

Electronic Supplementary Information for
Light-controlled efficient photoluminescence based on an europium β -diketonate with single-crystal-to-single-crystal [2+2] cycloaddition

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Experimental Section

X-ray crystallography. The X-ray measurements of complexes were carried out on Bruker Smart CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by using an ω scan mode at 296 K. The diffraction data were treated using SAINT,¹ and all absorption corrections were applied by using SADABS.² All non-hydrogen atoms were located by Patterson's method³ using the SHELXS programs of the SHELXTL package and by subsequent difference Fourier syntheses. The Hydrogen bonded to carbon were determined theoretically and refined with isotropic thermal parameters riding on their parents. H-atoms of methanol were first located by difference Fourier E-maps and then treated isotopically as riding. All non-hydrogen atoms were refined by a full-matrix least-squares technique based on F^2 . All calculations were performed by SHELXTL-2014.⁴

Analysis, spectroscopy and photophysics. Elemental analyses of C, H and N were measured by a PerkinElmer 240C elemental analyzer. Raman spectroscopy was recorded on LabRAM Aramis (HORIBA). Images of complexes **1** and **1a** were captured using an Olympus IX73 inverted fluorescence microscope and a confocal laser-scanning fluorescence microscope, LEICA TCS SP8 X. The fluorescence data were collected on a FluoroMax-4 spectrofluorometer (Horiba Scientific). The UV-vis absorption spectra were recorded on UV-3600 (SHIMADZU). The quantum yields and lifetimes were measured by Fluorolog (HORIBA). NMR spectra were taken on 400 MHz Bruker spectrometer with 400 MHz for ¹H NMR reported as parts per million (ppm) from the internal standard TMS. Thermogravimetric analyses (TGA) was measured from 30 to 600 °C on a NETZSCH STA 449F3 analyzer at a

heating rate 5 °C/min under N₂ atmosphere. The differential scanning calorimetry (DSC) was performed on DSC 823^e (METTLER TOLEDO).

Materials. All the commercially available chemicals are used without further purification. 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (97%, Energy Chemical), 1,2-bis(4-pyridyl)ethylene (98%+, Adamas), lanthanide chloride hexahydrate (EuCl₃·6H₂O and GdCl₃·6H₂O, 99.9%, Aladdin Co.) were purchased.

Synthesis of [Eu(tfnb)₃(bpe)(MeOH)] (1). The synthesis of complex **1** are similar to Carlos's work with some modifications.⁵ The precursor Eu(tfnb)₃·2H₂O (**P1**) was prepared as follows: 9 mmol of tfnb was dissolved in 30 mL ethanol, then 9 mmol KOH was added followed by adding EuCl₃·6H₂O. The mixed solution was stirred overnight and then the formed precipitate was filtered. Water was added to the filtrate to yield a pale yellow precipitate. This was filtered, washed with water and dried under vacuum. To obtain complex **1** 0.1 mmol **P1** was dissolved in 10 mL methanol, then 0.1 mmol bpe was added under gentle stirring. Crystals were obtained overnight by slow evaporation with a yield of 85%. Elemental analysis calcd (%) for C₅₅H₃₈EuF₉N₂O₇: C 56.81, N 2.410, H 3.271, found (%): C 56.37, N 2.387, H 3.486.

Synthesis of [Eu(tfnb)₃(MeOH)]₂(tpcb) (1a, tpcb = tetrakis(4-pyridyl)cyclobutane). Crystals of **1a** were obtained through the exposure of **1** under UV irradiation for 12 h using a high-pressure mercury lamp (λ = 360 nm). Elemental analysis calcd (%) for C₁₁₀H₇₆Eu₂F₁₈N₄O₁₄: C 56.81, N 2.410, H 3.271, found (%): C 55.95, N 2.422, H 3.686.

Synthesis of [Gd(tfnb)₃(bpe)(MeOH)] (2). The precursor Gd(tfnb)₃·2H₂O was synthesized as above except that EuCl₃·6H₂O was replaced with GdCl₃·6H₂O. Crystals of complex **2** were obtained through a similar way as **1** except that **P2** was used instead of **P1**. Elemental analysis calcd (%) for C₅₅H₃₈F₉GdN₂O₇: C 56.55, N 2.399, H 3.256, found (%): C 56.43, N 2.384, H 3.359.

Synthesis of [Gd(tfnb)₃(MeOH)]₂(tpcb) (2a). The way to obtain **2a** is similar to that of **1a**. Yellow crystals of **2a** were obtained by irradiating crystals of **2** under high-pressure mercury lamp (λ = 360 nm) for 12 h. Elemental analysis calcd (%) for C₁₁₀H₇₆F₁₈Gd₂N₄O₁₄: C 56.55, N 2.399, H 3.256, found (%): C 56.20, N 2.405, H 3.534.

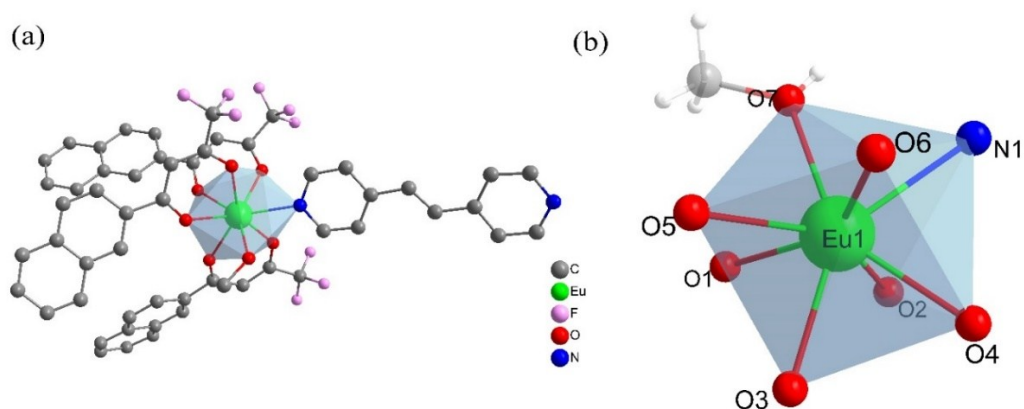


Fig. S1. (a) Mixed ball-and-stick and polyhedral representation of the molecular unit of complex **1**. (b) Detailed view of the distorted square antiprismatic coordination environment of the crystallographic independent Eu^{3+} center in complex **1**.

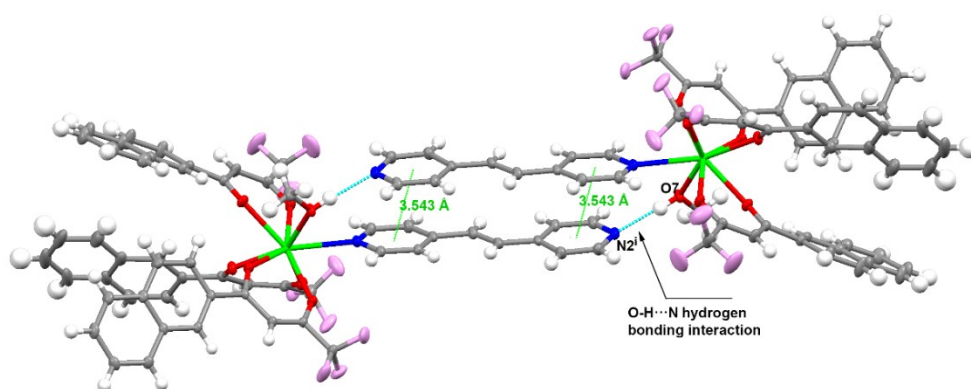
Table S1. Crystal data for complexes **1** and **1a**.

	1	1a
formula	$\text{C}_{55}\text{H}_{38}\text{EuF}_9\text{N}_2\text{O}_7$	$\text{C}_{110}\text{H}_{76}\text{Eu}_2\text{F}_{18}\text{N}_4\text{O}_{14}$
M_r	1161.83	2323.66
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.1610(13)	13.1434(11)
b (Å)	15.4629(15)	15.3452(13)
c (Å)	24.040(2)	23.763(2)
α (°)	90.00	90.00
β (°)	98.0640(10)	97.7680(10)
γ (°)	90.00	90.00
V (Å ³)	4843.8(8)	4748.8(7)
T (K)	296(2)	296(2)
Z	4	2
ρ_{calcd} (g cm ⁻³)	1.593	1.625
λ (Å)	0.71073	0.71073
number of ind. reflns	11270	8323
number of reflns with $I > 2\sigma(I)$	9961	7456
number of parameters	672	672
final R_1 , ωR_2 with $[I > 2\sigma(I)]$	0.0248, 0.0581	0.0359, 0.0882
R_1 , ωR_2 all data	0.0298, 0.0603	0.0408, 0.0915
goodness of fit, GOF	1.044	1.041
CCDC	1937946	1937947

$$R_1^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, \quad \omega R_2^b = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Eu1-O1	2.3822(13)	Eu1-O2	2.3629(15)
Eu1-O3	2.3755(13)	Eu1-O4	2.3933(13)
Eu1-O5	2.3758(14)	Eu1-O6	2.3730(13)
Eu1-O7	2.4283(14)	Eu1-N1	2.6003(16)
O1-Eu1-O2	70.67(5)	O1-Eu1-O3	73.73(5)
O1-Eu1-O4	131.69(5)	O1-Eu1-O5	72.88(5)
O1-Eu1-O6	142.61(5)	O1-Eu1-O7	73.72(5)
O2-Eu1-O3	85.28(5)	O2-Eu1-O4	74.94(5)
O2-Eu1-O5	142.34(5)	O2-Eu1-O6	146.48(5)
O2-Eu1-O7	98.07(5)	O3-Eu1-O4	70.55(5)
O3-Eu1-O5	75.72(5)	O3-Eu1-O6	105.54(5)
O3-Eu1-O7	144.00(5)	O4-Eu1-O5	125.96(5)
O4-Eu1-O6	78.98(5)	O4-Eu1-O7	145.02(5)
O5-Eu1-O6	70.90(5)	O5-Eu1-O7	80.40(5)
O6-Eu1-O7	91.33(5)	N1-Eu1-O1	127.91(5)
N1-Eu1-O2	76.84(5)	N1-Eu1-O3	142.63(5)
N1-Eu1-O4	73.20(5)	N1-Eu1-O5	135.59(5)
N1-Eu1-O6	75.72(5)	N1-Eu1-O7	71.84(5)

**Fig. S2.** Illustration of the O-H \cdots N hydrogen bonds (connecting bpe units to methanol molecules) and π - π contacts between the adjacent pyridyl groups in the crystal structure of complex **1**. Details on the represented hydrogen bonds are listed in Table S3.**Table S3.** Represented hydrogen bonding interactions in complex **1**. Distances are given in Å and interaction angles in degrees.

D-H \cdots A	d (D-H)	d (H \cdots A)	\angle (DHA)	d (D \cdots A)
O7-H7 \cdots N2 ⁱ	0.771	1.965	170.73	2.728

(i) Symmetry transformation used to generate equivalent atoms: 1-x, 2-y, 1-z

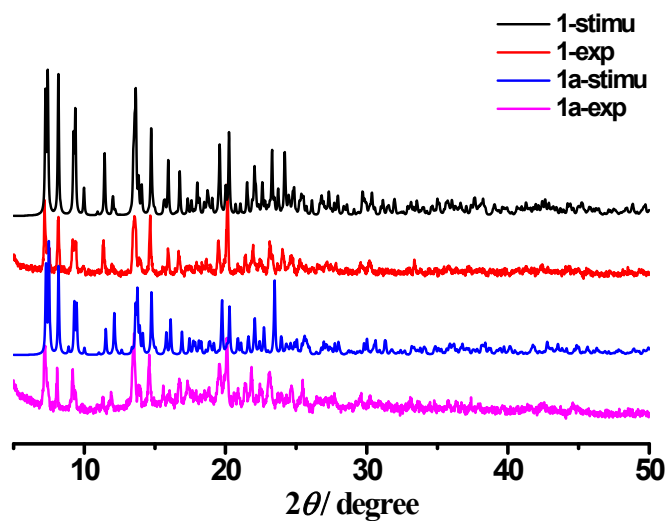


Fig. S3. X-ray powder diffraction of **1** and **1a**.

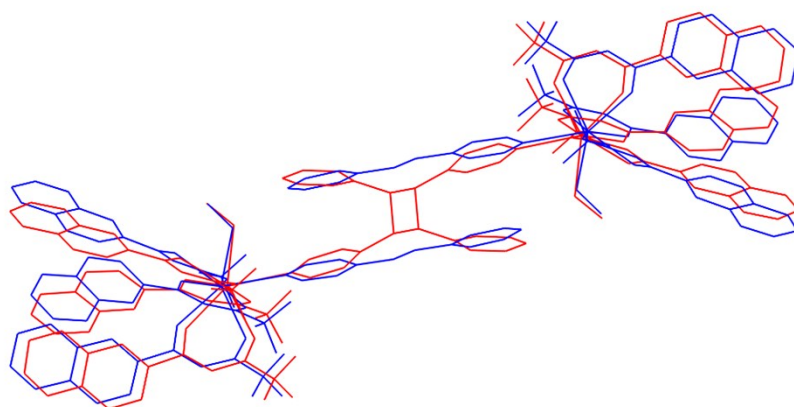


Fig. S4. Superimposition of the molecules in **1** (blue) and **1a** (red) which shows the [2+2] cycloaddition process.

Table S4. Selected bond lengths (Å) and angles (°) for **1a**.

Eu1-O1	2.387(3)	Eu1-O2	2.359(3)
Eu1-O3	2.366(3)	Eu1-O4	2.400(3)
Eu1-O5	2.385(3)	Eu1-O6	2.362(2)
Eu1-O7	2.451(3)	Eu1-N1	2.606(3)
O1-Eu1-O2	70.60(9)	O1-Eu1-O3	73.64(10)
O1-Eu1-O4	129.51(9)	O1-Eu1-O5	73.43(9)
O1-Eu1-O6	143.44(9)	O1-Eu1-O7	73.44(10)
O2-Eu1-O3	87.33(10)	O2-Eu1-O4	73.80(10)
O2-Eu1-O5	142.85(9)	O2-Eu1-O6	145.81(9)
O2-Eu1-O7	97.88(10)	O3-Eu1-O4	70.04(9)
O3-Eu1-O5	73.85(10)	O3-Eu1-O6	103.72(10)

O3-Eu1-O7	142.69(10)	O4-Eu1-O5	125.67(9)
O4-Eu1-O6	79.75(9)	O4-Eu1-O7	146.85(9)
O5-Eu1-O6	70.98(9)	O5-Eu1-O7	80.35(10)
O6-Eu1-O7	92.50(10)	N1-Eu1-O1	129.53(9)
N1-Eu1-O2	77.64(9)	N1-Eu1-O3	143.24(10)
N1-Eu1-O4	73.58(9)	N1-Eu1-O5	134.95(9)
N1-Eu1-O6	74.35(9)	N1-Eu1-O7	73.29(9)

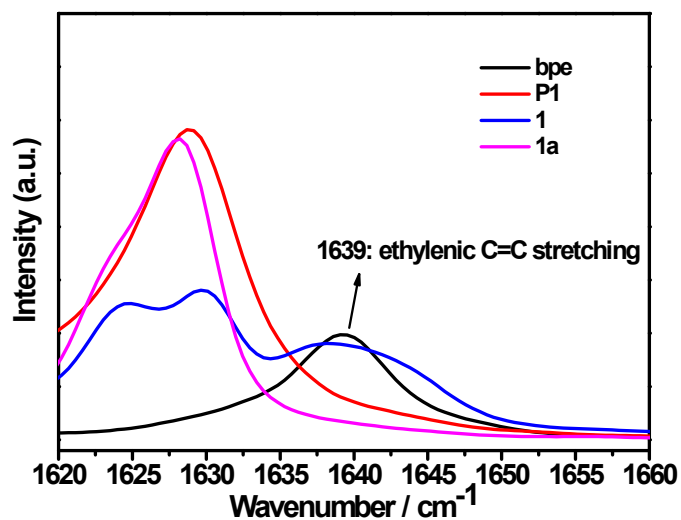


Fig. S5. Raman spectra of bpe, P1, 1 and 1a in solid state.

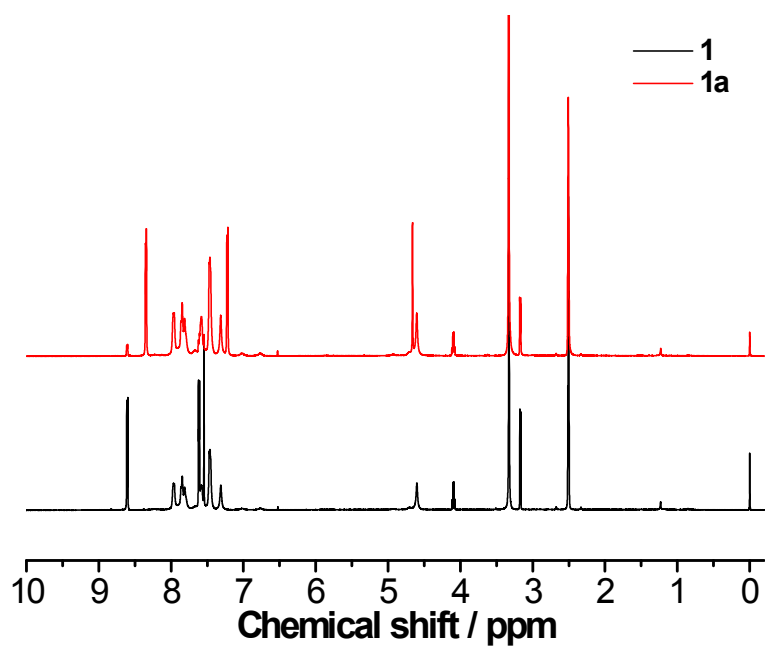


Fig. S6. ^1H NMR spectra of complex 1 and 1a in $\text{DMSO-}d_6$ solution (400 MHz).

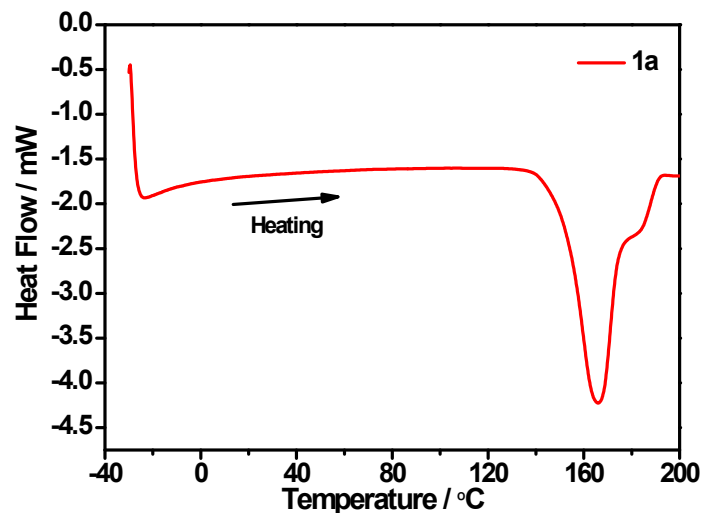


Fig. S7. DSC (heating process) curve of complex **1a**.

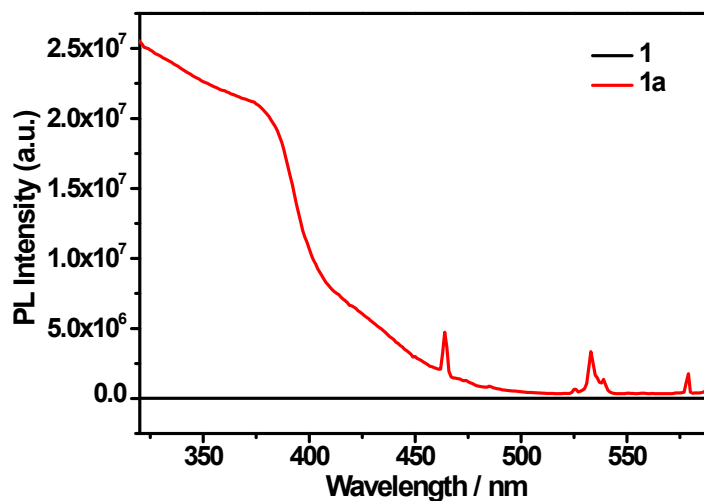


Fig. S8. Excitation spectra of complexes **1** and **1a** in solid state at room temperature ($\lambda_{\text{em}} = 612$ nm).

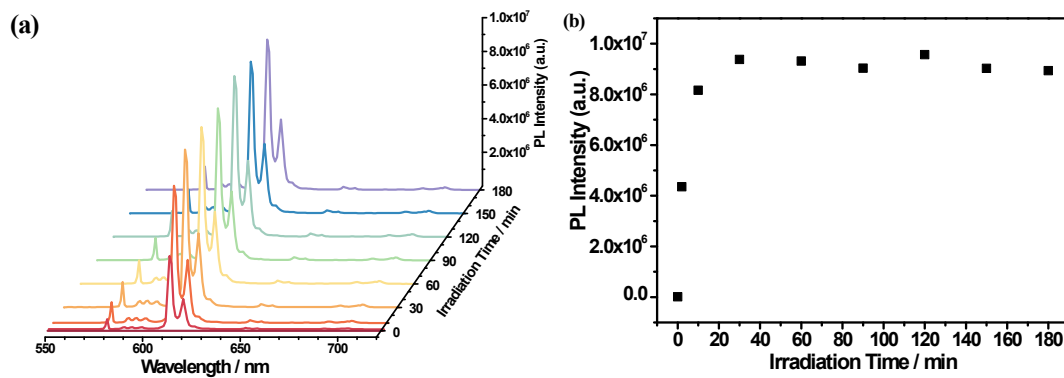


Fig. S9. (a) Emission spectra (300 K) of complex **1** ($\lambda_{\text{ex}} = 360$ nm) as function of irradiation time under high-pressure mercury lamp ($\lambda = 360$ nm). (b) The intensity at 612 nm variation with the irradiation.

Table S5. Crystal data for complexes **2** and **2a**.

	2	2a
formula	C ₅₅ H ₃₈ F ₉ GdN ₂ O ₇	C ₁₁₀ H ₇₆ F ₁₈ Gd ₂ N ₄ O ₁₄
<i>M_r</i>	1167.12	2334.24
crystal system	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	13.1610(13)	13.1434(11)
<i>b</i> (Å)	15.4629(15)	15.3452(13)
<i>c</i> (Å)	24.040(2)	23.763(2)
α (°)	90.00	90
β (°)	98.0640(10)	97.7680(10)
γ (°)	90.00	90
<i>V</i> (Å ³)	4843.8(8)	4748.8(7)
<i>T</i> (K)	296(2)	296(2)
<i>Z</i>	4	2
ρ_{calcd} (g cm ⁻³)	1.600	1.632
λ (Å)	0.71073	0.71073
number of ind. reflns	11209	10877
number of reflns with $I > 2\sigma(I)$	9756	8551
number of parameters	672	672
final $R_1, \omega R_2$ [$I > 2\sigma(I)$]	0.0246, 0.0504	0.0590, 0.1542
$R_1, \omega R_2$ all data	0.0322, 0.0528	0.0774, 0.1658
goodness of fit, GOF	1.029	1.026
CCDC	1937948	1937949

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

Table S6. Selected bond lengths (Å) and angles (°) for **2**.

Gd1-O1	2.3761(13)	Gd1-O2	2.3501(15)
Gd1-O3	2.3596(14)	Gd1-O4	2.3801(15)
Gd1-O5	2.3658(14)	Gd1-O6	2.3654(14)
Gd1-O7	2.4119(16)	Gd1-N1	2.5875(16)
O1-Gd1-O2	70.93(5)	O1-Gd1-O3	73.75(5)
O1-Gd1-O4	131.78(5)	O1-Gd1-O5	72.70(5)
O1-Gd1-O6	142.64(5)	O1-Gd1-O7	73.80(5)
O2-Gd1-O3	85.77(5)	O2-Gd1-O4	74.80(5)
O2-Gd1-O5	142.44(5)	O2-Gd1-O6	146.21(5)
O2-Gd1-O7	98.13(6)	O3-Gd1-O4	70.84(5)
O3-Gd1-O5	75.39(5)	O3-Gd1-O6	105.18(5)
O3-Gd1-O7	143.93(5)	O4-Gd1-O5	126.18(5)
O4-Gd1-O6	78.83(5)	O4-Gd1-O7	144.86(5)
O5-Gd1-O6	71.07(5)	O5-Gd1-O7	80.30(5)
O6-Gd1-O7	91.37(5)	N1-Gd1-O1	128.08(5)
N1-Gd1-O2	76.80(5)	N1-Gd1-O3	142.91(5)
N1-Gd1-O4	73.07(5)	N1-Gd1-O5	135.49(5)
N1-Gd1-O6	75.57(5)	N1-Gd1-O7	71.81(5)

Table S7. Selected bond lengths (Å) and angles (°) for **2a**.

Gd1-O1	2.385(3)	Gd1-O2	2.358(4)
Gd1-O3	2.347(4)	Gd1-O4	2.389(4)
Gd1-O5	2.381(4)	Gd1-O6	2.353(3)
Gd1-O7	2.439(4)	Gd1-N1	2.586(4)
O1-Gd1-O2	70.77(12)	O1-Gd1-O3	73.48(13)
O1-Gd1-O4	129.17(12)	O1-Gd1-O5	73.03(12)
O1-Gd1-O6	143.35(12)	O1-Gd1-O7	73.90(12)
O2-Gd1-O3	88.59(14)	O2-Gd1-O4	73.58(13)
O2-Gd1-O5	142.85(12)	O2-Gd1-O6	145.78(13)
O2-Gd1-O7	96.53(13)	O3-Gd1-O4	70.58(13)
O3-Gd1-O5	73.34(14)	O3-Gd1-O6	102.68(14)
O3-Gd1-O7	143.12(13)	O4-Gd1-O5	126.52(13)
O4-Gd1-O6	79.86(12)	O4-Gd1-O7	145.74(12)
O5-Gd1-O6	71.07(12)	O5-Gd1-O7	81.10(13)
O6-Gd1-O7	93.38(12)	N1-Gd1-O1	130.02(13)
N1-Gd1-O2	77.54(13)	N1-Gd1-O3	143.74(14)
N1-Gd1-O4	73.37(13)	N1-Gd1-O5	134.67(12)
N1-Gd1-O6	74.42(12)	N1-Gd1-O7	72.47(12)

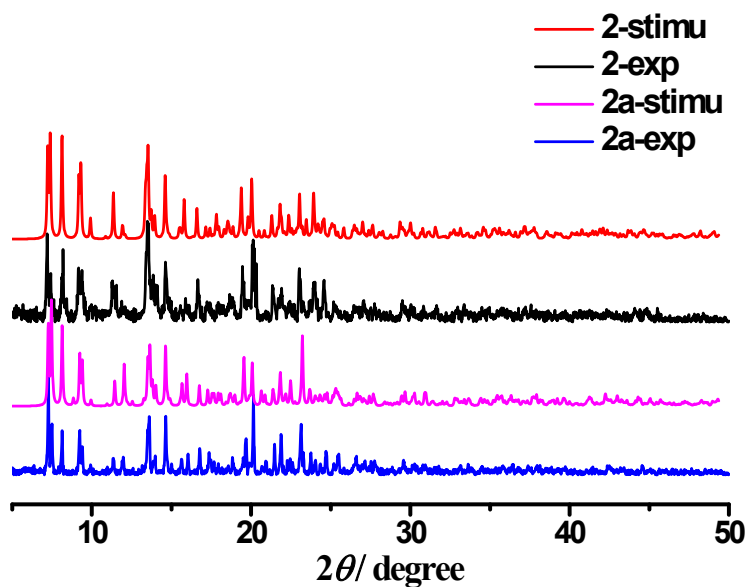


Fig. S10. X-ray powder diffraction of **2** and **2a**.

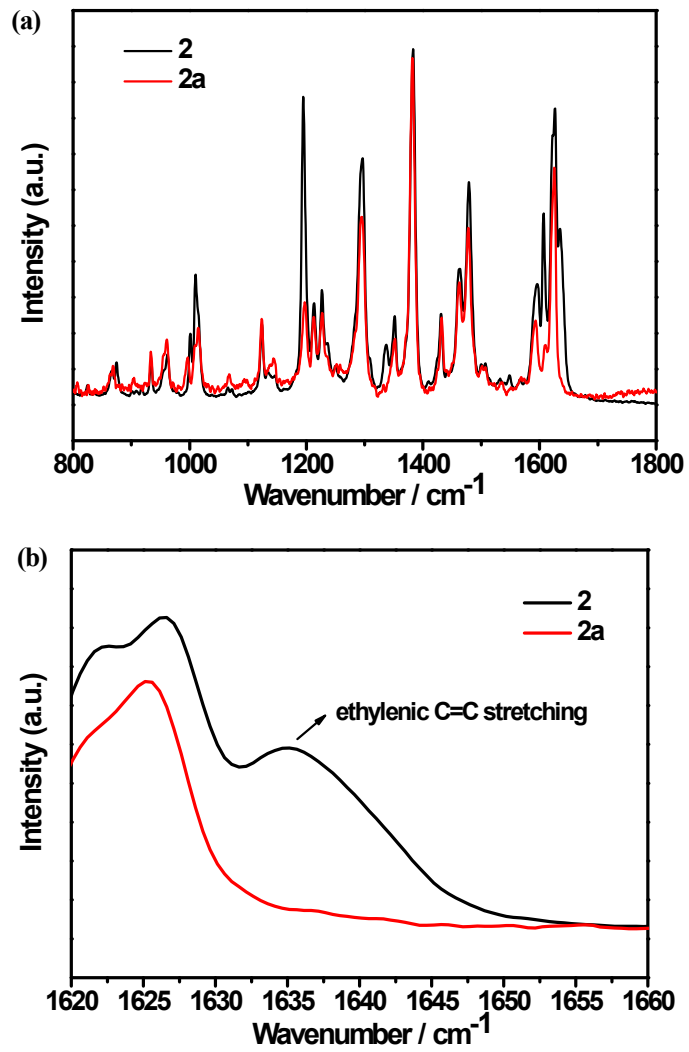


Fig.S11. Raman spectra of 2 and 2a in solid state.

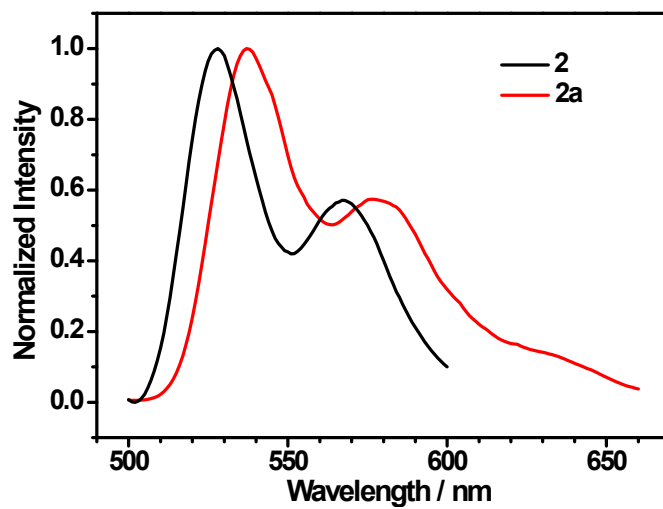


Fig. S12. Emission spectra (77 K) of polycrystalline samples of 2 and 2a.

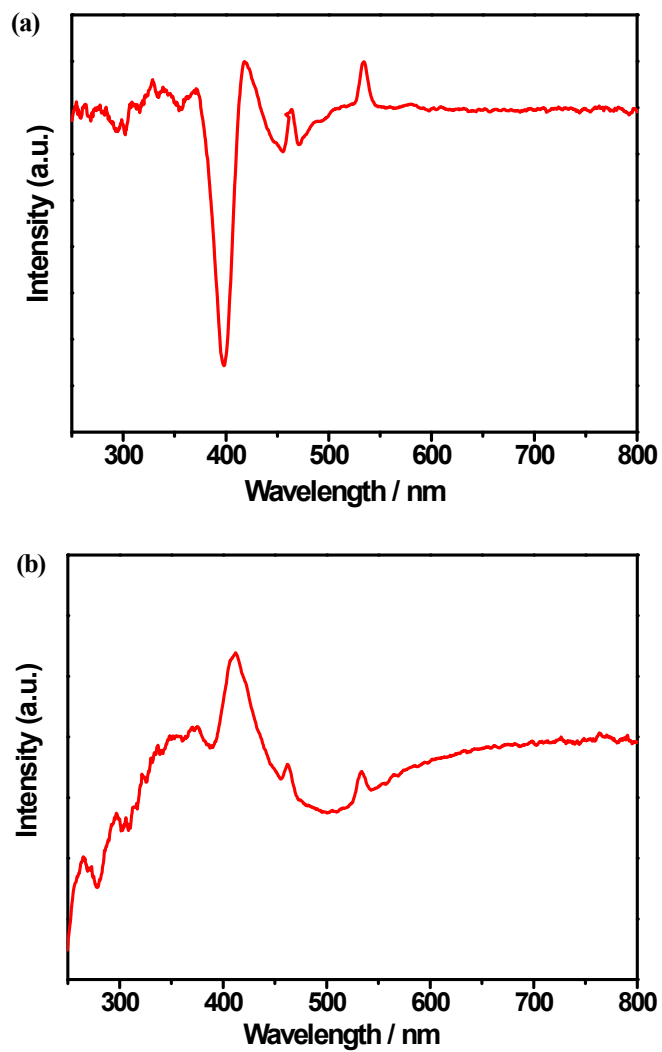


Fig.S13. (a) The arithmetic difference between curves of complexes **1** and **2**. (b) The arithmetic difference between curves of complexes **1a** and **2a**.

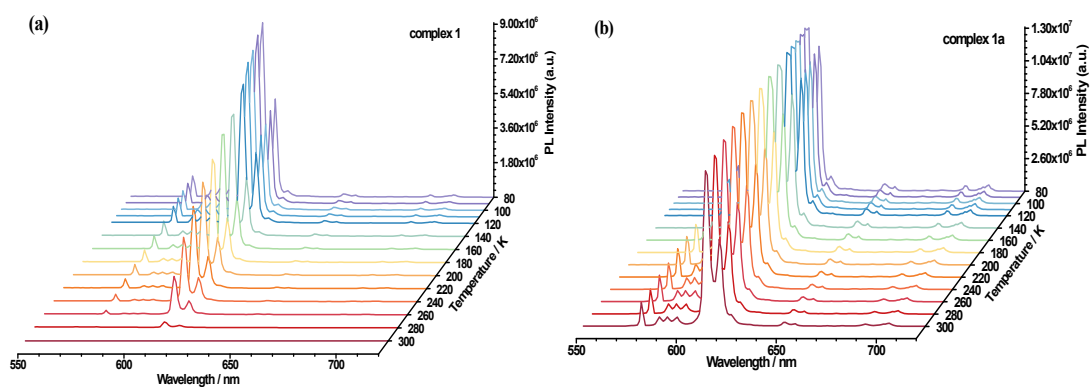


Fig. S14. (a) Photoluminescence spectra of complex **1** in solid state from 80 K to 300 K ($\lambda_{\text{ex}} = 360$ nm). (b) Photoluminescence spectra of complex **1a** in solid state from 80 K to 300 K ($\lambda_{\text{ex}} = 360$ nm)

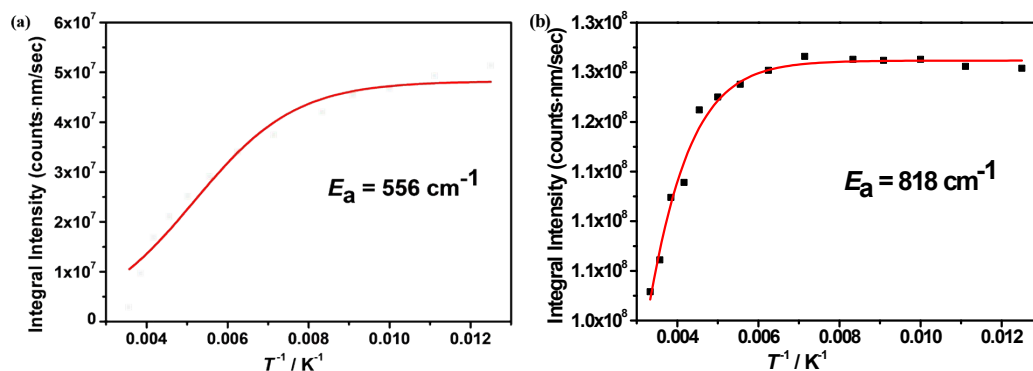


Fig. S15. (a) The temperature dependence of the integrated luminescence intensity of complex **1**. (b) The temperature dependence of the integrated luminescence intensity of complex **1a**.

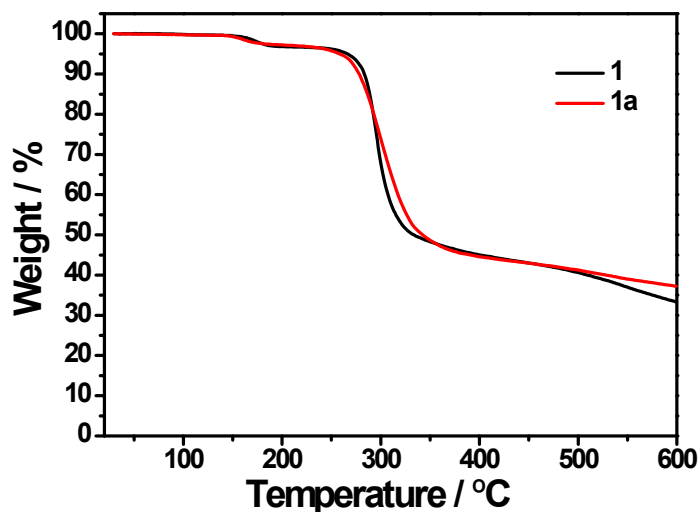


Fig. S16. TG curves of complexes **1** and **1a**. The first weight loss around 145-210 °C corresponds to the loss of coordinated methanol molecules (obsd: 2.72% for **1** and 2.41% for **1a**; calcd: 2.75% for **1** and **1a**).

References

- 1 *SAINT*, version 5.0-6.01; Bruker Analytical X-ray Systems Inc.: Madison, WI, USA, 1998.
- 2 Sheldrick, G. M. *SADABS*, An empirical absorption correction program; University of Göttingen: Göttingen, Germany, 1996.
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- 5 P. P. Lima, M. M. Nolasco, F. A. A. Paz, R. A. S. Ferreira, R. L. Longo, O. L. Malta and L. D. Carlos, *Chem. Mater.*, 2013, **25**, 586.