Supporting Information

Photo- and thermo-activated electron transfer system based on a luminescent europium organic framework with spectral response from UV to visible range

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General methods and materials

All of the reagents were purchased from commercial sources and used without further purification. The amount of hydrates of the purchased Eu(OAc)₃:xH₂O was determined as 2.66 by thermogravimetric analysis. 1,1'-dicarboxymethyl-4,4'-bipyridinium dichloride was synthesized according to a reported method.^{S1} ATA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N₂ at a rate of 10 °C min⁻¹. The X-ray powder diffraction data were collected with a Bruker D8 Advance X-ray diffractometer using CuK α radiation ($\lambda = 1.5406$ Å). Solid state diffuse-reflectance spectral measurements were carried out using a HITACHI U-3010 spectrometer equipped with an integral sphere. Photoluminescence spectra were obtained using a F-4500 FL Spectrophotometer. The excitation wavelength used for emission spectra is 375 nm and the excitation/emission slit width were set to 2.5/2.5 nm. IR spectra were collected by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm⁻¹ using a KBr tablet. ESR spectra were recorded at room temperature with a Bruker EMX-10/12 Electron Spin Resonance Spectrometer, with 1,1diphenyl-2-picrylhydrazyl as reference. The C, H and N microanalyses were carried out with a Vario EL III elemental analyzer. The luminescent quantum yields of the solid-state samples were determined by an absolute method using an integrating sphere (150 mm diameter, BaSO₄ coating) on Edinburgh Instrument FLS920. The excitation wavelength, excitation slit width, emission slit width were set as 375 nm, 3 mm, 0.13 mm respectively and the emission was monitored from 570 to 720 nm. Timeresolved luminescence spectroscopy was conducted by exponential fit time scan (FLS920, Edinburgh Instruments) under air ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 616$ nm). All of the samples exhibit second-order exponential decay.

Synthesis of compound 1

As methyl viologen easily decompose at higher temperature, an *in situ* MV^{2+} generation strategy was adopted. The starting material 1,1'-dicarboxymethyl-4,4'-bipyridinium ion is decarboxylated to methyl viologen dication in a basic condition, which was then incorporated and stabilized in the anionic framework after the solvothermal reaction. Eu(OAc)₃•xH₂O (80 mg, 0.2 mmol), 1,1'-dicarboxymethyl-4,4'-bipyridinium dichloride (55 mg, 0.15 mmol) and isophthalic acid (67 mg, 0.4 mmol) were added to a mixture of H₂O (2 mL), EtOH (5 mL) and DMF (5 mL). The slurry was then transferred into a 23 mL Teflon-lined autoclave and heated at 85 °C for 48 hours. The solution was allowed to cool at a rate of 5 °C/h. Block-shaped crystals were collected through filtration, washed with EtOH (3 × 20 mL) and ethyl ether (1 × 20 mL), dried at room temperature in a vacuum (46.7 mg, 40.8 % yield based on Eu). IR (KBr): v = 3270 (m), 3136 (m), 3061 (s), 1646 (vs), 1603 (vs), 1545 (vs), 1448 (vs), 1385 (vs), 1190 (m), 1161 (m), 1080 (m), 1026 (w), 960 (m), 908 (w), 823 (s), 754 (vs), 706 (vs), 650 (m), 575 (m), 517 (s) cm⁻¹. Eu₂C₄₄H₃₀O₁₆N₂ (M=1146.6): calcd. C 46.05 %, H 2.637 %, N 2.442 %; found C 45.31 %, H 2.410 %, N 2.420 %. Replacing Eu(OAc)₃ with Sm(OAc)₃, Gd(OAc)₃, Tb(OAc)₃, Dy(OAc)₃ also yields similar compounds. XRD patterns indicate that the Sm, Eu, Gd, Tb, Dy compounds are isostructural (Fig. S2).

Single Crystal Data

The measurements were taken on a Rigaku R-AXIS SPIDER CCD diffractometer with graphitemonochromated Mo/K α radiation. Data were collected at 298K, using the ω - and φ -scans to a maximum θ value of 25.03°. The data were refined by full-matrix least-squares techniques on F² with SHELXTL-97.^{S2} And the structures were solved by direct methods SHELXS-97.^{S3} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions. CCDC 1016434 contains the supplementary crystallographic data for this paper. These data can be Centre obtained free of charge from the Cambridge Crystallographic Data via www.ccdc.cam.ac.ukf/data request/cif.

 $Crystal data for 1: C_{44}H_{30}Eu_2N_2O_{16}$, fw = 1146.62 g·mol⁻¹, Triclinic, space group P-1, a= 11.046(2) Å, b= 11.633(2) Å, c= 16.246(3) Å, α = 78.69(3)°, β = 73.81(3)°, γ = 88.58(3)°, V = 1964.9(6) Å³, Z = 2, ρ_{calcd} = 1.938 g·cm⁻³, final R1 = 0.0454 and wR2 = 0.1113 for 6763 independent reflections [I>2 σ (I)].

Formula	$Eu_2C_{44}H_{30}O_{16}N_2$			
Formula weight	1146.62 g/mol			
Crystal system	triclinic			
Space group	P-1			
a (Å)	11.046(2)			
b (Å)	11.633(2)			
c (Å)	16.246(3)			
α (°)	78.69(3)			
β (°)	73.81(3)			
γ (°)	88.58(3)			
Volume (Å ³)	1964.9(6)			
Void volume (Å ³)	78.7			
Crystal density (g/cm ³)	1.938			
F (000)	1124			
Goodness-of-fit on F ²	1.059			
Final R indices $[I > 2\sigma (I)]^a$	$R_1 = 0.0454 \text{ w} R_2 = 0.1113$			
R indices (all data)	$R_1 = 0.0592 \text{ w} R_2 = 0.1189$			

Table S1. Crystal data for compound 1.

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|. wR_{2} = [\sum [w (F_{0}^{2} - F_{c}^{2})^{2}] / \sum [w (F_{0}^{2})^{2}]]^{1/2}.$

Crystal structure diagrams



Fig. S1 Diagrams to show: (a) the coordination environment of Eu^{3+} ; (b) linking mode of the BDC ligand; topological representation viewed from (c) *a* axis, (d) *b* axis, (e) *c* axis; (f) cavities generated from the Eu-BDC framework and the embedded viologen ions.



Fig. S2 (a) Experimental and simulated powder X-ray diffraction patterns of compound 1.

Optical band gap

Diffuse reflectance spectra were translated into the absorption spectra by the Kubelka – Munk method.^{S4} The energy gap (E_g) can be derived from the dependence of $(F(R_{\infty})E)^2$ on the photon energy E = hv. Extrapolating the tangential line from the high photon energy intersected $(F(R_{\infty})E)^2$ at $hv = E_g$.

 $F(R_{\boldsymbol{\infty}})$ was calculated according to the equations below:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
$$A = \log(\frac{1}{R_{\infty}})$$

A refers to diffuse reflectance absorbance, which is obtained from the solid state diffuse reflectance spectra.



Fig. S3 Optical band gap energy of compound 1.

Electron spin resonance (ESR)



Fig. S4 ESR spectra of (a) photo-irradiated (60 min); (b) heated (140 °C for 60 min) samples of compound **1**. Their spin density is 9.85×10^{15} Spins/g (1.129×10^{19} Spins/mol) and 4.11×10^{15} Spins/g (4.711×10^{18} Spins/mol) respectively.

Kinetic rate calculations

After irradiation for 1 min, 2 min, 3 min, 5 min, 10 min, 20 min, 30 min, 45 min, UV-Vis diffuse reflectance and photoluminescence spectra were recorded and the calculations of kinetics of photo-reaction kinetic rates were based on the intensity values of the wavelength at 616 nm,. The kinetic rate constants are determined by the literature calculation method.^{S5} The following equation is used for data treatment:

$$In\frac{A_{\infty}-A_{0}}{A_{\infty}-A_{t}}=kt$$

$$In\frac{I_{\infty}-I_{0}}{I_{\infty}-I_{t}}=kt$$

where A_0 , A_t , A_∞ refer to the observed absorption data at the beginning, versus time, and at the end of the reaction, respectively. I_0 , I_t , I_∞ refer to the observed emission intensity data at the beginning, versus time, and at the end of the reaction, respectively.



Fig. S5 Solid state photo-reaction kinetic traces of (a), (b): photo-coloration based on diffuse reflectance absorbance monitored at 616 nm; (c), (d): photoluminescence based on emission intensity monitored at 616 nm.

Emission quantum yield and lifetime

Table. S2 emission quantum yield, lifetime, kinetic constants for as-synthesized sample, sample heated at 140 °C for 20 min, sample irradiated by a Xenon lamp of compound **1**.

Sample	$\Phi_{Ln}/{}^{\!$	τ_1/ms	τ_2/ms	τ/ms	a_1 , rel%	a ₂ , rel%	$k_{\rm r}$ /×10 ² s ⁻¹	$k_{\rm nr}$ /×10 ³ s ⁻¹
As-synthesized	5.70	0.3106	0.9918	0.8831	415.2, 15.96%	684.6, 84.04%	0.6454	1.068
Heated	4.15	0.2485	0.9327	0.7839	583.8, 21.75%	559.8, 78.25%	0.5294	1.223
Irraideted	2.54	0.1989	0.8870	0.6717	719.8, 31.84%	345.4, 68.16%	0.3781	1.451

The emission lifetime τ was calculated according to the equation below:

$$\tau = \frac{a_1 \times \tau_1^2 + a_2 \times \tau_2^2}{a_1 \times \tau_1 + a_2 \times \tau_2}$$

 $k_{\rm r}$ and $k_{\rm nr}$ were obtained using the following two equations^{S6}:

$$\phi_{\rm Ln} = k_r / (k_r + k_{nr})$$
$$\tau = 1 / (k_r + k_{nr})$$



Fig. S6 Luminescent decay profile for the three samples, excited at 375 nm and recorded at 298K.

Long-lived charge separated state



Fig. S7 diffuse reflectance spectral changes of the photo-irradiated (60 min) sample stored at a dark place for a period of time. The inset shows slow declination of the absorbance monitored at 616 nm, indicating the formation of long-lived charge separated state.

Thermal stability



Fig. S8 (a) TGA curve of compound 1; (b) powder X-ray diffraction patterns of as-synthesized and calcinated samples of compound 1.

Visible-light-driven electron transfer



Fig. S9 Diffuse reflectance spectral changes of the sample after visible light illumination (controlled by an edge filter, $\lambda > 400$ nm) for 10 min.

The same MOF compounds with other lanthanide ions



Fig. S10 XRD patterns of the same MOF compounds with other lanthanide ions (Sm³⁺, Gd³⁺, Tb³⁺, Dy³⁺).

Note: The same MOF compounds with other lanthanide ions $(Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+})$ are successfully obtained (Fig. S10). They show similar photochromic behaviors as that of compound **1**, the Eu-MOF complex. However, only compound **1** displays good intermolecular resonance energy transfer characters. This can be attributed to the good spectral overlap between the main emission band of the Eu³⁺ and the arisen broad absorption bands around 616 nm of the colored photochromic unit.

References:

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