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Recent advances in lanthanide-based POMs for photoluminescent applications

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1. Introduction

As an exceptional subset of metal oxides, polyoxometalates (abbr. POMs) are a large exceptional family of assembled anionic compounds of polynuclear early transition metal oxides (MO_x) (e.g. notably V^V, Mo^{VI}, W^{VI}, Nb^V, and Ta^V).¹⁻⁶ POM materials with abundant structural units and chemical versatility are compellingly appealing⁷⁻¹⁰ and are widely recognized as the preferred choice in functional, magnetism, and catalysis materials.¹¹⁻¹⁵ Under certain conditions, condensation reactions are triggered between the MO_x components, in which the MO_x octahedrons are structurally assembled in the form of typically symmetrical assemblies via edge-, corneror face-sharing linkages. With the development of synthesis technology, a growing number of synthesis methods have been rapidly established, demonstrating that the composition of POMs can be customized by varying the constituent elements. Among them, introducing heteroatoms into the reaction system has been found to enable the synthesis of POM derivatives with more diverse structures. Moreover, the skeleton of POM readily dissociates from one or more MO_x octahedra, producing lacunary POMs with unique functions to trap additional electrophilic components (lanthanide/transition metal, etc.) yielding mixed-addenda POMs by tuning the number and position of substituted sites. Therefore, lacunary POMs, known as "superligands" or "metalloligands", are widely used as precursor units in the speciation of coordi-

Since the first formation of the famous "Peacock–Weakley" anions $[Ln(W_5O_{18})_2]^{8/9-}$, a steady stream of breakthroughs have been made in the chemistry of multitalented lanthanide (Ln)-based polyoxometalates (POMs) for their potentially desirable properties. In particular, Ln^{III} ions are generally recognised as the "vitamins of the modern industry" owing to their ability to cover a wide emission range, endowing Ln-based POMs with great potential for versatile and diverse luminescence-related applications. In this frontier, we discuss the synthesis strategies and intramolecular energy transfer in Ln-based POM derivatives. Then, the progressive improvements achieved with Ln-based POMs in photoluminescence applications are highlighted, focusing mainly on luminescent and fluorescent probes. Finally, the challenges for Ln-based POM materials for photoluminescence applications are discussed.

nation polymers with nearly endless structural and compositional diversities. To summarize, in relation to the composition of POMs, several review articles include a more detailed Introduction.^{6,16–20}

Lanthanide (Ln)-based luminescent materials with the high color purity of the emitted light have attracted considerable attention in broad areas of sciences as potent candidates owing to their resistance to photobleaching, narrow f-f transitions, and long excited-state lifetimes.21-23 Trivalent LnIII ions with many complicated 4f energy levels, known as the "vitamins of modern industry", feature fluorescence emission via intra-4f or 4f-5d transitions from visible (Eu^{III} or Tb^{III}) to near-infrared (Nd^{III} or Yb^{III}) light.^{22,24-29} This property can ensure the emergence of Ln ions with high color purity and Stokes shift, reducing excitation interference in the emission process.30-32 Consequently, in the field of luminescent materials, Ln-based materials could be employed as a crucial branch,^{33,34} generating considerable interest in applications as varied as bioimaging and biomedical analysis, lasers, chemical sensing, optical fibers, and amplifiers.35-38 Nevertheless, in principle, the direct excitation of 4f levels indicates a relatively inefficient process as a consequence of the Laporte forbidden f-f transitions, yielding extremely low molar absorption coefficients ($\varepsilon < 10 \text{ L mol}^{-1} \text{ cm}^{-1}$).^{39–41} In this regard, the limitations of intramolecular excitation can be overcome by the formation of hybrid materials with the introduction of photosensitizers, also known as the Ln-sensitization or optical antenna effect.40,42-44 The essence of the antenna effect is that the dopants as luminescent sensitizers can harvest light, and then transfer efficient energy to the Ln centers as the energy of emitting levels is higher than that in the emitting levels for Ln^{III} luminescence.⁴⁵ In relation to the luminescence prin-

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ciples of Ln ions, several reviews have introduced a detailed summary and provided some insightful comments.^{21,46,47}

The high coordination number is extremely advantageous for Ln^{III} ions to be linkers and stabilizers to endow mixedaddenda POMs with a considerable increase in structural diversity.^{34,46,47} It is important that the synergistic combination between lacunary POMs and Ln components results in coordination compounds with characteristic functions and unique physicochemical properties.⁴⁷⁻⁵¹ The thermal/chemical stability and acid/redox properties of POM moieties when judiciously combined with the highly peculiar properties of Ln ions (e.g. luminescence, magnetism) render Ln-based POMs as suitable candidates for implementation in different fields such as photoluminescence, magnetism, and photochromism. Dating back to the 1970s, a new field of Ln-based POM was opened up by a pioneering work, famous as "Peacock-Weakley" polyanions $[Ln(W_5O_{18})_2]^{8/9-}$, reported by Weakley et al.⁵²

Following the breakthrough of the "Peacock-Weakley" ions, research on Ln-based POM derivatives has witnessed dramatic developments, especially in the last few decades, judging from several review articles that have primarily introduced the synthesis and structure.53-55 Fundamental opinions on the principles of Ln-based POMs' luminescence were proposed, based on extensive research by Yamase et al.^{5,21,56} In fact, the W-O charge transfer (CT) transitions in POM components will be executed under the excitation, leading to strong absorption in the ultraviolet range, manifesting a particularly pronounced action in energy transfer processes in POMs to act as photosensitizers. Typically, the 2p orbital electrons of the ligand oxygen will transfer to the d orbitals of the metal M (LMCT) upon excitation. At this point, the state of the POM components changes from the ground state ${}^{1}A_{1g}$ to the excited state ${}^{1}T_{1u}$. The energy from the $^1T_{1u} \rightarrow \, ^3T_{1u}$ states is then transferred to the excited levels of the Ln^{III} ions, effectively enhancing the emission of the Ln centers. Among the luminescent Ln-based POMs, the Peacock-Weakley anion $[Eu(W_5O_{18})_2]^{9-}$ elucidates the long-lasting luminescent stability and the highest luminescent quantum yields.57

In this article, we would like to discuss the synthesis strategies from the view of energy transfer in Ln-based POM derivatives, and then further summarize the detailed study of photoluminescent applications such as those related to luminescence and fluorescence probes. In the final part, conclusions are discussed, together with further work that is urgently needed or challenges remaining in this field. We hope that this article will provide an overview of the recent novel functional developments of lanthanide-based POMs and provide inspiration for functional expansions.

2. Synthesis strategies and energy transfer in luminescent materials

Because the series usually have identical structures owing to the lanthanide contraction,^{46,58,59} it is feasible to introduce

different Ln^{III} ions into a system defined as a pre-functionalization strategy to emit a distinctive color. As could be expected, in the representative structure of this type, compound $\{[W_2O_5(OH)_2(H_2tart)_2](H_2tart)\}$

 $\{[W_3O_6Ln_2(H_2O)_6][SeW_9O_{33}]_2\}_2\}^{14-}$ will explicitly exhibit a different emission color under excitation, for Ln ions, *i.e.*, Eu (red), Tb (green), Dy (blue), and Ho (orange).⁴¹

Apart from that, the most popular solution to circumvent the limitation of low molar absorption coefficients of Ln^{III} ions is the co-doping of a sensitizer in the Ln system, as previously proposed, the so-called "antenna effect". Although the fact that the direct combination of POMs with Ln^{III} ions has produced a plethora of types of architectures with hybrid frameworks, the incorporation of organic ligands will enrich the family of functionalized POM-based architectures with enhanced processability and robustness. Indeed, organic ligands (most with highly conjugated structures) could be envisaged as another "antenna" where the sensitization generally concerns the population of a triplet excited state of the conjugated organic ligand, which intrinsically exhibits a long lifetime, thus enabling energy to be efficiently transferred to the emitting Ln^{III} center.

In this field, the feasible synthetic strategies can be primarily divided into three categories based on the energy transfer pathways: (1) between POM moieties and a single Ln^{III} center; (2) between POM moieties, organic ligands (heterocyclic and aromatic carboxylates) and Ln^{III} centers, (3) between POM moieties and doped Ln^{III} components (double and triple Ln^{III} centers). Moreover, the photostability could be effectively improved by preparing Ln-doped POM compounds.

In 2018, the Pr-based POMs presented that POM components can sensitize Pr^{III} ions *via* energy transitions.⁶⁰ There are a plethora of compounds of antenna effects caused by the transfer of energy from POM components to Ln^{III} ions $(Sm^{III}, {}^{30,61} Eu^{III}, {}^{30,61-63} Tb^{III}, {}^{63} Dy^{III}$, and $Ho^{III} {}^{64}$). Certain typical molecular structures are shown in Fig. 1, and the



Fig. 1 Some typical molecular structures for Ln-based POMs. $(1a, {}^{60}$ 1b, 61 1c, 30 1d, 62 1e, 67 1f, 68 and 1g. 69)



Fig. 2 (a) Mechanisms for the sensitized emission of $Pr^{III,60}$ (b) $Sm^{III,61}$ (c) Eu^{III} from POM components.⁶²

corresponding energy transfer mechanism is described in Fig. 2. It is worth mentioning the compound [Ln $(H_2O)_6(H_4(TaO_2)_6As_4O_{24})]^{3-}$ in which the $\{As_4Ta_6\}$ segment can transfer the energy to the Eu^{III} centers, facilitating Eu^{III} emissions.⁶⁵ In 2005, Zhang *et al.* developed a ternary system of Eu^{III}-based POM derivatives, representing the first "organic group modified Eu^{III}-based POMs". In this ternary system, the organic group was able to absorb energy and sensitize the emission of Eu^{III} ions through energy transfer.⁶⁶

In 2020, we confirmed that organic benzoic acid ligand in the compound $[Sm(C_7H_5O_2)(H_2O)_2(PW_{11}O_{39})]^{5-}$ can indeed sensitize Ln centers and improve the luminescence efficiency, corresponding to the $\pi^*-\pi$ transition of the benzoic acid group⁶⁷ (Fig. 3). There are many examples of efficient sensitizers among organic ligands such as benzoate ligand \rightarrow Sm^{III}/Eu^{III, 30} isonicotinic acid \rightarrow Sm^{III, 70} and 2-picolinic acid \rightarrow Eu^{III}/Dy^{III, 71,72}

In comparison, the energy transfer process in co-doped Lnbased POMs containing two or more Ln^{III} components is more complex. Initially, the ground state of Ln1 is converted under excitation, followed by the transfer of the f–f state photon energy to the ground state of Ln2. Finally, the conversion emission is successfully induced. Typically, for a known structured



Fig. 3 The mechanisms process for POMs, ${\rm Ln}^{\rm III}({\rm a}),$ and organic ligands (b). $^{\rm 30,67}$

POM derivative with one type of Ln^{III} ion, a series of isomorphic compounds could be purposefully obtained by introducing other Ln^{III} ions or controlling different molar ratios of Ln ions with two or more centers.

Employing this strategy, the double-mixed Dy^{III}/Tm^{III} ionbased POM derivatives, $[Dv_rTm_{1-r}(C_4H_2O_6)(PW_{11}O_{39})]_2^{16-73}$ verified the energy transfer $Tm^{III} \rightarrow Dy^{III}$ to efficiently facilitate emissions of the Dy^{III} centers. In 2022, we offered a family of co-Eu/Tb-doped compounds based [{(As₂W₁₉O₆₇(H₂O))Ln $(H_2O)_2$ ₂ (C_2O_4) ²⁴⁻, probing the existence of the energy transfer $(Eu^{III} \rightarrow Tb^{III})$ centers in the compound $Eu_{0,1}Tb_{0,99}$ -POM.⁶³ In addition, the energy transfer $(Dy^{III} \rightarrow Er^{III})$ was researched via the $Dy_x Er_{(1-x)}$ -POM (x = 0-1) derivatives based $[Dy(C_4H_2O_6)]$ $(PW_{11}O_{39})]_2^{16-,75}$ where the derivative with the optimal doping ratio obtained was Dy_{0.8}Er_{0.2}-POM with the best photostability. Note that the triple-Ln^{III} ion, due to the optimal doping ratio obtained in Dy0.8Er0.2-POM, showed the best photostability. Moreover, the triple-Ln^{III} ion-doped POM derivatives, $[Eu_xTb_yTm_{1-x-y}(C_7H_5O_2)(H_2O)_2(PW_{11}O_{39})]^{5-,76}$ representing a relatively high energy transfer efficiency between Eu^{III} and Tb^{III} ions.

Admittedly, Zhao's group achieved a lot of research progress in this field. In 2018, the Ho^{III}/Yb^{III} co-doped POM derivatives on the basis of $[Ln_2(OH)(TeW_7O_{28})Sn_2(CH_3)_4(W_5O_{18})]_2^{14-}$ demonstrated the maximum emission intensity in the $Er_{0.40}/$ Yb_{0.60} co-doped sample, primarily owing to the energy transfer between Yb^{III} ions and Er^{III.77} Furthermore, in 2020, they synthesized a series of Ho^{III}/Tm^{III}-co-doped POM derivatives based [SeO₄Ln₅(H₂O)₇(Se₂W₁₄O₅₂)₂]^{13-,74} confirming that Tm^{III} ions can sensitize the emission of Ho^{III} ions in the Ho_{0.5}/Tm_{0.5} derivative (Fig. 4a). Furthermore, the red emitter Eu^{III} ions and green emitter Tb^{III} ions are co-doped in the [Gd₂(C₂O₄) (H₂O)₄(OH)W₄O₁₆]₂¹⁰⁻. The compound **Gd**_{0.08}**Tb**_{3.6}**Eu**_{0.32}**W**₈ demonstrated the highest emission intensity, attributed to the energy transfer from Tb^{III} to Eu^{III} ions⁶⁸ (Fig. 4b). Following a similar synthetic method, Eu^{III}/Tb^{III}/Dy^{III}/Gd^{III}-codoped speciesbased [(WO₄){Tb(H₂O)(Ac)(SbW₉O₃₁(OH)₂)₃]¹⁷⁻ demonstrated a



Fig. 4 Energy transfer (ET) process of (a) POMs component, Ho^{III} , and $Tm^{III,74}$ (b) POMs component, Eu^{III} , and $Tb^{III;68}$ (c) POMs component, Dy^{III} , Tb^{III} , and $Eu^{III.69}$

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two-step successive $Dy^{III} \rightarrow Tb^{III} \rightarrow Eu^{III}$ energy transfer process in the compound $Dy_{1,2}Tb_{3z}Eu_{0,03}Gd_{1,77-3z}W_{28}^{69}$ (Fig. 4c).

In addition to POM components and organic ligands, cationic surfactant (CS) usually acted as a stabilizer and a regulator in the Ln system.^{78–81} Note that there is a novel method for sensitization of Ln^{III} ions in Ln-based POM composites with CS. Further exploration was conducted to study the influence of CS and Ln-based POMs with different mass ratios on the emission intensity. In 2017, Zhao *et al.* constructed a [{Sn (CH₃)W₂O₄(IN)}{(TeW₈O₃₁)Sm(H₂O)(Ac)}₂]₂^{20–}@CTAB composites with peanut-like and honeycombed morphologies (CTAB = cetyltrimethylammonium bromide).⁸² The energy transfer was performed from CTAB to Sm^{III} centers within CTAB/POMs = 0.033/0.05 consolidation.

Photoluminescent applications

3.1 Multi-color emission

The ability to achieve multi-color emission by Ln-based POM materials is a potential application in many fields such as WLED, lighting, and displays, as unique features of Ln-based luminescent materials. A plethora of strategies, such as adjusting the excitation wavelength and the relative intensity of the emission peaks, have been used to achieve different color emissions from Ln-based POM materials.^{83–89} The CIE chromaticity diagram is often adopted to visually represent the luminescence information of materials with CIE chromaticity coordinates obtained from the emission spectra according to the International Commission on Illumination.

Our group has performed several explorations in this field. In 2015, we synthesized a family of POM-ligated trinuclear Ln-clusters $[Ln_3(OH)(H_2O)_8(AsW_9O_{33})(AsW_{10}O_{35}(mal))]_2^{22-90}$. Different samples vielded different emission colors, from vellowish-green to green to reddish-orange by the introduction of different Ln ions. This method of changing the type of Ln^{III} ions in POM compounds to afford different colors of emission is already well established, mainly because the different Ln^{III} metals are typically isostructural.91 Furthermore, changing the excitation wavelength to coordinate the emission of Ln-based POMs is an obviously effective channel. In 2018, an Ln-based hybrid $[{Pr(H_2O)_2}_2 As_2W_{19}O_{68}]$ POM derivative, $\{WO_2(mal)\}_2^{12-}$, showed excitation wavelength-dependent emission properties, achieving a reversible emission color switching simply by changing the excitation wavelength (380-470 nm)⁶⁰ (Fig. 5a and b). In addition, we found that the novel reversible color-tunable photoluminescence Ln-based POM $[Sm(C_7H_5O_2)(H_2O)_2(PW_{11}O_{39})]^{5-}$ demonstrated emitting colors from blue to pink based on the excitation $(260-350 \text{ nm})^{67}$ (Fig. 5c).

In recent years, our group has devoted considerable efforts to co-doped Ln^{III}-based POM materials for optical applications. The main reasons are as follows: (I) different ratios of two Ln^{III} centres could produce multi-colour emission by changing the doping molar ratio of different Ln^{III} ions; (II) intramolecular energy transfer occurs between different Ln^{III} components



Fig. 5 (a) PL emission spectra of compound $[{Pr(H_2O)_2}_{2}{As_2W_{19}O_{68}}] {WO_2(mal)}_2]^{12-}$ under $\lambda_{ex} = 380-470$ nm, and the CIE diagram (b).⁶⁰ (c) The CIE 1931 diagram of Sm-based POMs on $\lambda_{ex} = 260-350$ nm.⁶⁷ (d) The CIE diagram of co-Tm^{III}/Dy^{III}-based POMs.⁷³

with similar energy values, which enhances the luminescence intensity of another Ln^{III} emission centre. There is an enormous variety of successful cases of achieving multi-colour luminescence by tuning the emission intensity of co-doped Ln^{III} emission centres. In 2018, a family of co- Tm^{III}/Dy^{III} -based POMs, $[Dy_xTm_{1-x}(C_4H_2O_6)(PW_{11}O_{39})]_2^{16-}$ was constructed, which displayed color reconcilable properties⁷³ (Fig. 5d). The successful implementation is that different samples could provide adjustable emission colours from blue to yellow by adjusting the combination of Tm^{III}/Dy^{III} .

In 2022, co-doped compounds, $[\{(As_2W_{19}O_{67}(H_2O))Ln (H_2O)_2\}_2(C_2O_4)]^{24-}$ {Eu_xTb_{1-x}-POM} (x = 0.01, 0.04, 0.1, and 0.2), could potentially generate coordinated emission colours transitioning from green to red by modulating the ratio of Eu^{III}/Tb^{III} components.⁶³ Moreover, we obtained another series of different ratios of doped-Dy_xEr_(1-x) ions POM (x = 0-1) derivatives, which represent [Dy(C₄H₂O₆)(PW₁₁O₃₉)]₂¹⁴⁻ as the parent Dy-POM⁷⁵ (Fig. 6). Among them, the compounds Dy_xEr_(1-x)-POM (x = 1, 0.9, and 0.8) can emit cover the blue LED chip to emit white light in practical applications. As the doping amount of Er^{III} increases, the emission intensity of Dy^{III} gradually decreases.

Zhao *et al.* demonstrated that multiple emission colors were achievable by doping Tb^{III} ions into the polyanion $[\text{Eu}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4(\text{OH})\text{W}_4\text{O}_{16}]_2^{10-}$. The samples emit green in the absence of Tb^{III} , while the color can change to red emission by adding Tb^{III} in different ratios.⁶⁸ Recently, a family of co-Er/Yb-doped POM-based on the $[\text{Er}(\text{OH})(\text{TeW}_7\text{O}_{28})]$ $\text{LnSn}_2(\text{CH}_3)_4(\text{W}_5\text{O}_8)]_2^{14-}$ polyanion with luminescence pro-



Fig. 6 (a) PL emission spectra and (b) the CIE diagram of $Dy_x Er_{(1-x)}$ -POM; (c) corresponding emission intensity at 480, 573, and 663 nm; (d) PL decay time diagrams upon excitation at 367 nm and emission at 573 nm (x is 0.1–1) of $Dy_x Er_{(1-x)}$ -POM ($\lambda_{ex} = 367$ nm).⁷⁵

perties in the visible/NIR regions was synthesized.⁷⁷ The emission intensity of Er^{III} ions reached the maximum with the ratio of Er/Yb of 0.40:0.60. Very recently, they probed the characteristic emission bands of co-HoIII/TmIII-existing in Ln-based POM-derivatives based the polvanion on $[SeO_4Ho_5(H_2O)_7(Se_2W_{14}O_{52})_2]^{13-}$. As the concentration of Tm^{III} ions increases, the characteristic emission band of Tm^{III} ions shifts slightly to red while the emission peak of Ho^{III} ions shifts slightly to blue.⁷⁴ When the concentration of Ho^{III} and Tm^{III} reaches a certain level (1:1), the strongest emission with the longest fluorescence lifetime can be generated by the energy transfer from the excited state Tm^{III} to Ho^{III}.

Surprisingly, by changing the excitation wavelengths, the emission color of the Eu^{III}/Tb^{III}/Dy^{III}/Gd^{III}-codoped derivatives the $\{(WO_4)|Ln(H_2O)(Ac)\}$ based on polyanion $(SbW_9O_{31}(OH)_2)]_3$ ¹⁷⁻ can vary from blue to yellow in which a near-white-light emission case was achieved on $\lambda_{ex} = 378$ nm.⁶⁹ In 2019, Zhao et al. synthesized the nanosized CTA-encapsulated POM composites using the microwave method (cetyltrimethylammonium bromide = CTABr).92 The $[SeO_4Dy_5(H_2O)_7(Se_2W_{14}O_{52})_2]^{13-}$ @CTA-5 min nanomaterial with the highly uniform small-sized nanoparticles demonstrated the highest emission among the nanomaterials at different stirring times.

Furthermore, as a hot trend in solid-state lighting, white light-emitting diodes (WLEDs) have attracted considerable attention for their high energy efficiency, high brightness, and low power consumption. As different Ln^{III} ions can emit inherent CIE luminescence color coordinates, they are widely used in the production of WLED materials. More commonly, Eu^{III} is widely used for red emission, Dy^{III} or Sm^{III} for yellow emission, Tb^{III} for green emission, and Tm^{III} for blue emis-

sion. Thus, Eu^{III}, Dy^{III}, Sm^{III}, and Tb⁺ are used as common elements in the production of WLED materials. The white light point is referred to as the equal energy point (x_{ee} , y_{ee}), which is located near the center of the chromaticity diagram with the standard chromaticity coordinates (0.33, 0.33).⁹³

At present, in the field of research on Ln^{III}-based POM materials with white light emission, the synthesis of co-Ln^{III}doped POM derivative ions is primarily obtained by adjusting the concentration of each Ln^{III} ion. As depicted in Fig. 7a, we report that the mixed Dy^{III}/Tm^{III}-based POM derivatives, $[Dy_{x}Tm_{1-x}(C_{4}H_{2}O_{6})(PW_{11}O_{39})]_{2}$, can emit a variety of colors from blue to white to yellow by adjusting the molar ratio of Dy^{III} and Tm^{III} .⁷³ Similarly, for $Dy_x Er_{(1-x)}$ -POM based [Dy $(C_4H_2O_6)(PW_{11}O_{39})]_2^{16-}$, the Dy_xEr_(1-x)-based POM (x = 1, 0.9, and 0.8) samples emit macroscopic white light under blue irradiation, indicating that the samples can cover the blue LED chip to emit white light in practical applications⁷⁵ (Fig. 7b). Zhao et al. confirmed that the co-doped Ln^{III}-based POMs, $Dy_{1,2}Tb_{1,2}Eu_{0,03}Gd_{0,57}W_{28}$ based $[(WO_4){Tb(H_2O)(Ac)}$ $(SbW_9O_{31}(OH)_2)_3]^{17-}$ represent a near-white-light emission case upon excitation at 378 nm⁶⁹ (Fig. 7c). Moreover, they that the co-doped Ln-based compound, illustrate $Tb_{3,92}Eu_{0.08}W_8$ -based $[Gd_2(C_2O_4)(H_2O)_4(OH)W_4O_{16}]_2^{10-}$, also displayed near white-light emission.⁶⁸ The multicenter-Ln codoped $[Eu_xTb_yTm_{1-x-y}(C_7H_5O_2)(H_2O)_2(PW_{11}O_{39})]^{5-}$ have been synthesized to study the white-light-emitting behavior with the molar ratio of Eu^{III}/Tb^{III}/Tm^{III} = 0.06 : 0.10 : 0.84.⁷⁶

3.2 Fluorescent probe

Fluorescent probe materials are often used as indicators and for the generation of excited fluorescence at a predetermined wavelength and are widely used in a variety of detection and labelling fields such as the determination of metal ions, pesticide residues, biomolecular content, traceability of bio-



Fig. 7 (a) CIE chromaticity coordinates, color purity, emitting color of co-Dy^{III}/Tm^{III} POMs derivatives.⁷³ (b) CIE diagram of $Dy_x Er_{(1-x)}$ -POM.⁷⁵ (c) CIE 1931 diagram of $Dy_{1.2}Tb_{1.2}Eu_{0.03}Gd_{0.57}W_{28}$ upon excitation at 378 nm.⁶⁹

molecules and cellular and subcellular structures. By detecting the changes in fluorescence intensity owing to the influence of the environment on the fluorescent probe, visual monitoring of the detected substance is achieved, providing the characteristics of the environment or specific information present in the environment. Based on the substance, there are many classifications of fluorescent probes, including metal ion fluorescent probes and biomolecular fluorescent probes.

The detection of trace metal ions in drinking and irrigation water is important for a better understanding of their role in humans and animals. In this field, Eu-based POMs have a prominent position, as a hotspot of research, primarily because of the undisturbed high-intensity luminescence and ultrahigh sensitivity.⁹⁵ In 2019, we found that the Eu-based POMs, [Eu $(PHBA)(H_2O)_2(PW_{11}O_{39})]^{5-}$, can serve as a luminescent probe for selective sensing of Cr^{III} with a detection limit of 1.423 μM (quenching) and Ca^{II} with the detection limit of 0.676 mM (enhancing) in an aqueous solution showing photoluminescence intensity⁹⁴ (Fig. 8). Furthermore, intense dynamic collision between Eu^{III} ions and Cr^{III} ions causes luminescence quenching, and the electrostatic interactions between hydroxyl groups and Ca^{II} ions lead to enhanced luminescence. In 2022, we fabricated a Ba^{II}-probe Ln-based arsenotungstate $[{(As_2W_{19}O_{67}(H_2O))Eu(H_2O)_2}_2(C_2O_4)]^{24-}$ with the detection limit of 0.0105 mM for the selective detection of Ba^{II} ions in the presence of other metal ions. We suggested that the increase in fluorescence intensity could be caused by a possible interaction between Ba^{II} ions and oxygen sites in the POM backbone.⁶³

In recent years, Zhao *et al.* synthesized a variety of Eu-based POM materials regarded as fluorescent probes. In 2020, a Ba^{II}-detector material, [$\{Eu_6W_{14}O_{40}(H_2O)_{18}(Htpdc)_2\}$ $\{AsW_9O_{33}\}_6$]³⁴⁻, was successfully obtained with high sensitivity, good selecti-



The fabrication of biological fluorescent probes as a possible research hotspot has been widely adopted in various fields such as medical imaging, bacterial detection, and biological warfare agents. Recently, Zhao *et al.* used the compound $[Eu_4(H_2O)_6(HPZDA)_2(HFMA)_2W_8O_{21}][SeW_9O_{33}]_4^{18-}$ to engineer a fluorescent sensor to detect the main marker of anthrax spores (DPA) in the aqueous solution with a detection limit of 3.83 µM (enhancing)⁹⁷ (Fig. 10). Moreover, the detection process could be followed through decay lifetime measurements of Eu-POMs with and without DPA.

3.3 Fluorescent switch

As is known, photochromic POM-based materials with stability and reversibility are attractive and promising for applications in many fields.¹⁰¹ Among them, most strikingly, the fluorescence of Ln-based POM materials displays an effectively switchable behavior under irradiation. Recently, photochromic Ln-based POM materials have emerged with interesting potential in the application of fluorescent switches owing to their colour-reversible ability.



Fig. 8 Changes of emission intensity with the addition of different concentrations of Cr^{III} ion (a) and Ca^{II} ion (b). The linear relationship between emission intensities of Cr^{III} (c) and Ca^{II} ions (d).⁹⁴



Fig. 9 (a) Variation in the intensity of Eu–Sm-POMs dissolved in aqueous solution with enhancement of the Cu^{II} concentration. (b) Plot of the strength of the 613 nm peak and the Cu^{II} concentration and the linear fitting result. (c) Variation of the intensity dissolved in an aqueous solution with increasing Zn^{II} concentration. (d) Plot of the intensity strength of the 613 nm peak and Zn^{II} concentration.⁷⁰



Fig. 10 (a) Comparison of the emission spectra with the addition of different concentrations of DPA. (b) A linear relationship between the *I*/ I_0 ratio and the DPA concentration. (c) Comparison of the FL emission intensity with the addition of DPA (0–400 μ M). (d) Comparison of the FL spectra in the presence of DPA and each different interferent.⁹⁷

Our group has made considerable progress in this field. In 2016, we isolated a photochromic mono-Dy-based POMs, [Dy $(C_4H_2O_6)(PW_{11}O_{39})]_2^{16-}$, which displayed an effectively switchable behavior upon irradiation⁹⁹ (Fig. 11a and b). Multinuclear Sm-implanted POMs $[\{(P_2W_{17}O_{61})Ln(H_2O)_3Sm(C_6H_5COO)(H_2O)_6\}]\{[(P_2W_{17}O_{61})Sm(H_2O)_3]\}_2^{26-}$ with switchable luminescence behavior induced by fast photochromism were synthesized.³⁰ Moreover, we synthesized $[\{As_4W_{44}O_{137}(OH)_{18}-(H_2O)_2(Ser)_2\}\{Sm_2(H_2O)_4(Ser)\}_2\{Ln(H_2O)_7\}_2]^{2-}$ in 2022, which possesses an effective luminescent switchable behavior, triggered by its fast-responsive photochromism effect⁶¹ (Fig. 11c and d). All these compounds demonstrated a gradual decrease in fluorescence intensity with the quenching phenomenon



Fig. 11 (a) The color evolution for Dy-POMs after irradiation; (b) emission spectral evolution after irradiation;⁹⁹ (c) the color transformation for Sm-POMs on irradiation; (d) emission spectral evolution for Sm-POMs on irradiation.⁶¹

during the photochromism process, and reversible fluorescent switch behavior *via* alternating from irradiation (OFF) to in-air (ON) states, without major structural rearrangements.

3.4 Drug activity

In recent decades, biological studies in medicine using Lnbased POM materials with broad-spectrum antiviral, antitumor, and antibacterial activities have become a burgeoning area of exploration.^{102–104}

Zhao *et al.* reported a series of Ln-bridged nanosized POM aggregates $[Ln_{10}W_{16}(H_2O)_{30}O_5(AsW_9O_{33})_8]^{46-}$ $[Ln = Tb^{III}, Tm^{III}]$ in 2016, and cytotoxicity tests indicated that Tb^{III} and Tm^{III} -based compounds can induce the apoptosis of human cervical cancer (HeLa) cells and human breast cancer (MCF-7) cells and kills cells, which was monitored from the evolution of fluorescence intensity.¹⁰⁵ In 2018, they measured the drug activity of Ln-based POMs [{Eu(H₂O)₈}{K₃Cu₂WO(H₂O)₁₀} {AsW₉O₃₃}₂]³⁻ *via* 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenylte-trazolium bromide (MTT) assays, inducing the apoptosis of HepG₂ cells and HCT-116 cells through the activation of caspase-3 and the autophagy of HepG₂ cells and HCT-116 cells through the involvement of lysosomes (Fig. 12).¹⁰⁰

3.5 Other applications

In recent years, a few novel co-doped Ln-based POM materials have emerged as potential new optical markers in the domain of biomedical imaging. In 2018, PEG–NaGd(WO₄)₂:Eu, considered the X-ray luminescence nanoprobe in optical bioimaging, was reported by Yang *et al.*¹⁰⁶ The maximum emission intensity was reached ($\lambda_{em} = 615$ nm) when the proportion of Eu^{III} in the complex was 10%, stronger than that in all the other reported luminescent X-ray nanoprobes, thereby rendering it a prime candidate for exploitation as a biomarker in biological imaging (Fig. 13). In 2019, the nanoparticles Gd₂(WO₄)₃:Yb^{III}/Ho^{III}@SiO₂ nanoparticles (Gd₂(WO₄)₃@SiO₂– Pt–PEG) displayed yellow emission behavior under near-infrared excitation.¹⁰⁷ After the invasion of the nanoparticles inside CT26 cells, fluorescence signals were detected at different invasion times. In addition, Gd₂(WO₄)₃@SiO₂–Pt–PEG demon-



Fig. 12 Compound $[{Ln_{10}W_{16}(H_2O)_{30}O_{50}}](AsW_9O_{33})_8]^{46-}$ on the MMP in HepG₂ cells. (a) Representative pictures from one of the three independent experiments with similar results. (b) The MMP (green) was detected with rhodamine 123/Hoechst staining through HCS of HepG₂ cells *in vitro*.¹⁰⁰



Fig. 13 Luminescence imaging of (a) the cell medium, cell lysis, and mouse hair, (b) mice before and after intramuscular injection of InP/ZnS QDs (left) and PEG–NGW:Eu nanorods (right), and (c) mice before and after (30 min) intravenous injection of InP/ZnS QDs (left) and PEG–NGW:Eu nanorods (right) excitation. (d) Comparison of the intensity ratio in mice under excitation with InP/ZnS QDs or PEG–NGW:Eu nanorods.¹⁰⁷

strated the magnetic resonance imaging property, which is positively correlated with the amount of Gd^{III}.

Furthermore, Ln-based POM materials have also shown a great deal of potential in the application of pH sensing and temperature sensing.¹⁰⁸ In 2017, Ocaña *et al.* synthesized Eudoped NaGd(WO₄)₂ nanophosphors, as a wide pH range (pH = 4–10) radiometric sensor: pH = 4 (blue), 7 (green), and 12 (red) (Fig. 14a and b).¹⁰⁹ In 2018, Tu *et al.* designed a portable all-fiber thermometer using Er^{III}/Yb^{III}-co-doped TWLN glasses, as a wide temperature range (293–569 K) radiometric sensor with the highest value of absolute temperature sensitivity (*S*_a) (86.7 × 10⁻⁴ K⁻¹ at 553 K) (Fig. 14c and d).¹¹⁰



Fig. 14 (a) Emission spectra of Eu:NaGd(WO₄)₂ NPs under pH-dependent; (b) intensity ratio of emissions at different pH values.¹⁰⁹ (c) emission spectra of Er^{III}/Yb^{III}-co-doped TWLN glass fiber with $T/^{\circ}$ C-dependent; (d) integrated up conversion intensities at 523 nm and 547 nm vs. $T/^{\circ}$ C.¹¹⁰

4. Conclusion

The ever-growing interest in Ln-based POMs is without doubt due to the compositional variability of these compounds, displaying unique chemical and physical properties because of the synergistic combination between POM coordinative structures and Ln^{III} constituents. In this review, we briefly reviewed the preparation of POMs, Ln-based materials, and Ln-based POM derivatives, and then comprehensively summarized the photoluminescent applications of these Ln-based POMs such as in multicolor emission, fluorescent probes, drug activity, and fluorescent switches.

However, as an important branch of photoluminescent materials, it is of great necessity to research how to improve the luminescence efficiency, which remains a challenging issue. Quantum yield and fluorescence intensity are essential parameters for the interpretation of luminescent materials. Firstly, Ln^{III} ions with Laporte forbidden f-f transitions have low molar absorption coefficients. Secondly, in Ln-based POMs, although a double antenna effect occurs from the organic and POM ligands to the Ln centers, a low energy transfer efficiency may occur due to the weak emission of the POM fragment. It is necessary to investigate how to improve the luminescence efficiency of the target products. It is expected that the high quantum yield of high-nuclearity Ln-based POMs may be achieved. In addition, organic ligands with high energy absorption efficiency can be introduced by experimental syntheses such as spiropyran and viologen to improve the energy transfer efficiency between organic ligands and Ln centers. In addition, the inherent optical properties of Ln-based POM materials are expected to emerge with high potential for applications in light-emitting security printing, anti-counterfeiting, and encrypted information storage at different availability levels.

Although the design and manufacture of functional Lnbased POMs with unique properties are still very limited, these are expected to be overcome and run in more fields in tomorrow's world.

Conflicts of interest

There are no conflicts to declare.

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