Supporting Information

Influence of Halide Ions on Chirality and Luminescent Property of Ionothermally Synthesized Lanthanide-based Metal-organic Frameworks

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Supporting information, S1

Materials and methods

All reagents used were commercially available and were used as received. The infrared spectra were recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curves were prepared on a SDT Q600 Thermal Analyzer. Elemental analyses (C, H and N) were performed using a Vario EL III analyzer. The solid-state circular dichroism spectra was taken by Circular Dichroism (CD) Spectrometer J-810 with pressed KCl pellets (simple:KCl=1:299). Solid‑state ultraviolet spectra were collected by Varian Cary 5000 with transmission and diffuse reflection modes. Solid‑state fluorescence spectra were recorded on Fluoromax-4 spectrofluorometer and photoluminescence efficiencies were calculated by HORIBA Jobin Yvon quantum yield and colour calculator. X-ray photoelectron spectroscopy were prepared on PHI Quantum-2000 XPS. All material were market sales analytical pure reagent used directly without purification. H_2O was deionized water.

Preparation of **1** to **4**:

1 and **2**: $LnCl_3 \cdot 6H_2O$ (0.5 mmol) , thiophene-2,5-dicarboxylic acid (0.173 g, 1 mmol), 1-methyl-3-ethylimidazolium bromide (0.955 g, 5 mmol) and H_2O (2.2 mmol, 0.04 g) were put into a 25 mL Teflon-lined Parr and heated to 170 °C for 4320 minutes, then cooled to room temperature at a rate of 1 °C/20min. Purple crystals of **1** were obtained in 54% yield based on $NdCl_3$. Anal. Calcd. for $C_{18}H_{15}Br_{0.50}ClN_2Nd_{1.50}O_8S_2$ (**1**): C, 29.07; H, 2.02; N, 3.77 (Found: C, 28.89; H, 2.16; N, 3.50;). IR Spectra for **1** (KBr, cm^{-1}): 3433(m), 3092(w), 1589(s), 1554(s), 1376(s), 1290(m), 1165(w), 1132(w), 1028(w), 930(w), 812(w), 769(m), 718(m), 622(w), 443(w). Yellow crystals of **2** were obtained in yield 31.5% based on $EuCl_3$. Anal. Calcd. for $C_{18}H_{15}Br_{0.25}Cl_{1.25}Eu_{1.50}N_2O_8S_2$ (**2**): C, 29.05; H, 2.02; N, 3.77 (Found: C, 28.92; H, 1.88; N, 3.49;). IR Spectra for **2** (KBr, cm^{-1}): 3434(w), 3098(w) 1564(w), 1537(s), 1554(s), 1381(s), 1168(m), 1022(w), 821(w), 772(m), 681(m), 646 (w), 619(w), 587(w), 464(s).

3 and **4**: Ln_2O_3 (0.25 mmol), thiophene-2,5-dicarboxylic acid (0.173 g, 1 mmol), 1-methyl-3-ethylimidazolium bromide (0.955 g, 5 mmol) and H_2O (2.2 mmol, 0.04 g) were put into a 25 mL Teflon-lined Parr and heated to 170 °C for 4320 minutes, then cooled to room temperature at a rate of 1 °C/20min. Purple crystals of **3** were obtained in 62% yield based on Nd_2O_3. Anal. Calcd. for $C_8H_{15}N_2NdO_8S_2$, (**3**): C, 36.26; H, 2.52; N, 4.70 (Found: C, 36.15; H, 2.27; N, 4.33;). IR Spectra for **3** (KBr, cm^{-1}): 3439(w), 3139(w), 3111(w), 3069(w), 1619(s), 1554(s), 1527(s), 1385 (s), 1163(m), 1121(w), 1022(w), 855(w), 822(m), 841(m), 728(s), 776(s), 750(m), 679(m), 650(w), 623(w), 536(w), 457(m). Yellow crystals of **4** were obtained in yield 31% based on Eu_2O_3. Anal. Calcd. for $C_8H_{15}N_2EuO_8S_2$, (**4**): C, 35.80; H, 2.49; N, 4.63 (Found: C, 35.75; H, 2.29; N, 4.82;). IR Spectra for **4** (KBr, cm^{-1}): 3434(w), 3098(w) 1564(w), 1537(s), 1554(s), 1381(s), 1168(m), 1022(w), 821(w), 772(m), 681(m), 646 (w), 619(w), 587(w), 464(s).

Supporting information, S2

Crystal data for **1**: $C_{18}H_{15}Br_{0.50}ClN_2Nd_{1.50}O_8S_2$, $M = 743.21$, orthorhombic, $a = 16.3890(3)$ Å, $b = 12.0113(2)$ Å, $c = 12.2966(2)$ Å, $V = 2420.63(7)$ Å^3, $T = 173(2)$ K, space group $P2_12_12$, $Z = 4$, $\rho_{calcd} = 2.039$ g·cm^{-3}. Of the 6424 reflections meassured, 4411 are unique ($R_{int} = 0.0211$) and 4114 are observed ($I > 2\sigma(I)$). On the basis of all these data and 318 refined parameters, R_1 R_1(obs.) = 0.0196, wR_2 (all data) = 0.0384 and Flack = 0.026(2) were obtained. The 8 H atoms associated with the mutual disorder of the ethyl and methyl C atoms were refined as follows: C14: This has two unit-occupancy H atoms H14A and H14B and one half-occupancy H atom H14C (which lies along the C14–C17 bond); C18: This two unit-occupancy H atoms H18A and H18B and one half-occupancy H atom H18C (which lies along the C18–C20 bond); C17 and C20: These have a half-occupancy and should each have three half-occupancy H atoms.

Crystal data for **2**: $C_{18}H_{15}Br_{0.25}Cl_{1.25}Eu_{1.50}N_2O_8S_2$, $M = 743.67$, orthorhombic, $a = 16.2850(5)$ Å, $b = 11.9314(3)$ Å, $c = 12.2099(4)$ Å, $V = 2372.42(12)$ Å^3, $T = 173(2)$ K, space group $P2_12_12$, $Z = 4$, $\rho_{calcd} = 2.082$ g·cm^{-3}. Of the 7680 reflections measured, 4506 are unique ($R_{int} = 0.0577$) and 4027 are observed ($I > 2\sigma(I)$). On the basis of all these data and 318 refined parameters, R_1(obs.) = 0.0469, wR_2 (all data) = 0.0838 and Flack = -0.01(2) were obtained. There are 32 restraints in the refinement of **2**, which is generated by using the instruction of ISOR 0.02 for the O8, C2, C5, C7 and C10 atoms in the organic ligand. If the instruction was not used, the refinement of **2** would result in these atoms non-positive definition. There is the highest residual peak (1.43), locating at about 1.09 Å around Eu atom in **2**. The 8 H atoms associated with the mutual disorder of the ethyl and methyl C atoms were refined as follows: C14: This has two unit-occupancy H atoms H14A and H14B and one half-occupancy H atom H14C (which lies along the C14–C17 bond); C18: This ha two unit-occupancy H atoms H18A and H18B and one half-occupancy H atom H18C (which lies along the C18–C20 bond); C17 and C20: These have a half-occupancy and should each have three half-occupancy H atoms.

Crystal data for **3**: $C_8H_{15}N_2NdO_8S_2$, $M = 595.68$, monoclinic, $a = 11.7380(4)$ Å, $b = 16.5818(4)$ Å, $c = 11.5785(4)$ Å, $\beta = 113.5(4)°$, $V = 2066.47(11)$ Å^3, $T = 173(2)$ K, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 1.915$ g·cm^{-3}. Of the 9618 reflections measured,

3630 are unique (R_{int} = 0.0450) and 3123 are observed ($I > 2\sigma(I)$). On the basis of all these data and 280 refined parameters, R_1(obs.) = 0.0335 and wR_2 (all data) = 0.1178 were obtained.

Crystal data for **4**: $C_8H_{15}N_2EuO_8S_2$, M = 603.40, monoclinic, a = 11.7636(3) Å, b = 16.3609(3) Å, c = 11.5890(3)) Å, β = 113.314(3)°, V = 2048.34(8) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, ρ_{calcd} = 1.957 g·cm^{-3}. Of the 9266 reflections measured, 3598 are unique (R_{int} = 0.0397) and 3204 are observed ($I > 2\sigma(I)$). On the basis of all these data and 280 refined parameters, R_1(obs.) = 0.0270, wR_2 (all data) = 0.0949 were obtained.

Supporting information, S3

Photoluninescence quantum yield
Theory
The sample is placed in the integrating sphere, and excited with a monochromatic source of wavelength λ. The file absorbance, A, is

$$A = \frac{L_b - L_c}{L_b}$$

where L_b is the integrated excitation profile when the sample is diffusely illuminated by the integrating sphere's surface; and Lc is the integrated excitation profile when the sample is directly excited by the incident beam.
The quantum yield Φ_f, is by definition, photons emitted to photons absorbed:

$$\Phi_f = \frac{E_c - (1-A) \cdot E_b}{L_a \cdot A} = \frac{E_c - E_a}{L_a - L_c}$$

Where E_c is the integrated luminescence of the film caused by direct excitation, and E_b is the integrated luminescence of the film caused by direct excitation, and E_b is the integrated luminescence of the film caused by indirect illumination from the sphere. The term L_a is the integrated excitation profile from an empty integrating sphere (without the sample, only a bank). Here E_a is the integrated luminescence from an empty integrating sphere (only a blank)

The luminescence decay curves of complex **2**, **4** and [(Eu$_2$(TDC)$_3$(CH$_3$OH)$_2$·(CH$_3$OH)] (Figures S10, S11 and S12) which were obtained from time-resolved luminescence experiments could fit to a monoexponential function.

$$y = A_1 * exp(-x/t_1) + y_0$$

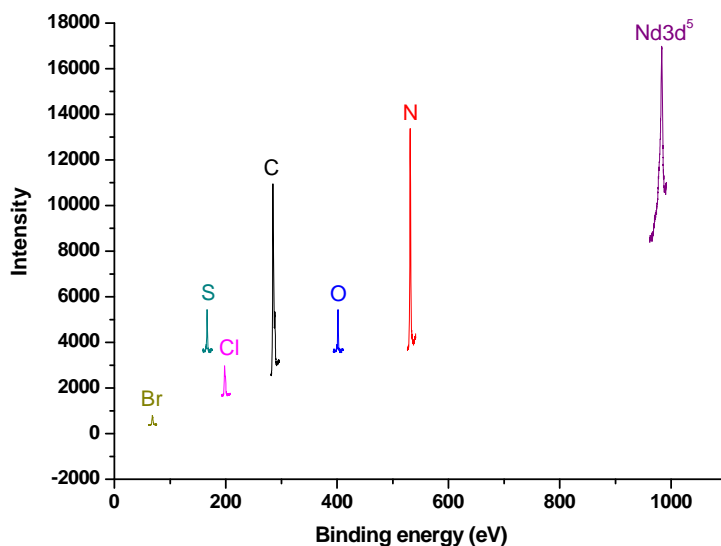where A is the pre-exponential factor obtained from the curve fitting, and t stands for the lifetimes.

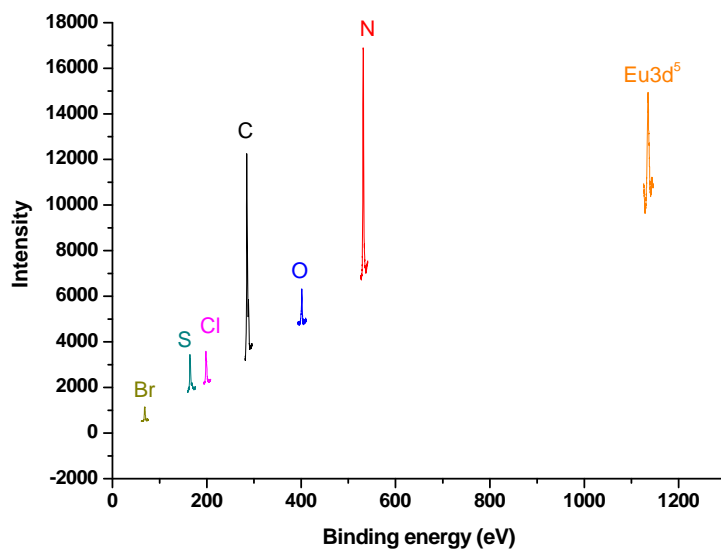**Fig. S1** The X-ray photoelectron spectroscopy spectrum for **1**.

Fig. S2 The X-ray photoelectron spectroscopy spectrum for **2**.
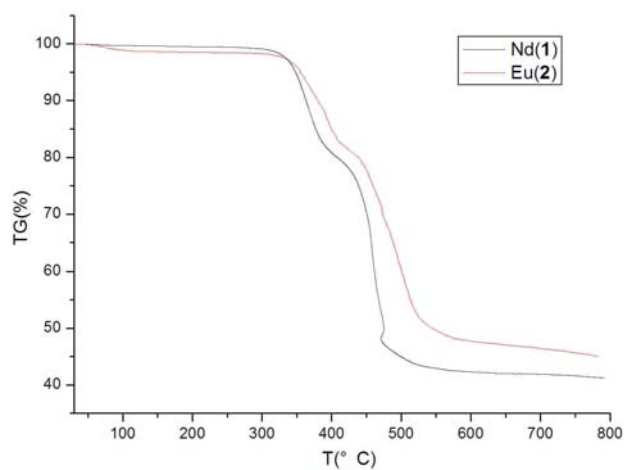
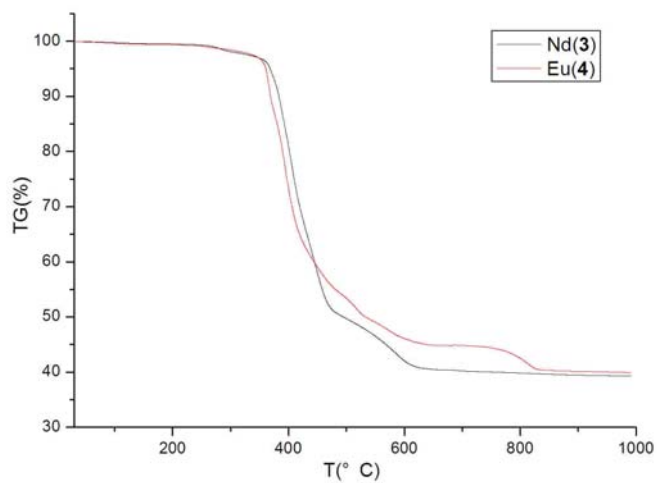**Fig. S3** TG curves for complexes **1** and **2**.

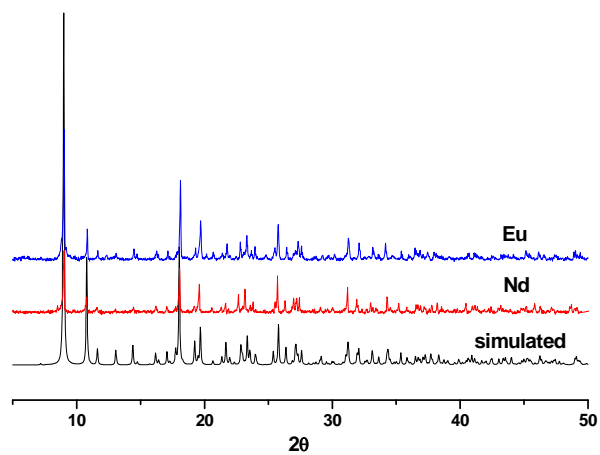**Fig. S4** TG curves for complexes **3** and **4**.

Fig. S5 The simulated (black) and actual (red) powder X-ray patterns for **1** and actual (blue) powder X-ray patterns **2**.
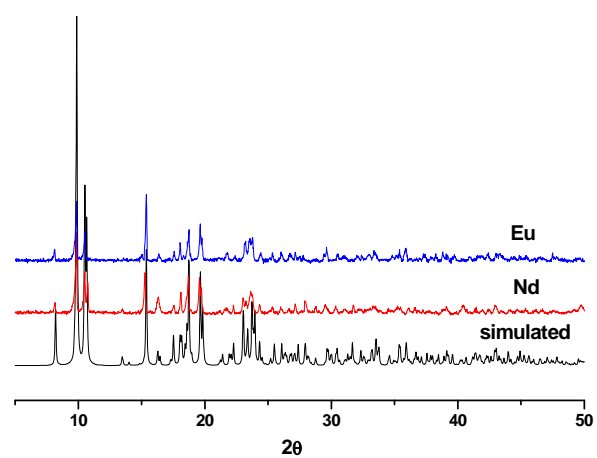

Fig. S6 The simulated (black) and actual (red) powder X-ray patterns for **3** and the actual powder X-ray patterns for **4** (blue).
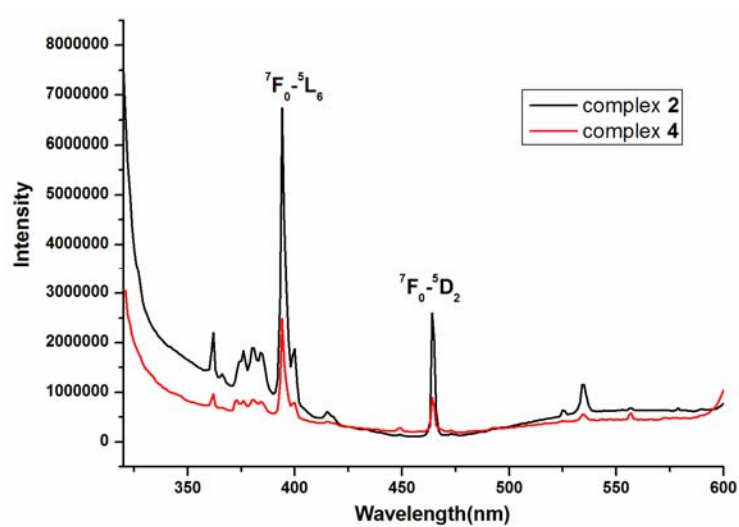

Fig. S7 Room-temperature excitation with emission monitored at approximately 610 nm for compound **2, 4** (excitation slit is 1.0 nm and emission slit 1.0 nm) in the solid state.
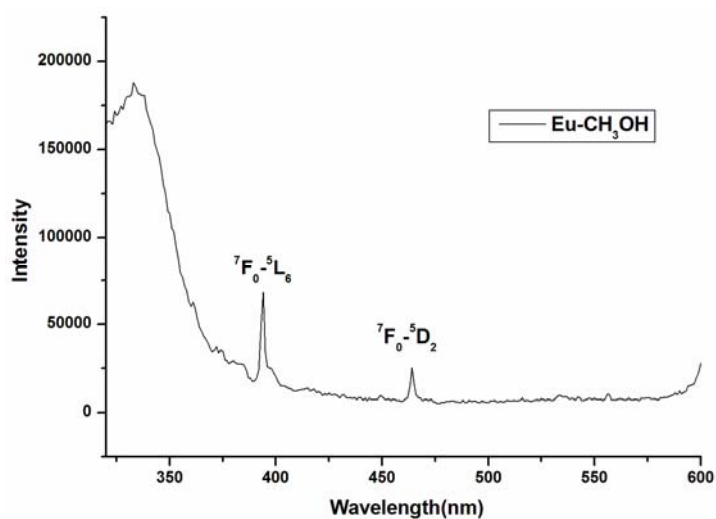
Fig. S8 Room-temperature excitation with emission monitored at approximately 610 nm for the [(Eu$_2$(TDC)$_3$(CH$_3$OH)$_2$·(CH$_3$OH)] (excitation slit is 1.0 nm and emission slit 1.0 nm) in the solid state.
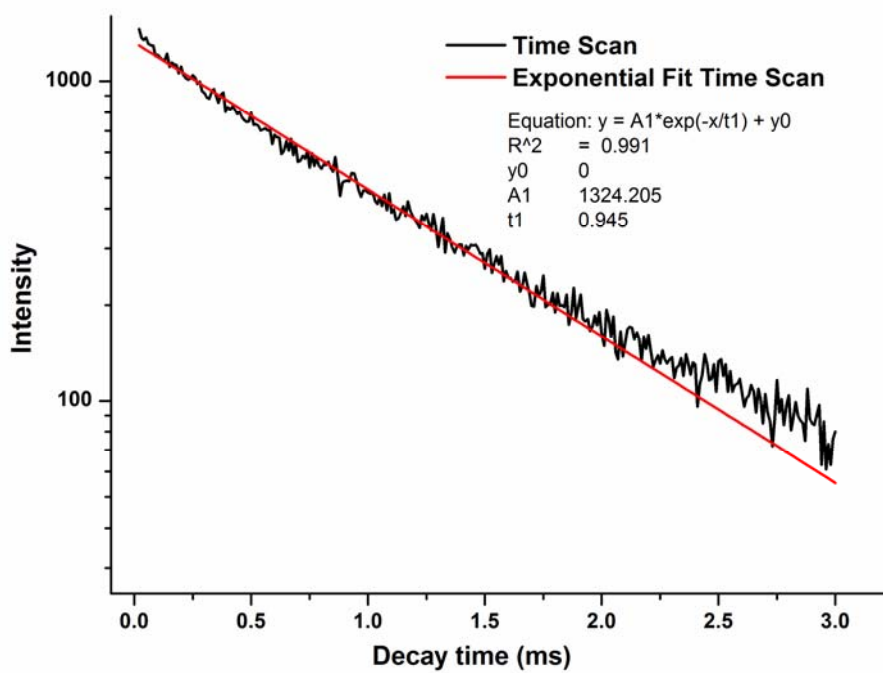

Fig. S9 Luminescence decay curve excitation at 395 nm of the complex **2** (excitation slit is 2 nm and emission slit 2 nm).
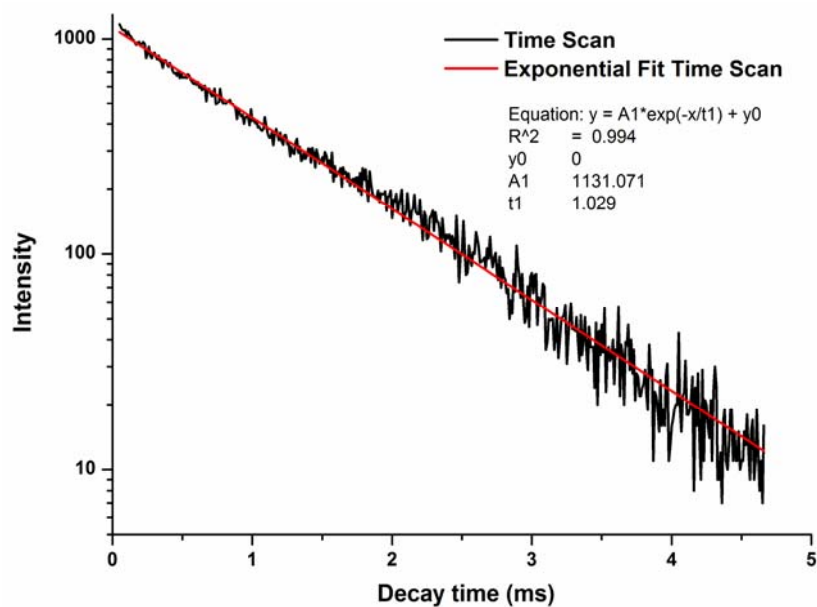
Fig. S10 Luminescence decay curve excitation at 395 nm of the complex **4** (excitation slit is 1.4 nm and emission slit 1.4 nm).
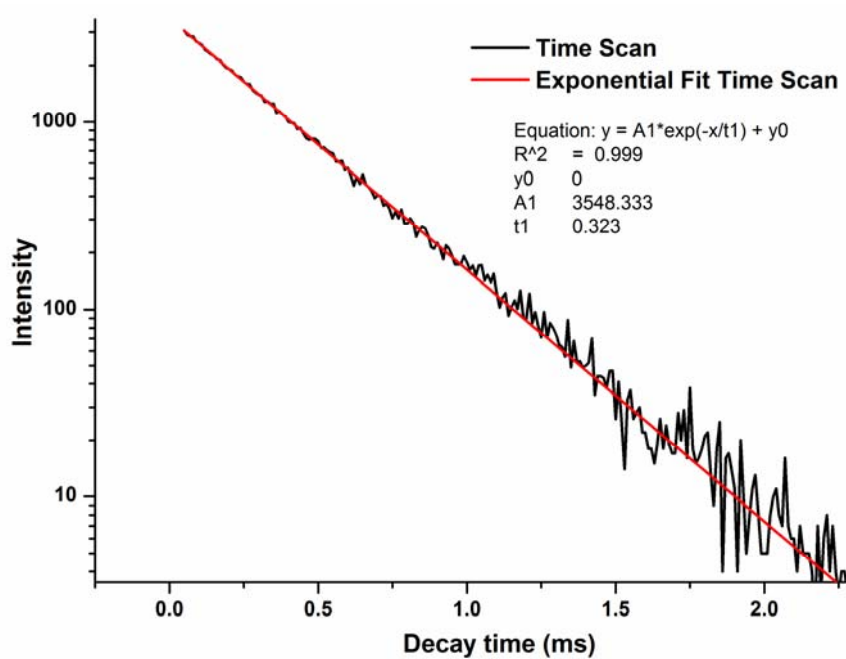

Fig. S11 Luminescence decay curve excitation at 395 nm of the compound [(Eu$_2$(TDC)$_3$(CH$_3$OH)$_2$·(CH$_3$OH)](excitation slit is 3 nm and emission slit 3 nm).
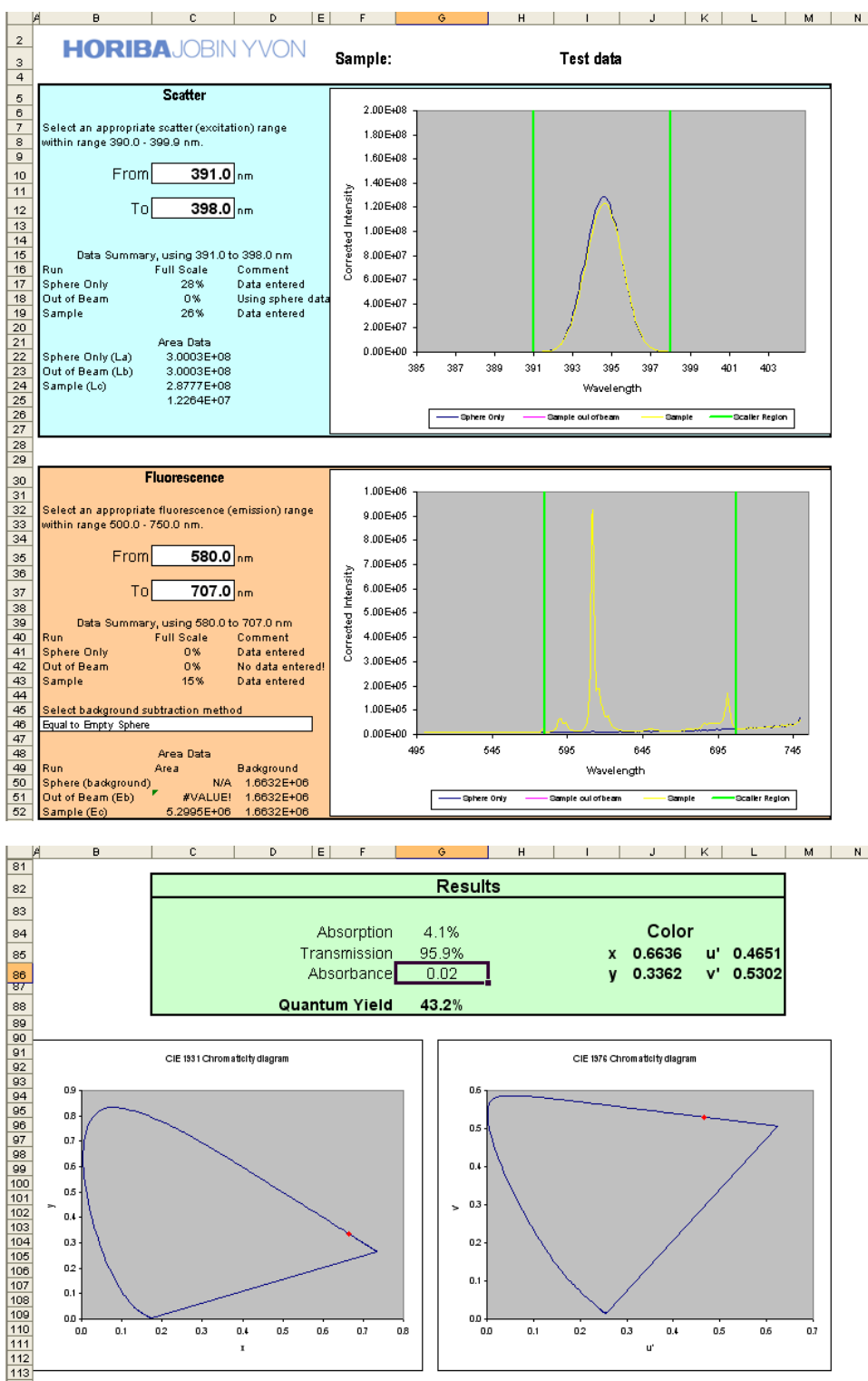
Fig. S14 Figures showing the quantum yield for **4** measured with excitation slits width:1.4 nm and emission slits width: 1.4 nm
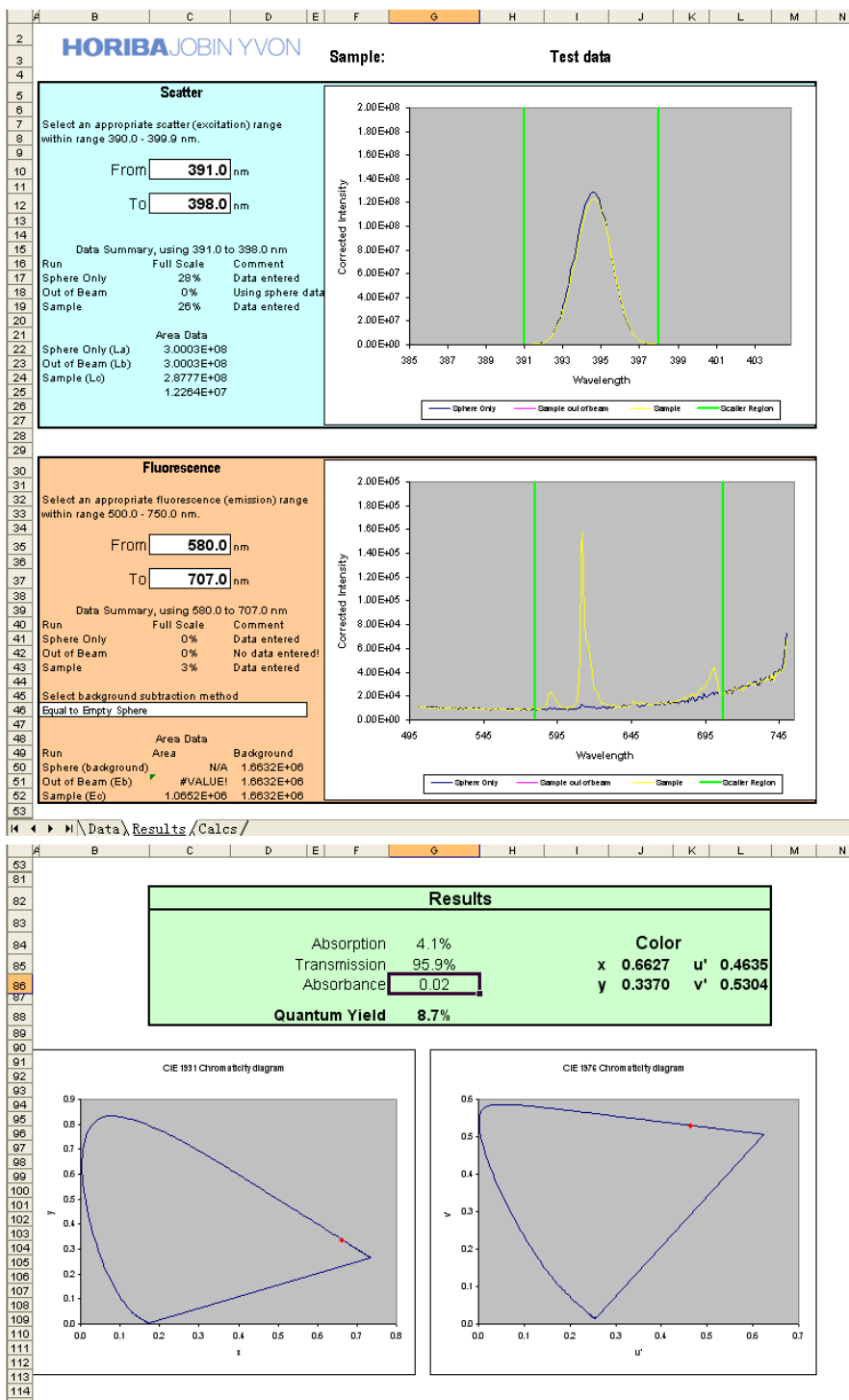
Fig. 15. Figures showing the quantum yield for **2** measured with excitation slits width:1.4 nm and emission slits width: 1.4 nm