Supplementary Information

Organic–inorganic Hybrid Rare Earth complexes based on Polymolybdates with Intrinsic Photosensitive Properties

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1. Experimental Section

1.1. Materials and measurements

All reagents were purchased commercially and used without further purification. Elemental analysis (C, H and N) was performed by a Perkin-Elmer 2400-II CHNS/O analyzer. Infrared spectra (IR) were obtained on a Bruker VERTEX 70 IR spectrometer in the range of 4000–400 cm\(^{-1}\) (using KBr in pellets). PXRD data were recorded on a Philips X'Pert-MPD instrument with Cu K\(\alpha\) radiation (\(\lambda = 1.54056 \text{ Å}\)) in the angular range 2\(\theta = 5\)–40° at 293K. TG analysis was measured on a Mettler-Toledo TGA/SDTA851\(^e\) instrument with a heating rate of 10 °C/min from room temperature (about 20 °C) to 800 °C in N\(_2\) flow. Diffuse reflectivity in the solid state (using BaSO\(_4\) as the reference) and UV spectrum pH=1 H\(_2\)SO\(_4\) solution (concentration: 100 and 1 \(\mu\)M) were obtained on HITACHI U4100 UV-vis spectrometer. The absorption (\(\alpha/S\)) data were calculated from the reflectivity using the Kubelka-Munk function: \(\alpha/S=(1-R)^2/2R\), where R is the reflectivity at a given wavelength, \(\alpha\) is the absorption coefficient, and S is the scattering coefficient. The optical gaps are determined from the reflectivity spectrum as the intersection point between the wavelength axis and the line extrapolated from the linear portion of the reflectivity threshold. The fluorescence properties were performed on a HITACHI F–7000 fluorescence spectrophotometer in solid state and pH=1 H\(_2\)SO\(_4\) solution (concentration: 100\(\mu\)M). Electrochemical measurements were carried out on a CHI 660A electrochemical workstation (pH=1 H\(_2\)SO\(_4\) as solvent) at room temperature. UV (\(\lambda = 365 \text{ nm}\)) and visible light (\(\lambda > 420 \text{ nm}\)) used in photosensitive experiment were generated by 300 W CEL-HXF300 Xenon Lamp from Zhong Jiao Jin Yuan company equipped with UV365 and UV\(\text{CUT420}\) transmission filter, respectively. The distance between the lamp and the sample was 5 cm.
1.2. Synthesis:

Na$_2$MoO$_4$·2H$_2$O (0.50 g, 1.7 mmol) was dissolved in distilled water (10 ml) and acetonitrile (5ml). The solution is acidified with concentrated HCl until the pH value was about 2.0 with stirring. Then PO (0.5 ml) was added and the pH value was adjusted to 1.3 with concentrated HCl. To the above solution, a distilled water (5 ml) solution containing Nd(NO$_3$)$_3$·6H$_2$O (0.22g, 0.05 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 30 mins, filtrated and the filtrate was kept in darkness for several days. The large amount of yellow block crystals of 1 were filtered, washed with cool water, and then dried in air. Compounds 2-10 are prepared similarly to 1 using the corresponding RE(NO$_3$)$_3$·6H$_2$O (RE= Sm, Eu, Gd, Dy, Er, Tm, Yb, Lu, Y) instead of Nd(NO$_3$)$_3$·6H$_2$O.

1: Yield: 42% (based on Mo). Anal. calcd for C$_{59}$H$_{231}$N$_{13}$O$_{185}$Mo$_{36}$Nd$_2$: C, 9.06; H, 2.98; N, 2.33. Found: C, 8.09; H, 2.45; N, 2.07. IR (KBr pellet, cm$^{-1}$): 3347, 2949, 1622, 1501, 1402, 1357, 1273, 1175, 1107, 981, 955, 878, 787, 646, 581.

2: Yield: 38% (based on Mo). Anal. calcd for C$_{59}$H$_{199}$N$_{13}$O$_{169}$Mo$_{36}$Sm$_2$: C, 9.39; H, 2.66; N, 2.41. Found: C, 8.28; H, 2.48; N, 2.08. IR (KBr pellet, cm$^{-1}$): 3341, 2949, 1622, 1501, 1402, 1356, 1273, 1173, 1107, 980, 955, 878, 787, 646, 579.

3: Yield: 52% (based on Mo). Anal. calcd for C$_{59}$H$_{201}$N$_{13}$O$_{170}$Mo$_{36}$Eu$_2$: C, 9.36; H, 2.68; N, 2.41. Found: C, 8.13; H, 2.40; N, 2.13. IR (KBr pellet, cm$^{-1}$): 3339, 2945, 1622, 1501, 1400, 1356, 1273, 1173, 1107, 980, 955, 878, 787, 646, 577.

4: Yield: 56% (based on Mo). Anal. calcd for C$_{59}$H$_{199}$N$_{13}$O$_{169}$Mo$_{36}$Gd$_2$: C, 9.37; H, 2.65; N, 2.41. Found: C, 8.01; H, 2.45; N, 2.18. IR (KBr pellet, cm$^{-1}$): 3337, 2947, 1622, 1501, 1402, 1356, 1273, 1173, 1107, 981, 952, 878, 787, 644, 577.
5: Yield: 30% (based on Mo). Anal. calcd for C_{59}H_{201}N_{13}O_{170}Mo_{36}Dy\_2: C, 9.33; H, 2.67; N, 2.40. Found: C, 8.26; H, 2.44; N, 2.12. IR (KBr pellet, cm\(^{-1}\)): 3345, 2949, 1624, 1501, 1404, 1355, 1273, 1175, 1107, 980, 955, 878, 787, 646, 579.

6: Yield: 28% (based on Mo). Anal. calcd for C_{59}H_{205}N_{13}O_{172}Mo_{36}Er\_2: C, 9.28; H, 2.71; N, 2.38. Found: C, 8.38; H, 2.46; N, 2.16. IR (KBr pellet, cm\(^{-1}\)): 3335, 2945, 1620, 1499, 1402, 1354, 1273, 1173, 1107, 981, 955, 878, 787, 644, 577.

7: Yield: 53% (based on Mo). Anal. calcd for C_{59}H_{199}N_{13}O_{169}Mo_{36}Tm\_2: C, 9.34; H, 2.64; N, 2.40. Found: C, 8.16; H, 2.40; N, 2.15. IR (KBr pellet, cm\(^{-1}\)): 3345, 2949, 1624, 1501, 1404, 1356, 1273, 1175, 1107, 981, 955, 878, 789, 646, 579.

8: Yield: 26% (based on Mo). Anal. calcd for C_{59}H_{203}N_{13}O_{171}Mo_{36}Yb\_2: C, 9.29; H, 2.68; N, 2.39. Found: C, 8.13; H, 2.39; N, 2.19. IR (KBr pellet, cm\(^{-1}\)): 3345, 2949, 1624, 1501, 1404, 1355, 1273, 1175, 1107, 981, 955, 878, 789, 646, 579.

9: Yield: 48% (based on Mo). Anal. calcd for C_{59}H_{235}N_{13}O_{187}Mo_{36}Lu\_2: C, 8.94; H, 2.99; N, 2.30. Found: C, 8.40; H, 2.41; N, 2.11. IR (KBr pellet, cm\(^{-1}\)): 3345, 2949, 1624, 1501, 1404, 1355, 1273, 1175, 1107, 980, 955, 878, 789, 646, 579.

10: Yield: 60% (based on Mo). Anal. calcd for C_{59}H_{197}N_{13}O_{168}Mo_{36}Y\_2: C, 9.56; H, 2.68; N, 2.46. Found: C, 8.56; H, 2.45; N, 2.00. IR (KBr pellet, cm\(^{-1}\)): 3345, 2949, 1624, 1501, 1404, 1355, 1273, 1175, 1107, 980, 955, 878, 789, 646, 579.

It should be noted that the contents of nitrogen and hydrogen are consistent with the calculated results in all compounds. However, the contents of carbon found by XRD were larger than those determined by elemental analysis (about 10% deviation). This may be explained from following two aspects: 1) the reference used for carbon analysis is 30%, but the carbon content of each
compound lower than 10%, and thus imprecise results may be obtained; 2) the crystals are easy to weather when exposed in air, which may also influence the analysis results. For overall consistency, the formulas in this work are same as those found by XRD. Thus the corresponding formulas should be: \([\{\text{RE}_2(\text{PO})_2(\text{H}_2\text{O})_{10}\}[\text{H}_2\text{Mo}_{36}\text{O}_{112}(\text{OH}_2)_{12}(\text{PO})_{12}]\} \cdot 5\text{PO} \cdot 2(\text{CH}_3\text{CN}) \cdot n\text{H}_2\text{O}\) [n= 40 for 1; n= 24 for 2, 4, 7; n= 25 for 3, 5; n= 27 for 6; n= 26 for 8; n= 42 for 9; n= 23 for 10].

1.3. Synthesis Discussion

After plenty of parallel experiments, we find that several factors have affected the formation of compounds 1-10: (a) The volume of the acetonitrile is quite important. When we increase the volume to 7.5 mL, the same crystals could be obtained after fewer days, but not suitable for the single-crystal diffraction. However, if the acetonitrile is stead of same volume of water, we can only get some unknown powder. (b) The pH value should be in the range of 1.0 to 1.6. When pH value below 1.0, some \{\text{Mo}_4\} derives will be crystallized. While pH value above 1.6, the quality of crystals can not reach the standard. (c) The addition order of PO and RE(NO\textsubscript{3})\textsubscript{3} does not affect the formation of the crystals, but each of them should be added after the Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O solution is acidified to pH=2.0. Otherwise, it is easy to form precipitation instead of crystallization. (d) The ion types of the RE salts seem to be of no significance for the formation of compounds. We try to use RECl\textsubscript{3} to replace RE(NO\textsubscript{3})\textsubscript{3}, the isostructures can be also formed. (e) The reaction temperature varies from the room temperature to 50°C has no effect on the formation or the quality of crystals. But if the reaction time exceeds 1 hour, only precipitation could be isolated.
1.4. X-ray Crystallography

The crystallographic data of compounds 1-10 were collected on a Bruker CCD Apex-II diffractometer with Mo Kα radiation (λ= 0.71073Å) at 296 K. The crystal data were solved by direct method and further refined by full-matrix least-squares refinements on F² using the SHELXL-97 software and an absorption correction was performed using the SADABS program. In the final refinement, the Mo and lanthanide atoms were refined anisotropically; the C, N and O atoms were refined isotropically. The hydrogen atoms of the confirmed PO and acetonitrile molecules were placed in calculated positions and then refined using a riding model. All H atoms on confirmed water molecules were directly included in the molecular formula. SQUEEZE procedure was applied to deal with the existence of the voids. The detailed crystal data and structural refinements for compounds 1-10 are given in Table S1. CCDC 1016517-1016526 contain the supplementary crystallographic data of compounds 1-10. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/date_request/cif.
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2. Bond Valence Sum (BVS) Calculations and Occupancy Values

![Diagram of atoms labeling in the \(\text{Mo}_{18}-(\text{PO}_2)\) unit of compound 4 (the protonized O atoms with different color).]

**Table S2** Bond valence sum parameters for Mo atoms and protonized O atoms in the \(\text{Mo}_{18}-(\text{PO}_2)\) unit of compounds 1-10.

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<td>5.889</td>
<td>5.941</td>
<td>5.896</td>
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Table S3 Occupancy values of the disordered Mo atoms in compounds 1-10.

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<tr>
<th>atom</th>
<th>Mo4/ Mo1X</th>
<th>Mo5/ Mo1Y</th>
<th>Mo12/ Mo1Z</th>
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<td>1</td>
<td>0.85/0.15</td>
<td>0.55/0.45</td>
<td>0.80/0.20</td>
</tr>
<tr>
<td>2</td>
<td>0.85/0.15</td>
<td>0.55/0.45</td>
<td>0.80/0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.85/0.15</td>
<td>0.60/0.40</td>
<td>0.80/0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.85/0.15</td>
<td>0.65/0.35</td>
<td>0.80/0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.85/0.15</td>
<td>0.70/0.30</td>
<td>0.85/0.15</td>
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<td>6</td>
<td>0.85/0.15</td>
<td>0.70/0.30</td>
<td>0.85/0.15</td>
</tr>
<tr>
<td>7</td>
<td>0.85/0.15</td>
<td>0.70/0.30</td>
<td>0.80/0.20</td>
</tr>
<tr>
<td>8</td>
<td>0.90/0.10</td>
<td>0.75/0.25</td>
<td>0.85/0.15</td>
</tr>
<tr>
<td>9</td>
<td>0.90/0.10</td>
<td>0.75/0.25</td>
<td>0.85/0.15</td>
</tr>
<tr>
<td>10</td>
<td>0.85/0.15</td>
<td>0.70/0.30</td>
<td>0.80/0.20</td>
</tr>
</tbody>
</table>
3. Additional Physical Measurements

3.1. IR Spectra

In the IR spectroscopy of compounds 1-10, the characteristic bonds range from 700 to 960 cm\(^{-1}\) was assigned to characteristic asymmetric vibrations from \{Mo\(_{36}\}\) polyanions \(^2-^4\). The characteristic bonds at 1622 and 1107 cm\(^{-1}\) are attributed to the C=O and N-H vibrations of PO molecules, respectively \(^5\). The aqueous vibrations at 3335-3345 cm\(^{-1}\) show that there are some water molecules in all compounds \(^4\). It is in accordance with the result of the crystal structure study.

![Fig. S2 IR spectra of compounds 1-10](image-url)
The reference compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$ was synthesized via the literature procedure (ref. 22 in the manuscript), the structure of which was confirmed by IR spectrum. Obviously, the characteristic asymmetric vibrations of $\{Mo_{36}\}$ polyanions also appear at the range of 700 to 960 cm$^{-1}$.

![IR spectrum of compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$](image)

**Fig. S3** IR spectrum of compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$
3.2. Powder X-ray Diffraction (PXRD) Spectra

The phase purities of compounds 1-10 were supported by the powder X-ray diffraction (PXRD) pattern of the bulk samples, which are consistent with the calculated patterns.

Fig. S4. X-ray powder diffraction (XPRD) pattern of compounds 1-10 (a-j).
3.3. Thermogravimetric Analysis

As shown in Table S4 and Fig. S4, the TG curve of each compound shows a first step of weight loss below 210 °C, which is attributed to the decompositions of the crystallization water and acetonitrile molecules, plus water molecules coordinated with RE(III) ion. A second weight loss between 210 and 550 °C is assigned to the decompositions of 12 coordination water molecules of Mo atoms and 11 organic PO molecules. For temperature over 550 °C, the TG curve shows a sharp weight loss indicating the sublimation of MoO$_3$.

Table S4. Weight loss (%) of compounds 1-10

<table>
<thead>
<tr>
<th>compounds</th>
<th>found (calc.) $T&lt;210$ °C</th>
<th>found (calc.) $T=210-550$ °C</th>
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<tr>
<td>1</td>
<td>7.90 (12.65)</td>
<td>15.24 (16.67)</td>
</tr>
<tr>
<td>2</td>
<td>7.21 (9.30)</td>
<td>15.83 (17.29)</td>
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<tr>
<td>3</td>
<td>7.13 (9.50)</td>
<td>16.57 (17.24)</td>
</tr>
<tr>
<td>4</td>
<td>8.22 (9.28)</td>
<td>15.82 (17.25)</td>
</tr>
<tr>
<td>5</td>
<td>8.36 (9.48)</td>
<td>16.28 (17.19)</td>
</tr>
<tr>
<td>6</td>
<td>8.43 (9.90)</td>
<td>16.20 (17.09)</td>
</tr>
<tr>
<td>7</td>
<td>8.25 (9.25)</td>
<td>15.34 (17.20)</td>
</tr>
<tr>
<td>8</td>
<td>7.72 (9.67)</td>
<td>15.42 (17.10)</td>
</tr>
<tr>
<td>9</td>
<td>8.49 (12.95)</td>
<td>15.67 (16.47)</td>
</tr>
<tr>
<td>10</td>
<td>8.01 (9.23)</td>
<td>16.16 (18.02)</td>
</tr>
</tbody>
</table>
Fig. S5. TGA curves of compounds 1-10 (a-j).
3.4. UV-vis spectroscopy

In pH=1.0 H₂SO₄ solution (concentration: 1μM), the characteristic absorption bands of compounds 1-10 are at about 213 nm, which exhibits red-shift by contrast with classical {Mo₃⁶} (at 209 nm). This is probably due to the π- π* conjugate action between the {Mo₃⁶} unit with the covalently bonded PO molecules. However, it can be confirmed that compounds 1-10 could maintain their {Mo₃⁶} backbone in pH=1.0 H₂SO₄ solution.

![UV spectra of compounds 1-10 in pH=1 H₂SO₄ solution (concentration: 1μM)](image)

**Fig. S6.** UV spectra of compounds 1-10 in pH=1 H₂SO₄ solution (concentration: 1μM)
3.5. Electrochemistry

The electrochemical properties of the compounds 1-10 were detected in pH=1 H₂SO₄ solution at the scan rate of 100 mV s⁻¹. Different from the reported functionalized {Mo₃₆} cluster ², ³, only one irreversible redox peak appears for each compound (Fig. S6) and the mean peak potential \( E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \) is about 0.055 V (versus SCE), corresponding to the redox of the Mo⁶⁺ in the polyoxoanion framework ², ³. At scan rates lower than 250 mV·s⁻¹, the peak currents were proportional to the scan rate, which indicates that the redox process of each compound is surface-controlled ³. Interestingly, the solutions show similar cathodochromic phenomenon as reviewed by Yamase ⁷.
Fig. S7. The cyclic voltammograms of compounds 1-10 (a-j) in pH=1 H₂SO₄ solution at different scan rates (from inner to outer: 50, 100, 150, 200, 250 mV·s⁻¹).
4. Coloration of each compound in solid state via visible light irradiation

<table>
<thead>
<tr>
<th></th>
<th>0 min</th>
<th>2 min</th>
<th>4 min</th>
<th>6 min</th>
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Fig. S8. Color variations of compounds 1-10 (a-j) in solid state after 0-20 min irradiation via visible light.
Fig. S9. Reflectance $R(t)$ of 4 in the 350 – 1000 nm range measured after irradiating the sample for $t$ min with visible light ($\lambda > 420$ nm). From top to bottom, $t= 0, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16, 20$ and 40 min, respectively. The vertical dashed line at 768 nm indicates that the local minimum of the reflectance occurs at 768 nm.

Fig. S10. IR spectra of the compound 4 in solid state, before (a) and after (b) visible light irradiation.

Fig. S11. No Color variation of the compound K$_8$[Mo$_{36}$O$_{112}$(H$_2$O)$_{18}$]·36H$_2$O before (a) and after (b) 40 min irradiation via visible light in solid state.
5. Additional fluorescence spectroscopy in solid state

**Fig. S12.** Excitation (black) and emission (blue) spectra of compounds 2-10 (a-i) and $K_8[Mo_{36}O_{112}(H_2O)_{18}]\cdot36H_2O$ (j) in solid state.
6. Fluorescence spectroscopy in solution

**Fig. S13.** Emission spectra of compounds 1-10 in pH=1 H$_2$SO$_4$ solution ($\lambda_{ex}=410$ nm, concentration: 100 µM).

7. References