Supporting information

A new type of photomagnetic system: Photoinduced charge transfer in polyoxometalate-based organic-inorganic hybrid

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Section 1 Experimental Section

Materials and measurements

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. metal elemental analyses were determined by a Leaman inductively-coupled plasma (ICP) spectrometer. IR spectra were obtained with an Alpha Centaurt FT/IR spectrometer with KBr pellets in the range 400–4000 cm^{-1}. Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 5ºC min^{-1}. XRD was performed on a Philips X'Pert-MPD instrument with CuKα radiation ($\lambda = 1.54056$ Å) in the range $2\theta = 5$–$50°$ at 293 K. The UV/Vis spectra were recorded with a 756 CRT spectrophotometer (Shanghai Optical Instrument Company, China). Quartz cuvettes with an optical path of 1.00 cm were used. Electron paramagnetic resonance signals were recorded on a JES-FE3AX EPR spectrometer; all measurements were carried out using solid samples; frequency: 100 kHz, microwave power: 9.44 GHz and time constant: 0.03 s. A 300 W xenon lamp (320 nm $\leq \lambda \leq$ 780 nm) was used as a light source, and the average intensity reaching the powder sample of **1** was measured to be ca. 5.6mW·cm^{-2}. Diffuse reflectance UV-Vis spectra were measured from 200 to 800 nm on a Varian Cary 500 UV-Vis NIR spectrometer equipped with a 110 mm diameter integrating sphere at room temperature. Barium sulfate ($BaSO_4$) pellet was used as the standard with 100% reflectance. Magnetic susceptibility data were recorded using a Quantum Design SQUID MPMS XL-5 magnetometer. Variable temperature susceptibility measurements were carried out in the temperature range of 2–300 K at a magnetic field of 1000 Oe on polycrystalline samples. The experimental susceptibilities were corrected for Pascal's constants.

Synthesis of polyanion $[(VMo_6O_{22})_2\{O_2C(CH_2)_2CO_2\}_3]^{12-}$

$(NH_4)_{12}[(VMo_6O_{22})_2\{O_2C(CH_2)_2CO_2\}_3]\cdot 23H_2O$ (1) : $NaVO_3\cdot 2H_2O$ (0.1896 g, 1.2 mmol) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.4943 g, 0.4 mmol) were successively dissolved in water (20 mL). The pH was adjusted to 5.0 by 3.45 M ammonium hydroxide. The resulting suspension was heated to about 60°C, Solid succinic acid (0.708g, 6mmol) was added to the hot solution and the pH was adjusted to 5.0 by adding 3.45 M ammonium hydroxide. Then the solution was heated at 90℃ for an additional 1h. The mixture was filtered and allowed to cool to ambient temperature. The Colorless block crystals of **1** were isolated after two weeks in 25% yield (based on Mo). Elemental analysis (%) calc (found): V 3.47(3.69), Mo 39.21 (40.28), C 4.91 (5.12), H 3.63 (3.98), N 5.72 (6.02). IR (2% KBr pellet, ν/cm^{-1}): 3427(m), 3159(m), 1629(w), 1549(s), 1407(s), 1238(m), 1150(m), 974(s), 901(s), 769(s), 629(s), 518(m).

Section 2 Crystallography

Crystal data of **1** was measured on a Bruker Apex CCD diffractometer using MoKα radiation (λ=0.71073 Å) at 293(2) K. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELX-TL package. The CCDC data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC number 1010483 for **1**. The H atoms on water molecules cannot be determined from the difference Fourier maps due to the limited quality of the data. The crystal structures exhibit the frequent appearance of disorder in the range of counterions and water molecules. So the exact molecular formulas were determined by elemental analysis and thermal gravimetric (TG). The crystal data and structure refinement parameters for compound **1** are summarized in Table 1.

Table S1. X-ray crystallographic data for **1**

	1
formula	$H_{106}N_{12}C_{12}V_2Mo_{12}O_{79}$
M_r [g]	2936.24
crystal system	monoclinic
space group	$P2_1/n$
Z	8
a [Å]	19.7845(9)
b [Å]	28.1745(9)
c [Å]	30.7109(15)
α [°]	90 °
β [°]	103.989(1) °
γ [°]	90°
V [Å]	16611(14)
ρ_{calcd} [g cm^{-3}]	2.348
μ [mm^{-1}]	2.090
Reflections collected	33646
Radiation type	MoKα
R_1 [$I>2\sigma(I)$][a]	0.0570
wR_2 [all data][b]	0.1725
GOF on F^2	0.991

[a] $R_1=\sum|F_o|-|F_c|/\sum|F_c|$; [b] $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ with $1/w=\sigma^2F_o^2+aP^2+bP$ and $P=F_o^2+2F_c^2/3$.

Section 3 Supplementary Physical Characterizations

The phase purity of **1** was confirmed by the agreement between the experimental powder X-ray diffraction pattern and the simulated pattern based on the structure analysis (Fig. S1).

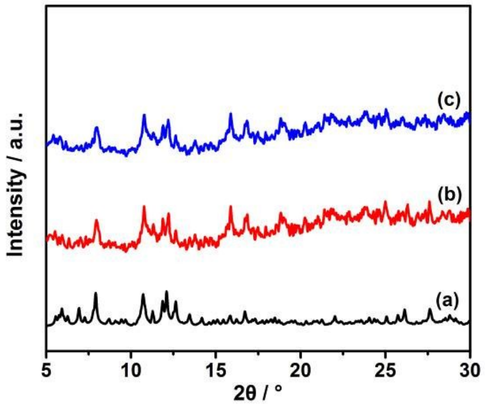

Fig. S1 The PXRD patterns of compound **1**: (a) calculated, (b) as-synthesized, (c) after 2h irradiation.

In the IR spectrum of complex **1**, the characteristic peaks at 974, 901, 769, 629 and 518 cm^{-1} are assigned to the *v*(V–O$_a$), *v*(Mo–O$_d$), *v*(Mo–O$_b$–Mo) and *v*(Mo–O$_c$–Mo) vibrations of the [VMo$_6$O$_{22}$]$^{6-}$ fragment respectively. Furthermore, the *v*(C=O) bands appear in the region 1622−1401 cm^{-1}, which demonstrate the grafting of organic ligands onto the surface of POMs. Compared to the uncoordinated carboxylic acid (1700−1740 cm^{-1}), the *v*(COO) vibrations of **1** are shifted to low frequency because of the interaction between carboxylate and metal ion.[1] Accordingly, the results of these IR data are consistent with the single-crystal X-ray analysis (Fig. S2).

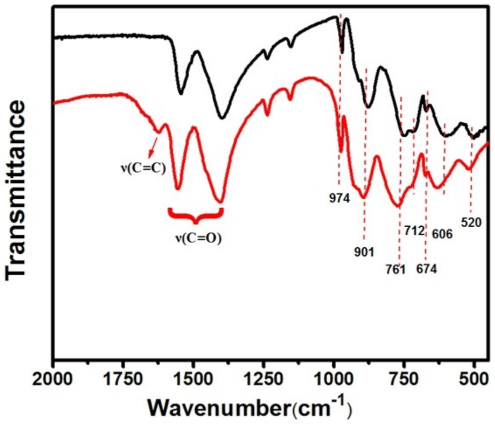

Fig. S2 The IR spectra of **1** before irradiation (black line) and after 2h irradiation (red line).

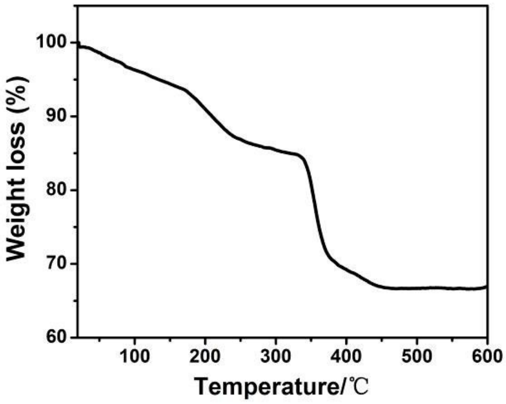

Fig. S3 The TGA curve of **1.**

The thermal stability of **1** has been determined by thermal gravimetric analysis. The plot shows three steps of weight loss in the temperature range 20-600 °C (Figure S3). The first weight loss of 19.8% in the temperature range 20-338°C corresponds to the release of 23 crystalline water molecules and 12 NH_3 molecules (21.1% calculated). The second weight loss of 11.2% (12.1% calculated), which occurs from 338 to 374 °C, is attributed to the loss of three carboxylate ligands. The last stage is the decomposition of the V–Mo–O framework, and the total weight loss (33.8%) agrees with the calculated value (34.2 % calculated).

Section 4 photochromic and photomagnetic studies

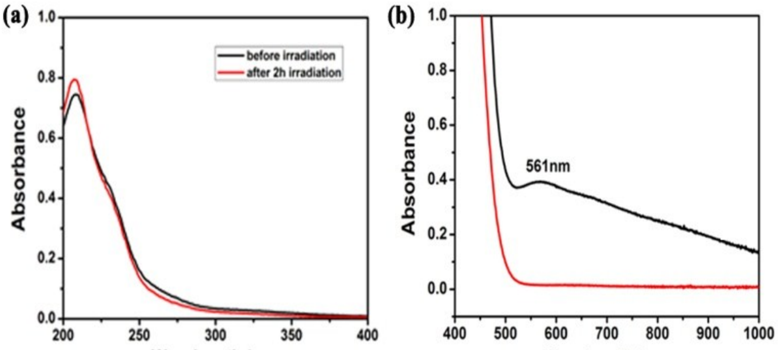

Fig. S4 (a) UV/Vis spectra of **1** in the pH=5.0 aqueous solution in the range from 200 to 400 nm. (b) UV/Vis spectra of **1** without irradiation in the pH=5.0 aqueous solution (red spectrum); UV/Vis spectra of **1** after 2h irradiation(black spectrum).

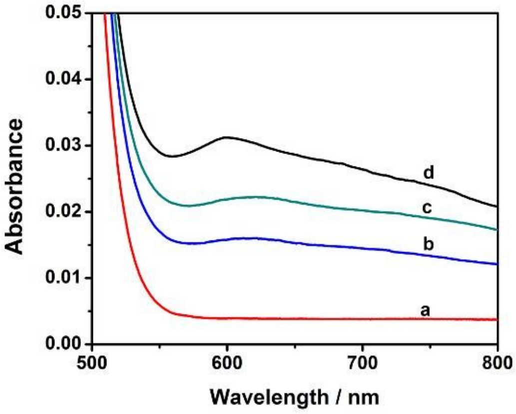

Fig. S5 UV/Vis spectrum of **1** in the pH=5.0 aqueous solution, without irradiation (a) , with irradiation for 20 min (b), 40 min (c), 60min (d).

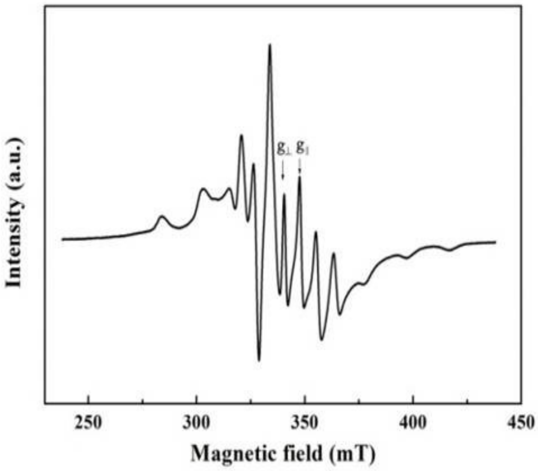

Fig. S6 Solid state EPR spectra of compound **1** after 2h irradiation.

Optical Band Gap

To explore semiconductivity potentials of compound **1**, the measurement of diffuse reflectivity for a powder sample was used to obtain band gap (E_g) (Figure S5), which was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka-Munk function F against energy E.[2-3] Kubelka—Munk function, $F = (1-R)^2/2R$, was converted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at a given wavelength. For compound **1**, the band gap can be assessed at 3.08eV. The reflectance spectra reveal the nature of semiconductivities with a large energy gap for compound **1**.

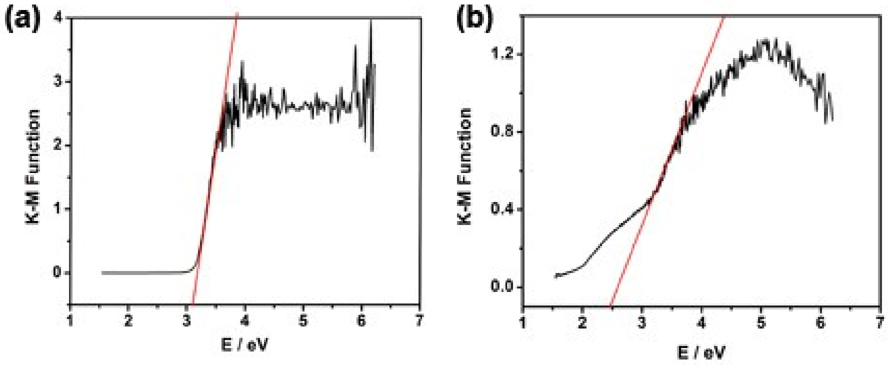

Fig. S7 The diffuse reflectance UV–vis–NIR spectra of K–Mfunction vs. energy (eV) of compound **1**. (a) before irradiation, (b) after 2h irradiation.

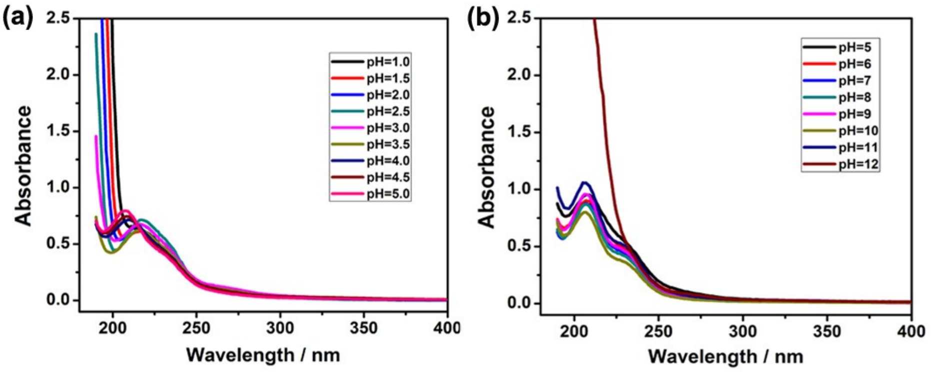

Fig. S8 Influence of the pH values on the stability of **1** in aqueous solution: (a) The UV spectral evolution in acidic direction; (b) The UV spectral evolution in alkaline direction.

To investigate the solution stability of **1**, the in-situ UV spectra of **1** was measured in aqueous solution of different pH value. As shown in Figure S8, the UV spectra of **1** in aqueous solution displays two absorption bands at ca. 208 and 231 nm at pH = 5.0. The high energy band is assigned to the charge transfer transition of $O_t \rightarrow Mo$, whereas the low energy band is attributed to those of $O_{b,c} \rightarrow Mo$ band. At pH value ranging from 3 to 10, there are not obvious changes in the UV spectra. With decreasing pH value further decreasing, the absorption band at 208 nm is gradually red-shifted, while the absorption band at 231 nm slowly disappears. However, as pH value of the solution is higher than 10, the band intensity at 208 and 231nm appears from weakening to vanishing, being indicative of the decomposition of skeleton of **1**. Therefore, the stability of **1** in aqueous solution could be determined to be stable in pH values ranging from 3 to 10.

References

[1] B. Modec, D. Dolenc, *Inorg. Chem.*, 2008, **47**, 3625.
[2] Liao, J. H.; Juang, J. S.; Lai, Y. C. *Cryst. Growth Des.* 2006, **6**, 354.
[3] Xia, Y.; Wu, P. F.; Wei, Y. G.; Wang, Y.; Guo, H. Y. *Cryst. Growth Des.* 2006, **6**, 253.