

Supporting Information

A viologen-based multifunctional Eu-MOF: photo/electric-modulated chromism and luminescence

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Materials and Measurements.

All reagents and solvents, including $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 4,4'-dipyridine and acetonitrile (CH_3CN) were purchased commercially without further purification. Thermogravimetric analysis (TGA) were recorded by a SDT 2960 thermal analyzer from room temperature to 800 °C under N_2 atmosphere using a heating rate of 10 °C /min. Elemental analyses for C, H and N were collected on a Perkin-Elmer 240 elemental analyzer. Single Crystal X-Ray Diffraction measurement were conducted with a Rigaku XtaLAB Pro diffractometer equipped with $\text{Cu-K}\alpha$ radiation. Powder X-ray diffraction were carried out with a Rigaku B/Max-RB X-ray diffractometer using $\text{Cu-K}\alpha$ radiation. The Fourier transform infrared spectra were performed on ALPHA II spectrometer with KBr pellets. Photoluminescence and fluorescence lifetime were carried out using an Edinburgh FLS980 fluorescence spectrometer. ESR for solid state were recorded on Bruker A300. Solid-state UV-vis diffuse reflectance spectra were collected on UH4150 spectrophotometer using BaSO_4 as the reference. Cyclic voltammetry was carried out on an electrochemical working station CHI 660E (Shanghai) in 0.1 M acetonitrile and water solution. Electronic absorption spectra measurements were performed on America PINE spectroelectrochemical. A typical three-electrode system was employed, using Eu-MOF in ITO glass as working electrode, a platinum wire as counter electrode, and an Ag/AgCl electrode as reference electrode.

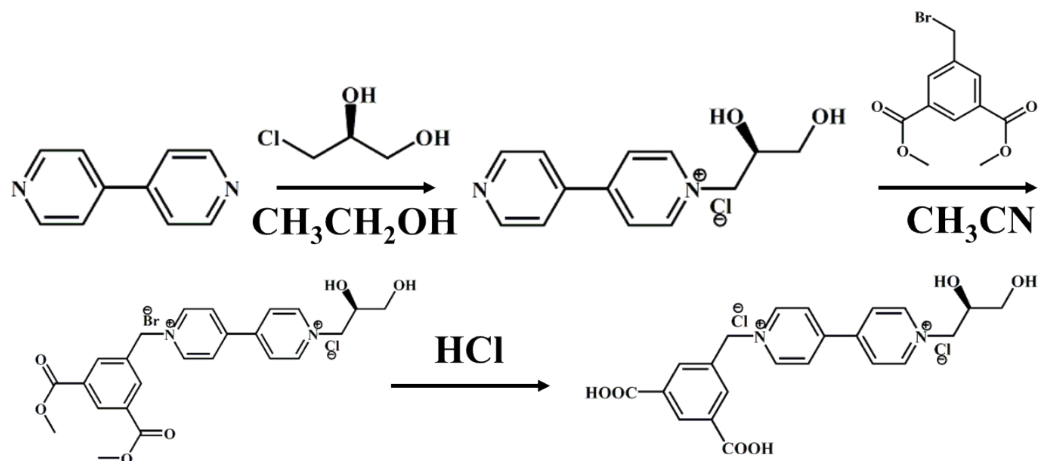
Synthesis of {1-(3,5-dicarboxybenzyl)-1'-(R-2,3-dihydroxypropyl)-4,4'-bipyridinium dichloride} ($\text{H}_3(\text{R-L})\text{Cl}_2$).

5-bromomethylisophthalic acid dimethyl ester was synthesized according to previously reported procedure in the literature.^{S1}

Synthesis of {1-(R-2,3-dihydroxypropyl)-4,4'-bipyridinium chloride}. 4,4'-bipyridine (15.6 g, 100 mmol) and 50 mL ethanol were taken into a 100 mL round bottomed flask. The mixture was stirred for 10 min. R-3-chloro-1,2-propanediol (12 g, 108 mmol) was added into the solution at 8 °C and stirred for 3 h. After that, the mixture was heated at 90 °C and stirred for 5 days. The reaction was cooled down to room temperature and 300 mL acetone was added into the mixture. Immediately a large amount of precipitate was formed. The precipitate was collected by filtration and washed with acetone. The white solid powder was obtained in vacuum. Yield: 11.5 g, 43.15%.

Synthesis of $\text{H}_3(\text{R-L})\text{Cl}_2$. 1-(R-2,3-dihydroxypropyl)-4,4'-bipyridinium dichloride (0.4 g, 1.5 mmol), 5-bromomethylisophthalic acid dimethyl ester (1.29 g, 4.5 mmol) were added into a 100 mL round bottomed flask with 30 mL acetonitrile. The mixture was reacted at 90 °C for 3 days. The

reaction was cooled down to room temperature. The precipitate was filtered, washed three times with acetonitrile, and dried to obtain yellow solid powder. Then, the resulting yellow powder and 15 mL hydrochloric acid were placed in a 50 mL round-bottom flask, and the mixture was reacted for 12 h at 100 °C. After the reaction was cooled down to room temperature, the precipitate was filtered and dried to obtain yellow powder. Yield: 0.55 g, 93.13%.



Scheme S1 Synthetic route of {1-(3,5-dicarboxybenzyl)-1'-(R-2,3-dihydroxypropyl)-4,4'-bipyridinium dichloride}.

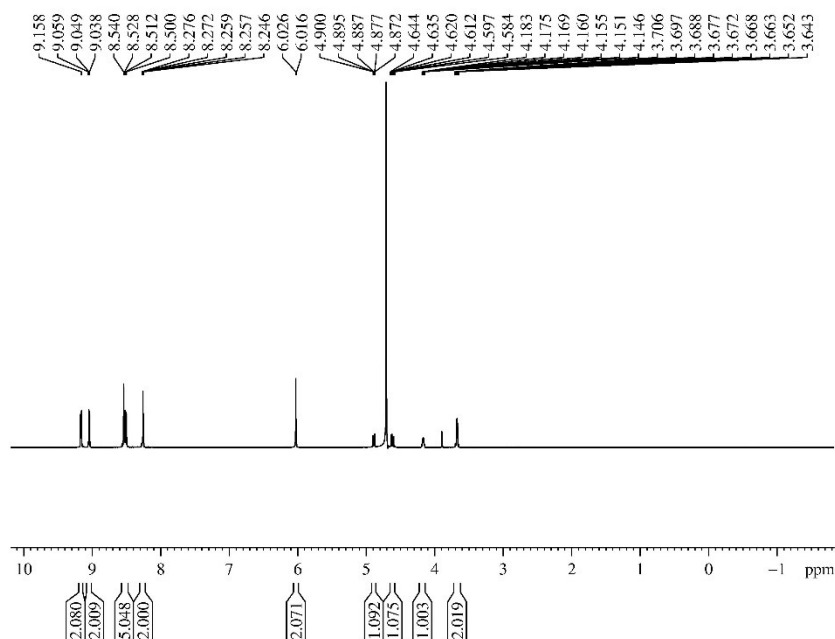


Figure S1 ^1H NMR of $\text{H}_3(\text{R-L})\text{Cl}_2$. (600 MHz, D_2O): δ 9.1, d, 2H; 9.0, d, 2H; 8.5, d, 3H; 8.5, d, 2H; 8.2, s, 1H; 6.0, s, 2H; 4.9, q, 1H; 4.6, q, 1H; 4.2, m, 1H; 3.7, q, 2H.

Synthesis of $\{[\text{Eu} \cdot (\text{R-L}) \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\}_n$ (Eu-MOF) crystal.

A mixture of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (30 mg, 0.067 mmol), $\text{H}_3(\text{R-L})\text{Cl}_2$ (8 mg, 0.018 mmol), H_2O (0.5 mL) and CH_3CN (3 mL) were sealed in a 25 mL Teflon lined stainless steel container and heated at 120 °C for 3 days. The container temperature was cooled down to room temperature within 12 hours. The yellow flake crystals were collected by filtered and washed. Yield: 20% (based on Eu). Anal Calcd for $\{[\text{Eu} \cdot (\text{R-L}) \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\}_n$ (Eu-MOF): H 3.20, C 36.71, N 7.78%. Found: H 2.78, C 36.27, N 7.88%.

The preparation of Eu-MOF working electrode

Clean and dry the ITO glass with water, ethanol and acetone in turn. 10 mg Eu-MOF crystal, 0.5 mL methanol and 20 μL 5% Nafion were added to the bottle and the mixture was ultrasonic for 30 min. The solution was dispersed to ITO glass by Pipetting gun and let it dry overnight at room temperature to obtain the Eu-MOF working electrode.

The preparation of Eu-MOF suspension.

1 mg crystals were dispersed in 0.5 M LiClO_4 aqueous solution and dispersed uniformly in the solution by ball mill.

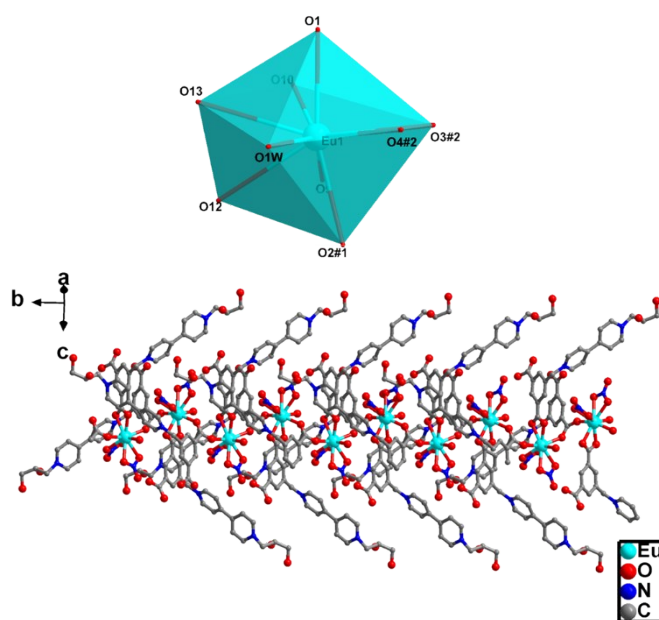


Figure S2 The coordination geometry of Eu center atom and the one-dimensional chain structure of Eu-MOF (#1: $1 - x, -0.5 + y, 1.5 - z$, #2: $x, 0.5 - y, 0.5 + z$).

Table S1. The crystal data and structure refinements of Eu-MOF.

Compound	Eu-MOF
CCDC number	2013647
Empirical formula	C ₂₂ H ₂₃ EuN ₄ O ₁₄
Formula weight	719.41
Temperature / K	219.99(10)
Crystal system	monoclinic
Space group	<i>P2₁/c</i>
<i>a</i> / Å	16.3413(6)
<i>b</i> / Å	10.2541(4)
<i>c</i> / Å	15.7957(4)
<i>α</i> / °	90
<i>β</i> / °	91.960(3)
<i>γ</i> / °	90
Volume / Å³	2645.26(16)
<i>Z</i>	4
ρ_{calc} g / cm³	1.804
μ / mm⁻¹	17.683
F(000)	1432
Crystal size / mm³	0.03x0.025x0.02
Radiation	Cu K α (λ = 1.5418)
2Θ range for data collection / °	5.43 to 135.74
Index ranges	-19 ≤ <i>h</i> ≤ 19, -10 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 18
Reflections collected	12074
Independent reflections	4832 [<i>R</i> _{int} = 0.0944, <i>R</i> _{sigma} = 0.0921]
Data / restraints / parameters	4848 / 297 / 365
Goodness-of-fit on F²	1.089
Final R indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.1031, <i>wR</i> ₂ = 0.2765
Final R indexes [all data]	<i>R</i> ₁ = 0.1161, <i>wR</i> ₂ = 0.2942
Largest diff. peak/hole / e Å⁻³	3.57/-3.89

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \cdot wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

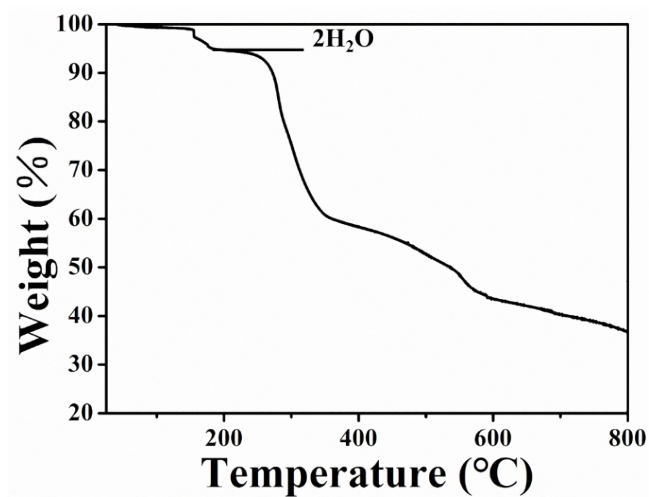


Figure S3 TGA plot of Eu-MOF crystal.

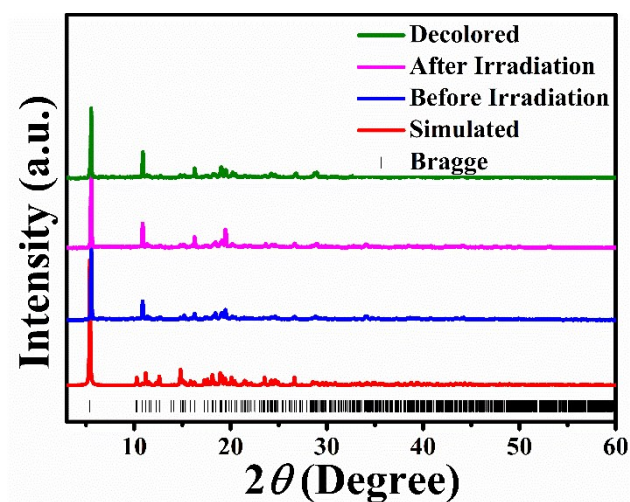


Figure S4 Powder X-ray diffraction (PXRD) patterns of Eu-MOF before irradiation (blue), after irradiation (magenta) and decolored (olive).

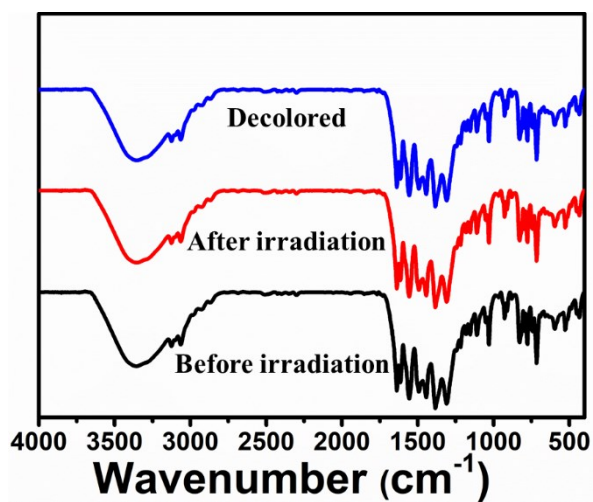


Figure S5 FT-IR spectra of Eu-MOF at different conditions.

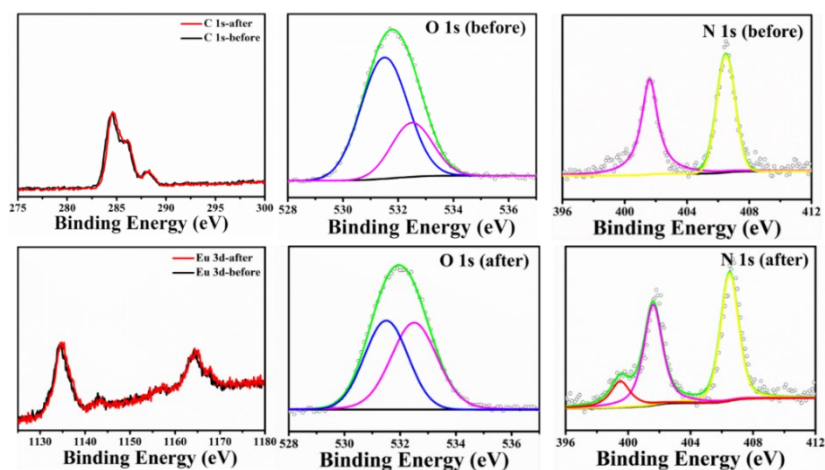


Figure S6 High-resolution XPS spectra of Eu-MOF before and after irradiation.

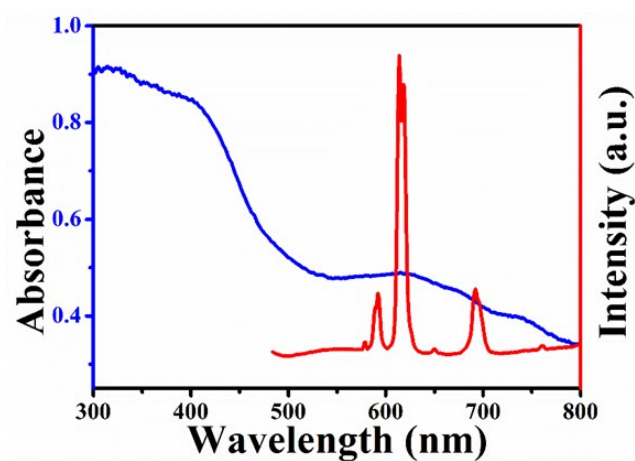


Figure S7 UV-vis spectrum of Eu-MOF after UV irradiation for 15 min (blue) and the fluorescence emission spectrum of Eu-MOF (red).

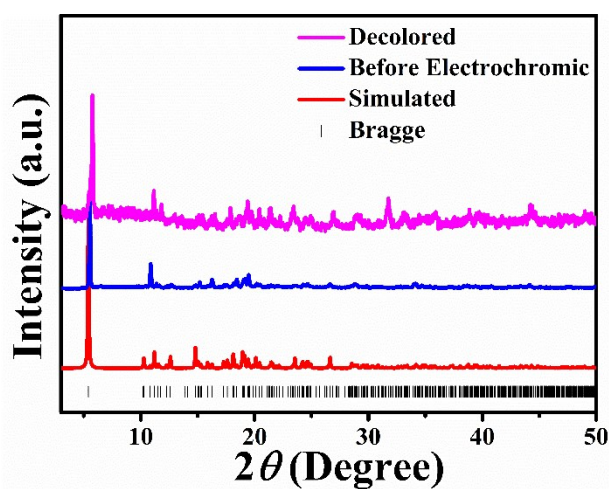


Figure S8 Powder X-ray diffraction (PXRD) spectra of Eu-MOF before electrochromic (blue) and decolored (magenta).

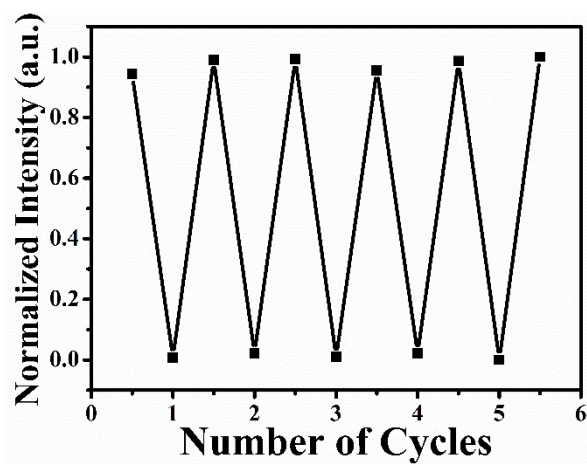


Figure S9 The repeated switching of luminescence emission of Eu-MOF between the initial and colored states.

Supplementary References

S1 C. Stackhouse, J. Ren, C. Shan, A. Nafady, A. M. Al-Enizi, M. Ubaidullah, Z. Niu and S. Ma, *Cryst. Growth Des.*, 2019, **19**, 6377–6380.