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Electronic Supplementary Information

A novel naphthalenediimide-based lanthanide-organic framework with polyoxometalate templates exhibiting reversible photochromism

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1. Materials and Physical Measurements

All chemicals were obtained from commercial sources and used as received without further purification. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu Kα radiation (λ = 1.5406 Å). IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. XPS studies were performed in Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer. EPR spectra were recorded on a Bruker BioSpin E500 EPR spectrometer with a 100 kHz magnetic field modulation at room temperature. Thermal analyses were performed on a TGA/DSC 1 STARe system from room temperature to 1000°C at a heating rate of 10K/min under nitrogen. A 460 nm LED (gaoke BZ(100-240)/AC LED (λ = 460-465nm), 220V, 3W) was employed as the irradiation source.

2. Experimental Section

Synthesis of N,N'-bis(5-isophthalic acid)-1,4,5,8-naphthalenediimide (H4BINDI) ligand. H_4BIDNI was synthesized according to a previously reported procedure.[S1] A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NDA) (1.34 g, 5.0 mmol) and 5-aminoisophthalic acid (1.81 g, 10.0 mmol) in DMF (20 mL) was heated under reflux for 12 h. After gradually cooling to room temperature and standing for one night, the product was precipitated out after standing for one night. The product was collected by filtration, washed with ethanol and dried in vacuum to yield 2.0 g of yellow solid (yield 68%).

Synthesis of LONF-1. The mixture of $Ce(NO_3)_3 \cdot 6H_2O$(0.007 mmol, 30.4 mg) and H_4BIDNI (0.035 mmol, 21 mg) were dissolved in N,N-dimethylacetamide (DMA) (4 mL), and 1.5mL of a acetonitrile (MeCN) solution of silicotungstic acid ($H_4SiW_{12}O40 \cdot xH_2O$) (0.017 mmol, 50 mg) was added dropwise to the solution. The reaction mixture was then sealed in a glass bottle and heated at 95 °C for 3 days, resulting in light yellow single crystals of **LONF-1** were collected and washed with DMA and ethanol, and air-dried. The yield of is ca. 66 %. Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. Anal. Calcd for $C_{136}H_{191}N_{23}O_{83}SiW_{12}Ce_4$: C 26.05, H 3.07, N 5.14%. Found: C 25.85, H 3.06, N 5.09%.

3. Crystallographic data collection and refinement

Suitable single crystal of **LONF-1** was mounted on glass fiber for the X-ray measurement. Diffraction data was collected on a Saturn724 + CCD diffractometer equipped with graphitemonochromatic Mo Kα (λ = 0.71073 Å) radiation by using an *ω*-scan model technique at 123 K. 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 ordered non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed geometrically and refined with a riding model. The highly disordered solvent molecules could not be well modeled in the refinement, therefore, a *SQUEEZE* option implemented in *PLATON* was performed to calculate electron densities corresponding to disordered solvent molecules. The diffuse electron density in the pore cavities, calculated from *SQUEEZE*, was 288 electrons per unit cell, corresponding to ca. 3DMA per formula, which has been confirmed by elemental analysis and TGA. The crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1528863. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

4. Crystal data for compound LONF-1

Table S1. Crystal Data and Structure Refinement Parameters for **LONF-1**

Compound reference	**LONF-1**
Chemical formula	$C_{124}H_{164}N_{20}O_{80}SiW_{12}Ce_4$
Formula Mass	6009.52
Crystal system	Tetragonal
a/Å	23.714 (3)
b/Å	23.714 (3)
c/Å	16.575 (3)
α/°	90.00
β/°	90.00
γ/°	90.00
Unit cell volume/Å^3	9168.2
Temperature/K	173
Space group	$P4_2/n$
No. of formula units per unit cell, Z	2
No. of reflections measured	67391
No. of independent reflections	10574
R_{int}	0.053
Final R_1[a] values ($I > 2\sigma(I)$)	0.0761
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.1907
Final R_1[a] values (all data)	0.0897
Final $wR(F^2)$[b] values (all data)	0.2001
Goodness-of-fit on F^2	1.06

[a]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. [b]$wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$

5. Figures of LONF-1

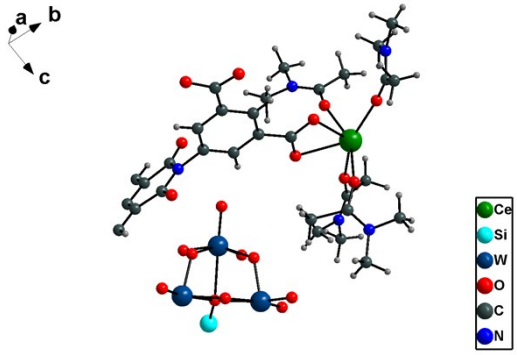

Fig. S1 The asymmetric unit of **LONF-1**, containing one Ce center, half of deprotonated BINDI ligand, four coordinated DMA molecules and one-quarter of the $[SiW_{12}O_{40}]^{4-}$ Keggin anion. Ce (green), C (gray), O (red), N (blue), Si (turquoise), W (dark teal), H (light gray).

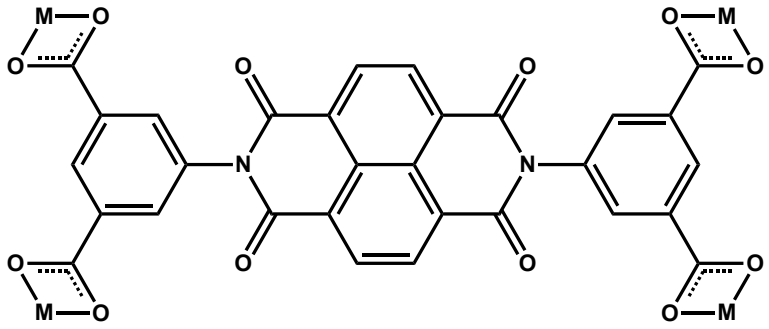

Fig. S2 The coordination mode of fully deprotonated BINDI ligand.

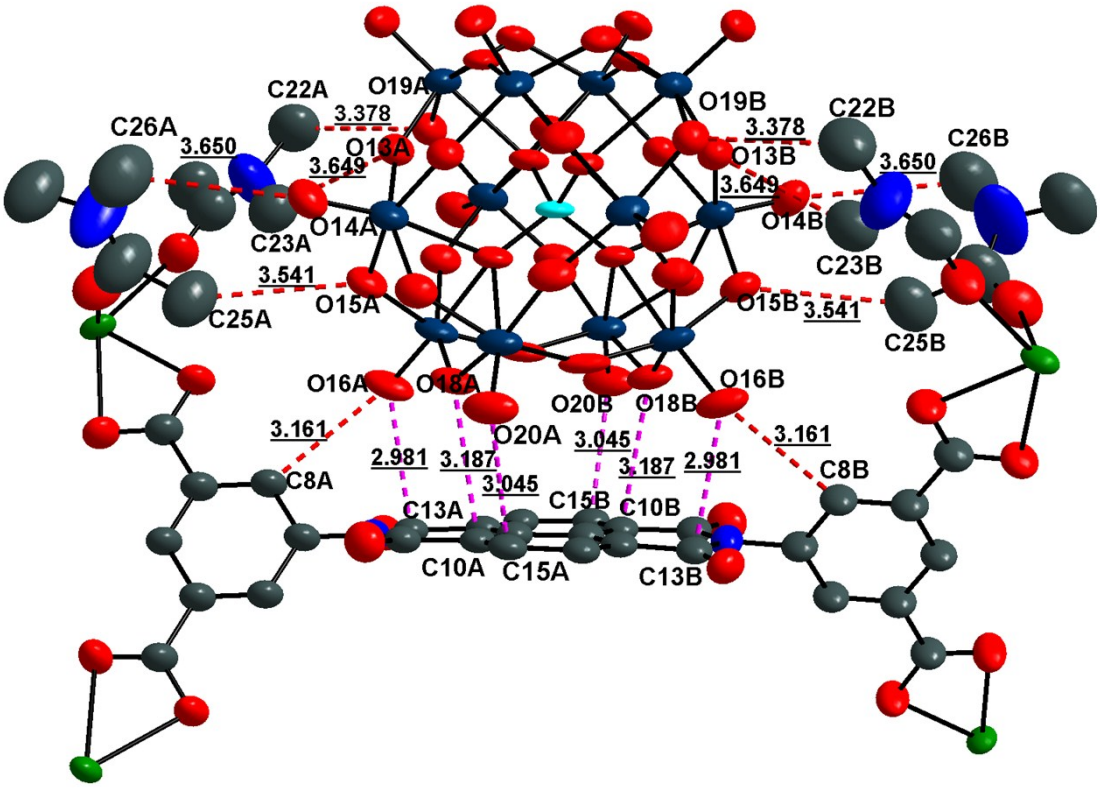

Fig. S3 Anion–π (pink dashed line) (average distance from O_{POM} to NDI centroids is ~ 3.06 Å) and C–H···O H-bonds (red dashed line) (The average C–H…O distance is ~ 3.39 Å) interactions with p-acidic BINDI and DMA molecules. Ce (green), C (gray), O (red), N (blue), Si (turquoise), W (dark teal), H atoms are omitted for clarity.

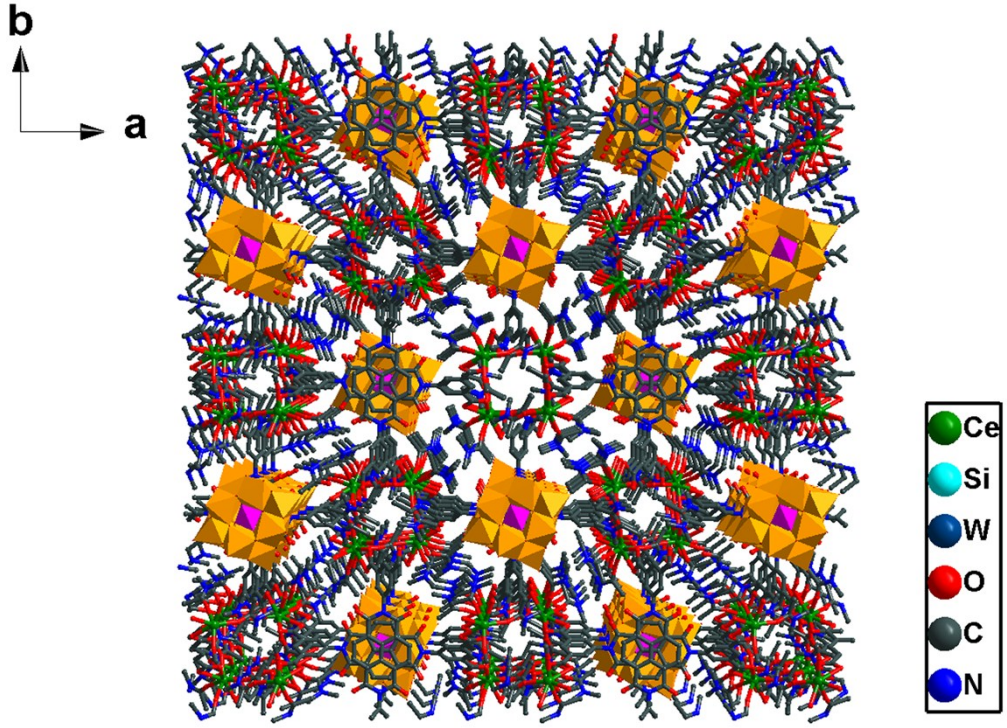

Fig. S4 The 3-D framework of **LONF-1** viewing along the *c* axis. Ce (green), C (gray), O (red), N (blue), Si (turquoise), W (dark teal), POMs (light orange and pink polyhedron), H atoms are omitted for clarity.

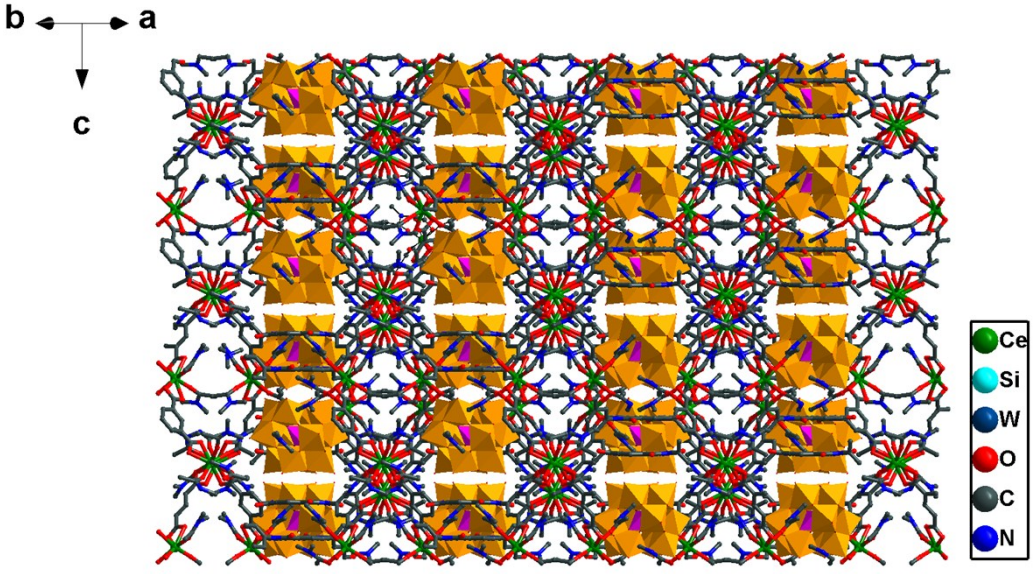

Fig. S5 The 3-D framework of **LONF-1** viewing along the [110] direction. Ce (green), C (gray), O (red), N (blue), Si (turquoise), W (dark teal), POMs (light orange and pink polyhedron), H atoms are omitted for clarity.

6. The estimated energy band gap

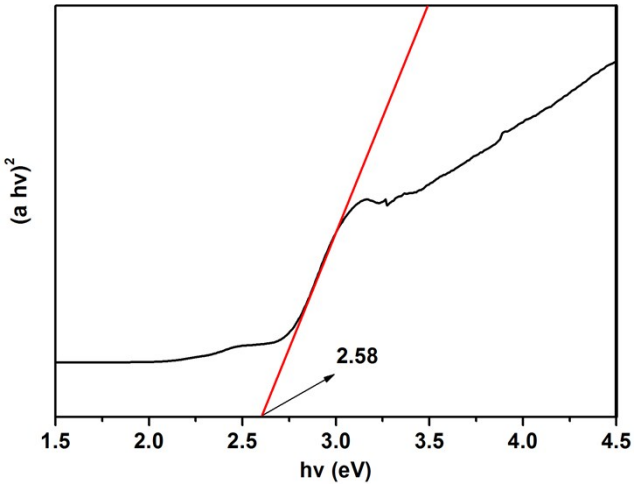

Fig. S6 The estimated energy band gap of **LONF-1** by the UV-Vis DRS based on the Kubelka-Munk Function.

7. X-ray Photoelectron Spectroscopy

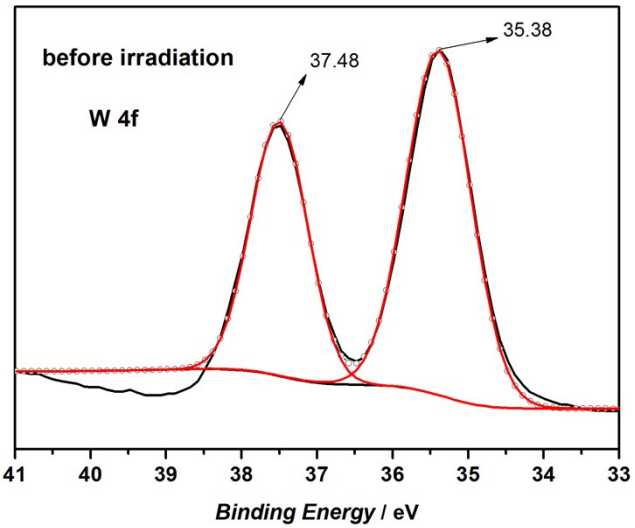

Figure S7 Resolved W4f XPS core-level spectra of **LONF-1**.

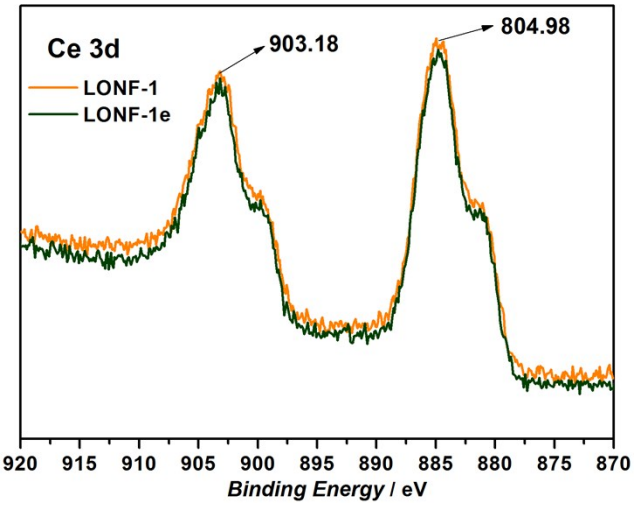

Figure S8 Ce3d XPS core-level spectra of **LONF-1** and **LONF-1e**.

8. IR spectroscopy

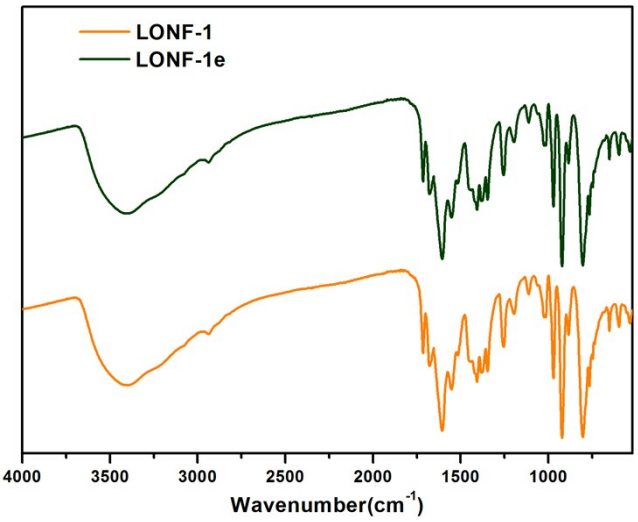

Fig. S9 The IR spectra of **LONF-1** and **LONF-1e**.

9. Thermogravimetric analyses

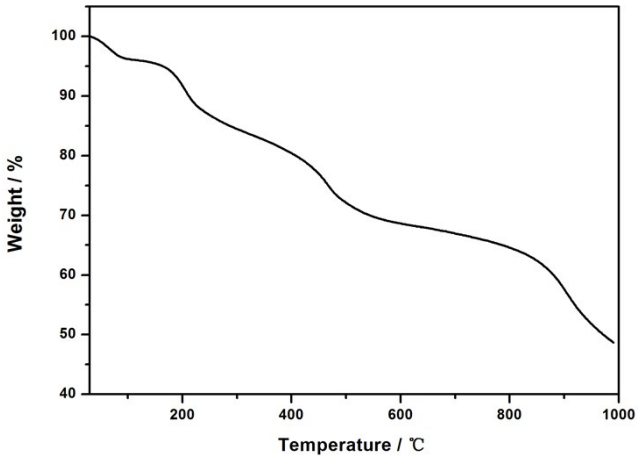

Fig. S10 The TGA curve of **LONF-1**.

10. References

S1. S1. D. Singh and J. B. Baruah, *Tetrahedron Lett*., 2008, **49**, 4374.
S2. G. Sheldrick. *Acta Cryst*. 2008, **A64**, 112.