

Cluster Compounds |Hot Paper|

Unprecedented {Fe₁₄}/{Fe₁₀} Polyoxotungstate-Based Nanoclusters with Efficient Photocatalytic H₂ Evolution Activity: Synthesis, Structure, Magnetism, and Electrochemistry

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Abstract: Novel Fe₁₀ and Fe₁₄ clusters [Rb₉Cs₄H₃₇Fe₁₀O₃₄(A- α -PW₉O₃₁)₃(OH)₃]-36H₂O (1) and [H₃Rb₃Fe₁₄(OH)₁₂(PO₄)₆(B- α -PW₉O₃₄)₂]-21H₂O (2) were synthesized and characterized in the solid state by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis (TGA), and magnetic studies, and in solution by electrochemistry. Cluster 1 is a decameric Fe^{III} polyanionic cluster encapsulating a cesium atom in the center. Cluster 2 is a unique tetradecanuclear Fe^{III} sandwich structure with phosphate-linked units featuring two quasicubic Fe₄O₄ moieties. Apparently, 2 has the highest nuclearity of all known Fe^{III} sandwich-type polyoxometalate

clusters. Clusters **1** and **2** also act as photocatalysts with platinum as cocatalyst for H_2 evolution from light-driven water splitting. Changes in the cyclovoltammetric patterns with variations in pH were observed for **1** and **2**, most likely due to intermolecular interactions among the high-nuclearity Fe^{III} cluster cores and subsequent changes in the acidbase properties of the two reduced POMs. Magnetic studies provide evidence of antiferromagnetic interactions in **1** and **2**. TGA showed that complexes **1** and **2** decompose between 580 and 590 °C.

Introduction

In recent years, the chemistry of d-block transition-metal-substituted polyoxometalates (POMs) has continued to attract much attention, owing to their fascinating electronic properties and many useful applications.^[1-3] The use of POMs is attractive because they facilitate the development of new synthetic procedures to obtain high nuclearity. In particular, the class of lacunary polyoxotungstates has been widely used as ligands to obtain a multitude of clusters, specially engineered with a view to their appealing properties.^[4] Recently, attempts were made to obtain new nanosized molecular clusters by using lacunary POMs with restricted geometries and ions such as PO_4^{3-} , CO_3^{3-} , and F^- , but such work is very rare.^[5] Nevertheless, these ions with transition metals may produce unprecedented nanocluster cores, change the oxidation states, particularly of transition and rare earth metal ions, and also effect the shell functionalities by increasing/decreasing the vacant posi-

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tions in POMs,^[6] and thus result in the formation of new basic building blocks by serendipitous molecular assembly. However, rational tailoring of their structural features by self-assembly of transition metal substituted POMs (TMSPs) by using ionic linkers remains a challenge. In recent years, lacunary POMs were widely implemented with 3d metal ions, particularly with earth-abundant transition metals. Among them, the polyoxometalates involving high-nuclearity ferric ions attracted several research groups owing to their multifarious applications.^[7] Pioneering works with higher-nuclearity ferric ions in polyoxometalates have been reported by various groups. Müller et al. reported 30 Fe^{III} centers in Mo- and W-based porous nanocapsules and a {Mo₇₂Fe₃₀} ball.^[8a,b] Gouzerh et al. synthesized phosphotungstates containing iron atoms, namely, $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{26-} \quad and \quad [H_4P_2W_{12}Fe_9O_{56}(OAc)_7].^{[8c]} \quad Mialane$ et al. reported the single-molecular magnetic behavior of $Na_{14}(C_4H_{12}N)_5[{Fe_4W_9O_{34}(H_2O)}_2(FeW_6O_{26})] \cdot 50H_2O$ $Na_{6}(C_{4}H_{12}N)_{4}[Fe_{4}(H_{2}O)_{2}(FeW_{9}O_{34})_{2}]$ ·45 H₂O.^[8d] Cronin et al. reported [KFe₁₂(OH)₁₈(α -1,2,3-P₂W₁₅O₅₆)₄] nanoscale polyoxometalate clusters.^[7a] Kortz et al. synthesized tetrameric, multi-Fe^{III}-containing polyoxotungstates.^[7b] Recently, Wang et al. observed the photophysical activity of $H_{146}Fe_{10}N_9Na_{19}O_{286}Se_8W_{62}$ and $C_8H_{136}Fe_6N_4Na_{14}O_{184}Se_6W_{34}\ Dawson-type\ nanoscale\ Fe-based\ se$ lenotungstate clusters.^[7c] Song, Zhao, et al. reported the remarkable H_2 evolution activity of $Na_{27}[Fe_{11}(H_2O)_{14}(OH)_2(W_2O_{10})_2(SbW_9O_{33})_6].103\,H_2O.^{[7d]} \quad These \quad dimensional equation (M_2O)_{14}(OH)_2(W_2O_{10})_2(SbW_9O_{33})_6].103\,H_2O.^{[7d]}$ verse Fe^{III} clusters based on POMs have applications in various areas of research, mainly for the preparation of magnetic materials and catalytic oxygenation and water splitting reactions for

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 $\rm H_2$ and $\rm O_2$ evolution. In particular, oxo and hydroxo iron clusters are highly efficient in the last-named process. However, the field is still developing and therefore provides the chemist with important new challenges.^[8e]

In this context and given our interest in developing new architectures for novel polyoxometalates and understanding the role of cluster-core molecular assembly and its applicability in diverse areas of research, we synthesized some electroactive Fe^{III} oxo or hydroxo clusters using Rb⁺ and Cs⁺ cations and PO₄³⁻ anions as linkers. The use of these linkers in the formation of clusters 1 and 2 enables us to propose reliable models for building up giant molecular assemblies and structural tailoring via PO₄ linkers in polyoxometalates. Herein, we report the synthesis and characterization of the unprecedented nanoclusters 1 and 2. $[Rb_9Cs_4H_{37}Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]$ ·36H₂O (1) consists of a decanuclear Fe^{III} oxoanion assembly with a domelike core encapsulating cesium in the center, and $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-PW_9O_{34})_2]$ ·21 H₂O (**2**) forms a tetradecanuclear sandwich structure with a unique three-winged motif in its cluster core. Interestingly, the polyanionic Keggin anions in clusters **1** and **2** have A- and B-type $\{\alpha$ -PW₉ $\}^{[9]}$ bonding features but essentially can be obtained from A-type { α -PW₉} polyanions by means of slight variations in pH and cation/anion linkers.

Results and Discussion

Synthesis

Yellowish-green Fe₁₀[Rb₉Cs₄H₃₇Fe₁₀O₃₄(PW₉O₃₁)₃(OH)₃]·36 H₂O (1) and Fe₁₄, [H₃Rb₃Fe₁₄(OH)₁₂(PO₄)₆(B- α -PW₉O₃₄)₂]·21 H₂O (2) were readily synthesized from the trilacunary A-type α -PW₉O₃₄ polyanion by one-pot reactions in slightly acidic medium. The crystals of cyclic Fe₁₀ Keggin trimer 1 were obtained at pH 3–4 by using 2 α HCl in the reaction mixture of Fe(NO₃)₂·9H₂O and A- α -PW₉O₃₄ polyanion with mixed Rb⁺/Cs⁺ countercations. However, slight variations in reaction pH, addition of Na₃PO₄, and minor changes in reaction stoichiometry result in the formation of **2** (Scheme 1), which has a rare sandwich-type Fe₁₄ B- α -



Scheme 1. Representation of the formation of clusters [Rb₉ Cs₄H₃₇Fe₁₀O₃₄(A- α -PW₉O₃₁)₃(OH)₃]·36 H₂O (1) and [H₃Rb₃Fe₁₄(OH)₁₂(PO₄)₆(B- α -PW₉O₃₄)₂]·21 H₂O (2) from A-(α -PW₉O₃₄)·9H₂O. Fe green, W cyan, oxygen red, P purple.

PW₉O₃₄ trivacant Keggin structure. Interestingly, the cluster core in **2** is encapsulated between two B- α -PW₉O₃₄ polyanions. During the preparation, a series of parallel experiments were performed for successful isolation of **1** and **2**. The current synthetic methodology demonstrates that small variations in cation and PO₄³⁻ anion together with slight fluctuations in pH played a key role in isolating structures based on A- and B-type α -PW₉O₃₄ isomeric polyanions. We also tried the same reaction strategy with other 3d metal ions to investigate structural ambiguity with the A-type α -PW₉O₃₄ polyanion but failed to obtain suitable crystals for structure determination.

Crystal structures

Crystallographic data, structure refinement, and selected bond lengths and angles for **1** and **2** are presented in Tables S1–S3 of the Supporting Information. The structure of **1**, which crystallizes in trigonal space group $R\bar{3}m$, contains $[Cs_4H_{37}Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{9-}$ anions (Figure 1) with crystallographically imposed threefold symmetry, nine Rb cations for charge balance, and 36 solvent water molecules.

The anion contains three nonequivalent types of Fe^{III} atoms Fe1, Fe2, and Fe3 with population factors of 1, 0.5, and 0.166, respectively, derived from the trivacant A-type Na₉(α -PW₉O₃₄) Keggin anion. There are two nonequivalent Cs ions Cs1 and Cs2 with population parameters of 1 and 0.33, respectively. Both Cs1 and Fe3 lie on the threefold *z* axis at the center of the cluster anion. All three iron atoms are six-coordinate, bonded to six oxygen atoms in a distorted octahedral environment. Both Fe1 and Fe2 are bonded to three oxygen atoms that form bridges to other iron atoms, two that form bridges to tungsten atoms, and one from PO₄. In all cases the bond lengths are in the order Fe–O(Fe) < Fe–O(W) < Fe–O(P) (Table S2, Supporting Information). Fe3 sits on the threefold axis and is bonded to three O9 atoms that form bridges to



Figure 1. Ball-and-stick representation of 1. Fe green, W cyan, O red, Cs blue, PO_4 purple.

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other iron atoms and three O10 atoms that are terminal and can therefore be identified as belonging to water molecules according to bond valence sum (BVS) values (Table S4, Supporting Information). Fe1 and Fe2 are bonded to two oxygen atoms of different WO₄ units and thus fill the vacancies of the trivacant A-type α -PW₉O₃₄ polyanion.

The trivacancy-substituting Fe1 and Fe2 ions are connected through Fe1-O-Fe1 and Fe1-O-Fe2 bridges via monoprotonated μ_3 -O25 and tetrahedrally coordinated μ_3 -O23 atoms, as confirmed by BVS values (Table S4, Supporting Information) with Fe-O bond lengths in the range 1.81(1)-1.95(1) Å. Notably, all the Fe1 atoms form a trimer through μ_3 -O24 units bonded to two Fe and one central Cs atom thus forming an outer Fe1-O24-Fe1 hexagonal ring {Fe₆O₆} perimeter with an O24-Fe1-O25 bond angle of 102.3(13)° and Cs1–O24 distance of 3.22(3) Å. The Fe1 atoms are further connected to Fe2 atoms by μ_4 -O23 units through six Fe-O-Fe bridges, and the three Fe2 atoms are further connected to the apical Fe3 atom by μ_3 -O9 atoms in three Fe2-O-Fe3 bridges. Notably, the μ_3 -O9 atom is also bonded to the centrally located Cs1 atom through a nonprotonated bridging atom, and thus a crown-like core assembly is created (Figure S1, Supporting Information). The core in 1 exhibits an apical Fe3 atom lying at the top of the anion on the threefold rotation axis. The nine remaining Fe^{III} ions (Fe1 and Fe2 and their symmetry equivalents) make up the outer ring of the cluster core, lying alternately above and below the plane perpendicular to the threefold rotation axis. This unprecedented bonding core differentiates 1 from the other reported tri-Keggin and tetra-Keggin Fe^{III} clusters, in which the ten iron atoms are distributed with six in an outer ring, three in a central ring, and one in an apical position. Interestingly, 1 shows a porous solid-state framework, since the tri-Keggin polyoxotungstate further forms supramolecular coordination polymeric chains through the Rb/Cs-O-directed molecular assembly in which the corners of the trimeric units are connected through Rb/Cs oxo or hydroxo bridges (Figure 2).



Figure 2. Packing of **1** in the solid state showing the porous coordination framework due to connection of the corners of the cluster anion by rubidium/cesium-directed molecular assembly through oxo and hydroxo bridges. W cyan, Fe green, O red, Rb brown, Cs blue.

The structure of cluster **2** is shown in Figure 3. It crystallizes in the space group $R\bar{3}c$ with six unique Fe^{III} atoms paired in three different octahedral coordination environments, that is, Fe1–Fe3, Fe4, Fe5, and Fe2–Fe6. The center of the cluster is



Figure 3. Ball-and-stick representation of cluster 2. Fe green, W cyan, O red, Rb brown, PO_4 purple.

based around a core containing eight Fe^{III} atoms. Fe1 and Fe3 atoms are situated on the central threefold axis, while Fe4 and Fe5 atoms are in general positions coordinated with the oxygen atoms of six PO₄ anions, whereby they are bonded to four μ -O atoms of two different PO₄ units in an arrangement in which three wings emanate from the central frame (Figure 4).



Figure 4. Front and side views of the cluster core of **2** showing the threewinged motif and two Fe_4O_4 quasicubes, three sides of which are connected to three Fe-O-Fe bridges via six PO₄ units.

Furthermore, these adjacent Fe centers are bridged through the hydroxide O atom μ_2 -O21, as is confirmed by calculated BVS values (Table S5, Supporting Information), with an Fe4-O21-Fe5 bond angle of 125.9(7)° and Fe4–O21 and Fe5–O21 distances of 1.949(12)–1.947(12) Å (Table S3, Supporting Information). Fe4 and Fe5 have similar coordination environments, bonded to oxygen atoms O17 (aqua) and O41 (hydroxide), with bond lengths of 2.070(12) and 2.183(12) Å respectively. Interestingly, two Fe atoms, that is, Fe1 and Fe3, occupy the threefold axis on the perimeter of the cluster core, bridged to the trivacancy-occupying Fe6 and Fe2 atoms via μ -O10 and μ -O20 atoms, respectively, with formation of two Fe₄O₄ quasicubes (Figure 4). Also, the μ -O10 and μ -O20 atoms of the Fe₄O₄ cubane units are monoprotonated, as is clear from their BVS values (Table S5, Supporting Information). In the Fe₄O₄

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quasicubanes, the Fe–O bond lengths lie in the range pf 2.043(12)–2.321(9) Å. The Fe–O distances for O bridges to P and to three Fe atoms, for example, Fe6–O8 and Fe2–O7, are the longest (ca. 2.31 Å) with Fe···Fe distances of 3.16(2)–3.44(2) Å, and these dimensions are similar to those found for **1**. The three sides of two Fe₄O₄ quasicubes are connected with the six Fe-O-Fe bridges through six PO₄ units encapsulating three rubidium atoms inside the core, and thus the gigantic cluster core sandwiched in between the two B-type α -PW₉O₃₄ polyanions is completed. The cluster **2** forms a supramolecular network through solvent-assisted hydrogen bonding (Figure S2, Supporting Information) and shows a type ABA packing motif (Figure S3, Supporting Information).

Electronic absorption spectroscopy

The UV/Vis absorption spectra of **1** and **2** were recorded in 3×10^{-4} M aqueous solutions. The UV/Vis spectra show sharp maxima at 265 nm ($\varepsilon = 5066$) and 270 nm ($\varepsilon = 5700$) for **1** and **2**, respectively, which correspond to the dominant oxygen-to-tungsten charge-transfer bands of the polyoxoanion framework (Figure 5). The Fe-centered d–d transition bands appear



Figure 5. UV/Vis absorption spectra of 1 and 2 in $3 \times 10^{-4}\,\text{m}$ aqueous solution.

at 410 (ε =416) and 430 nm (ε =473 Lmol⁻¹ cm⁻¹) for **1** and **2** respectively. To evaluate the stability of the polyanion clusters **1** and **2**, their UV/Vis spectra were recorded at regular time intervals up to 48 h (Figure S4, Supporting Information). The peaks corresponding to both ligand-to-metal charge-transfer and d–d transitions appeared in the same region with slightly decreased absorbance, and thus the spectral reproducibility during this period of time confirms the structural stability of both clusters.

Cyclic voltammetry

Cyclic voltammograms (CVs) of clusters **1** and **2** in aqueous solution were recorded at different pH values by using 0.2 M Na₂SO₄ + H₂SO₄ and 0.4 M CH₃COONa + CH₃COOH buffers. The reproducibility of the spectra from pH 3 to 6 confirms their stability in this pH range (Figure S5, Supporting Information). The CV of the trilacunary species {PW₉} was recorded to compare the redox behavior of clusters **1** and **2**. The CV of {PW₉} shows

W^{VI} reduction waves at -0.53 V and -0.72 V (Figure S6, Supporting Information), whereas the redox potential of the ten Fe^{III} centers in the polyanion of cluster **1** lies in a more positive direction, that is, before the first reduction wave of W^{VI}, and they are reduced in stepwise manner in three distinct reduction waves at ($E_{p,c1} - 0.47$ V, $E_{p,a1} - 0.34$ V; $E_{p,c2} = 0.017$ V, $E_{p,a2} = 0.057$ V; $E_{p,c3} = 0.35$ V and $E_{p,a3} = 0.52$ V versus SCE at pH 4; Figure 6a). Interestingly, the W^{VI} reduction wave of {PW₉} at -0.53 V shifts to a more negative potential at -0.63 V in **1**.



Figure 6. a) Cyclic voltammogram of 1 (3×10^{-4} m) in 0.2 m Na₂SO₄/H₂SO₄ solution/pH 4 in different scan rates. b) CVs of 1 (3×10^{-4} m) in 0.2 m Na₂SO₄/H₂SO₄ solution from pH 2 (red) to 3 (black) at 20 mVs⁻¹.

The 14 Fe^{III} centers in 2 at pH 4 are also reduced in a stepwise manner similar to 1 (Figure S7a, Supporting Information), with Fe^{III/II} reduction potentials of -0.35, -0.043, and 0.14 V. Stepwise reduction of the Fe^{III} centers has previously been reported for some polyoxometalate iron clusters.^[8a] This phenomenon is probably due to interactions among the various adjacent Fe^{III} centers.^[8c] To rationalize the effect of pH on protonation in both clusters 1 and 2, which are based on isomeric $A-\alpha$ -PW₉O₃₄ and $B-\alpha$ -PW₉O₃₄ Keggin polyanions, the CVs of **1** and **2** in the pH range 2–6. The CV of 1 at pH 2 shows one broad W^{VI} reduction wave at -0.62 V along with the three Fe^{III/II} reduction peaks at -0.47, 0.085, and 0.43 V, and on increasing the pH to 3, a slight shift in Fe^{III/II} reduction and oxidation peaks is observed (Figure 6b). However, in the case of 2, the CV at pH 2 shows a broad, merged peak corresponding to the Fe^{III/II} reduction process, which subsequently splits at pH 3-4 into two separate $\mathrm{Fe}^{\scriptscriptstyle III/II}$ peaks at -0.043 and 0.14~V (Figure S7b, Supporting Information). This slight variation observed for the reduction of Fe^{III} centers in 1 and 2 highlights the different acid–base properties of the two clusters.^[9]

Magnetic studies

The solid-state magnetic behavior of **1** and **2** was investigated in the temperature range 1.43–300 K in a field of 1000 Oe. The plots of $\chi_m T$ versus *T* and χ_m versus *T* (χ_m = molar magnetic susceptibility) are shown in Figure 7. The χ_m values for **1** and **2** slowly increase from 0.10 and 0.12 cm³mol⁻¹ (300 K) to 4.06 and 4.45 cm³mol⁻¹ (1.43 K), respectively, whereas the $\chi_m T$ values exhibit a continuous decrease with decreasing temperature, from 39.46 to 7.76 cm³mol⁻¹ K for **1** and from 36.88 to 8.67 cm³mol⁻¹ K for **2**, in the temperature 301 to 1.43 K. This type of behavior indicates the presence of dominant antiferro-

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Figure 7. χ_m versus *T* and $\chi_m T$ versus *T* for **1** and **2** in the temperature range of 1.43–300 K.

magnetic interactions in **1** and **2**. The $\chi_m T$ values at 300 K are smaller than the theoretical values of 43.75 cm³ mol⁻¹K for 10 Fe centers and 61.26 cm³ mol⁻¹K for 14 Fe centers in **1** and **2**, respectively. The $\chi_m T$ values at the lowest temperature, obtained from the extrapolated plot at approximately 0 K of 8.40 and 8.12, cm³ mol⁻¹K for **1** and **2**, respectively, are similar to the magnetic moment for two unpaired electrons. It is significant that these values are nonzero although the clusters are even-electron systems, and this is presumably due to some antiferromagnetic interactions in both **1** and **2**. Furthermore, the $1/\chi_m$ versus *T* plot obeys the Curie–Weiss law between 25 and 300 K (Figure S8, Supporting Information), with Curie constants of C = 45.45 and $38.44 \text{ cm}^3 \text{ Kmol}^{-1}$ and Weiss constants of $\theta = -18.08$ and -15.29 K for **1** and **2**, respectively.

Photocatalytic activity

After careful examination of the stability of compounds **1** and **2** in aqueous solution by UV/Vis spectroscopy and cyclic voltammetry for up to 48 h (Figures S4 and S9, Supporting Information), their photocatalytic activity was also tested. Photocatalytic water-splitting studies were performed by using 100 mg of compounds **1** and **2** as catalyst. Encouraging photocatalytic hydrogen evolution occurred when of H₂PtCl₆ (1 mL of a 1 g H₂PtCl₆ solution in 250 mL water; concentration 9 mM)) was added as a cocatalyst with **1** and **2** in a 20% aqueous solution of MeOH (20 mL), which was used as sacrificial electron donor. The photocatalytic H₂ evolution rates from water under UV irradiation were remarkably high, namely 61.70 and 51.21 µmolg⁻¹ h⁻¹ (Figure 8), and the total amounts of H₂ pro-



Figure 8. Rate of H₂ production versus irradiation time for 1 and 2 as photocatalysts with 1 mL H₂PtCl₆ as cocatalyst. The experiments were performed in 100 mL of solution containing 20 mL of CH₃OH, 80 mL of water, 100 mg of catalyst (1 or 2), and 1 mL of H₂PtCl₆ solution as photocatalyst.

duced in 9 h were 493.66 and 401.55 μmol for $1+H_2 PtCl_6$ and $\mathbf{2} + H_2 PtCl_6$, respectively. Since the H_2 evolution rates were observed every hour, they vary a little from linearity, but they are almost linear. Interestingly, the increase in H_2 evolution rate was larger in the case of $1 + H_2PtCl_6$. Furthermore, H_2 was consistently evolved from the reaction mixture in both cases. The turnover numbers [(moles of H₂ formed)/(moles of 1 or 2)] obtained up to 9 h of reaction were 38.12 and 30.88 for 1+ H_2PtCl_6 and $2 + H_2PtCl_6$, respectively. Clearly, the true values may be much higher, as the reaction continues in both cases. During photocatalytic reactions, an electron is excited from the valence band (O 2p) to the conduction band of the metal cation. $^{\left[7c,\,8e,f\right] }$ The electron is then transferred from the metal center to H₂O to produce H₂. This characteristic behavior is akin to that reported for semiconductor metal oxides, as the bandgaps of 1 and 2 of 2.34 and 2.82 eV, calculated from diffuse-reflectance spectra (Figure S10, Supporting Information), are similar to those reported for photocatalytically active semiconductor metal oxides. We also investigated the photocatalytic hydrogen-evolution activities of compounds 1 and 2 under the same reaction conditions but without using H₂PtCl₆ as cocatalyst and found that 1 and 2 still facilitate H₂ evolution by photocatalytic H₂O reduction, but at a slower rate. It is therefore clear that the H₂PtCl₆ cocatalyst increases the photocatalytic efficiencies of 1 and 2.

The blank reaction of H₂PtCl₆ (1 mL), that is, without catalyst 1 or 2, was also tested under the same reaction conditions, and the amount of H_2 produced in 9 h was 0.649 μ mol, which is a very small amount. Moreover, the reactions of 1 or 2 and CH₃OH without light irradiation were also been investigated, and H₂ evolutions after 9 h of photocatalysis were 0.979 and 0.658 µmol, that is, extremely low in both cases. Furthermore, the PXRD patterns of 1 and 2 after UV irradiation (300 W Xe lamp) were examined. Before doing so, the photocatalytic solutions of 1 and 2 were centrifuged to determine whether any precipitate had formed, but the solutions remained homogeneous. They were then vacuum dried and washed three to four times with acetone. The XRD patterns were then measured and showed that these photocatalysts retain their structure even after the experiment (Figure 9). Dynamic light scattering (DLS) experiments were also performed to detect Fe₂O₃ nanoparticle formation after 9 h of photocataytic reactions of



Figure 9. XRD patterns of photocatalysts 1 (a) and 2 (b) before (middle) and after (top) photocatalytic water splitting reaction under UV irradiation (300 W Xe lamp).

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1 and **2** (Figure S11, Supporting Information). However, no nanoparticles were detected in both cases, which indicated that the catalytically active species were homogeneously dissolved molecules. The photocatalysis of **1** and **2** exhibits the characteristic color change from yellow-green to blue due to the reduction of W^{V1} to W^{V} . The color remained blue if the system was protected from oxygen. However, on exposure to air both **1** and **2** recover their yellowish green color due to reoxidation of W^{V1} to W^{V1} .

Mass spectrometry

The ESI mass spectra of **1** and **2** (Figure 10 and Figure S12, Supporting Information) were recorded in aqueous solution. The trimeric anion **1** was observed in solution as the cluster



Figure 10. ESI mass spectrum of 1.

anions $[Cs_4H_{37}Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{9-.36}H_2O$ and $[Cs_4H_{37}Rb_3Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{6-.6}H_2O$ (*m/z* obsd/calcd: 990.28/990.55 and 1438.12/1438.56 respectively; Table 1). In the frag-

Table 1. Peak assignments of the fragmented polyanion in the negative-mode mass spectrum of 1.				
Obsd m/z	Calcd m/z	Charge	Polyanion	
990.28 1438.12 1044.26 1002.36	990.55 1438.56 1044.49 1002.46	-9 -6 -6 -6	$\begin{array}{l} [Cs_4H_{37}Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{9-}{\cdot}36H_2O~(1) \\ [Rb_3H_{37}Cs_4Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{6-}{\cdot}6H_2O~(1) \\ [Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-PW_9O_{34})_2]^{6-}{\cdot}14H_2O~(2) \\ [Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-PW_9O_{34})_2]^{6-}~(2) \end{array}$	

ment anionic peak of $[H_{37}Rb_3Cs_4Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]^{6-}\cdot 6H_2O$ at 1438.12, the three Rb atoms most likely originate from the three Rb2 atoms, which are bonded to the anion more strongly in the crystal structure than the six Rb1 atoms. The ESI mass spectrum of **2** shows fragment anionic peaks corresponding to cluster anions $[Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-PW_9O_{34})_2]\cdot 14H_2O$ and $[Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-PW_9O_{34})_2]\cdot 1044.26/1044.49$ and 1002.36/1002.46, respectively), which support their stability in aqueous solution (Figure S12, Supporting Information). This observation is important, since it is confirmation that cluster anions **1** and **2** are stable in solution.

Conclusion

Novel high-nuclearity Fe^{III} clusters [Rb₉Cs₄H₃₇Fe₁₀O₃₄(A-α- $PW_9O_{31}_3(OH)_3]$ ·36 H₂O (1) and $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-M_3)]$ ·37 O (1) and $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-M_3)]$ ·38 O (1) and $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-M_3)]$ ·38 O (1) and $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(B-\alpha-M_3)]$ ·38 O (1) and $[H_3Rb_3Fe_{14}(OH)_{12}(OH)_{12}(PO_4)_{12}$ $PW_{9}O_{34})_{2}$ ·21 H₂O (2) were obtained from the {A- α -PW₉} trilacunary polyanion. Cluster 1 encapsulates Cs⁺ in the center and contains a porous coordination framework formed through Rb/Cs oxo or hydroxo linkages, whereas cluster 2 has the highest Fe^{III} nuclearity known in a sandwich POMS and encapsulates three Rb⁺ cations in a three-winged core. Clusters 1 and 2 proved to be efficient catalysts for light-driven H₂ evolution by water splitting. Both clusters show antiferromagnetic behavior. CVs of 1 and 2 show pH-dependent changes in their reduction and oxidation potentials, which may be due to intermolecular interactions among the high-nuclearity Fe^{III} cluster cores and subsequent changes in the acid-base properties of the reduced POMs. Clusters 1 and 2 serve as an ideal models for the design and formation of other high-nuclearity TMSP architectures with interesting properties.

Experimental Section

Synthesis of $[Rb_9Cs_4H_{37}Fe_{10}O_{34}(PW_9O_{31})_3(OH)_3]$ ·36H₂O (1)

An aqueous solution (5 mL) of Fe(NO₃)₃·9H₂O (0.280 g, 1.00 mmol) was slowly added to an aqueous solution (20 mL) of Na₉[A- α -PW₉O₃₄]·7H₂O (0.493 g, 0.20 mmol), synthesized as reported,^[10] and the pH of the reaction mixture was maintained at 4, by using 2 m HCl followed by the addition of 2–3 drops of 1 m RbCl. The reaction mixture was kept at 80 °C for 3 h. The resulting solution turned yellowish green in color and was then cooled, followed by the addition of 3–4 drops of 1 m CsCl, and subsequently decanted by centrifugation. The obtained clear solution was kept in an open vial for slow evaporation. The greenish yellow crystals were collected after three weeks. Yield: 0.165 g (26.41 % based on W). IR (KBr pellet, cm⁻¹): $\tilde{\nu}$ = 1628, 1110(s), 1089(s), 1031.48(m), 926(s), 881(m), 821(w), 765(w), 590(w), 552(w).

Synthesis of $[H_3Rb_3Fe_{14}(OH)_{12}(PO_4)_6(\alpha - PW_9O_{34})_2] \cdot 21 H_2O$ (2)

Fe(NO₃)₃·9H₂O (0.229 g, 0.85 mmol) was dissolved in 15 mL of H₂O, and Na₉[A- α -PW₉O₃₄]·7H₂O (0.321 g, 0.13 mmol) was added with stirring until a clear, dark brown solution formed, followed by slow addition of Na₃PO₄ (0.163 g, 1 mmol) at room temperature while the pH of the reaction mixture was maintained at 4 with 2 M aqueous HCl. The color of the reaction mixture became yellowish green. The reaction mixture was stirred for 3 h, and then heated in a water bath at 80 °C for 6 h and subsequently cooled slowly to room temperature, followed by the addition of 3–4 drops of 1 M RbCl. The solution was kept for crystallization at room temperature. Slow evaporation resulted in the formation of yellowish green crystals in about 20 d. Yield: 0.156 g (37.68% based on W). IR data (KBr pellet, cm⁻¹): $\tilde{\nu} = 1650(s)$, 1143(m), 1115(m), 1063(s), 957(s), 889(s), 815(w), 783(s), 724(s), 593(m), 514(m).

CCDC 1455107 (1) and 1455108 (2) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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