

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 ($\lambda = 1.54056 \text{ \AA}$) in the angular range $2\theta = 5\text{--}40^\circ$ at 293K. TG analysis was measured on a Mettler-Toledo TGA/SDTA851^e instrument with a heating rate of 10 $^\circ\text{C}/\text{min}$ from room temperature (about 20 $^\circ\text{C}$) to 800 $^\circ\text{C}$ in N_2 flow. Diffuse reflectivity in the solid state (using BaSO_4 as the reference) and UV spectrain pH=1 H_2SO_4 solution (concentration: 100 and 1 μM) were obtained on HITACHI U4100 UV-vis spectrometer. The absorption (α/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, α 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_2SO_4 solution (concentration: 100 μM). Electrochemical measurements were carried out on a CHI 660A electrochemical workstation (pH=1 H_2SO_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 UVCUT420 transmission filter, respectively. The distance between the lamp and the sample was 5 cm.

1.2. Synthesis:

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (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 $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (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 $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE= Sm, Eu, Gd, Dy, Er, Tm, Yb, Lu, Y) instead of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

1: Yield: 42% (based on Mo). Anal. calcd for $\text{C}_{59}\text{H}_{231}\text{N}_{13}\text{O}_{185}\text{Mo}_{36}\text{Nd}_2$: 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 $\text{C}_{59}\text{H}_{199}\text{N}_{13}\text{O}_{169}\text{Mo}_{36}\text{Sm}_2$: 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 $\text{C}_{59}\text{H}_{201}\text{N}_{13}\text{O}_{170}\text{Mo}_{36}\text{Eu}_2$: 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 $\text{C}_{59}\text{H}_{199}\text{N}_{13}\text{O}_{169}\text{Mo}_{36}\text{Gd}_2$: 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: $\{[\text{RE}_2(\text{PO})_2(\text{H}_2\text{O})_{10}][\text{H}_2\text{Mo}_3\text{O}_{11}(\text{OH})_2(\text{PO})_4]\} \cdot 5\text{PO} \cdot 2(\text{CH}_3\text{CN}) \cdot n\text{H}_2\text{O}$ [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 instead 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 $\{\text{Mo}_8\}$ derivatives 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 $\text{RE}(\text{NO}_3)_3$ does not affect the formation of the crystals, but each of them should be added after the $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 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_3 to replace $\text{RE}(\text{NO}_3)_3$, 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 K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The crystal data were solved by direct method and further refined by full-matrix least-squares refinements on F^2 using the SHELXL-97 software and an absorption correction was performed using the SADABS program ¹. 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/data_request/cif.

Table S1 Crystal Data and Structure Refinements for Compounds **1-10**

	1	2	3	4	5
Empirical formula	C ₅₉ H ₂₃₁ N ₁₃ O ₁₈₅ Mo ₃₆ Nd ₂	C ₅₉ H ₁₉₉ N ₁₃ O ₁₆₉ Mo ₃₆ Sm ₂	C ₅₉ H ₂₀₁ N ₁₃ O ₁₇₀ Mo ₃₆ Eu ₂	C ₅₉ H ₁₉₉ N ₁₃ O ₁₆₉ Mo ₃₆ Gd ₂	C ₅₉ H ₂₀₁ N ₁₃ O ₁₇₀ Mo ₃₆ Dy ₂
Formula weight	7825.89	7549.85	7571.09	7563.65	7592.17
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Space group / Crystal system	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n
a / Å	18.1342(6)	18.1715(9)	18.1150(9)	18.1061(13)	18.1552(7)
b / Å	18.9297(6)	18.9571(10)	18.8634(9)	18.8800(12)	18.9640(7)
c / Å	31.2954(10)	31.3002(17)	31.2063(16)	31.161(2)	31.1861(12)
β / deg	103.2550(10)	103.3210(10)	103.4020(10)	103.4280(10)	103.4730(10)
V / Å ³	10456.7(6)	10492.2(9)	10373.1(9)	10360.8(12)	10441.7(7)
Z	2	2	2	2	2
D _c / g cm ⁻³	2.486	2.390	2.424	2.424	2.415
μ / mm ⁻¹	2.687	2.733	2.803	2.841	2.900
F(000)	7576	7264	7288	7272	7300
Limiting indices	-21 ≤ h ≤ 17 -22 ≤ k ≤ 15 -32 ≤ l ≤ 37	-19 ≤ h ≤ 21 -17 ≤ k ≤ 22 -37 ≤ l ≤ 30	-20 ≤ h ≤ 21 -17 ≤ k ≤ 22 -37 ≤ l ≤ 29	-21 ≤ h ≤ 15 -22 ≤ k ≤ 13 -33 ≤ l ≤ 37	-16 ≤ h ≤ 21 -14 ≤ k ≤ 22 -37 ≤ l ≤ 34
□□ for data collection / deg	1.19-25.00	1.60-25.00	1.19-25.00	1.19-25.00	1.19-25.00
reflns collected / unique	53965 / 18422	53769 / 18481	53180 / 18266	50263 / 18236	53332 / 18393
R _(int)	0.0307	0.0306	0.0401	0.0343	0.0339
Goodness-of-fit on F ²	1.069	1.041	1.082	1.088	1.055
final R indices	R ₁ = 0.0493	R ₁ = 0.0469	R ₁ = 0.0486	R ₁ = 0.0465	R ₁ = 0.0462
[I > 2σ(I)]	wR ₂ = 0.1398	wR ₂ = 0.1176	wR ₂ = 0.1327	wR ₂ = 0.1271	wR ₂ = 0.1215
R indices	R ₁ = 0.0607	R ₁ = 0.0564	R ₁ = 0.0607	R ₁ = 0.0592	R ₁ = 0.0572
(all data)	wR ₂ = 0.1465	wR ₂ = 0.1226	wR ₂ = 0.1399	wR ₂ = 0.1340	wR ₂ = 0.1275

	6	7	8	9	10
Empirical formula	C ₅₉ H ₂₀₅ N ₁₃ O ₁₇₂ Mo ₃₆ Er ₂	C ₅₉ H ₁₉₉ N ₁₃ O ₁₆₉ Mo ₃₆ Tm ₂	C ₅₉ H ₂₀₃ N ₁₃ O ₁₇₁ Mo ₃₆ Yb ₂	C ₅₉ H ₂₃₅ N ₁₃ O ₁₈₇ Mo ₃₆ Lu ₂	C ₅₉ H ₁₉₇ N ₁₃ O ₁₆₈ Mo ₃₆ Y ₂
Formula weight	7637.72	7587.01	7631.26	7923.38	7408.96
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Space group / Crystal system	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n	Monoclinic / P2(1)/n
a / Å	18.1548(7)	18.1417(15)	18.1439(7)	18.1063(8)	18.1596(17)
b / Å	18.9687(7)	18.9738(16)	18.9549(7)	18.8830(9)	18.9673(18)
c / Å	31.1244(12)	31.066(3)	31.0336(12)	30.9085(14)	31.122(3)
β / deg	103.4860(10)	103.4910(10)	103.4890(10)	103.5380(10)	103.499(2)
V / Å ³	10422.9(7)	10398.4(15)	10378.5(7)	10274.0(8)	10423.4(17)
Z	2	2	2	2	2
D _c / g cm ⁻³	2.434	2.423	2.442	2.561	2.361
μ / mm ⁻¹	2.994	3.046	3.099	3.192	2.746
F(000)	7348	7292	7336	7660	7152
Limiting indices	-21 ≤ h ≤ 21 -22 ≤ k ≤ 10 -37 ≤ l ≤ 37	-20 ≤ h ≤ 21 -22 ≤ k ≤ 17 -36 ≤ l ≤ 30	-20 ≤ h ≤ 21 -22 ≤ k ≤ 12 -36 ≤ l ≤ 36	-11 ≤ h ≤ 21 -22 ≤ k ≤ 22 -36 ≤ l ≤ 36	-21 ≤ h ≤ 11 -22 ≤ k ≤ 22 -37 ≤ l ≤ 37
θ for data collection / deg	1.60-25.00	1.19-25.00	1.19-25.00	1.20-25.00	1.60-25.00
reflns collected / unique	53212 / 18346	53214 / 18301	53381 / 18263	52839 / 18096	53404 / 18346
$R_{(int)}$	0.0315	0.0321	0.0313	0.0629	0.0257
Goodness-of-fit on F ²	1.043	1.060	1.083	1.042	1.048
final R indices	$R_1 = 0.0432$	$R_1 = 0.0440$	$R_1 = 0.0447$	$R_1 = 0.0542$	$R_1 = 0.0434$
[I > 2 σ (I)]	$wR_2 = 0.1105$	$wR_2 = 0.1160$	$wR_2 = 0.1199$	$wR_2 = 0.1462$	$wR_2 = 0.1105$
R indices	$R_1 = 0.0510$	$R_1 = 0.0538$	$R_1 = 0.0539$	$R_1 = 0.0779$	$R_1 = 0.0527$
(all data)	$wR_2 = 0.1147$	$wR_2 = 0.1213$	$wR_2 = 0.1248$	$wR_2 = 0.1590$	$wR_2 = 0.1149$

2. Bond Valence Sum (BVS) Calculations and Occupancy Values

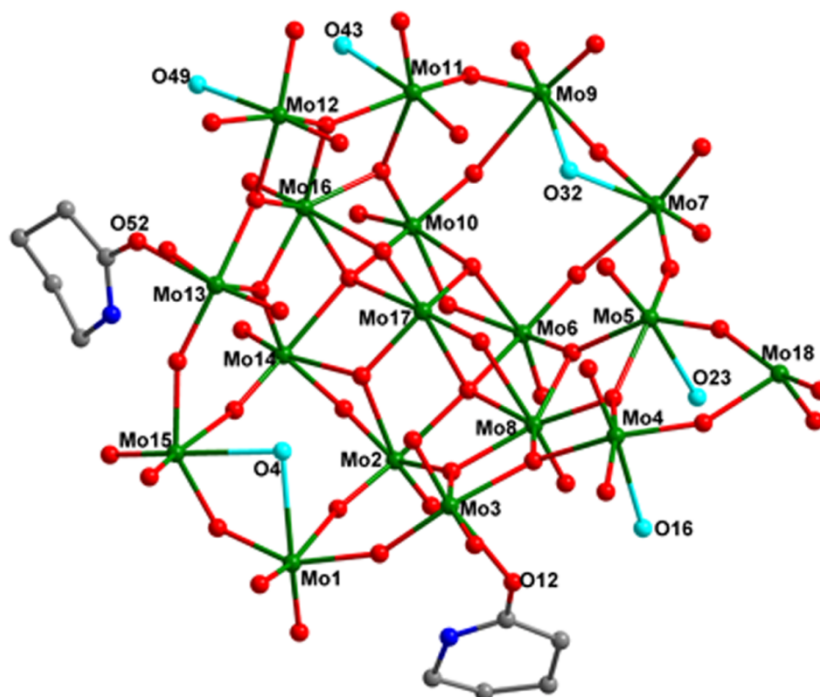


Fig. S1 The representation of atoms labeling in the $\{\text{Mo}_{18}\text{-(PO)}_2\}$ unit of compound **4** (the protonized O atoms with different color).

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**.

compound atom	1	2	3	4	5	6	7	8	9	10
Mo1	5.964	5.977	6.046	6.011	6.014	6.002	6.061	6.027	6.195	5.990
Mo2	6.124	6.023	6.119	6.148	6.061	6.034	6.101	6.102	6.154	6.080
Mo3	6.075	6.048	6.070	6.118	6.061	6.092	6.080	6.063	6.132	6.054
Mo4	6.064	6.055	6.078	6.190	6.048	6.077	6.090	6.108	6.257	6.107
Mo5	6.006	6.049	6.127	6.107	6.117	6.144	6.153	6.220	6.287	6.108
Mo6	6.077	6.027	6.117	6.153	6.059	6.051	6.059	6.071	6.132	6.072
Mo7	6.113	6.066	6.127	6.151	6.076	6.079	6.144	6.165	6.142	6.106
Mo8	5.940	5.911	5.934	5.941	5.953	5.939	5.975	5.948	6.032	5.954
Mo9	6.036	6.027	6.100	6.104	6.054	6.039	6.042	6.080	6.133	6.045
Mo10	6.048	5.987	6.040	6.089	6.044	6.019	6.077	6.064	6.147	6.020
Mo11	6.168	6.093	6.113	6.105	6.122	6.127	6.148	6.153	6.228	6.163
Mo12	6.209	6.107	6.188	6.212	6.147	6.193	6.190	6.231	6.181	6.184
Mo13	6.034	6.034	6.117	6.036	6.073	6.104	6.152	6.137	6.166	6.093
Mo14	6.014	6.019	6.099	6.126	6.037	6.058	6.056	6.073	6.119	6.019
Mo15	6.010	5.993	6.032	6.036	6.007	5.978	6.038	6.014	5.989	6.013
Mo16	5.934	5.932	5.991	6.009	5.926	5.909	5.967	5.930	6.064	5.953
Mo17	5.899	5.806	5.895	5.896	5.885	5.879	5.927	5.889	5.941	5.896

Mo18	6.195	6.139	6.258	6.244	6.197	6.193	6.228	6.243	6.386	6.201
O4	0.479	0.464	0.473	0.473	0.470	0.465	0.465	0.469	0.473	0.460
O16	0.278	0.277	0.275	0.274	0.261	0.261	0.268	0.262	0.264	0.267
O23	0.301	0.303	0.293	0.289	0.277	0.267	0.262	0.261	0.251	0.272
O32	0.430	0.427	0.425	0.425	0.428	0.424	0.425	0.429	0.436	0.422
O43	0.292	0.293	0.288	0.288	0.283	0.292	0.288	0.290	0.294	0.288
O49	0.243	0.243	0.240	0.247	0.243	0.243	0.245	0.249	0.236	0.244

Table S3 Occupancy values of the disordered Mo atoms in compounds **1-10**.

atom compound	Mo4/ Mo1X	Mo5/ Mo1Y	Mo12/ Mo1Z
1	0.85/0.15	0.55/0.45	0.80/0.20
2	0.85/0.15	0.55/0.45	0.80/0.20
3	0.85/0.15	0.60/0.40	0.80/0.20
4	0.85/0.15	0.65/0.35	0.80/0.20
5	0.85/0.15	0.70/0.30	0.85/0.15
6	0.85/0.15	0.70/0.30	0.85/0.15
7	0.85/0.15	0.70/0.30	0.80/0.20
8	0.90/0.10	0.75/0.25	0.85/0.15
9	0.90/0.10	0.75/0.25	0.85/0.15
10	0.85/0.15	0.70/0.30	0.80/0.20

3. Additional Physical Measurements

3.1. IR Spectra

In the IR spectroscopy of compounds **1-10**, the characteristic bands range from 700 to 960 cm^{-1} was assigned to characteristic asymmetric vibrations from $\{\text{Mo}_{36}\}$ polyanions ²⁻⁴. The characteristic bands 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.

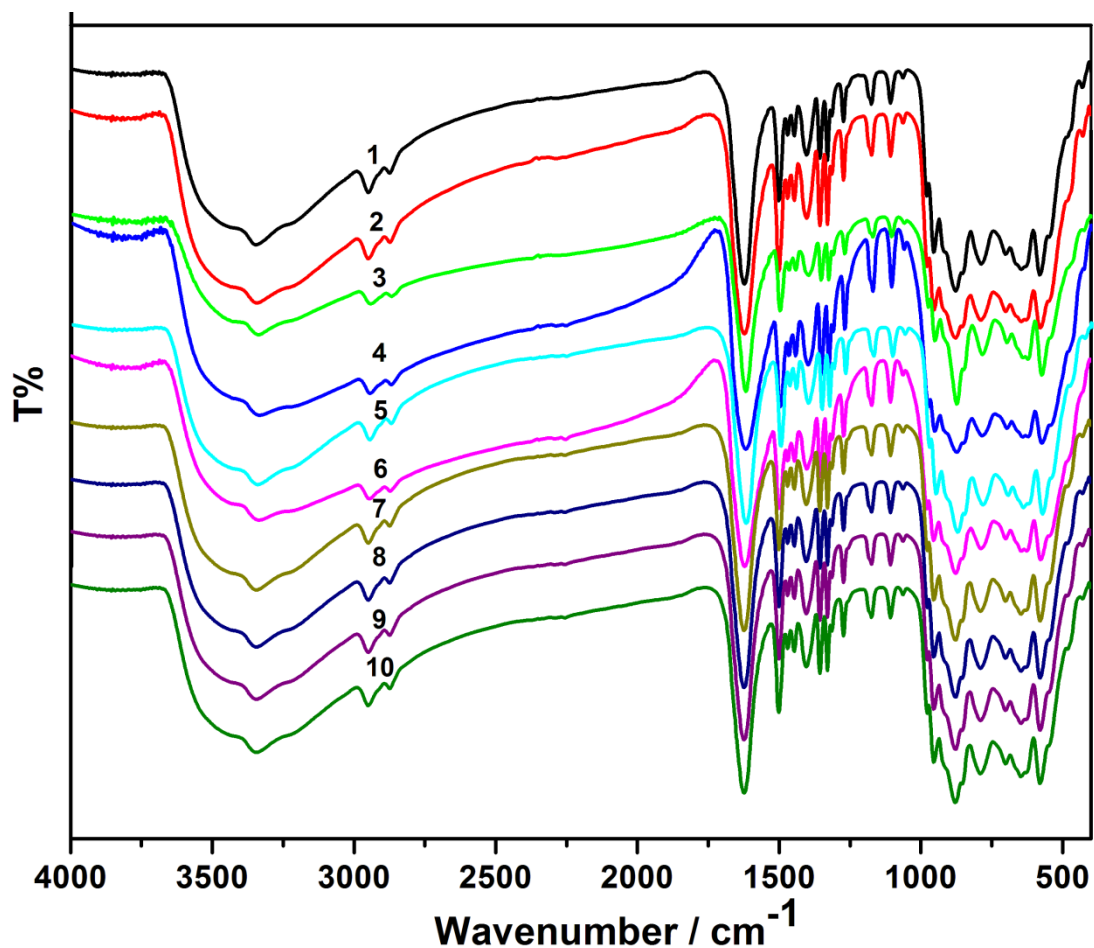


Fig. S2 IR spectra of compounds 1-10

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} .

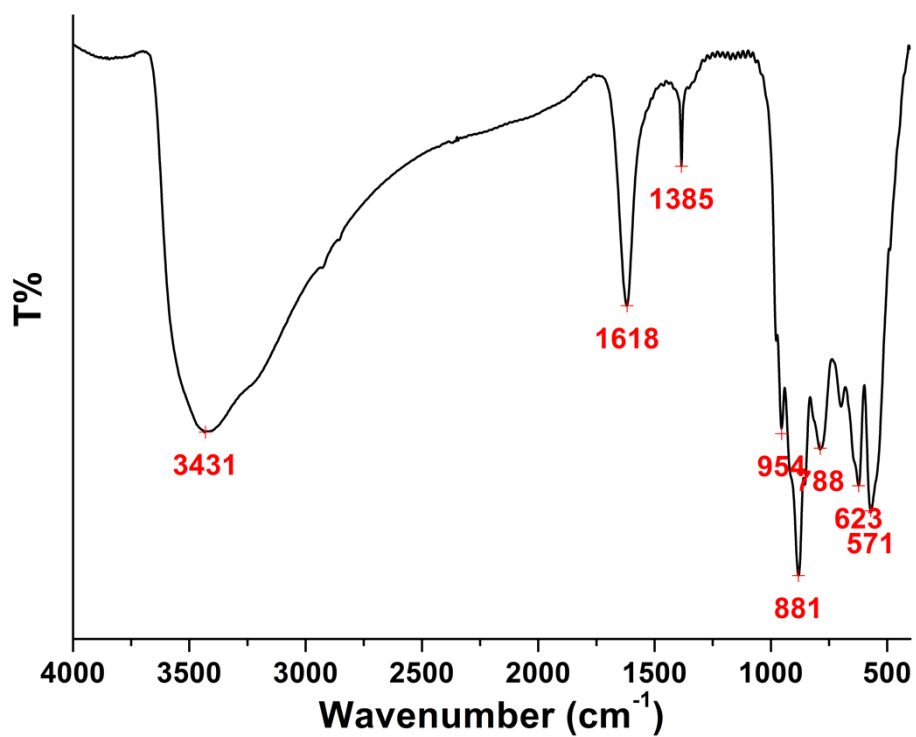


Fig. S3 IR spectrum of compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$

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.

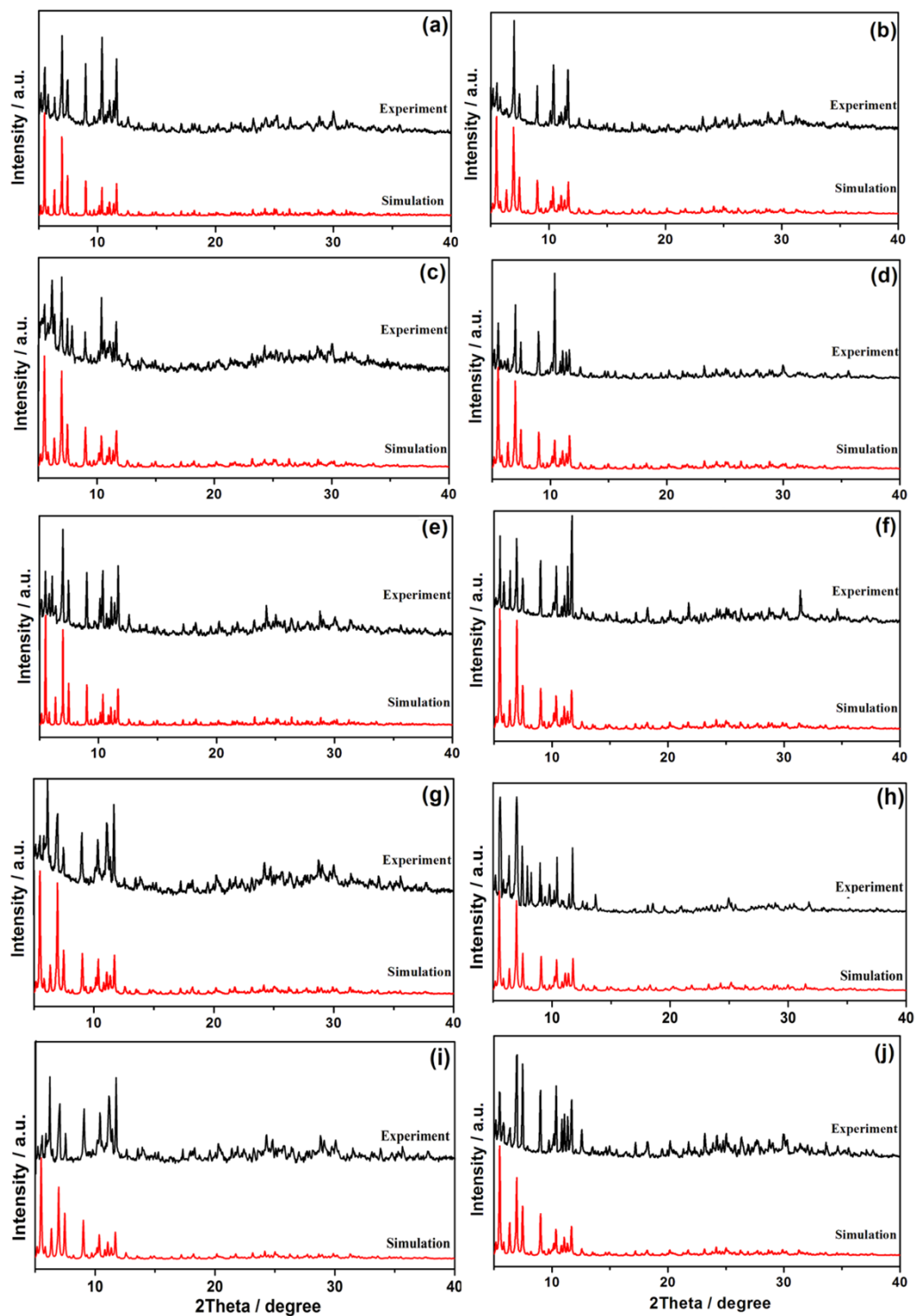


Fig. S4. X-ray powder diffraction (XPRD) pattern of compounds **1-10** (a-j).

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 MoO₃⁶.

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

compounds	found (calc.) T<210 °C	found (calc.) T=210-550 °C
1	7.90 (12.65)	15.24 (16.67)
2	7.21 (9.30)	15.83 (17.29)
3	7.13 (9.50)	16.57 (17.24)
4	8.22 (9.28)	15.82 (17.25)
5	8.36 (9.48)	16.28 (17.19)
6	8.43 (9.90)	16.20 (17.09)
7	8.25 (9.25)	15.34 (17.20)
8	7.72 (9.67)	15.42 (17.10)
9	8.49 (12.95)	15.67 (16.47)
10	8.01 (9.23)	16.16 (18.02)

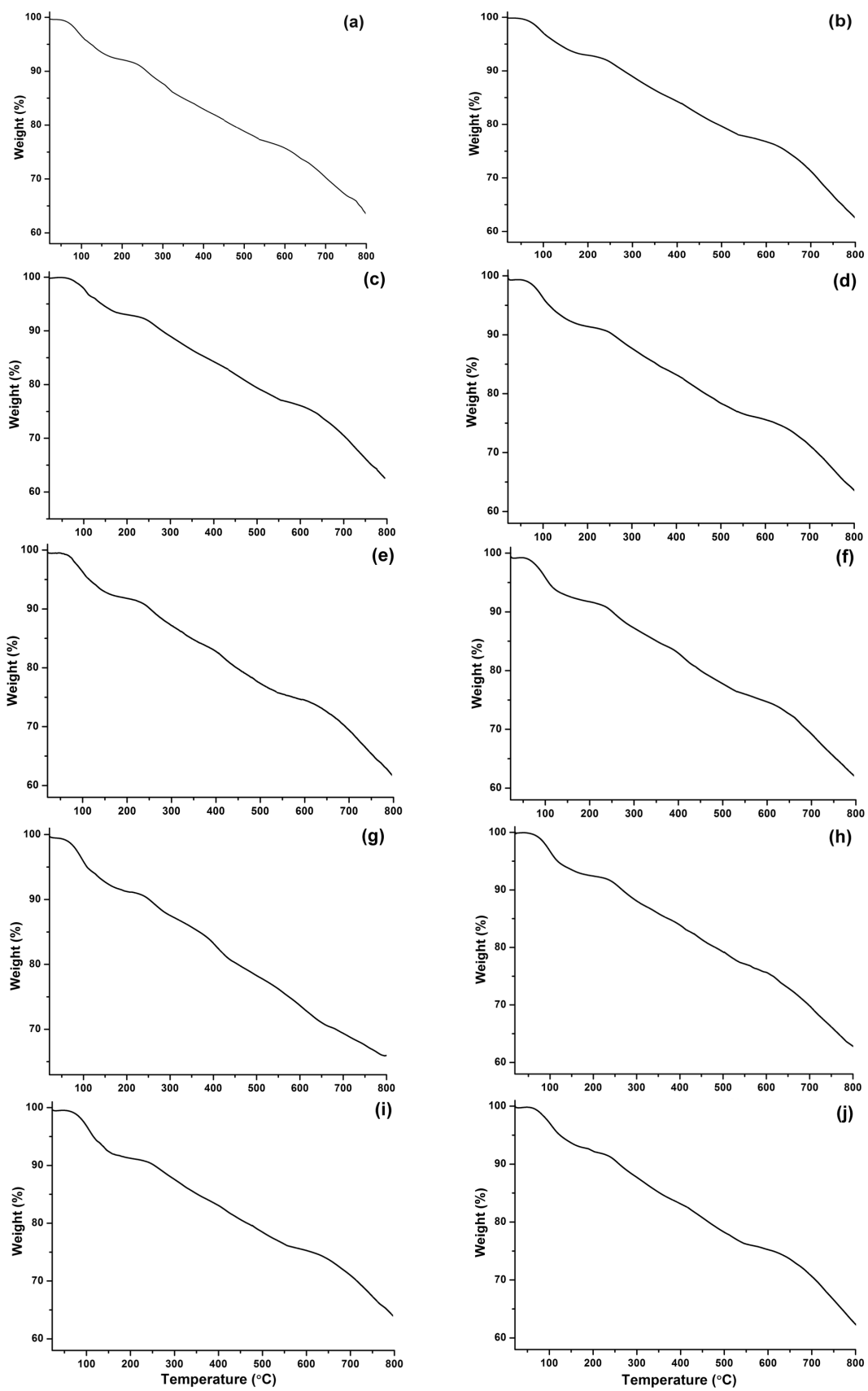


Fig. S5. TGA curves of compounds 1-10 (a-j).

3.4. UV-vis spectroscopy

In pH=1.0 H₂SO₄ solution (concentration: 1 μM), 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)³. This is probably due to the π-π* conjugate action between the {Mo₃₆} unit with the covalently bonded PO molecules³. However, it can be confirmed that compounds **1-10** could maintain their {Mo₃₆} backbone in pH=1.0 H₂SO₄ solution.

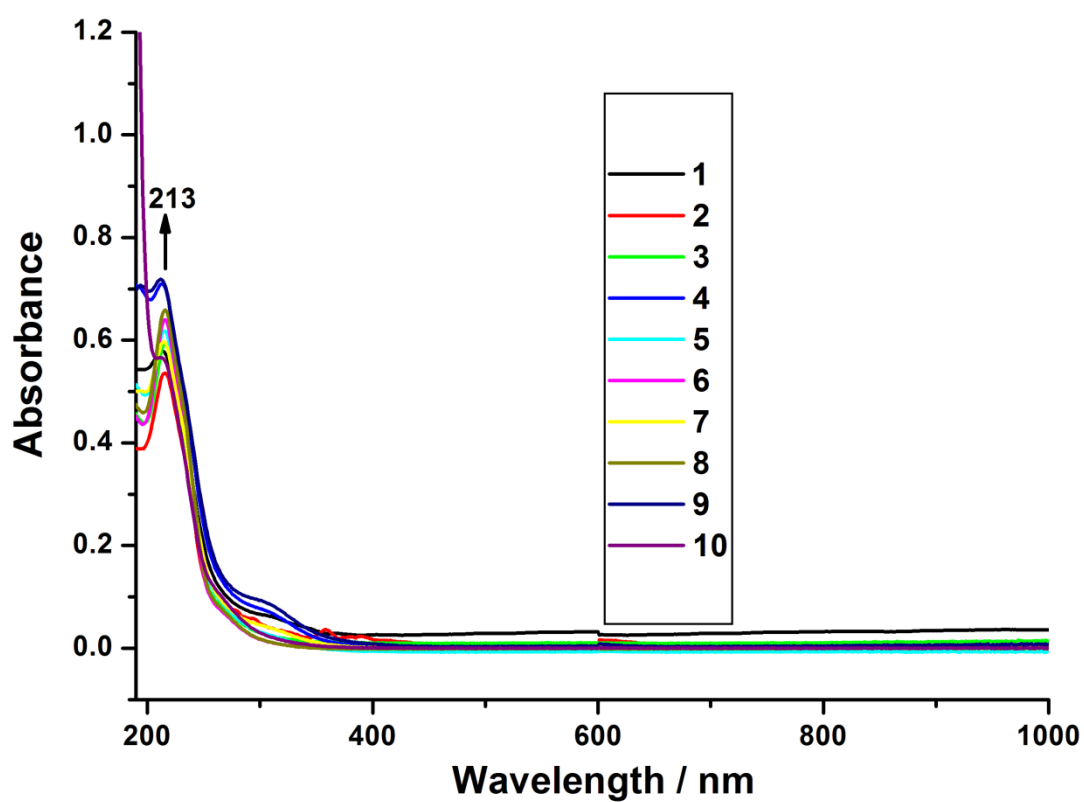


Fig. S6. UV spectra of compounds **1-10** in pH=1 H₂SO₄ solution (concentration: 1 μM)

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 $E_{1/2} = (E_{pa} + E_{pc}) / 2$ 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-controlled³. Interestingly, the solutions show similar cathodochromic phenomenon as reviewed by Yamase⁷.

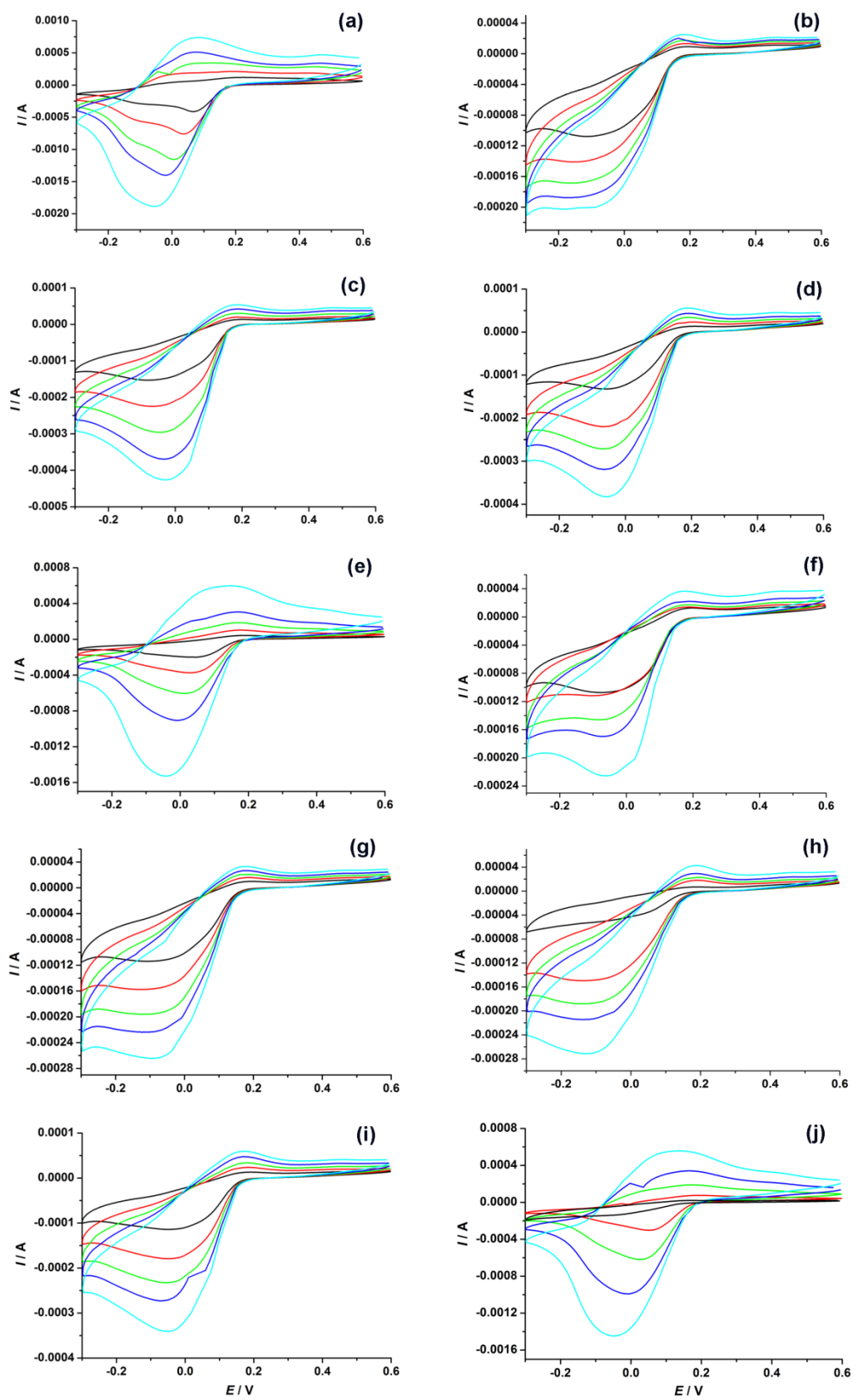


Fig. S7. The cyclic voltammograms of compounds **1-10** (a-j) in pH=1 H₂SO₄ solution at different scan rates (from inner to outer: 50,100, 150, 200, 250 mV·s⁻¹).

4. Coloration of each compound in solid state via visible light irradiation

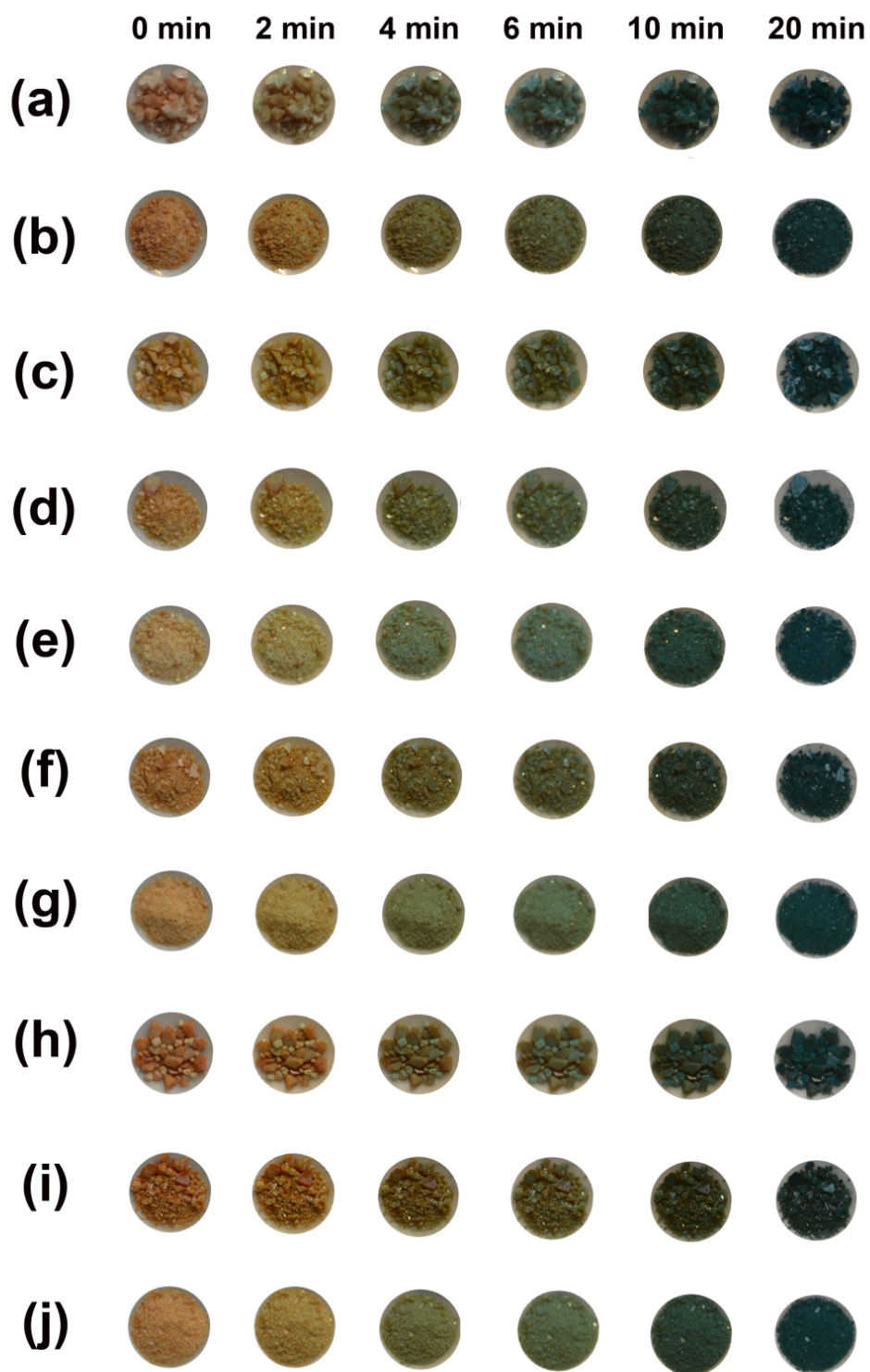


Fig. S8. Color variations of compounds 1-10 (a-j) in solid state after 0-20 min irradiation via visible light.

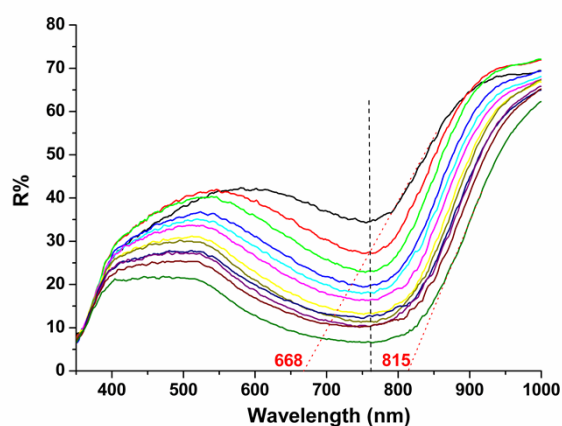


Fig. S9. Reflectance $R(\lambda)$ of **4** in the 350 – 1000 nm range measured after irradiating the sample for t min with visible light ($\lambda > 420$ nm). From top to bottom, $t = 0, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16, 20$ and 40 min, respectively. The vertical dashed line at 768 nm indicates that the local minimum of the reflectance occurs at 768 nm.

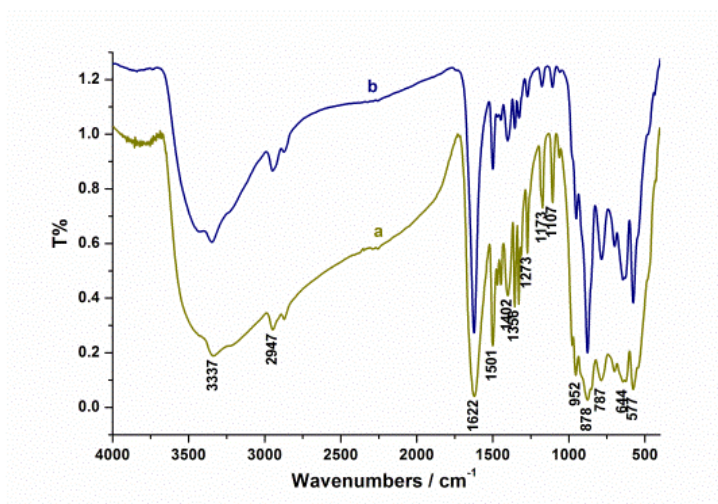


Fig. S10. IR spectra of the compound **4** in solid state, before (a) and after (b) visible light irradiation.

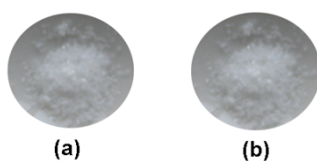


Fig. S11. No Color variation of the compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$ before (a) and after (b) 40 min irradiation via visible light in solid state

5. Additional fluorescence spectroscopy in solid state

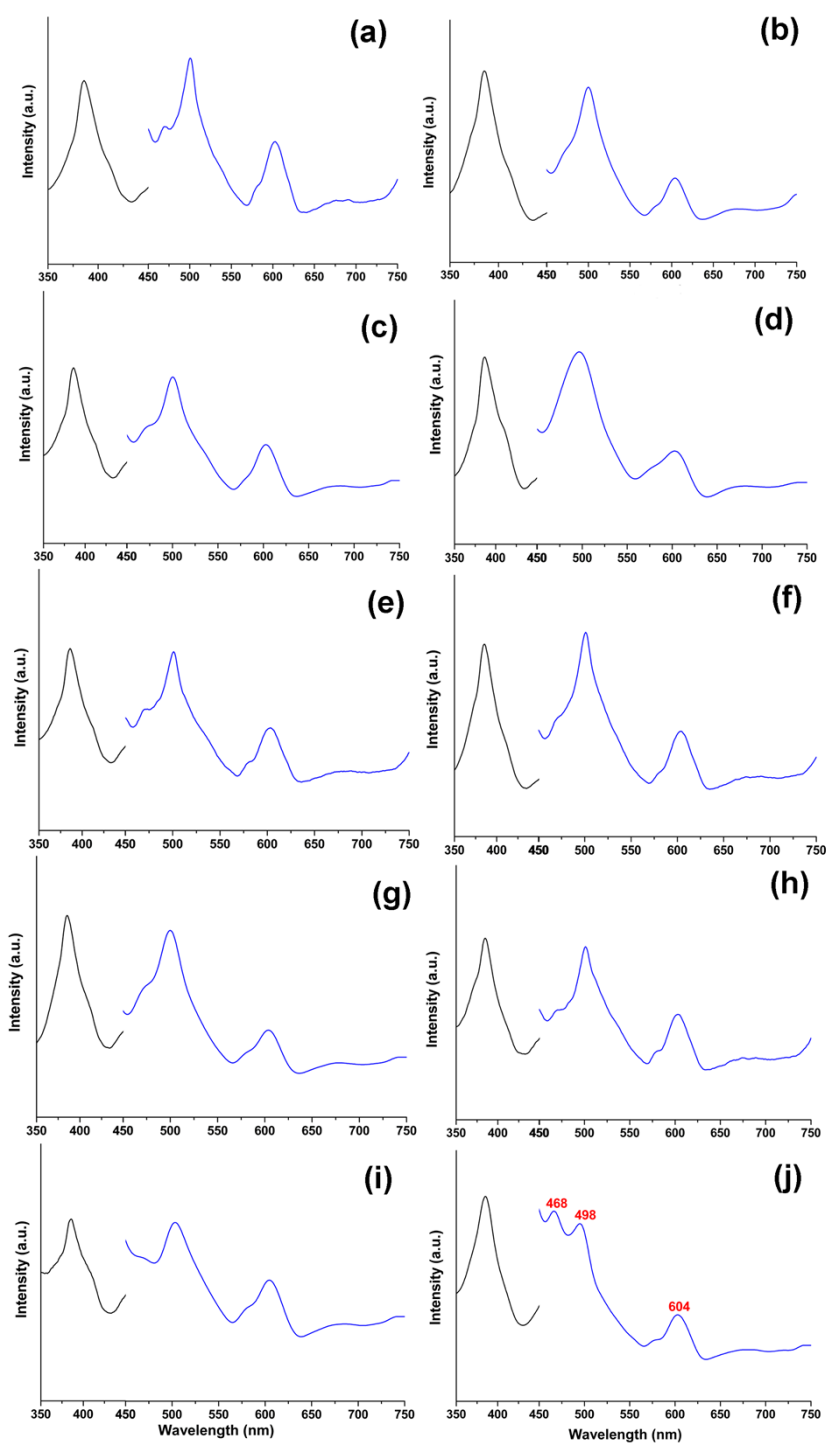


Fig. S12. Excitation (black) and emission (blue) spectra of compounds **2-10** (a-i) and $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$ (j) in solid state.

6. Fluorescence spectroscopy in solution

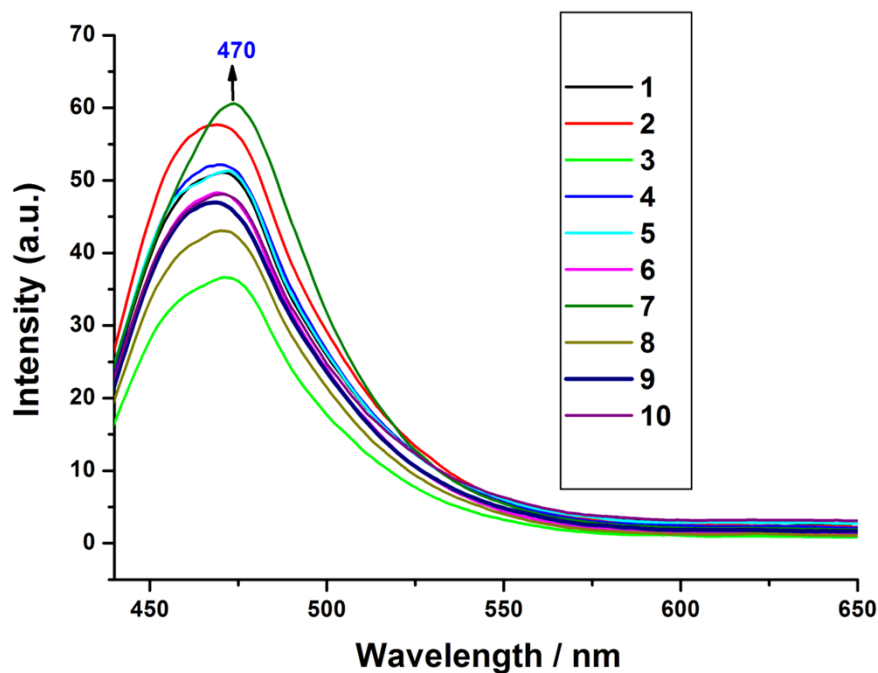


Fig. S13. Emission spectra of compounds **1-10** in pH=1 H₂SO₄ solution ($\lambda_{\text{ex}} = 410$ nm, concentration: 100 μM).

7. References

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