Terbium Oxalatophosphonate as Efficient Multiresponsive Luminescent Sensors for Chromate Anions and Tryptophan Molecules

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Abstract: A stable 2D terbium oxalatophosphonate with green luminescence, namely, [ Tb2(H3L)(C2O4)3(H2O)]·2H2O (1), has been hydrothermally obtained using (4-carboxypiperidyl)-N-methylenephosphonic acid (H3L) and oxalate ligand. The luminescent investigation indicates that the emission behavior of compound 1 shows high water and pH stabilities. It can be applied as a multiresponsive luminescent probe with high selectivity, high sensitivity, recycling capability, and fast sensing of CrO4

INTRODUCTION

In recent years, luminescent metal−organic frameworks (MOFs) as a new type of sensor have attracted a great deal of interest because of their distinct advantages such as intense and visible emission by the naked eye, simplicity in operation, and high sensitivity and selectivity. A variety of luminescent MOFs have been explored for sensing of different cations, temperature, organic molecules, and nitroaromatic explosives.

CrO4

and Cr2O7

anions serve as oxidants, playing a crucial role in industry. Meanwhile, they are also toxic and easily soluble in water. Long-term exposure to these substances can result in pulmonary congestion, skin allergy, and several water-borne diseases. Therefore, it is very important and urgently required to develop luminescent sensors for CrO4

and Cr2O7

anions with high selectivity and sensitivity. However, some reported luminescent MOFs for detecting those ions are in nonaqueous solvents. The use of an organic solvent is disadvantageous for health and environmental protection. In addition, as there are more than one type of pollutant ions in waste water, high selective sensing is very important. However, the corresponding reports are rare. Thus, it remains a challenge to construct luminescent MOFs as probes to detect CrO4

and Cr2O7

anions in water, simultaneously, especially for excluding the interference of other mixed anions.

As is known, as the building blocks of proteins and enzymes, amino acids play vital roles in food, chemical, and pharmaceutical industries. Among them, tryptophan (Trp) is an essential amino acid and plays an important part in various physiological processes such as protein biosynthesis, animal growth, and plant development. An abnormal level of Trp is considered as a strong indicator for some diseases, including pellagra, delusions, chronic hepatitis, and parkinsonism. At present, the most used analytical strategies to detect Trp are based on capillary electrophoresis, gas chromatography, high-performance liquid chromatography, UV−vis spectrophotometry, and electrochemical methods. However, there are many drawbacks in these methods, such as high costs, complicated operation, and poor portability, which limit their widespread applications. Therefore, the development of cheap and easy detective methods for rapid and sensitive detection of Trp is still more imminently needed. Fortunately, luminescent MOF sensors can provide an alternative to solve these problems. However, compared to the ones for sensing ions and molecules, only a few investigations were reported for detecting Trp based on luminescent MOFs and coordination polymers, which did not achieve the visible sensor by the naked eye. Hence, it is very important and urgent from the point of view of security and practical considerations to exploit the luminescent sensors for Trp.

In order to achieve the aims, we focus on the construction of the lanthanide luminescent MOFs (Ln-MOFs). Compared with transition-metal-based luminescent MOFs, Ln-MOFs...
have been regarded as very promising luminescent-sensing materials because of their distinct optical advantages, such as large Stokes shift, high color purity, relatively long luminescent lifetimes, visible and very bright luminescent colors, especially for Eu- and Tb-MOFs.\textsuperscript{45–49} In previous reports, some Ln-MOFs have been made for the luminescent sensor; however, very few Ln-MOFs could be observed to show multiresponsive luminescent sensing for different analytes.\textsuperscript{32,33,50,51} In the assembly of structures and functions of Ln-MOFs, the choice of the organic ligand is very vital. Traditionally, organic carboxylic acid was mainly selected as the ligand to construct Ln-MOFs.\textsuperscript{45–49} Recently, the phosphonate ligands, especially, attaching additional functional groups to the phosphonic acid (such as $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, etc.), can also provide access to obtain Ln-MOFs. Compared with carboxylates, the introduction of the phosphonate groups can yield many different structural topologies and a fascinating luminescent property.\textsuperscript{52,53} Moreover, the uncoordinated functional groups can also serve as the recognition site to achieve luminescent detection. More importantly, metal phosphonates are generally prepared in hydrothermal conditions. Therefore, the as-synthesized compounds can exhibit high thermal and chemical stabilities,\textsuperscript{54} providing a chance to detect the analytes in the aqueous system. For example, several Cd/Pb phosphonates have been investigated in the detection of metal ions, anions, and amino acids by our group.\textsuperscript{45,55,56} However, these sensors cannot achieve visible sensors because of the near UV luminescent property. The introduction of luminescent lanthanide ions can solve this problem. Fu et al. prepared a luminescent terbium phosphonate, which achieved a rapid and recyclable sensing of CrO$_4^{2-}$/Cr$_2$O$_7^{2-}$ anions and Trp. Therefore, it is still a challenge to achieve multiresponsive and visible luminescent sensing for different ions and molecules based on these materials. Meanwhile, the preparation and characterization of lanthanide phosphonates is still difficult because these materials generally exhibit high insolubility and poor crystallinity.\textsuperscript{57,59} To resolve this problem, two types of synthetic strategies were employed: (1) modifying the phosphonic acid ligand with other functional groups can improve the solubility and crystallinity of these materials;\textsuperscript{59,60} (2) Introducing a second metal linker such as an organic carboxylic acid is also one of the effective approaches.\textsuperscript{61} It can not only solve the solubility and crystallinity problems but also enhance luminescent intensity and lifetime of the synthesized lanthanide phosphonates through the so-called “antenna effect”. By using these methods, more and more lanthanide phosphonates with luminescent property have been successfully obtained.\textsuperscript{57,59,60,62} As an expansion of our work, by using H$_2$O$_2$,PCH$_2$–NC$_3$H$_7$–COOH (H$_3$L) as the phosphonate ligand and oxalate (H$_2$C$_2$O$_4$) as the second ligand, we successfully obtained a 2D terbium oxalatophosphonate, namely, [Tb$_2$(H$_3$L)$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$]·2H$_2$O (1). It shows high selective, visible, and recyclable sensing of CrO$_4^{2-}$/Cr$_2$O$_7^{2-}$ anions and Trp. Meanwhile, the probable mechanisms for the quenching behavior are also discussed.

## RESULTS AND DISCUSSION

### Crystal Structure of 1

X-ray crystallographic analysis indicated that compound 1 crystallized in a monoclinic space group $P2_1(1)/n$ (Table S1). The crystal structure consists of two Tb$^{III}$ ions, one H$_2$L ligand, three C$_2$O$_4^{2-}$ anions, four coordinated water molecules, and two lattice water molecules (Figure 1a). The Tb$^{III}$ ion adopts a nine-coordinated geometry with six oxygen atoms (O6, O7, O10, O11, O14, and O15) from three C$_2$O$_4^{2-}$ anions, one phosphate oxygen atom (O2) from one H$_2$L ligand, and two coordinated water molecules (O18 and O19). The Tb$^{II}$ ion employs an eight-coordinated environment, consisting of six oxygen atoms (O8A, O9A, O12B, O13B, O16, and O17) from three C$_2$O$_4^{2-}$ anions and two coordinated water molecules (O20 and O21).

![Figure 1](image-url)
Bond distances of Tb–O are in the range of 2.260(4)–2.616(4) Å, in accordance with those reported for other TbIII oxalatophosphonates (Table S2).63 Using the program SHAPE 2.0,64,65 the continuous shape measures (CSHMs) of the Tb centers relative to the ideal spherical capped square antiprism for Tb1 and triangular dodecahedron for Tb2 are calculated to be 0.778 and 0.874, respectively. All C2O42− anions employ the same coordination mode, chelating to two TbIII ions forming two stable five-membered rings (Tb–O–C–C–O). On the basis of charge balances, the phosphonate oxygen atom (O1), the nitrogen atom (N1), and the carboxyl oxygen atom (O5) of the H3L ligand are protonated.

In compound 1, the interconnection of TbIII ions via cheating C2O42− anions to form a 2D layer structure (Figure 1b). The carboxyl groups of the H3L ligand are uncoordinated, distributing on the two sides of the layer (Figure S1). A 24-atom window is formed, including six TbIII ions, twelve O atoms, and six C atoms, and the approximate dimension is 5.97 Å (O11–O12) × 9.02 Å (O14–O15) (Figure 1c). From a topological perspective, each TbIII ion can be regarded as a three-connected node; thus, the 2D layer structure can be simplified as a unidonal three-connected network with the point Schlüff symbol of {63} (Figure 1d).

**Luminescence Property.** The luminescence spectrum of compound 1 was investigated in the solid state. First, the purity of bulk samples of compound 1 was verified by X-ray powder diffraction (Figure S2). Second, the UV–vis absorption spectrum of compound 1 consists of a broad band between 200 and 600 nm with a maximum absorption of 256 nm (Figure S3). The broad band may be assigned to the synergetic absorption strongly depends on the crystal field of the host matrix because of the low shielding of the 5d orbital.66 On the basis of the UV–vis absorption spectrum of compound 1, a 254 nm light was selected to induce the luminescent emission. Compound 1 shows four emission peaks at 491, 547, 587, and 623 nm, contributing to the 1D4f → 7Fj (J = 6, 5, 4, 3) transitions of the TbIII ion (Figure 2). Among them, the 1D4f → 7F5 transition is the strongest, which is assigned to magnetic-dipole-induced transitions. The room temperature lifetime of the TbIII ion in the 1D4f → 7Fj transition is measured to be 0.85 ms (Figure S4). Compound 1 displays strong green luminescence under UV irradiation of 254 nm (in the inset of Figure 2), which is visible by the naked eye. The strong visible emission provides the possibility for compound 1 acting as a luminescent sensor.

**Thermal and Chemical Stabilities.** Considering practical applications, the physical and chemical stabilities of compound 1 were investigated. First, the thermogravimetric analysis (TGA) indicates that all water molecules are removed upon heating to 167 °C; the resulting desolvated structure is stable up to 234 °C (Figure S5). Second, we examined the aqueous and pH stabilities of compound 1 in water. The luminescent intensities of this sample have almost no change after soaking in the water solution for 10 days or immersing into water solutions with different pH values from 3 to 13 for 24 h (Figures 3 and S6). In addition, powder X-ray diffraction (PXRD) patterns of the different pH-treated samples (pH = 3–13) completely overlap that of the simulated one (Figure S7), indicating that the framework is still retentive in a broad range of pH values. The results of thermal, luminescent, pH, and water stabilities indicate that compound 1 is stable and provides a suitable platform for further luminescent sensing.

**Sensing of Anions.** Compound 1 was first examined for the potential application of detecting anions. As shown in Figures 4a and S8, results indicate that CrO42− and Cr2O72− anions afford significant luminescence quenching effect compared with other anions. It reveals that most suspensions display green color, except for CrO42− and Cr2O72− suspensions that show dark color upon excitation at 254 nm (Figure 4b). Meanwhile, anti-interference experiments were carried out to verify the high selectivity for detection of CrO42− and Cr2O72− anions (Figure 4c). First, the mixture of anion suspensions except CrO42− and Cr2O72− anions was prepared, which shows green luminescence. Once CrO42− or Cr2O72− anions were added into the above suspension of compound 1 with other anions, the luminescence of suspension was significantly quenched from green to dark. The above results indicate that compound 1 can be regarded as a selective and sensitive luminescent sensor for detecting the CrO42− and Cr2O72− anions.

The sensing sensitivities of compound 1 toward CrO42− and Cr2O72− anions were measured by a series of titration experiments. As shown in Figure 5a,c, the luminescence intensities are gradually quenched, and the quenching efficiency can reach 78.9% for CrO42− and 82.7% for Cr2O72− anions as the concentration increases to 4.4 × 10−4 M for CrO42− and 3.3 × 10−4 M for Cr2O72− anions. To further investigate the relationship between the quenching efficiency and CrO42− or Cr2O72− concentration, the quenching curve was analyzed by the Stern–Volmer equation

$$I_0/I = K_{sv}[C] + 1 (I_0 and I are the luminescence intensities before and after the addition of CrO42− or Cr2O72− anions, respectively; [C] represents the molar concentration of CrO42− or Cr2O72− anions; K_{sv} is the quenching constant).$$

As shown in Figure 5b,d, the curves of Stern–Volmer display a good linear relationship at a low concentration, and the Ksv values are fitted to be 3.63 × 1010 M−1 for CrO42− and 7.78 × 109 M−1 for Cr2O72− anions. The LODs are calculated to be 3.7 μM for CrO42− and 4.2 μM for Cr2O72− anions (Figure S9), which are calculated using the equation: LOD = 3δ/s (δ is the standard deviation from 10 blank measurements and s is the slope of the calibration curve).15,16,51 Compared with the reported MOFs sensors for Cr3+ anions, this LOD is comparable and even lower (Table S3).13–17,32–36 Furthermore, the LODs are lower, comparing with the largest standard of Cr3+ in wastewater of 10 μM, defined by an integrated wastewater.
As is known, the luminescent sensors are not widely used in our actual life mainly because of their non-recoverable performance and high cost; thus, recyclable experiments were performed. After quenching, the luminescence intensity of compound 1 can recover by simply washing with water several times (Figure S10). As shown in Figure S11, the luminescence intensity of each recycle remains basically unchanged. Furthermore, the time of luminescence discharge standard of China. As is known, the luminescent sensors are not widely used in our actual life mainly because of their non-recoverable performance and high cost; thus, recyclable experiments were performed. After quenching, the luminescence intensity of compound 1 can recover by simply washing with water several times (Figure S10). As shown in Figure S11, the luminescence intensity of each recycle remains basically unchanged. Furthermore, the time of luminescence discharge standard of China. As is known, the luminescent sensors are not widely used in our actual life mainly because of their non-recoverable performance and high cost; thus, recyclable experiments were performed. After quenching, the luminescence intensity of compound 1 can recover by simply washing with water several times (Figure S10). As shown in Figure S11, the luminescence intensity of each recycle remains basically unchanged. Furthermore, the time of luminescence discharge standard of China. As is known, the luminescent sensors are not widely used in our actual life mainly because of their non-recoverable performance and high cost; thus, recyclable experiments were performed. After quenching, the luminescence intensity of compound 1 can recover by simply washing with water several times (Figure S10). As shown in Figure S11, the luminescence intensity of each recycle remains basically unchanged. Furthermore, the time of luminescence discharge standard of China.
intensity reaching the minimum value is estimated to be within 10 s with the addition of CrO$_4^{2-}$ or Cr$_2$O$_7^{2-}$ anions (Figure S12), which is obviously shorter than those of previously reported compounds (Table S3). The results indicate that compound 1 can realize the fast and recyclable luminescent sensor for detecting CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions.

The mechanisms of detecting CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions were also explored. PXRD patterns of compound 1 treated with different anions completely overlap those of the simulated one, ruling out the mechanism of collapse of the crystal structure (Figure S13). The solid particles of compound 1 with chromate anions were analyzed by inductively coupled plasma (ICP). The ICP results verify that the chromate anions in solution cannot be fixed into the channels of compound 1 (Table S4). In addition, the Cr peaks have not been observed by energy-dispersive X-ray spectroscopy of the sample treated with the chromate anion aqueous solution, which also further identifies that chromate anions do not combine with compound 1 (Figure S14). On the basis of these results, there are no direct interactions between the chromate anions and compound 1, which is not the primary factor in fluorescence quenching. The UV−vis absorption spectra of compound 1 and anions are shown in Figure S15. It is obvious that the absorption bands of CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions are partly overlapped by the absorption band of compound 1; however, other anions have no obvious overlaps in the absorption range. Thus, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions can absorb the excitation energy and then hinder the absorption of compound 1, resulting in the decrease of the luminescence intensity. Therefore, the probable mechanisms for the quenching behavior can be mainly defined to the competitive absorption of excitation energy between compound 1 and CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions, which accords with the previously reported compounds that sensing of the CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions.

**Sensing of Amino Acids.** To further explore the potential application of compound 1 for detecting the amino acid molecules, the luminescence spectra were recorded with the addition of 20 different kinds of amino acids. As shown in Figures 6a and S16, different amino acids exhibit different quenching efficiencies toward the intensity of compound 1. Among them, Trp has a significant quenching effect. As shown in Figure 6b, the suspension with Trp displays an evident blue color, but the suspensions with other amino acids show bright green color upon excitation at 254 nm. Meanwhile, anti-interference experiments further prove that compound 1 has good selectivity for detecting Trp even in the presence of other amino acids (Figure 6c). The luminescence intensity is significantly quenched with the addition of Trp, which indicates that compound 1 can serve as a selective and sensitive luminescent probe for detecting Trp.

To check the selective sensing behavior of compound 1 toward Trp, titration experiments were performed. As anticipated, the luminescence intensity gradually decreases with increasing concentration of Trp (Figure 6d). The quenching efficiency reaches 95.4% with the concentration of Trp increasing to 2.5 × 10$^{-3}$ M. At a low concentration, the plot of Stern−Volmer shows a good line relationship, and the $K_q$ is calculated to be 3.86 × 10$^3$ M$^{-1}$ (Figure 6e). The LOD value is estimated to be 25.2 μM (Figure S17). In addition, the luminescence intensity of each recycle can be recovered, indicating that it is a recyclable luminescent sensor for Trp (Figures S18 and S19). Meanwhile, the luminescence can also reach the most quenching efficiency within 10 s with the addition of Trp (Figure S20). To the best of our knowledge, compound 1 is the first metal phosphonate that can be used for the visible, fast, and recyclable luminescent probe for sensing Trp.

To date, the reasons for luminescent quenching caused by Trp may be due to three approaches: (1) weak intermolecular interactions (hydrogen bonds and/or π−π interactions); (2) chemical reaction between Trp and the parent compound; (3) resonance energy transfer. In compound 1, the carboxyl oxygen atom of the H$_2$L ligand is not coordinated, making it possible to form intermolecular hydrogen bonds between compound 1 and Trp. However, all of the amino acid molecules have the same access to form hydrogen bonds with the uncoordinated carboxyl groups; thus, it is difficult to conclude whether the hydrogen bond interaction is the main reason for the luminescence quenching. In addition, there is no
π−π interaction site in compound 1; the mechanism of π−π interactions can be ruled out. IR spectra of compound 1 have no changes before and after being immersed in Trp solution, indicating no chemical reaction between Trp and compound 1 (Figure S21). The UV−vis absorption spectra of compound 1 and amino acids are shown in Figure S22. Lys, Tyr, and Trp all show a wide absorption band in the absorption range of compound 1. Among them, Trp has the highest absorption intensity; thus, it can adsorb the most excitation energy and results in the strongest luminescence quenching. According to the above discussion, it can be speculated that competitive adsorption of excitation energy between compound 1 and Trp should be the main reason for the luminescence quenching.

■ CONCLUSIONS

In summary, a stable 2D terbium oxalatophosphonate with green emission has been prepared via hydrothermal reaction. This compound can be regarded as a high selectivity and sensitivity luminescent sensor for detecting the CrO₄²⁻, CrO₂⁻² ions and Trp through the luminescence quenching effect. Further study and speculation of the mechanism indicate that competitive adsorption of excitation energy between compound 1 and the analytes can be the main reason for the luminescence quenching. To the best of our knowledge, it is first observed that compound 1 can be used for the fast and recyclable luminescent probe for detecting Trp by the naked eye in metal phosphonates. This work has confirmed that luminescent metal phosphonates can be rationally designed to achieve multiresponsive luminescent sensors for detecting different ions and biomolecules.

■ EXPERIMENTAL SECTION

Materials and General Methods. The H₂O,PCH₃−
NC₃H₆−COOH (H₃L) was prepared according to a method described previously.⁶³ All other chemical reagents were obtained from commercial sources and directly used. The contents of C, H, and N were measured by employing a PE-2400 elemental analyzer. Contents of Tb and P were analyzed using an ICP atomic absorption spectrometer. IR spectra were measured on a Bruker AXS Smart APEX II CCD X-diﬀractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 ± 2 K. An empirical absorption correction was applied using the SADAB program. The structure was resolved by direct methods and refined by full matrix least-squares fitting on F² by using SHELXS-2014.⁶⁹ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were located anisotropically. The hydrogen atoms for the solvent water molecules excepting O1W were disordered, which were split with partial occupancy. Crystal data and structure refinements of compound 1 are summarized in Table S1. Bond distances and angles of compound 1 are listed in Table S2.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02486.

(CIF) Additional crystal structures, IR spectra, TG curves, PXRD curves, UV-vis spectra, and emission spectra (PDF)

Accession Codes

CCDC 1503486 contains the supplementary crystallographic data for this paper.

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The authors declare no competing financial interest.

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