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# A family of functional Ln-organic framework constructed by iodine-substituted aromatic polycarboxylic acid for turn-off sensing of ${\rm UO_2}^{2+}$

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#### **1** | INTRODUCTION

At the end of the twentieth century, with the rapid development of inorganic materials as the main body of the crystallization, which promote the birth of a new type of

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With the rapid development of nuclear energy, one of the main constraints restricting the development of nuclear energy is the long-term safe disposal of strong uranium waste. Here it is a great significance that we use four new synthetic Ln (III)-based coordination polymers to test the uranium solution. In this study, four three-dimensional coordination polymers **1–4** (CPs-(**1–4**); Ln = Eu, Gd, Sm, Nd) were successfully synthesized through 1:1 complexation of Ln (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with poly-carboxylic acid ligand H<sub>3</sub>TIBTC (2,4,6-Triiodo-1,3,5-benzene tricarboxylic acid) which contains substituents of the carboxylic acid group and halogen atom, respectively. Based on the ligand being excellent fluorescent properties in the solution, it prompted us to further study the fluorescence properties of the coordination polymers. Experimental results show that the coordination polymers are favorable materials for the simultaneous selective detection uranium solution from water, being potentially useful in monitoring water quality and treating uranium-wastewater.

#### KEYWORDS

2,4,6-Triiodo-1,3,5-benzene tricarboxylic acid, coordination polymers, luminescence sensor, luminescent property, uranyl

crystal material---organic-inorganic hybrid coordination polymer (coordination polymer).<sup>[1-9]</sup> And the metalorganic materials have continued to expand in the fields of biochemistry, green chemistry and pharmaceutical chemistry.<sup>[10-13]</sup> Therefore, the design synthesis, mechanispolymerm and performance research of metal organic coordination polymers have developed rapidly into interdisciplinary research hotspots. At the same time,

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environmental problems that endanger human health and social sustainable development have become increasingly concerned and urgent issues to be solved, such as water pollution, air pollution, industrial waste pollution, etc.<sup>[14]</sup> Over the past few years, the use of nuclear power generation has greatly alleviated the demand for electricity, but in uranium water treatment, uranium enrichment and nuclear fuel reprocessing process will produce a lot of uranium-containing wastewater, which brought unprecedented pressure to the global environment and human survival safety.<sup>[15-19]</sup> Nowadays, governments and scientists have invested a lot of manpower, material and financial solution to the uranium-containing environmental problems. At present, the commercial methods used to test uranium contaminants and the instruments based on science and technologies are expensive and poor versatility. Therefore, develop a new and efficient method which has the ability to detect the uranium pollutant is extremely urgent need.

In recent years, porous coordination polymers crystalline material is an important branch, it has shown a certain value in the uranium detection and absorption, causing the scientific workers are widely concerned about it and research it.<sup>[20,21]</sup> Using different interactions between host and guest, coordination polymers have been developed in terms of molecular recognition and fluorescent probes, and many well-known scientists have made outstanding contributions in this field.<sup>[22-25]</sup> Coordination polymers materials for chemical testing must have a suitable conversion signal, the chemical effect into measurable physical quantities in which fluorescence is a very good signal<sup>[26–29]</sup> and it usually has the characteristics of the naked eye can be observed. Due to the unique luminescent properties of rare earth ions, lanthanide coordination polymers have been used as fluorescent probes.<sup>[30-35]</sup> In addition, a suitable signal conversion medium immobilized on the framework of the fluorescent coordination polymers material is also important, which should have a specific recognition at the molecular level with analytical and can continuously affect the signal change.<sup>[36]</sup> In the past, a large number of studies based on coordination polymers have focused on the application of single signal conversion media, unsaturated metal centers or Lewis base sites, and they have excellent responsiveness to individual components of organic molecules, metal ions or explosives. A variety of pre-functionalization and post-synthesis methods facilitate the introduction of different signal conversion media into the bulk coordination polymers material, the structure of a variety of organic ligands and easy functionalized pore surfaces to provide further possibilities for the introduction of different signal conversion media, which is beneficial to produce coordination polymers based

#### HIGHLIGHTS

- Four isostructural 3D network lanthanide coordination polymers
- 2,4,6-Triiodo-1,3,5-benzene tricarboxylic acid (H<sub>3</sub>TIBTC)
- Effective fluorescence detection of  $UO_2^{2+}$

fluorescence sensors with multiple response recognition capabilities.<sup>[37,38]</sup>

Coordination polymers based on carboxylic acid ligands have always been a hotspot for coordination chemists.<sup>[39-41]</sup> Relative to other nitrogen-containing ligands (such as pyridine, schiff base, imidazole), carboxvlic acid ligands have great advantages. Since carboxylic acids are extremely sensitive to pH, the different degree of deprotonation of the carboxyl groups at different pH values results in different coordination modes (Figure 1).<sup>[42]</sup> Carboxylic acid groups have a strong ability to bridge, which can take either double-dentate bridging or single-dentate bridging. Among many reported coordination polymers, the carboxyl groups have taken the coordination of multiple atoms in the case of a single ligand coordination mode, with the exception of a few auxiliary ligands (or water molecules) involved mode.<sup>[43,44]</sup> A wide range of coordination modes for poly-carboxylic acids can meet the needs of coordination and pattern of different metal ions and coordination angles. In addition, the carboxylic acid can also form the strong hydrogen bonds in the molecular packing.

Depending on the degree of deprotonation, a carboxyl group can be used as a donor for hydrogen bonds or as a hydrogen bond. Sometimes a number of carboxyl groups in a polycarboxylic acid ligand may be partially deprotonated, and in this case in the supramolecular weak force or coordination of the bond force driven by self-assembly, it can be provided as hydrogen donor and acceptor at the same time.<sup>[45]</sup> The poly-carboxylic acid ligand includes an aromatic carboxylic acid and an aliphatic carboxylic acid, and the aromatic carboxylic acid has the following characteristics with respect to the aliphatic carboxylic acid: i) Because it has the aromatic ring and does not have the rotation make it has an aromatic ring rigid, rigid ligand is more conducive to crystal growth than flexible ligand. ii) Due to the rigidity of the ligand itself, it is easier to connect metal ions to form a high-dimensional structure. The structure usually accompanied by the existence of holes, so these coordination polymers tend to have a novel topology. iii) The presence of conjugated systems in aromatic rings favors the



**FIGURE 1** Carboxylic acid with different coordination modes: (a) Single tooth; (b) Bridge double teeth; (c) Bridging single and double teeth; (d) Chelate bidentate; (e) Chelating bridge combined with double teeth; (f) Bridging single tooth; (g) Bridge double monocular; (h) Bridge type four tooth type

transmission of electrons, resulting the coordination polymers often have some special properties such as electrical and magnetic properties. Therefore most of them have great research value.<sup>[46]</sup> Trimesic acid is one of the most widely used and most studied ligands in the construction of new structures for the coordination polymers. The majority chemists love it the main reason not only because the above-mentioned aromatic carboxylic acid has the characteristics, but also its symmetrical arrangement of three carboxyl and benzene ring in the same plane. At the same time we independently synthesized this ligand on the basis of the trimesic acid which introduced iodide atoms and the conjugate system is conducive to electronic transfer, making the coordination polymers have some special properties in the field of fluorescence.<sup>[47-49]</sup> Because of the unique structure and properties of rare earth ions, lanthanide coordination polymers have wide application prospect in light, electricity, magnetism and catalysis. The luminescence of it has the advantages of long life, strong strength and pure color. In recent years, people have great interest in it and it has been becoming an active research field.

In this work, we have chosen a functional organic ligand (Scheme 1) containing both a polycarboxylic acid group and a halogen atom based on the following three points: i) Rigidity is advantageous for constructing the pore structure; ii) Overcoming the effect by the antenna effect that the rare earth ion absorption coefficient is low, easy to sensitize the light; iii) The conjugate ring can use the Lewis base site can be a variety of host and guest interaction to enhance its ability to



**SCHEME 1** The structure of 2,4,6-Triiodo-1,3,5-benzene tricarboxylic acid

detect. Using the solvent thermal reaction method, we successfully designed and synthesized four new rare earth-organic coordination polymers, and constructed a multi-responsive fluorescence sensor. It has a good fluorescence quenching response to uranium solution. To our knowledge, structures and properties of poly [tris (dimethylformamide)( $\mu_3$ -2,4,6-triiodol-1,3,5-benzene tricarboxylic acid)-lanthanide (III)] [Ln (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> (H<sub>3</sub>TIBTC = 2, 4, 6-Triiodo-1, 3, 5-benzene tricarboxylic acid) are reported rarely. In the work, we not only research synthesis and structure, but also investigate selective UO<sub>2</sub><sup>2+</sup> ion detection firstly. The experimental results indicate that the coordination polymers can be used as candidate materials for selective detection of uranium.

#### 2 | EXPERIMENTAL SECTION

#### 2.1 | Materials and methods

All chemicals purchased commercially were analytical grade or better and used without further purification. Solvents were purified according to the standard methods. The ligand 2,4,6-triiodo-1,3,5-benzene tricarboxylic acid (H<sub>3</sub>TIBTC) was prepared as reported previously and appropriately modified the methods. Elemental analyses of C, H, and N were conducted on a Perkin-Elmer 240C automatic analyzer at the analysis center of Liaoning Normal University. All IR measurements were obtained using a Bruker AXS TENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 400–4000  $\text{cm}^{-1}$  at room temperature. UV-Vis-NIR spectra for the coordination polymer and ligand were recorded on a JASCO V-570 UV/VIS/NIR microspectrophotometer (200-2500 nm, in form of solid sample). Thermogravimetric analysis (TG) was performed on a Perkin Elmer Diamond TG/DTA under atmosphere from room temperature to 800 °C with a heating rate of 10 °C/min. The morphology of the coordination polymer was investigated using 4 of 13 WILEY Organometallic Chemistry

scanning electron microscope and X-ray analyzer (SEM, SU8010). X-ray powder diffraction patterns were obtained on a Bruker Advance-D8 equipped with Cu-K $\alpha$  radiation, in the range 5° < 2 $\theta$  < 55°, with a step size of 0.02° (2 $\theta$ ) and an count time of 2 s per step. The photoluminescent spectra of the coordination polymers were measured on a HORIBA Fluoromax-4-TCSPC spectrofluorometer equipped with Spectra LED Pulsed LED sources at room temperature (200–1000 nm). Solid-state circular dichroism (CD) measurements were performed on MOS-500/ALX300 (50160HZ 250 W) (Scheme 2).

#### 2.2 | Synthesis

2,4,6-Triiodo-1,3,5-benzene tricarboxylic acid was synthesized on the basis of the modified method in related literature.<sup>[50]</sup> Specific synthetic steps are given in the supporting information.

[Ln (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> (Ln = Eu, Gd, Sm, Nd) (CPs-(1-4)). The CP-1 was synthesized by blending Ln (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0250 g, 0.05 mmol), H<sub>3</sub>TIBTC (0.0250 g, 0.04 mmol) and added solvent (DMF: EtOH = 1: 1) 2 ml. The mixture solution was placed in a 20 ml Pyrex vial and stirred for 1 hr at room temperature and then heated statically at 85 °C for 3 days. Slowly cool down and green crystals of the CP-1 were obtained after filtration and washing thoroughly with absolute ethanol (EtOH). The solution pH was 5 before the reaction and 5 at the end. And the CPs-(2-4) were synthesized in the same manner. Detailed analysis data are as follows:

[Eu (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> (CP-1) Yield: 55% (based on H<sub>3</sub>TIBTC), anal. Calc. for C<sub>18</sub>H<sub>21</sub>I<sub>3</sub>N<sub>3</sub>O<sub>9</sub>Eu (956.05): C, 22.61; H, 2.21; N, 4.40%. Found: C, 22.66; H, 2.25; N, 4.44%. IR data (KBr, cm<sup>-1</sup>): 3410, 3126, 2924, 2395, 1645, 1580, 1389, 1310, 1108, 939, 740, 675, 515.

[Gd (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> (CP-2) Yield: 55% (based on H<sub>3</sub>TIBTC), anal. Calc. for  $C_{18}H_{21}I_3N_3O_9Gd$  (961.33): C, 22.49; H, 2.20; N, 4.37%. Found: C, 22.53; H, 2.26; N, 4.41%. IR data (KBr, cm<sup>-1</sup>): 3415, 3126, 2922, 2350, 1651, 1583, 1387, 1305, 1111, 940, 738, 671, 506.

[Sm (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> (CP-3) Yield: 55% (based on H<sub>3</sub>TIBTC), anal. Calc. for  $C_{18}H_{21}I_3N_3O_9Sm$  (954.44): C, 22.65; H, 2.22; N, 4.40%. Found: C, 22.68; H, 2.26; N, 4.45%. IR data (KBr, cm<sup>-1</sup>): 3405, 3128, 2925, 2370, 1656, 1581, 1380, 1313, 1109, 935, 738, 678, 506.

 $[Nd (TIBTC)(DMF)_3]_n (CP-4)$  Yield: 55% (based on H<sub>3</sub>TIBTC), anal. Calc. for C<sub>18</sub>H<sub>21</sub>I<sub>3</sub>N<sub>3</sub>O<sub>9</sub>Nd (948.32): C,

22.80; H, 2.22; N, 4.44%. Found: C, 22.86; H, 2.22; N, 4.44%. IR data (KBr, cm<sup>-1</sup>): 3417, 3123, 2925, 2357, 1656, 1589, 1397, 1307, 1111, 932, 736, 676, 509.

## 2.3 | X-ray crystal structure determination

A single crystal of suitable dimensions for the coordination polymer was mounted on glass fibers for the X-ray structure determinations. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A semiempirical absorption correction was applied by the program SADABS.<sup>[51]</sup> The program suite SHELXTL-97 was used for space-group determination (XPREP), direct method structure solution (XS), and least-squares refinement (XL).<sup>[42,53]</sup> All nonhydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms around the carbon atoms were included using a riding model. Hydrogen atoms of coordination water molecules and lattice water molecules were found in the difference Fourier map. The details of the crystal parameters, data collection, and refinement for the CPs-(1-4) are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table S1-S4. Hydrogen bond lengths (Å) and angles (°) for the CPs-(1-4) are listed in Table S5. Further details are provided in the Supporting Information.

#### **3** | RESULTS AND DISCUSSION

#### 3.1 | Structure descriptions

X-ray diffraction analysis revealed that the CPs-(1-4) crystallized in the cubic system and the space group are all  $P2_13$ . CPs-(1-4) have the same structure, here we choose the CP-1 [Eu (TIBTC)(DMF)<sub>3</sub>]<sub>n</sub> as an example to discuss. The molecular structure of the CP-1 consisted of one Eu atom, three H<sub>3</sub>TIBTC ligands, three coordinated DMF ligands. The coordination pattern of the center metal is shown in Figure 2a. In the structure, the linking pattern of ligand H<sub>3</sub>TIBTC is  $\mu_3$ - $\eta_0^1\eta_0^1\eta_0^{-1}\eta_0^{-1}$ , where two oxygen atoms on each carboxyl group take the coordination mode of bidentate chelating (Figure 2b), and coordinating DMF as a terminal ligand prevents the unit linkage in other directions. The Eu



**SCHEME 2** Synthesis route of ligand 1,3,5-Triiodo-2,4,6-trimethylbenzene

#### TABLE 1 Crystallographic data for the CPs-(1-4)

<b>Coordination polymers</b>	CP-1	CP-2	CP-3	CP-4
Chemical formula	$C_{18}H_{21}I_3N_3O_9Eu$	$C_{18}H_{21}I_{3}N_{3}O_{9}Gd$	$C_{18}H_{21}I_3N_3O_9Sm$	$C_{18}H_{21}I_3N_3O_9Nd$
$M (\text{g mol}^{-1})$	956.05	961.33	954.44	948.32
Crystal system	cubic	cubic	cubic	cubic
Space group	<i>P</i> 2(1)3	P2(1)3	P2(1)3	<i>P</i> 2(1)3
a (Å)	14.1345 (2)	14.1149 (2)	14.1171 (2)	14.1918 (3)
<i>b</i> (Å)	14.1345 (2)	14.1149 (2)	14.1171 (2)	14.1918 (3)
<i>c</i> (Å)	14.1345 (2)	14.1149 (2)	14.1171 (2)	14.1918 (3)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
$V(Å^3)$	2823.85(7)	2812.12(7)	2813.43(7)	2858.33(10)
Ζ	4	4	4	4
$D_{\text{calc}} (\text{g-cm}^{-3})$	2.249	2.271	2.253	2.204
Crystal size (mm)	$0.51\times0.40\times0.31$	$0.51\times0.41\times0.30$	$0.51\times0.42\times0.30$	$0.50\times0.41\times0.30$
F(000)	1776	1780	1772	1764
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	5.547	5.698	5.426	5.102
$\theta$ (deg)	2.04-31.26	2.04-31.31	2.04-31.30	2.03-31.28
Reflections collected	19701	19616	19627	19947
Independent reflections	2929(2504)	2915(2587)	2939(2609)	2992(2765)
Parameters	106	106	105	106
R <sub>int</sub>	0.0354	0.0340	0.0333	0.0227
$\Delta(\rho)$ (e Å <sup>-3</sup> )	0.697 and – 0.629	0.702 and - 0.640	2.144 and - 1.075	0.858 and - 0.648
Goodness of fit	1.016	1.034	1.040	1.037
R <sup>a</sup>	0.0224 (0.0341) <sup>b</sup>	0.0256 (0.0338) <sup>b</sup>	0.0342 (0.0427) <sup>b</sup>	0.0203 (0.0246) <sup>b</sup>
$WR_2^a$	0.0411 (0.0442) <sup>b</sup>	0.0563 (0.0595) <sup>b</sup>	0.0857 (0.0901) <sup>b</sup>	0.0425 (0.0441) <sup>b</sup>

 ${}^{a}R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, wR_{2} = [\Sigma w (Fo^{2} - Fc^{2})^{2} / \Sigma w (Fo^{2})^{2}]^{1/2}; [Fo > 4\sigma(Fo)].$ 

<sup>b</sup>Based on all data.

atom is nine-coordinated by three oxygen atoms (O1) from the DMF ligand with bond lengths of Ln-O bond length is 2.534 Å, six oxygen atoms (O2, O3) from the three coordination H<sub>3</sub>TIBTC ligands with the bond lengths are 2.574 Å and 2.644 Å, forming a LaO9 irregular tetradecahedron which has the chirality (Figure 2c). The contact of Eu-Eu bond distance is 10.0039 (2) Å. All these bond lengths are similar to the relevant literature, which is shown they are in a reasonable range.<sup>[37]</sup> For the structural unit [Eu (COO)<sub>3</sub>(DMF)<sub>3</sub>] in the CP-1, when viewed along the direction, five structural units form a ringshaped twisted pores (Figure 2d), these twisted pores are connected by the C-bonding of the H<sub>3</sub>TIBTC ligand to extend the dimensionality, yielding a 3D cage structure (Figure 2e). In consideration of the complexity of the structure, we try to interpret the framework topologically and the ligands being viewed as nodes, respectively. The simplified structure is shown in Figure 2f. Each Eu is simplified as a 3-connected node, and each ligand is also simplified as a 3-connected node, and the whole structure is a 3, 3-connected srs topology. Although one related CP-**3** have been previously reported,<sup>[54]</sup> its detailed molecular structural descriptions are not specific enough, especially its functional properties have not been well studied. Therefore, it is necessary for us to carry out a systematic study of the properties of the coordination polymers.

#### 3.2 | IR spectra

The IR spectra of the CPs-(1-4) are similar to each other, shown in Figure S1. Here we take the IR spectra of the CP-1 to discuss. The broad absorption bands appearing at 3417 cm<sup>-1</sup> of coordination polymer indicates the



**FIGURE 2** Structure of the CP-1: (**a**) coordination environment of Eu<sup>3+</sup> ion (#1: 1-z, x + 0.5, 1.5-y; #2: y-0.5, 1.5-z, 1-x); (**b**) connection fashions of H<sub>3</sub>TIBTC ligand; (**c**) rotationally symmetric EuO<sub>9</sub> tetradecahedron; (**d**) a ring-shaped twisted pore structure formed by five metal ions and five ligands; (**e**) 3D cage structure of the CP-1 (**f**) simplified topology of the CP-1. Symmetry transformations used to generate equivalent atoms: A = x, y, z; B = 1/2-x, -y, 1/2 + z; C = 1/2 + x, 1/2-y, -z; D = -x, 1/2 + y, 1/2-z; E = z, x, y; F = y, z, x; G = 1/2-z, -x, 1/2 + y; H = -y, 1/2 + z, 1/2-x; I = 1/2 + z, 1/2-x, -y; J = 1/2-y, -z, 1/2 + x; K = -z, 1/2 + x, 1/2-y; L = 1/2 + y, 1/2-z, -x

presence of water molecules. The peaks around 1645 and 1397 cm<sup>-1</sup> are assigned to the asymmetrical stretching vibration ( $\nu_{asCOO}^{-}$ ) and symmetrical stretching vibration ( $\nu_{sCOO}^{-}$ ) of C=O bond, and 1310, 1589 and 2925 cm<sup>-1</sup> ( $\nu_s$  of C=C and C-C bonds) are attributed to the skeletal vibrations of the organic aromatic rings. And the peaks at the position of 937–740 cm<sup>-1</sup> can be assigned to characterization vibration of  $\delta_{=C-H}$  in the 1,2,4-position substitution on the benzene ring, respectively. Table S6 shows the attribution of IR (cm<sup>-1</sup>) for ligand and CPs-(**1–4**).

#### 3.3 | Chiral analysis

Studying shown that achiral ligands can form pure chiral crystals under certain chiral induction factors. In this work, we use the ligand tri-iodophthalic acid belongs to a kind of achiral substance, and the X-ray single crystal diffraction data show that the crystal has a chiral structure. Solid-state circular dichroism (CD) measurements were performed on solid material in KBr plates to illustrate the chiral nature of the CP-1, and groups of

randomly selected single crystals of the CP-1 were used for the CD spectrum. As shown in Figure S2 that single crystal structure of the CP-1 is homochiral and the bulk sample may be a pure chiral crystal.

#### 3.4 | UV-vis assignment

The UV–Vis spectrum of the ligand H<sub>3</sub>TIBTC and CP-1 is shown in Figure S3, to be recorded in the form of solid sample. And the characteristics data of UV–Vis spectra is listed in Table S7. CP-1 presented three peaks, the peak at 218 nm was attributed to the  $\pi \rightarrow \pi^*$  transition of the H<sub>3</sub>TIBTC ligand, the peak of 292 nm was attributed to the n  $\rightarrow \pi^*$  transition of the H<sub>3</sub>TIBTC ligand. At the same time, the broad peak at around 353 nm for the coordination polymer should be attributed to LMCT.

#### 3.5 | Thermal properties

The thermogravimetric analysis of the coordination polymer generally refers to dynamic thermogravimetric analysis, which is performed according to a preprogrammed procedure. The weight of the sample was recorded while the sample was heated at a constant speed varying temperature. The thermal stability of the coordination polymer is an important means of characterizing the properties of the coordination polymer. The heat of the coordination polymer system stability includes the removal of guest molecules, ligand substitution, isomerization, conversion of coordination structures, thermal dissociation, thermal decomposition and many other processes. Therefore, by analyzing the thermogravimetric properties of the coordination polymer, the structural important information of the coordination polymer can be derived.

To examine the thermal stability of the coordination polymers, thermal gravimetric analysis (TG) was carried out at a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere with the temperature range from 30 to 800 °C, and the thermalgravimetric curves of the CPs-(1-4) are shown in Figure S4. The TG curves of the coordination polymers are similar to each other. Take the CP-1 as an example. The TG curve of the CP-1 is divided into two steps. The CP-1 shows a first weight loss between 200 and 400 °C attributable to the loss of three coordinating DMF molecules (obsd: 22.39%; calcd: 23.21%). The second loss (obsd: 40.00%) between 400 and 600 °C corresponds to the decomposition of the whole organometallic coordination polymer frame structure collapses (calcd: 40.19%), the residual mass of the final metal oxide residue is 37% of the original weight.

#### 3.6 | PXRD analysis

In order to confirm whether the crystal structures were truly representative of the bulk materials, the PXRD patterns of the coordination polymers were recorded (Figure S5). Comparing with the corresponding simulated single-crystal diffraction data, all the peaks present in the measured patterns closely match the simulated patterns generated from single crystal diffraction data, which indicated that coordination polymer in the pure phase.

#### 3.7 | Application and exploration

## 3.7.1 | Coordination polymer for the reduction of potassium permanganate

Based on the synthesized three-dimensional skeleton single-crystal coordination polymer having a halogen atom such as iodine, we sought to harness the halogen atom of the coordination polymer to discolor the acidic potassium permanganate solution. In this part of the

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experiment the CP-1 is added to the prepared acidic potassium permanganate solution, the partial decoloration of the solution and the change in color of the crystals were evident to the naked eye (Figure 3), finally, almost complete decoloration of the solution was detected after 6 hr (in which KMnO<sub>4</sub> has been undergone a substantial change, the CP-1 have changed to another black material). We tried to separate the new material from the solvent, but unfortunately, this idea failed to be realized because in practice we found that it was difficult to completely separate the newly formed material from the solution. The absorbance curves of potassium permanganate with time were shown in Figure 3.

In general, we have synthesized a rigid water-stable 3D coordination polymers. The coordination polymer is a good example of a coordination polymers based material, which is effective to reduce the environmental pollution of potassium permanganate. This work requires us to further explore it in detail.

## 3.7.2 | General fluorescent property of the coordination polymer

The fluorescence of inorganic–organic coordination polymers has been currently drawing significant attention in the development of fluorescent materials. Here we take the CP-1 as an example. Regarding the luminescence properties of europium, CP-1 was studied at an excitation wavelength of 390 nm with slit width (1:1) and Figure 4 gives the excitation spectrum and emission spectrum of CP-1. The characteristic  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 1–4) transitions of Eu (III) ion at 591, 615, 650, and 693 nm show efficient ligand to-Eu energy transfer. The fairly weak emission band  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  at 581 nm is attributed to the



**FIGURE 3** Visible potassium permanganate color change chart and the absorbance of potassium permanganate curve with time (the arrows indicate the change in the absorption spectra with time)



**FIGURE 4** Luminescent spectra of the CP-1 ( $\lambda_{ex} = 390$  nm) in the solid state

symmetry-forbidden emission of the Eu (III) ions in the CP-1. The emission band  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  pertained to the prominent magnetic dipole transition, which is almost influenced by the coordination environment. On the other hand, the outstanding  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission band, possessing strong electric dipole character, is hypersensitive to the coordination environment. Herein Eu (III) ions luminescence can act as a sensitive probe of the lanthanide coordination environment. In particular, the ratio of the intensity  $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ :  $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  transition is very sensitive to the symmetry of the Eu (III) ion center. In the spectrum, it can be obviously seen that the intensity of the electric dipole transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is much stronger than that of the magnetic dipole transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ , which implies that the Eu (III) ions in CP-1 are located in a lower symmetric coordination environment. This can be confirmed by analysis of the single crystal diffraction data. Among these emission lines, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is almost striking, indicating intense red luminescence of CP-1.

#### 3.7.3 | Fluorescence lifetime

In order to explore Luminescent characterization, we tested the fluorescence lifetime of solid CP-1 and the test chart as is shown in Figure S6. The measured fluorescence lifetime of CP-1 is approximately 670  $\mu$ s. At the same time, after the metal and the ligand were mixed and ground in the same ratio, the fluorescence lifetime value of the sample was measured (171  $\mu$ s). It can be seen that the metal and the ligand undergo a reaction coordination to greatly improve the fluorescence lifetime. It is shown that the energy of ligand efficiently transfer to

Eu<sup>3+</sup> ion. Compared with lifetime values of the previously reported lanthanide coordination polymers, the lifetime value of the CP-**1** is longer than those of Tb (PBI)<sub>3</sub>(DPEPO) (where HPBI = 3-phenyl-4-benzoyl-5-isoxazolone, DPEPO = bis(2-(diphenylphosphino) phenyl), lifetime = 168  $\mu$ s),<sup>[55]</sup> [Eu<sub>3</sub>(bpydb)<sub>3</sub>(HCOO)( $\mu$ <sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)]·(x solvent) (where bpydbH<sub>2</sub> = (4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoic acid, lifetime = 258  $\mu$ s)<sup>[56]</sup> and Eu(L)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O) (where HL = 4-(Dipyridin-2-yl) aminobenzoic acid), lifetime = 428  $\mu$ s).<sup>[57]</sup>

## 3.7.4 | Fluorescence quenching response to metal cations

In terms of the CPs-(1-4) have the 3D network framework with evenly arranged porous and excellent chemical stability, the CPs-(1-4) were explored for the application in the detection of metal ions in a solvent system based on fluorescent sensing. It was found that their emissions are strong and almost not affected by solvent effect. The CPs-(1-4) all show intense fluorescent emissions in water. The high water stability together with good fluorescent performance of the four coordination polymers, thus prompt us to explore their fluorescent sensing properties in water. CPs-(1-4) are structurally similar, here we select CP-1 as a representative to describe its fluorescence efficacy.

To explore the ability of sensing a trace quantity of metal ions and  $UO_2^{2+}$  ion, the grounded powder samples of the CP-1 (10 mg) were immersed in 30 ml of deionized water and ultrasonicated over 30 min to form a steady turbid suspension. Then, 2 ml of the as-made CP-1 suspension was added to a cuvette containing 2 ml of

1 mM aqueous solutions of 14 different metal ions of  $Co^{2+}$ ,  $Ni^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Ba^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ , and  $UO_2^{2+}$  ion respectively, to form the metal ion incorporated CP-1-M<sup>n+</sup> suspensions for fluorescence studies. The fluorescent intensities of these CP-1 suspensions were recorded at room temperature and compared (Figure 5). Interestingly, it was found that the fluorescent intensities of them are greatly dependent on the identities of the metal ions. For the CP-1,  $Co^{2+}$ ,  $Ni^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Ba^{2+}$ ,  $Fe^{2+}$  show negligible effects on its fluorescence, and Fe<sup>3+</sup> and Al<sup>3+</sup> exhibits a moderate degree of quenching, whereas Fe<sup>3+</sup> gives the quenching with the efficiency as 27.40%, Al<sup>3+</sup> is about 9.96%. They are much lower than that of  $UO_2^{2+}$  ion (Figure 6).

#### 3.7.5 | Selective $UO_2^{2+}$ ion detection based on fluorescence quenching

High energy efficiency, low pollution and low cost, these advantages allow nuclear energy to develop well throughout the world. China's nuclear power development report pointed out that "China's nuclear power has formed a large-scale development pattern". In the development process of nuclear energy industry, one of the main constraints restricting the development of nuclear energy is the long-term safe disposal of strong uranium waste. So, here we use the new compounds to test the uranium solution will be a great significance.

In experiment the powder samples of the CP-1 (10 mg) were immersed in 30 ml of deionized water and ultrasonicated over 30 min to form a steady turbid



suspension. Then, 2 ml of the as-made CP-1 suspension was added to a cuvette containing 2 ml of aqueous solutions of 10 different concentrations of uranium solution to form the suspensions for fluorescence studies. The fluorescent intensities of these CP-1 suspensions were recorded at room temperature and compared (Figure 7). Interestingly, it was found that the fluorescent intensities are greatly dependent on the identities of the concentrations of uranium solution. The CP-1 has obvious fluorescence quenching effect for different concentrations of uranium solution.

The detection limit of the CP-1 for the  $UO_2^{2+}$  ions is calculated by following equation:

Detection limit = 
$$3 \sigma/k$$
 (1)

Where, k represents the slope between the luminescence intensity vs.  $\log[UO_2^{2^+}]$ ;  $\sigma$  represents the standard deviation of blank determination. The detection limit of the CP-1 is calculated to be 0.011 mM (5.54 mg/L) for  $UO_2^{2^+}$  ions detection, which is lower than the MOF-76 reported to detect uranyl ions in solution carried out by Sun *et al.* with the poor detection limits of 23.8 mg/ L.<sup>[58]</sup> The lower detection limits indicate the feasibility and sensitivity of the CP-1 to detect biological molecule of  $UO_2^{2^+}$  ions.

To furthermore understand the luminescence sensitivity, the quenching efficiency was quantified using the Stern-Volmer (SV) equation:

$$I_0/I = K_{SV}[Q] + 1$$
 (2)

Where,  $I_0$  is the initial emission peak intensity, I is the emission peak intensity after the addition of the analytes



**FIGURE 5** Fluorescence intensity curves of CP-1 for different metal ions and  $UO_2^{2+}$ 



**FIGURE 6** Comparison of quenching efficiency of CP-1 for different metal ions and  $UO_2^{2+}$ 



FIGURE 7 Quenching curves of CP-1 for different concentrations of uranium solution

 $({\rm UO_2}^{2^+}$  ions), [Q] is molar concentration of the analytes (quencher), and  $K_{\rm SV}$  is the quenching constant, which was used to quantitatively evaluate the performance of the CP-1 as a  ${\rm UO_2}^{2^+}$  ions sensing material.<sup>[38]</sup> As shown in Figure 8, the quenching efficiency of the CP-1 in different concentrations of uranium ion solution (20  $\mu$ M, 40  $\mu$ M, 60  $\mu$ M, 100  $\mu$ M, 200  $\mu$ M, 400  $\mu$ M, 600  $\mu$ M, 800  $\mu$ M, 1000  $\mu$ M, 2000  $\mu$ M) is different. The quenching constant (K<sub>SV</sub>) was 4 × 10<sup>3</sup> M<sup>-1</sup>. The greater K<sub>SV</sub> values revealed an extremely high sensitivity, which made the CP-1 one of the best sensitive luminescence based metal–organic detectors of different concentrations of uranium solution.



FIGURE 8 Fluorescence intensity curve of CP-1 for different concentrations of uranium solution

In addition, further experiments also showed that the quenching efficiency of the CP-1 toward  $UO_2^{2+}$  ions can almost reach the maximum value within 1 min. This rapid response is quite appealing and may be attributed to the fact that  $UO_2^{2+}$  ions can rapidly diffuse into the channels of the CP-1 and interact with luminophores on the pore surface.

The forbidden f-f transition of rare earth ions result in its low molar absorption coefficient.<sup>[59]</sup> In order to overcome the shortcoming of low molar absorption coefficient, organic iodine substituted polycarboxylic acid ligands, which possess electron conjugate induction effect, are introduced to coordinate with rare earth ions. The energy of the organic ligand is transmitted to the rare earth ions through the antenna effect and so that the rare earth ions are sensitized. For CP-1, the luminescence of the rare earth ion Eu<sup>3+</sup> is mainly in suspension derived from the energy transfer of the ligand. However, it is found that the energy of the ligand is not well transferred to  $Eu^{3+}$  in the aqueous solution. That is to say, the emission peaks of both ligands and metal ions appear, and the peak of the ligand is slightly stronger than the characteristic peak of the metal ion, when detecting uranium ions. Therefore, we have further studied the luminescence sensing properties of CP-1 for the detection of uranium ions by monitoring the characteristic peak intensity of the ligand in the aqueous solution. Meanwhile, the main factor affecting the energy transfer is the energy difference of the triplet state of the ligand and the excited state of the rare earth ion Eu<sup>3+</sup>. So, the reason why the uranium ion affects the fluorescence intensity of the ligand is that the interaction between the uranium ion and the ligand of the coordination polymer lead to the change of triplet energy level of the ligand. The  $UO_2^{2+}$  ions may enter the channels of the CP-1 and interact with the iodine atoms on the ligand when the uranium solution was added. The SEM micrographs of the CP-1 before and after detection may further confirmed (Figure S7-S8). Thereby iodine substitution absorbs a part of the excited state energy of the ligand, so that the energy transfer from the ligand to the rare earth ions is weakened, resulting in fluorescence quenching. In other words, it is inferred from the Figure 9 that there may be both static quenching and dynamic quenching processes. The interaction between the  $UO_2^{2+}$  ions and the CP-1 is the cause of static quenching. The dynamic quenching can be attributed to the energy and electron transfer processes between the  $UO_2^{2+}$  ions and the CP-1.



**FIGURE 9** Linear relationship of  $I_0/I$  ratio and the concentration of uranium



**FIGURE 10** Quenching efficiency of the CP-1 for  $UO_2^{2+}$  in repetitive experiments



FIGURE 11 PXRD before and after methanol washing

#### 3.7.6 | Repetitive experiment

As a sensor, it is necessary to be able to use it stably. Therefore, we also investigated the fluorescent properties of regenerated CP-1, which was simply obtained by washing with methanol. It was found that the quenching efficiencies of CP-1 for  $UO_2^{2+}$  ions are basically unchanged up to six cycles, demonstrating its good stability for the detection applications (Figure 10). At the same time we tested the crystals with methanol washing for PXRD and found that the purity of the crystal structure did not change significantly (Figure 11).

#### 4 | CONCLUSIONS

In this work, we have successfully synthesized four porous structure coordination polymers [Ln (TIBTC)  $(DMF)_3]_n$  (Ln = Eu, Gd, Sm, Nd) (CPs-(1-4)) under the hydrothermal condition by using a poly-carboxylic acid H<sub>3</sub>TIBTC which contains carboxylic acid group

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and halogen atom. From the single crystal analysis, the new coordination polymers possessed a fascinating 3D network framework. Fluorescence experiments have shown that the coordination polymers exhibited good fluorescence quenching effects in the fluorescence detection experiments of uranium solutions. This finding could open up a new avenue to address the issues for uranium fuel waste treatment and detection in an aqueous solution.

#### ASSOCIATED CONTENT

Selected bond lengths (Å) and angles (deg) for CPs-(1-4) are listed in Table S1-S4. Hydrogen bond lengths (Å) and angles (°) for the CPs-(1-4) are listed in Table S5. Table S6 shows the attribution of IR  $(cm^{-1})$  for ligand H<sub>3</sub>TIBTC and CPs-(1-4). And the characteristics data of UV-Vis spectra is listed in Table S7. Infrared spectra of the ligand H<sub>3</sub>TIBTC and CPs-(1-4) are shown in Figure S1. Solid dichroism of CP-1 and its isomeric crystal coordination polymers are shown in Figure S2. UV-vis spectrum of the ligand H<sub>3</sub>TIBTC and CP-1 is shown in Figure S3. The TG curves of the CPs-(1-4) are shown in Figure S4. PXRD patterns for the CPs-(1-4) are shown in Figure S5. The fluorescence lifetime of the CP-1 is shown in Figure S6. The EDAX spectra of the CP-1 before and after detection are shown in Figure S7. The SEM micrographs of the CP-1 before and after detection are shown in Figure S8. CIF files have also been deposited at the Cambridge Crystallographic Database Centre and may be obtained from http://www.ccdc.cam.ac.uk by citing CCDC for the CP-1: 1554191; CP-2: 1554192; CP-3: 1554195; CP-4: 1554193.

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