

以环己二酸及咪唑基化合物为配体的镉配合物的合成、 晶体结构及荧光性质

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摘要: 以硝酸镉、环己二酸(H₂CDC)和 2,3,5,6-四氟-1,4-二咪唑基二甲苯(FBIX)为原料, 在水热条件下得到了 1 个配位聚合物 [Cd(CDC)(FBIX)_{0.5}]_n (**1**), 并利用元素分析、红外光谱以及 X-射线单晶衍射对其进行了表征。该晶体属三斜晶系, $P\bar{1}$ 空间群, $a=0.880\,53(18)$ nm, $b=0.888\,31(18)$ nm, $c=1.091\,7(2)$ nm, $\alpha=97.349(2)^\circ$, $\beta=95.688(2)^\circ$, $\gamma=105.495(2)^\circ$, $V=0.808\,1(3)$ nm³, $D_c=1.799$ g·cm⁻³, $Z=2$, $F(000)=434$, $Goof=1.094$, $R_1=0.025\,6$, $wR_2=0.072\,3$ 。Cd(II)离子通过 2 个 CDC 配体桥联形成一维双绞链, 再通过 FBIX 配体连接成二维层状结构。室温下该配合物表现出较强的荧光发射。

关键词: 镉配合物; 环己二酸; 晶体结构; 荧光

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Synthesis, Crystal Structure and Fluorescent Property of a Cadmium(II) Coordination Polymer Constructed from 1,4-Cyclohexanedicarboxylic Acid and Imidazole Ligand

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Abstract: A two-dimensional coordination polymer of [Cd(CDC)(FBIX)_{0.5}]_n (**1**) (H₂CDC=1,4-cyclohexanedicarboxylic acid and FBIX=2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-yl-methyl)benzene) has been prepared and characterized by elemental analysis, IR spectroscopy, TGA and single-crystal X-ray diffraction. The crystal is of triclinic system, space group $P\bar{1}$ with $a=0.880\,53(18)$ nm, $b=0.888\,31(18)$ nm, $c=1.091\,7(2)$ nm, $\alpha=97.349(2)^\circ$, $\beta=95.688(2)^\circ$, $\gamma=105.495(2)^\circ$, $V=0.808\,1(3)$ nm³, $D_c=1.799$ g·cm⁻³, $Z=2$, $F(000)=434$, $Goof=1.094$, $R_1=0.025\,6$, $wR_2=0.072\,3$. Complex **1** shows a two-dimensional layer structure based on paddle-wheel building units. Moreover, it shows intense fluorescent property at room temperature. CCDC: 785745.

Key words: Cd(II) complex; 1,4-cyclohexanedicarboxylic acid; crystal structure; fluorescence

Great interest has been focused on the rapidly expanding field of the construction of novel functional metal-organic frameworks (MOFs) owing to their variety of intriguing architectures and topologies and their

potential applications in magnetism, electric conductivity, molecular adsorption, heterogeneous catalysis, nonlinear optics and fluorescent materials^[1-6]. The selection of the special ligand is very important in the

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construction of these coordination polymers. As an important family of multidentate O-donor ligands, organic aromatic polycarboxylate ligands have been extensively employed in the preparation of metal-organic complexes with multidimensional networks and interesting properties. Hence, the reported coordination polymers are mostly constructed by rigid polycarboxylate ligands^[7-10]. Recently, more and more attention has been paid to the flexible polycarboxylate ligands, but studies about flexible polycarboxylate ligands are relatively few^[11-13].

A particularly promising class of ligand, where two imidazole units are interconnected by chains or groups of different types, has been explored to form open frameworks^[14-15]. 1,4-Bis(imidazol-1-yl-methyl)-benzene (bix), which has comparatively longer linkers, was a good candidate for the formation of novel supramolecular architectures^[16-18]. This ligand formed ordered, open networks defined by metal coordination geometries but also frequently suffered from the phenomenon of interpenetration and supramolecular isomerization leaving no void space in the solid for enclathrating guests. One strategy was to design programmed organic ligands that prevent this interpenetration. This was achieved by introducing substituents on the bix ligand. By using electron deficient coordinated imidazolium groups and replacing electron-rich phenylene with electron-deficient tetrafluorophenylene, the resulting flexible networks are unlikely to be constricted or interpenetrated, but, because of the weak intermolecular interactions in fluorine-containing compounds, they may prefer to interact with guest molecules to form clathrate compounds^[19-20]. In the paper, we report the synthesis, structural characterization, fluorescent properties of a new two-dimensional coordination polymer $[\text{Cd}(\text{CDC})(\text{FBIX})_{0.5}]_n$ (**1**) (H_2CDC = 1,4-cyclohexanedicarboxylic acid and FBIX = 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-yl-methyl) benzene).

1 Experimental

1.1 Materials and general methods

All reagents for syntheses and analyses were

purchased from commercial sources and used as received without further purification. The ligand FBIX was prepared according to the reported method^[21]. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. The luminescent spectra for the powdered solid samples were obtained at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$.

1.2 Synthesis of $[\text{Cd}(\text{CDC})(\text{FBIX})_{0.5}]_n$ (**1**)

A mixture of H_2CDC (0.1 mmol, 17.2 mg), FBIX (0.1 mmol, 31.0 mg), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol, 24.1 mg) and H_2O (15 mL) was stirred for 30 min, and the pH value of the solution was adjusted to about 5 with pyridine. After stirring for another 30 min, the mixture was transferred to a 25 mL Teflon-lined stainless steel vessel and heated at 140 $^\circ\text{C}$ for 3 d. Then the reaction system was cooled to room temperature, and colorless block crystals of **1** were obtained. Yield: 65% (based on Cd). Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_2\text{N}_2\text{O}_4\text{Cd}$ (%): C, 41.16; H, 3.45; N, 6.40. Anal. Found (%): C, 40.97; H, 3.53; N, 6.46. IR spectrum: 3 577, 2 926, 2 851, 1 609, 1 548, 1 512, 1 421, 1 365, 1 297, 1 267, 1 174, 931, 742, 675 and 471 cm^{-1} .

1.3 X-ray crystallography

The single crystals of complex **1** with approximate dimension of 0.18 mm×0.16 mm×0.10 mm was placed on a Bruker Smart Apex II CCD diffractometer. The diffraction data were collected using a graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293(2) K. The Lp factor and semi-empirical adsorption corrections were applied to the intensity data. The structure was solved by the direct method using SHELXS-97^[22] and refined by full-matrix least squares on F^2 using SHELXL-97^[23]. All of the non-hydrogen

atoms were refined anisotropically. The details of the crystal parameters, data collection and refinement for **1** are summarized in Table 1, and selected bond lengths

and angles with their estimated standard deviations are listed in Table 2.

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Table 1 Crystal data and structure refinement for **1**

Formula	C ₁₅ H ₁₅ F ₂ N ₂ O ₄ Cd	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.799
Formula weight	437.69	Absorption coefficient / mm	1.394
Temperature	293(2)	θ range / (°)	2.41~25.50
Crystal system	Triclinic	Limiting indices	$-10 \leq h \leq 10, -10 \leq k \leq 10, -13 \leq l \leq 11$
Space group	$P\bar{1}$	$F(000)$	434
a / nm	0.880 53(18)	Reflections collected	5 664
b / nm	0.888 31(18)	Independent reflections (R_{int})	2 958 (0.019 5)
c / nm	1.091 7(2)	Reflections observed ($I > 2\sigma(I)$)	2 732
$\alpha / (^\circ)$	97.349(2)	Data / restraints / parameters	2 958 / 0 / 217
$\beta / (^\circ)$	95.688(2)	Goodness-of-fit on F^2	1.094
$\gamma / (^\circ)$	105.495(2)	R_1, wR_2 ($I > 2\sigma(I)$)	0.025 6, 0.07 23
V / nm^3	0.808 1(3)	R_1, wR_2 (all data)	0.028 4, 0.074 2
Z	2	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	507, -291

Table 2 Selected bond lengths (nm) and angles (°) for **1**

Cd(1)-N(1)	0.221 9(3)	Cd(1)-O(4) ⁱⁱⁱ	0.224 0(2)	Cd(1)-O(2) ⁱ	0.222 4(3)
Cd(1)-O(1)	0.225 5(3)	Cd(1)-O(3) ⁱⁱ	0.223 2(2)		
N(1)-Cd(1)-O(2) ⁱ	101.92(11)	O(3) ⁱⁱ -Cd(1)-O(4) ⁱⁱⁱ	159.67(11)	N(1)-Cd(1)-O(3) ⁱⁱ	105.07(10)
N(1)-Cd(1)-O(1)	98.15(11)	O(2) ⁱ -Cd(1)-O(3) ⁱⁱ	89.03(10)	O(2) ⁱ -Cd(1)-O(1)	159.73(12)
N(1)-Cd(1)-O(4) ⁱⁱⁱ	95.11(10)	O(3) ⁱⁱ -Cd(1)-O(1)	88.47(10)	O(2) ⁱ -Cd(1)-O(4) ⁱⁱⁱ	89.23(11)
O(4) ⁱⁱⁱ -Cd(1)-O(1)	86.19(10)				

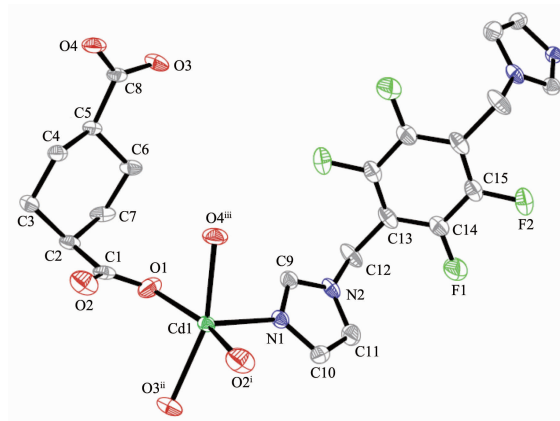
Symmetry code: ⁱ $-x+2, -y+1, -z$; ⁱⁱ $x+1, y, z$; ⁱⁱⁱ $-x+1, -y+1, -z$.

2 Results and discussion

2.1 Crystal structure

Single-crystal X-ray analysis shows that the structure of **1** is a 2D network with binuclear paddle-wheel motif. The asymmetric unit of **1** contains one Cd(II) ion, half of one FBIX ligand and one CDC anion. As shown in Fig.1, each Cd(II) ion is five coordinated and its equatorial plane is occupied by four oxygen atoms, O1, O2ⁱ, O3ⁱⁱ and O4ⁱⁱⁱ, from four different CDC anions, while the apical position is occupied by one nitrogen atom, N1, from FBIX ligand, giving a slightly distorted square-pyramidal geometry. The Cd-O distances range from 0.222 4(3) to 0.225 5(3) nm, and the Cd-N distance is 0.221 9(3) nm. The O-Cd-O bond angles range from 86.19(10)° to 159.73(12)° and the N-Cd-O bond angles range from 95.11(10)° to

105.07(10)°, which are similar to those observed in the reported complexes^[24]. Each carboxylate group of CDC anion exhibits bidentate coordination mode and

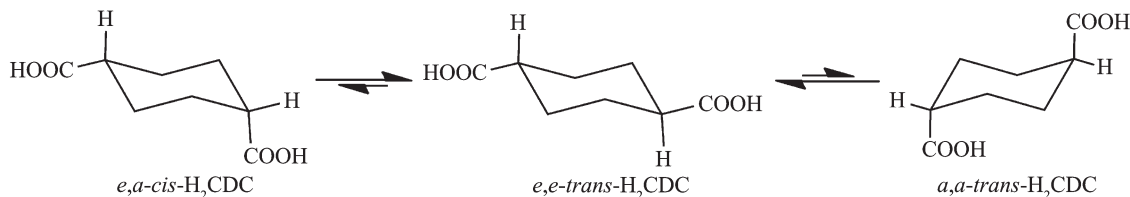


Symmetry code: ⁱ $-x+2, -y+1, -z$; ⁱⁱ $x+1, y, z$; ⁱⁱⁱ $-x+1, -y+1, -z$; Hydrogen atoms are omitted for clarity

Fig.1 ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability

connects two Cd(II) ions. A lantern-like dimer is formed via two Cd(II) connected by four carboxylate groups from four different CDC anions, in which two carboxylate groups and two Cd(II) ions constitute an approximately coplanar eight membered ring. The dimer consists of two approximately perpendicular eight membered rings (dihedral angle: 91.23°). The Cd1-Cd1ⁱ distance is 0.297 27(6) nm and the Cd-Cd-O angles range from $71.28(9)^\circ$ to $88.46(8)^\circ$.

H₂CDC possesses one *cis*- and two *trans*- conformations, that is, *e,a-cis*-, *e,e-trans*- and *a,a-trans*-H₂CDC (Scheme 1). The *e,e-trans*-form is the most thermodynamically stable due to its two equatorial substituents and the *a,a-trans*-form is the least stable because of 1,3-diaxial hindrance^[25]. Due to the rotation



Scheme 1 Three conformations of H₂CDC

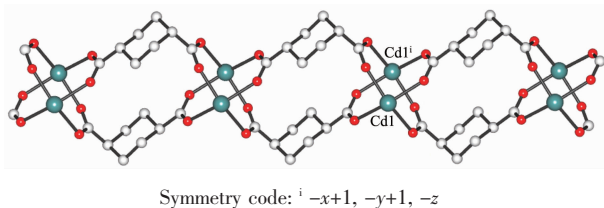


Fig. 2 1D double-chain structure with rhombic voids in complex **1**

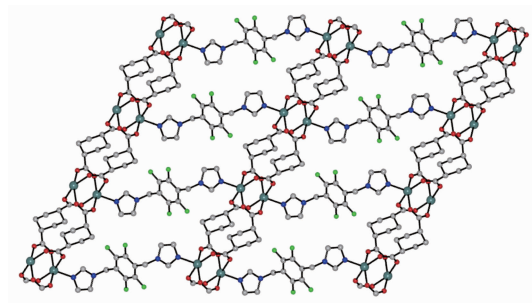


Fig. 3 2D layer framework of complex **1**

2.2 IR spectra

The IR spectrum of **1** shows characteristic bands of carboxylate groups at 1 609 and 1 512 cm^{-1} for the antisymmetric stretching and at 1 421 cm^{-1} for symmetric stretching. The separations ($\Delta\nu$) between $\nu_{\text{asym}}(\text{CO}_2)$

of flexible C-C bond and the spontaneous conformational inversion of H₂CDC, the *e*- and *a*-positions of H₂CDC can be interconverted. Therefore, thermodynamic equilibrium exists among the three conformations of H₂CDC though the *e,e-trans*-form is the preferential conformation. The interesting feature in the structure of **1** is that the flexible CDC anions possess only one kind of *e,a-cis*-form and empty cavity is left within the double strands of CDC-bridge (Fig. 2). No solvent molecules occupy the cavity and the empty channel is *ca.* 0.001 7 nm^2 in terms of the C1-C8 (0.498 51 nm) and C1-C8ⁱ distance (0.368 68 nm). When the introduction of FBIX ligands, these 1D [Cd(CDC)]_n double-chains are pillared to generate 2D square-grids (Fig. 3).

and $\nu_{\text{sym}}(\text{CO}_2)$ bands indicate the presence of bidentate coordination mode^[26]. Single-crystal X-ray diffractions show that carboxylate groups coordinate to the metal atoms in **1** in an absolutely same fashion. The absence of the characteristic bands at around 1 700 cm^{-1} in **1** attributed to the protonated carboxylate group indicates the complete deprotonation of H₂CDC ligand upon reaction with Cd ion. The IR spectra of **1** exhibit a serial of characteristic peaks of imidazole in the 742~1 365 cm^{-1} range.

2.3 Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing N₂ with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Complex **1** is stable up to *ca.* 310 $^\circ\text{C}$, and then the structure collapses slowly. The remaining weight corresponds to CdO (obsd. 31.02%, calcd. 29.25%).

2.4 Luminescent properties

Luminescent complexes are currently of great interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display^[27-28]. The luminescent properties of Zn and

Cd carboxylate compounds have been investigated^[29]. In the solid state, complex **1** exhibits an intense emission at 455 nm in the blue region ($\lambda_{\text{ex}}=354$ nm) at room temperature (Fig.4). The free FBIX exhibit fluorescent emission bands at 467 nm ($\lambda_{\text{ex}}=362$ nm). In order to understand the nature of the emission band, the photoluminescence properties of the H₂CDC ligand are analyzed. A weak emission ($\lambda_{\text{max}}=425$ nm) could be observed. In comparison to the free ligands, the emission maximums of complex **1** have changed. This may be caused by a change in the HOMO and LUMO energy levels of deprotonated CAM anions and neutral ligands coordinating to metal centers, a charge-transfer transition between ligands and metal centers, and a joint contribution of the intraligand transitions or charge-transfer transitions between the coordinated ligands and the metal centers^[30-31]. These observations indicate that they may be excellent candidates for potential photoactive materials.

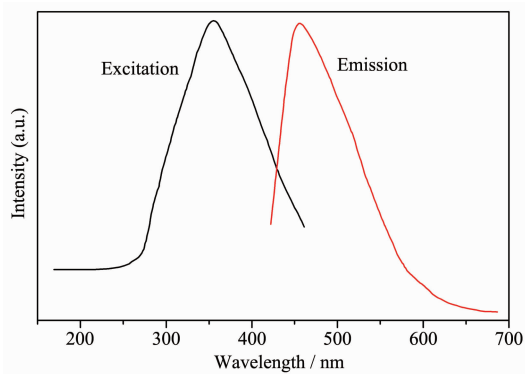


Fig.4 Solid-state photoluminescent spectra of **1** at room temperature

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