Supporting Information

Reversible Luminescence Switch in a Photochromic Metal-Organic Framework

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Section 1. Experimental Section

General: All chemicals were obtained from commercial sources and of GR/AR grade. FT-IR spectra (KBr pellets) were recorded on a Bomen MB-102 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851^e thermal analyzer in flowing air atmosphere at a heating rate of 10 °C·min^{-1} from 30 to 800 °C. Elemental analysis of C, H and N was performed on a Vario EL III CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Philips PW3040/60 high resolution diffractometer at 45 kV, 40 mA for Cu Kα (λ = 1.5406 Å), with a scan speed of 4 °/min. The photochromic reaction was induced by irradiation with a Xe lamp (Beijing, 500 W) equipped with optical fiber cable and interference filters of appropriate wavelengths. UV-vis diffuse reflectance spectral measurements were carried out using a Perkin–Elmer Lambda 900 spectrometer. The spectrophotometer was calibrated against the surface of $BaSO_4$ for 100% reflectance over the wavelength range under consideration. The photoluminescence spectra were determined at room temperature by a FLS920 and FSP920C fluorescence spectrometer at room temperature. Electron spin resonance (ESR) signals were recorded with a Bruker A300 spectrometer.

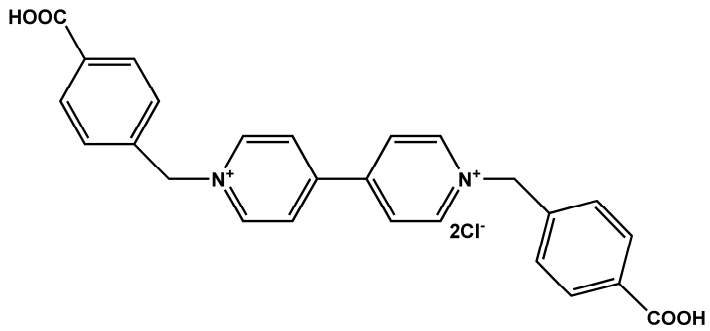
X-ray crystallography. The X-ray diffraction data for **1** was collected on a Rigaku Saturn 70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 294 K. The CrystalClear program was used for the absorption correction. The structure was solved by direct methods with SHELXS-90 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of aromatic rings were placed in a calculated position with isotropic displacement parameters set to 1.2Ueq of the attached atom. However, the H atoms of the water molecules had not been included in the final refinement. The disordered water molecule(O4W, O5W) positions were modeled with equally occupancy ratios and were refined isotropically. The disordered benzoate ligand was subjected to geometric restraints during the refinements.

Crystal data for **1** : $C_{46}H_{47}EuN_5O_{20}$ $\{[Eu(BA)\cdot(Bpybc)_{1.5}(H_2O)]\cdot 2NO_3\cdot 5H_2O\}_n$, M_r = 1141.85, space group $P2_1/c$, a = 12.219(3), b = 16.005(4), c = 24.834(6) Å, β = 92.817(3)°, T = 294 K, Z = 4, V = 4851.0(19) Å^3, D_c = 1.563 g·cm^{-3}, μ = 1.378 mm^{-1}, $F(000)$ = 2324 and GOF = 1.048. 35823 reflections collected, 10822 unique (R_{int} = 0.0358). R_1 = 0.0427, wR_2 = 0.1125 [$I > 2\sigma(I)$], 642 parameters, 1 restraints.

Synthesis of 1: $H_2BpybcCl_2$ was synthesized by the reported procedure[1]. $H_2BpybcCl_2$ (49.7 mg, 0.1 mmol) was dissolved in water (5 mL) and the pH value was adjusted to 7 with 0.1 mol/L NaOH solution. Then sodium benzoate (14.4 mg, 0.1 mmol) and $EuNO_3$ aqueous solution (0.1 mol/L, 1 mL) were added to the solution and stirred for 1 min. The filtrate was allowed to stand at room temperature for slow evaporation. Yellow prism crystals of **1** were obtained within a few days (Yield: 45%). Elemental analysis: Calc. for $C_{46}H_{47}Eu_1N_5O_{20}$: C, 48.38; H, 4.15; N, 6.13. Found: C, 48.32; H, 4.39; N, 5.93 %. IR data(KBr, cm^{-1}): 3406.30(s), 3119.63(m), 3048.80(m), 1635.67(s), 1613.89(w), 1593.72(s), 1539.00(s), 1415.05(s), 1384.69(s), 1221.10(m), 1165.24(s), 1019.16(w), 860.10(m), 814.50(m), 770.93(m), 730.08(m), 684.08(w), 648.89(w), 599.53(w), 521.77(w).

Reference: [1] Sun, Y. Q.; Zhang, J.; Ju, Z. F.; Yang, G. Y. *Cryst. Growth Des*. **2005**, *5*, 1939.

Section 2. Additional characterization data and structural figures



Scheme S1. 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium dichloride (**$H_2BpybcCl_2$**).

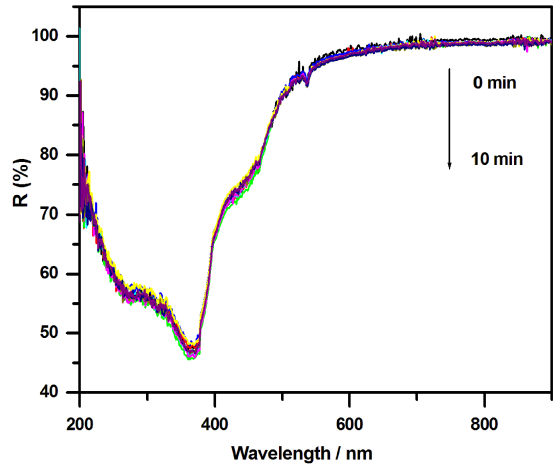


Fig S1. UV-vis diffuse reflectance spectra of **1** before (black) and after continuous light irradiation (red) (λ > 460 nm).

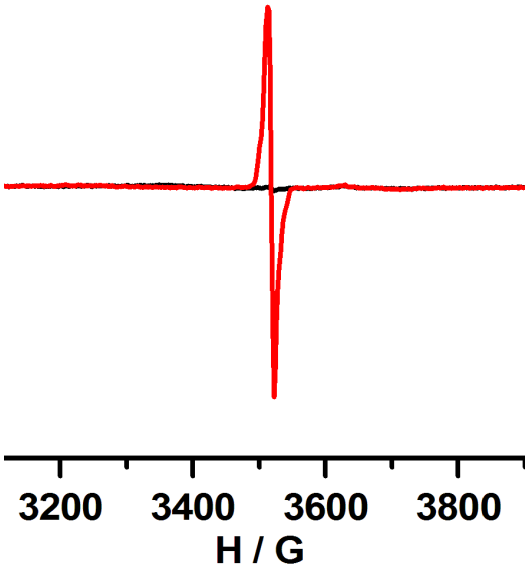


Fig S2. The ESR spectra of **1** before (dark) and after (red) UV irradiation (g = 2.0016).

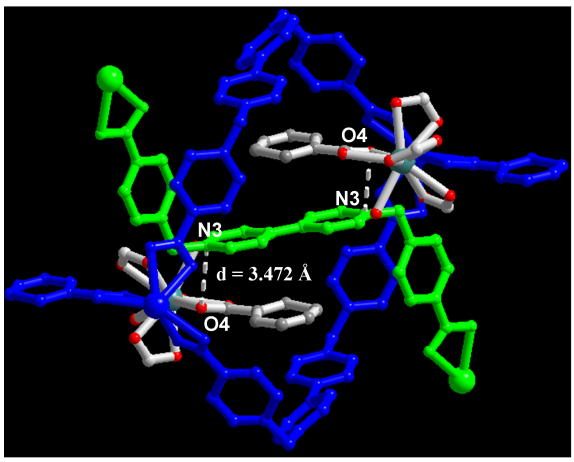


Fig S3. The distance and orientation between the donor (O4) and accepter (N3) in **1**. All hydrogen atoms and some disordered carbon atoms of benzoate ligands are omitted for clarity.

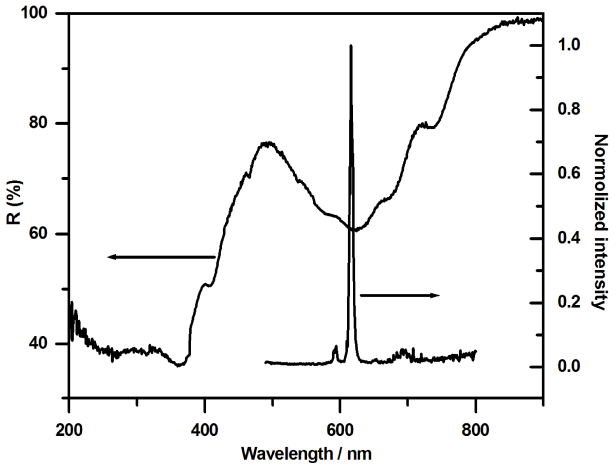


Fig S4. The luminescence spectrum of **1** in the initial state and UV-vis diffuse reflectance spectrum of **1** in the colored state.

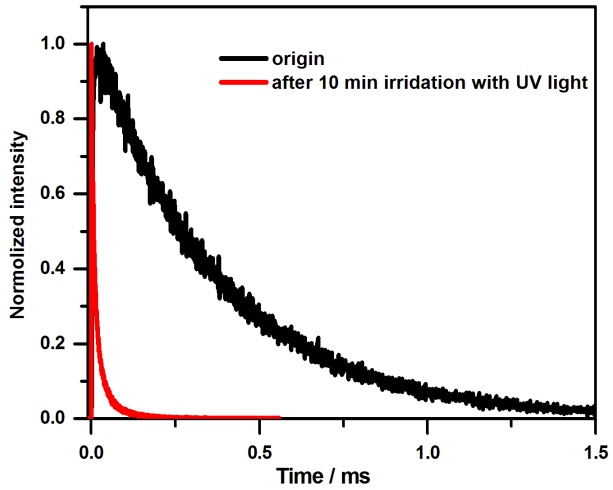


Fig S5. Luminescence-decay profiles of the **1** detected at 616 nm before (the excited-state lifetime τ = 0.35 ms) and after UV irradiation for 10min (τ = 0.009 ms).

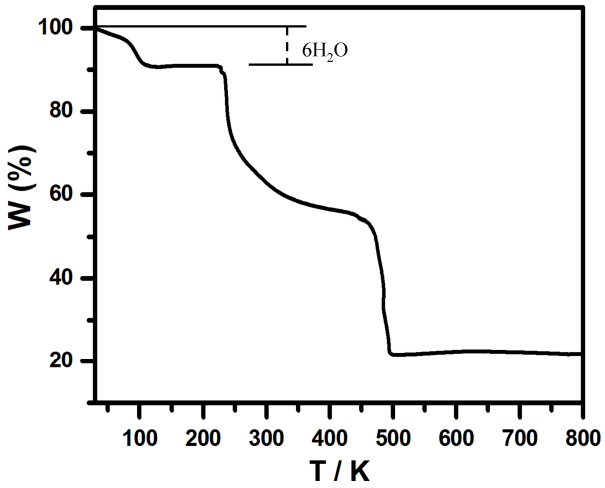


Fig S6. Thermogravimetric analysis of **1** under air atmosphere.

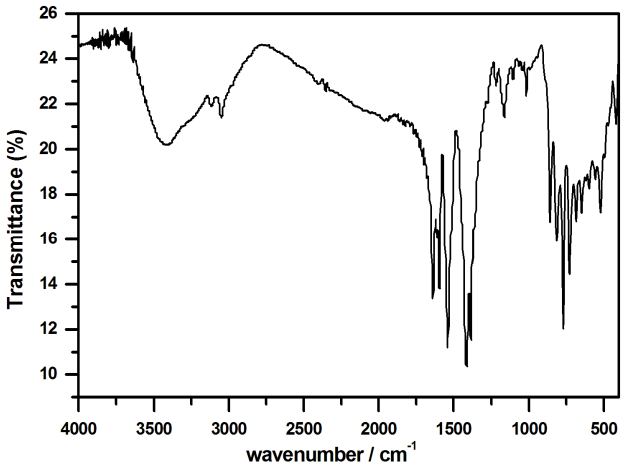


Fig S7. IR spectrum of **1**.

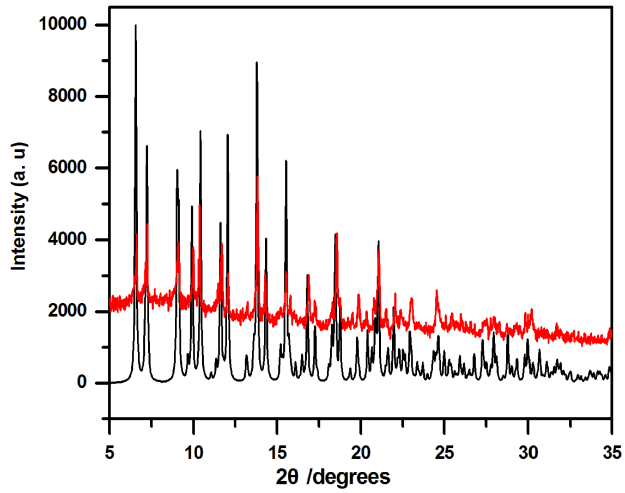


Fig S8. Calculated (black) and experimental (red) XRPD patterns of **1**.