Supporting Information for

Viologen-functionalized chiral Eu-MOF as a platform for multifunctional switchable material

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Experimental Details

All chemicals were of reagent grade quality and gained from commercial sources. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max-2500PC diffractometer with Cu Kα radiation (λ = 1.5406 Å) over the 2θ range of 5−50° with a scan speed of 5°/min at room temperature. Elemental analyses for C, H and N were measured on a Perkin-Elmer 240 elemental analyzer. TGA-DTG measurement was performed on a PE Diamond TG/DTA unit under air atmosphere at a rate of 10 °C min^{-1} in the temperature range of 30 °C – 700 °C. UV-vis diffuse reflectance spectra were measured on an Agilent Cary 5000 UV-VIS-NIR Spectrophotometer with $BaSO_4$ as the reference. Electron-spin resonance (ESR) signals were recorded on a Brucker A300 spectrometer at room temperature. Luminescence spectra for the solid samples were collected on a Hitachi 850 fluorescence spectrophotometer. Powder SHG measurement on the sample was performed on a modified Kurtz-NLO system using 1064 nm laser radiation. The SHG signal was detected using a CCD detector. The piezoelectric coefficients of single crystal (5.0×2.5×1.0 mm^3) samples were recorded from a ZJ-6A static piezoelectric analyzer.

Synthesis of $H_2L^+NO_3^-$ {1-(3,5-dicarboxybenzyl)-4,4'-bipyridinium nitrate}

The $H_2L^+Cl^-$ was synthesized according to the reported literature. $H_2L^+Cl^-$ (1 g, 2.7 mmol) was dissolved in 10 mL deionized water, AgNO3 was dissolved in deionized water and added dropwise, filtered and washed with deionized water, concentrated and dried in vacuum oven.

Synthesis of {[Eu(μ_2–OH)(L)(H_2O)]·NO_3·H_2O}$_n$.

The reaction mixture containing $Eu(NO_3)_3·6H_2O$ (0.0130 g, 0.029 mmol), $H_2L^+NO_3^-$ (0.0110 g, 0.030 mmol), acetonitrile (2 mL) and water (1 mL) were sealed in a 25 mL Teflon reactor autoclave and heated to 120 °C for 3 days. After cooling down to room temperature at a rate of 5 °C /h, light-yellow crystals suitable for single crystal X-ray crystallographic analysis were obtained. Anal. Calcd for {[Eu(μ_2–OH)(L)(H_2O)]·NO_3·H_2O}$_n$ (Eu-MOF): H 2.92, C 38.01, N 7.00%. Found: H 3.25, C 38.20, N 6.85%.

X-ray Crystallographic Studies.

Single-crystal X-ray diffraction measurement was measured on a Bruker SMART1000 CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation Mo Kα radiation (λ = 0.71073 Å) at 150K using the ω-scan technique. Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. The structure was solved by direct methods with SHELXS-97 and refined using a full-matrix least-squares refinement on F^2.[1] Difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the coordination water molecules, and ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The hydrogen atoms of the solvent water molecules were located from the difference Fourier maps, then restrained at fixed positions and refined isotropically. Crystal data and structure refinement results for the Eu-MOF are summarized in Table S1. Crystallographic data for the structure reported in this paper have also been deposited with the CCDC as deposition no. CCDC 1406260 (available free of charge, on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K.; e-mail deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinements for Eu-MOF.

Compound	Eu-MOF
Formula	$C_{19}H_{18}EuN_3O_{10}$
Formula weight	600.33
Temperature (K)	150(2)
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	9.7675(9)
b (Å)	7.1607(6)
c (Å)	15.8901(19)
α(°)	90
β(°)	107.90
γ(°)	90
V (Å^3)	1057.59(18)
Z	2
D_c (Mg/m^3)	1.885
μ (mm^{-1})	3.028
F(000)	592
Reflns collected	4721
Independent reflns	4308
Completeness	98.7%
R(int)	0.0362
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3269/476/298
GOF on F^2	1.009
Flack parameters	0.04(3)
[a]$R_1[I>2\sigma(I)]$, wR_2	0.0416,0.1043
R_1[all data], wR_2	0.0489,0.1102

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

Table S2. Selected bond lengths (Å) and bond angles (°) for Eu-MOF.

bond lengths (Å)			
Eu(1)–O(5)#1	2.328(9)	Eu(1)–O(5)	2.332(8)
Eu(1)–O(1)	2.446(6)	Eu(1)–O(4)#2	2.449(7)
Eu(1)–O(2)#3	2.459(8)	Eu(1)–O(1W)	2.488(8)
Eu(1)–O(3)#4	2.516(6)	Eu(1)–O(4)#4	2.592(7)
Eu(1)–O(2)	2.669(7)		
bond angles (°)			
O(5)#1–Eu(1)–O(5)	145.4(2)	O(5)#1–Eu(1)–O(1)	93.2(3)
O(5)–Eu(1)–O(1)	96.8(3)	O(5)#1–Eu(1)–O(4)#2	79.3(3)
O(5)–Eu(1)–O(4)#2	72.2(3)	O(1)–Eu(1)–O(4)#2	72.9(2)
O(5)#1–Eu(1)–O(2)#3	79.7(2)	O(5)–Eu(1)–O(2)#3	70.9(3)
O(1)–Eu(1)–O(2)#3	138.6(2)	O(4)#2–Eu(1)–O(2)#3	65.7(2)
O(5)#1–Eu(1)–O(1W)	134.5(3)	O(5)–Eu(1)–O(1W)	80.1(3)
O(1)–Eu(1)–O(1W)	74.6(2)	O(4)#2–Eu(1)–O(1W)	133.9(3)
O(2)#3–Eu(1)–O(1W)	137.0(3)	O(5)#1–Eu(1)–O(3)#4	100.7(3)
O(5)–Eu(1)–O(3)#4	87.4(3)	O(1)–Eu(1)–O(3)#4	148.9(2)
O(4)#2–Eu(1)–O(3)#4	136.8(2)	O(2)#3–Eu(1)–O(3)#4	71.8(2)
O(1W)–Eu(1)–O(3)#4	75.9(2)	O(5)#1–Eu(1)–O(4)#4	69.7(3)
O(5)–Eu(1)–O(4)#4	135.0(3)	O(1)–Eu(1)–O(4)#4	110.5(2)
O(4)#2–Eu(1)–O(4)#4	148.94(17)	O(2)#3–Eu(1)–O(4)#4	105.1(2)
O(1W)–Eu(1)–O(4)#4	74.0(3)	O(3)#4–Eu(1)–O(4)#4	51.1(2)
O(5)#1–Eu(1)–O(2)	67.2(3)	O(5)–Eu(1)–O(2)	141.3(3)
O(1)–Eu(1)–O(2)	50.9(2)	O(4)#2–Eu(1)–O(2)	109.7(2)
O(2)#3–Eu(1)–O(2)	146.7(2)	O(1W)–Eu(1)–O(2)	71.5(3)
O(3)#4–Eu(1)–O(2)	109.8(2)	O(4)#4–Eu(1)–O(2)	60.8(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y - 1/2, -z + 2$; #2 $-x + 1, y + 1/2, -z + 2$; #3 $-x, y + 1/2, -z + 2$; #4 $x - 1, y, z$

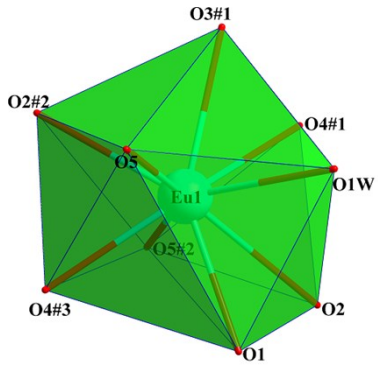

Figure S1. The coordination geometry of Eu center in Eu-MOF. Symmetry codes: #1: – *x*, *y* – 1/2, – *z* + 2; #2: – *x* + 1, *y* + 1/2, – *z* + 2; #3: – *x*, *y* + 1/2, – *z* + 2.

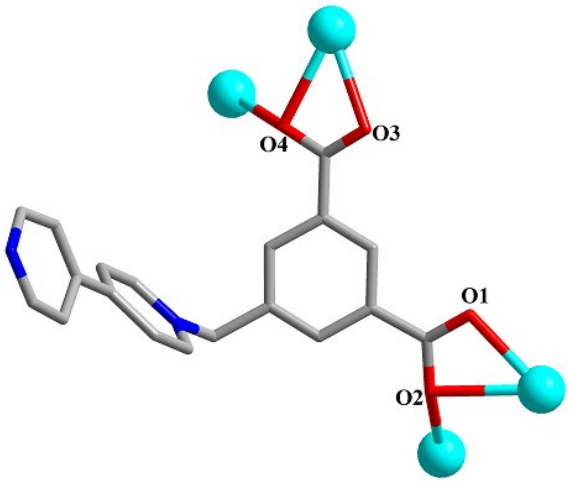

Figure S2. Coordination modes of carboxylate groups in Eu-MOF.

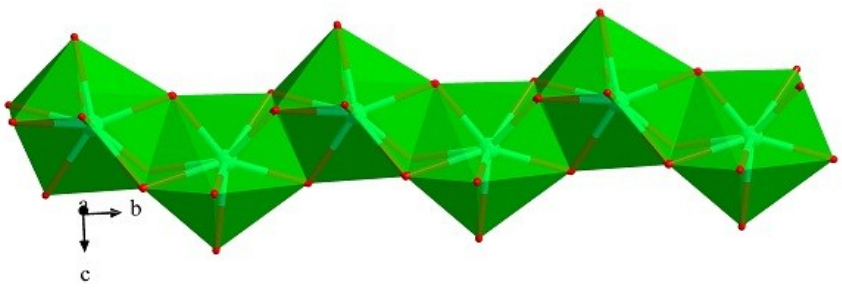

Figure S3. The infinite rod-like 1D chain along the *b* axis in Eu-MOF.

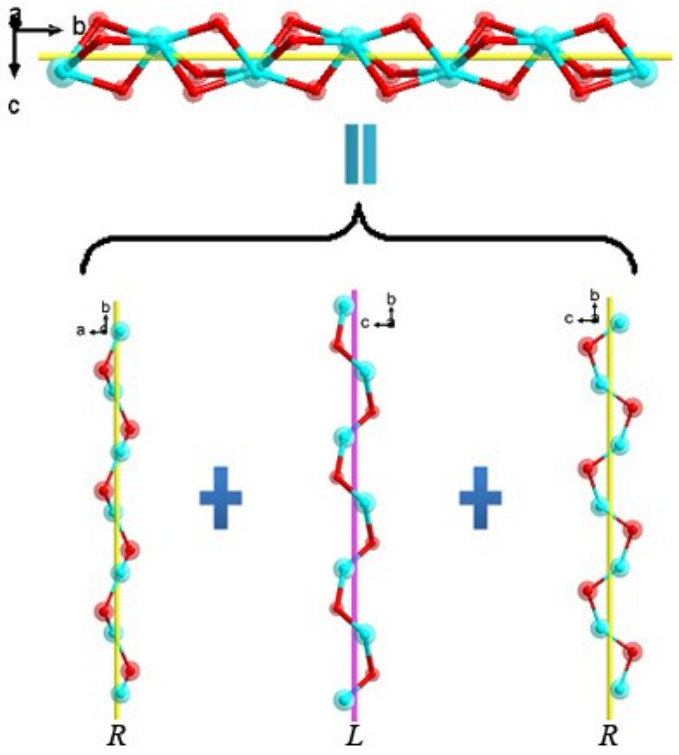

Figure S4. Three co-axial helical chains of the 1D rod-like chain in Eu-MOF.

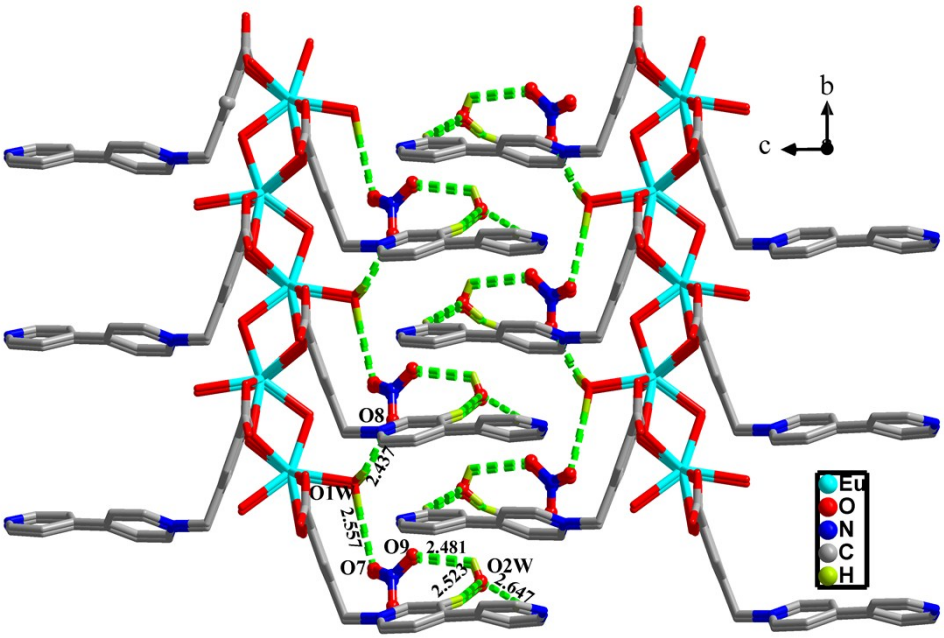

Figure S5. Hydrogen bonds of the Eu-MOF. O8···H1WA–O1W = 2.437 Å; O7···H1WB–O1W = 2.557 Å; O9···H2WB–O2W = 2.481 Å; O2W···H11–C11 = 2.523 Å; O2W···H18–C18 = 2.647 Å. Only the hydrogen atoms involved in supramolecular interactions are shown for clarity.

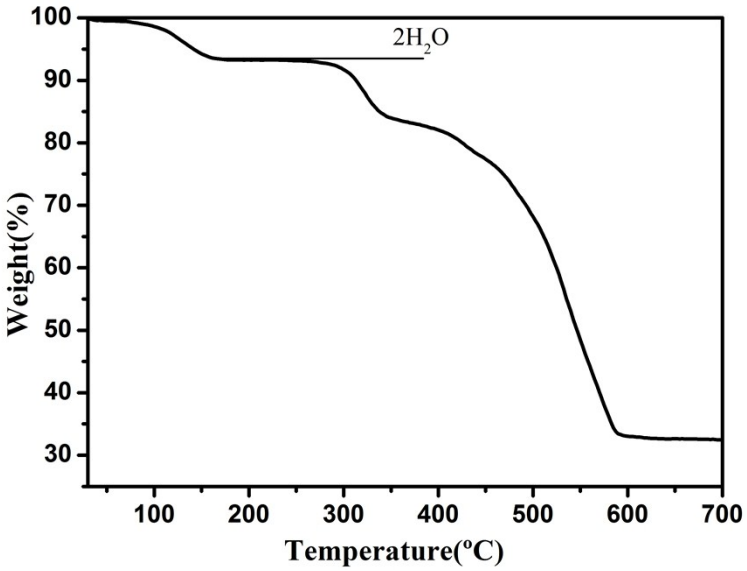

Figure S6. TG Plot of Eu-MOF. The weight loss of 6.23% (calcd 6.01%) up to 150 °C corresponds to the loss of one free and one coordinated water molecule.

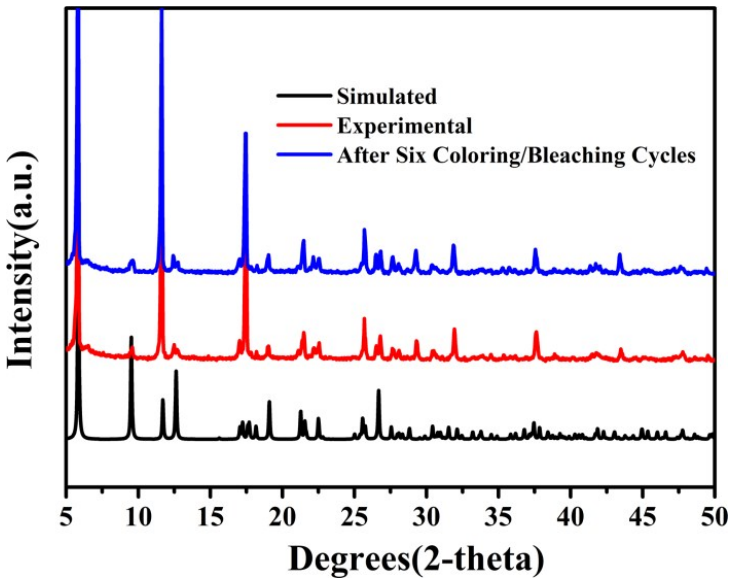

Figure S7. The Powder X-ray diffraction (XRD) profiles for simulated (black), experimental (red) and after six coloring/bleaching cycles (blue) of Eu-MOF samples.

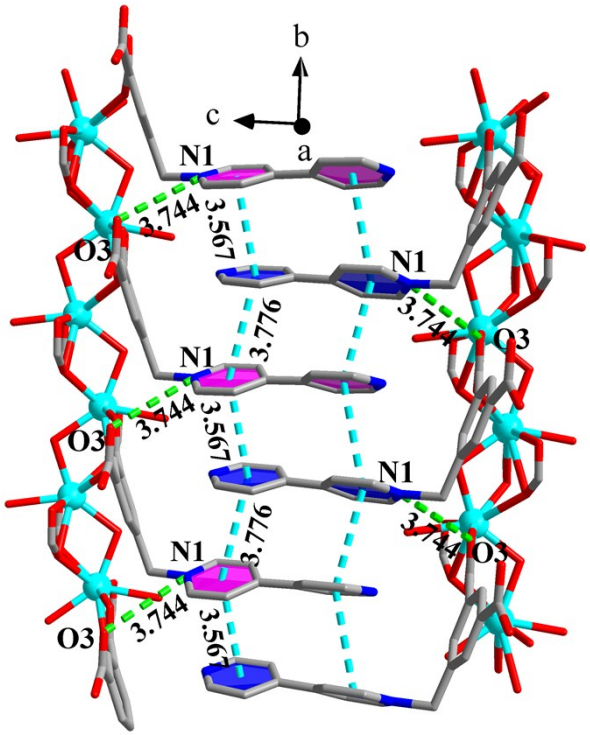

Figure S8. Two kinds of possible electron transfer pathways in Eu-MOF. Distances are in angstrom (Å).

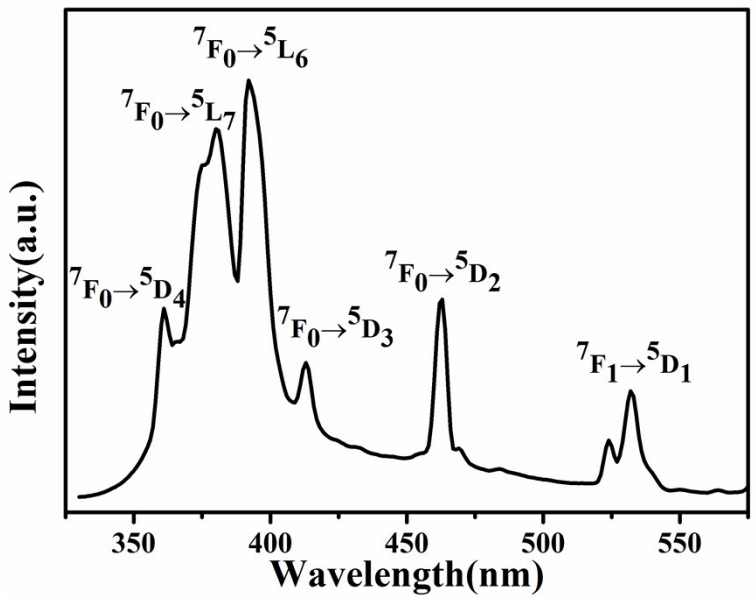

Figure S9. The excitation spectrum of Eu-MOF monitored at 618 nm.

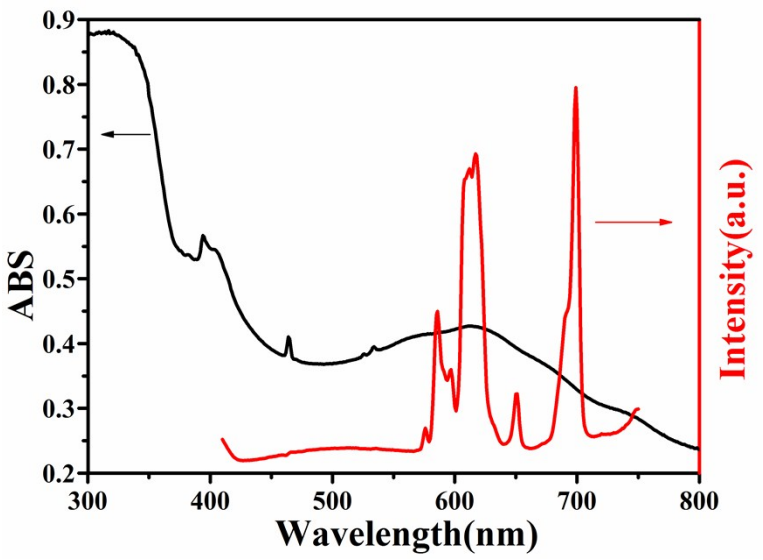

Figure S10. The fluorescent emission spectrum of Eu-MOF (red) and UV−Vis diffuse reflectance spectrum of colored samples (black).

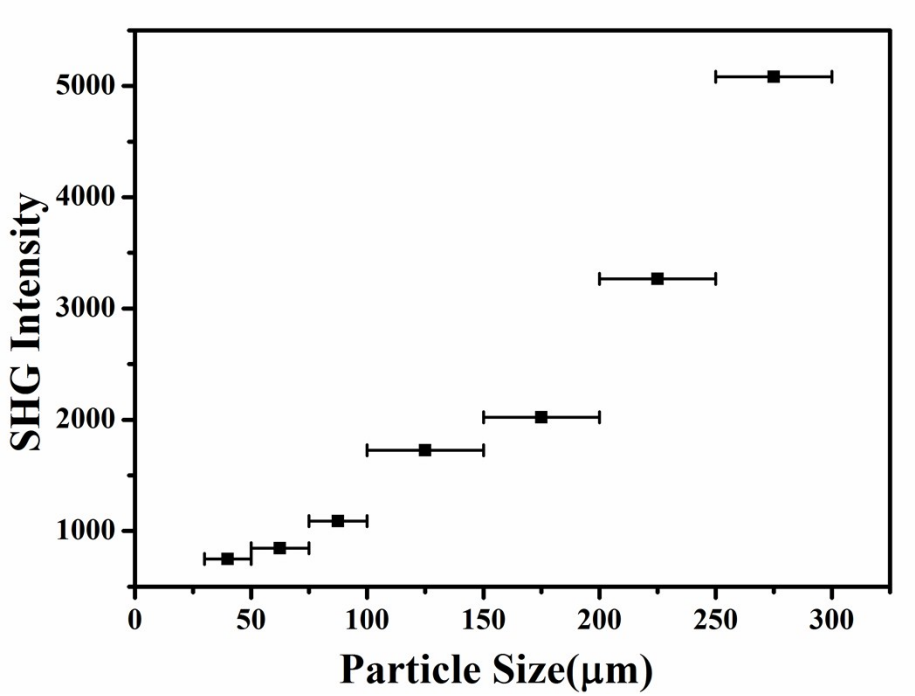

Figure S11. The curve of measured SHG activity and particle size.

References

[1] G. M. Sheldrick, *Acta Crystallogr. A*. **2008**, *64*, 112.