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Electronic Supplementary Information

"Reversible" photochromism of polyoxomolybdate-viologen hybrids without the

need of proton transfer

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1. Experimental Section

1.1 Materials.

(Bpyen)Br₂ (Scheme S1, ESI^{\dagger}) and (Pbpy)Cl₂ (Scheme S2, ESI^{\dagger}) were prepared as reported.¹ Other chemicals and solvents of reagent grade quality were obtained commercially and used as received without further purification.

1.2 Methods.

1) Single crystal X-ray diffraction analysis of 1

Single-crystal X-ray diffraction data for **1** was collected at 294 K on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator Mo-K α radiation ($\lambda = 0.71073$ Å) by using the Φ/ω scan technique. The structure was solved and refined by full-matrix least squares on F^2 using the SHELXL-97 software package² with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the organic ligands were generated theoretically and refined with isotropic thermal parameters. The hydrogen atoms of the free water molecules were theoretically generated by using the O–H distance restrained to a target value of 0.85 Å. The entry of CCDC-1554658 contains the supplementary crystallographic data for **1**.

2) Single crystal X-ray diffraction analysis of 2

Single-crystal X-ray diffraction data for compounds **2** using an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by using ω -scan technique. The structure was solved and refined by full-matrix least squares on F^2 using the SHELXL-2016 software package³ and Olex-2 program⁴. The hydrogen atoms of the organic ligands were generated theoretically and refined with isotropic thermal parameters. The hydrogen atoms of the free water molecules were theoretically generated by using the O–H distance restrained to a target value of 0.85 Å. The entry of CCDC-1545410 contains the supplementary crystallographic data for **2**.

3) Theoretical calculations

The calculation was conducted using the Gaussian 09 package.⁵ We chose the widely used B3LYP⁶ as an exchange correlation function in view of its good compromise between accuracy and computational cost. The energy levels of frontier orbitals of ligands, getting from the crystal structure, were achieved at the B3LYP/6-31+G(d,p) level. The oscillator strength *f* for viologen radicals were obtained through TD-DFT calculations using the 6-31G+g(d,p) basis set. The results were dealt with the GaussView 5.0 software.

Electrostatic potential surfaces of **1** and **2** were obtained using DFT method (6-31g(d,p) for C H N O; Lanl2dz for Mo). The results were analyzed by Multiwfn.⁷

4) FT-IR spectroscopy

The FT-IR spectra were measured by a Mattson Alpha-Centauri spectrometer over the scope 4000-400 cm⁻¹ with the pure KBr pellets as the references.

5) Powder X-ray diffraction (PXRD) analysis

A Rigaku D_{max} 2000 X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) was used to measure the PXRD data for **1** and **2** at 293 K. Simulated PXRD patterns were derived from the Mercury Version 1.4.2 software using the X-ray single crystal diffraction data.

6) Thermogravimetric (TG) analysis

TG analyses of **1** and **2** were performed on a Perkin-Elmer model TG-7 analyzer from room temperature to 800 $^{\circ}$ C under nitrogen at a heating rate of 10 $^{\circ}$ C min⁻¹.

7) Elemental analyses

Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer.

8) Ultraviolet-visible (UV-vis) absorption

UV–Vis absorption spectra were measured in the reflectance mode at room temperature on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer with an integrating sphere attachment and BaSO₄ as a reference.

9) Electron spin resonance (ESR)

ESR spectra were recorded at X-band frequency (9.867 GHz) on a Bruker ELEXSYS E500 spectrometer.

10) X-ray photoelectron spectroscopy (XPS)

XPS studies were performed with a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al $K\alpha$ radiation ($\lambda = 8.357$ Å).

11) Fluorescence analasis

Fluorescence spectra for compound **1** and **2** were obtained with a FLSP920 fluorescence spectrometer equipped with a 450 W Xe lamp and a R928P PMT detector.

12) Light source

A PLSSXE300C 300 W xenon lamp (ca. 2.4 W/cm²) system was used to illuminate samples for achieving

various spectra.

1.3 Synthesis.

1.3.1 [(Bpyen)₂(Mo₈O₂₆)] 2H₂O (1)

Compound **1** was obtained by a hydrothermal reaction of $(Bpyen)Br_2$ (0.025 g, 0.05 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.062 g, 0.05 mmol) and 1 mol/L HCl (0.05 mL) in a 25 mL Teflon-lined stainless steel autoclave at 90 °C for 72 h. Pale brown crystals were collected by filtration, washed by water, and dried at room temperature. The yield of **1** based on the $(Bpyen)Br_2$ was 47.81%. Elem. Anal. calcd for $C_{44}H_{44}Mo_8N_8O_{28}$ (%): C 27.78, H 2.32, N 5.89. Found (%): C 27.12, H 2.28, N 5.56.

1.3.2 [(Pbpy)₂(Mo₈O₂₆)] 4H₂O (2)

Compound **2** was obtained by a hydrothermal reaction of (Pbpy)Cl₂ (0.025 g, 0.05 mmol), $(NH_4)_6Mo_7O_{24}$ 4H₂O (0.062 g, 0.05 mmol) and 1 mol/L HCl (0.06 mL) in a 25 mL Teflon-lined stainless steel autoclave at 120 °C for 96 h. Antique white crystals were collected by filtration, washed by water, and dried at room temperature. The obtained yield based on the (Pbpy)Cl₂ was 80.32%. Elem. Anal. calcd for C₅₆H₅₆Mo₈N₈O₃₀ (%): C 32.17, H 2.68, N 5.36. Found (%): C 31.96, H 2.61, N 5.27.

2. Graphics.



Scheme 1. The molecular structure of (Bpyen)Br₂.



Scheme 2. The molecular structure of (Pbpy)Cl₂.



Fig. S1 (a) $p \cdots \pi$ stacking interactions around Bpyen cations and O_{Mo-O} atoms in compound **1** (d₁ = 4.2986(2) Å, d₂ = 4.2986(2) Å; (b) $p \cdots \pi$ and $\pi \cdots \pi$ stacking interactions in compound **2** (d₃ = 3.7037(3) Å, d₄ = 3.8785(3) Å, d₅ = 3.7886(4) Å, d₆ = 3.8378(1) Å). H atoms and H₂O are omitted for clarity.



Fig. S2 PXRD patterns of **1** (left) and **2** (right). Labels: **1a** and **2a**: before irradiation; **1b-P** and **2b-P**: after photo irradiation; **1b-T**: after thermal excitation for **1**; **p-decolored** (**1**) and **decolored** (**2**): heating in 120 °C for 1 h and 1.5 h, respectively; **simulated**: simulated patterns from single-crystal X-ray structure data.



Fig. S3 FT-IR spectra of **1** (left) and **2** (right). Labels: **1a** and **2a**: before irradiation; **1b-P** and **2b-P**: after photo irradiation; **1b-T**: after thermal excitation for **1**; **p-decolored** (**1**) and **decolored** (**2**): heating in 120 °C for 1 h and 1.5 h, respectively.



Fig. S4 TGA curves of compounds **1** (a) and **2** (b) were investigated using powder samples under N_2 . The weight loss of **1** is 2.0% (calcd 1.9%) up to 141 °C corresponding to the loss of two free H₂O, while the **2** is 3.2% (calcd 3.1%) up to 83 °C corresponding to the loss of four free H₂O.



Fig. S5 ESR spectra of 1. Black line: before irradiation (two weak signals due to rather sensitive to ambient light). Labels: 1a, before irradiation; 1b-P, after photo irradiation; 1b-T, after thermal excitation.



Fig. S6 UV–Vis absorption spectra of **2** in the photochromic process. **2a**: before photo irradiation; **2b-P**: after exposure in a 300 W Xe lamp; **decolored**: heating in 120 °C for 1.5 h; **2b-P'**: decolored sample immediately photo irradiation.



Fig. S7 (a) UV–Vis absorption spectra of **1** in the photochromic process. (b) UV–Vis absorption spectra of **1** before and after thermal excitation. **1a**: before irradiation; **1b-P**: after exposure in a 300W Xe lamp; **1b-T**: after annealing at 90 °C for five hour; **p-decolored**: heating in 120 °C for 1 h; **1b-P'**: decolored sample immediately photo irradiation.



Fig. S8 Photochromism of compounds 1 and 2 at room temperature in N_2 . The balloon is filled with nitrogen.



Fig. S9¹H NMR of compound 1 in DMSO.





Fig. S10¹H NMR of compound 2 in DMSO.



Fig. S11 ESR spectrum (v = 319.2 GHz) of compounds 1 and 2 at 4 K.



Fig. S12 (a) The **nearest** distance between **H** atoms in H₂O and O_{M0-0} in compound 1 (d₁ = 10.169 Å), (b) The nearest distance between H atoms in H₂O and O_{M0-0} in compound 2 (d₂ = 2.604 Å).

3. Tables.

Empirical formula	C ₄₄ H ₄₄ Mo ₈ N ₈ O ₂₈ (1)	C ₅₆ H ₅₆ Mo ₈ N ₈ O ₃₀ (2)
Formula weight	1900.39	2088.60
Temperature /K	294	293

Table S1. Crystal Data and Structure Refinements for 1 and 2

Crystal system	Triclinic	Monoclinic	
Space group	<i>P</i> –1	$P2_{1}/c$	
a /Å	10.6571(6)	10.946(2)	
<i>b</i> /Å	11.0273(6)	22.138(4)	
c /Å	13.8362(7)	14.603(3)	
α /deg	73.772(2)	90	
eta /deg	75.933(2)	109.77(3)	
γ/deg	64.238(2)	90	
Volume /Å ³	1392.09(13)	3330.1(13)	
Z	1	2	
$D_c/\mathbf{g}\cdot\mathbf{cm}^{-3}$	2.267	2.083	
Absorption coefficient /mm ⁻¹	1.839	1.550	
Goodness-of-fit on F^2	1.048	1.130	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0243, wR_2 = 0.0526$	$\mathbf{R}_1 = 0.0371, \mathbf{wR}_2 = 0.0636$	
R indices (all data)	$R_1 = 0.0347, wR_2 = 0.0567$	$\mathbf{R}_1 = 0.0562, \mathbf{w}\mathbf{R}_2 = 0.0692$	
$\overline{{}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} , {}^{b}wR_{2} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})_{2}]^{2}\}^{1/2}.$			

1		2	
Mo(1)-O(2)	2.167(2)	Mo(1)-O(12)	1.711(3)
Mo(2)-O(6)	1.691(2)	Mo(2)-O(5)	1.698(3)
Mo(3)-O(9)	1.703(3)	Mo(3)-O(7)	1.750(3)
Mo(4)-O(5)	2.385(2)	Mo(4)-O(3)	2.241(3)
N(1)-C(9)	1.345(4)	N(1)-C(27)	1.334(6)
C(2)-C(3)	1.488(5)	C(2)-C(6)	1.385(7)
N(4)-C(22)	1.318(6)	N(4)-C(16)	1.325(7)

Table S2. Selected bond lengths (Å) for $1 \mbox{ and } 2$

1		2	
O(10)-Mo(1)-O(3)	155.82(10)	O(2)-Mo(1)-O(7)	71.44(10)

O(6)-Mo(2)-O(5)	104.35(12)	O(1)-Mo(2)-O(2)	84.26(11)
O(9)-Mo(3)-O(10)	105.70(12)	O(7)-Mo(3)-O(3)	102.36(14)
N(1)-Mo(3)-O(2)	106.00(9)	O(1)-Mo(4)-N(1)	164.28(13)
O(1)-Mo(4)-O(7)	96.81(11)	O(1)-Mo(4)-O(3)	77.47(12)
Mo(2)-O(2)-Mo(3)	103.08(10)	Mo(4)-O(1)-Mo(2)	113.80(15)
C(1)-N(2)-C(5)	119.2(3)	C(27)-N(1)-Mo(4)	120.0(3)
N(3)-C(6)-C(20)	121.3(3)	C(10)-N(2)-C(14)	120.2(4)
C(14)-C(10)-C(19)	123.0(3)	N(3)-C(1)-C(6)	120.1(5)
C(22)-C(17)-C(2)	119.4(4)	C(9)-C(3)-C(24)	122.7(4)
Mo(2)-O(13)-Mo(4)#1	108.64(10)	Mo(1)-O(8)-Mo(3)#1	104.78(13)
Mo(1)#1-O(13)-Mo(2)#1	93.57(7)	Mo(4)#1-O(8)-Mo(3)#1	104.64(12)

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