⅱ) centers in **3**; (b) Co(Ⅱ) hybrid calix[4]arene; (c) View of a 1D chain of **3**; (d) View of two contiguous chains structure of **3**

Two adjacent hybrid calix[4]arene of complex **3** were linked by a μ_2-oba^{2-} ion to formed the zigzag *cis*-vconfiguration chain (Fig.3c). Because of steric effects, two adjacent chains were *trans*-configuration (Fig.3d). Furthermore the solvent accessible volume of complex **4** is 20.96% which was found by Platon analysis.

2.3　Thermal gravimetric analysis and PXRD patterns

The thermal stability of **1**, **2**, **3** and **4** was investigated by TGA and the results are shown in Fig. 4. Complexes **1** and **2** lost solvent molecules in the ranges of 30~222 ℃ (Obsd. 6.19% and Calcd. 6.72% for **1**) and 30~213 ℃ (Obsd. 3.61% and Calcd. 3.70% for **2**), respectively. Frameworks of complexes **1** and **2** are stable up to 342 ℃ and 368 ℃, respectively, and then frameworks begin to collapse. The complex **3** has two different process of weight loss: an initial weight loss of 0.80% corresponds to the loss of lattice water molecules (Calcd. 0.92%); the removal of DMA molecules occurs in the range of 139 ~324 ℃ (Obsd. 17.99%, Calcd. 17.94%). Framework can stable up to 534℃ and then begins to collapse. Complex **4** shows a weight loss of 9.88% in the temperature range of 41~169 ℃, which is attributed to the loss of DMA molecules from the frameworks (Calcd. 9.89%), then it decomposes at 392 ℃. The experimental and simulated PXRD patterns of **1** ~**4** were shown in Fig.S1 ~S4. Their experimental and simulated peaks are in good agreement, implying the phase purity of these samples are good.

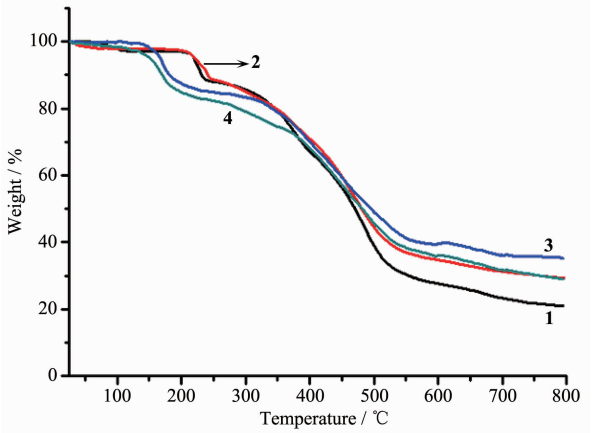


Fig.4　TGA curves for complexes **1**, **2**, **3** and **4**

2.4 UV-Vis spectrum

As shown in Fig.S5, complexes **3** and **4** show wide absorption peaks at 240~260 nm, which should be considered as π-π* transition of the ligands. The lower energy bands of **3** and **4** are at 200~220 nm, which can be attributed to metal-to-ligand charge-transfer transitions[27-28].

3 Conclusions

In conclusion, we have successfully synthesized four one-dimensional coordination polymers, which concluded metal hybrid calix[4]arene and dicarboxmlates. The better thermal stability of four complexes was demonstrated by thermal gravimetric analysis. Further experiments exploring the property and potential applications are underway in our laboratory.

Supporting information is available at http://www.wjhxxb.cn

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