

Supporting Information for

**Photogeneration of Two Reduction-active Charge-separated States in a Hybrid Crystal of Polyoxometalates and Naphthalene Diimides**

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## 1. Experimental Details and Synthesis

**Materials and Methods:** *N*-methylpyrrolidin-2-one (NMP, analytical reagent grade),  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ ,  $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ , methanol (analytical reagent grade) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. NMR spectra were recorded with a Bruker Avance III 500 MHz NMR spectrometer. ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. IR spectra were recorded in the range 4000-400  $\text{cm}^{-1}$  on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. The electron spin resonance (ESR) measurements were recorded on a Bruker A300 instrument operating in the X-band at room temperature. The XPS studies were performed with a Thermo Fisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al  $K\alpha$  radiation ( $\lambda = 8.357 \text{ \AA}$ ). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.6 eV. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku MiniFlex-II X-Ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). TGA measurements were performed on a TG-209 system with a heating rate of 10  $^\circ\text{C}/\text{min}$  under an  $\text{N}_2$ -atmosphere. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere.

**Synthesis of DPNDI:** The organic ligand *N,N'*-di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI) was synthesized following the reported process.<sup>[S1]</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CF}_3\text{COOD}$ , 298K):  $\delta = 9.12$  (d,  $J=7\text{Hz}$ , 4H), 9.05 (s, 4H), 8.38 (d,  $J=7\text{Hz}$ , 4H). ESI-MS  $m/z$ : Calculated for  $\text{C}_{24}\text{H}_{12}\text{N}_4\text{O}_4$ : 420.09, Found: 420.09.

**Synthesis of complex 1.** A solution (0.5 mL) of NMP/MeOH (1:1, v/v) was carefully layered over a NMP (5 mL) solution of NDI (0.1mmol, 0.042g) and  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ , (0.05mmol, 0.068g), and then the solution of  $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$  (0.1mmol, 0.021g) in MeOH (5 mL) was carefully added as a second layer. Light yellow crystals of complex **1** were obtained after several days in the dark (*ca.* 23% yield based on polyoxometalates). IR data (KBr,  $\text{cm}^{-1}$ ): 3507(m), 3056(w), 2956(w), 2895(w), 1685(s), 1343(s), 1250(m), 1124(w), 1024(w), 981(w), 859(w), 757(m), 642(m), 537(w).

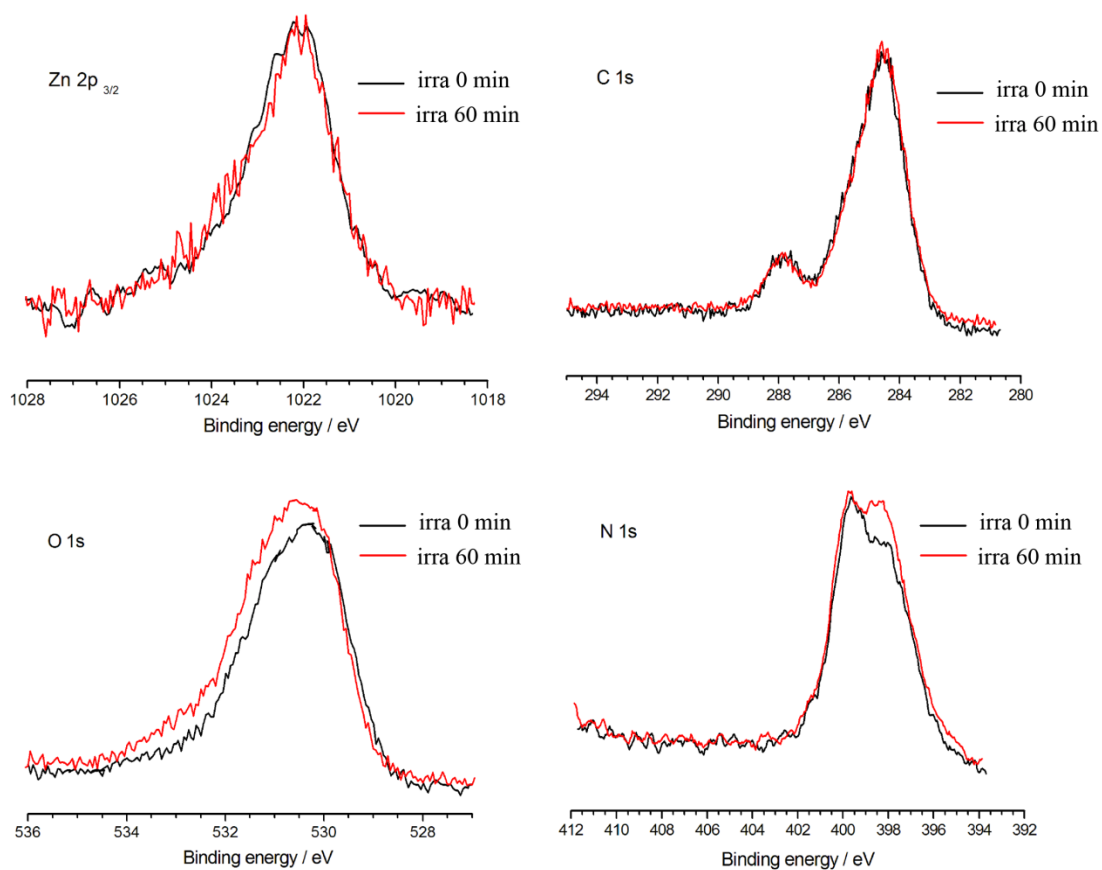
## 2. Crystallographic data collection and refinement

Suitable single crystal of complex **1** was mounted on glass fiber for the X-ray measurement. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD area-detector system. The measurement was made by using graphic monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 113 K under a cold nitrogen stream. The frame data were integrated and absorption correction using a Rigaku *CrystalClear* program package. All calculations were performed with the *SHELXTL-97* program package<sup>[S2]</sup>, and structures were solved by direct methods and refined by full-matrix least-squares against F<sup>2</sup>. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The diffraction data were treated by the “SQUEEZE” method as implemented in PLATON<sup>[S3]</sup> to remove diffuse electron density associated with these badly disordered solvent molecules. Due to the mixed solvents were used during the synthesis of complex **1**, the solvent content could not be precisely specified. But combined with TGA data and volume/count\_electrons analysis, there are approximately 16 NMP molecules and 20 MeOH molecules per unit cell were squeezed. In addition, one of the two independent bis(pyridyl)naphthalenediimide ligands in the complex **1** shows partly occupied with about 33% occupancy, accordingly 67% site is occupied by water molecule. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1022530. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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

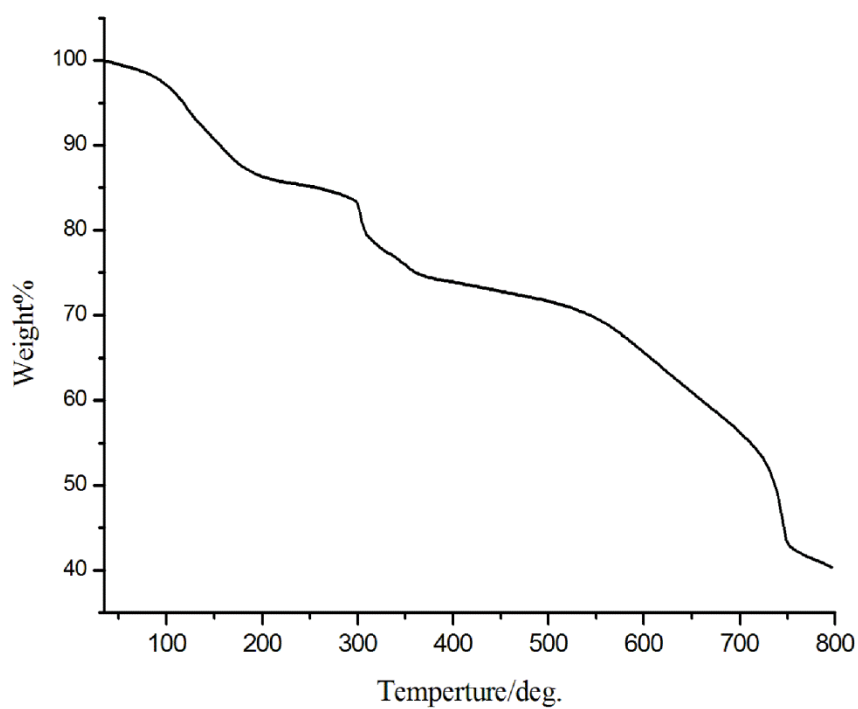
<b>Complex</b>	1
<b>Crystal size (mm)</b>	0.38×0.25×0.17
<b>Empirical Formula</b>	$C_{62.5}H_{67.33}Mo_6N_{10.67}O_{32.83}Zn$
<b>Formula weight</b>	2134.28
<b>Crystal system</b>	Monoclinic
<b>Space group</b>	$C2/c$
<b><i>a</i> (Å)</b>	18.484(4)
<b><i>b</i> (Å)</b>	54.534(11)
<b><i>c</i> (Å)</b>	18.076(4)
<b><i>α</i> (°)</b>	90
<b><i>β</i> (°)</b>	103.40(3)
<b><i>γ</i> (°)</b>	90
<b><i>V</i> (Å<sup>3</sup>)</b>	17725(6)
<b><i>Z</i></b>	8
<b><i>D<sub>c</sub></i> (g/ cm<sup>3</sup>)</b>	1.600
<b><i>μ</i>(Mo <i>Kα</i>) (mm<sup>-1</sup>)</b>	1.169
<b><i>F</i>(000)</b>	8493
<b>Collected reflections</b>	47236
<b>Independent reflections</b>	12656 (0.0616)
<b>Goodness-of-fit on <i>F</i><sup>2</sup></b>	1.135
<b><i>R</i><sub>1</sub><sup><i>a</i></sup>, <i>wR</i><sub>2</sub><sup><i>b</i></sup> (<i>I</i>&gt;2σ(<i>I</i>))</b>	0.1003, 0.2996
<b><i>R</i><sub>1</sub><sup><i>a</i></sup>, <i>wR</i><sub>2</sub><sup><i>b</i></sup> (all data )</b>	0.1150, 0.3178

### 3. X-ray photoelectron spectroscopy



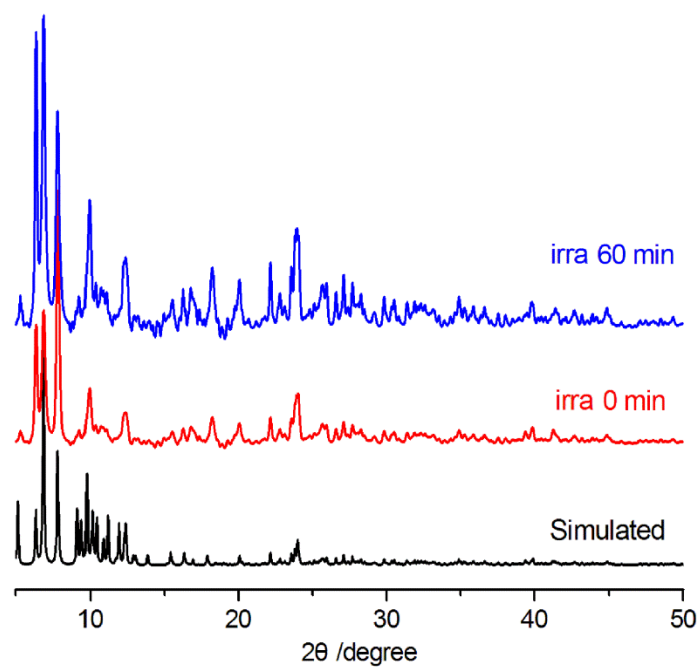
**Figure S1.** XPS core-level spectra of 1 upon irradiation.

#### 4. Thermogravimetric analyses

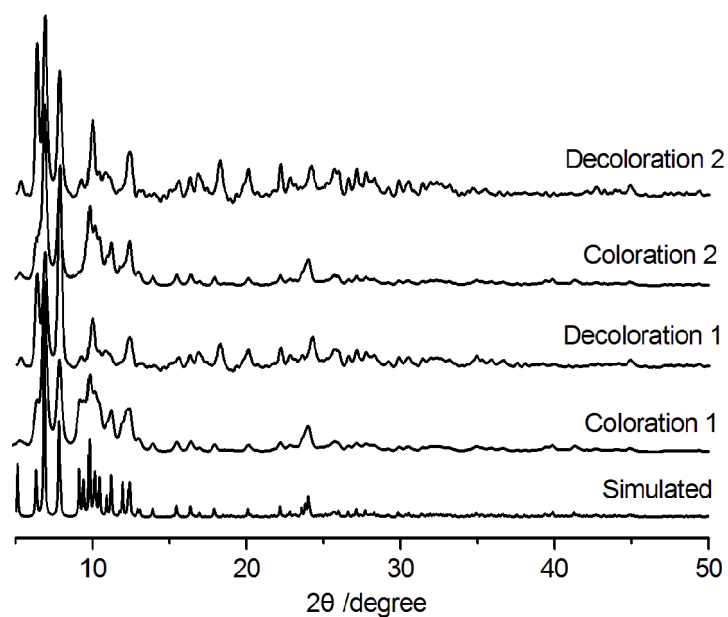


**Figure S2.** TGA data of 1

## 5. X-ray Powder Diffraction

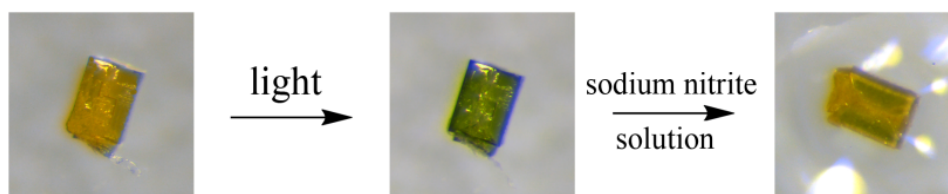


**Figure S3.** Comparison of the simulated and synthesized PXRD for hybrid 1.



**Figure S4.** PXRD pattern about the stability of crystal **1**.

## 6. Photograph



**Figure S5.** The coloration and decoloration process of **1** from photographic images

## 7. References

- S1. Guha, S.; Goodson, F. S.; Corson, L. J.; Saha, S. *J. Am. Chem. Soc.*, 2012, **134**, 13679.  
 S2. Sheldrick, G. *Acta Cryst.* 2008, **A64**, 112-122.  
 S3. Spek, A. L. *Acta Crystallogr.*, 2009, **D65**, 148-155.