Supporting information

A Photochromic Naphthalene Diimide Coordination Networks Sensitized by Polyoxometalates

Jian-Jun Liu,[a] Yao Wang,[a] Yu-Jian Hong,[a] Mei-Jin Lin,*[ab] Chang-Cang Huang*[a] and Wen-Xin Dai[a]

[a] State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, China, 350116; and [b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, CAS, China, 350002. Email: meijin_lin@fzu.edu.cn, cchuang@fzu.edu.cn, Tel: 0086 591 2286 6143

Table of Contents:

1. Experimental Details and Synthesis

Materials and Methods: *N*-methylpyrrolidin-2-one (NMP, analytical reagent grade), $H_3PMo_{12}O_{40}$, $ZnSiF_6 \cdot 6H_2O$, ethanol (analytical reagent grade) and 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. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^1H coupling constants J are given in Hertz (Hz). ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. IR spectra were recorded in the range 4000-400 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 Kα radiation (λ = 8.357 Å). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.7 eV. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku MiniFlex-II X-Ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). TGA measurements were performed on a TG-209 system with a heating rate of 10 °C/min under an 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.

The organic ligand *N*, *N'*-di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI) was synthesized following the reported process.[S1]

Synthesis of compound 1. A solution (0.5 mL) of NMP/EtOH (1:1, v/v) was carefully layered over a NMP (5 mL) solution of NDI (0.1mmol, 0.042g) and $H_3PMo_{12}O_{40}$ (0.025mmol, 0.046g), and then the solution of $ZnSiF_6 \cdot 6H_2O$ (0.2mmol, 0.041g) in EtOH (5 mL) was carefully added as a second layer. Yellow crystals of compound **1** were obtained after several days in the dark (*ca.* 30% yield based on polyoxometalates). IR(KBr, cm^{-1}): 3543 (w) 3062(w), 2947(w), 1709(m), 1645(s), 1536(m), 1351(m), 1253(m), 1079(s), 984(m), 818(s), 753(m), 517(w).

2. Crystallographic data collection and refinement

Suitable single crystal of compound **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 Kα radiation (λ= 0.71073 Å) 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 [S2], and structures were solved by direct methods and refined by full-matrix least-squares against F^2. 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[S3] to remove diffuse electron density associated with these badly disordered solvent molecules. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with reference number CCDC 1020295. 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 **1**.

Complexes	**1**
Crystal size (mm)	0.35×0.23×0.20
Empirical Formula	$C_{68}H_{60}FMo_{12}N_{12}O_{54}PZn_2$
Formula weight	3241.27
Crystal system	Monoclinic
Space group	*P2/c*
a (Å)	19.693(4)
b (Å)	16.245(3)
c (Å)	26.761(8)
α (°)	90
β (°)	132.800(18)
γ (°)	90
V (Å^3)	6282(3)
Z	2
Dc (g/ cm^3)	1.714
μ(Mo Kα) (mm^{-1})	1.624
F(000)	3144
Collected reflections	52158
Independent reflections	14511 (0.0795)
Goodness-of-fit on F^2	1.094
$R_1{}^a$, $wR_2{}^b$ ($I>2\sigma(I)$)	0.0914, 0.2212
$R_1{}^a$, $wR_2{}^b$ (all data)	0.1089, 0.2318

3. XPS spectra

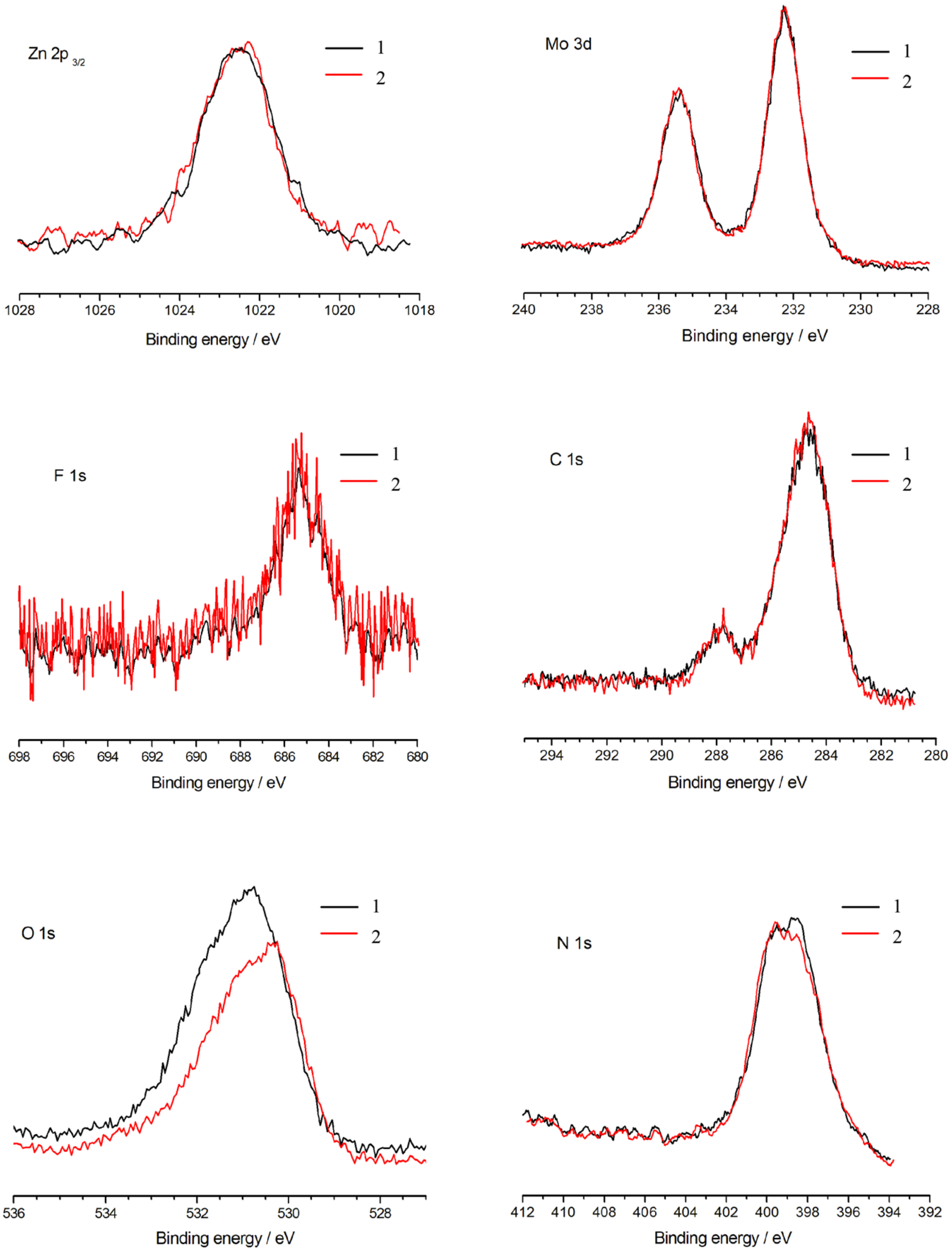

Figure S1. XPS core-level spectra of **1** and **2**.

4. Thermogravimetric analyses

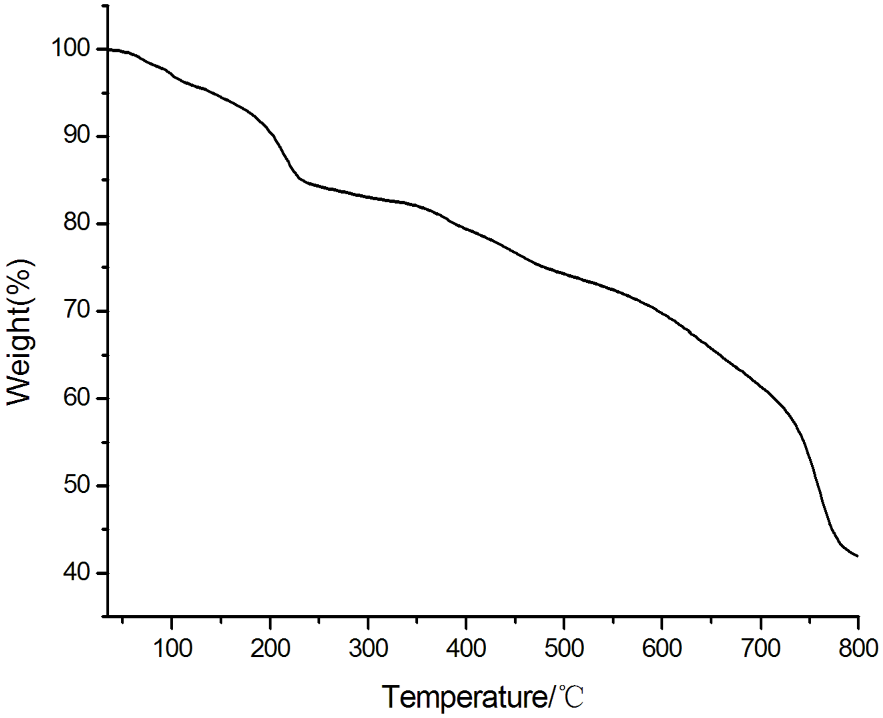

Figure S2. TGA data of the **1**.

5. X-ray Powder Diffraction

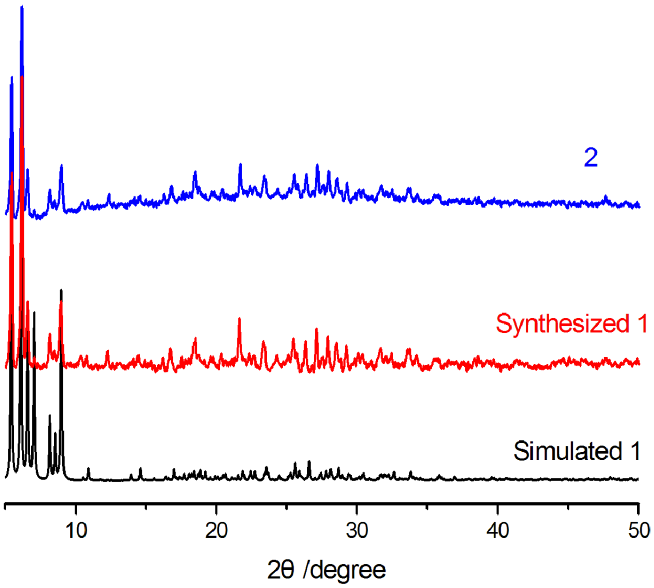

Figure S3. PXRD patterns of **1** and **2**.

6. Photograph

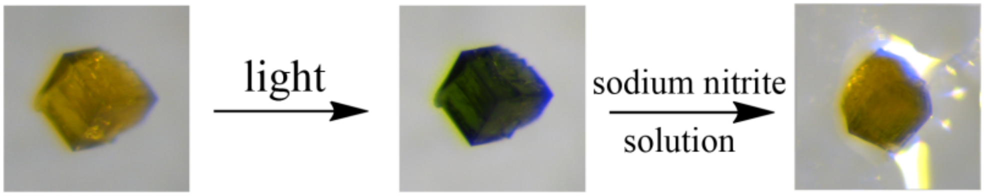

Figure S4. The coloration and decoloration process of **1** from photographic images

7. References

S1. S. Guha, F. S. Goodson, L. J. Corson and S. Saha. *J. Am. Chem. Soc.,* 2012, **134**, 13679.

S2. G. Sheldrick. *Acta Cryst.* 2008, **A**64, 112-122.

S3. Spek, Acta Crystallogr., 2009, **D**65, 148-155.