Supporting Informations

A Novel Photocholoremetric and Photofluorometric Europium(III) Complex for Advanced Encryption

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Experimental section

Materials and general measurements. The chemicals and solvents were purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification. NMR (^{1}H) spectra were recorded on a Bruker DRX 400 NMR spectrometer in deuterated solvents at room temperature (298 K). UV-Vis spectra were measured on a UV-3600 spectrophotometer. Photoluminescence (PL) spectra were measured by Hitachi F-4600 PL spectrophotometer. Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART APEX CCD based on diffractometer operating at room temperature. Thermal stability studies were carried out on a Perkin-Elmer Pyris 1 TGA analyzer by heating the sample from room temperature to 800 °C at a heating rate of 10 °C/min in N_2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference numbers: 1440297.

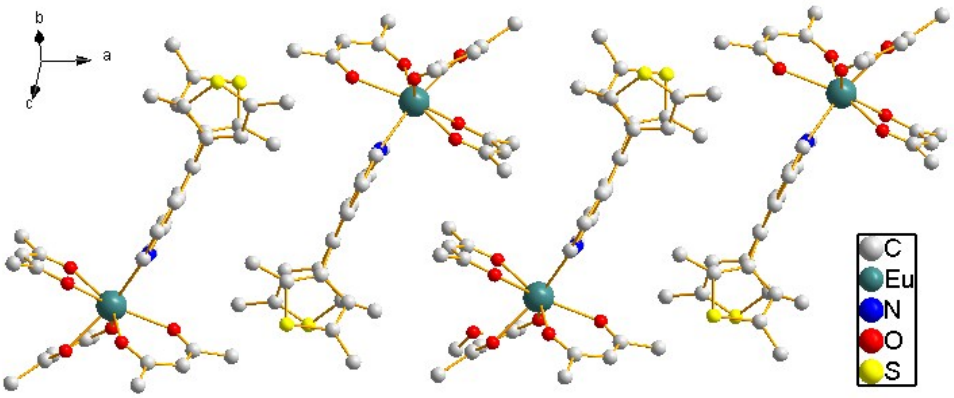
Synthesis of Eu(L_o)(acac)$_3$. The white solid $\mathbf{L_o}$ (23.4 mg, 0.05 mmol) and Eu(acac)$_3$·H_2O (20.0 mg, 0.05 mmol) were added to 10 mL methanol and stirred at room temperature for one night. The solvent was slowly evaporated for **Eu(L_o)(acac)$_3$** crystal precipitation (Yield: 90%.).

Table S1. Crystallographic data of complex **Eu(L_o)$(acac)_3$**

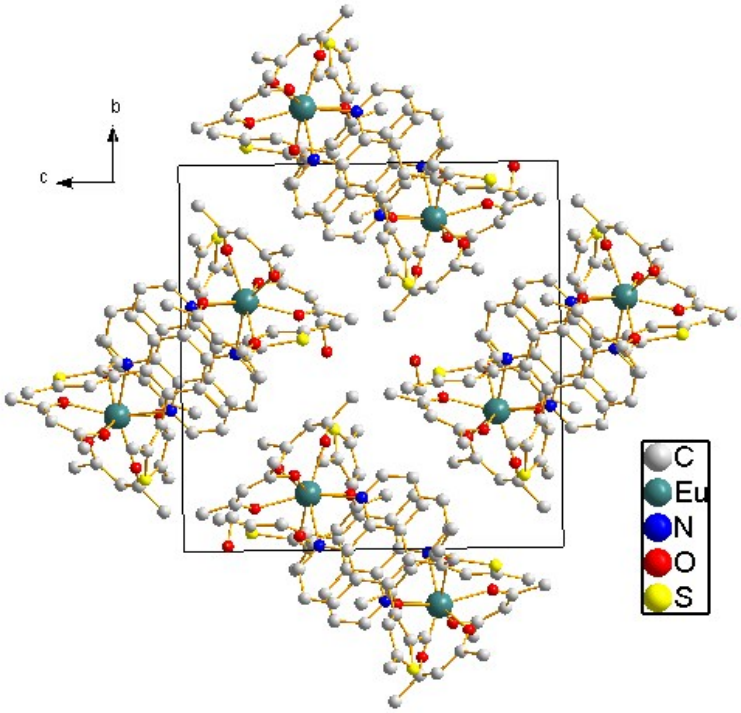
Formula	$EuC_{40}H_{45}N_2O_7S_2$
Mr/g mol^{-1}	881.86
crystal system	Monoclinic
Space group	*P*2(1)/n
a/Å	15.514(8)
b/Å	16.468(8)
c/Å	16.153(8)
α/ °	90.00
β/ °	98.977(8)
γ/ °	90.00
V/Å^3	4076(4)
Z	4
T /K	296(2)
Radiation, *λ* /Å	0.71073
D_{calcd}, g/cm^{-3}	1.437
μ/mm^{-1}	1.690
F(000)	1800
Crystal size/mm^3	0.26×0.18×0.12
θ range/°	1.69 to 25.00
Reflections measured	21693
Unique reflections	7185
R_{int}	0.0797
Reflections with $F^2 > 2\sigma(F^2)$	4072
Number of parameters	418
Goodness-of-fit on F^2	1.023
R_1 [$F^2 > 2\sigma(F^2)$]	0.0842
wR_2 (all data)	0.2650
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	2.972, -2.315

Table S2. Bond lengths [Å] and angles [°] of complex **Eu(L_0)$(acac)_3$**.

Bond Length			
Eu1−N1	2.622(9)	N1−Eu1−N2	62.1(3)
Eu1−N2	2.635(9)	N1−Eu1−O1	79.9(3)
Eu1−O1	2.359(7)	N1−Eu1−O2	147.6(3)
Eu1−O2	2.373(9)	N1−Eu1−O3	71.0(3)
Eu1−O3	2.348(8)	N1−Eu1−O4	113.4(3)
Eu1−O4	2.357(8)	N1−Eu1−O5	134.5(3)
Eu1−O5	2.374(9)	N1−Eu1−O6	76.2(2)
Eu1−O6	2.422(4)	N2−Eu1−O1	140.4(3)
Bond Angles			
N2−Eu1−O2	147.6(3)	N2−Eu1−O3	101.1(3)
N2−Eu1−O4	73.4(3)	N2−Eu1−O5	81.1(3)
N2−Eu1−O6	80.7(2)	O1−Eu1−O2	72.1(3)
O1−Eu1−O3	74.9(3)	O1−Eu1−O4	137.1(3)
O1−Eu1−O5	123.8(3)	O1−Eu1−O6	79.6(2)
O2−Eu1−O3	86.0(3)	O2−Eu1−O4	79.0(3)
O2−Eu1−O5	76.3(3)	O2−Eu1−O6	113.3(2)
O3−Eu1−O4	72.2(3)	O3−Eu1−O5	146.8(3)
O3−Eu1−O6	141.2(2)	O4−Eu1−O6	142.0(2)
O4−Eu1−O5	76.9(3)	O5−Eu1−O6	72.0(2)



(a)



(b)

Figure S1. The molecular packing diagram of **Eu(L_o)$(acac)_3$**. (a) View along *a* axis; (b) View in *bc* plane.

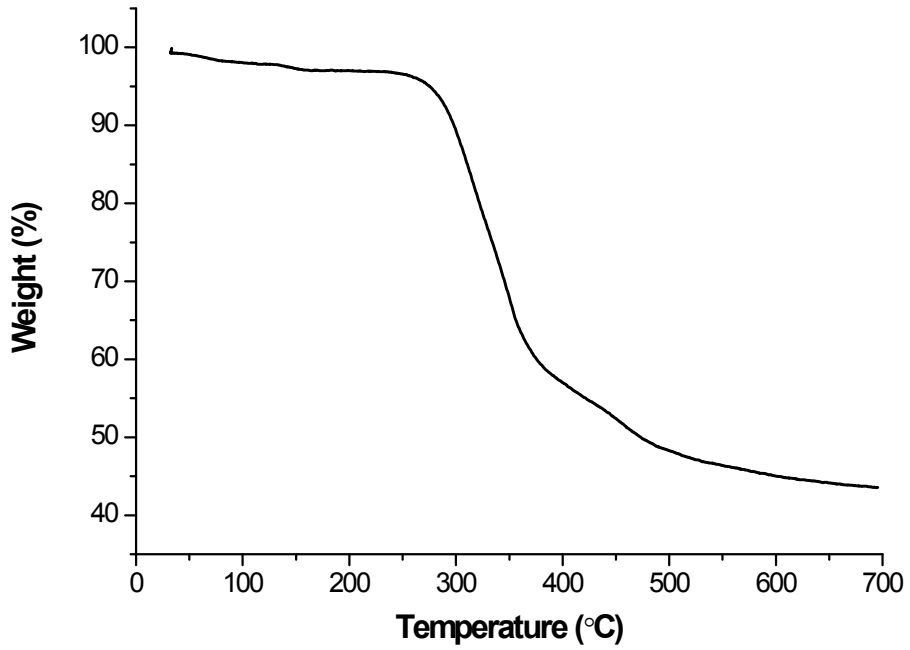


Figure S2. The TGA curve of **Eu(L_o)(acac)$_3$**.

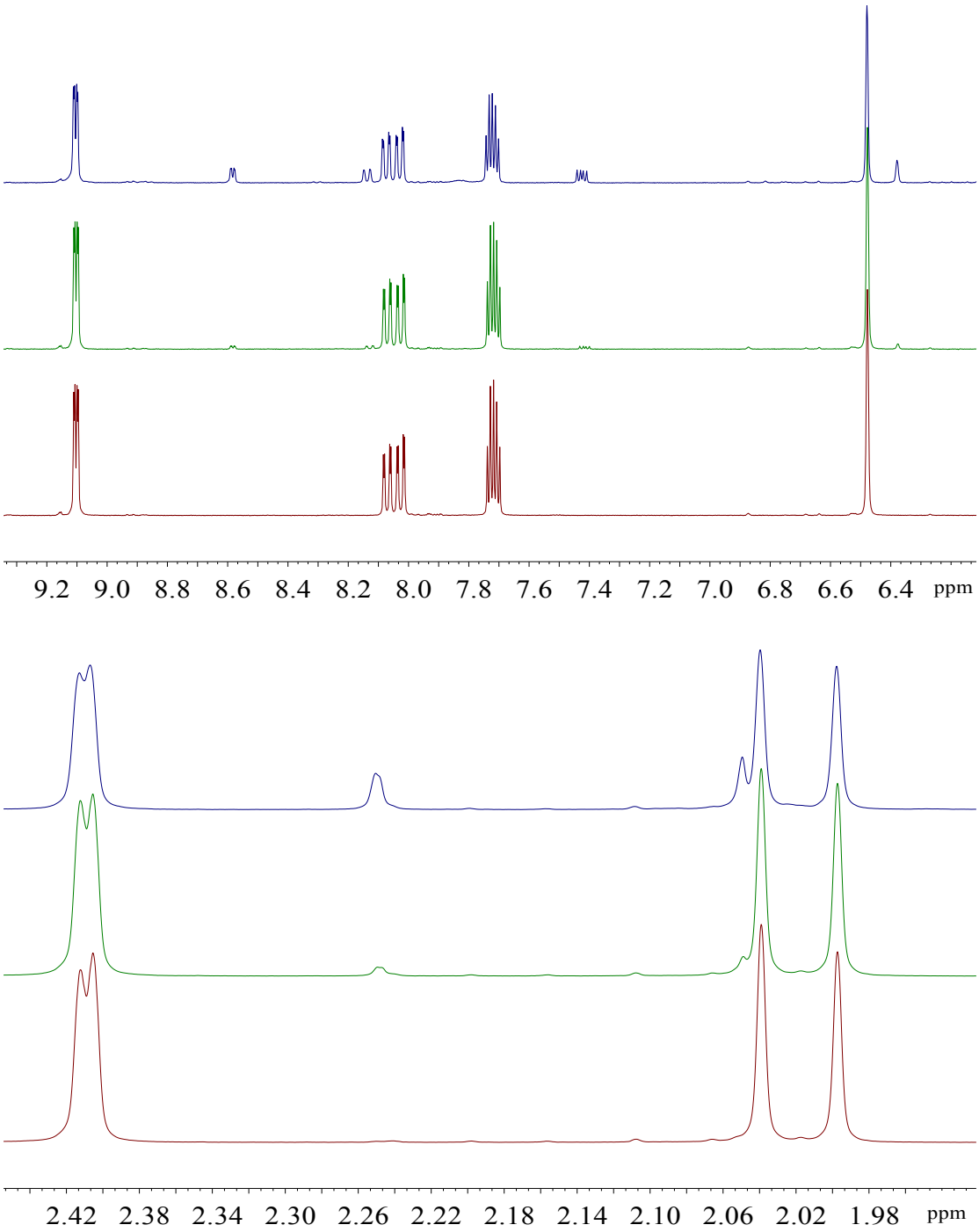


Figure S3. ^{1}H NMR spectral changes of the ligand $\mathbf{L_o}$ upon UV light irradiation. ^{1}H NMR (400 MHz, CD3OD, 298 K): δ 1.978 (s, 3H, anti-parallel conformation), 2.020 (s, 3H, parallel conformation), 2.386 (s, 3H, anti-parallel conformation), 2.393 (s, 3H, parallel conformation), 6.459 (s, 2H), 7.699 (s, 2H), 8.029 (m, 2H), 9.084 (m, 2H). The new peaks are assigned to the closed form.

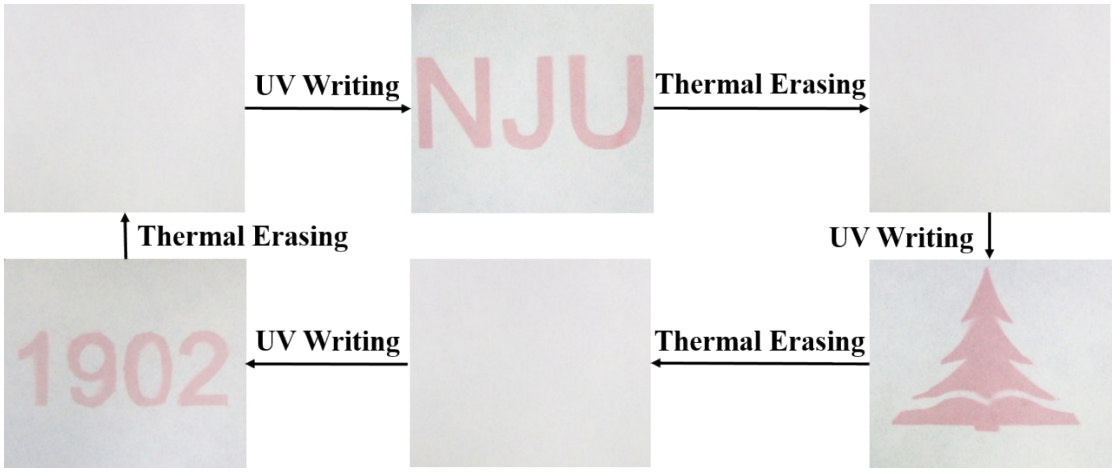


Figure S4. Photographs of rewritable paper with several cycles of writing-erasing process.

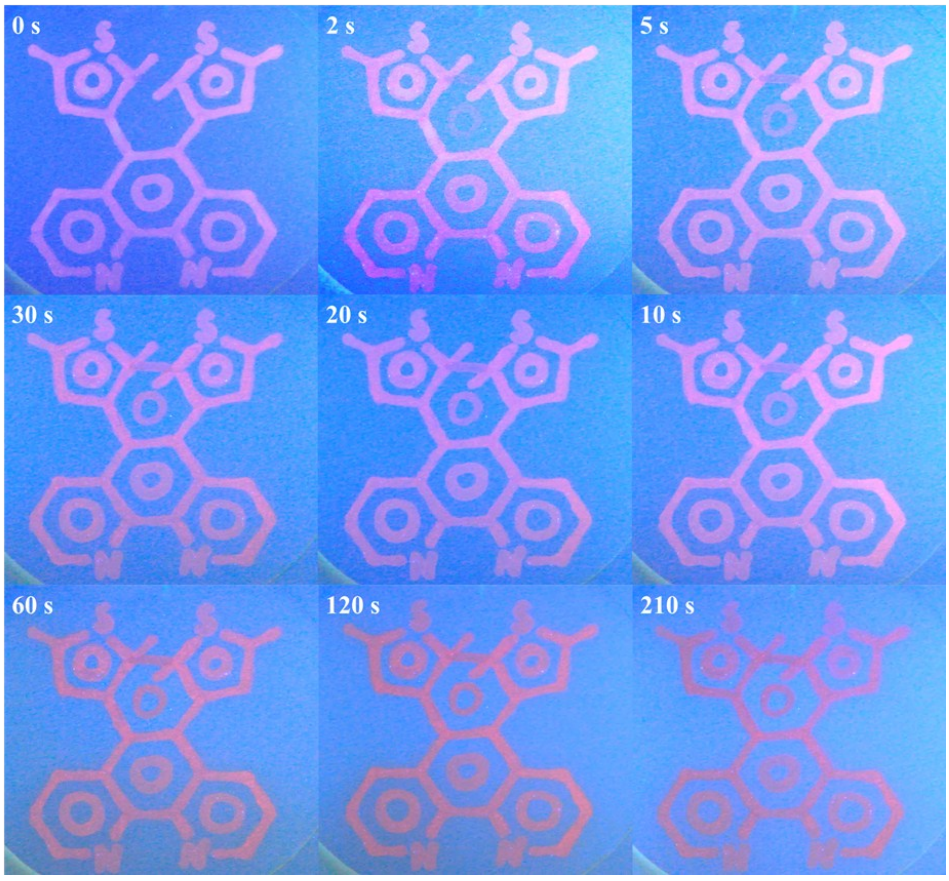


Figure S5. Photographs of information decryption with UV light irradiation.