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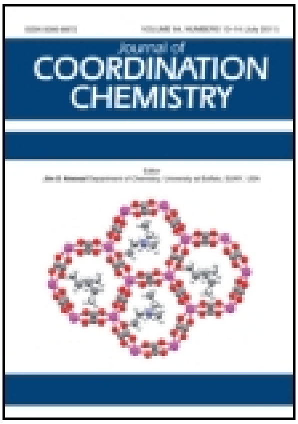

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pH-Controlled assembly of two polyoxometalate chains based on $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ and Eu^{3+}: syntheses, crystal structures, and properties

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pH-Controlled assembly of two polyoxometalate chains based on [α-$GeW_{11}O_{39}$]$^{8-}$ and Eu^{3+}: syntheses, crystal structures, and properties

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Utilizing reactions of [α-$GeW_{11}O_{39}$]$^{8-}$ and Eu^{3+} under different pH conditions, two types of polymer chains, $Cs_3K[Eu_4(H_2O)_{18}Ge_2W_{22}O_{78}]\cdot 16.5H_2O$ (**1**) and $Cs_3K_2[Eu(H_2O)_2GeW_{11}O_{39}]\cdot 10H_2O$ (**2**), have been isolated and characterized by elemental analysis, IR spectroscopy, thermal analysis, and single-crystal X-ray diffraction. The Eu/[α-$GeW_{11}O_{39}$]$^{8-}$ ratio is 1 : 1 in polyanion **2a** and is an infrequent 2 : 1 in polyanion **1a**. The Ln : POM ratio can be increased by controlling the reaction conditions. The solid photoluminescence spectra of **1** and **2** have been investigated at room temperature. The luminescence of **1** and **2** are distinctly different owing to their different Eu coordination geometries. UV spectra and electrochemical properties of **1** and **2** have been investigated. Compound **1** displays good electrocatalytic activity toward the reduction of nitrite.

Keywords: Cluster compounds; Europium; Luminescence; Polyoxometalates; Self-assembly

1. Introduction

Polyoxometalates (POMs), discrete anionic metal–oxygen clusters, are remarkable for their molecular and electronic structural diversity [1, 2]. They have a wide range of properties and significant applications in many fields, including catalysis, medicine, and materials science [3–5]. Because of the multiple coordination requirements and high-oxophilic activities of lanthanide (Ln) ions, they are suitable for linking POM building blocks to form new classes of materials with extended metal–oxygen frameworks. Furthermore, lanthanides can impart useful functionality such as luminescence [6], magnetism [7], and Lewis acid catalysis [8] to POMs, which extend the range of physical and chemical properties of the resulting lanthanide-containing POMs.

In 1971, Peacock and Weakley first proposed that monovacant Keggin anions $[XW_{11}O_{39}]^{n-}$ ($X = Si^{IV}$, P^{V}) form both 1 : 2 and 1 : 1 (lanthanide : POMs) compounds with lanthanide ions in solution [9]. For a period of time, only 1 : 2 complexes were isolated and characterized. Finally, Pope *et al.* [10] reported the structural

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characterization of a 1-D 1 : 1 compound, $[Ln(R\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{3+}$, Ce^{3+}), and showed that these anions are polymeric in the solid state, provoking interest in Ln/monovacant POM systems [11, 12]. This work was mainly on conventional 1 : 1 and 1 : 2 configurations and species of other ratios were rarely reported.

Among the monolacunary Keggin anions, although the monolacunary germanotungstate $[GeW_{11}O_{39}]^{8-}$ was reported for the first time by Hervé and Tézé [13], derivatives based on the monovacant germanotungstate are less reported. Tourné *et al.* [14] reported the first example of the lanthanide derivative of the monolacunary germanotungstate, $Cs_{12}[U(GeW_{11}O_{39})_2] \cdot 13\text{–}14H_2O$. Liu *et al.* [15] reported a series of compounds of bis(undecatungstogermanate) lanthanides, in which all the anions have a structure similar to that of $Cs_{12}[U(GeW_{11}O_{39})_2] \cdot 13\text{–}14H_2O$. Recently, Niu *et al.* [16, 17] reported a series of compounds based on the monovacant polyanion $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ and lanthanide ions including organic–inorganic hybrids based on the lanthanide-substituted germanotungstates. $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ has larger bite angle in the vacant site than that of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$, and this is favorable to accommodate lanthanide cations [17, 18]. So it is interesting and challenging to break through the conventional 1 : 1 and 1 : 2 configurations in Ln/monovacant POM systems, especially in the Ln/monovacant germanotungstate system. In this article, we report the synthesis, structures, and properties of two polyoxometalate chains based on monovacant germanotungstate and Eu, $Cs_{3.5}K_{0.5}[Eu_4(H_2O)_{18}Ge_2W_{22}O_{78}] \cdot 18H_2O$ (**1**) and $Cs_3K_2[Eu(H_2O)_2GeW_{11}O_{39}] \cdot 14H_2O$ (**2**). Compounds **1** and **2** both display 1-D chain-like structure and **2** possesses an infrequent 2 : 1 Ln/POM configuration. The pH plays an important factor in their synthesis. They display different photoluminescence properties owing to different coordinate environments of Eu in **1** and **2**.

2. Experimental

2.1. *Materials and measurement*

The precursor $\alpha\text{-}K_8GeW_{11}O_{39} \cdot nH_2O$ was prepared according to the literature [19] and confirmed by IR spectroscopy. All other reagents were readily available from commercial sources and used as-received. IR spectra in KBr pellets were recorded from 400 to 4000 cm^{-1} with an Alpha Centaurt FT/IR spectrophotometer. Ge, W, Cs, Eu, and K analyses were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Thermogravimetric (TG) analyses were carried out using a Perkin-Elmer TGA7 instrument, with a heating rate of 10°C min^{-1}, under nitrogen. Photoluminescence spectra were measured using an FLSP 920 Edinburgh instrument (Eng) with 450 W Xenon lamp monochromated by double grating.

2.2. *Syntheses*

2.2.1. $Cs_{3.5}K_{0.5}[Eu_4(H_2O)_{18}Ge_2W_{22}O_{78}] \cdot 18H_2O$ (1). A 1.52 g (0.5 mmol) sample of $\alpha\text{-}K_8GeW_{11}O_{39} \cdot nH_2O$ was dissolved in 25 mL of water at 70°C, followed by dropwise addition of 0.30 g (1.16 mmol) of $EuCl_3$ in 5 mL of NaOAc/HOAc buffer (1.0 mol L^{-1} pH 3.5). The pH of the solution was carefully adjusted to 5.8 with 1 mol L^{-1} K_2CO_3.

After 1 h, 0.5 mL CsCl solution (2 mol L^{-1}) was added dropwise. The resulting solution was cooled to room temperature and the precipitate was removed by filtration. The filtrate was left to evaporate at room temperature. Colorless block crystalline product started to appear within 5 days (Yield: 72%). IR (KBr disks): 958(s), 889(s), 816(s), 767(s), 525(w), 462(w). Elemental Anal. Calcd for $Cs_{3.5}K_{0.5}[Eu_4(H_2O)_{18}Ge_2W_{22}O_{78}] \cdot 18H_2O$ (**1**): K, 0.27; Ge, 2.02; Cs, 6.48; Eu, 8.47; W, 56.34. Found: K, 0.35; Ge, 1.89; Cs, 6.95; Eu, 8.42; W, 56.71.

2.2.2. $Cs_3K_2[Eu(H_2O)_2GeW_{11}O_{39}] \cdot 14H_2O$ (2). A 1.52 g (0.5 mmol) sample of α-$K_8GeW_{11}O_{39} \cdot nH_2O$ was dissolved in 30 mL of water at 70°C, followed by dropwise addition of 0.2 g (0.78 mmol) of $EuCl_3$ dissolved in 5 mL of water. After 1 h, 0.5 mL of CsCl solution (2 mol L^{-1}) was added dropwise. The resulting solution was cooled to room temperature and a small amount of precipitate was removed by filtration. The filtrate (final pH 4.0) was left to evaporate at room temperature. Colorless block crystalline product started to appear within 5 days (Yield: 86%). IR (KBr disks): 953(s), 875(s), 815(s), 772(s), 526(w), 459(w). Elemental Anal. Calcd for $Cs_3K_2[Eu(H_2O)_2GeW_{11}O_{39}] \cdot 14H_2O$ (**2**): K, 2.15; Ge, 2.00; Cs, 10.97; Eu, 4.18; W, 55.62. Found: K, 1.98; Ge, 1.88; Cs, 11.15; Eu, 4.22; W, 55.38.

2.3. *X-ray crystallography*

Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD diffractometer with Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [20]. Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through full matrix least-squares on F^2 using SHELXS-97 [21]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception for some oxygen atoms. Those hydrogen atoms attached to lattice water were not located. Crystallization of water molecules were estimated by thermogravimetry and only partial oxygen atoms of water were found with the X-ray structure analysis. The crystal data and structure refinement results of **1** and **2** are summarized in table 1 (Supplementary material).

3. Results and discussion

3.1. *Synthesis*

Compounds **1** and **2** were synthesized by similar synthetic procedure, with the only difference that they were obtained at different pHs. Pure crystal of **2** can be obtained in the pH range of 3.0–4.8. Increasing the pH of the reaction solution above 5.5, crystals of **1** can be obtained. Note that in the synthesis of **2**, Eu^{3+} was introduced to the reaction system by dissolving $EuCl_3$ in water and then adding dropwise to the reaction system. Adjusting the acidity of the reaction solution of **2** above pH 5.5 results in massive deposition and only simple germanotungstate containing no Eu can be obtained.

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

Formula	$Cs_7Eu_8Ge_4KO_{225.5}W_{44}$	$Cs_6Eu_2Ge_2K_4O_{98.50}W_{22}$
Formula weight ($gmol^{-1}$)	14,172.63	7023.50
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	16.8068(3)	11.937(5)
b	17.6347(3)	12.613(5)
c	18.0764(4)	18.188(5)
α	76.583(2)	76.633(5)
β	85.763(2)	82.787(5)
γ	86.092(1)	85.904(5)
Volume (Å^3), Z	5189.88(18), 1	2640.6(17), 1
Calculated density ($Mg\,m^{-3}$)	4.535	4.417
Absorption coefficient (mm^{-1})	28.562	27.874
$F(000)$	6096.0	3012.0
Crystal size (mm^3)	0.18 × 0.18 × 0.16	0.20 × 0.20 × 0.14
Goodness-of-fit on F^2	1.007	1.058
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0626$, $wR_2{}^a = 0.1585$	$R_1{}^a = 0.0793$, $wR_2{}^a = 0.2223$
R indices (all data)	$R_1{}^a = 0.0844$, $wR_2{}^a = 0.1642$	$R_1{}^a = 0.1030$, $wR_2{}^a = 0.2325$

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

However, this can be avoided by dissolving $EuCl_3$ in 5 mL of NaOAc/HOAc buffer, which was then added dropwise to the reaction system (as shown in the synthesis of **1**). Though there is no acetic acid in the structure of **1**, acetic acid plays an important role in the formation and crystallization of **1**.

3.2. *Structure description*

The polymeric structure of the two polyanions (**1a** and **2a**) have analogous structures consisting of 1-D chains based on $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ building blocks. The linear structures are further connected by potassium and cesium ions, yielding an extended network of parallel chains.

The striking structural feature of **1a** is that there are three kinds of coordination environments for Eu, EuI, EuII and EuIII (figure 1), which are responsible for the formation of polymeric structures. EuI (Eu2 and Eu4 in the crystal data have similar coordination environment with only slight differences in bond length and bond angle) reside in the vacancy of the polyanions, bound to two adjacent $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ subunits *via* two O_d oxygen atoms (dEu1-O = 2.39–2.48 Å). Two water molecules complete the coordination sphere of EuI, which is eight-coordinate adopting a distorted Archimedean antiprism geometry. Compound **1a** adopts a 1-D arrangement with zigzag chains directed along the a axis (figure 1). EuII and EuIII reside at the gaps of adjacent $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ subunits. Comparing with **1a**, EuII and EuIII are absent in **2a** and only Eu1 exists, which resides in the vacancy and connects the polyanions to a 1-D chain. The structure of polyanion **2a** is closely related to that previously reported for $(NH_4)_5[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]$ by Pope *et al.* [10] and $Na_{0.5}Cs_{4.5}[Eu(\alpha\text{-}SiW_{11}O_{39})(H_2O)_2]$ by Sécheresse *et al.* [11]. A comparison between **2a** and the Si analogs in the structure of their vacant sites is shown in table S2, which indicates

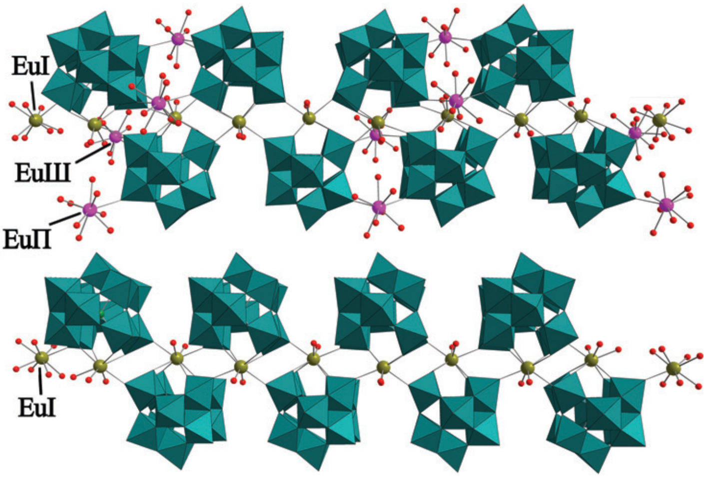

Figure 1. Polyhedral representation of polyanions **1a (top)** and **2a (bottom)**, forming 1-D chains in the solid state. EuI in **1a** and **2a** are shown in dark yellow; EuII and EuIII are shown in pink. WO_6 octahedra (teal), O (red).

the vacancy in **2a** is larger than that in Si analogs. The shortest intrachain EuI–EuI distances are 6.33 Å, 6.42 Å for **1a** and 6.52 Å, 6.69 Å for **2a**, respectively. The Ge–Ge distance in **2a** is 11.94 Å; however, the average Ge–Ge distance in **1a** is 11.75 Å. The combination of EuII and EuIII makes the Ge–Ge distance in **1a** remarkably shorter than that in **2a**. Every EuI in both **1a** and **2a** is eight-coordinate (see table S1) and links to six O_t(W) (terminal O bonded to W) and two terminal water molecules. EuII and EuIII in **1a** are nine-coordinate, to two O_t(W) and seven terminal water molecules. Bond valence sums (BVS) analysis suggests that in **1** and **2** all Ge's are in the +4 oxidation state, all W's are in the +6 oxidation state, and the Eu sites are in +3 oxidation state.

3.3. *FTIR spectroscopy and TG analysis*

As shown in figure 2, IR spectra of **1** and **2** are very similar, showing the characteristic asymmetric vibration patterns of the Keggin heteropolyanion in the low-wavenumber region ($<1000\,cm^{-1}$) [22–24], ν_{as}(W–O_d), ν_{as}(W–Ob), ν_{as}(W–Oc), and ν_{as}(Ge–Oa) [25], appearing at 958(s), 889(s), 816(s), 767(s), 525(w) for **1** and 953(s), 875(s), 815(s), 772(s), 526(w) for **2**. In comparison with the parent anion $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$, the ν_{as}(W–O_d) vibration frequencies have red shifts of 64 and 65 cm^{-1}. The major reason may be that the lanthanide cations have stronger interactions to terminal oxygen atoms of the polyoxoanions, impairing the W–O_d bond, reducing the W–O_d bond force constant, leading to a decrease in the W–O_d vibration frequency.

Thermal behaviors of **1** and **2** have been studied by TG measurements. The TG curves of **1** and **2** (figure 3) exhibit one step of weight loss. From 30°C to 300°C, the weight loss of **1** is 8.2% (Calcd 7.9%) and the weight loss of **2** is 9.1% (Calcd 9.0%), corresponding to the release of crystal water and coordination water molecules [26–28].

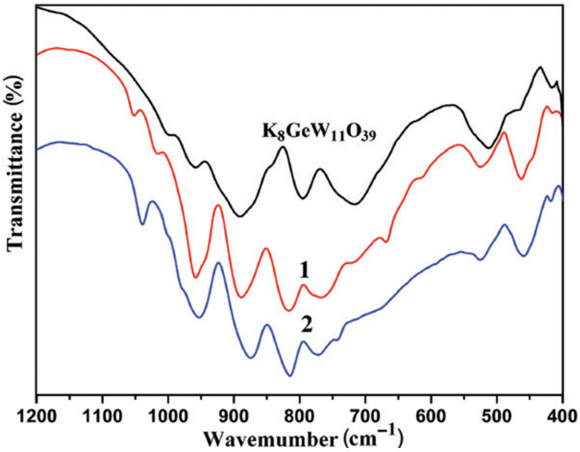

Figure 2. IR spectra of $K_8GeW_{11}O_{39}$, **1** and **2**.

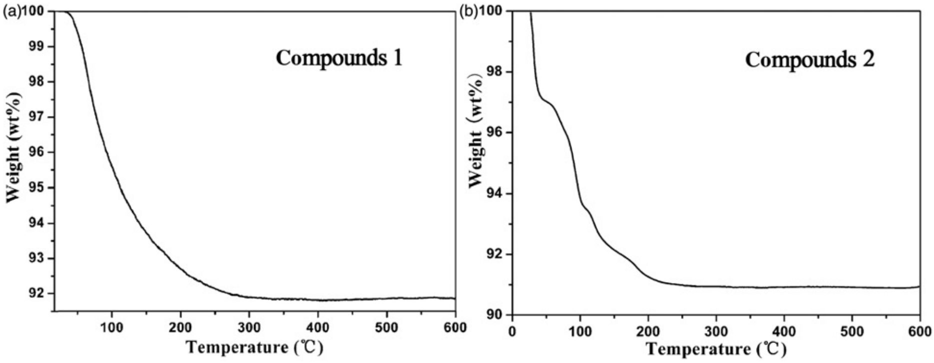

Figure 3. TG curve of **1** (a) and **2** (b).

3.4. *Photoluminescence properties*

Solid photoluminescence spectra of **1** and **2** have been measured at room temperature. Under the excitation wavelength (394 nm), the solid emission spectra of **1** and **2** (figure 4) both exhibit the characteristic transitions of Eu^{3+} (at 579, 592, 616, 651, 698 nm for **1** and at 579, 592, 613, 651, 699 nm for **2**), corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4), respectively. The spectrum of **2** is similar with the previously reported data for $Na_{0.5}Cs_{4.5}[Eu(\alpha\text{-}SiW_{11}O_{39})(H_2O)_2]$ [11]. The $^5D_0 \rightarrow {}^7F_0$ transition corresponds to the symmetry-forbidden emission, which is strictly forbidden in a field of symmetry. The presence of $^5D_0 \rightarrow {}^7F_0$ transition in **1** and **2** reveals that the site symmetry of Eu^{3+} is low without an inversion center in **1a** and **2a**. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are ascribed to magnetic and electric dipole transitions, respectively. The former mainly depends on the ligand field strength acting on Eu^{3+} and is fairly insensitive to the coordination environment of the Eu^{3+}, while the latter that corresponds to the strongest emission at 614 nm is quite sensitive to chemical bonds in the vicinity of Eu^{3+},

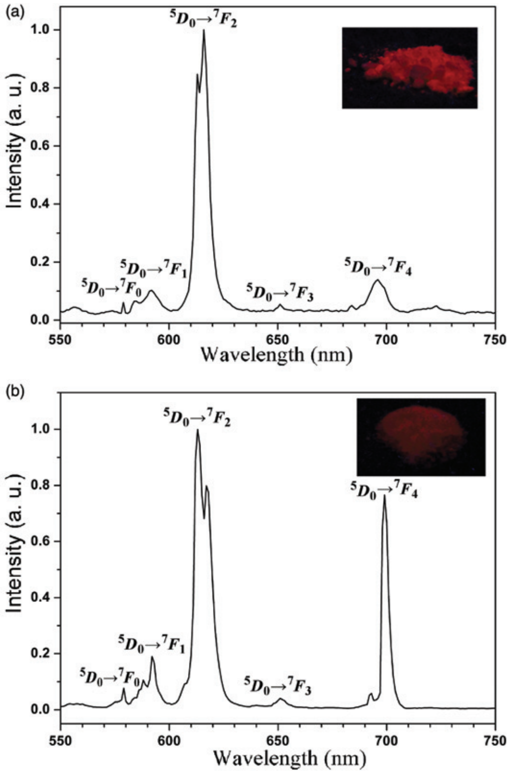

Figure 4. The emission spectrum ($\lambda_{ex} = 394$ nm) of **1** (a) and **2** (b) at solid sate (inset: digital photographs of **1** and **2** under UV irradiation (365 nm)).

increasing as the site symmetry of Eu^{3+} decreases. Consequently, the $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ ratio is widely used as a measure of the coordination state and site symmetry of lanthanide [29–32]. This ratio for **1** is bigger than **2,** indicating lower symmetry in **1** than **2**, which is consistent with the results of the single-crystal X-ray analysis. The solution photoluminescence spectra of **1** and **2** were not detected for two possible reasons. First, the fluorescence may be strongly quenched in water, upon coupling with OH oscillators [33]. Second, **1** and **2** both contain Cs^+ as counterions, so their solubility is low.

Under the UV irradiation (365 nm), **1** exhibits remarkable red fluorescent emission. However, under the same conditions, the emission is extremely weak for **2** (see figure S4 and the inset of figure 4). To explain this, we studied detailed bond angles and coordination geometries of the Eu^{3+} centers for **1** and **2**. It has been reported that the emission efficiency of Eu^{3+} is strongly interrelated with the Eu–O–W bond angles of approximately 150° for Eu-containing POMs, as this angle allows for effective d^1 hopping through $f\pi$–$p\pi$–$d\pi$ orbital mixing [6]. As shown in table S1, the Eu–O–W bond angles in **1** are closer to 150° than that in **2**. The presence of these Eu–O–W bonds, especially for bond angles of 149.6° and 151.9° in **1**, is responsible for the intense red luminescence.

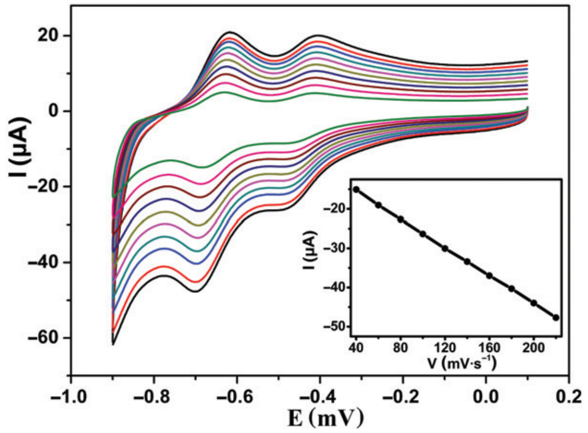

Figure 5. The UV-Vis spectra of **1** (2.1×10^{-3} mol L^{-1} in water) at different pHs. The initial pH was adjusted with aqueous HCl and was adjusted to 5.8–7.4 by careful addition of K_2CO_3 solution (0.1 mol L^{-1}).

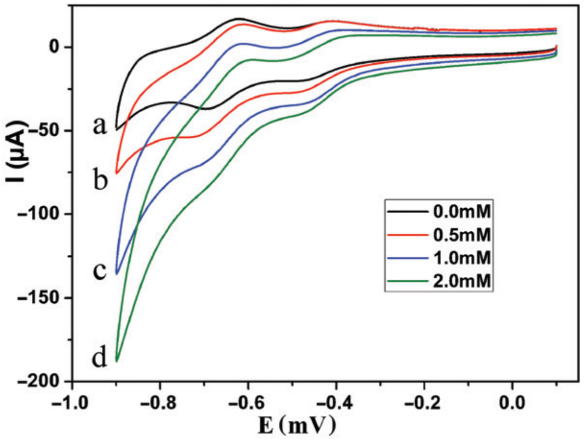

Figure 6. Cyclic voltammogram of **1** in NaOAc/HOAc buffer (0.5 mol L^{-1} pH 5.8) at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, and 220 mVs^{-1}). The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

3.5. *UV-Vis spectra and electrochemistry properties*

The UV spectra of **1** and **2** in aqueous solution were studied from 200 to 400 nm. Absorption spectra of **1** and **2** exhibit peaks centered at 261 nm and 257 nm, respectively (figures S7 and S8), assigned to pπ–dπ charge–transfer transitions of the $O_{b(c)}$–W bond [34, 35]. It is interesting to observe that (as shown in figure 5) above pH 6.8, absorption spectra of **1** remarkably changed, shifting to low wavelength (~254 nm), which may be a result of the disassembly of **1**.

The electrochemical properties of **1** were investigated in NaOAc/HOAc buffer (1.0 mol L^{-1} pH 5.8) at room temperature. Two one-electron reversible redox processes I–I', II–II' at $E_{1/2} = -444.3$ mV, −659.0 mV arise from W centers [36]. Taking the

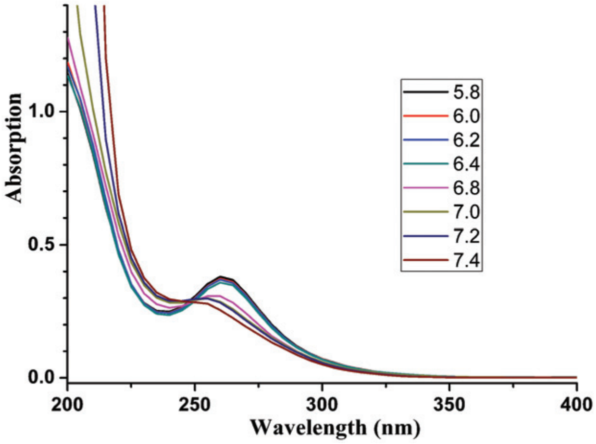

Figure 7. Electrocatalytic reduction of NO^{2-} in the presence of 1.0 mM **1** in NaOAc/HOAc buffer (1.0 mol L^{-1} pH 5.8), at a scan rate of 200 mVs^{-1}, containing NO^{2-} concentrations of 0.0 mmol L^{-1} (a), 0.5 mmol L^{-1} (b), 1.0 mmol L^{-1} (c), and 2.0 mmol L^{-1} (d). The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

reduction peak (II) of **1** as representative, at scan rates lower than 200 mV s^{-1}, the peak currents were proportional to the scan rate, which indicates that the redox process of **1** is surface-controlled (figure 6). Electrochemical properties of **2** (investigated in NaOAc/HOAc buffer (1.0 mol L^{-1}, pH 4.0) at room temperature) are similar to **1**. Two one-electron reversible redox processes I–I′, II–II′ at $E_{1/2} = -0.448$ mV, -667 mV were observed. As shown in figure S9, the redox process of **2** is also surface-controlled.

The electrocatalytic activity of **1** toward the reduction of NO^{2-} was tested in 1.0 mol L^{-1} NaOAc/HOAc buffer (1.0 mol L^{-1}, pH 5.8). As shown in figure 7, with the addition of nitrite, all the reduction peak currents gradually increase while the corresponding oxidation peak currents decrease, which indicates that the reduced species of the polyoxoanions show electrocatalytic activities toward reduction of nitrite.

4. Conclusions

Two lanthanide-containing POM chains based on monovacant germanotungstate and Eu^{3+} have been synthesized from conventional synthesis under different pH conditions. The Eu/[α-$GeW_{11}O_{39}$]$^{8-}$ ratio is 1 : 1 in the anion of **2** (**2a**) and is the infrequent 2 : 1 in the anion of **1** (**1a**). The Ln : POM ratio can be increased by controlling the reaction conditions. Luminescence properties of **1** and **2** are distinctly different owing to the different coordinate environments of Eu. The UV spectra of **1** were very sensitive to the change of pH. The results of the electrocatalysis studies indicate that **1** displays good electrocatalytic activity toward the reduction of nitrite.

Supplementary material

CSD-423155 (**1**) and CSD-423156 (**2**) contain the supplementary crystallographic data for this article. The data can be obtained free of charge from Fachinformationszentrum

Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (http://www.fiz-karlsruhe.de/request_for_deposited_data.html). Additional figures and X-ray crystallographic information files (CIF) are available.

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[25] Oa is the oxygen atom bond to the Ge atom, Ob is the bridging oxygen atom shared by two W atoms of different W_3O_{13} clusters, Oc is thebridging oxygen atom shared by two W atoms from the same W_3O_{13} cluster, Od is the terminal oxygen atom combined with only one W atom.
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