

# Reactivity of Polyoxoniobates in Acidic Solution: Controllable Assembly and Disassembly Based on Niobium-Substituted Germanotungstates

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**Abstract:** The reactivity of polyoxoniobates has been studied in acidic solution by grafting niobium onto trivacant Keggin-type germanotungstates. Four niobium-containing compounds were obtained in the course of this study.  $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9(\text{NbO}_2)_3\text{O}_{37}]\cdot 6\text{H}_2\text{O}$  ( $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$ ) synthesized by the reaction of  $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]$  and  $\text{A-}\alpha\text{-Na}_{10}\text{-}[\text{GeW}_9\text{O}_{34}]$  in  $\text{H}_2\text{O}_2$  solution is a tris-(peroxoniobium)-substituted  $\text{A-}\alpha\text{-GeW}_9$  derivative.  $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9\text{Nb}_3\text{O}_{40}]\cdot 10\text{H}_2\text{O}$  ( $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$ ) is a peroxy-free compound obtained by eliminating the peroxy groups in **1**. Monomers **1** and **2** as precursors can each afford two

nanoscale POMs, dimer  $\text{Cs}_5[\text{H}_{15}\text{Ge}_2\text{W}_{18}\text{Nb}_8\text{O}_{88}]\cdot 18\text{H}_2\text{O}$  ( $\text{Cs}_5\text{-3}$ ) and tetramer  $\text{Cs}_8\text{K}_3\text{H}_9[\text{Ge}_4\text{W}_{36}\text{Nb}_{16}\text{O}_{166}]\cdot 27\text{H}_2\text{O}$  ( $\text{Cs}_8\text{K}_3\text{H}_9\text{-4}$ ), through the formation of Nb–O–Nb bridges. Disassembly through the cleavage of Nb–O–Nb bonds from **4** to **2** and **1** was achieved by controlling the pH and by adding  $\text{H}_2\text{O}_2$ , respectively. The transition from **1** to **2** can be achieved by simply adding  $\text{H}_2\text{O}_2$  to a solution of **1**.

**Keywords:** cluster compounds • nanostructures • niobium • polyoxometalates • reactivity

All four compounds were characterized in the solid state by elemental analysis, infrared spectroscopy, thermogravimetry, and single-crystal X-ray diffraction.  $^{183}\text{W}$  NMR analysis proved that the solid-state structures of polyanions **1–4** were retained after dissolution. Disassembly from **4** to **1** and **2** in solution was observed by  $^{183}\text{W}$  NMR spectroscopy. The UV/Vis spectra of **1** at different pH confirmed that it is stable in the pH range of 0.1–14.0 at room temperature.

## Introduction

The synthesis and reactivity of polyoxoniobates are important in polyoxometalate (POM) chemistry owing to their unique characteristics and potential applications in diverse areas such as nuclear waste treatment, antiviral therapy, and catalysis.<sup>[1–3]</sup> Unlike POMs based on molybdenum or tungsten, which have been well examined under acidic conditions,<sup>[4]</sup> the study of polyoxoniobates have been dominated for a very long time by the Lindquist  $[\text{Nb}_6\text{O}_{19}]^{8-}$  ion, which exists only under alkaline conditions, forming  $\text{Nb}_2\text{O}_5$  precipi-

tates under acidic conditions, and this has severely restricted the development of polyoxoniobates.<sup>[5]</sup> However, great progress has been made in polyoxoniobate chemistry in recent years owing to the discovery and development of heteropoly-niobates by Nyman and co-workers,<sup>[6]</sup> the research presented by Casey and co-workers,<sup>[7]</sup> and the recent reports on  $[\text{Nb}_{20}\text{O}_{54}]^{8-}$ ,<sup>[8]</sup>  $[\text{H}_9\text{Nb}_{24}\text{O}_{72}]^{15-}$ ,<sup>[9]</sup>  $[\text{Nb}_7\text{O}_{22}]^{9-}$ ,<sup>[10a]</sup>  $[\text{Cu}(\text{H}_2\text{O})\text{L}]_2(\text{CuNb}_{11}\text{O}_{35}\text{H}_4)^{5-}$  (L = 1,10-phenanthroline, 2,2'-bipyridine),<sup>[10b]</sup>  $[\text{HNb}_{27}\text{O}_{76}]^{16-}$  and  $[\text{H}_{10}\text{Nb}_{31}\text{O}_{92}(\text{CO}_3)]^{23-}$ .<sup>[11]</sup> However, the development of polyoxoniobate chemistry is still at an early stage and is dominated by reactions performed under alkaline and mainly hydrothermal conditions. The potential of polyoxoniobates is expected to be explored in acidic solution in which other POMs and transition-metal and lanthanide ions widely exist.

Inspired by the work of Finke<sup>[3c,d,12]</sup> and Hill<sup>[13]</sup> and their co-workers, we considered that niobium-substituted POMs synthesized by the reaction of lacunary POMs and  $[\text{Nb}_6\text{O}_{19}]^{8-}$  in  $\text{H}_2\text{O}_2$  solution are appropriate candidates for studying polyoxoniobates in acidic solution. Interestingly,  $\text{H}_2\text{O}_2$ , which is used to solubilize the  $\text{Nb}^{5+}$  and prevent the formation of  $\text{Nb}_2\text{O}_5$  under acidic conditions, allows the graft-

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ing of peroxo groups onto the niobium atoms of the products.<sup>[3c,12a]</sup> The terminal oxygen atoms (O<sub>t</sub>) bonded to the niobium atoms are nucleophilic and the Nb–O bonds are labile.<sup>[14,15]</sup> Once the peroxo groups have been eliminated, the exposed NbO<sub>6</sub> units become the reactive center of the POM. Therefore some novel reactions can be expected and rationally designed. For example, if a way to realize the self-aggregation of niobium is found, the lacunary POM segments will be aggregated. This will not only result in high-nuclearity niobium clusters, but also provide a strategy for the design and synthesis of giant POM assemblies.

In this work we chose trivalent Keggin-type germanotungstate as the niobium carrier, obtaining the tris(peroxoniobium)-containing compound Cs<sub>6.5</sub>K<sub>0.5</sub>[GeW<sub>9</sub>(NbO<sub>2</sub>)<sub>3</sub>O<sub>37</sub>]·6H<sub>2</sub>O (Cs<sub>6.5</sub>K<sub>0.5</sub>-**1**) and the peroxo-free compound Cs<sub>6.5</sub>K<sub>0.5</sub>[GeW<sub>9</sub>Nb<sub>3</sub>O<sub>40</sub>]·10H<sub>2</sub>O (Cs<sub>6.5</sub>K<sub>0.5</sub>-**2**). Used as precursors, these two monomers assemble to form two nano-scale POMs, dimeric Cs<sub>5</sub>[H<sub>15</sub>Ge<sub>2</sub>W<sub>18</sub>Nb<sub>8</sub>O<sub>88</sub>]·18H<sub>2</sub>O (Cs<sub>5</sub>-**3**) and tetrameric Cs<sub>8</sub>K<sub>3</sub>H<sub>9</sub>[Ge<sub>4</sub>W<sub>36</sub>Nb<sub>16</sub>O<sub>166</sub>]·27H<sub>2</sub>O (Cs<sub>8</sub>K<sub>3</sub>H<sub>9</sub>-**4**), by the self-aggregation of niobium grafted onto the {GeW<sub>9</sub>O<sub>34</sub>} fragment. The disassembly of **4** to monomers **1** and **2** occurred by cleavage of the Nb–O–Nb bonds. The conditions of assembly and disassembly have been studied in detail.

## Results and Discussion

The structures of compounds **1–4** were determined by single-crystal X-ray diffraction. Polyanion **1** is a tris(peroxoniobium)-substituted A- $\alpha$ -GeW<sub>9</sub> derivative. Each of the three niobium atoms is ligated by five oxygen atoms and one terminal  $\eta^2$ -coordinated peroxo unit. The average O–O distance in the peroxo groups in **1** (1.48 Å) is comparable to the bond length observed in the crystal structure of hydrogen peroxide (1.49 Å)<sup>[16]</sup> and similar to those in the peroxo groups in other reported POMs.<sup>[4c,13a–c,17]</sup> Two [GeW<sub>9</sub>(NbO<sub>2</sub>)<sub>3</sub>O<sub>37</sub>]<sup>7-</sup> units are linked by a six-coordinated potassium ion forming a sandwich-like structure (see Figure S1-1 of the Supporting Information). The coordination of the potassium ion may stabilize the peroxo groups in the solid state and indicates the strong coordination ability of the peroxo groups. The peroxo-free polyanion **2** has a perfect Keggin structure. There is crystallographic orientational disorder and the metal sites are statistically occupied by tungsten and niobium in anion **2**. As shown in Figure 1, the polyanion **3**, with a length of about 1.89 nm, has perfect C<sub>2h</sub> symmetry. It includes a cubic-like Nb<sub>8</sub>O<sub>12</sub> core sandwiched between two A- $\alpha$ -GeW<sub>9</sub> Keggin moieties. The Nb<sub>8</sub>O<sub>12</sub> core, made up of two equivalent {Nb<sub>4</sub>O<sub>4</sub>} quadrangle units that are linked by four  $\mu_2$ -O atoms, has never previously been observed in polyoxoniobates. And the analogous cubic-like structure has not been reported in the well-studied transition-metal-substituted POMs. The eight niobium atoms in the Nb<sub>8</sub>O<sub>12</sub> core can be divided into two groups (NbA: Nb3(a), Nb4(a); NbB: Nb1(a), Nb2(a)) in accord with the positions in the NbO<sub>6</sub> octahedra (Figure 1b). NbA atoms are located at the

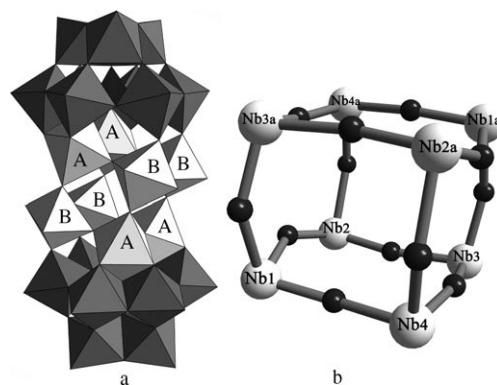


Figure 1. (a) Polyhedral representation of polyanion **3**. (b) Ball-and-stick representation of the central Nb<sub>8</sub>O<sub>12</sub> core in **3**. NbA: Nb3(a), Nb4(a), NbB: Nb1(a), Nb2(a). NbA is located at the vacant sites of the {GeW<sub>9</sub>O<sub>34</sub>} units. The WO<sub>6</sub> octahedra are shown in gray, GeO<sub>4</sub> octahedron in black, NbO<sub>6</sub> octahedra in white, and the balls represent niobium (white), and oxygen (black).

vacant sites of the {GeW<sub>9</sub>O<sub>34</sub>} units with no terminal ligands, whereas every NbB has two terminal *cis* oxygen ligands, which is infrequent in polyoxoniobate chemistry. As far as we know, only the {Nb<sub>24</sub>} cluster ([H<sub>9</sub>Nb<sub>24</sub>O<sub>72</sub>]<sup>15-</sup> reported by Bontchev and Nyman<sup>[9]</sup> and [K<sub>0.5</sub>Nb<sub>24</sub>O<sub>72</sub>H<sub>14.5</sub>] reported by Wang et al.<sup>[10c]</sup>) possesses a niobium atom with two terminal oxygen ligands, in contrast to the two terminal oxygen atoms (with BVS values of 0.2–0.3) in the {Nb<sub>24</sub>} cluster located at two *trans* positions. The exposed terminal oxygen ligands bonded to NbB may be active sites for replacement by a variety of organic ligands or binding the electrophilic reagents. The bond valence sums (BVS) for **3** (see Figures S1–4 of the Supporting Information) show that the BVS values are 0.41–0.44 for eight terminal oxygen atoms (with Nb–O<sub>t</sub> bonds 2.215–2.237), which indicates the most likely sites for protonation. In addition, the BVS values of –1.48 to –1.65 for 10 O<sub>t</sub>(W) suggest that some terminal oxygen atoms bonded to tungsten atoms may be monoprotonated. Although they cannot be accurately located from the BVS values or by X-ray diffraction, these protons must be localized or delocalized in the polyanion.<sup>[9,18]</sup> Polyanion **4** can be described as a tetramer consisting of one Nb<sub>4</sub>O<sub>6</sub> core and four {GeW<sub>9</sub>Nb<sub>3</sub>O<sub>40</sub>} Keggin units (Figure 2). They are con-

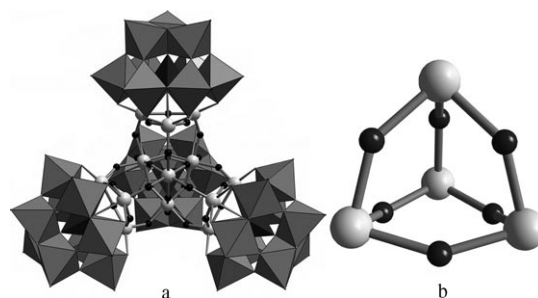
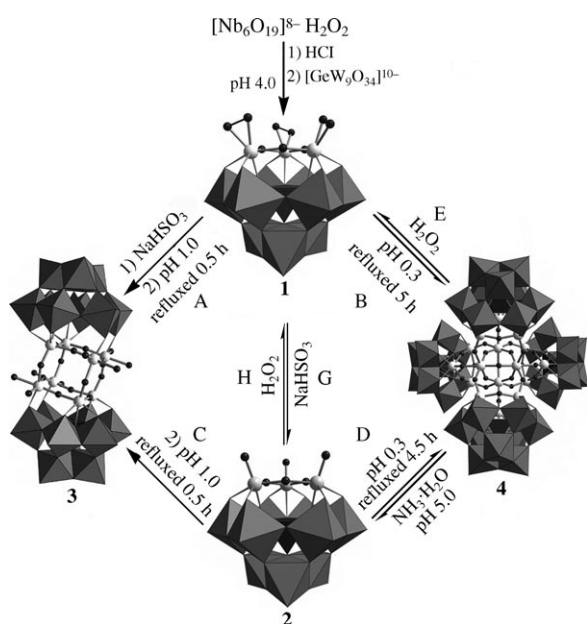


Figure 2. (a) Combined polyhedral/ball-and-stick representation of polyanion **4**. (b) Ball-and-stick representation of the central Nb<sub>4</sub>O<sub>6</sub> core in **4**. The color code is the same as in Figure 1.

nected by 12 Nb–O–Nb bridges, which are formed between four Nb<sub>3</sub>–O<sub>3</sub> faces of the {Nb<sub>4</sub>O<sub>6</sub>} core and Nb<sub>3</sub> clusters of the four [GeW<sub>9</sub>Nb<sub>3</sub>O<sub>40</sub>]<sup>7-</sup> Keggin units. The structure of the polyanion **4** with approximate *T<sub>d</sub>* symmetry can be viewed as a tetrahedron: A {Nb<sub>16</sub>O<sub>30</sub>} core lies in the center, four {GeW<sub>9</sub>O<sub>34</sub>} units are located at four vertices, and the vertex–vertex distance is about 2.13 nm (see Figures S1–3 of the Supporting Information). BVS analysis based on the observed bond lengths for **1**, **3**, and **4** suggests the formal valences of W<sup>6+</sup>, Nb<sup>5+</sup>, and Ge<sup>4+</sup>, respectively.

The synthesis of **1–4** and the transformations between them were achieved by strictly controlling the reaction conditions, as shown in Scheme 1. The peroxo-containing com-



Scheme 1. Synthesis of **1–4** and the interconversions between them (the eight reaction routes are labeled as letters **A–H**). The color code is the same as in Figure 1.

pound (Cs<sub>6.5</sub>K<sub>0.5</sub>-**1**) was prepared by the reaction of [GeW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup> and [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> in H<sub>2</sub>O<sub>2</sub> solution. By dissolving Cs<sub>6.5</sub>K<sub>0.5</sub>-**1** in 0.5 M HCl solution (pH~0.3) and heating the mixture at reflux for 5 h, it assembled to tetramer **4** (Route B in Scheme 1). By adjusting the pH of the solution of **4** with ammonia to pH 5.0, the tetramer disassembled to peroxo-free monomer **2** (Route F). By using **2** as precursor, dissolved in 0.5 M HCl (pH~0.3) and heated at reflux for 4.5 h, it also polymerized to **4** (Route D). Disassembly of **4** into monomer **1** occurred by adding excess H<sub>2</sub>O<sub>2</sub> (Route E). Dimer **3** can be assembled from both monomers **1** and **2** by adjusting the pH to 1.0 and heating at reflux for 0.5 h (Routes A and C). Pure crystals of **1–4** with distinct shapes were obtained in high yield by the methods shown in Scheme 1. A series of synthetic experiments showed that **4** can be obtained in a broader acidity range (0.5–1.0 M HCl) by heating at reflux for 3–5 h, whereas **3** can be gained only by performing the reaction for 0.5 h in the range pH 0.9–1.0. We

attempted to find the species {Ge<sub>2</sub>W<sub>18</sub>Nb<sub>6</sub>O<sub>77</sub>}, which is the analogue of the known [Si<sub>2</sub>W<sub>18</sub>Nb<sub>6</sub>O<sub>77</sub>]<sup>8-</sup> reported by Hill and co-workers,<sup>[3b]</sup> but failed even by using <sup>183</sup>W NMR spectroscopy. This may be because the reactive systems based on germanium and silicon are distinguishing.

The assembly reaction is mainly based on the reactivity of peroxo-free Nb<sub>3</sub> clusters in monomer **2**. Therefore it was necessary to eliminate the peroxo groups in polyanion **1**. This was achieved by two methods in our study: Oxidation by NaHSO<sub>3</sub> and heating at reflux in acidic aqueous solution. Note that acidity and temperature are both crucial to the latter method and the resulting peroxo-free species were converted into other species under the reaction conditions. Heating at reflux in aqueous solution for more than 36 h was necessary for the yellow solution of **1** to become colorless. And the acidic solution of **1** could be kept without change under ambient temperature for months. However, the time could be shortened by heating at reflux in acidic solution, and the more acid that was used, the less time was needed. About 5 h was necessary in 0.5 M hydrochloric acid and only 3 h in 1.0 M hydrochloric acid before **1** reacted completely. Nevertheless, the conversion of **2** into **1** could be easily achieved by adding H<sub>2</sub>O<sub>2</sub>.

To learn more about the behavior of **1–4** in solution and the conversions between them, we carried out <sup>183</sup>W NMR experiments. The <sup>183</sup>W NMR spectra of **1–4** are shown in Figure S3 of the Supporting Information. The signals of **1–4** (at  $\delta = -75.8$  and  $-137.4$  ppm with intensity ratios of 2:1 for **1**, at  $\delta = -85.1$  and  $-133.6$  ppm with intensity ratios of 2:1 for **2**, at  $\delta = -92.1$ ,  $-100.2$ ,  $-118.8$ ,  $127.4$ , and  $130.8$  ppm with intensity ratios of 2:2:2:2:1 for **3**, and at  $\delta = -107.5$  and  $-115.7$  ppm with intensity ratios of 2:1 for **4**) confirmed that their solid-state structures were all maintained after being dissolved. As expected, disassembly from **4** to **1** was observed by <sup>183</sup>W NMR analysis, which was performed by adding 0.5 equiv of H<sub>2</sub>O<sub>2</sub> to the solution of **4** (D<sub>2</sub>O, pD~0.3; Figure 3). <sup>183</sup>W NMR experiments were performed on **4** at different pD by adding ammonia to the solution of **4** (D<sub>2</sub>O, 1.0 M DCl). The spectrum recorded at pD 0.0 ([D]<sup>+</sup>=1.0) was identical to that recorded at pD 0.3, which accounts for the retention of polyanion **4**. However, at pD 3.0, the

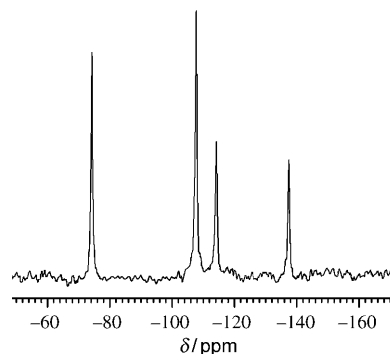


Figure 3. <sup>183</sup>W NMR spectrum of **4** (0.5 equiv of H<sub>2</sub>O<sub>2</sub> was added to a solution of **4** (D<sub>2</sub>O, pD 0.3)).

$^{183}\text{W}$  NMR spectra displayed two new signals assigned to **2**. At pD 4.5, the signals of **4** disappeared completely and only two signals of **2** were observed, which indicates that all of the polyanion **4** had decomposed into **2** (see Figure 4).

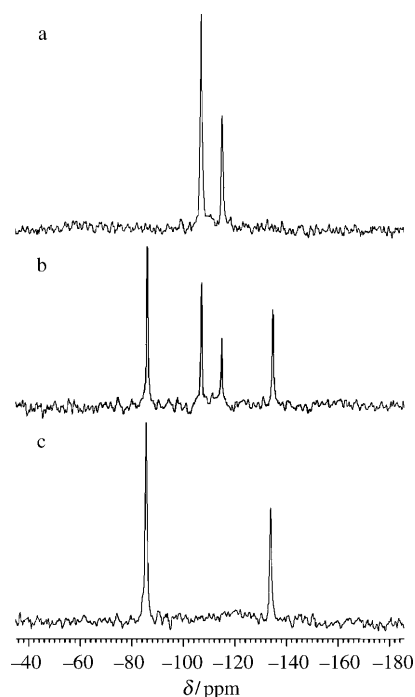
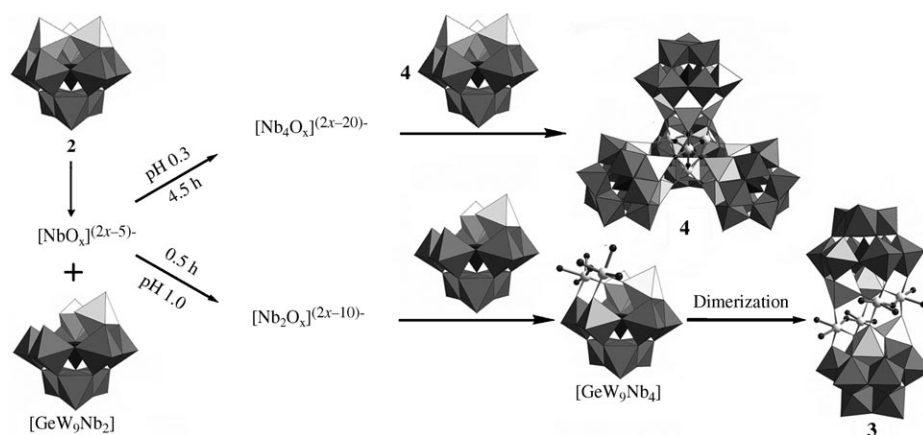


Figure 4.  $^{183}\text{W}$  NMR spectra of **4** at different pD in aqueous ( $\text{D}_2\text{O}$ ) solution. (a) pD 0.0, (b) pD 3.0, (c) pD 4.5.

Note that the ratio of niobium and tungsten in monomers **1** and **2** is 3:9 whereas it is 4:9 in aggregates **3** and **4**. We conjecture that the additional niobium in aggregates is released from precursor  $\{\text{GeW}_9\text{Nb}_3\}$ . As shown in Scheme 2, under the reaction conditions, niobium fragments are likely to be released from the peroxo-free monomer **2** and reassemble into dimer  $[\text{Nb}_2\text{O}_x]^{(2x-10)-}$ . The  $[\text{Nb}_2\text{O}_x]^{(2x-10)-}$  com-



Scheme 2. Graphical representation of the formation of aggregates **3** and **4**. The color code is the same as in Figure 1.

bins with a one-niobium-releasing  $\{\text{GeW}_9\text{Nb}_2\}$  segment to give the  $\{\text{GeW}_9\text{Nb}_4\}$  subunit, which further concentrates to **3** through four Nb–O–Nb bridges. Under more acidic conditions and longer reaction times, the niobium fragments may assemble to form tetramer  $[\text{Nb}_4\text{O}_x]^{(2x-20)-}$ , which may attach to four  $\alpha\text{-}[\text{GeW}_9\text{O}_{40}\text{Nb}_3]^{7-}$  units leading to the formation of **4**.

A small amount of a white insoluble solid removed by filtration in the “assembly reactions” (Routes A–D in Scheme 1) and the “disassembly reaction” (Route F in Scheme 1) was confirmed to be niobium oxide. This may derive, respectively, from unreacted niobium fragments released from precursors in “assembly reactions” and the decomposition of the  $\text{Nb}_4\text{O}_6$  core in the “disassembly reaction” of **4**. In the crystallization process of the “assembly reactions” (Routes A–D in Scheme 1), when the mother liquor vaporized nearly completely, a small amount of byproduct (a soluble white powder) appeared, which was confirmed to be an alkali metal salt of  $[\alpha\text{-GeW}_{12}\text{O}_{40}]^{4-}$ . This may derive from unreacted  $\{\text{GeW}_9\text{Nb}_2\}$ , which further releases niobium fragments and finally forms Keggin-type germanotungstate in the strong acidic solution. The appearance of niobium oxide and  $[\alpha\text{-GeW}_{12}\text{O}_{40}]^{4-}$  supports the hypothesis concerning the formation of **3** and **4**.

An attempt to introduce an additional niobium source ( $\text{H}_2\text{O}_2$  solution containing  $[\text{Nb}_6\text{O}_{19}]^{8-}$ ) into the reaction system of Route B did not obviously improve the yield of **4**. The excess niobium finally led to the formation of an insoluble oxide and  $[\alpha\text{-GeW}_{12}\text{O}_{40}]^{4-}$  was still observed. This evidences that even in the presence of excess niobium, niobium fragments will be released from the  $\{\text{GeW}_9\text{Nb}_3\}$  precursor. We tried to monitor the intermediates (such as  $\{\text{GeW}_9\text{Nb}_2\}$  segments) formed during the reaction, but neither  $^{183}\text{W}$  NMR nor ESI MS experiments gave any meaningful results.

The major bands of **1** in the IR spectrum are very similar to those observed for **2**, but three additional bands were observed at  $\tilde{\nu}=857.73$ ,  $656.09$ , and  $593.50\text{ cm}^{-1}$ , which were assigned to  $\nu_{\text{O}-\text{O}}$ ,  $\nu_{\text{sym,NbO}_2}$ , and  $\nu_{\text{asym,NbO}_2}$ , respectively.<sup>[13d,19]</sup> The strong IR bands at  $\tilde{\nu}=703.74\text{ cm}^{-1}$  for **3** and  $\tilde{\nu}=708.77\text{ cm}^{-1}$  for **4** are consistent with the existence of Nb–O–Nb bridges.<sup>[12a]</sup> The IR spectra of **1–4** are shown in Figure S4 of the Supporting Information.

The thermal gravimetric (TG) curves of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$ ,  $\text{Cs}_5\text{-3}$ , and  $\text{Cs}_8\text{K}_3\text{H}_9\text{-4}$  all exhibit one-step weight losses corresponding to the loss of lattice water with no further weight loss being observed until  $600^\circ\text{C}$ , which indicates high thermal stability (TG curves for the four compounds are shown in Figure S6 of the Supporting

Information). The second weight loss between 175 and 350 °C in the TG graph of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  corresponds to the loss of 2.95 oxygen atoms with no further weight loss being observed until 600 °C. We speculate that only one oxygen atom in each peroxy group is lost and the Keggin POM framework is still intact. To support this idea, the yellow crystal sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  was heated to 350 °C for 30 min, which resulted in a white solid that exhibited an IR spectrum and solution  $^{183}\text{W}$  NMR spectrum identical to that of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$ . Digital photographs and IR spectra are shown in the Supporting Information.

Although active under the reaction conditions (thermodynamically unstable), the peroxy-containing anion **1** is stable at room temperature. The retention of the characteristic absorption peak ( $\lambda=254.9$  nm) of **1** in the UV/Vis spectra at different pH confirmed that it is stable in the pH range 0.1–14.0 at room temperature. However, the decline of the characteristic absorption peak ( $\lambda=257.6$  nm) of **2** above pH 8.5 demonstrates its decomposition (see Figure S4 of the Supporting Information.). This not only indicates the stability of **1** but also implies that the presence of peroxy groups plays an important role in the stability of the POM framework towards pH change. The electrochemical properties of **1** were investigated and only two reversible redox peaks corresponding to tungsten centers were found in the cyclic voltammograms (see Figure S7 of the Supporting Information).

## Conclusion

Two niobium-containing germanotungstate monomers have been successfully synthesized that subsequently assemble to form two nanoscale POMs by the aggregation of niobium under acidic conditions. Their structures have all been unambiguously confirmed in both the solid and solution state. The  $\text{Nb}_8\text{O}_{12}$  core observed in dimer **3** is unprecedented in POM chemistry. The conditions for niobium-based assembly and disassembly between monomers and aggregates were studied in detail. The results indicate the following: 1) There is a strong tendency for niobium to form Nb–O–Nb bonds in acidic solution. 2) The use of niobium-substituted POMs as building blocks is a feasible approach to the construction of large-sized POMs by the aggregation of niobium. 3) Niobium fragments may be released gradually from monomer **2**, which provides a route for introducing niobium into acidic reaction systems and the flexible connection of these niobium fragments can lead to diverse reactions. 4) Disassembly by cleavage of Nb–O–Nb bonds may occur by controlling the pH or by adding  $\text{H}_2\text{O}_2$  solution. 5) The reactivity of polyoxoniobates presented in this paper is instructive for the further development of polyoxoniobate chemistry in acidic solution and provides a theoretical basis for subsequent work.

In future work we will extend the synthetic strategy described herein to other lacunary POM systems in acidic conditions, thus more assemblies of a larger size and with novel structures can be expected. Moreover, we plan to perform

catalytic studies on the peroxy-containing polyanion **1**. Another exciting possibility is to exploit the nucleophilicity of  $\text{O}(\text{Nb})$  in niobium-containing POMs to combine 3d or 4f metal ions so that new niobium-based species with interesting structures and properties can be constructed. Some progress in these fields has been made and will be reported in due course.

## Experimental Section

**Synthesis:** All chemicals were obtained commercially and used without additional purification. The  $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$ <sup>[20]</sup> and  $\text{A-}\alpha\text{-Na}_{10}\text{-}[\text{GeW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ <sup>[21]</sup> precursors were synthesized according to the procedures described in the literature and characterized by IR spectra. All other reagents were readily available from commercial sources and used as received without further purification.

### $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9(\text{NbO}_2)_3\text{O}_{37}]\cdot 6\text{H}_2\text{O}$ ( $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$ )

**Method 1:**  $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$  (1.91 g, 1.39 mmol) was dissolved in  $\text{H}_2\text{O}_2$  solution (consisting of 15 mL of ca.33% aqueous  $\text{H}_2\text{O}_2$  and 200 mL of water; 215 mL) with moderate stirring. HCl solution (16 mL, 1.0 M) was added dropwise to give a yellow, effervescent solution of pH 2.0. Finely powdered  $\text{A-}\alpha\text{-Na}_{10}\text{-}[\text{GeW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$  (7.80 g, 2.76 mmol) was added in a single step while the mixture was rapidly stirred to give a clear, orange-yellow solution of pH 4.0. Next, solid CsCl (20 g, 119 mmol) was added. After stirring for about 1 h, the yellow precipitate was collected by filtration, washed with diethyl ether ( $2\times 15$  mL), and dried in air to give 9.10 g of a yellow powder (yield: 86.6% based on the hexaniobate precursor). Well-formed yellow rod-like single crystals suitable for X-ray crystallography were obtained by recrystallization from deionized water and slow evaporation (yield: 90%).  $^{183}\text{W}$  NMR:  $\delta = -75.8$  (6W),  $-137.4$  ppm (3W). IR (KBr disks):  $\tilde{\nu} = 957$  (m), 892 (s), 858 (sh), 799 (vs), 767 (vs), 656 (vw), 593 (w), 546 (vw),  $456\text{ cm}^{-1}$  (w); elemental analysis calcd (%) for  $\text{K}_{0.5}\text{GeNb}_3\text{Cs}_{6.5}\text{W}_9\text{O}_{49}\text{H}_{12}$ : K 0.53, Ge 1.97, Nb 7.56, Cs 23.44, W 44.89; found: K 0.51, Ge 1.98, Nb 7.55, Cs 23.36, W 44.87.

**Method 2:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$  (0.80 g, 0.22 mmol) was dissolved in water (25 mL) and 30%  $\text{H}_2\text{O}_2$  solution (0.2 mL) was added. The colorless solution turned to yellow immediately. The yellow solution was stirred for about five minutes and allowed to evaporate at room temperature. Well-formed yellow bar-shaped crystals started to appear within 1 week (yield: 91%).

**Method 3:** A sample of  $\text{Cs}_8\text{K}_2\text{H}_9\text{-4}$  (0.80 g) was dissolved in hot water (28 mL) and 30%  $\text{H}_2\text{O}_2$  solution (0.2 mL) was added. The colorless solution turned to yellow immediately. The yellow solution was stirred for about five minutes and allowed to evaporate at room temperature. Well-formed yellow bar-shaped crystals started to appear within 1 week (yield: 85%).

### $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9\text{Nb}_3\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ ( $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$ )

**Method 1:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  (0.80 g, 0.21 mmol) was dissolved in hot water (30 mL) and sodium bisulfite (0.15 g, 2.88 mmol) was added. The yellow solution turned colorless within minutes. This solution was cooled to room temperature and filtered. The filtrate (pH~5.0) was allowed to evaporate at room temperature. A colorless block crystalline product started to appear within 1 week (yield: 82%).  $^{183}\text{W}$  NMR:  $\delta = -85.1$  (6W),  $-133.6$  ppm (3W). IR (KBr disks):  $\tilde{\nu} = 957$  (s), 886 (s), 805 (s), 764 (vs), 747 (sh), 526 (vw),  $443\text{ cm}^{-1}$  (w); elemental analysis calcd (%) for  $\text{K}_{0.5}\text{GeNb}_3\text{Cs}_{6.5}\text{W}_9\text{O}_{50}\text{H}_{20}$  ( $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$ ): K 0.53, Ge 1.96, Nb 7.51, Cs 23.29, W 44.60; found: K 0.51, Ge 1.95, Nb 7.49, Cs 23.33, W 44.56.

**Method 2:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  (0.80 g, 0.21 mmol) was dissolved in HCl solution (0.5 M, 30 mL). The yellow solution was heated at reflux until the yellow color disappeared (about 5 h) and then dilute ammonia was added dropwise under stirring (final pH~5.0). The solution was cooled to room temperature. After a small amount of white insoluble solid had been removed by filtration, the filtrate was allowed to evapo-

rate at room temperature. A colorless block crystalline product started to appear within 1 week (yield: 69%)

**Method 3:** A sample of  $\text{Cs}_8\text{K}_3\text{H}_{11}\text{-4}$  (0.80 g, 0.06 mmol) was dissolved in hot water (28 mL). Dilute ammonia was added dropwise under stirring (final pH ~5.0). This solution was cooled to room temperature. After a small amount of white insoluble solid had been removed, the filtrate was allowed to evaporate at room temperature. A colorless block crystalline product started to appear within 1 week (yield: 82%)

**$\text{Cs}_5\text{H}_5[\text{Ge}_2\text{W}_{18}\text{Nb}_8\text{O}_{88}]\cdot 18\text{H}_2\text{O}$  ( $\text{Cs}_5\text{-3}$ )**

**Method 1:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$  (0.80 g, 0.22 mmol) was dissolved in water (30 mL) and a solution of HCl (1.0 M, 2.8 mL) was added dropwise (the final pH was about 1.0). The resulting solution was heated at reflux for 0.5 h and then cooled to room temperature. After a small amount of white insoluble solid had been removed by filtration, the filtrate was allowed to evaporate at room temperature. Colorless rod-like crystals suitable for X-ray crystallography were obtained within 1 week (yield: 52%).  $^{183}\text{W}$  NMR:  $\delta = -92.1$  (4 W),  $-100.2$  (4 W),  $-118.8$  (4 W),  $127.4$  (4 W) and  $130.8$  ppm (2 W). IR (KBr disks):  $\tilde{\nu} = 964$  (s),  $881$  (vs),  $806$  (sh),  $768$  (vs),  $704$  (s),  $533$  (vw),  $458$   $\text{cm}^{-1}$  (w); elemental analysis calcd (%) for  $\text{Ge}_2\text{Nb}_8\text{Cs}_5\text{W}_{18}\text{O}_{106}\text{H}_{33}$ : Ge 2.20, Nb 11.24, Cs 10.05, W 50.07; found: Ge 2.22, Nb 11.25, Cs 10.00, W 50.04. (A small amount of a white powder appeared as a byproduct when the mother liquor had vaporized nearly completely.)

**Method 2:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  (0.80 g, 0.21 mmol) was dissolved in hot water (30 mL) and sodium bisulfite (0.20 g, 2.8 mmol) was added. After the yellow solution had turned colorless, a solution of HCl (1.0 M, 3.3 mL) was added dropwise (final pH 1.0). The resulting solution was heated at reflux for 0.5 h and then cooled to room temperature. After a small amount of a white insoluble solid had been removed, the filtrate was allowed to evaporate at room temperature. Colorless rod-like crystals started to appear within 1 week (yield: 50%).

**$\text{Cs}_8\text{K}_3\text{H}_9[\text{Ge}_4\text{W}_{36}\text{Nb}_{16}\text{O}_{166}]\cdot 27\text{H}_2\text{O}$  ( $\text{Cs}_8\text{K}_3\text{H}_9\text{-4}$ )**

**Method 1:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  (0.80 g, 0.21 mmol) was dissolved in HCl solution (0.5 M, 30 mL). The clear yellow solution was heated at reflux for about 5 h until the color disappeared and then it was cooled to room temperature. After a small amount of white insoluble solid had been removed by filtration, the filtrate was allowed to evaporate at room temperature. Colorless polyhedral crystals suitable for X-ray crystallography were obtained within 1 week (yield: 66% based on precursor  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$ ).  $^{183}\text{W}$  NMR:  $\delta = -107.5$  (24 W),  $-115.7$  ppm (12 W). IR (KBr disks):  $\tilde{\nu} = 965$  (s),  $889$  (vs),  $811$  (sh),  $769$  (vs),  $709$  (s),  $535$  (vw),  $459$   $\text{cm}^{-1}$  (w); elemental analysis calcd (%) for  $\text{K}_3\text{Ge}_4\text{Nb}_{16}\text{Cs}_8\text{W}_{36}\text{O}_{193}\text{H}_{63}$ : K 0.92, Ge 2.28, Nb 11.68, Cs 8.35, W 52.00; found: K 0.90, Ge 2.28, Nb 11.65, Cs 8.38, W 52.03. (A small amount of a white powder appeared as a byproduct when the mother liquor had vaporized nearly completely in Methods 1–3.)

**Method 2:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$  (0.80 g, 0.22 mmol) was dissolved in HCl solution (0.5 M, 30 mL). The colorless solution was heated at reflux for about 4.5 h and then cooled to room temperature. After a small amount of white insoluble solid had been removed by filtration, the filtrate was al-

lowed to evaporate at room temperature. A colorless polyhedral crystalline product started to appear within 1 week (yield: 50%).

**Method 3:** A sample of  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$  (0.80 g, 0.21 mmol) was dissolved in HCl solution (0.6 M, 25 mL). A solution (5 mL) containing 30%  $\text{H}_2\text{O}_2$  (0.5 mL) and  $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$  (0.08 g) was added to the solution. The clear yellow solution was heated at reflux for about 5.5 h until the color disappeared and then it was cooled to room temperature. The white insoluble solid was removed by filtration and the filtrate was allowed to evaporate at room temperature. (The white insoluble solid formed during the reaction was clearly more than that obtained by Method 1). A colorless polyhedral crystalline product started to appear within 1 week (yield: 68% based on precursor  $\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$ ).

**X-ray crystallography:** Single-crystal diffraction was conducted on a Bruker Smart Apex CCD diffractometer with Mo KR 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.<sup>[22]</sup> Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the full-matrix least-squares method on  $F^2$  using SHELXS-97.<sup>[23]</sup> 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 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 **1–4** are summarized in Table 1. Selected bond lengths and bond angles for **1** and **3** are provided in Tables S1 and S3. 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:

Table 1. Crystal data and structural refinement for compounds **1–4**.

	$\text{Cs}_{6.5}\text{K}_{0.5}\text{-1}$	$\text{Cs}_{6.5}\text{K}_{0.5}\text{-2}$	$\text{Cs}_5\text{-3}$	$\text{Cs}_8\text{K}_3\text{H}_9\text{-4}$
formula	$\text{Cs}_{13}\text{Ge}_2\text{KNb}_6\text{O}_{97.40}\text{W}_{18}$	$\text{Cs}_7\text{GeNb}_3\text{O}_{50}\text{W}_9$	$\text{Cs}_{10}\text{Ge}_4\text{Nb}_{16}\text{O}_{209}\text{W}_{36}$	$\text{Cs}_8\text{Ge}_4\text{K}_3\text{Nb}_{16}\text{O}_{190}\text{W}_{36}$
formula weight	7337.13	7349.07	13068.34	12615.82
[ $\text{g mol}^{-1}$ ]				
$T$ [K]	296(2)	296(2)	296(2)	296(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	cubic	monoclinic	monoclinic
space group	$C2/c$	$Fm\bar{3}m$	$P21/c$	$C2/c$
$a$ [Å]	18.585(4)	23.0721(18)	13.1899(12)	34.235(5)
$b$ [Å]	21.193(49)	23.0721(18)	12.4939(11)	30.320(5)
$c$ [Å]	26.285(5)	23.0721(18)	33.695(3)	23.279(5)
$\alpha$ [°]	90.000	90.000	90.000	90.000(5)
$\beta$ [°]	92.647(4)	90.000	95.018(1)	124.008(5)
$\gamma$ [°]	90.000	90.000	90.000	90.000(5)
$V$ (Å <sup>3</sup> )	10342 (4)	12281.8(17)	5531.4(9)	20031(6)
$Z$	4	4	1	4
$D_{\text{calcd}}$ [ $\text{mg m}^{-3}$ ]	4.712	3.974	3.923	4.183
$\mu$ [ $\text{mm}^{-1}$ ]	25.794	21.726	21.683	23.643
$F(000)$	12620.8	12644.7	5670.0	21860.0
crystal size [mm]	0.25 × 0.12 × 0.12	0.22 × 0.22 × 0.12	0.24 × 0.11 × 0.13	0.25 × 0.25 × 0.24
goodness-of-fit on $F^2$	1.049	1.113	1.071	1.056
final $R$ indices	$R_1 = 0.0698$ , $wR_2 = 0.1605$	$R_1 = 0.0391$ , $wR_2 = 0.1068$	$R_1 = 0.0567$ , $wR_2 = 0.1635$	$R_1 = 0.0625$ , $wR_2 = 0.1672$
$[I > 2\sigma(I)]^{\text{[a]}}$	$R_1 = 0.1005$ , $wR_2 = 0.1731$	$R_1 = 0.0412$ , $wR_2 = 0.1086$	$R_1 = 0.0866$ , $wR_2 = 0.1774$	$R_1 = 0.1005$ , $wR_2 = 0.1823$
$R$ indices <sup>[a]</sup> (all data)	4.678/–2.592	2.632/–2.413	5.054/–4.592	8.173/–3.044
largest diff. peak and hole [ $\text{e Å}^{-3}$ ]	–22 ≤ $h$ ≤ 21	–27 ≤ $h$ ≤ 24	–13 ≤ $h$ ≤ 15	–40 ≤ $h$ ≤ 40
limiting indices	–25 ≤ $k$ ≤ 21	–26 ≤ $k$ ≤ 27	–14 ≤ $k$ ≤ 14	–26 ≤ $k$ ≤ 36
	–30 ≤ $l$ ≤ 31	–26 ≤ $l$ ≤ 27	–40 ≤ $l$ ≤ 39	–27 ≤ $l$ ≤ 26
refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$

$$[a] R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}$$



crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-380461 (1), CSD-421620 (2), CSD-421630 (3), and CSD-421621 (4).

**<sup>183</sup>W NMR spectroscopy:** <sup>183</sup>W NMR spectra were measured with an Avance-400 Bruker NMR spectrometer at an operating frequency of 16.66 MHz with a 2.5 kHz sweep width, 50-*t*s pulse width, and 5 s pulse delay, NS 58256, LB 10.00 Hz. Samples of 1 (pD 6.8) and 2 (pD 6.5) for analysis were prepared by dissolving the crystals (0.5 g) in D<sub>2</sub>O (1.5 M LiClO<sub>4</sub>; 1.2 mL) solution and ultrasonicated the solution for 20 min. After CsClO<sub>4</sub> and the oversaturated sample were deposited, the upper clear solution was removed with a pipette for testing. Samples of 3 and 4 were prepared similarly to 1 and 2, except that 3 and 4 were dissolved in different D<sub>2</sub>O solutions (for 3: DCl, [D<sup>+</sup>]=0.07 M, LiClO<sub>4</sub>, [Li<sup>+</sup>]=1.5 M; for 4: DCl, [D<sup>+</sup>]=0.5 M, LiClO<sub>4</sub>, [Li<sup>+</sup>]=1.5 M). The final pD for the sample of 3 was 1.0 and for the sample of 4 it was about 0.3. The <sup>183</sup>W NMR experiments performed on 4 at different pD values were performed as follows: Crystals of 4 (1.0 g) were dissolved in D<sub>2</sub>O (DCl, [D<sup>+</sup>]=1.0 M, LiClO<sub>4</sub>, [Li<sup>+</sup>]=1.5 M; 2.5 mL) solution and the upper clear solution (pD 0.0) was removed with a pipette for testing. The residual sample was adjusted to pD 3.0 with ammonia and the upper clear solution was removed with a pipette for testing. Then the residual sample was adjusted to pD 4.5 for testing.

**Physical measurements:** IR spectra in KBr pellets were recorded in the range 400–4000 cm<sup>-1</sup> with an Alpha Centaur FT/IR spectrophotometer. Elemental analyses for germanium, tungsten, niobium, caesium, and potassium were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Thermogravimetric analyses were carried out by using a Perkin-Elmer TGA7 instrument at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. UV/Vis absorption spectra were obtained by using a 752 PC UV-Vis spectrophotometer.

**Electrochemical:** Electrochemical measurements were performed with a CHI660B electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A three-electrode system was employed in this study. A glass carbon electrode (*d*=3 mm) was used as the working electrode, an Ag/AgCl electrode as the reference electrode, and platinum coil as the counter electrode. All potentials were measured and reported versus the Ag/AgCl electrode. All experiments were conducted at ambient temperature (25–30 °C).

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