

## Assembly of Saturated Nb/W Mixed-Addendum Polyoxometalate $[P_2W_{15}Nb_3O_{62}]^{9-}$ and Lanthanide Ions (Ln = Eu, Ce)

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Two isostructural polyoxotungstates,  $K_6Na_4H_8[Eu_6(H_2O)_{38}-(P_2W_{15}Nb_3O_{62})_4] \cdot 45H_2O$  (**1**) and  $K_6Na_4H_8[Ce_6(H_2O)_{38}(P_2W_{15}Nb_3O_{62})_4] \cdot 56H_2O$  (**2**), have been synthesized by reaction of saturated Nb/W mixed-addendum polyoxometalate  $[P_2W_{15}Nb_3O_{62}]^{9-}$  and lanthanide ions in acidic solution. They are the first examples of lanthanide derivatives based on saturated Dawson-type Nb/W mixed-addendum polyoxometalates. All the compounds were fully characterized by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis, elemental analysis, and electrochemistry. XRD analysis reveals that **1** and **2** display one-dimensional chains

constructed from sandwich-type fragment  $\{Ln_3-(P_2W_{15}Nb_3O_{62})_2\}$  linked by alternating Ln–O–W bridging bonds. In **1** and **2**, all the lanthanide ions selectively bind to  $O_t(Nb)$  of  $\{P_2W_{15}Nb_3O_{62}\}$  fragments ( $O_t$ : terminal oxygen atoms), indicating the high nucleophilicity of  $O_t(Nb)$ . The photoluminescence behavior of **1** in the solid state was investigated at room temperature; it exhibits the characteristic transition of Eu under the excitation wavelength (394 nm). Additionally, the cyclic voltammogram of **2** indicates good electrocatalytic activity towards the reduction of nitrite.

### Introduction

Polyoxoniobates are an important subfamily of polyoxometalates (POMs). They have potential applications in diverse areas such as antiviral therapy, nuclear waste treatment, and catalysis.<sup>[1–3]</sup> Conventional polyoxoniobates (such as isopolyniobate clusters<sup>[4]</sup> and heteropolyniobate clusters<sup>[5]</sup>) are prepared under basic conditions mainly by hydrothermal synthesis, and they always decompose to niobium oxide under acidic conditions. However, among numerous polyoxoniobates, Nb/W mixed-addendum POMs explored by Klemperer,<sup>[6]</sup> Hill,<sup>[3a,3b,7]</sup> and Finkel<sup>[3c,3d,8]</sup> et al., including Lindqvist-type  $(Nb_xW_{6-x}O_{19}^{(2+x)-})$ ,<sup>[9]</sup> Keggin-type  $(XW_9Nb_3O_{40})^{n-}$  ( $n = 7, X = Si^{IV}, Ge^{IV}; n = 6, X = P^V, As^V$ ),<sup>[7a,7b,10]</sup> and Dawson-type  $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$ ,<sup>[7e]</sup>  $[P_2W_{15}Nb_3O_{62}]^{9-}$ ,<sup>[8a]</sup> and  $[P_2W_{17}(NbO_2)O_{61}]^{7-}$ ,<sup>[11]</sup> attracted our attention because of their unique characteristics. Firstly, all the primary Nb/W mixed-addendum POMs are prepared in the form of peroxo compounds by reaction of  $[Nb_6O_{19}]^{8-}$  with lacunary polyoxotungstates or sodium tungstate in acidic  $H_2O_2$  solution. Secondly, they have good stability in acidic media owing to the presence of the peroxide groups.<sup>[10]</sup> Finally, inheriting the properties of poly-

oxoniobates, the Nb/W mixed-addendum POMs also possess high nucleophilicity especially on  $O_t(Nb)$ , after elimination of the peroxide groups.<sup>[7d,8b,12]</sup> Such acidic stability and basic sites are comparable to those of lacunary polyoxotungstates, which are widely used as multidentate ligands to coordinate with electrophilic groups, such as lanthanide ions.<sup>[13]</sup> Thus, we consider that Nb/W mixed-addendum POMs can also be regarded as suitable candidates for combining with lanthanide ions just like the lacunary polyoxotungstates.

However, up to now, the chemistry of lanthanide-containing POMs has been mainly based on lacunary POMs,<sup>[14]</sup> and there are only a few examples of plenary POMs.<sup>[15]</sup> Lacunary POMs are formed by eliminating one or more  $(WO)^{4+}$  fragments from plenary POMs, which leave them with a higher negative charge and make them more reactive towards electrophiles. On the other hand, the derivatives of Nb/W mixed-addendum POMs are mainly organometallic complexes<sup>[6,8b–8d]</sup> and products of self-aggregation (dimers and tetramers).<sup>[3a,7c,7d,10]</sup> Although Yamase et al. discovered the only example of europium-containing polyoxoniobates in 1994,<sup>[16]</sup> there are no reports in the literature on lanthanide derivatives based on Nb/W mixed-addendum POMs.

We realize that the Dawson-type  $[P_2W_{15}Nb_3O_{62}]^{9-}$  is a promising building block to coordinate with lanthanide ions not only because the “ $Nb_3O_3$ ” cap has sufficient charge density and a lot of exposed  $O_t(Nb)$  atoms but also because it is larger than Keggin-type  $(XW_9Nb_3O_{40})^{n-}$  ( $n = 7, X = Si^{IV}, Ge^{IV}; n = 6, X = P^V, As^V$ ). Although

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$[\text{P}_2\text{W}_{12}(\text{NbO}_2)_6\text{O}_{56}]^{12-}$  has the largest niobium-oxo cluster among all the primary Nb/W mixed-addendum POMs, it is unstable in solution.<sup>[7e]</sup>

Herein, we chose  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$  as a precursor to react with the lanthanide ions under acidic conditions and obtained two 1D compounds,  $\text{K}_6\text{Na}_4\text{H}_8[\text{Eu}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]\cdot 45\text{H}_2\text{O}$  (**1**) and  $\text{K}_6\text{Na}_4\text{H}_8[\text{Ce}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]\cdot 56\text{H}_2\text{O}$  (**2**). In these two compounds, Ln atoms are all located between the  $\text{NbO}_6$  octahedra to form Nb–O–Ln bonds, because of the high nucleophilicity of  $\text{O}_t(\text{Nb})$ . Furthermore, they display 1D architectures by forming Ln–O–W bridging bonds between two vicinal  $\{\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\}$  units.

## Results and Discussion

### Synthesis

Compounds **1** and **2** are synthesized by reaction of  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$  and  $\text{LnCl}_3$  (Ln = Eu, Ce) in a ratio of 1:1.5 in aqueous solution with pH = 2.0 at 85 °C for 2 h. Before adding lanthanide ions to the solution,  $[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{62}]^{9-}$  is reduced to peroxide-free  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$  by  $\text{NaHSO}_3$  because the presence of peroxide groups could prevent the  $\text{O}_t(\text{Nb})$  from connecting with Ln atoms.

The maintenance of  $\{\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\}$  units in **1** and **2** under such highly acidic conditions (pH = 2.0) indicates the stability of the products in acidic medium, which is higher than that of lacunary polyoxotungstates that are usually sensitive to pH and sometimes undergo disassembly and reassembly in the reaction process.<sup>[13a,17]</sup> Therefore, the saturated mixed-addendum POMs are not only active but also more stable in retaining their structure type in a broad pH range. In addition to compounds **1** and **2**, we also obtained the Pr and Nd analogues under the same synthesis conditions. However, the quality of the single crystals were not good enough for analysis by X-ray diffraction.

It is noteworthy that the pH value is crucial for the successful preparation of **1** and **2**. The pH should be strictly controlled in the range 1.5–2.5. When the pH value is higher than 2.5,  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$  is easily deposited as the lanthanide salt. In contrast, no crystals of the products can be isolated, except for some amorphous precipitation, when the pH value is lower than 1.5.

### Structure Determination

Single-crystal X-ray diffraction analysis reveals that the polyanions of **1** and **2** (**1a** and **2a**) crystallize in the space group  $P\bar{1}$ . For compounds **1** and **2**, which are isomorphic with only slight differences in bond lengths and angles and the number of lattice water molecules, **1** is described as an example below. As shown in Figure 1, polyanion **1a** displays novel 1D infinite chains with  $\{\text{Eu}_6(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4\}$  as the asymmetric subunit.

The asymmetric subunit (Figure 2) contains two identical sandwich-type fragments,  $\{\text{Eu}_3(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_2\}$ , which are arranged in a centrosymmetric form and linked by two Eu–O– $\text{W}_a$  ( $\text{W}_a$ : the equatorial W atoms that are away from Nb atoms and linked to Eu atoms) bridges. To the best of our knowledge, the lanthanide atoms are preferentially coordinated with terminal oxygen atoms, because of their higher basicity, rather than bridging oxygen atoms. Moreover,  $\text{O}_t(\text{Nb})$  is more nucleophilic than  $\text{O}_t(\text{W})$ , because the formal valence of Nb is +5 and that of W is +6. Therefore, all the Eu atoms bind to the  $\text{NbO}_6$  octahedra through Eu– $\text{O}_t(\text{Nb})$  bonds. In particular, the three Eu centers in each sandwich-type fragment are not connected directly by  $\mu$ -O atoms to form a metal cluster, which is in difference to the arrange-

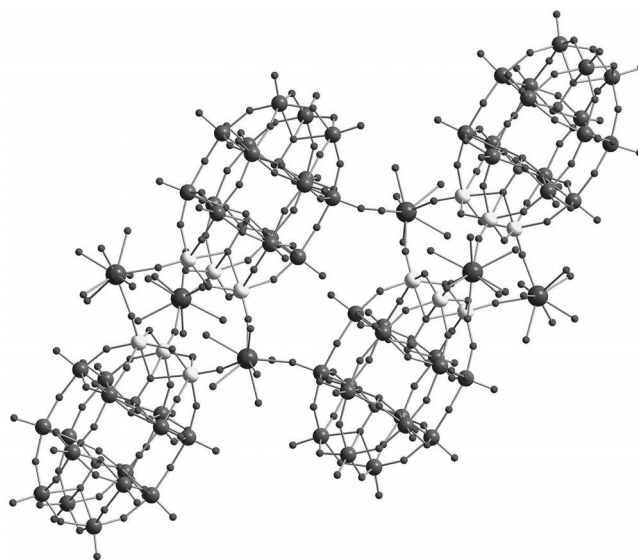


Figure 2. Ball-and-stick representation of the asymmetric subunit of **1a**.

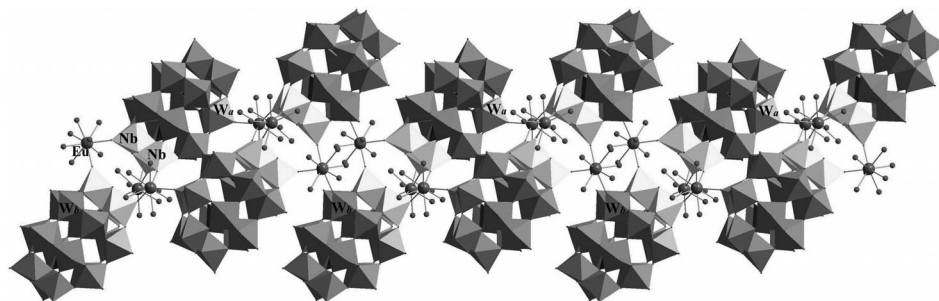


Figure 1. Combined polyhedral/ball-and-stick representation of polyanion **1a**.

ment of most sandwiched metal centers.<sup>[17c,18]</sup> Each pair of adjacent asymmetric subunits  $\{\text{Eu}_6(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4\}$  is joined together by two Eu–O–W<sub>b</sub> (W<sub>b</sub>: the equatorial W atoms that are adjacent to Nb atoms and linked to Eu atoms) bridges, resulting in an overall 1D zigzag chain arrangement of polyanion **1a** (Figures S2–S4 in the Supporting Information). All the Eu atoms of polyanion **1a** are nine-coordinate and coordinated with two O<sub>i</sub>(Nb) from different  $\{\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\}$  subunits. The remaining coordination sites of Eu atoms are filled by aqua ligands.

The bond valence sum (BVS)<sup>[19]</sup> analysis for compounds **1** and **2** confirms that the oxidation states of W, Nb, P, and Ln atoms are +IV, +V, +V, and +III, respectively. Six K<sup>+</sup> and four Na<sup>+</sup> can be located crystallographically. The overall charge of all atoms obtained from the single-crystal structure determination is –8. Thus, to balance the negative charges of **1** and **2**, eight protons should be added; those cannot be located crystallographically and are assumed to be delocalized over the entire structures.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) on **1** and **2** were performed under a nitrogen atmosphere (Figures S5 and S6 in the Supporting Information). The thermograms all show one step of weight loss between 30 and 350 °C corresponding to the loss of lattice and coordinated water molecules. The weight loss is 7.82% for **1** and 8.80% for **2**. In addition, there is no further weight loss until 600 °C.

### Electrochemistry

The electrochemical behavior of **2** and its electrocatalytic activity in the reduction of NO<sub>2</sub><sup>–</sup> were studied in 0.5 M (CH<sub>3</sub>COOK + CH<sub>3</sub>COOH) pH 4.7 buffer solution (scan rate: 100 mV s<sup>–1</sup>, Figure 3a). There are three reversible redox peaks, II–II', III–III', and IV–IV', with midpoint potentials,  $E_{\text{mid}}$ , of –450, –601, and –811 mV [ $E_{\text{mid}} = (E_{\text{pa}} + E_{\text{pc}})/2$ ], respectively, corresponding to the redox processes of W centers.<sup>[20]</sup> In addition, the irreversible anodic peak I at 304 mV is assigned to the oxidation process of Ce<sup>IV</sup>/Ce<sup>III</sup>.<sup>[21]</sup>

As we know, niobium is not electrochemically active. When it is introduced into polyoxotungstates, the negative ionic charge of the polyanions increases and their reducibility decreases, which was demonstrated by Dabbabi et al.<sup>[22]</sup> Their study of the electrochemical properties of Nb<sub>n</sub>W<sub>6–n</sub>O<sub>19</sub><sup>(2+n)–</sup> indicates that the introduction of niobium can weaken the electrochemical activity of tungsten. For example, the cyclic voltammogram of W<sub>6</sub>O<sub>19</sub><sup>2–</sup> exhibits two reversible redox peaks corresponding to the redox processes of W centers, while that of Nb<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4–</sup> exhibits only one reversible redox peak. Comparatively, because the ratio of Nb/W is low in compound **2**, we can see three reversible redox peaks corresponding to W centers, which is consistent with the cyclic voltammogram of  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6–}$ .

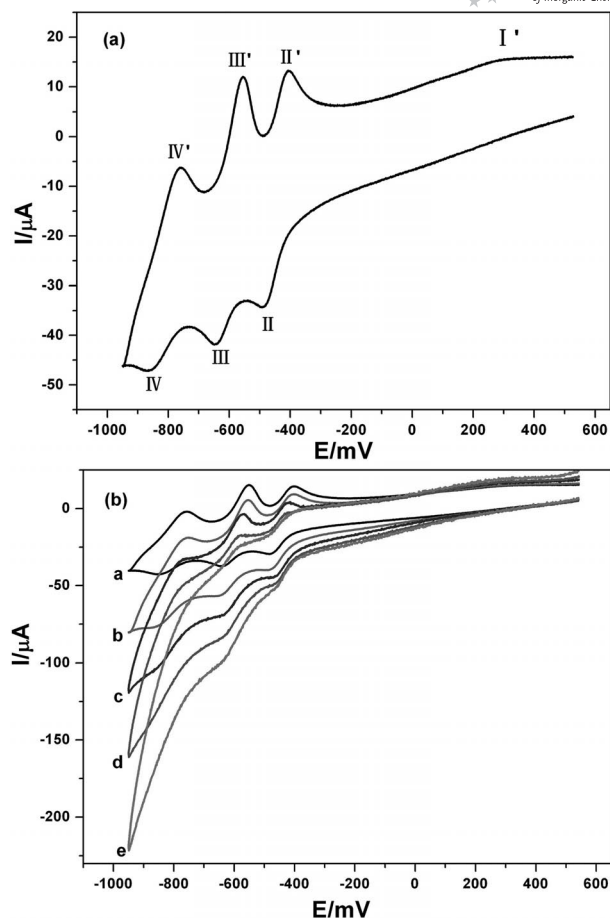


Figure 3. (a) Cyclic voltammogram of **2** in pH = 4.7 buffer solution (0.4 M CH<sub>3</sub>COOK + CH<sub>3</sub>COOH) at a scan rate of 100 mV s<sup>–1</sup>; (b) Cyclic voltammograms of **2** in pH = 4.7 buffer solution (0.4 M CH<sub>3</sub>COOK + CH<sub>3</sub>COOH) at a scan rate of 100 mV s<sup>–1</sup> containing: a) 0.0 mM, b) 1 mM, c) 2 mM, d) 4 mM, and e) 8 mM NaNO<sub>2</sub>. The working electrode is glassy carbon, and the reference electrode is Ag/AgCl.

The determination of the amount of nitrite in environmental and food samples is important because of its potential toxicity.<sup>[23]</sup> In general, the direct electroreduction of nitrite is not possible because of the high overpotential. POMs can act as the appropriate catalyst in the electroreduction process by lowering the overpotential as a result of their capability of delivering electrons to other species. They can serve as powerful electron reservoirs for multielectron reductions.<sup>[24]</sup> Nevertheless, the electrocatalytic reduction of nitrite remains to be a challenge in the NO<sub>x</sub> series, because the complete process requires several electrons. Therefore, the electrocatalytic reduction of NO<sub>2</sub><sup>–</sup> by **2** constitutes a further step in the study of its electrocatalytic activity. We found that **2** displays remarkable electrocatalytic activity in the reduction of NO<sub>2</sub><sup>–</sup> (Figure 3b). On addition of NO<sub>2</sub><sup>–</sup>, all the reduction peak currents increase and the corresponding oxidation peak currents decrease dramatically, which indicates that both of the reduced species show electrocatalytic activity towards the reduction of nitrite.



### Photoluminescence Properties

The photoluminescence behavior of **1** in the solid state was investigated at room temperature. It exhibits intense photoluminescence upon excitation at 394 nm, the typical  $\text{Eu}^{\text{III}}$  red fluorescent emission. The emission spectrum of solid **1** (Figure 4) displays five characteristic emission bands at 579, 591, 613, 653, and 699 nm corresponding to the  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 0-4$ ) transitions. The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition is allowed for low symmetry, which shows that the site symmetry of  $\text{Eu}^{\text{III}}$  is low without an inversion center in **1**. The  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is a magnetic dipole transition, which varies with the ligand field strength acting on  $\text{Eu}^{\text{III}}$  and is fairly insensitive to the coordination environment of  $\text{Eu}^{\text{III}}$ . The highest relative intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission at 613 nm corresponds to the electric dipole transition. The intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is greatly sensitive to chemical bonds in the vicinity of  $\text{Eu}^{\text{III}}$  and it increases as the site symmetry of the  $\text{Eu}^{\text{III}}$  center decreases. Therefore, the  $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$  ratio is widely used as a measure of the coordination state and site symmetry of the lanthanide.<sup>[25]</sup> The value of this ratio for compound **1** is 15.43, which shows the low site symmetry of  $\text{Eu}^{\text{III}}$ . It is noteworthy that compound **1** exhibits remarkable red fluorescent emission from its colorless and transparent crystals under irradiation (365 nm) from a UV lamp (Figure S7 in the Supporting Information).

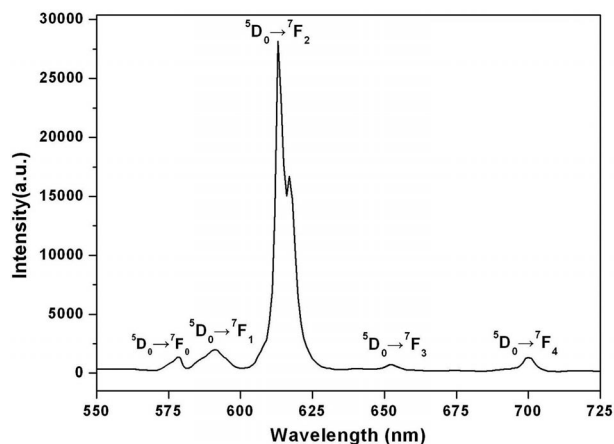


Figure 4. Emission spectrum ( $\lambda_{\text{ex}} = 394$  nm) of solid sample **1**.

Furthermore, the luminescence properties of **2** and  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$  were also studied at room temperature (Figures S8 and S9 in the Supporting Information). The emission spectrum of **2** in the solid state exhibits a maximum at 556 nm upon excitation at 265 nm, which is assigned to the  $5d(^2\text{A}_{1g}) \rightarrow 4f(^2\text{F}_{5/2})$  transition of  $\text{Ce}^{\text{III}}$ .<sup>[26]</sup> The precursor  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$  displays weak photoluminescence at 427 nm when excited at 364 nm, which is attributed to the  $\text{O} \rightarrow \text{W}$  and  $\text{O} \rightarrow \text{Nb}$  charge transfer.

### Conclusions

In summary, we have synthesized two 1D Ln-containing POMs,  $\text{K}_6\text{Na}_4\text{H}_8[\text{Eu}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]\cdot 45\text{H}_2\text{O}$  (**1**)

and  $\text{K}_6\text{Na}_4\text{H}_8[\text{Ce}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]\cdot 56\text{H}_2\text{O}$  (**2**), by reaction of Dawson-type saturated triniobium-substituted phosphotungstate and lanthanide ions in acidic aqueous medium. They have been fully characterized in the solid state by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis, elemental analysis, and electrochemical studies. Photoluminescence measurements show that europium-based compound **1** exhibits expected luminescence, and cerium-based compound **2** shows good electrocatalytic activity in the reduction of nitrite. In view of the high coordination numbers especially a good deal of aqua ligands of lanthanide ions in this system, we are interested in preparing new derivative species by the introduction of organic ligands such as amino acids or carboxyl ligands. Furthermore, this result gives us new inspiration for designing Nb/W mixed-addendum POMs. We can try to introduce transition metal ions or other lanthanide ions into Nb/W mixed-addendum POMs, as  $\text{O}_t(\text{Nb})$  is highly nucleophilic.

### Experimental Section

**Materials and Instruments:** Precursors  $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$ ,<sup>[4a]</sup>  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 24\text{H}_2\text{O}$ ,<sup>[27]</sup> and  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$ <sup>[11]</sup> were synthesized according to the procedures described in the literature, and their purity was determined by IR spectroscopy. All other reagents were readily available from commercial sources and were used as received without further purification. The IR spectra in KBr pellets were recorded in the range  $400\text{--}4000\text{ cm}^{-1}$  with an Alpha Centauri FTIR spectrophotometer. Elemental analyses (C, H, and N) were performed with a Perkin-Elmer 2400 CHN Elemental Analyzer. P, W, Nb, Ce, Eu, Na, and K were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. The thermogravimetric analyses (TGA) were carried out by using a PerkinElmer TGA7 instrument, with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ , under a nitrogen atmosphere. Electrochemical measurements were performed with a CHI660B electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A three-electrode system was employed in this study. A glassy carbon electrode ( $d = 3$  mm) was used as a working electrode, a  $\text{Ag}/\text{AgCl}$  electrode as a reference electrode, and a Pt coil as a counterelectrode. All potentials were measured and reported vs.  $\text{Ag}/\text{AgCl}$ . All the experiments were conducted at ambient temperature ( $25\text{--}30\text{ }^\circ\text{C}$ ). The photoluminescence properties were measured with a FLS920 Edinburgh Fluorescence Spectrometer.

**$\text{K}_6\text{Na}_4\text{H}_8[\text{Eu}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]\cdot 45\text{H}_2\text{O}$  (**1**):** A sample of  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}]\cdot 12\text{H}_2\text{O}$  (1.00 g, 0.22 mmol) was dissolved in  $\text{H}_2\text{O}$  (20 mL) at  $90\text{ }^\circ\text{C}$  whilst stirring. Then,  $\text{NaHSO}_3$  (0.15 g, 1.44 mmol) was added to the solution. After 10 min, the yellow solution turned colorless. The pH value of the solution was carefully adjusted to 2.0 with aqueous HCl (1 M). Afterwards, a solution of  $\text{EuCl}_3\cdot 7\text{H}_2\text{O}$  (0.15 g, 0.39 mmol) in  $\text{H}_2\text{O}$  (2 mL) was added dropwise. The mixture was vigorously stirred at  $85\text{ }^\circ\text{C}$  for 2 h. The resulting solution was filtered and concentrated at room temperature. After a week, single crystals suitable for X-ray crystal structure determination were obtained (yield: 51% based on W).  $\text{H}_{174}\text{Eu}_6\text{K}_6\text{Na}_4\text{Nb}_{12}\text{O}_{331}\text{P}_8\text{W}_{60}$  (19103.15): calcd. H 0.92, Eu 4.77, K 1.23, Na 0.48, Nb 5.84, P 1.30, W 57.74; found H 0.85, Eu 4.85, K 1.35, Na 0.39, Nb 6.02, P 1.42, W 57.51. IR (KBr disks):  $\tilde{\nu} = 1620$  (w), 1090 (m), 953 (s), 916 (s), 762 (vs), 519 (s)  $\text{cm}^{-1}$ .

Table 1. Crystal data and structural refinement for compounds **1** and **2**.

Formula	H <sub>174</sub> K <sub>6</sub> Na <sub>4</sub> P <sub>8</sub> W <sub>60</sub> Nb <sub>12</sub> Eu <sub>6</sub> O <sub>331</sub>	H <sub>196</sub> K <sub>6</sub> Na <sub>4</sub> P <sub>8</sub> W <sub>60</sub> Nb <sub>12</sub> Ce <sub>6</sub> O <sub>342</sub>
Formula weight (g mol <sup>-1</sup> )	19102.58	19229.66
<i>T</i> (K)	296	296
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	18.0538(14)	18.105(5)
<i>b</i> (Å)	23.4546(18)	23.473(7)
<i>c</i> (Å)	23.685(3)	23.709(7)
$\alpha$ (°)	110.839(1)	110.545(4)
$\beta$ (°)	107.679(1)	107.824(4)
$\gamma$ (°)	105.035(1)	104.979(4)
<i>V</i> (Å <sup>3</sup> )	8134.7(14)	8191(4)
<i>Z</i>	1	1
<i>D</i> <sub>calcd.</sub> (Mg m <sup>-3</sup> )	3.859	3.849
$\mu$ (mm <sup>-1</sup> )	22.888	22.420
<i>F</i> (000)	8223.2	8270.0
Crystal size (mm)	0.24 × 0.23 × 0.23	0.24 × 0.23 × 0.23
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.997	0.983
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> <sup>[a]</sup> = 0.0686, <i>wR</i> <sub>2</sub> <sup>[a]</sup> = 0.1603	<i>R</i> <sub>1</sub> <sup>[a]</sup> = 0.0635, <i>wR</i> <sub>2</sub> <sup>[a]</sup> = 0.1481
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> <sup>[a]</sup> = 0.1295, <i>wR</i> <sub>2</sub> <sup>[a]</sup> = 0.1833	<i>R</i> <sub>1</sub> <sup>[a]</sup> = 0.1277, <i>wR</i> <sub>2</sub> <sup>[a]</sup> = 0.1727

[a]  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

**K<sub>6</sub>Na<sub>4</sub>H<sub>8</sub>[Ce<sub>6</sub>(H<sub>2</sub>O)<sub>38</sub>(P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>)<sub>4</sub>]-56H<sub>2</sub>O (2)**: The same procedure was followed as that for **1**, except for using CeCl<sub>3</sub>·7H<sub>2</sub>O instead of EuCl<sub>3</sub>·7H<sub>2</sub>O (yield: 57% based on W). H<sub>196</sub>Ce<sub>6</sub>K<sub>6</sub>Na<sub>4</sub>Nb<sub>12</sub>O<sub>342</sub>P<sub>8</sub>W<sub>60</sub> (19230.28): calcd. H 1.03, Ce 4.37, K 1.22, Na 0.48, Nb 5.80, P 1.29, W 57.36; found H 1.12, Ce 4.25, K 1.15, Na 0.33, Nb 5.69, P 1.43, W 57.58. IR (KBr disks):  $\tilde{\nu}$  = 1610 (w), 1090 (m), 955 (s), 910 (s), 766 (vs), 519 (s) cm<sup>-1</sup>.

**X-ray Crystallography**: Single-crystal diffractometry was conducted with a Bruker Smart Apex CCD diffractometer with Mo-*K*<sub>α</sub> monochromated radiation ( $\lambda$  = 0.71073 Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.<sup>[28]</sup> Empirical absorption corrections were applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on *F*<sup>2</sup> with SHELXS-97.<sup>[29]</sup> Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for some oxygen atoms. Those hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules were estimated by thermogravimetry and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. The crystal data and structure refinement results of **1** and **2** are summarized in Table 1. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-423718 (for **1**) and CSD-423719 (for **2**).

**Supporting Information** (see footnote on the first page of this article): Additional structural figures of **1**; TG curves and IR spectra of **1** and **2**; emission spectra of **2** and K<sub>8</sub>H[P<sub>2</sub>W<sub>15</sub>(NbO<sub>2</sub>)<sub>3</sub>O<sub>59</sub>]-12H<sub>2</sub>O; the digital photograph of **1** under UV irradiation; and cyclic voltammograms of **2**.

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