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Three Types of Distinguishing L-Alanine-Decorated and Rare-Earth-Incorporated Arsenotungstate Hybrids Prepared in a Facile One-Step Assembly Strategy

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Supporting Information

ABSTRACT: Three kinds of distinguishing ala-decorated RE-incorporated (ala = L-alanine, RE = rare-earth) polytungstoarsenate hybrids containing {As₂W₁₉O₆₈} building blocks [H₂N(CH₃)₂]₁₃Na₃H₂[Eu₄W₅(H₂O)₁₀(ala)₃O₁₄(As₂- $W_{19}O_{68}_{2}$]·35H₂O (1), $[H_2N(CH_3)_2]_{12}Na_2H_2$ - $[RE_4W_6(H_2O)_8(ala)_4O_{15}(OH)_2(As_2W_{19}O_{68})_2] \cdot 36H_2O$ [RE = Gd^{3+} (2), Tb^{3+} (3)], and $[H_2N(CH_3)_2]_{12}Na_4[RE_4W_6 (H_2O)_{10}(ala)_2O_{15}(OH)_2(As_2W_{19}O_{68})_2]\cdot 40H_2O$ [RE = Dy³⁺ (4), Ho^{3+} (5), Er^{3+} (6), Yb^{3+} (7), Lu^{3+} (8)] were made in a facile one-step assembly strategy. The polyoxoanion skeletons of 1-8 are very similar, and all can be described as two [As₂W₁₉O₆₈]¹⁶⁻ moieties encapsulating an ala-decorated W-O-RE heterometallic cluster $([Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$



for 1, $[RE_4W_6(H_2O)_8(ala)_4O_{15}(OH)_2]^{16+}$ for 2-3, and $[RE_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2]^{16+}$ for 4-8, resulting in a four-leaf-clover-shaped tetrameric structure; however, the major discrepancy in the ala-decorated W-O-RE heterometallic clusters lies in the number of ala molecules equaling to three, four, and two, which may result from the various coordination geometries of RE ions and the different construction modes of W-O-RE heterometallic clusters. It should be emphasized that the carboxyl groups of ala ligands only coordinate to the W centers in 4-8, while they not only bridge the W centers together but also combine RE ions together in 1-3. Besides, the solid luminescent properties and lifetime decay behaviors of 1, 3, 4, 5, and 6 were systematically investigated at ambient temperature, and time-resolved fluorescence spectra of 1, 3, and 5 were also examined. Furthermore, the electrochemical response properties of composite CS-CMWCNs-1, 3, or 5/GCE electrochemical sensors toward the dopamine detection were investigated, which will offer the possibility of RE-incorporated polyoxometalates for acting as electrochemical response electrode materials.

INTRODUCTION

Polyoxometalates (POMs) are particular polynuclear metal-oxo cluster compounds of early transition metals (mainly including V, Mo, W, Nb, and Ta) in their high oxidation states and continue to attract increasing interest on account of their extremely widespread applications in catalysis, medicine, magnetism, optics, electrics, and material science.¹⁻⁹ In the territory of POM chemistry, arsenotungstates (ATs), as a very important subfamily carrying various structures and tantalizing properties, have attracted tremendous attention over the past several decades.^{3,4,10,11} It can be found that lacunary AT fragments are able to be self-polymerized to the various larger aggregates such as $[As_2W_{19}O_{67}(H_2O)]^{14-}$, $[As_4W_{40}O_{140}]^{28-}$ (Figure S1a), and $[As_6W_{65}O_{217}(H_2O)_7]^{26-}$ (Figure S1b) under appropriate conditions,^{12,13} which provide abundant initial materials to search and exploit their derivatives. More importantly, these lacunary AT aggregates can serve as

multidentate inorganic ligands and incorporate diverse transition-metal (TM) cations, giving rise to rapidly growing TM-substituted ATs (Figure S1c-d).¹⁴⁻²⁶ It should be pointed out that the flexible coordination ability and oxophilicity of rareearth (RE) cations can make RE cations easily combine with different AT precursors to design and synthesize novel REcontaining ATs (RECATs).^{27,28} Over the past two decades, great progress on RECATs has been made due to the versatile and ingenious assembly between AT fragments and RE linkers.^{29–35} Some representative RECATs (Figure S1e-f) are demonstrated in the Supporting Information.³⁰⁻³⁵ Obviously, most of those previously reported RECATs principally are purely inorganic; however, related reports on organic-inorganic RECAT hybrids remain underdeveloped. Recently, organic-

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inorganic hybrid RECATs have come to attract incremental attention because of the special functions that organic ligands can readily coordinate with RE or W atoms, bridge AT building blocks and RE centers together, and transfer their properties to the resulting compounds. Thus, some organic-inorganic RECAT hybrids have been isolated, such as acetate-modified $[Gd_{6}As_{6}W_{65}O_{229}(OH)_{4}(H_{2}O)_{12}(OAc)_{2}]^{38-,36}$ picolinate-decorated $[Tb_8 (pic)_6 (H_2O)_{22} (B-\beta-AsW_8O_{30})_4 (WO_2(pic))_6]^{12-1}$ (Figure S1g),³⁷ tartrate-bridging $[RE_2(C_4H_4O_6)(C_4H_2O_6)-(AsW_9O_{33})]_2^{18-}$ (RE = Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺, Y³⁺),³⁸ double-malate-bridging $[RE_3(\mu_3-OH)(H_2O)_8 (AsW_9O_{33}) (AsW_{10}O_{35}(mal))]_2^{22-}$ (RE = Dy³⁺, Tb³⁺, Gd³⁺, Eu³⁺, Sm³⁺), and citrate-participating $[RE_3(H_2O)_7(RE_2(H_2O)_4As_2W_{19}O_{68^-}(WO_2)_2(C_6O_7H_4)_2]_3]^{32^-}$ (RE = Y³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺) (Figure S1h).⁴⁰ These remarkable achievements have confirmed the versatile coordination ability and connection function of organic ligands in the structural construction of organic-inorganic RECAT hybrids, which provide us an excellent opportunity to continuously explore organic-inorganic RECAT hybrids.

Amino acids (AAs), as a kind of carboxyl-and-aminocontaining flexible multidentate ligand, are excellent candidates for acting as organic modifiers in the construction of novel structures. However, AA-embedded RECATs have been reported very rarely, to the best of our knowledge; Wang's group reported the first AA-containing RECATs $[Ce_4As_4W_{44}O_{151}(ala)_4(OH)_2(H_2O)_{10}]^{12-}$ in 2007,⁴¹ and then a type of RE-bridging and proline-including one-dimensional (1-D) chains in 2013.⁴² Boskovic and co-workers also reported a series of glycine-decorated RECATs [RE₄As₅W₄₀O₁₄₄(H₂O)₁₀- $(gly)_2]_3^{21-}$ (RE = Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Y³⁺) in 2011⁴³ and several norleucine- or glycine-decorated yttrium- containing As–W or As–W–Mo tetramers in 2016 (Figure S1i).⁴⁴ What is more, our lab also synthesized a family of L-threonine-inserted and RE-supporting Kreb-type AT dimers in 2015 (Figure S1j),45 and three families of serine-decorated RECATs by controlling the usage of RE salts in 2017.⁴⁶ By summarizing the previously reported AA-embedded RECATs, it can be easily found that most of them were obtained by the step-by-step method with the versatile $[As_2W_{19}O_{67}(H_2O)]^{14-}$ precursor utilized as the starting material, $\frac{41-45}{5}$ whereas the one-step self-assembly strategy of raw materials to prepare AA-embedded RECATs was less developed.⁴⁶ Therefore, this background offers us with some precious opportunities to prepare novel AA-embedded RECATs via the facile one-step self-assembly method of raw materials. Thus, we have begun to exploit this domain by the one-step selfassembly strategy of raw materials in order to discover neoteric AA-embedded RECAT aggregates. As a result, several series of serine-based RECATs were fabricated by our group in 2017,⁴⁶ which gives us more confidence for continuing the execution of this strategy, and then the introduction of ala into RECATs was focused on. Ala possesses one less hydroxy than serine, resulting in fewer ligating atoms but smaller steric hindrance, which may lead to a discriminating coordination mode in the analogous reaction system. Besides, ala with N and O ligating atoms also possesses a potential capacity to simultaneously link W and RE atoms to construct bigger clusters. Here, ala was employed to synthesize ala-based RECATs. Furthermore, according to the our previous results,46,47 we found that the introduction of dimethylamine hydrochloride plays a key role in preparing target RECATs by the one-step self-assembly strategy of raw materials. On one hand, there exist competitive reaction between protonated dimethylamine cations and RE cations with AT

anions in solution, which will result in a lower chance for RE ions to directly touch AT fragments and decrease precipitations derived from the rapid combination of RE cations and AT anions. On the other hand, protonated dimethylamine cations could act as counter cations to stabilize in situ formed REcontaning AT fragments since they have relatively larger bulk than Na⁺ or K⁺ cations, which can be better to match with the big in situ formed RE-containing AT fragments. Besides, different RE cations can affect the structural construction of resultant products. In the paper, introducing dimethylamine hydrochloride and ala to the one-step self-assembly system of raw materials, we synthesized three families of distinguishing ala-decorated RECAT hybrids [H2N- $(CH_3)_2]_{13}Na_3H_2[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}(As_2W_{19}O_{68})_2]$. $35H_2O$ (1), $[H_2N(CH_3)_2]_{12}Na_2H_2[RE_4W_6(H_2O)_8(ala)_4O_{15} (OH)_2(As_2W_{19}O_{68})_2] \cdot 36H_2O$ [RE = Gd³⁺ (2), Tb³⁺ (3)], and $[H_2N(CH_3)_2]_{12}Na_4[RE_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2(As_2W_{19} O_{68}_{2}$]·40H₂O [RE = Dy³⁺ (4), Ho³⁺ (5), Er³⁺ (6), Yb³⁺ (7), $Lu^{3+}(8)$] respectively. The fluorescence properties and lifetime decay behaviors of 1, 3, 4, 5, and 6 as well as the time-resolved luminescence spectra of 1, 3, and 5 were probed. In addition, the electrochemical response properties of composite CS-CMWCNs-1, 3, or 5/GCE (CS = chitosan, CMWCNs = arboxyl functionalized multiwalled carbon nanotubes, GCE = glassy carbon electrode) electrochemical sensors toward dopamine were also measured, manifesting that the 1, 3, or 5modified electrode can improve the electrochemical response to dopamine (DA), which may provide the promising prospect of RECATs as modified electrode materials for realizing the detection of small biomolecules.

RESULTS AND DISCUSSION

Synthesis. According to our previous work, it is not difficult to find that the introduction of dimethylamine hydrochloride (DAH) to the reaction system can facilitate construction of novel RECATs because DAH not only can act as an organic solubilizer to improve the solubility RE ions and promote the combination of RE cations with in situ generated POM fragments, but also it can form the larger protonated dimethylamine organic cations to stabilize RE-incorporated POM fragments and thus give rise to novel RECATs.^{33,46,47} Meanwhile, the sluggish development of AA-containing RECATs provides us with a outstanding opportunity to introduce ala into the RE-AT-system to fabricate ala-decorated RECATs.⁴³⁻⁴⁶ Ala, owning simultaneously N and O ligating atoms as well as a small steric hindrance, is a suitable polydentate ligand to chelate different metal centers to create bigger POM aggregates. Under this background, we performed this work. However, the experimental facts suggest that the coordination ability of carboxylic O atoms in ala is stronger than the N atom, often resulting in uncoordinated N atoms. It can be found that the number of ala in three types of ala-decorated RECATs is different, which may be related to the effect of RE cations on the structures. Specifically, there are three, four, and two ala molecules in types 1, 2-3, and 4-8 respectively. In 4-8, the two ala molecules are just linked to W atoms via two carboxyl O atoms, but in 1-3, the newly added one or two ala molecule(s) is (are) combined with two RE ions through the same method. Of course, the coordination mode of ala may also affect the coordination geometry of RE ions, resulting in RE ions in 2-3just adopting bicapped triangular prism configuration while adopting simultaneously the monocapped triangular prism and bicapped triangular prism in 1 and 4-8. In summary, the

synthesis of all products is identical except for the various RE ions, and the synthetic process is displayed in Scheme 1.

Scheme 1. Schematic Synthetic Processes of Three Types of ala-Decorated RECATs



Structure Description. Crystal data and structural parameters for 1–8 are illustrated in Table S1. Three types of four-leaf-clover-shaped structures all belong to the triclinic space group $P\overline{1}$ and can be described as two $[As_2W_{19}O_{68}]^{16-}$ moieties linked by an ala-decorated W–O–RE heterometallic cluster $([Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ for 1, $[RE_4W_6(H_2O)_8(ala)_4O_{15}-(OH)_2]^{16+}$ for 2–3 and $[RE_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2]^{16+}$ (Figure 1a) moiety is made up of two trivacant Keggin $[B-\alpha-AsW_9O_{33}]^{9-}$ (Figure 1b) fragments bridged by a corner-sharing $\{WO_6\}$ octahedron (Figure 1c), which is somewhat different from the $[As_2W_{19}O_{67}(H_2O)]^{14-}$ precursor that was first found by Tourné et al. in 1973 and structurally determined by Kortz et al. in 2001.⁴⁶

The molecular unit of **1** comprises an organic–inorganic hybrid four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}-(As_2W_{19}O_{68})_2]^{18-}$ polyoxoanion (Figure 1d), 13 $[H_2N(CH_3)_2]^+$ cations, 3 Na⁺ cations, 2 H⁺ cations, and 35 lattice water molecules. The four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}-(ala)_3O_{14}(As_2W_{19}O_{68})_2]^{18-}$ polyoxoanion is constructed from two $[As_2W_{19}O_{68}]^{16-}$ moieties encapsulating an interesting triala-decorated W–O–Eu heterometallic $[Eu_4W_5(H_2O)_{10}-(ala)_3O_{14}]^{14+}$ cluster (Figure 1e–f) through 20 μ_2 -O atoms from two $[As_2W_{19}O_{68}]^{16-}$ moieties. In the four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}-(ala)_3O_{14}]^{14+}$ cluster (Figure 1e–f) through 20 μ_2 -O atoms from two $[As_2W_{19}O_{68}]^{16-}$ moieties. In the four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}(As_2W_{19}O_{68})_2]^{18-}$ polyoxoanion, every Eu³⁺ ion employs two neighoring vacant μ_2 -O atoms from a $[B-\alpha$ -AsW₉O₃₃]⁹⁻ fragment (O117, O143 for Eu1³⁺;

O56, O74 for Eu2³⁺; O17, O79 for Eu3³⁺; O31, O8 for Eu4³⁺) and one terminal μ_2 -O atom (O42 for Eu1³⁺; O87 for Eu2³⁺; O54 for Eu3³⁺; O68 for Eu4³⁺) from the corner-sharing $\{WO_6\}$ octahedron connecting two $[B-\alpha-AsW_9O_{33}]^{9-}$ fragments in each $[As_2W_{19}O_{68}]^{16-}$ moiety. In the $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ heterometallic cluster, $Eu1^{3+}$ and $Eu4^{3+}$ ions are combined together via the $\{W5O_6\}$ octahedron, and Eu2³⁺ and Eu3³⁺ ions are bridged together through the $\{W110_6\}$ octahedron. Most intriguingly, $Eu3^{3+}$ and $Eu4^{3+}$ ions are also joined together by the central { $W6O_6$ } octahedron, while Eu1³⁺ and Eu2³⁺ ions are free from the central $\{W6O_6\}$ octahedron. A further observation reveals that Eu1³⁺ and Eu2³⁺ ions are linked together via an ala ligand, whereas Eu3³⁺ and Eu4³⁺ ions are connected together via a $\{W_2O_3(ala)\}$ group. To the best of our knowledge, the tri-aladecorated heterometallic [Eu₄W₅(H₂O)₁₀(ala)₃O₁₄]¹⁴⁺ cluster is first discovered in coordination chemistry. Upon further inspection, the tri-ala-decorated $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ heterometallic cluster can be viewed as an aggregation of a mono-ala-decorated $\{W_2O_3(ala)Eu_2(H_2O)_4\}$ cluster (Figure 1g) and a di-ala-decorated $\{W_2O_3(ala)_2Eu_2(H_2O)_6\}$ cluster (Figure 1h) in the help of a central bridging $\{WO_6\}$ group (Figure 1i) through sharing four μ_2 -O atoms. Noteworthily, in the mono-ala-decorated $\{W_2O_3(ala)Eu_2(H_2O)_4\}$ cluster, W2 and W4 atoms are fused together by sharing one μ_2 -O atom and one ala ligand (Figure 1g); in the contrast, in the di-aladecorated $\{W_2O_3(ala)_2Eu_2(H_2O)_6\}$ cluster, W1 and W3 atoms are also linked together by sharing one μ_2 -O atom and one ala ligand; however, another ala ligand directly combines Eu1³⁺ and $Eu2^{3+}$ ions together (Figure 1h). From the side view, when the tri-ala-decorated heterometallic central cluster is rotated to 90° (Figure 1f), a distorted U-shaped skeleton (Figure 1j) was seen, in which Eu3, Eu4, W2, and W4 centers construct one side plane, Eu1, Eu2, W1, and W3 centers form the other side plane, and Eu3, Eu4, W3, and W1 centers build the bottom plane. Of particular concern is that the ala ligand linking Eu1³⁺ and Eu2³⁺ ions together is almost perpendicular to the Eu1-Eu2-W1-W3 plane. It is not difficult to find that four crystallographically unique Eu³⁺ ions are almost symmetric along the "mirror plane" formed by three ala ligands (Figure 1k) with the Eu1³⁺ ion corresponding to the Eu2³⁺ ion and the Eu3³⁺ ion corresponding to the Eu4³⁺ ion. Thereinto, the Eu1³⁺ and Eu2³⁺ ions inhabit the eight-coordinate distorted bicapped trigonal prism geometries (Figure 11) defined by three O atoms from a $[As_2W_{19}O_{68}]^{16-1}$ fragment (O42, O117, and O143 for Eu1³⁺; O56, O74, and O87 for $Eu2^{3+}$), one O atom from the {WO₆} octahedron belonging to the $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ central cluster (O34 for $Eu1^{3+}$; O89 for $Eu2^{3+}$), one carboxyl O atom from an ala ligand (O156 for $Eu1^{3+}$; O142 for $Eu2^{3+}$), and three water ligands (O1W, O2W, and O3W for Eu1³⁺; O4W, O5W, and O6W for $Eu2^{3+}$), in which the carboxyl O atom and one water ligand occupy two cap sites of the bicapped trigonal prism geometry. Meanwhile, Eu3³⁺ and Eu4³⁺ bind to three O atoms from a [As₂W₁₉O₆₈]¹⁶⁻ fragment (O17, O54, and O79 for Eu3³⁺; O8, O31, and O68 for Eu4³⁺), two O atoms from $\{WO_6\}$ octahedra on the $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ central cluster (O19 and O26 for Eu 3^{3+} ; O39 and O78 for Eu 4^{3+}), and two water ligands (O7W and O8W for Eu 3^{3+} ; O9W and O10W for Eu 4^{3+}), achieving the seven-coordinate distorted monocapped trigonal prism configurations (Figure 11) where one water ligand takes up the cap site of the monocapped trigonal prism geometry. The Eu–O bond lengths vary from 2.29(3) to 2.44(3)(3) Å, and the O-Eu-O bond angles are in the range of 69.1(10)- $146.4(8(7)^{\circ})$



Figure 1. (a) The $[As_2W_{19}O_{68}]^{16-}$ moiety. (b) The trivacant Keggin-type $[B-\alpha-AsW_9O_{33}]^{9-}$ fragment. (c) The corner-sharing $\{WO_6\}$ octahedron in the $[As_2W_{19}O_{68}]^{16-}$ moiety. (d) The four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}(As_2W_{19}O_{68})_2]^{18-}$ polyoxoanion of **1**. (e) Front view of the triala-decorated heterometallic $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ cluster. (f) Bottom view of the tri-ala-decorated heterometallic $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]^{14+}$ cluster. (g) The mono-ala-decorated $\{W_2O_3(ala)Eu_2(H_2O)_4\}$ cluster. (h) The di-ala-decorated $\{W_2O_3(ala)_2Eu_2(H_2O)_6\}$ cluster. (i) The central bridging $\{WO_6\}$ group connecting the mono-ala-decorated $\{W_2O_3(ala)Eu_2(H_2O)_4\}$ cluster and the di-ala-decorated $\{W_2O_3(ala)_2Eu_2(H_2O)_6\}$ cluster. (k) The mirror symmetry of Eu^{3+} ions in **1** with the $Eu1^{3+}$ ion corresponding to the $Eu2^{3+}$ ion and the $Eu3^{3+}$ ion corresponding to the $Eu4^{3+}$ ion. (l) The coordination configurations of four Eu^{3+} ions. Color distribution: purple octahedron for WO_6 in $[As_2W_{19}O_{68}]^{16-}$ fragments, red balls for O atoms, azure balls for linker-O atoms, blue balls for N atoms, green balls for Eu atoms; brown balls for As atoms, orange balls for C atoms. H atoms were omitted for clarity.



Figure 2. (a) The polyoxoanion packing view of 1 viewed along the *a* axis. (b) The adjacent A- and B-layers in type I. (c) The adjacent A- and B-layers in type II. (d) The distance between two polyanions along the *c* axis in type II. (e) The distance between two polyanions along the *c* axis in type II. (e) The distance between two polyanions along the *c* axis in type II. (f) The simplified view of the packing of 1 viewed along the *a* axis. (g) Layer A viewed along the *c* axis. (h) Layer B viewed along the *c* axis. (i) The chirality of polyoxoanions in layer A and B. The color distribution is same as Figure 1 and red octahedra for WO₆.

In addition, countercation ions such as Na⁺ ions, H⁺ ions, $[NH_2(CH_3)]^+$ ions, and crystal water molecules in **1** are distributed in the space among polyoxoanions and interact with polyoxoanions through hydrogen-bonding interactions and electrostatic attraction interactions, resulting in the 3-D supramolecular structure (Figure S2) with the N-H···O distances ranging from 2.03 to 2.71 Å. The stacking diagram viewed from *a* axis is shown in Figure 2a, and it can be apparently

found that the molecular units of 1 are orderly aligned in the -ABAB- pattern along the *c* axis and the -AAA- mode along the *b* axis. Further, it is also seen that the packing modes between neighboring layer A and layer B are not identical (Figure 2b–c). In type I (Figure 2b), layer A and layer B are arranged in a "back to back" pattern, while in type II (Figure 2c), layer A and layer B are stacked in a "face to back" pattern. When the four-leaf-clover-shaped [Eu₄W₅(H₂O)₁₀(ala)₃O₁₄(As₂W₁₉O₆₈)₂]¹⁸⁻ polyoxoan-

ion is simplified as a bow-tie-shaped skeleton (Figure 2d-f), the 3-D supramolecular packing can be easily understood, and the distances between two polyanions along the c axis are 20.8569(12) Å in type I (Figure 2d) and 24.9856(12) Å in type II (Figure 2e) because of the different spatial orientations of four-leaf-clover-shaped $[Eu_4W_5(H_2O)_{10}(ala)_3O_{14}]$ $(As_2W_{19}O_{68})_2]^{18-}$ polyoxoanions. The simplified view in the *bc* plane (Figure 2f) further narrates the –ABAB– packing style. When we focus on layer A or layer B (Figure 2g-h), it is obvious that the polyoxoanions in both layers display the same -AAApacking mode along the *b* and *c* axes. However, the stacking of polyoxoanions viewed along the c axis (Figure S3) displays a interlaced mode in order to decrease the steric hindrance. When we specifically observe the single polyanion in layer A and layer B, although the polyoxoanions in layer A and layer B display mirror symmetry, the whole structure is achiral (Figure 2i).

The structure of **5** as a representative was described here in detail to demonstrate the feature of **4**–**8**. The organic–inorganic hybrid four-leaf-clover-shaped $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}-(OH)_2(As_2W_{19}O_{68})_2]^{16-}$ polyoxoanion (Figure 3a) in **5** is



Figure 3. (a) The four-leaf-clover-shaped $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2(As_2W_{19}O_{68})_2]^{16-}$ polyoxoanion of **5.** (b) Front view of the diala-decorated heterometallic $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2]^{16+}$ central cluster in **5.** (c) Bottom view of the di-ala-decorated heterometallic $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2]^{16+}$ central cluster in **5.** (d) The zigzag hexanuclear $\{W_6(ala)_2O_{15}(OH)_2\}$ cluster. (e) The mono-ala-modified $\{W_3(ala)(OH)\}$ subunit. (f) The triangle connection mode of W1, W3, and W18 atoms. (g) The almost vertical relation between the ala ligand and the W1–W3–W18 plane. (h) The rectangular parallelepiped of the di-ala-decorated heterometallic $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2]^{16+}$ central cluster. (i) The coordination geometries of Ho1³⁺ and Ho2³⁺ ions. Color distribution is same as Figure 2. Symmetry operation A: -x, -y, 1 - z.

assembled from two $[As_2W_{19}O_{68}]^{16-}$ moieties anchoring a diala-decorated W–O–Ho heterometallic $[Ho_4W_6(H_2O)_{10}-(ala)_2O_{15}(OH)_2]^{16+}$ central cluster (Figure 3b–c) through a similar bridging mode to **1**. As a result, the similar bridging mode between $[As_2W_{19}O_{68}]^{16-}$ moieties and the heterometallic central clusters is not described herein, and only the main difference in the heterometallic center cluster in **5** is highlighted. In **5**, the di-ala-decorated heterometallic $[Ho_4W_6(H_2O)_{10^-}(ala)_2O_{15}(OH)_2]^{16+}$ central cluster can be viewed as four Ho³⁺ ions linked by a unique zigzag hexanuclear W–O { $W_6(ala)_2O_{15^-}(OH)_2$ } cluster (Figure 3d). It should be pointed out that the zigzag hexanuclear { $W_6(ala)_2O_{15}(OH)_2$ } cluster is looked on as two mono-ala-modified { $W_3(ala)(OH)$ } subunits (Figure 3e)

linked by a W18-O66-W18A bond. In each mono-alamodified $\{W_3(ala)(OH)\}$ subunit, W1, W3, and W18 atoms are combined with each other in a triangle connective motif (Figure 3f) through a vertex-sharing fashion, in which the ala ligand bridges W1 and W3 atoms together via two carboxyl O atoms, and the ala ligand is almost perpendicular to the W1-W3-W18 plane (Figure 3g). From the side view, the 90°rotated di-ala-decorated heterometallic [Ho₄W₆ (H₂O)₁₀- $(ala)_2O_{15}(OH)_2$ ¹⁶⁺ central cluster (Figure 3c) displays a rectangular parallelepiped with Ho2-Ho1A-W3A-W1 defining the upper bottom surface and Ho2A-Ho1-W3-W1A forming the lower bottom surface (Figure 3h). Upon further inspection, two ala ligands are almost perpendicular to the upper and lower bottom surfaces, and W18 and W18A are respectively located in the centers of the two bottom surfaces and O66 inhabits the center of the rectangular parallelepiped. From the viewpoint of crystallography, there exist two crystallographically independent Ho³⁺ ions (Ho1³⁺ and Ho2³⁺) in 5, which display two kinds of coordination geometries (Figure 3i). Specifically, the eight-coordinate Ho1³⁺ ion links to three O atoms (O74, O54, O42) from one $[As_2W_{19}O_{68}]^{16-}$ moiety [Ho-O: 1.917(9)-1.972(10) Å], two O atoms (O49, O79) from the zigzag hexanuclear W–O $\{W_6(ala)_2O_{15}(OH)_2\}$ cluster [Ho-O:1.917(9)-1.972(10) Å], and three coordinate water molecules (O1W, O2W, O3W) [Ho-O: 2.050(11)-2.104(10) Å], finishing a bicapped trigonal prism geometry (Figure 3i) with O1W and O3W occupying two cap sites. Whereas the monocapped trigonal prism geometry of the seven-coordinate $Ho2^{3+}$ ion is constituted by three O atoms (O35, O40, O45) from one $[As_2W_{19}O_{68}]^{16-}$ moiety [Ho-O: 1.917(9)-1.972(10) Å], two O atoms (O1, O73) from the zigzag hexanuclear W-O $\{W_6(ala)_2O_{15}(OH)_2\}$ cluster [Ho-O: 1.917(9)-1.972(10) Å], and two coordinate water molecules (O4W, O5W) [Ho-O: 2.050(11)-2.104(10) Å] and with O4W occupyng the cap site. In addition, the four-leaf-clovershaped $[Ho_4W_6(H_2O)_{10}(ala)_2O_{15}(OH)_2(As_2W_{19}O_{68})_2]^{16-}$ polyoxoanions in 5 (Figure S4a-b) along the a and c manifest the -AAA- alignment fashion through electrostatic attraction and hydrogen-bonding interactions. The distribution of the fourleaf-clover-shaped polyoxoanions viewed along the c direction (Figure S4b) shows a wave-like motif (Figure S4c), and the distances between adjacent polyanions are 23.760 Å along the a axis, 14.125 Å along the b axis, and 19.662 Å along the c axis, respectively.

3 was selected as the representative to elaborately describe the structural features of 2-3. The organic-inorganic hybrid fourleaf-clover-shaped $[Tb_4W_6(H_2O)_8(ala)_4O_{15}(OH)_2$ - $(As_2W_{19}O_{68})_2]^{16-}$ polyoxoanion (Figure 4a) of 3 is very similar to that of 5 except that the tetra-ala-decorated heterometallic $[Tb_4W_6(H_2O)_8(ala)_4O_{15}(OH)_2]^{16+}$ central cluster (Figure 4bc) includes two extra ala ligands, each of which links two neighboring Tb³⁺ ions together (Figure 4d). Four Tb³⁺ ions are almost symmetric along the plane defined by four ala ligands if ignoring the asymmetry of ala ligands (Figure 4e). Albeit there still exist two crystallographically independent Tb³⁺ ions (Figure 4f) in 3, both $Tb1^{3+}$ and $Tb2^{3+}$ ions reside in the eightcoordinate distorted bicapped trigonal prism geometries defined by three O atoms from one $[As_2W_{19}O_{68}]^{16-}$ moiety [Tb-O:2.35(2)-2.42(2) Å], two O atoms from the zigzag hexanuclear $\{W_6(ala)_2O_{15}(OH)_2\}$ cluster [Tb-O: 2.31(1)-2.37(2) Å], and two coordinate water molecules [Tb-O: 2.38(3)-2.42(3) Å], and one carboxyl O atom from one ala ligand [Tb-O: 2.35(3)-2.41(3) Å]. The two cap sites are occupied by one carboxyl O



Figure 4. (a) The four-leaf-clover-shaped $[Tb_4W_6(H_2O)_8-(ala)_4O_{15}(OH)_2(As_2W_{19}O_{68})_2]^{16-}$ polyoxoanion of **3.** (b) Front view of the tetra-ala-decorated $[Tb_4W_6(H_2O)_8(ala)_4O_{19}(OH)_2]^{8+}$ heterometallic central cluster of **3.** (c) Bottom view of the tetra-ala-decorated heterometallic central cluster in **3.** (d) The rectangular parallelepiped of the tetra-ala-decorated heterometallic $[Tb_4W_6(H_2O)_8(ala)_4O_{19}-(OH)_2]^{8+}$ central cluster. (e) The mirror symmetry of Tb³⁺ ions in **3** with the Tb1³⁺ ion corresponding to the Tb2³⁺ ion. (f) The coordination configurations of two crystallographically independent Tb³⁺ ions. Symmetry operation A: $1 - x_1 - y_1 - z$.

atom from the ala ligand and one water ligand. Comparing the coordination environments of the Tb1³⁺ and Tb2³⁺ ions in 3 with the Ho1³⁺ ion in 5, it is found that the coordinate water molecule in one cap site in 5 was replaced by one carboxyl O atom from one ala ligand, giving rise to the coordination environments of the Tb1³⁺ and Tb2³⁺ ions in 3. In comparison with the Ho2³⁺ ion in 5, there exist one more carboxyl O atom in

the coordination spheres of the Tb1³⁺ and Tb2³⁺ ions in 3, which result in the difference of their coordination configurations. Therefore, the most obvious discrepancy of structures between 3 and 5 stems from the introduction of two additional ala ligands leading to the distinction of the coordination geometry of RE ions. With regard to the packing alignment of 3-Tb, only the packing viewed along the *b* axis was shown in Figure S5. The polyoxoanion packing representations along the three axes all adopt the -AAA- mode, and the interval distances between adjacent layers are 22.324 Å along the *a* axis, 19.894 Å along the *b* axis, and 32.927 Å along the *c* axis.

To compare the aforementioned structural features of three types of ala-decorated RECATs, their common structure feature is that they include a four-leaf-clover-shaped structure (Figure S6a-c) constructed from two $[As_2W_{19}O_{68}]^{16-}$ fragments (Figure S6d) sandwiching a RE₄-functionalized heterometallic central cluster (Figure S6e–g) through the same connection modes: two $[As_2W_{19}O_{68}]^{16-}$ fragments are linked by sharing eight μ_2 -O atoms with W atoms and $12 \mu_2$ -O atoms with RE ions in the center cluster. Thereinto, the former eight μ_2 -O (O_W) atoms are from the vacant sites of four trivacant Keggin-type [B α -AsW₉O₃₃]⁹⁻ subunits, while the latter 12 μ_2 -O atoms (O_{RE}) are from the remaining vacant sites of four [B- α -AsW₉O₃₃]⁹⁻ subunits and bridging {WO₆} octahedra in the two $[As_2W_{19}O_{68}]^{16-}$ fragments. Undoubtedly, the main discrepancies among them are observed: (1) 1 contains a tri-ala-decorated U-shaped W–O–Eu heterometallic cluster (Figure S6e) consisting of five {WO₆} groups (Figure S6h) and three ala



Figure 5. (a) The emission spectrogram of 1 in the visible region. (b) The fitted lifetime decay profile of 1. (c) Time-resolved fluorescence spectra of 1. (d) The emission spectrogram of 3 in the visible region. (e) The fitted lifetime decay profile of 3. (f) Time-resolved fluorescence spectra of 3. (g) The emission spectrogram of 5 in the visible region. (h) The fitted lifetime decay profile of 5 in the visible region. (i) Time-resolved fluorescence spectra of 5 in the visible region. (j) The emission spectrogram of 5 in the NIR region. (k) The fitted lifetime decay profile of 5 in the NIR region. (l) Time-resolved fluorescence spectra of 5 in the NIR region. (k) The fitted lifetime decay profile of 5 in the NIR region. (l) Time-resolved fluorescence spectra of 5 in the NIR region.

molecules (Figure S6i), 5 includes a bi-ala-decorated rectangular parallelepiped W-O-RE heterometallic cluster (Figure S6f) consisting of six $\{WO_6\}$ groups (Figure S6h) and two ala molecules (Figure S6i), while 3 contains a tetra-ala-decorated rectangular parallelepiped W-O-Tb heterometallic cluster (Figure S6g) consisting of six $\{WO_6\}$ groups (Figure S6h) and four ala molecules (Figure S6i); (2) ala ligands only coordinate with W centers in 4-8 (Figure S6f), whereas ala ligands coordinate simultaneously with W and RE centers in type 1, 2, and 3 (Figure S6e,g); (3) the RE ions in 1 and 4-8adopt the monocapped trigonal prism and bicapped trigonal prism geometry; in contrast, the RE ions in 2 and 3 only utilize the bicapped trigonal prism geometry (Figure S6j-k); (4) from the viewpoint of the stacking pattern, the polyoxoanions in 1 are orderly aligned in the –ABAB– pattern along the *a* axis (Figure S61) and in the -AAA- pattern along the *b* and *c* axes; meanwhile, the polyoxoanions in 5 or 3 are orderly aligned in the -AAA- pattern along the *a*, *b*, and *c* axes (Figure S6m-n).

Luminescence Properties. As is known to us all, RE cations at their stable +3 oxidation state possess amazing characteristics of photoluminescence chiefly stemming from the internal electron transitions in the 4f shell of RE ions.⁴⁶ Therefore, the luminescence properties of lots of RE-containing complexes have been widely studied due to their worldwide applications in biomarkers, drug carriers, optical switches, displays, information storage in photovoltaic devices, and so on.^{46–62} Here, the solid-state fluorescence properties of 1, 3, 4, 5, and 6 were studied at room temperature.

As for 1, the characteristic emission spectrogram in the visible region was made upon excitation at 394 nm (Figure 5a) and exhibits five groups of characteristic signal bands appearing at 579 nm, 589 and 592 nm, 614 and 617, 651, and 701 nm, which are successively derived from the ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow$ $^{7}F_{2}$, $^{5}D_{0} \rightarrow ^{7}F_{3}$, and $^{5}D_{0} \rightarrow ^{7}F_{4}$ electron transitions of the Eu³⁺ ions. As the literature revealed, the intensity ratio of $I({}^{5}D_{0} \rightarrow$ ${}^{7}F_{2}$) and I(${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) often acts as a touchstone of evaluating the symmetry of the coordination environment of a Eu³⁺ cation with the larger ratio manifesting the higher symmetry and the smaller ratio suggesting the lower symmetry,⁴⁶ and herein the intensity ratio of $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ and $I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ is 3.1, which reveals that Eu³⁺ ions in 1 lie in the lower-symmetry ligand field. This coincides with the fact that four crystallographically unique Eu^{3+} ions in 1 show two types of lower-symmetry coordination configurations (monocapped trigonal prism and bicapped trigonal prism). Moreover, splitting of both ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ peaks can be observed, indicating that Eu³⁺ ions in 1 lie in the distorted coordination environments or inhibit the different coordination surroundings, which can be further supported by four Eu³⁺ ions in 1 dwelling in the distorted monocapped trigonal prism and bicapped trigonal prism. The excitation spectrogram acquired by monitoring the emission at 614 nm (Figure S7a) offers five groups of noteworthy peaks emerging at 362 nm, 376 nm, 380 and 385 nm, 394 nm, 416 and 465 nm, which are assigned to the electron transitions among energy levels of ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_0 \rightarrow {}^5G_2$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$, and ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ of the Eu³⁺ centers.^{46,52} What is more, the lifetime profile of 1 was further tested based on the strongest emission (614 nm) and excitation (394 nm) with the decay curve (Figure 5b) fitted by a single exponential function $I = A \exp^{(-t/\tau)} (\tau \text{ is the})$ lifetime, A is the pre-exponential factor). The fitting results lead to τ = 333.77 μ s and *A* = 8197.05. While it is a little strange that there are two types of coordination surroundings of Eu³⁺ ions in

1 but only one fitting lifetime is obtained, here we speculate that the influence of two types of similar trigonal prism coordination environments (monocapped trigonal prism and bicapped trigonal prism) on lifetime is ignorable. In order to probe whether energy transfer between W–O clusters and Eu³⁺ ions exists or not, the time-resolved fluorescence spectra of 1 were collected (Figure 5c), and it is obvious that the shapes of emission spectra remain unchanged, but the emission intensity decreases in order along the increase of time. This phenomenon just confirms the absence of intramolecular energy transfer in 1.⁴⁷

The emission spectrogram of 3 (Figure 5d) in the visible region was obtained upon the excitation at 378 nm and contains four groups of characteristic peaks appearing at 491 nm, 544 nm, 583 and 589 nm, and 622 nm, being assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$, and ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ electron transitions of Tb³⁺ centers, respectively.⁴⁶ Besides, the excitation spectrum (Figure S7b) was also tested through monitoring the most intense emission peak at 544 nm, where four typical excitation peaks of Tb³⁺ centers are observed at 352 nm, 358 nm, 369 and 378 nm, which are in agreement with the electron transitions of Tb³⁺ centers from the ground state (${}^{7}F_{6}$) to the excited states (${}^{5}L_{6}$, ${}^{5}L_{9}$, ${}^{5}L_{10}$, ${}^{5}G_{6}$ in the order). 46,53,54 Its lifetime decay profile upon the most intense emission (544 nm) can also be fitted by a single exponential function with $\tau = 179.1 \ \mu s$ and A = 418.01(Figure 5e), which is in accordance with the fact that all Tb^{3+} ions dwell in the bicapped trigonal prism coordination configuration. Similarly, the time-resolved fluorescence spectra (Figure 5f) also manifest the absence of intramolecular energy transfer.4

The emission spectra of 5 in the visible region (Figure 5g) and the NIR region (Figure 5j) were both recorded upon the excitation at 454 nm. The obvious emission band at 659 nm in the visible region stems from the ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ electron transition of Ho³⁺ ions; in contrast, the emission band at 974 nm in the NIR region is attributed to the ${}^{5}F_{5} \rightarrow {}^{5}I_{7}$ electron transition of Ho³⁺ ions.^{46,52,55} The excitation spectrogram of 5 (Figure S7c) based on monitoring the emission at 974 nm shows three characteristic excitation peaks at 416 nm, 451 and 479 nm induced by the ${}^{\rm 5}\mathrm{I}_8$ $\rightarrow {}^{5}G_{5}, {}^{5}I_{8} \rightarrow {}^{5}G_{6}$, and ${}^{5}I_{8} \rightarrow {}^{5}F_{5}$ electron transitions of Ho³⁺ ions in sequence.⁴⁶ The decay time profiles of 5 in the visible region (Figure 5h, λ_{em} = 659 nm) and the NIR region (Figure 5k, $\lambda_{\rm em}$ = 974 nm) were respectively measured, and both decay behaviors obey the double exponential function $I = A_1 \exp^{(-t/\tau 1)}$ + $A_2 \exp^{(-t/\tau^2)}$. The fitted τ_1, τ_2, A_1 , and A_2 parameters in the visible region are 1009.2 ns (56.29%), 8749.91 ns (43.71%), 1277.98, and 114.48, and the average lifetime (τ^*) is indexed to 4392.66 ns according to the equation $\tau^* = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1)$ + $A_2\tau_2$),⁴⁶ whereas the fitted τ_1 , τ_2 , A_1 , and A_2 parameters in the NIR region are 968.14 ns (58.05%), 12096.45 ns (41.95%), 330.11, and 19.10, and the average lifetime (τ^*) is calculated to 5637.49 ns. On the basis of previous knowledge, the high frequency O-H oscillators in water ligands accelerate the quenching of the luminescence,⁴⁷ and it is very pronounced that the longer fitting lifetime (τ_2) is assigned to the Ho2³⁺ ions, while the shorter one (τ_1) is assigned to the Ho1³⁺ ions because the Ho1³⁺ ion coordinates to three water molecules but the Ho2³⁺ ion just coordinates to two water ligands. The timeresolved emission spectra of 5 in the visible region (Figure 5i) and in the NIR region (Figure 51) showed the unchanged spectral shape and ordered decreasing intensity along the decay of time, which evidences the default of energy transfer.⁵⁶



Figure 6. (a) The emission spectrogram of **4** in the visible region. (b) The fitted lifetime decay profile of **4** in the visible region. (c) The emission spectrogram of **4** in the NIR region. (d) The fitted lifetime decay profile of **4** in the NIR region. (e) The emission spectrogram of **6** in the visible region. (f) The fitted lifetime decay profile of **6** in the visible region. (g) The emission spectrogram of **6** in the NIR region. (h) The fitted lifetime decay profile of **6** in the NIR region. (h) The fitted lifetime decay profile of **6** in the NIR region.

In the case of 4, the emission spectra in the visible region (Figure 6a) and the NIR region (Figure 6c) were separately recorded under the excitation of 388 nm. Three obvious emission signals arise at 479, 573, and 662 nm in the visible region and respectively stem from the electron transitions between the energy levels of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ of the Dy³⁺ ions. Four conspicuous emission bands appearing at 850 nm, 936 nm, 1006 nm, and 1172 nm in the NIR region are respectively assigned to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{7/2} + {}^{6}F_{9/2}, {}^{4}F_{9/2} \rightarrow {}^{6}H_{5/2}, {}^{4}F_{9/2} \rightarrow {}^{6}F_{7/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{6}F_{5/2}$ transitions of the Dy³⁺ ions. 46,57 By monitoring the emission at 574 nm, the excitation spectrogram of 4 was also acquired (Figure S7d) and exhibits four noteworthy excitation peaks at 352 nm, 366 nm, 388 and 427 nm that are derived from the electron transitions between the energy levels of ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$, ${}^{6}H_{15/2} \rightarrow {}^{6}P_{5/2}$, ${}^{6}H_{15/2} \rightarrow {}^{4}I_{13/2}$, ${}^{6}H_{15/2} \rightarrow {}^{4}G_{11/2}$ of the Dy³⁺ ions in sequence. What is more, the luminescent lifetime decay behaviors of 4 in the visible and NIR regions are also tested by respectively detecting the emissions at 574 and 850 nm, and the fitted decay profiles (Figure 6b,d) keep to the second-order exponential function. The fitted lifetimes are $\tau_1 = 4022.69$ ns (61.58%), $\tau_2 =$ 9862.54 ns (38.42%), and τ^* = 6266.36 ns with A_1 = 582.74 and A_2 = 148.30 in the visible region, while τ_1 = 3812.18 ns (53.71%), $\tau_2 = 9745.89$ ns (46.29%), and $\tau^* = 6558.89$ ns with $A_1 = 155.48$ and $A_2 = 52.42$ in the NIR region.

The emission spectra of **6** in the visible (Figure 6e) and NIR regions (Figure 6g) were also tested upon the excitation at 381 nm. Three noticeable emitting peaks at 557 nm, 670 and 701 nm in the visible region and one broad band at about 1540 nm in the NIR region are successively vested in the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{9/2} \rightarrow {}^{4}I_{11/2}$, and ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er^{3+} ions.^{59,60} The excitation spectrum between 350 and 420 nm (Figure S7e) was gathered by tracing the emission at 556 nm, and it can be seen that three excitation signals at 366, 378, and 407 nm result from the f–f electron transitions of Er^{3+} ions. ^{61,62} The decay curves of **6** both obey the second-order exponential function fitting (Figure 6f in the visible region, $\lambda_{em} = 556$ nm and Figure 6h in the NIR region, $\lambda_{em} = 1536$ nm), and the relevant

results are listed as follows: $\tau_1 = 1073.68$ ns (47.62%), $\tau_2 = 9046.99$ ns (52.38%), $A_1 = 956.96$, $A_2 = 124.90$, and $\tau^* = 5250.10$ ns in the visible region as well as $\tau_1 = 1283.76$ ns (60.55%), $\tau_2 = 9929.84$ ns (39.45%), $A_1 = 540.72$, $A_2 = 45.55$, and $\tau^* = 4694.64$ ns in the NIR region.

What is more, the chromaticity coordinates of 1, 3, 4, 5, and 6 derived from their visible PL spectra in the visible region are displayed in the CIE 1931 diagram to show the specific emission colors of the above materials (Figure S8). The CIE chromaticity coordinates (X, Y) for 1, 3, 4, 5, and 6 are (0.64938, 0.35017), (0.32829, 0.57833), (0.39692, 0.44404), (0.52449, 0.45836), and (0.64938, 0.35017), indicating that they exhibit the red, green, yellowish-green, orange, and dark-yellow emission, respectively. The systematic study on the luminescence properties of these products are useful to the applications of RE-containing POMs in the field of optical materials. In the future, the further investigations will be carried out, and more significant achievements are expected to be obtained.

Electrochemical Sensing Properties. Electrochemical detection for small biomolecules is an increasingly attractive field because of the high sensitivity of the electrochemical detection method and the essential significance of the trace amounts of biomolecules in the physiological mechanism.^{63,64} POMs were also employed as the modifiers synergized with carbon materials (such as ordered mesoporous carbon, singlewalled carbon nanotubes, reduced graphene oxide, multiwall carbon nanotubes) to improve the electrochemical response of electrodes for the target substance to be examined.⁶⁴⁻ However, the previously reported examples are only involved in some simple POMs (such as $[\alpha-\text{SiMo}_{12}\text{O}_{40}]^{4-}$, $[\alpha-\text{SiMo$ $PW_{12}O_{40}$ as modified electrode materials to electrochemically detect small biomolecules; however, there are very rare reports on RECATs as the modified electrode materials to electrochemically detect small biomolecules. Therefore, in this paper, the as-synthesized RECATs 1, 3, and 5 as the modified electrode materials were used to fabricate CS-CMWCNs-RECAT/GCE ESs (CS = chitosan, CMWCNs = arboxyl functionalized multiwalled carbon nanotubes, RECAT = 1, 3, or

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5, GCE = glass carbon electrode, ESs = electrochemical sensors). The specific preparation process of CS-CMWCNs-RECAT/GCE ESs is shown in the Supporting Information, and the schematic preparation process is displayed in Scheme 2.

Scheme 2. Schematic Preparation Process of CS-CMWCNs-RECAT/GCE ESs through "Layer by Layer" Assembly



Thereinto, CS is used as a main component in the film of the ES because CS can be protonated in the acetic acid solution and the protonated CS carrying positive charges, which is in favor of the combination of negatively charged RECAT on the GCE through electrostatic interactions. The electrochemical response properties of CS-CMWCNs-1, 3, or 5/GCE ESs toward DA detection (Figures 7, S12–S13) were further investigated by cyclic voltammetry (CV) in the 0.10 mol·L⁻¹ H₂PO₄⁻/HPO₄²⁻ solution (pH = 3).

First, in order to observe whether the prepared CS-CMWCNs-1/GCE ES can be employed to detect DA or not, we compared the cyclic voltammograms (CVs) of the CS-CMWCNs-1/GCE ES in the 0.10 mol·L⁻¹ $H_2PO_4^{-}/HPO_4^{2-}$ solution (pH = 3) with DA (30 μ mol·L⁻¹) or without DA (Figure 7a). It is very obvious that there appeared a pair of redox peaks at $E_{1/2} = 0.373$ V that is attributed to the redox process of DA when DA was added to the $H_2PO_4^{-}/HPO_4^{2-}$ solution. This phenomenon indicates that the CS-CMWCNs-1/GCE ES can function as a candidate of sensoring DA. What is more, the sensoring CVs toward DA of CS-CMWCNs-1/GCE ESs containing different dosages of CMWCNs and Nafion are presented in Figure S9. It can be seen that among the synthesized CS-CMWCNs-1/GCE ESs, the usage of 20 mg of CMWCNs and 10 μ L of Nafion in step 2 and 3 of the preparation procedure of CS-CMWCNs-1/GCE ESs can highly improve the electrochemical sensoring signals toward DA. Thus, the sensoring CVs toward DA of the CS-CMWCNs-1/GCE ES was investigated by comparing the CVs behaviors of bare GCE, CS-CMWCNs/GCE, and CS-CMWCNs-1/GCE ES in 0.10 $mol \cdot L^{-1} H_2 PO_4^{-} / HPO_4^{2-}$ solution (pH = 3.0) in the presence of 30 μ mol L⁻¹ DA over a potential range of -1.0-1.0 V at a scan rate of 100 mV s⁻¹ (Figure 7b). Apparently, there is not a response signal at the bare GCE, while there are one oxidation peak at 0.249 V and two reduction peaks at 0.102 V and -0.647 V at the CS-CMWCNs/GCE that may result from the CS or CMWCNs in the film of the CS-CMWCNs/GCE ES. However, a pair of obvious electrochemical response signals attributable to the DA redox process are observed at the CV curve of the CS-CMWCNs-1/GCE ES (Figure7b); moreover, the newly appearing four oxidation peaks at 0.062 V, -0.133 V, -0.493 V_{2} –0.666 V and two reduction peaks at –0.245 V and –0.795 V are assigned to the redox process of the WVI centers in the polyoxoanion of 1. In conclusion, the CS-CMWCNs-1/GCE ES shows a striking response toward the DA redox process

Figure 7. (a) Comparison of the CVs of CS-CMWCNs-1/GCE ES in the 0.10 mol·L⁻¹ H₂PO₄^{-/}/HPO₄²⁻ solution (pH = 3.0) solution with DA (30 μ mol L⁻¹) and without DA. (b) The CVs of the bare GCE, CS-CMWCNs/GCE, and CS-CMWCNs-1/GCE ESs in the 0.10 mol·L⁻¹ $H_2PO_4^{-}/HPO_4^{2-}$ solution in the presence of 30 μ mol·L⁻¹ DA in a potential range of -1.0-1.0 V at a scan rate of 100 mV·s⁻¹. (c) Effect of pH on the CVs of CS-CMWCNs-1/GCE ES in the H₂PO₄^{-/} HPO₄²⁻ solution in the presence of 30 μ mol·L⁻¹ DA (scan rate: 100 mV·s⁻¹). (d) Effect of the pH on the anodic peak current of DA using the CS-CMWCNs-1/GCE ES as a working electrode in the H₂PO₄^{-/}/HPO₄²⁻ solution in the presence of 30 μ mol·L⁻¹ DA (scan rate: 100 mV·s⁻¹). (e) The CVs of CS-CMWCNs -1/GCE ES in the H₂PO₄⁻/HPO₄ solution in the presence of 30 μ mol·L⁻¹ DA (scan rate: 100 mV·s⁻¹) from the second round to the 180th round, inset: the enlarged view of the anodic peak currents. (f) The variation of anodic peak currents from the second round to the 180th round in the $H_2PO_4^{-1}/HPO_4^{2-}$ solution in the presence of 30 μ mol·L⁻¹ DA (scan rate: 100 mV·s⁻¹). (g) The CVs of CS-CMWCNs-1/GCE ES in the $H_2PO_4^{-}/HPO_4^{2-}$ solution in the presence of 30 μ mol·L⁻¹ DA at the different scan rates (from inner to outer: 20, 50, 80, 100, 120, 150, 180, and 200 mV·s⁻¹). (h) The linear relationship between peak current of DA and scan rate. (i) The variation of the anodic peak currents of DA in the $H_2PO_4^{-}/HPO_4^{-2}$ solution (pH = 3.0) using CS-CMWCNs-1/GCE ES as a working

Figure 7. continued

electrode with the DA concentration changing from 4 to 30 $\mu mol \cdot L^{-1}$ (scan rate: 100 mV·s⁻¹). (j) Plot of the anodic peak currents of DA versus the different concentrations of DA.

compared with bare GCE and CS-CMWCNs/GCE, which suggests that 1 plays the major role in the improvement of sensing performance of the CS-CMWCNs-1/GCE ES. Besides. the characteristic redox peaks of the W^{VI} centers also identify the load of 1 onto the CS-CMWCNs-1/GCE ES. The mechanism of the electrochemical response of the CS-CMWCNs-1/GCE ES toward DA can be hypothesized as follows: (1) there exist hydrogen bonding interactions between protonated [HAD]⁺ cations in the electrolyte and Nafion as well as chitosan on the surface of ES, which make a nonignorable contribution to the electrochemical response toward DA; (2) the load of RECAT onto the CS-CMWCNs-1/GCE accelerates electron transfer rates because of the electrostatic attraction between the positively charged DA in the electrolyte and negatively charged ES electrode; ^{63,66} (3) conductively efficient heterogenization of RECAT by CS over CMWCNs offers a synergistic effect between RECAT and CMWCNs, which improves the electron transport on the electrode/electrolyte interface.⁶³ These abovementioned factors account for the enhanced electrochemical signals of CS-CMWCNs-1/GCE ES toward DA.

The pH of the electrolyte solution has a significant influence on the redox process of DA; therefore, the influence of pH on the CVs of the CS-CMWCNs-1/GCE ES in the $H_2PO_4^{-}/$ HPO_4^{2-} solution in the presence of 30 μ mol·L⁻¹ DA (Figure 7c) was explored at different pH values. The pH of the electrolyte solution was adjusted by adding phosphonic acid. The results shown in Figure 7c indicate that the peak potential of DA is gradually shifted to the lower potential region, and peak currents gradually decrease by increasing the pH value. The correlation between the anodic peak potential (E_{pa}) and the pH value of electrode follows the equation: $E_{pa}/(V) = 0.61739 - 0.0673(pH)$ $(R^2 = 0.996)$ (Figure 7d), and the slope of -67.3 mV/pH is close to the value of -59.2 mV/pH at 25 °C for the one-electron/ monoproton electrode reaction, which shows that the electron transfer was accompanied by an equal number of protons.⁶⁷ The results are in good agreement with the literature where the oxidation of DA was reported to be a monoproton and oneelectron process.⁶⁸ In addition, the influence of pH on the CVs of CS-CMWCNs-1/GCE ES in the H₂PO₄^{-/}HPO₄²⁻ solution in the absence of DA (Figure S10) was explored at different pH values. Figure S10 suggests that the excessively strong acidity (pH < 3) leads to the dramatic change of the CV curves, which may result from the decomposition of POM fragments in 1. So the optimal pH was determined to be 3.0, and all the measurements were performed at pH = 3.0.

The stability of CS-CMWCNs-1/GCE ES was investigated by using a newly fabricated CS-CMWCNs-1/GCE ES as a working electrode in the $H_2PO_4^{-}/HPO_4^{2-}$ solution in the presence of 30 μ mol·L⁻¹ DA (pH = 3.0) under 180-round CV scanning conditions in the potential range of -1.0-1.0 V with the scan rate of 100 mV·s⁻¹. As shown in Figure 7e, the CVs on CS-CMWCNs-1/GCE ES from the second round to the 180th round do not show a significant change, which manifests the comparative stability of CS-CMWCNs-1/GCE. Figure 7f shows the slight variation of the anodic peak current of DA under different circles, in which the anodic peak currents slightly increases in the first 50 rounds and negligibly decreases in the subsequent circles. When it comes to the reason, it may result from the slow electrochemical response of ES toward DA in the first 50 rounds, and the slight drop of 1 from ES leads to the inappreciable decrease of the anodic peak current in the subsequent measurement.

Next, the effect of the scan rate on the peak current of DA at the CS-CMWCNs-1/GCE ES was also researched (Figure 7g). It is extremely obvious that the anodic and cathodic peak currents of DA increase with increasing the scan rate and are linearly proportional to the scan rate (Figure 7h), and they can be respectively fitted by $I_{pa}/(mA) = 0.00178\nu(mV\cdot s^{-1}) + 0.07283$ ($R^2 = 0.999$) and $I_{pc}/(mA) = -0.00119\nu(mV\cdot s^{-1}) + 0.00161$ ($R^2 = 0.994$), which demonstrates that the electrode reaction process is adsorption-controlled.⁶³ Moreover, when the scan rate increases, the potential difference (ΔE_p) between the redox peaks also increases, which is related to the limitations associated with charge transfer at the surface of CS-CMWCNs-1/GCE ES.⁶³

Figure S11a exhibits the CVs of CS-CMWCNs-1/GCE ES in the $H_2PO_4^{-}/HPO_4^{2-}$ solution with the changeable concentration of DA (pH = 3.0, scan rate = $100 \text{ mV} \cdot \text{s}^{-1}$). The variation of the anodic peak currents of DA in the $H_2PO_4^{-}/HPO_4^{2-}$ solution (pH = 3.0) using the CS-CMWCNs-1/GCE ES as a working electrode with the DA concentration changing from 4.0 to 30 μ mol·L⁻¹ (Figure 7i) shows that the anodic peak currents of DA increase with successive addition of DA. Figure 7j shows the good linear dependence of the anodic peak currents of DA with increasing the concentration of DA in the range of 4.0-30 μ mol·L⁻¹, which can be fitted by the equation I_{pa} (mA)= 0.00511 (μ mol·L⁻¹) + 0.15008 with $R^2 = 0.993$. The linear relation in the range of 4.0–30 μ mol·L⁻¹ and the good linear relation between the current signals and concentration of DA demonstrate that the CS-CMWCNs-1/GCE ES can be used to detect DA in the aforesaid concentration range. The detection limit of CS-CMWCNs-1/GCE ES toward DA was calculated to be 0.943 μ mol·L⁻¹ based on three times the standard deviation of the blank sample measurement.⁶⁹

Investigations on electrochemical sensing properties of CS-CMWCNs-3/GCE ES and CS-CMWCNs-5/GCE ES toward the DA detection are seen in the Supporting Information (Figures S12–S13). The results indicate that CS-CMWCNs-1, 3, or 5/GCE ESs show a similar electrochemical response signals of toward the DA detection, mainly because they have similar four-leaf-clover-shaped structures formed by two [As₂W₁₉O₆₈]¹⁶⁻ moieties encapsulating an ala-decorated W-O-RE heterometallic cluster. The good linear relation between the peak current and the concentration of analyte can provide a good opportunity for developing CS-CMWCNs-RECAT/GCE ESs as efficient biosensors to detect the small biomolecules in biological environments. In addition, the chemical components in the surfaces of CS-CMWCNs-1, 3, or 5/GCE ESs have been confirmed by energy dispersive spectrometer (EDS) (Figure S14), and the results manifest that RECATs 1, 3, or 5 are loaded onto the surfaces of the ESs because of the existence of the signals of As, W, and RE elements. Meanwhile, the signals of S and F elements in the EDS spectra indicate the participation of Nafion; what is more, the C signals are mainly from CMWCNs, CS, and RECATs 1, 3, or 5. The mass percentages and atomic percentages of all the elements are provided in Table S2. It can be easily found that the atomic ratios of As and W are close to 1:11 in the EDS results of CS-CMWCNs-1, 3, or 5/GCE ESs, and the atomic ratios of As and W in the solid samples of 1, 3, or 5 are also close to 1:11. Two similar atomic percentages

demonstrate the maintaining of the polyoxoanion skeletons of 1, 3, or 5 during the course of preparing CS-CMWCNs-1, 3, or 5/GCE ESs, which can be further proved by the good agreements of IR spectra in the range of $1000-500 \text{ cm}^{-1}$ of 1 and CS-CMWCNs-1, 3, and CS-CMWCNs-3, and 5 and CS-CMWCNs-5 (Figure S15).

CONCLUSIONS

In conclusion, three kinds of unique ala-decorated RECATs 1-8 containing $[As_2W_{19}O_{68}]^{16-}$ building blocks were manufactured through a facile one-step assembly strategy in traditional aqueous solution and structurally characterized. Their structure differences rest on the central ala-decorated W-O-RE heterometallic cluster surrounded by $[As_2W_{19}O_{68}]^{16-}$ building blocks, where the number of ala molecules are three, four, and two, which may result from the various coordination geometries of RE ions and the different construction modes of W-O-RE heterometallic clusters. The PL performance and lifetime decay behaviors of 1, 3, 4, 5, and 6 were studied, and their emission spectra primarily originate from 4f electrons transitions of RE ions. The time-resolved luminescence emission spectra of 1, 3, and 5 were characterized and confirmed the lack of energy transfer between the AT building blocks and the RE ions. In addition, the electrochemical sensing properties of CS-CMWCNs-1, 3, or 5/GCE ESs toward the DA detection were for the first time investigated, suggesting that 1, 3, and 5 may be used in the electrochemical biosensing field. In the future work, we will continue to exploit much more novel RE-containing POM-based materials and explore their luminescence and electrochemical biosensing properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00004.

Experimental section, IR spectra, TG curves, relevant structural figures and electrochemistry curves and discussion (PDF)

Accession Codes

CCDC 1887690–1887697 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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