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Two three-dimensional cadmium(II) coordination polymers based on 5-amino-tetrazolate and 1,2,4,5-benzenetetracarboxylate: pH value controlled syntheses, crystal structures, and luminescent properties

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† Electronic supplementary information (ESI) available: crystallographic data in CIF, supplementary figures, PXRD, FT-IR spectra, and Table S1 (selected bond lengths and angles) (PDF). CCDC reference numbers 913253 and 979408 for **1** and **2**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: ××××××××××

By pH value controlled synthesis strategy, hydrothermal reactions of $Cd(NO_3)_2{\cdot}4H_2O$ with mixed-ligands of 5-amino-tetrazole (Hatz) and 1,2,4,5-benzenetetracarboxylic acid (H_4btec) yielded two 3D cadmium(II) coordination polymers (CPs) of $\{K[Cd_2(atz)(btec)(H_2O)_2]\}_n$ (**1**) and $[Cd_3(OH)(atz)(btec)(H_2O)_2]_n{\cdot}nH_2O$ (**2**). Their structures were determined by elemental analysis (EA), infrared spectra (IR), thermogravimetric analysis (TGA), and single-crystal/powder X-ray diffraction. The result reveals that both **1** and **2** are 3D architectures. In **1**, the Cd(II) ions are connected together by μ_2-atz and μ_6-btec^{4-}, generating a rare (4,6)-connected anion framework. The anti-cations K^+ ions locate the micropores and weakly interact with the carboxyl oxygen of μ_6-btec^{4-} ligands. In **2**, six Cd(II) ions are linked together through two μ_3-OH$^-$ and two μ_3-atz$^-$ to form a $[Cd_6(\mu_3\text{-}OH)_2(\mu_3\text{-}atz)_2]^{8+}$ unit, which is further connected with other equivalent units by μ_9-btec^{4-} spacers, resulting in a rare (5,10)-connected porous framework. Photoluminescent investigation illustrates that **1** and **2** show strong emission at 470 and 457 nm upon excitation at 350 and 370 nm, respectively.

Introduction

Over the past two decades, the design and syntheses of coordination polymers (CPs) have received remarkable attention due to their intriguing topological structures and potential applications in fields of gas separation and storage,[1] catalysis,[1b,2] photoluminescence,[3] molecular magnet,[4] and so on.[5] However, rational design and construction of CPs with desired structure and geometry is still a great challenge. As many factors such as solvent,[6] pH value,[7] ratio of reactants,[8] temperature,[9] counteranion,[10] and so on, can affect the final product of the reaction. Among these factors, the pH value has proven significant effect on the product formation. A common observation is that at different pH values polycarboxylic acid shows different deprotonation and thus exhibits rich coordination modes to coordinate with metal ions to form diverse CPs.[7c.d] In addition, at higher pH value, the excess OH^- anions can act as bridges to connect metal ions to generate polynuclear clusters, which usually leads to the formation of novel CPs with highly-connected topological network.[11] Therefore, pH value controlled syntheses is an effective approach for the constructions of CPs.

To date, most reported metal CPs are assembled from aromatic polycarboxylates[11a,12,13] or N-heterocyclic carboxylates.[14,15] Because these types of ligands can employ flexible and diverse coordination modes during the assembly processes. Recently, 1*H*-tetrazole (Htz) and its derivatives have also been used as ligands to construct functional CPs.[16-18] 5-amino-tetrazole (Hatz), as one of the Htz's derivatives, has currently attracted much interest in coordination chemistry. Numerous Hatz-based CPs have been synthesized from *in situ* or *ex situ* reactions during the past several years.[19,20] However, CPs constructed from mixed ligands including Hatz and polycarboxylic acid are still limitedly reported so far.[20]

The use of mixed ligands has proved to be an effective and useful strategy for constructions of CPs with intriguing architectures and topologies.[18,20,21] Our recent research interest focuses on the use of mixed ligands of Hatz and polycarboxylic acid to construct functional CPs. In this paper, we selected Hatz and 1,2,4,5-benzenetetracarboxylic acid (H_4btec) as the mixed ligands. By controlling pH values of reactions, we obtained two Hatz-H_4btec-based 3D cadmium(II) coordination polymers, $\{K[Cd_2(atz)(btec)(H_2O)_2]\}_n$ (**1**) and $[Cd_3(OH)(atz)(btec)(H_2O)_2]_n \cdot nH_2O$ (**2**). Their syntheses, crystal structures and luminescent properties have been investigated and discussed.

Experimental Section

Materials and physical measurements

All the reagents were commercially obtained and used without further purification. Elemental analyses (EA) were determined using an Elementar Vario EL elemental analyzer. The infrared spectra (IR) were recorded in the 4000-400 cm^{-1} region using KBr pellets with a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) data were carried out on a Netzsch TG-209 thermogravimetry analyzer under N_2 atmosphere in the temperature range of 20-800 °C with a heating rate of 10 °C/min. The powder X-ray diffraction (PXRD) measurements were recorded on Bruker D8 ADVANCE powder X-ray diffractometer (Cu $K\alpha$, $\lambda = 1.5418$ Å). Photoluminescent measurements were conducted on a Shimadzu RF-5301PC fluorescence spectrophotometer for the solid polycrystalline samples under ambient temperature.

Synthesis of $\{K[Cd_2(atz)(btec)(H_2O)_2]\}_n$ (1). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.308 g, 1.0 mmol), Hatz (0.086 g, 1.0 mmol), H_4btec (0.127 g, 0.5 mmol), KOH (0.168 g, 3.0 mmol), and distilled water (10 mL) was stirred for 30 minutes, and then sealed in a 25 mL Teflon-lined stainless steel container under autogenous pressure and heated at 170 °C for 72 hours. After the oven was cooled to the room temperature at a rate of 5 $°C \cdot h^{-1}$, colorless block-shaped crystals were collected, washed with distilled water and dried in air. The pH values of the mixture before and after reaction were ~6. Yield: 76% (based on $Cd(NO_3)_2 \cdot 4H_2O$). Elemental analyses calcd (%) for $C_{11}H_8N_5O_{10}Cd_2K$ (**1**): C, 20.83; H, 1.27; N, 11.04. Found: C, 20.90; H, 1.32; N, 11.12. IR (KBr, cm^{-1}; Fig. S1): 3438 (m), 3346 (m), 3244 (b), 1646 (m), 1556 (s), 1484 (s), 1438 (s), 1382 (s), 1324 (m), 1144 (m), 1098 (w), 922 (w), 876 (m), 828 (m), 812 (m), 766 (m), 752 (w), 672 (w), 590 (m), 514 (m), 466 (m), 450 (w).

Synthesis of $[Cd_3(OH)(atz)(btec)(H_2O)_2]_n \cdot nH_2O$ (2). These colorless crystals were obtained by a similar procedure to that for **1** except using 4.0 mmol (0.224 g) KOH instead of 3.0 mmol (0.168 g) KOH. The pH values of the mixture before and after reaction were ~9. Yield: 64% (based on $Cd(NO_3)_2 \cdot 4H_2O$). Elemental analyses calcd (%) for $C_{11}H_{11}N_5O_{12}Cd_3$ (**2**): C, 17.79; H, 1.49; N, 9.43. Found: C, 17.90; H, 1.52; N, 9.62. IR (KBr, cm^{-1}; Fig. S1): 3562 (m), 3427 (vs), 3315 (vs) 3248 (s), 1649 (s), 1570 (s), 1531 (s), 1433 (s), 1385 (s), 1327 (m), 1142 (m), 1095 (w), 877 (m), 833 (m), 756 (w), 729 (m), 677 (m), 575 (m), 534 (m), 500 (w).

Determination of Crystal Structures

Single-crystal data for **1** and **2** were collected on an Agilent Xcalubur Nova CCD diffractometer with graphite monochromatic Mo *K*α radiation (λ = 0.71073 Å). Cell refinement and data reduction were applied using the program of CrysAlis PRO. The structures were solved using the direct method, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms of the betc^{4-} and atz^{-} ligands were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of coordinated water molecules in **1** and **2**, and hydroxy in **2** were located in the difference Fourier maps and refined isotropically. The hydrogen atoms of the disordered lattice water molecules in **2** were not assigned. All calculations were performed using the SHELXTL-97 system of computer programs.[22] The crystallographic data and structural refinements were summarized in Table 1, and the selected bond lengths and angles were listed in Table S1.

Results and Discussion

Syntheses

Although the formation of CPs are very sensitive to the pH values of the reaction systems, reports on constructions of CPs by delicately tuning the pH value are limited.[7,11] With the same reactants and synthetic conditions, we, by tuning the pH values of the reaction systems, have constructed two Hatz-H_4btec-based cadmium(II) CPs with completely different structures. At pH ~6 (adjusted with KOH), the ligands Hatz and H_4btec deprotonate and coordinate to the central metal Cd(II) ion to form **1**. At a higher pH value of ~9, the ligands Hatz and H_4btec also deprotonate and bond with the central metal Cd(II) ions. Additionally, the excess OH^- anion, acting as a μ_3-brigde, participates in the assembly process of the framework, which leads to the formation of a new coordination polymer (**2**). This observation reveals that pH value controlled syntheses is really a powerful strategy for fabrication of functional coordination polymers with diverse structures, which is consistent with the conclusion demonstrated in literatures.[7,11] Additionally, we have found that the hydrothermal reactions of $CdCl_2$/$Cd(Ac)_2$ with Hatz and H_4btec can also produce **1** and **2** under the same condition (Fig. S3), which indicates that the influence of the metal precursor to the formation of **1** or **2** is negligible, and further reveals that in this reaction system the pH value is the most important factor that determines the final product of the reaction. Considering Zn(II) ion has similar coordination modes to Cd(II), we tried to use Zn(II) instead of Cd(II) to assemble coordination polymers. However, we can not get the Hatz-H_4btec-based Zn(II) CPs under the same condition, which may be attributed to the smaller ion radii of Zn(II) ion.

Crystal structures

The result of single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic system with the space group of *C*2/*c*. The asymmetrical unit of **1** contains one $[Cd_2(atz)(btec)(H_2O)_2]^-$ coordinated unit and one anti-cation K^+. As shown in Fig. 1a, the central metal Cd(1) ion is six-coordinated with four oxygen atoms (O(1), O(2), O(3B) and O(4A)) from three carboxylate groups of three individual μ_6-btec^{4-} ligands (Scheme 1a), one nitrogen atom (N(2)) from one μ_2-atz$^-$ ligand (Scheme 1c), and one coordinated water molecule (O(1W)), resulting in a slightly distorted octahedral geometry (Fig. S2a). O(1), O(2), O(4A) and N(2) locate the equatorial quasi-plane. O(1W) and O(3B) occupy the axial positions. The four carboxylate groups of H_4btec and the imine group of Hatz deprotonate. The resulted btec^{4-} and atz$^-$ anions employing μ_6- and μ_2- bridging coordination modes respectively (Scheme 1a and 1c), bond with six and two Cd(II) ions. The bond lengths of Cd-O (2.243(3)-2.429(3) Å) and Cd-N (2.210(4) Å) (Table S1) are comparable with those reported in other Cd(II) compounds.[8,12c,15b,e,16,19c] Through the bridging of μ_6-btec^{4-} and μ_2-atz$^-$ anions, the Cd(II) ions are connected together to generate a 3D anionic microporous framework along the *c* axis (Fig. 1b). The K$^+$ ions, as anti-cations to balance the charge of the framework, locate the micropores and weakly interact with the carboxyl oxygen atoms of μ_6-btec^{4-} ligands (Fig. 1b).

To well understand the structure of **1**, the topological approach was applied to simplify and analyze the framework of **1**. Obviously, the μ_2-atz$^-$ anion, connecting two Cd(II) ions, should be considered as a linker. The Cd(II) ions, connecting three μ_6-btec^{4-} and one μ_2-atz$^-$ anions, can be regarded as a 4-connected node (Fig. 1c). The μ_6-btec^{4-} anion, bonded with six Cd(II) ions, can be viewed as a 6-connected node (Fig. 1d). Therefore, a (4,6)-connected network with the Schläfli symbol of $\{4^2\cdot5\cdot6^3\}\{4^4\cdot5^4\cdot6^3\cdot7^4\}$ is formed (Fig. 1e), which has not been reported in literature before this work.[23]

Raising the pH value to ~9, we obtained a new coordination polymer (**2**). Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in the triclinic system with space group of $P\bar{1}$. The structure contains three crystallographically independent Cd(II) ions. As illustrated in Fig. 2a, all Cd(II) ions are six-coordinated and show similar distorted $\{CdNO_5\}$ octahedral geometry. The nitrogen atom coordinating with Cd(1)/Cd(2)/Cd(3) is from μ_3-atz$^-$ ligand (Scheme 1d). The five oxygen atoms (O(1), O(2), O(8A), O(5B) and O(7B)) bonding with Cd(1) come from three individual μ_9-btec^{4-} ligands (Scheme 1b) (Fig. S2b), while those (O(1), O(6D), O(3E), O(9), and O(1W)) around Cd(2) are from three individual μ_9-btec^{4-} ligands (Scheme 1b), one coordinated water molecule and one μ_3-OH$^-$ bridge (Fig. S2c), and those (O(3G), O(4B), O(9B), O(9F) and O(2W)) binding with Cd(3) come from two individual μ_9-btec^{4-} ligands, two μ_3-OH$^-$ bridges and one coordinated water molecule (Fig. S2d). In contrast to **1**, the ligands of btec^{4-} and atz$^-$ anions in **2** employ more complicated coordination modes (Scheme 1b and 1d). The btec^{4-} anion acts as a μ_9- bridge connecting nine Cd(II) ions, which is rarely observed in H$_4$btec-based coordination polymers.[18e,f,24] The atz$^-$ anion serves as a μ_3- bridge linking three Cd(II) ions. The bond lengths of Cd-N (2.250(4)-2.392(5) Å) and Cd-O bond (2.218(4)-2.490(3) Å) are in good agreement with literature values (Table S1).[8,12c,15b,e,16,19c] It should be noted that the OH$^-$ anion, adopting a μ_3- bridging coordination mode, takes part in the construction of the framework. Two μ_3-OH$^-$ anions connect two Cd(2) and two Cd(3) to form a tetra-nuclear [Cd$_4$(μ_3-OH)$_2$] cluster, which is further linked with two Cd1 by the bridges of two μ_3- atz$^-$ anions, generating a [Cd$_6$(μ_3-OH)$_2$(μ_3-atz)$_2$]$^{8+}$ structural unit (Fig. 2b). The [Cd$_6$(μ_3-OH)$_2$(μ_3-atz)$_2$]$^{8+}$ structural units are further connected together by μ_9-btec^{4-} ligands, resulting in a 3D porous structure (Fig. 2e), in which each [Cd$_6$(μ_3-atz)$_2$(μ_3-OH)$_2$]$^{8+}$ structural unit connects ten μ_9-btec^{4-} ligands (Fig. 2c), and each μ_9-btec^{4-} ligand links five hexanuclear Cd(II) clusters (Fig. 2d). Consequently, a rare (5,10)-connected 3D topological network with the Schläfli symbol of $\{4^{10}\}_2\{4^{28}\cdot6^{16}\cdot8\}$ is generated (Fig. 2f). To the best of our knowledge, **2** represents the first (5,10)-connected network among reported CPs.[23]

X-ray powder diffraction, thermal stability analysis and luminescent properties

The phase purity of the bulk sample of **1** and **2** were identified by powder X-ray diffraction

(PXRD). As shown in Fig. S3, all the peaks displayed in the measured patterns at room temperature closely match to those in the simulated patterns generated from single-crystal diffraction data, indicating that single phases of **1** and **2** have been formed. The thermogravimetric analyses (TGA) for **1** and **2** were estimated under N_2 atmosphere from 20 to 800 °C at a heating rate of 10 $°C{\cdot}min^{-1}$ (Fig. 3). The TGA curve of **1** shows a weight loss of 5.9% in the temperature range of 150-227 °C, corresponding to the loss of the coordinated water molecules (calcd. 5.7%). The desolvated 3D framework is stable up to 280 °C, followed by another two continuous weight losses after that temperature. **2** loses its lattice and coordinated water in the 50-380 °C temperature range. The weight loss of 9.6% is consistent with that calculated (9.5%). Upon further heating, the desolvated framework began to decompose by another two step of continuous weight losses.

Constructed from a metal center with d^{10} electronic configuration and two mixed-ligands with conjugated systems, **1** and **2** may exhibit excellent photoluminescent behaviors. Hence, we measured their photoluminescent properties in the solid state at room temperature. As shown in Fig. 4, **1** and **2** show blue photoluminescence emission at 470 and 457 nm upon excitation at 350 and 370 nm, respectively. According to the literature,[18f,g,19c,20a] the free H_4btec and Hatz ligands exhibit weaker luminescent emission bands at 397 and 325 nm, respectively. Compared with the emission spectra of the free H_4btec and Hatz ligands, the emission peaks of **1** and **2** significantly red shift, which may be attributed to the deprotonated effects of H_4btec and Hatz ligands, the cooperative effects of intraligand emission, and the coordination interactions between ligands and Cd(II) ions. As the Cd(II) ion is difficult to be oxidized or reduced, the photoluminescence emissions of **1** and **2** may be assigned to intraligand (n-π^* or π-π^*) fluorescent emission.[3a,13e,18f,25]

Conclusions

In summary, by pH value controlled strategy, we have successfully synthesized two 3D Cd(II)

CPs with mixed-ligands of H_4btec and Hatz under the same reaction condition. **1** is a 3D coordination polymer with rare (4,6)-connected topological network, and **2** is a 3D porous framework with rare (5,10)-connected topological network. Photoluminescent investigations indicate that **1** and **2** may be potential blue materials.

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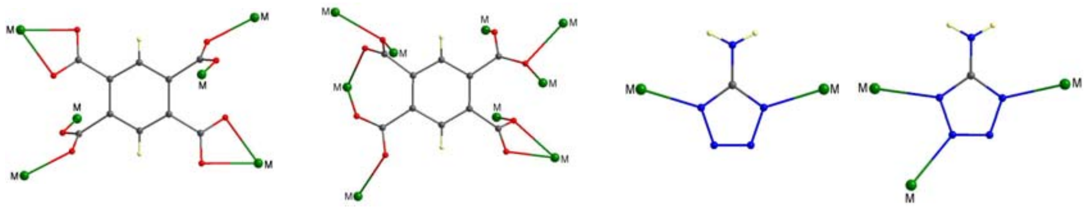
Table 1. Crystal Data and Structure Refinements for **1** and **2**

	1	**2**
Formula	$C_{11}H_8Cd_2KN_5O_{10}$	$C_{11}H_{11}Cd_3N_5O_{12}$
Fw.	634.12	742.45
Temperature (K)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	10.9578(3)	6.5950(4)
b (Å)	16.3093(5)	9.1653(5)
c (Å)	9.2414(3)	14.1958(10)
α (°)	90.00	85.873(5)
β (°)	97.956(3)	82.166(5)
γ (°)	90.00	74.734(4)
V (Å^3)	1635.67(9)	819.48(9)
Z	4	2
D_c (g·cm^{-3})	2.575	3.009
F(000)	1216	704
θ range(°)	2.50 to 27.00	2.68 to 27.00
Reflections collected/Unique *R*(int)	3486/1778(0.0380)	6240/3555(0.0296)
Data/restraints/parameters	1778/4/142	3555/0/295
GOF on F^2	1.044	1.060
$R_1[I\geq2\sigma(I)]$	0.0341	0.0364
$wR_2[I\geq2\sigma(I)]$	0.0560	0.0593



(a) μ_6-btec^{4-} (b) μ_9-btec^{4-} (c) μ_2-atz$^-$ (d) μ_3-atz$^-$

Scheme 1 Coordination modes of btec^{4-} and atz$^-$ ligands observed in **1** and **2**.

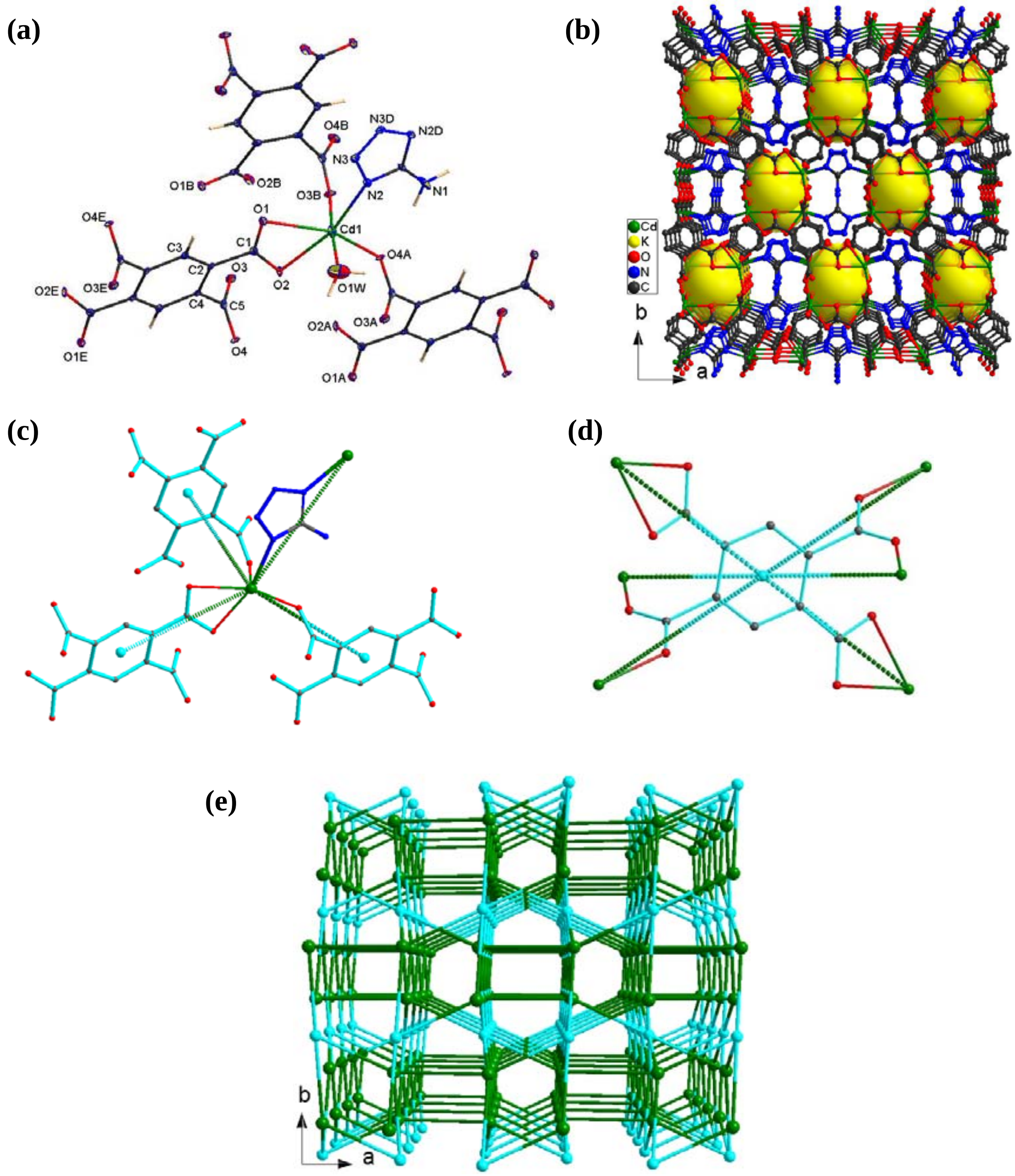


Fig. 1 (a) Coordination environment of Cd(II) ion in **1** (thermal ellipsoids are drawn at a 30% probability level. Symmetry codes: A -*x*, -*y*+1, -*z*; B -*x*, *y*, -*z*+1/2; D -*x*+1, *y*, -*z*+1/2; E -*x*-1/2, -*y*+1/2, -*z*). (b) 3D framework of **1** (K^+ ions are shown in space-filling model). (c) 4-Connected Cd(II) node. (d) 6-Connected μ_6-$betc^{4-}$ node. (e) Binodal (4,6)-connected topological network in **1**.

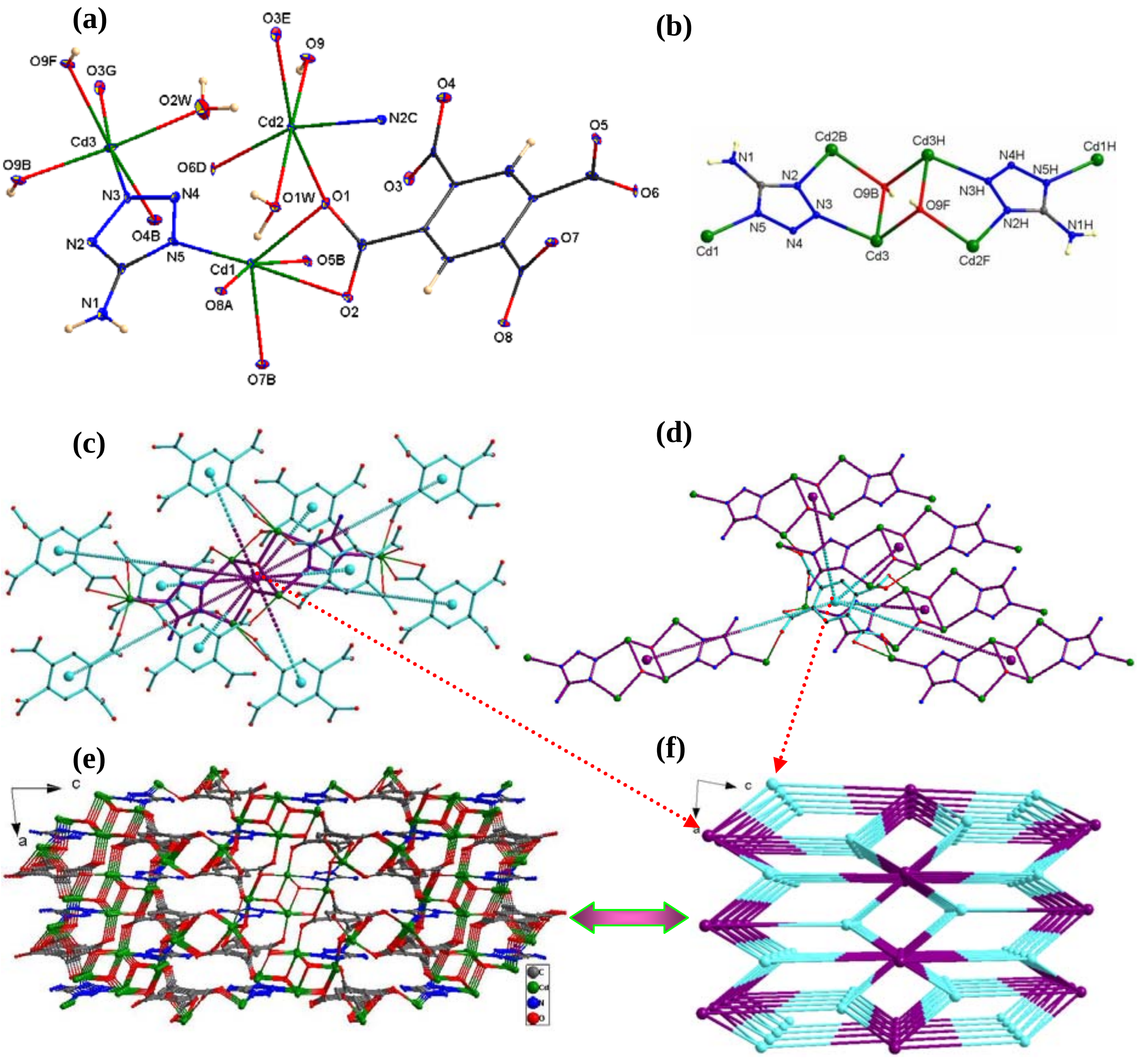


Fig. 2 (a) Coordination environments of Cd(II) ions in **2** (thermal ellipsoids are drawn at a 30% probability level. Symmetry codes: A -*x*+1, -*y*, -*z*; B *x*, *y*+1, *z*; C *x*, *y*-1, *z*; D *x*-1, *y*+1, *z*; E *x*-1, *y*, *z*; F -*x*, -*y*+1, -*z*+1; G -*x*+1, -*y*+1, -*z*+1; H -*x*, 2-*y*, 1-*z*). (b) $[Cd_6(\mu_3\text{-OH})_2(\mu_3\text{-atz})_2]^{8+}$ unit in **2**. (c) 10-Connected node of $[Cd_6(\mu_3\text{-atz})_2(\mu_3\text{-OH})_2]^{8+}$. (d) 5-Connected node of μ_9-betc^{4-}. (e) 3D framework of **2**. (f) Binodal (5,10)-Connected topological network of **2**.

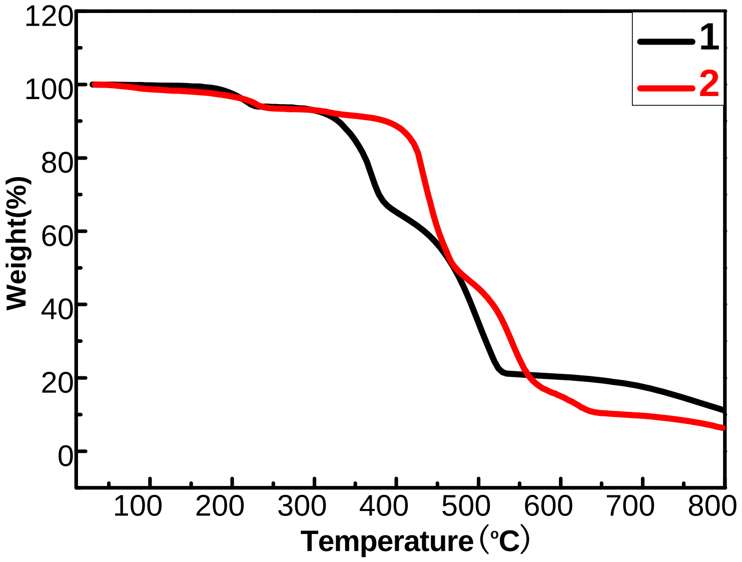


Fig. 3 TGA curves for **1** and **2**.

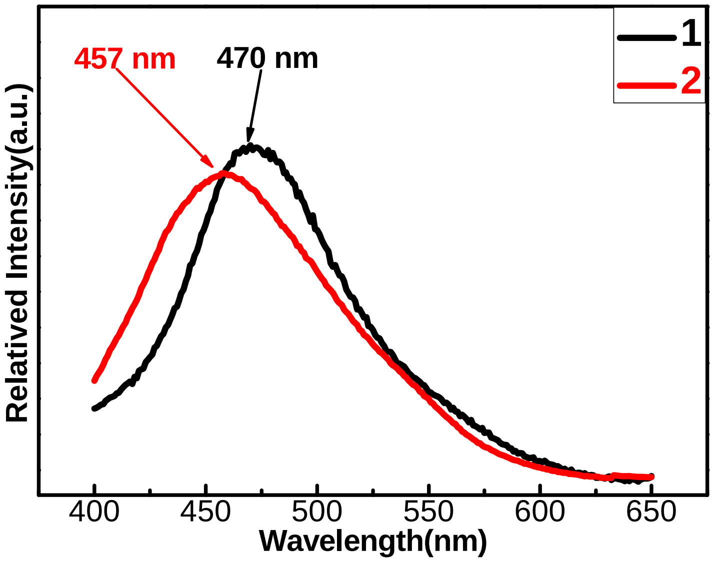


Fig. 4 Solid-state luminescent emission spectra of **1** and **2** at room temperature (λ_{ex} = 350 and 370 nm, respectively).

TOC graphic for

Two three-dimensional cadmium(II) coordination polymers based on 5-amino-tetrazolate and 1,2,4,5-benzenetetracarboxylate: pH value controlled syntheses, crystal structures, and luminescent properties

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Two 3D cadmium(II) coordination polymers based on mixed-ligands of 5-amino-tetrazole (Hatz) and 1,2,4,5-benzenetetracarboxylic acid (H_4btec) have been prepared by controlling the pH values of the reaction mixture.