

REVIEW

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11, 5004A dual-heteroatom–lanthanide cluster-embedded polyoxotungstate for sequential fluorescence detection of Fe³⁺ and pyrophosphate†Siyu Zhang,^{‡a,b} Tiantian Gong,^{‡b} Chenyun Liu,^{a,b} Qiuyu Wang,^b Fuxiu Chen,^b Jiancai Liu,^{*a,b} Lijuan Chen^{*b} and Junwei Zhao^{†a,b}

A neoteric inorganic–organic hybrid dual-heteroatom (HA) and lanthanide (Ln) cluster-bridged polyoxotungstate (POT) [H₈BTHMMAP]_{1.5}[H₂N(CH₃)₂]₄Na₃H[Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄][(W₅O₁₈)(B-α-BiW₉O₃₃)₂].44H₂O (**1**, H₆BTHMMAP = 1,3-bis[tris-(hydroxymethyl)methylamino]propane, Hpdca = 2-pyridinic acid) was prepared by the dual-HA template strategy. The skeleton of **1** possesses a three-bladed propeller-shaped [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄]¹³⁺ core wrapped by two Keggin [B-α-BiW₉O₃₃]⁹⁻ and one Lindqvist [W₅O₁₈]⁶⁻ segments. Noteworthy, the intricate [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄]¹³⁺ unit consisting of a Bi–Te dual-HA-bridged Ln–W polynuclear cluster is rather attractive and rarely seen in POT crystal engineering. Prominently, **1** exhibits an “ON–OFF” luminescence response triggered by Fe³⁺ based on dynamic quenching and competitive absorption, and the subsequent addition of pyrophosphate (PPI) leads to the recovery of luminescence due to the efficient interaction of Fe³⁺ and PPI. The developed “ON–OFF–ON” switch allows the consecutive discrimination of Fe³⁺ and PPI with low detection limits of 1.23 μM and 2.16 μM, respectively. This work provides a profound understanding of the dual-HA template approach in assembling complicated POTs, and shows the great potential of POT materials in environmental and biological detection.

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Introduction

The template strategy with the ingenious use of anions to achieve selective assembly has emerged as a versatile and valuable route to discover new reaction phenomena and access intricate molecular structures.^{1–6} A large number of examples have demonstrated that the template strategy can promote the ordered arrangement of building blocks (BBs) around them and is critical in influencing the overall architectures (nuclearity, size, and geometry) and physicochemical properties (stability, redox properties, acidity, *etc.*).^{1–9} Heteropolyoxotungstates (HPOTs) are a class of heteroatom (HA)-templated metal oxides and have been extensively applied in luminescence, catalysis, medicine, magnetism, materials science, *etc.*^{10–15}

Within HPOTs, HA species are wide ranging (from III to VI main groups such as B^{III}, Si^{IV}, Ge^{IV}, P^{III/V}, As^{III/V}, Sb^{III}, Bi^{III}, Se^{IV} and Te^{IV}), and the combination of diverse HA templates with tungstates leads to a large library of extraordinary HPOTs,^{16–20} denoting a versatile subclass of the polyoxometalate (POM) family.

Apart from the common function of HAs as interior structure-directing templates for generating BBs to capture metal ions [transition metal (TM) or lanthanide (Ln)], they can also work as extra linkers to control metal or inter-cluster aggregation.^{21–32} For example, Cronin *et al.* isolated a series of gigantic pure HPOTs [(H₈W₁₀₀Se₁₆O₃₆₄)WO(H₂O)₂]⁵²⁻ (Fig. S1a†), [W₂₈Te₈O₁₁₂]²⁴⁻, [W₂₈Te₉O₁₁₅]²⁶⁻ and [W₂₈Te₁₀O₁₁₈]²⁸⁻, where the *in situ*-formed [Se₃W₂₅O₉₁]²⁰⁻ or [TeW₇O₂₈]⁸⁻ BBs are connected by additional Se^{IV} or Te^{IV} linkers.^{23,24} Later, Wang *et al.* showed the effectiveness of P^V linkers in gathering Co²⁺ ions for the formation of the high-nuclear-Co²⁺ substituted HPOT [(Co₄(OH)₃(PO₄)₄(PW₉O₃₄)₄]²⁸⁻ (Fig. S1b†).²⁶ Noteworthy, besides the discrete HA linkers, the HA cluster linkers utilized for constructing HPOT BBs have also been discovered.^{27–32} For instance, Long and Kong *et al.* obtained a heterometallic tetramer [Ln₃(H₂O)₅Ni(H₂O)₃(Sb₄O₄)(SbW₉O₃₃)₃(NiW₆O₂₄)(WO₂)₃(CH₃COO)]¹⁷⁻ (Ln = La³⁺, Pr³⁺, Nd³⁺) (Fig. S1c†), featuring three [SbW₉O₃₃]⁹⁻ and one

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[Ni^{II}W₉O₃₃]¹⁰⁻ BB linked by a tetrahedral [Sb₄O₄]-connected metal core [Ln₃(H₂O)₅Ni(H₂O)₃(Sb₄O₄)(CH₃COO)]^{14+ 29}. Recently, Zheng *et al.* have reported a POM species [Sb₁₅Tb₇W₃O₂₉(OH)₃(DMF)(H₂O)₆ (SbW₈O₃₀)(SbW₉O₃₃)₅]²⁷⁻ with the highest-nuclear Sb^{III/IV} centers, in which the Sb-rich cluster cores contain dimeric {Sb₂O₆} and {Sb₂O₇}₂, trimeric {Sb₃O₁₀} and pentameric {Sb₅O₁₂(OH)} linkers (Fig. S1d†).³⁰ Besides, Bi^{III} cluster linkers generally in the form of {Bi₆O_x} were also used to obtain Ln³⁺ ions and BBs, which have been previously seen in HPOTs such as [(BiW₉O₃₃)₄(WO₃){Bi₆(μ₃-O)₄(μ₂-OH)₃}(Ln₃(H₂O)₆CO₃)]²²⁻ (Fig. S1e†) and {[(W₁₄Ce^{IV}O₆₁)([W₃Bi₆Ce^{III}(H₂O)₃O₁₄][B-α-BiW₉O₃₃]₂)]³⁴⁻ (Fig. S1f†).^{31,32}

Based on these innovative works, particular attention has been paid to the designed fabrication of novel HPOTs by judiciously choosing mixed-HA components. In principle, the synergetic assembly of two or more types of HAs can not only give access to novel HPOTs with diverse architectures, but also provide a great opportunity for generating novel BBs or functionalities. Hitherto, some unprecedented dual-HA-directed HPOTs have been synthesized by reasonably selecting HA pairs.³³⁻⁴³ However, those reported species are generally predominated by one kind of HA linker, and those with two kinds of HA linkers remain underexplored. Therefore, exploring mixed-HA-bridged HPOTs is still a challenging task.

In this work, a multicomponent self-assembly system by applying two kinds of HA materials (K₂TeO₃ and Bi(NO₃)₃·5H₂O) to react with tungstates and Ln ions in the presence of organic components (1,3-bis[tris(hydroxymethyl)methylamino]propane (H₆BTHMMAP), 2-pyridinic acid (Hpdca), and dimethylamine hydrochloride) in acidic aqueous medium was established. The selection of Te^{IV} and Bi^{III} HAs is largely due to their flexibility in structural regulation and ease of crystallographical differentiability. To be specific, the lone-electron-pair stereochemical effect of Te^{IV} and Bi^{III} HAs can to some extent impede the closure of *in situ*-generated BBs. Another reason is that they can work as bridges individually or together to integrate Ln centers or BBs into larger aggregates. In terms of organic ligands, the polydentate H₆BTHMMAP and Hpdca molecules with flexible N and O binding sites are excellent synthons as potential chelating and bridging units by coordinating N or O donors to Ln or W centers, which can effectively control Ln hydrolysis. The protonated species of organic molecules can also serve as counteranions. With this strategy, an inorganic-organic Hpdca-ornamented dual-HA-Ln cluster-bridged HPOT trimer [H₈BTHMMAP]_{1.5}[H₂N(CH₃)₂]₄Na₃H[Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄][(W₅O₁₈)(B-α-BiW₉O₃₃)₂]₄·44H₂O (**1**) was achieved. Polyanion **1** is composed of two [B-α-BiW₉O₃₃]⁹⁻ and one [W₅O₁₈]⁶⁻ BBs unified by one neoteric decanuclear heterometallic [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄]¹³⁺ cluster, which represents an extremely rare case that contains mixed HA cluster linkers in POM chemistry. **1** was preliminarily characterized by infrared (IR) and thermogravimetric (TG) analyses (Fig. S2 and S3†), and the powder X-ray diffraction (PXRD) analysis confirmed the good phase purity of **1** (Fig. S4†). Furthermore, an “ON-OFF-ON” system was proposed by developing **1** as a luminescent probe for the

sensitive and selective detection of Fe³⁺ and pyrophosphate (P₂O₇⁴⁻, PPI) in an aqueous environment. Specifically, the emission of **1** was significantly quenched by Fe³⁺ owing to the dynamic quenching and competitive absorption, while the selective binding effect of PPI with Fe³⁺ could gradually restore the luminescence with a recovery rate of about 78%. Such a probe can be practically employed in water and serum sample analyses.

Results and discussion

Structural description

1 crystallizes in the monoclinic space group *P*21/*c* (Table S1†) and its molecular skeleton comprises a trimeric polyoxoanion [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄][(W₅O₁₈)(B-α-BiW₉O₃₃)₂]¹¹⁻ (**1a**). **1a** displays a triangular arrangement of two trivalent Keggin [B-α-BiW₉O₃₃]⁹⁻ ({BiW₉}) BBs and one monovacant Lindqvist [W₅O₁₈]⁶⁻ ({W₅}) BB connected by an intriguing three-bladed “propeller-shaped” [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄]¹³⁺ ({Eu₂Bi₃(Hpdca)₃Te₂W₃}) cluster (Fig. 1a, e and f). As exhibited in Fig. 1a, **1a** can be viewed as one {W₅} BB capped on a dimeric [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄][(B-α-BiW₉O₃₃)₂]⁵⁻ fragment, where the Eu¹³⁺ ion in {Eu₂Bi₃(Hpdca)₃Te₂W₃} is just inserted into the vacant position of {W₅} BB and two metal-organic [Bi(Hpdca)]³⁺ (Bi4 and Bi5) cations simultaneously work as connectors to link one {W₅} and two {BiW₉} BBs (Fig. 1a and b), producing four Eu–O–W and two Bi–O–W bonds to reinforce the structural stability of **1a**. Remarkably, in the [Eu₂Bi₃(Hpdca)₃(H₂O)₃Te₂W₃O₁₄][(B-α-BiW₉O₃₃)₂]⁵⁻ dimer, one peculiar dual-HA-participated multi-nuclear [EuBi₂(Hpdca)₂(H₂O)₂Te₂O₅]⁷⁺ cluster is anchored onto the “open” [EuBi(Hpdca)(H₂O)W₃O₉][(B-α-BiW₉O₃₃)₂]¹²⁻ dimeric midbody by coordinating two Bi^{III} (Bi4^{III}, Bi5^{III}) and two Te^{IV} (Te1^{IV}, Te2^{IV}) atoms with four terminal-O (O_t) atoms from two {BiW₉} BBs as well as coordinating two Te^{IV} (Te1^{IV}, Te2^{IV}) atoms and one Eu¹³⁺ ion with three vertex O₂, O₁ and O₂₅ atoms from one bridging {WO₆} octahedron (Fig. 1b and c). For the [EuBi(Hpdca)(H₂O)W₃O₉][(B-α-BiW₉O₃₃)₂]¹²⁻ fragment, it can be explicitly observed that two {BiW₉} BBs are firstly interlinked by one [Eu₂(Hpdca)]³⁺ unit *via* four O_t atoms (O₃₃, O₄₁, O₁₇, O₅₆) into an open [Eu(Hpdca)][(B-α-BiW₉O₃₃)₂]¹⁵⁻ dimer, followed by the accommodation of one [BiW₃(H₂O)O₁₁]⁻ BB *via* four Bi–O_t–W (O_t: O₂₃, O₄₁, O₉, O₅₆) and four W–O_t–W (O₂₃, O₅₄, O₉, O₂₀) bonds (Fig. 1c, d and S5†).

A prominent characteristic of **1a** is the intricate three-bladed propeller-shaped {Eu₂Bi₃(Hpdca)₃Te₂W₃} core (Fig. 1f). Interestingly, three Hpdca ligands, like blades, are aligned in three different directions around the “propeller shaft” [Eu₂Bi₃(H₂O)₃Te₂W₃O₁₄]¹³⁺ ({Eu₂Bi₃Te₂W₃}) cluster (Fig. 1g) by fixing to Eu₂, Bi₄ and Bi₅ atoms through N and carboxyl-O sites, giving rise to two five-membered “–Eu–O–C–C–N–” and “–Bi–O–C–C–N–” rings (Fig. 1h). Noticeably, the phenomenon of Hpdca ligands in tethering with the Bi atom is rarely encountered. {Eu₂Bi₃Te₂W₃} can be viewed as a combination

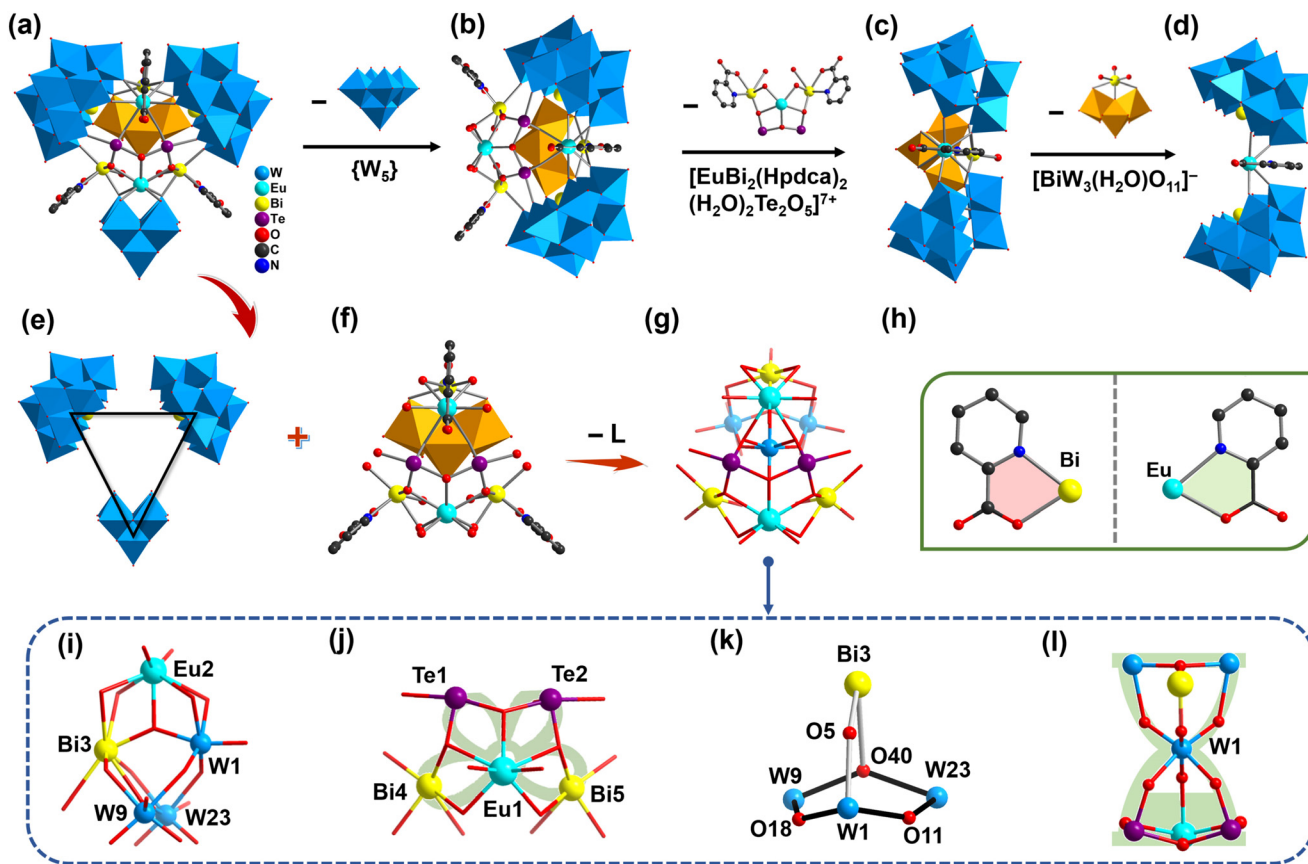


Fig. 1 (a) The structure of **1a**. (b) The $[\text{Eu}_2\text{Bi}_3(\text{Hpdca})_3(\text{H}_2\text{O})_3\text{Te}_2\text{W}_3\text{O}_{14}][(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]^{5-}$ fragment formed by removing the $\{\text{W}_5\}$ BB from **1a**. (c) The $[\text{EuBi}(\text{Hpdca})(\text{H}_2\text{O})\text{W}_3\text{O}_9][(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]^{12-}$ fragment formed by removing one $[\text{EuBi}_2(\text{Hpdca})_2(\text{H}_2\text{O})_2\text{Te}_2\text{O}_5]^{7+}$ cluster from the $[\text{Eu}_2\text{Bi}_3(\text{Hpdca})_3(\text{H}_2\text{O})_3\text{Te}_2\text{W}_3\text{O}_{14}][(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]^{5-}$ dimer. (d) The $[\text{Eu}(\text{Hpdca})][(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]^{15-}$ fragment formed by removing one $[\text{BiW}_3(\text{H}_2\text{O})\text{O}_{11}]^-$ BB from the $[\text{EuBi}(\text{Hpdca})(\text{H}_2\text{O})\text{W}_3\text{O}_9][(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]^{12-}$ fragment. (e) The arrangement of two $\{\text{BiW}_9\}$ and one $\{\text{W}_5\}$ subunits showing the triangular motif. (f) The three-bladed “propeller-shaped” $\{\text{Eu}_2\text{Bi}_3(\text{Hpdca})_3\text{Te}_2\text{W}_3\}$ cluster. (g) The $\{\text{Eu}_2\text{Bi}_3\text{Te}_2\text{W}_3\}$ cluster by removing three Hpdca ligands, where L represents the Hpdca ligand. (h) Two five-membered “-Bi-O-C-C-N-” and “-Eu-O-C-C-N-” rings. (i) and (j) The $[\text{EuBi}(\text{H}_2\text{O})\text{W}_3\text{O}_{10}]^{4+}$ and $[\text{EuBi}_2(\text{H}_2\text{O})_2\text{Te}_2\text{O}_4]^{9+}$ fragments constituting the $\{\text{Eu}_2\text{Bi}_3\text{Te}_2\text{W}_3\}$ cluster. (k) The $\{\text{BiW}_3\text{O}_4\}$ fragment showing the bridged hydrocarbon-shaped geometry. (l) The “hourglass-shaped” $[\text{EuBiW}_3(\text{H}_2\text{O})\text{Te}_2\text{O}_{14}]^{4+}$ fragment.

of $[\text{EuBi}(\text{H}_2\text{O})\text{W}_3\text{O}_{10}]^{4+}$ and $[\text{EuBi}_2(\text{H}_2\text{O})_2\text{Te}_2\text{O}_4]^{9+}$ clusters (Fig. 1i and j). In the $[\text{EuBi}(\text{H}_2\text{O})\text{W}_3\text{O}_{10}]^{4+}$ cluster, the $[\text{BiW}_3(\text{H}_2\text{O})\text{O}_{11}]^-$ BB comprises three vertex-shared $\{\text{WO}_6\}$ octahedra in a triangle motif, in which Bi3 and W1 atoms are ligated to the Eu2 atom *via* five O atoms (Fig. 1i). Besides, a unique octa-membered $\{\text{BiW}_3\text{O}_4\}$ segment with a novel bridged hydrocarbon-shaped geometry such as bicyclo[2,2,2]-octane was noticed in $[\text{BiW}_3(\text{H}_2\text{O})\text{O}_{11}]^-$ BB (Fig. 1k), quite distinct from the well-known cubane structure. The $[\text{EuBi}_2(\text{H}_2\text{O})_2\text{Te}_2\text{O}_4]^{9+}$ cluster comprises a centric Eu1 atom surrounded by outward two Te and two Bi atoms in the order of “Bi4-Te1-Te2-Bi5” *via* five O bridges, and each Te or Bi atom is in conjunction with the Eu1 atom by sharing two $\mu_3\text{-O}$ atoms, generating a petal-like motif with one side opening (Fig. 1g). This arrangement also gives rise to a folded $[\text{EuTe}_2\text{O}_3]^{5+}$ quadrangle along the “Eu1-O3” line (Fig. S6†). Actually, two Te and two Bi atoms are almost coplanar to build a trapezoid plane whereas the Eu1 atom is located above the plane with a distance of 1.992 Å (Fig. S7†). A close inspection

into the $\{\text{Eu}_2\text{Bi}_3\text{Te}_2\text{W}_3\}$ cluster unveils a peculiar “hourglass-shaped” $[\text{EuBiW}_3(\text{H}_2\text{O})\text{Te}_2\text{O}_{14}]^{4+}$ fragment based on $[\text{BiW}_3(\text{H}_2\text{O})\text{O}_{11}]^-$ BB and $[\text{EuTe}_2\text{O}_3]^{5+}$ section, which can be reasonably divided into the upper $\{\text{BiW}_3\text{O}_4\}$ and the lower $\{\text{EuTe}_2\text{O}_6\}$ parts sharing one middle W1 atom (Fig. 1j).

Noteworthy, five crystallographically independent Bi^{III} atoms in a **1a** polyoxoanion play two roles: Bi1^{III} and Bi2^{III} atoms as templates are embedded in $\{\text{BiW}_9\}$ BBs while Bi3^{III}-Bi5^{III} atoms as linkers are situated between BBs. In particular, Bi3^{III}-Bi5^{III} linkers are involved in different binding environments: the Bi3^{III} atom is surrounded by seven O-coordinate spheres with four from two adjacent $\{\text{BiW}_9\}$ BBs, two from the $\{\text{BiW}_3\}$ BB, and one from the water ligand (Fig. S8†); Bi4^{III} and Bi5^{III} atoms are coordinated by Hpdca ligands *via* N and carboxyl O sites and then encircled by two O_t atoms from $\{\text{BiW}_9\}$ and $\{\text{W}_5\}$ BBs, one $\mu_3\text{-O}$ atom from the $[\text{EuTe}_2\text{O}_3]^{5+}$ fragment and one from the water ligand, both displaying the hexa-coordinate configuration (Fig. S8†). Three Bi^{III} linkers have an average Bi-O and Bi-N bond lengths of 2.421 and 2.372 Å, and

the Bi–O bond lengths are a bit longer than those in BBs (2.133 Å). Both Te^{IV} atoms play the bridging role and are in a four-coordinate geometry defined by two, one and one O atoms from [EuTe₂O₃]⁵⁺, [BiW₃(H₂O)O₁₁][−] and {BiW₉} BBs with Te–O distances of 1.857(8)–2.223(9) Å (Fig. S9†). The Eu¹³⁺ ion displays the octa-coordinate bicapped triangular prism geometry completed by four O_t atoms from the {W₅} BBs, three μ₃-O atoms from the [EuTe₂O₃]⁵⁺ fragment and one μ₂-O atom from the [BiW₃(H₂O)O₁₁][−] BBs, whilst the Eu²³⁺ ion adopts a non-coordinate mono-capped square antiprism geometry defined by four O_t atoms from two {BiW₉} BBs, three μ₃-O atoms from the {W₁₀} octahedron as well as one carboxyl O and N atoms from the Hpdca ligand (Eu–O: 2.277(9)–2.776(9) Å) (Fig. S10†).

In the stacking diagram, trimeric **1a** polyoxoanions are packed together to form an interesting supra-molecular architecture through intermolecular interactions, where the charge compensating cations ([H₈BTHMMAP]²⁺, [H₂N(CH₃)₂]⁺, H⁺ and Na⁺) and water molecules fill in the pores among **1a** polyoxoanions. For clarity, countercations and water molecules are omitted, and the stacking framework along the *c* axis reveals that neighboring layers (named layer A and B) are stacked in an –ABAB– sequence (Fig. S11†). Hereinto, two adjacent **1a** polyoxoanions are intersected and distributed in a “face-to-face” pattern, constituting a repeating unit in each layer. Unlike the “back–front” order of two **1a** polyoxoanions in the repeating unit in layer A, the **1a** polyoxoanion in layer B shows a converse “back–front” order. The simplified graph by visualizing **1a** as a triangle (built by Bi1, Bi2 and W15 atoms) makes us more clearly understand the arrangement of **1a** polyoxoanions (Fig. S11†).

Stability studies of **1a** in solution

The stability of **1a** in water was explored by electrospray ionization mass spectrometry (ESI-MS) in negative mode and UV-vis absorption spectra. As shown in Fig. S12 and Table S2,† there are three groups of charged peaks with negative charges of 6– (*m/z* values: 1364.31, 1410.49, 1457.82), 5– (*m/z* values: 1680.28, 1755.27) and 4– (*m/z* values: 2151.93, 2203.94). The peak at *m/z* 1364.31 can be assigned to {[H₂N(CH₃)₂]₂Na₃[Eu₂Bi₃(H₂O)₄Te₂W₃O₁₄][(W₅O₁₈)(BiW₉O₃₃)₂]}^{6−}, implying that three Hpdca ligands are released from **1a**. The remaining peaks correspond to the species of [Eu₂Bi₃(Hpdca)₃(H₂O)_{*n*}Te₂W₃O₁₄][(W₅O₁₈)(BiW₉O₃₃)₂]^{11−} poly-anions with different numbers of counter cations ([H₂N(CH₃)₂]⁺, H⁺, [H₈BTHMMAP]²⁺, or Na⁺). These results corroborate that the skeleton of **1a** is basically stable in water. By extending time, the first two groups (*m/z* values less than 2000) of signal peaks gradually weakened while the third group (*m/z* values between 2000–2400) gradually disappeared at 24 h (Fig. 2a). By contrast, **1a** is more sensitive to pH because partial peaks have completely vanished when pH is lower than 3.3 or higher than 9.3 (Fig. 2b). Besides, UV-vis spectra were also recorded to explore its stability in water. Evidently, one strong absorption band at 192 nm and one weak absorption band around 260 nm were observed, respectively corresponding to O_t → W and O_{b(c)} → W π–π charge-transfer tran-

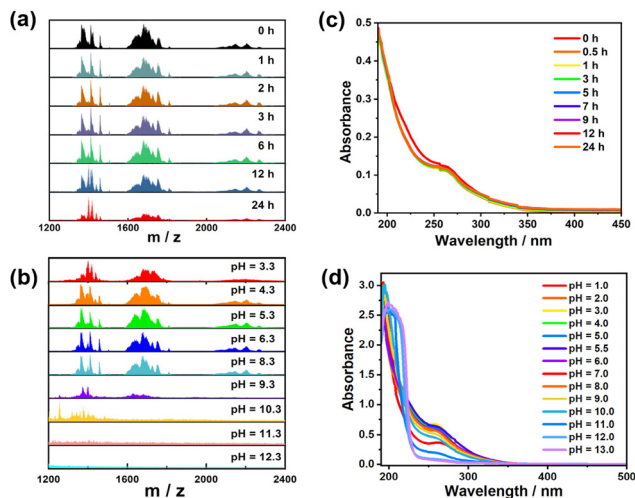


Fig. 2 (a) Time-dependent ESI-MS spectra of **1** in water. (b) The pH-dependent ESI-MS spectra of **1** in water. (c) Time-dependent UV-vis spectra of **1** in water. (d) The pH-dependent UV-vis spectra of **1** in water.

sitions. Notably, the UV-vis spectra of **1** didn't show obvious changes by prolonging time to 24 h, indicating that **1a** is basically stable for 24 h (Fig. 2c). However, the intensity of O_{b(c)} → W and O_t → W bands slowly shifted and decreased when the pH is out of the 3–10 range, as revealed in pH-dependent UV-vis spectra (Fig. 2d). Overall, the UV-vis result basically matches with ESI-MS data. Thus, the structural stability of **1a** can be maintained for 24 h, or in the pH range of 3.3–8.3.

Photoluminescence (PL) sensing properties

Ferric ion (Fe³⁺) is an essential trace element for the human body, and is also an important component of hemoglobin, many enzymes and immune system compounds.^{44–46} However, the abnormalities of Fe³⁺ in the human body can lead to various diseases such as anemia, renal failure, liver damage and hemochromatosis. In addition, an excess of Fe³⁺ threatens the ecological environment.^{47,48} Hence, the detection of Fe³⁺ is vital to the early warning of underlying diseases or environmental damage. Among the diverse detection strategies, PL sensing methods have aroused great interest owing to their high selectivity and sensitivity, convenient operation, and low sample consumption. As a water-stable and easy-to-prepare Eu-based PL material, **1** could be developed as a probe to detect Fe³⁺.

Motivated by this idea, the PL behaviors of **1** in water were studied. Five well-resolved emission peaks at 578, 594, 620, 654 and 699 nm were observed in the spectrum of **1** (2 mg mL^{−1}) that can be identified as the ⁵D₀ → ⁷F_{*J*} (*J* = 0–4) transitions of Eu³⁺ ions upon excitation at 397 nm (Fig. S13a†).^{49,50} The ⁵D₀ → ⁷F₂ transition at 620 nm is dominated by a splitting peak at 618 nm. Monitored at the strongest emission, the excitation spectrum of **1** exhibits one broad band at around 350 nm attributed to the O → W charge transfer of {BiW₉} and {W₅} BBs, as well as five typical peaks at 363 nm (⁷F₀ → ⁵D₄), 383 nm (⁷F₀ → ⁵G₂), 397 nm (⁷F₀ → ⁵L₆), 418 nm (⁷F₀ → ⁵D₃)

and 467 nm (${}^7F_0 \rightarrow {}^5D_2$) from Eu^{3+} ions (Fig. S13b \dagger). Additionally, the decay lifetime of **1** under the 397 nm excitation peak and 620 nm emission peak can be calculated as 816.04 μs by fitting with the mono-exponential function $I = A \exp(-t/\tau_1)$ (Fig. S13c \dagger), where A represents pre-exponential factor and τ_1 represents the luminescence lifetime. Moreover, the time-dependent PL emission of **1** (2 mg mL^{-1}) in water was studied (Fig. S14 \dagger). The intensity shows a slow attenuation that may be caused by dynamic exchange between water molecules in **1** and solution, and a total decrease of 9% within 10 h at 620 nm indicates the PL emission of **1** is basically stable in water for a long time.

Based on the excellent PL behavior in water, sensing experiments were carried out by employing **1** (2 mg mL^{-1}) as a probe. As revealed in Fig. 3a, the emission evolution of **1** towards Fe^{3+} triggers an “ON-OFF” response as the emission intensity gradually decreases to approximately 26% with the concentration of Fe^{3+} ranging from 0 to 400 μM . Additionally, a good linear Stern–Volmer (S - V) function fitted by $I_0/I = 0.992 + 0.00218[C_{\text{Fe}}]$ with a correlation coefficient (R^2) of 0.994 was obtained between intensity ratio (I_0/I , I_0 and I represent the emission intensity without or with the addition of Fe^{3+}) at 620 nm and Fe^{3+} concentration ($[C_{\text{Fe}}]$, 0–150 μM) (Fig. 3b), implying that the quantitative detection of Fe^{3+} by **1** is applicable over a wide $[C_{\text{Fe}}]$ range. As $[C_{\text{Fe}}]$ continues to increase, the fitting curve gradually deviates from linearity and bends upward, which can be perfectly fitted by an exponential function. The limit of detection (LOD) was determined to be

1.23 μM based on the definition of $\text{LOD} = 3s/k$, where s indicates the standard deviation of three blank tests, and k is the slope of the linear fitting curve (Table S3 \dagger).⁵¹ This LOD value is apparently lower than the permissible limit of Fe^{3+} in drinking water given by the World Health Organization (WHO) (5.37 μM).

By comparison, other cations $\text{M}(\text{Cl})_x$ ($\text{M}^{x+} = \text{Na}^+, \text{K}^+, \text{Li}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Al}^{3+}$, and Cd^{2+}) or anions Na_xN ($\text{N}^{x-} = \text{CH}_3\text{COO}^-, \text{NO}_3^-, \text{H}_2\text{PO}_4^-,$ and SO_4^{2-}) with the same concentration of 400 μM can hardly quench **1** (Fig. S15 \dagger). Furthermore, hierarchical cluster analysis (HCA) was applied for classifying analytes, which was calculated by the HCA algorithm based on PL intensity at 620 nm. Evidently, Fe^{3+} can be completely recognized from other ions from the root node of the clustering tree (Fig. 3c). Fig. 3d also shows the distance of HCA between ions where blue suggests they are far away and red suggests that they are close. The coexistence of interfering species with Fe^{3+} led to minor or negligible effects on the emission intensity (Fig. 3e), indicative of the remarkable anti-interference ability of **1** towards the determination of Fe^{3+} . The excellent detection performances of **1** drive us to evaluate its potential utility in actual samples. A series of lake water, tap water and human serum samples were filtered and spiked with various amounts of Fe^{3+} by standard addition method. And Fe^{3+} concentration in the above samples was computed by PL intensity tests and compared with the actual amount added. As manifested in Table S4 \dagger , the recoveries of 99.19%–100.50% with a relative standard deviation (RSD) of 0.83%–1.82% in tap water,

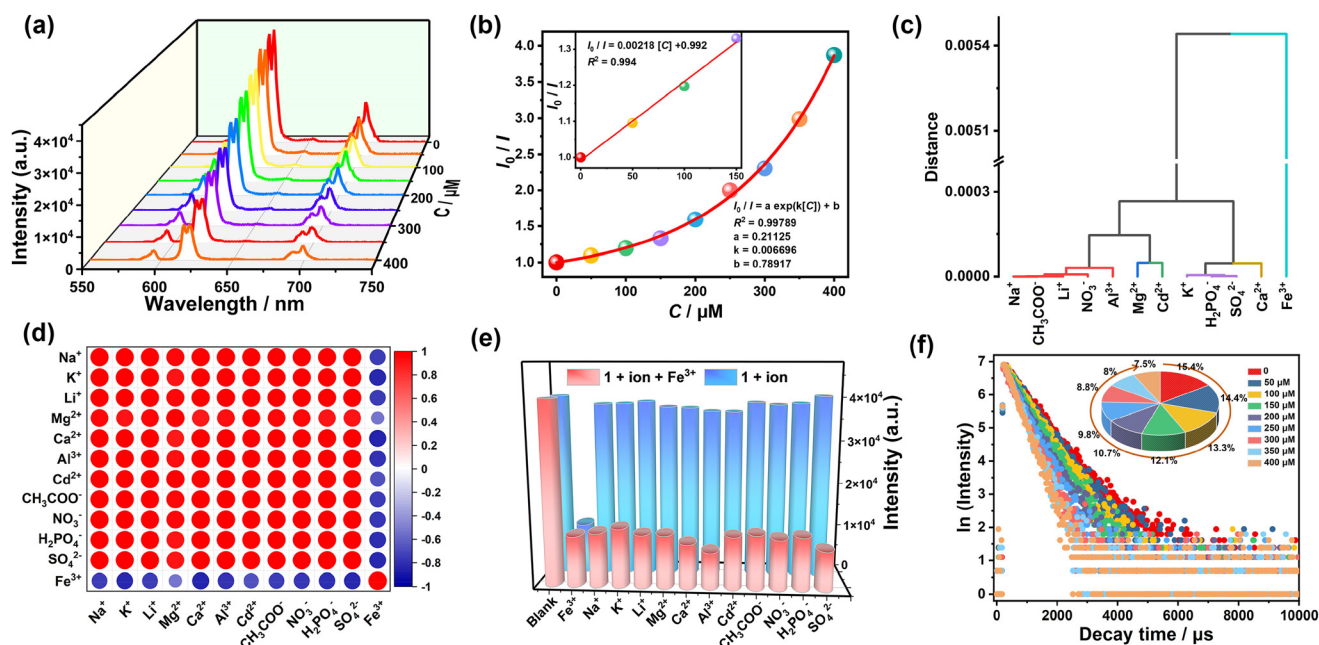


Fig. 3 (a) Evolution of the emission spectra of the 1-based sensor with different concentrations of Fe^{3+} . (b) Plot of PL intensity ratio vs. the concentrations of Fe^{3+} . Inset: the linear variation of I_0/I with the concentration of Fe^{3+} in the range of 0–150 μM . (c) Dendrogram of different ions in hierarchical cluster analysis. (d) Hot plot of distances between different ions based on hierarchical cluster analysis. (e) Fluorescence responses of the 1-based sensor under different interferences. (f) Lifetime decay curves of the 1-based sensor under different concentrations of Fe^{3+} (Inset: the pie chart of PL lifetime at different concentrations of Fe^{3+}).

99.00%–100.18% with an RSD of 0.27%–0.94% in lake water, and 99.56%–101.78% with an RSD of 0.34%–1.23% in human serum were found, indicating that the developed sensor was viable for the quantitative detection of Fe^{3+} in real samples.

To figure out the sensing mechanism, the PL decay lifetime curves of **1** were recorded at 397 nm excitation peak and 620 nm emission peak, all obeying the mono-exponential function. The lifetimes of **1** showed a definite dependency on the concentration changes, which decreased drastically from 816.04 (0 μM) to 400.14 μs (400 μM) (Fig. 3f and Table S5[†]). This phenomenon suggests that dynamic quenching based on the collision between **1** and Fe^{3+} may play an important role in the Fe^{3+} -induced “ON–OFF” process. Generally, the quenching rate constant (K_q) can be obtained from the equation $K_{SV} = K_q\tau_0$ (τ_0 means the decay lifetime of **1** without Fe^{3+}), and the intermolecular collision frequency in a dynamic process is usually less than $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁵² Here, τ_0 is 816.04 μs and the quenching rate constant (K_{SV}) is estimated to be $2.18 \times 10^3 \text{ M}^{-1}$ from the linear S - V function of $I_0/I = 0.992 + 0.00218[C_{\text{Fe}}]$, therefore K_q was calculated to be $2.67 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This value also confirms that the dynamic quenching pathway is predominant in Fe^{3+} detection. Moreover, the UV–vis spectrum of Fe^{3+} ion was recorded to further proclaim the quenching mechanism, which shows a broad absorption band (200–450 nm) centered around 297 nm. Clearly, the excitation spectrum of **1** exhibits large overlaps with the UV–vis absorption of Fe^{3+} ions, while the emission shows negligible overlap (Fig. S16[†]). This result precludes the fluorescence resonance energy transfer, but suggests the existence of competitive

absorption.^{53,54} That's to say, Fe^{3+} ions show strong competition with BBs or Eu^{3+} ions for light energy, which can weaken the excitation energy of BBs or Eu^{3+} ions, thus causing significant quenching.

Pyrophosphate ($\text{P}_2\text{O}_7^{4-}$, PPI) is the hydrolysis product of adenosine triphosphate, and is closely related to numerous fundamental chemical and biological processes such as DNA replication, cellular metabolism and enzymatic catalysis.^{55,56} An adequate level of PPI can block calcification in blood plasma, synovial fluid and urine, exhibiting a vital effect on arthritis and chondrocalcinosis. Therefore, accurate detection of PPI is essential.^{57,58} On account of the intense affinity of PPI towards metal ions causing emission quenching or enhancement, the resulting Fe^{3+} -quenched system might be a feasible way for recognizing PPI.

As illustrated in Fig. 4a and b, the emission intensity of Fe^{3+} -quenched system was progressively recovered with the continuous addition of PPI, and a recovery rate of about 78% was ultimately achieved when PPI concentration reached 800 μM . Thus, a bidirectional “ON–OFF–ON” PL sensing assay was developed for the successive detection of Fe^{3+} and PPI. To gain more insight into the relationship between emission intensity and analyte concentration, the PL enhancement coefficient (K_{EC}) was quantitatively analyzed from the equation $I_0/I = 1 + K_{EC}[C]$,⁵⁹ where $[C]$ denotes the concentration of analyte, and I_0 and I are PL emission intensities without and with analyte, respectively. In the present system, the I/I_0 at 620 nm shows a good linear response to PPI with the equation of $I/I_0 = 1.0035 + 0.00282[C]$ over a wide concentration scope

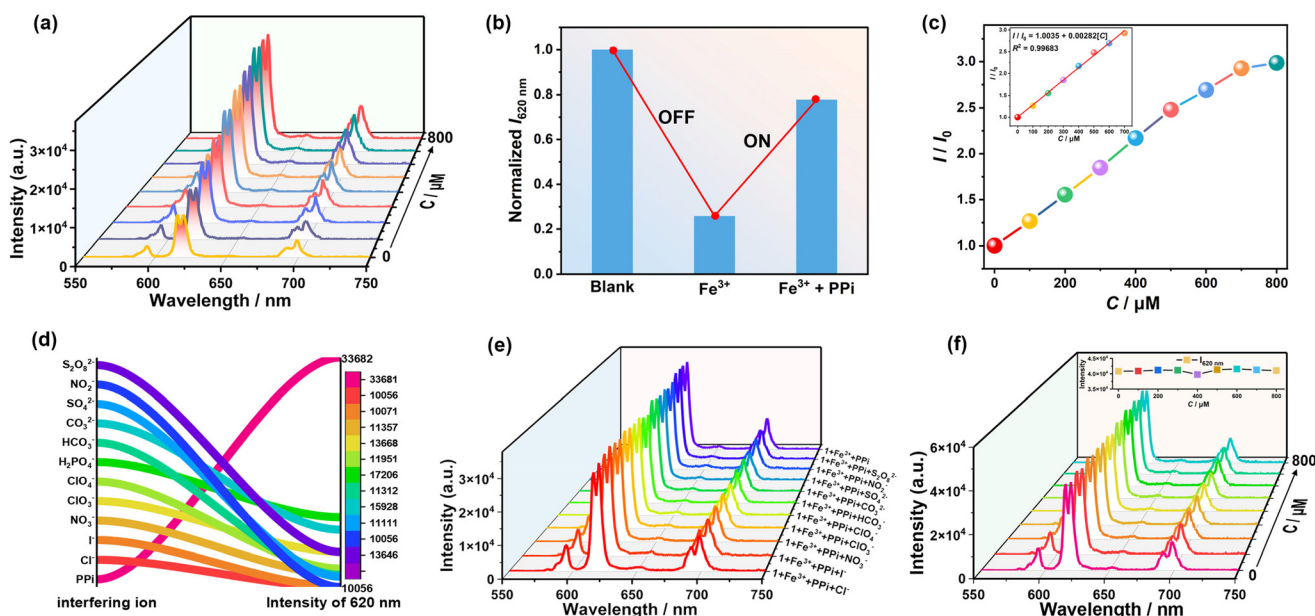


Fig. 4 (a) Evolution of the emission spectra of the Fe^{3+} -quenched system with different concentrations of PPI. (b) The variation of PL intensity during the whole ON–OFF–ON process. (c) Variation of I_0/I values at 620 nm of the Fe^{3+} -quenched system with the concentration of PPI ($C_{\text{Fe}} = 400 \mu\text{M}$). Inset: the linear variation of I_0/I with PPI concentration in the range of 0–700 μM . (d) Classification of different anions depending on their response patterns in the Fe^{3+} -quenched system. (e) Fluorescence responses of the Fe^{3+} -quenched system in the presence of PPI and other interfering anions. (f) Evolution of the emission spectra of the **1**-based sensor in different concentrations of PPI. (Inset: the PL intensity at 620 nm).

between 0 and 700 μM (Fig. 4c). The K_{EC} of the Fe^{3+} -quenched system for detecting PPI was found to be $2.82 \times 10^3 \text{ M}^{-1}$, suggestive of the effective interaction between Fe^{3+} and PPI. The LOD of PPI was calculated to be 2.16 μM by the $3s/k$ rule (Table S6[†]), comparable to the previously reported sensors for detecting Fe^{3+} and PPI (Table S7[†]).

Next, the selectivity and anti-interference of Fe^{3+} -quenched system were studied by measuring its response to various anions including Cl^- , I^- , NO_3^- , ClO_3^- , ClO_4^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , NO_2^- and $\text{S}_2\text{O}_8^{2-}$ (Fig. 4d, e and S17[†]). These interfering anions induced very low recoveries in intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ at the same concentrations of 800 μM , which was negligible in comparison with that of PPI. Besides, the recovery for PPI sensing was not affected by these interferents. Based on the good selectivity and anti-interference, the Fe^{3+} -quenched system can be established as a potential sensor for detecting PPI. Additionally, to exclude the potential impact of PPI on the **1**-based sensor, the PL evolution of the **1**-based sensor was recorded with the introduction of different concentrations of PPI. As exhibited in Fig. 4f, the impact of PPI on PL intensity was minimal, with PL intensity keeping steady even at concentrations up to 800 μM . As a consequence, the recovery of PL intensity is probably attributed to the affinity of Fe^{3+} towards PPI, and their combination greatly reduced the content of Fe^{3+} in the detection system, blocking the dynamic quenching process, thus the PL intensity of the Fe^{3+} -quenched system could be recovered. The PL lifetimes of the Fe^{3+} -quenched system with the addition of PPI were also investigated, which ultimately increased to 831.11 μs when PPI concentration was 800 μM (Fig. S18a, and Table S8[†]). As a comparison, the introduction of PPI alone into sensor **1** also caused the change in the lifetimes with a maximum up to 900 μs (Fig. S18b, and Table S9[†]), a bit higher than the initial lifetime of 816.04 μs of **1**, suggesting that PPI alone may also affect the recovery of PL lifetimes of the Fe^{3+} -quenched system apart from its combination with Fe^{3+} .

As another important criterion for evaluating sensor performance, the response times of sensor **1** towards Fe^{3+} and PPI were recorded. When Fe^{3+} (400 μM) was added into solution **1**, the emission intensity decreased immediately and quickly reached a plateau in less than 5 s (Fig. S19a[†]). By adding PPI (800 μM) into the above quenched system, the intensity dramatically increased and eventually achieved a stable level within 40 s (Fig. S19b[†]). These results manifest the response of **1** towards Fe^{3+} and the combination of Fe^{3+} with PPI are fast. Then the developed sensor was applied to detect Fe^{3+} and PPI in the serum to verify its applicability. Human serum was diluted 100-fold with deionized water, and **1** (2 mg mL^{-1}) was dissolved in the above serum. Then, a total of 400 μM Fe^{3+} was successively added to the **1**-containing serum to construct the Fe^{3+} -quenched luminescence system. The standard addition method was used in this system on subsequent addition of PPI. As manifested in Table S10,[†] recoveries of 99.69%–102.58% with RSDs of 0.56%–1.48% were found, indicating that the developed sensor has the effectiveness and practicality of detecting PPI in real samples.

Conclusions

In summary, a novel Bi–Te–Eu cluster embedded HPOT **1** has been fabricated, demonstrating the feasibility of combining HA pairs with Ln cations in the tungstate system to prepare mixed-HA-directed HPOTs. Particularly, the phenomenon that two types of HAs like a Bi–Te pair work together as linkers to grasp Ln and HPOT BBs has not been previously reported, and their tight connection modes endow **1** with excellent structural stability in water. Therefore, **1** was employed as a luminescence sensor to detect Fe^{3+} in water with remarkable selectivity, strong anti-interference ability and a low LOD (1.23 μM). This Fe^{3+} -quenched system was further applied to sensitively recognize PPI based on the strong affinity of Fe^{3+} and PPI, thus realizing a sequential detection system. This work highlights the vast potential of designing novel HPOTs directed by judiciously selected mixed-HA components and their promising applications in luminescence sensing in biological and environmental systems. More future efforts will be devoted to the controlled synthesis of poly-HA-templated HPOTs with higher structural complexity and functional properties.

Data availability

The data are available from the corresponding author on reasonable request.

Author contributions

Siyu Zhang and Tiantian Gong contributed equally to this work. They and Jiancai Liu performed the preparation, characterization, and photoluminescence sensing property determination and wrote the manuscript. Chenyun Liu, Qiuyu Wang and Fuxiu Chen participated in IR, TG, UV-vis spectroscopy and ESI-MS studies. Lijuan Chen and Junwei Zhao are responsible for proposing research ideas, determining crystal structures and revising the manuscript.

Conflicts of interest

There are no conflicts to declare.

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