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### pH-dependent synthesis of a cadmium coordination compound from a compound based on Hpytz ligand [Hpytz = 5-(4-pyridyl)tetrazole]

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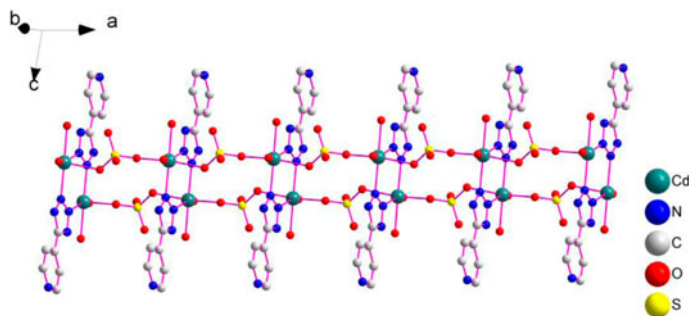
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## pH-dependent synthesis of a cadmium coordination compound from a compound based on Hpytz ligand [Hpytz = 5-(4-pyridyl)tetrazole]

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Two new cadmium coordination compounds were synthesized under different pH values. The luminescent properties were investigated at room temperature in the solid state.

Reactions of  $\text{CdSO}_4 \cdot 6\text{H}_2\text{O}$  and Hpytz [Hpytz = 5-(4-pyridyl)tetrazole] under high pH values produced a known compound,  $[\text{Cd}(\text{pytz})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  (**1**), which can be used to prepare  $[\text{Cd}(\text{Hpytz})(\text{SO}_4)(\text{H}_2\text{O})_2]$  (**2**) by adjusting the pH to a lower level using sulfuric acid under hydrothermal conditions. These compounds were characterized by elemental analysis, IR spectroscopy, and single-crystal diffraction. X-ray analysis reveals that **1** features a mononuclear structure, while **2** affords a 1-D polymeric chain structure. Compound **1** displays a 2-D network, while **2** shows a 3-D network by hydrogen bonding interactions. Furthermore, the luminescent properties were investigated at room temperature in the solid state.

*Keywords:* pH; Cadmium; Crystal structure; Luminescence

### 1. Introduction

Tetrazole along with its derivatives plays an important role in all fields of chemistry, owing to their unique structures and potential applications in advanced materials [1–8]. Numerous

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tetrazole derivatives such as 5-methyl-, 5-ethyl-, 5-amino-, 5-(2-pyridyl)-, 5-(3-pyridyl)-, 5-(4-pyridyl)-tetrazole, have been extensively researched, and a number of complexes based on these ligands have been reported [9–14]. To extend the previous work, we have investigated 5-(4-pyridyl)tetrazole (Hpytz, scheme 1) coordination compounds with cadmium because cadmium still remains one of the most commonly encountered toxic metal pollutants in the environment; therefore, there is a need for exploiting the unique coordination chemistry of Cd(II) [15] for the development of practical ligands as extractants, cadmium-poisoning treatment agents, and sensors. In this article, we describe the synthesis of a Cd-Hpytz-SO<sub>4</sub><sup>2-</sup> coordination compound that may be taken advantage of, as an effective approach to reducing the Cd(II) ions. By reacting 5-(4-pyridyl)-tetrazole (Hpytz) and CdSO<sub>4</sub>·6H<sub>2</sub>O under high pH values, [Cd(pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (**1**) was obtained, which can be further used to prepare [Cd(Hpytz)(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] (**2**) by adjusting the pH to a lower level under hydrothermal conditions. Herein, we will describe the synthesis, crystal structures, and luminescent properties.

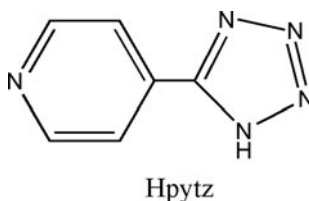
## 2. Experimental

### 2.1. Materials and instrumentations

5-(4-Pyridyl)tetrazole (designated as Hpytz) was prepared by [2 + 3] cycloaddition by treating 4-cyanopyridine with NaN<sub>3</sub> in toluene in the presence of triethylammonium chloride. Other chemicals were commercially available reagents of analytical grade and were used without purification. Elemental analyses for C, H, and N were performed with a PE2400 elemental analyser. IR spectra were obtained on a NICOLET380 spectrum using KBr disks from 4000 to 400 cm<sup>-1</sup>. Photoluminescent analyses were performed on an F-4600 fluorescence spectrometer. Single-crystal X-ray diffraction was carried out by a Rigaku SCXmini-CCD diffractometer. The pH was measured on a PHS-3C instrument.

### 2.2. Synthesis of [Cd(pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (**1**)

Hpytz (0.0147 g, 0.1 mM) was dissolved in 2 mL distilled water; then 2 mL ethanol and CdSO<sub>4</sub>·6H<sub>2</sub>O (0.0317 g, 0.1 mM) were added and stirred at room temperature for 2 h. Colorless crystals of **1** were obtained after one week. For **1**, yield: 46% based on Cd<sup>2+</sup> consumed. Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>10</sub>O<sub>13</sub>Cd, H: 3.93%, C: 28.11%, N: 27.32%. Found: H: 3.95%, C: 28.07%, N: 27.38%. IR (KBr, cm<sup>-1</sup>): 3381(w), 3098(w), 1626(s), 1528(s), 1383(s), 1119(w), 1042(w), 1018(w), 846(m), 750(m), 713(w).



Scheme 1. Schematic drawing for Hpytz.

### 2.3. Synthesis of $[Cd(Hpytz)(SO_4)(H_2O)_2]$ (**2**)

Compound **2** was prepared from **1** by adjusting the pH to 2 with  $H_2SO_4$  ( $0.2\text{ ML}^{-1}$ ) and the solution was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at  $120\text{ }^\circ\text{C}$  for 24 h and cooled to room temperature. Slow evaporation gave colorless crystals of **2**. For **2**, yield: 54% based on  $Cd^{2+}$  consumed. Anal. Calcd for  $C_6H_9N_5O_6SCd$ , H: 2.32%, C: 18.40%, N: 17.88%. Found: H: 2.25%, C: 18.34%, N: 17.96%. IR (KBr,  $cm^{-1}$ ): 3427(m), 3223(m), 3158(m), 3097(m), 1677(m), 1633(s), 1531(m), 1440(w), 1384(s), 1221(w), 1096(w), 1045(w), 982(m), 845(w), 794(w).

### 2.4. X-ray crystallography

Suitable single crystals of **1** and **2** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) at 291 K. All absorption corrections were performed using the Crystal-Clear program. The crystal structures of **1** and **2** were solved by direct methods and refined on  $F^2$  by full matrix least-squares method, using anisotropic displacement parameters for all non-hydrogen atoms [16]. For **1** and **2**, important crystal data and collection and refinement parameters are summarized in table 1, selected bond lengths and angles are given in table 2, and hydrogen-bonding geometries are listed in table 3.

Table 1. Selected crystallographic data and structure refinement for **1** and **2**.

| Compound  | <b>1</b>                  | <b>2</b>          |
|---|---------------------------|-------------------|
| Empirical formula                                 | $C_{12}H_{20}CdN_{10}O_6$ | $C_6H_9CdN_5O_6S$ |
| Formula mass                                      | 512.79                    | 390.63            |
| Crystal system                                    | Triclinic                 | Triclinic         |
| Space group                                       | $P\bar{1}$                | $P\bar{1}$        |
| $a$ ( $\text{\AA}$ )                              | 7.3436(15)                | 6.7256(13)        |
| $b$ ( $\text{\AA}$ )                              | 7.8978(16)                | 9.2788(19)        |
| $c$ ( $\text{\AA}$ )                              | 8.8561(18)                | 10.056(2)         |
| $\alpha$ ( $^\circ$ )                             | 90.50(3)                  | 106.27(3)         |
| $\beta$ ( $^\circ$ )                              | 90.43(3)                  | 104.66(3)         |
| $\gamma$ ( $^\circ$ )                             | 99.68(3)                  | 101.65(3)         |
| $V$ ( $\text{\AA}^3$ )                            | 506.29(18)                | 557.09(19)        |
| $Z$   | 1                         | 2                 |
| $T$ (K)   | 291(2)                    | 291(2)            |
| $D_{\text{calcd}}$ ( $g\text{ cm}^{-3}$ )         | 1.682                     | 2.329             |
| $\mu$ ( $mm^{-1}$ )                               | 1.130                     | 2.182             |
| Reflections collected                             | 5266                      | 5760              |
| Unique reflections ( $R_{\text{int}}$ )           | 2311 (0.0297)             | 2539 (0.0273)     |
| No. observations [ $I > 2.00\sigma(I)$ ]          | 6799                      | 2340              |
| No. variables                                     | 148                       | 172               |
| $R^a$ , $wR^b$                                    | 0.0322, 0.0820            | 0.0345, 0.0856    |
| GOF <sup>c</sup>                                  | 1.023                     | 1.019             |
| $\Delta\rho_{\text{max}}$ ( $e\text{ \AA}^{-3}$ ) | 0.455                     | 1.042             |
| $\Delta\rho_{\text{min}}$ ( $e\text{ \AA}^{-3}$ ) | -0.756                    | -0.956            |

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

$$^c \text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}, \text{ where } n = \text{number of reflections and } p = \text{total numbers of parameters refined.}$$

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

|   |            |                   |            |
|---|------------|-------------------|------------|
| [Cd(pytz) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]·2H <sub>2</sub> O ( <b>1</b> ) |            |                   |            |
| Cd(1)–O(2)  | 2.3021     | Cd(1)–O(2A)       | 2.3021     |
| Cd(1)–O(1)  | 2.3102     | Cd(1)–O(1A)       | 2.3102     |
| O(2)–Cd(1)–O(2A)  | 180.0      | O(2)–Cd(1)–O(1)   | 90.2       |
| O(2A)–Cd(1)–O(1)  | 89.8       | O(2)–Cd(1)–O(1A)  | 89.8       |
| O(2A)–Cd(1)–O(1A)   | 90.2       | O(2)–Cd(1)–O(1A)  | 180.0      |
| O(1)–Cd(1)–N(1A)  | 88.78(6)   | O(1A)–Cd(1)–N(1A) | 91.22(12)  |
| O(2)–Cd(1)–N(1A)  | 87.27(7)   | O(2A)–Cd(1)–N(1A) | 92.73(7)   |
| O(2)–Cd(1)–N(1)   | 92.73(7)   | O(2A)–Cd(1)–N(1)  | 87.27(7)   |
| O(1)–Cd(1)–N(1)   | 91.22(6)   | O(1A)–Cd(1)–N(1)  | 88.78(7)   |
| N(1A)–Cd(1)–N(1)  | 180.0      |                   |            |
| [Cd(Hpytz)(SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ] ( <b>2</b> )              |            |                   |            |
| Cd(1)–O(3B)   | 2.257(3)   | Cd(1)–O(6)        | 2.285(3)   |
| Cd(1)–N(2)  | 2.312(4)   | Cd(1)–O(5)        | 2.318(3)   |
| Cd(1)–O(1)  | 2.336(3)   | Cd(1)–N(3A)       | 2.393(4)   |
| O(3B)–Cd(1)–O(6)  | 108.61(13) | O(3B)–Cd(1)–N(2)  | 87.87(14)  |
| O(6)–Cd(1)–N(2)   | 93.92(13)  | O(3B)–Cd(1)–O(5)  | 93.89(13)  |
| O(6)–Cd(1)–O(5)   | 80.99(12)  | N(2)–Cd(1)–O(5)   | 174.91(12) |
| O(3B)–Cd(1)–O(1)  | 165.92(13) | O(6)–Cd(1)–O(1)   | 83.80(13)  |
| N(2)–Cd(1)–O(1)   | 84.59(13)  | O(5)–Cd(1)–O(1)   | 94.64(12)  |
| O(3B)–Cd(1)–N(3A)   | 85.57(13)  | O(6)–Cd(1)–N(3A)  | 158.17(13) |
| N(2)–Cd(1)–N(3A)  | 103.34(13) | O(5)–Cd(1)–N(3A)  | 81.57(13)  |
| O(1)–Cd(1)–N(3A)  | 84.63(13)  |                   |            |

Note: Symmetry codes for **1** A: 2 - x, 1 - y, -z; for **2**: A: 2 - x, 2 - y, 1 - z; B: 1 + x, y, z.

Table 3. Hydrogen-bonding geometry (Å and °) for **1** and **2**.

| D–H···A   | D–H  | H···A   | D···A    | D–H···A |
|---|------|---------|----------|---------|
| [Cd(pytz) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]·2H <sub>2</sub> O ( <b>1</b> ) |      |         |          |         |
| O(1)–H(1A)···O(3)#1   | 0.84 | 1.93    | 2.7633   | 171     |
| O(1)–H(1B)···N(5)#2   | 0.85 | 2.00(3) | 2.8137   | 162     |
| O(2)–H(2A)···O(3)   | 0.84 | 1.92    | 2.7465   | 168     |
| O(2)–H(2B)···N(4)#3   | 0.85 | 2.06(4) | 2.8762   | 164     |
| O(3)–H(3A)···N(2)#4   | 0.85 | 1.99(4) | 2.8344   | 176     |
| O(3)–H(3B)···N(3)#5   | 0.70 | 2.09(5) | 2.7849   | 171     |
| [Cd(Hpytz)(SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ] ( <b>2</b> )              |      |         |          |         |
| N(4)–H(4A)···O(5)#1   | 0.86 | 2.42    | 2.947(6) | 120     |
| O(5)–H(5B)···O(2)   | 0.85 | 1.95    | 2.713(6) | 149     |
| O(5)–H(5C)···O(2)#2   | 0.85 | 2.27    | 3.072(5) | 157     |
| O(6)–H(6B)···O(4)#3   | 0.85 | 2.54    | 2.199(6) | 135     |
| O(6)–H(6B)···N(1)#4   | 0.85 | 2.38    | 2.958(6) | 131     |
| O(6)–H(6C)···O(4)#5   | 0.82 | 1.98    | 2.751(5) | 158     |
| C(2)–H(2A)···O(2)#6   | 0.93 | 2.39    | 3.286(7) | 161     |
| C(3)–H(3A)···O(5)#4   | 0.93 | 2.56    | 3.183(6) | 125     |
| C(5)–H(5A)···O(2)#7   | 0.93 | 2.44    | 3.359(6) | 169     |

Note: Symmetry codes for **1**: #1 1 + x, y, z; #2 2 - x, 1 - y, 1 - z; #3 x, 1 + y, -1 + z; #4 x, 1 + y, z; #5 1 - x, -y, 1 - z; for **2**: #1 2 - x, 2 - y, 1 - z; #2 2 - x, 2 - y, 2 - z; #3 1 + x, y, -z; #4 2 - x, 1 - y, 1 - z; #5 1 - x, 1 - y, 1 - z; #6 x, -1 + y, -1 + z; #7 x, y, -1 + z.

### 3. Results and discussion

#### 3.1. General characterization of **1** and **2**

Both compounds **1** and **2** are air stable. All general characterizations were carried out with the crystal samples. The elemental analyses show that the components of these complexes

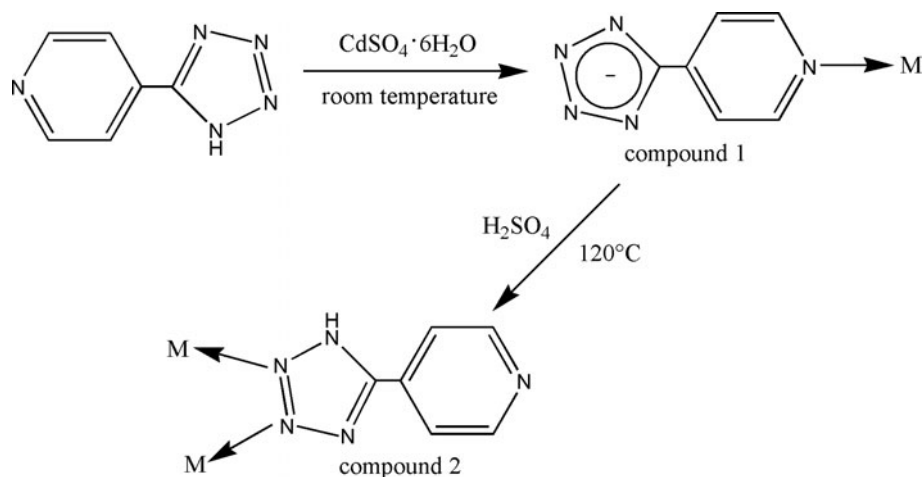
are in accord with the results of the structural analysis. IR spectra of the products show typical peaks (1383–1683  $\text{cm}^{-1}$ ) of the tetrazolyl and pyridyl groups. Peaks at 3351–3443  $\text{cm}^{-1}$  are from water, including coordinated water and perhaps uncoordinated water. The identities of **1** and **2** are confirmed by X-ray crystallography.

### 3.2. *pKa* of ligand

To characterize the acidity of the ligand, the *pKa* of Hpytz was measured at room temperature in aqueous solutions. Four different masses of the Hpytz ligand were dissolved in 100 mL distilled water (table S1, see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.965163>). From table S1, we calculate the *pKa* value to be 5.04. The acidity of Hpytz is lower than acetic acid. When the pH is high, one hydrogen of the tetrazolyl ring will be released to form pytz anion; while pH is low, pytz anion will combine with a hydrogen ion to form Hpytz, as shown in the synthesis procedure (scheme 2) and the crystal structures mentioned below.

### 3.3. Crystal structure of $[\text{Cd}(\text{pytz})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (**1**)

The X-ray analysis reveals that **1** crystallizes in triclinic space group  $P\bar{1}$  and the asymmetric unit contains only half of a  $[\text{Cd}(\text{pytz})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  molecule. As shown in figure 1, each Cd(II) is six-coordinated by two nitrogens from two independent pytz ligands (N1, N1A) and four oxygens from four water molecules (O1, O1A, O2, O2A) to give a distorted octahedral coordination geometry. Compared to the previously reported 1-D coordination polymers  $[\text{Cd}(\text{pn})_2(\text{trans-AT})]$  or  $[\text{Cd}(\text{en})_2(\text{trans-AT})]\cdot 4\text{H}_2\text{O}$  [17] in which 5,5'-azotetrazolate is a bidentate bridging ligand via its two nitrogens from two tetrazolyl rings, pytz ligand in **1** adopts a simpler mode. Each pytz is monodentate via nitrogen of the pyridyl ring to form a mononuclear structure, whereas tetrazolyl nitrogens are uncoordinated [18]. Adjacent  $[\text{Cd}(\text{pytz})_2(\text{H}_2\text{O})_4]$  molecules are further held together through six kinds of hydrogen bonding interactions between coordinated water and oxygen of solvent water  $[\text{O}(1)\text{--H}(1\text{A})\cdots\text{O}(3)$  2.7633Å/171°;  $\text{O}(2)\text{--H}(2\text{A})\cdots\text{O}(3)$  2.7465Å/168°], between coordinated water and nitrogen



Scheme 2. The synthesis procedure and changes in coordination mode caused by the pH value.

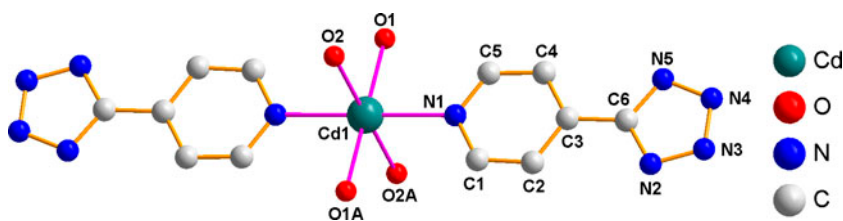


Figure 1. The coordination environment of Cd(II) of **1**. Hydrogens are omitted for clarity.

of the tetrazolyl ring [O(1)–H(1B)···N(5) 2.8137Å/162°; O(2)–H(2B)···N(4) 2.8762Å/164°], and between solvent water and nitrogen of the tetrazolyl ring [O(3)–H(3A)···N(2) 2.8344Å/176°; O(3)–H(3B)···N(3) 2.7849Å/171°], forming a 2-D supramolecular network extending along the *ac* plane (figure 2, table 3).

### 3.4. Crystal structure of [Cd(Hpytz)(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] (**2**)

Compound **2** crystallizes in triclinic space group *P* $\bar{1}$  and the asymmetric unit contains half of a [Cd(Hpytz)(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] molecule. Each Cd(II) center is six-coordinated by two nitrogens of the tetrazolyl ring from two independent Hpytz ligands (N2, N3A), two waters (O5, O6), and two oxygens from two independent sulfates (O1, O3B), generating a distorted octahedral coordination geometry (figure 3). Compared to **1**, each Hpytz in **2** is bidentate via its two nitrogens from the tetrazolyl ring to connect two independent Cd(II) centers and simultaneously each Cd(II) center is bridged by two oxygens from sulfate,

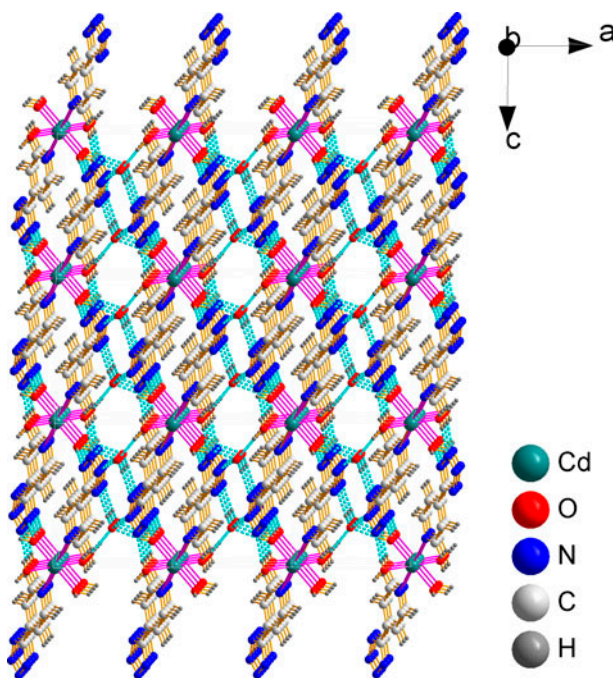


Figure 2. The 2-D network of **1** formed by hydrogen bonding interactions, extending along the *ac* plane.



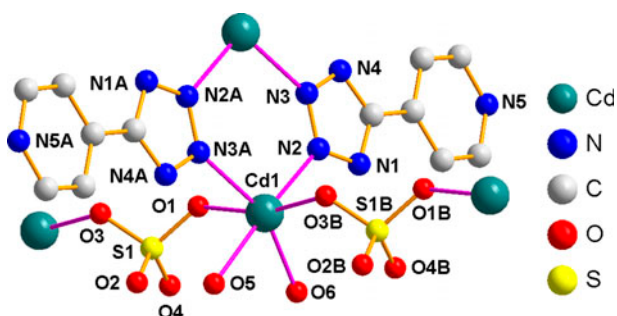


Figure 3. The coordination environment of Cd(II) of **2**. Hydrogens are omitted for clarity.

thereby displaying a 1-D polymeric chain with Cd $\cdots$ Cd distance of 6.7256 Å and Cd $\cdots$ Cd $\cdots$ Cd bite angle of 180° (figure 4). Compared to the previously reported Cd-5,5'-azotetrazolate complex [17], coordination mode of Hpytz in **2** is different since two nitrogens of the tetrazolyl ring (N1,N2) are connected to two Cd(II) centers, while in [Cd(pn)<sub>2</sub>(trans-AT)] or [Cd(en)<sub>2</sub>(trans-AT)]·4H<sub>2</sub>O, only one nitrogen of the tetrazolyl ring does.

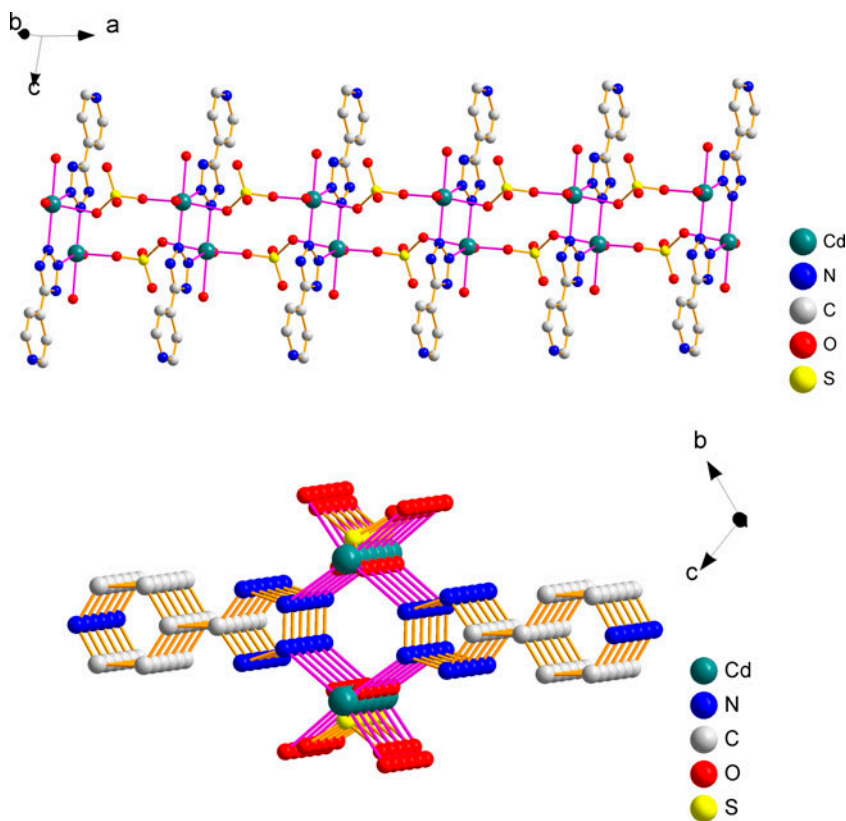


Figure 4. The 1-D polymeric chain structure of **2** (a) extending along the *a* axis, and (b) extending along the *c* axis.

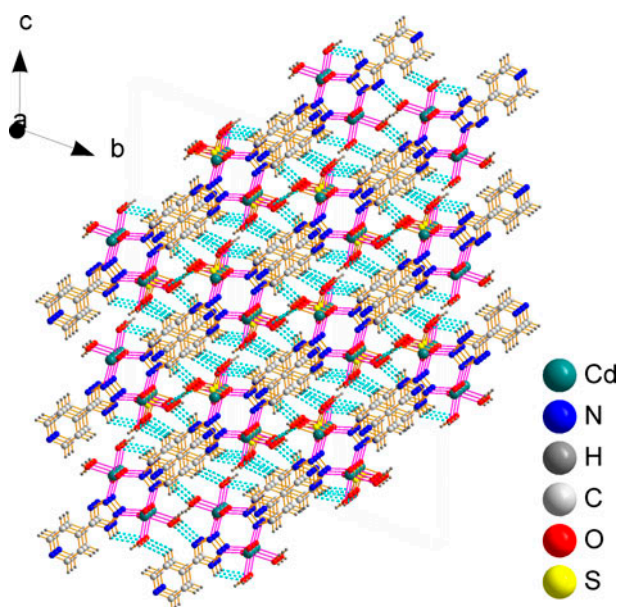


Figure 5. The 3-D structure of **2** formed by hydrogen bonding interactions.

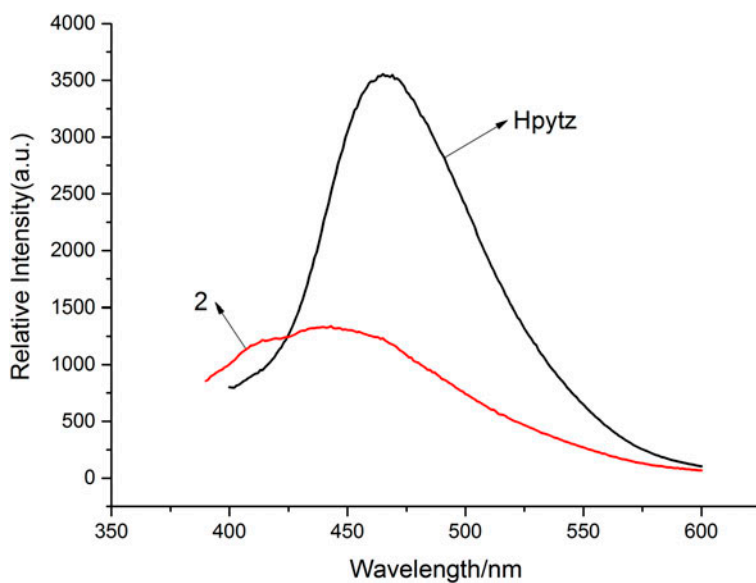


Figure 6. The emission spectra of free Hpytz and **2** at room temperature in the solid state (for Hpytz,  $\lambda_{\text{ex}} = 383$  nm; for **2**,  $\lambda_{\text{ex}} = 370$  nm).

Compound **2** shows a linear chain, while  $[\text{Cd}(\text{pn})_2(\text{trans-AT})]$  and  $[\text{Cd}(\text{en})_2(\text{trans-AT})] \cdot 4\text{H}_2\text{O}$  display zigzag chains. Within the 1-D chain, three hydrogen bonding interactions exist between coordinated water and the oxygen of sulfate  $[\text{O}(5)\text{--H}(5\text{B}) \cdots \text{O}(2)]$

2.713 Å/149°, O(5)–H(5C)⋯O(2) 3.072 Å/157°; O(6)–H(6B)⋯O(4) 2.199 Å/135°. The neighboring 1-D chains are linked through four kinds of hydrogen bonds: between the tetrazolyl ring and oxygen of coordinated water [N(4)–H(4A)⋯O(5) 2.947 Å/120°], between the coordinated water and nitrogen of the tetrazolyl ring [O(6)–H(6B)⋯N(1) 2.958 Å/131°], between coordinated water and the oxygen of sulfate [O(6)–H(6C)⋯O(4) 2.751 Å/158°], and between the C–H of the tetrazolyl ring and coordinated water [C(2)–H(2A)⋯O(2) 3.286 Å/161°; C(3)–H(3A)⋯O(5) 3.183 Å/125°; C(5)–H(5A)⋯O(2) 3.359 Å/169°], displaying a 3-D supramolecular network (figure 5, and table 3).

### 3.5. Luminescent properties

The luminescent properties of **2** and the free ligand were investigated at room temperature in the solid state. As shown in figure 6, **2** exhibits photoluminescence with maximum intensity at 440 nm upon excitation at 370 nm. The fluorescent emissions are tentatively assigned to intraligand emissions, because similar emissions were also observed for free Hpytz (465 nm) upon excitation at 383 nm. The weaker fluorescence observed with **2** is likely to be a result of fluorescence quenching by O–H oscillators of coordinated water and sulfate ligands. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the  $\pi$  and  $\pi^*$  molecular orbitals of the free ligand, which is related to the extent of  $\pi$  conjugation [19, 20].

## 4. Conclusion

We are the first to report the synthesis of a Cd-Hpytz-SO<sub>4</sub><sup>2-</sup> complex from Cd(II)-pytz molecule by changing the pH. When the pH is high, one hydrogen will be released to form pytz anion; however, when low, Hpytz will remain the same, which is demonstrated by the synthesis and crystal structures of **1** and **2**. The luminescence show the intraligand emissions of the ligand. Our results indicate that Cd-Hpytz(II)-based complexes are sensitive to pH values and further endeavors of other complexes are under way.

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