Supporting Information

Polyoxotungstates Incorporating Organotriphosphonate Ligands and Lanthanide Ions: Syntheses, Characterization, Magnetism and Photoluminescence Properties

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Section 1. IR spectra of $^{1}\text{Ce}–4\text{Eu}$

Solid state IR spectra of $^{1}\text{Ce}–4\text{Eu}$ have been recorded between 4000 and 450 cm$^{-1}$ to investigate the structural characters of targeted samples (Fig. S1). The spectra are very similar to each other with only slight shifts in the position of the bands, indicating that $^{1}\text{Ce}–4\text{Eu}$ almost have the same basic framework, and that is in good agreement with the results of the single-crystal X-ray structural analysis. The characteristic peaks detected at 711, 775, 871 and 980 cm$^{-1}$ for $^{1}\text{Ce}$; 715, 763, 882 and 983 cm$^{-1}$ for $^{2}\text{Nd}$; 718, 763, 886 and 978 cm$^{-1}$ for $^{3}\text{Sm}$; 716, 768, 886 and 985 cm$^{-1}$ for $^{4}\text{Eu}$; are assigned to the vibrations of $\nu$(W–O$_c$), $\nu$(W–O$_b$), $\nu$(As–O$_a$) and $\nu$(W–O$_t$), respectively. The absorption bands in the range 1184–1035 cm$^{-1}$ of $^{1}\text{Ce}–4\text{Eu}$ are assigned to the vibration bands of P–O bonds, and the ones in the range 673–666 cm$^{-1}$ are assigned to the vibrations of the P–C groups, which demonstrate the grafting of organic ligands onto the surface of POMs. The broad peaks around 3450 cm$^{-1}$ for $^{1}\text{Ce}–4\text{Eu}$ are assigned to the stretching vibration $\nu$(O–H), as well as signals appearing at 1618–1627 cm$^{-1}$ are attributed to the bending vibration $\delta$(O–H) of crystal and coordinated water molecules.

Section 2. Powder X-ray diffraction patterns of simulated and experimental for $^{1}\text{Ce}–4\text{Eu}$

The Powder X-ray diffraction (PXRD) patterns of $^{1}\text{Ce}–4\text{Eu}$ have been characterized by the good agreement with the simulated patterns derived from single-crystal X-ray diffraction (Fig. S2), implying the good phase purity for $^{1}\text{Ce}–4\text{Eu}$. The disparities in intensity of some diffraction peaks may be attributed to the variation of preferred orientation of the powder sample during the course of collecting the experimental PXRD patterns.
Fig. S2 Simulated (black) and experimental PXRD patterns (blue) of $^{1}\text{Ce} - ^{4}\text{Eu}$

Section 3. BVS values of selected oxygen atoms in $^{1}\text{Ce} - ^{4}\text{Eu}$

![Ball-and-stick representation of polyanion for $^{1}\text{Ce}$](image)

**Fig. S3** Ball-and-stick representation of polyanion for $^{1}\text{Ce}$

<table>
<thead>
<tr>
<th>atom</th>
<th>BVS</th>
<th>protonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O43</td>
<td>0.850 0.797 1.056 0.898</td>
<td>monoprotonated</td>
</tr>
<tr>
<td>O1W</td>
<td>0.348 0.318 0.349 0.321</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O2W</td>
<td>0.341 0.363 0.358 0.361</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O3W</td>
<td>0.305 0.305 0.288 0.322</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O4W</td>
<td>0.354 0.334 0.349 0.359</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O5W</td>
<td>0.339 0.328 0.346 0.323</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O6W</td>
<td>0.282 0.292 0.328 0.310</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O7W</td>
<td>0.400 0.333 0.417 0.365</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O8W</td>
<td>0.359 0.336 0.365 0.396</td>
<td>diprotonated</td>
</tr>
<tr>
<td>O9W</td>
<td>0.379 0.320 0.264 0.355</td>
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<tr>
<td>O10W</td>
<td>0.136 0.618 0.587 0.546</td>
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</tr>
<tr>
<td>O11W</td>
<td>0.297 0.194 0.205 0.229</td>
<td>diprotonated</td>
</tr>
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Table S1 BVS values of selected oxygen atoms in $^{1}\text{Ce} - ^{4}\text{Eu}$
Section 4. EDX spectra of single crystal of $\text{1Ce}^-$-$\text{4Eu}$ and EDX analyses

![Fig. S4 EDX spectra of single crystal of $\text{1Ce}^-$-$\text{4Eu}$](image)

EDX analyses

EDX was used to characterize the composition of $\text{1Ce}^-$-$\text{4Eu}$ using single crystals. According to the EDX spectra, W : K and As : K were respectively detected with approximate ratio of 10.6 : 1, 0.97 : 1 and this result has been checked using multiple samples to reduce the error in the value. In consideration of the error of EDX measurements, we combine EDX, structural data, BVS analyses, magnetic property, TG analyses, elemental analyses and charge balance arguments to estimate the formula of the isostructural compounds $\text{1Ce}^-$-$\text{4Eu}$. Using these approach we can give the formula is $\text{K}_2[\text{Ln(H}_2\text{O)}_4(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)(\text{O}_3\text{PCOHCH}_3\text{PO}_3)\text{Ln(H}_2\text{O)}_7]_2\cdot15\text{H}_2\text{O}$ [Ln = Ce ($\text{1Ce}$), Nd ($\text{2Nd}$), Sm ($\text{3Sm}$) and Eu ($\text{4Eu}$)] (W : K = 11 : 1, As : K = 1 : 1).

Section 5. The Ln–O bond lengths analyses with lanthanide contraction

![Fig. S5 The variation trend of Ln–O average bond lengths](image)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Average length (Å)</th>
<th>Atom</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Average length (Å)</th>
</tr>
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<tbody>
<tr>
<td>Ce1</td>
<td>Ce1–O14</td>
<td>2.544(14)</td>
<td>2.530</td>
<td>Ce1–O32</td>
<td>2.397(15)</td>
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<td></td>
</tr>
<tr>
<td>Ce1</td>
<td>Ce1–O34</td>
<td>2.503(14)</td>
<td>2.353(16)</td>
<td>Ce1–O5W</td>
<td>2.551(16)</td>
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<td></td>
</tr>
<tr>
<td>Ce1</td>
<td>Ce1–O35</td>
<td>2.480(14)</td>
<td>2.549</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Section 6. Thermal gravimetric analyses of 1Ce−4Eu

Thermal gravimetric analyses (TGA) of the four compounds have been analyzed upon heating to 800 °C under N₂ atmosphere (Fig. S6). All the TG curves show two slow steps of weight loss, the first weight loss of 9.18% for 1Ce (calcd 9.45%), 8.97% for 2Nd (calcd 9.43%), 9.62% for 3Sm (calcd 9.39%) and 9.53% for 4Eu (calcd 9.38%) in the temperature of 25−380 °C, respectively, which correspond to the release of fifteen crystal water molecules and twenty-two coordinated water molecules. From 380 to 800 °C, the second weight loss of 3.98% (calcd 4.05%), 4.48% (calcd 4.04%), 4.64% (calcd 4.03%) and 4.17% (calcd 4.03%) for 1Ce−4Eu, respectively.
can be ascribed to the loss of two \{-COHCH\_3\} groups and the sublimation of As\_2O\_3 molecules.

![Fig. S6 TG curves of 1Ce−4Eu](image)

**Fig. S6** TG curves of 1Ce−4Eu

Section 7. The 1/\(\chi\) versus T plots and the best-fit by the Curie-Weiss law for 1Ce and 2Nd

![Fig. S7 The temperature dependence of 1/\(\chi\) for 1Ce (a) and 2Nd (b), and the red solid for 1Ce and the blue solid for 2Nd lines represent the best-fit by the Curie-Weiss law.](image)

**Fig. S7** The temperature dependence of 1/\(\chi\) for 1Ce (a) and 2Nd (b), and the red solid for 1Ce and the blue solid for 2Nd lines represent the best-fit by the Curie-Weiss law.

Section 8. Some other additional figures

![Fig. S8 The crescent inorganic-organic hybrid module \{(W\_2O\_3)(O\_3P\text{COHCH\_3}PO\_3)Ce(H\_2O)\_7\}](image)

**Fig. S8** The crescent inorganic-organic hybrid module \{(W\_2O\_3)(O\_3P\text{COHCH\_3}PO\_3)Ce(H\_2O)\_7\}
**Fig. S9** Excitation spectra of $^{3}\text{Sm}$ (a) and $^{4}\text{Eu}$ (b) in the solid state at room temperature.

**Fig. S10** The NIR excitation spectra of $^{2}\text{Nd}$ (a) and $^{3}\text{Sm}$ (b) in solid state at room temperature.

**Fig. S11** (a) The solid-state emission spectrum of $\{\text{As}_2\text{W}_{19}\}$ under a light of 402 nm, (b) The solid-state emission spectrum of $\{\text{As}_2\text{W}_{19}\}$ under a light of 395 nm.

**Fig. S12** (a) The decay curve of $\{\text{As}_2\text{W}_{19}\}$ under the excitation at 402 nm, (b) The decay curve of $\{\text{As}_2\text{W}_{19}\}$ under the excitation at 395 nm.
Section 9. CIE color chromaticity coordinates of 3Sm and 4Eu

The CIE 1931 diagram is an international standard approach for studying all the possible colors by combining the three primary colors, in which the chromaticity coordinates $x$ and $y$ are always used to confirm the exact emission color for the tested samples. The CIE chromaticity coordinates $(x, y)$ for 3Sm and 4Eu are identified on the basis of the corresponding photoluminescence spectra and are indexed to $(0.60368, 0.39432)$ and $(0.64901, 0.34968)$, respectively (Fig. S11), which can be easily observed the reddish orange for 3Sm and red for 4Eu.

![Fig. S13 The CIE chromaticity diagrams of 3Sm and 4Eu.](image-url)