Supporting Information (ESI) for

A Highly Pure Red Luminescent Europium(III) Complex with a Schiff Base Znic(II) Complex as Neutral Ligand

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General Methods: All chemicals were commercial products of reagent grade and were used without further purification. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. UV-Vis absorption spectra were obtained from ethanol solutions with a HP-8453 UV-vis spectrophotometer. PL, EL spectra and quantum yield were recorded on HORIBA JOBIN YVON Fluoro Max-P spectrophotometer. The overall quantum yield (Φ) obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby[1] by using [Eu(tta)$_3$(phen)] as a reference[2]. Cyclic voltammetry (CV) measurements were carried out in 1.0×10^{-3} mol L^{-1} of substrate in anhydrous degassed DMF containing 0.1 mol L^{-1} tetrabutyl ammonium perchlorate (n-Bu_4NClO_4) as a supporting electrolyte. Platinum electrode was used as a counter electrode and carbon electrode was used as a working electrode and Ag / AgCl as a reference electrode.

Measurement of quantum yield of [EuZnL(tta)$_2$(μ-tfa)]: The overall luminescent quantum yields (Φ) of [EuZnL(tta)$_2$(μ-tfa)] (5.0×10^{-6} mol L^{-1} in THF) was measured by using [Eu(tta)$_3$(phen)] (5.0×10^{-6} mol L^{-1} in THF, Φ_{ref} = 36.5%) as a reference and was calculated according to the well-known method given[1,2].

$$\frac{\Phi}{\Phi_{ref}} = \frac{n^2 A_{ref} I}{n^2_{ref} A I_{ref}}$$

Here n, A, and I denote the refractive index of solvent, the area of the emission

spectrum, and the absorbance at the excitation wavelength, respectively. Subscript ref denotes the reference [Eu(tta)$_3$(phen)], and no subscript denotes the sample [EuZnL(tta)$_2$(μ-tfa)]. For Eu(III) typical emissions, the wavelength used to get the quantum yield value is the total wavelength scale (total area of the five emission peaks at 580, 590, 612, 651 and 701 nm correspond to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively).

The excitation wavelength used to get the quantum yield value is 361nm, which is the intersection point of UV-Vis absorption spectra of both [Eu(tta)$_3$(phen)] and [EuZnL(tta)$_2$(μ-tfa)].

Synthesis of ZnL(H$_2$O): 1,2-propanediamine (0.74 g, 10 mmol) was added to a solution of salicylaldehyde (2.44 g, 20 mmol) in absolute ethanol (30 mL). The resulting mixture was stirred and refluxed for 1 hour. Then, zinc (II) acetate dihydrate (10 mmol) in 10 mL ethanol solution was added. After refluxing for 2 hours, the reaction mixture was cooled and the resulting precipitate was filtered off. The precipitate was recrystallized in ethanol as white needle crystals. The product was dried in vacuum. Yield: 2.87g (79%). m.p.: 195-198^{o}C. Anal. calcd for $C_{17}H_{18}N_2O_3Zn$ (M= 363.74): C, 56.13; H, 4.99; N, 7.70 %. Found: C, 56.08; H, 5.06; N, 7.64%.

Synthesis of [EuZnL(tta)$_2$(μ-tfa)][3]*:* To a stirred suspension of ZnL(H$_2$O) (0.36 g, 1 mmol) in 30mL absolute ethanol, a solution of $EuCl_3$ (1 mmol) in ethanol (2 mL), htta (0.44 g, 2 mmol) and htfa (0.11 g, 1 mmol) were added. The mixture was then neutralized with EtONa ethanol solution and heated under refluxing for 50 minutes. The clear pale yellow solution was then cooled to room temperature and allowed to evaporate slowly at R.T., pale yellow single crystals of $C_{35}H_{24}N_2O_8F_9S_2ZnEu$ were obtained in about 2 weeks. Yield: 0.58g (56%). m.p. 136-139^{o}C. Anal. calcd for $C_{35}H_{24}N_2O_8F_9S_2ZnEu$ (M= 1053.06): C, 39.92; H, 2.30; N, 2.66%. Found: C, 39.85; H, 2.39; N, 2.61%.

Absorption and emission spectra of [EuZnL(NO$_3$)$_3$(H$_2$O)]: In order to confirm that ZnL can act as a long wavelength sensitizer for Eu^{3+} typical emissions, the complex

[EuZnL$(NO_3)_3(H_2O)$] has been synthesized. Reaction of ZnL(H_2O) with $Ln(NO_3)_3 \cdot 6H_2O$ in 1:1 molar ratio in MeCN produced a pale yellow solution. The reaction mixture was heated under refluxing for 50 minutes and then cooled to room temperature. The resulting precipitate was filtered off and recrystallized in MeCN as pale yellow solids. Elemental analyses result confirmed that the heterodinuclear complex has the molecular formula of [EuZnL$(NO_3)_3(H_2O)$]. Anal. calcd for $EuZnC_{17}N_5O_{12}H_{18}$ (M= 701.7): C, 29.10; H, 2.58; N, 9.98%. Found: C, 29.03; H, 2.62; N, 9.92%.

The absorption spectrum of complex EuZnL$(NO_3)_3(H_2O)$] (1.0×10^{-5} mol L^{-1} in MeCN solution) has broad band absorptions at 240, 270 and 350 nm (Fig. S1). When excited with the ligand-centered absorption at 350 nm at room temperature, the complex exhibits apparent red emissions typical of Eu^{3+} and no emission band at 445 nm from ZnL is observed (Fig. S2), suggesting that ZnL can act as a long wavelength sensitizer for Eu^{3+} typical emissions.

Single crystal X-Ray diffraction determination: Crystal data for complex $C_{35}H_{24}N_2O_8F_9S_2ZnEu$ was collected on a Bruker SMART APEXII CCD diffractometer with graphite monochromatic MoKα radiation (λ = 0.71073 Å) using the SMART and SAINT programs, and the structure was solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2. Anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic data and other pertinent information for the complex are summarized in Table S1. Selected bond distances and bond angles with their estimated standard deviations are listed in Table S2.

Table S1 Crystal data and structure refinement for [EuZnL$(tta)_2(\mu\text{-}tfa)$]

Identification code	P-1
Empirical formula	$C_{35}H_{24}N_2O_8F_9S_2ZnEu$
Formula weight	1053.06
Temperature / K	291.0
Crystal system	triclinic
Space group	P-1

a / Å, b / Å, c / Å	10.581(2), 11.669(2), 17.239(3)
α/°, β/°, γ/°	72.23(3), 79.69(3), 75.14(3)
Volume / Å^3	1947.5(7)
Z	2
ρ_{calc} / mg mm^{-3}	1.796
μ / mm^{-1}	2.414
F(000)	1036
Crystal size / mm^3	0.30 × 0.20 × 0.10
Theta range for data collection	2.24 to 53°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	21958
Independent reflections	7971[R(int) = 0.0662]
Data/restraints/parameters	7971/90/548
Goodness-of-fit on F^2	1.054
Final R indexes [I>2σ (I)]	R_1 = 0.0690, wR_2 = 0.1371
Final R indexes [all data]	R_1 = 0.1055, wR_2 = 0.1558
Largest diff. peak/hole / e Å^{-3}	0.663/-0.683

Table S2 Selected Bond Distances (Å) and Angles (deg) of [EuZnL(tta)$_2$(μ-tfa)]

	Distances (Å)		Angles (deg)
Eu1- Zn1	3.3354(13)	Zn1-O1-Eu1	97.93(13)
Eu1- O1	2.346(4)	Zn1-O2-Eu1	99.35(13)
Eu1- O2	2.354(3)	O2-Eu1-O7	77.98(13)
Eu1- O3	2.334(3)	O2-Zn1-O1	85.35(13)
Eu1- O4	2.330(4)	O2-Zn1-O8	97.83(16)
Eu1- O5	2.341(4)	O2-Zn1-N1	153.98(19)
Eu1- O6	2.299(4)	O2-Zn1-N2	92.27(18)
Eu1- O7	2.436(3)	O3-Eu1-O1	85.57(12)
Zn1- O1	2.069(3)	O3-Eu1-O2	133.74(14)
Zn1- O2	2.011(4)	O3-Eu1-O5	72.98(13)
Zn1- O8	2.029(4)	O3-Eu1-O7	135.59(13)
Zn1- N1	2.039(5)	O4-Eu1-O1	109.06(14)
Zn1- N2	2.023(6)	O4-Eu1-O2	78.34(13)
		O4-Eu1-O3	71.41(12)
		O4-Eu1-O5	124.15(13)
		O4-Eu1-O7	152.83(12)
		O5-Eu1-O1	109.48(12)
		O5-Eu1-O2	152.40(13)
		O5-Eu1-O7	75.92(12)
		O6-Eu1-O4	89.76(14)
		O6-Eu1-O5	72.93(13)
		O6-Eu1-O7	78.51(13)
		O8-Zn1-O1	100.01(15)

		O8-Zn1-N1	108.18(19)
		N1-Zn1-O1	89.63(17)
		N2-Zn1-O1	150.2(2)
		N2-Zn1-O8	109.7(2)
		N2-Zn1-N1	79.6(2)

The crystallographic data for [EuZnL(tta)$_2$(μ-tfa)] has been deposited in the Cambridge Crystallographic Data Centre with the deposition number CCDC 807139. This data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Device fabrication and measurements: The substrate was an indium tin oxide (ITO) coated glass with a sheer resistance of ~30 Ω/□. Pre-patterned ITO substrates were cleaned sequentially by sonication in detergent solution, doubly distilled water, and EtOH for 5 min in turn before being blown dried with a stream of nitrogen. The ITO substrates were then treated with oxygen plasma for 5 min before being loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of 0.1-0.3 nm/s under a pressure of 5.0×10^{-4} Pa. Current-voltage-light intensity (*I*-*V*-*L*) and EL spectra were measured and recorded by using a Keithley 2000 digital multimeter and ST-900M spectrometer luminance meter.

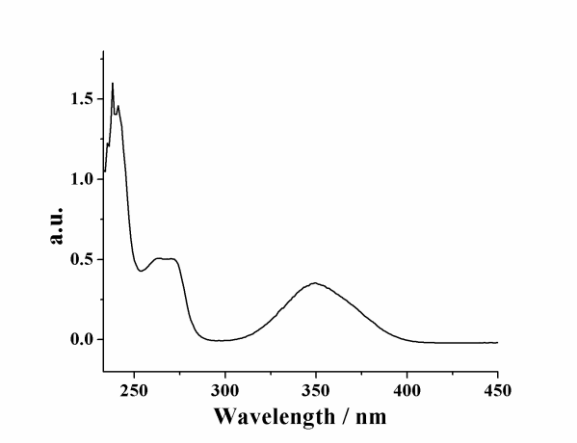

Fig. S1 UV-Vis spectrum of [EuZnL(NO$_3$)$_3$(H$_2$O)] (1.0×10^{-5} mol L^{-1} in MeCN)

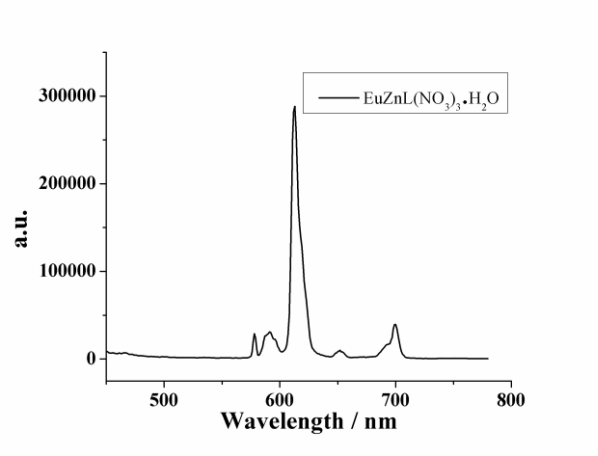

Fig. S2 Emission spectrum of $[EuZnL(NO_3)_3(H_2O)]$ in MeCN (λ_{ex}=350 nm)

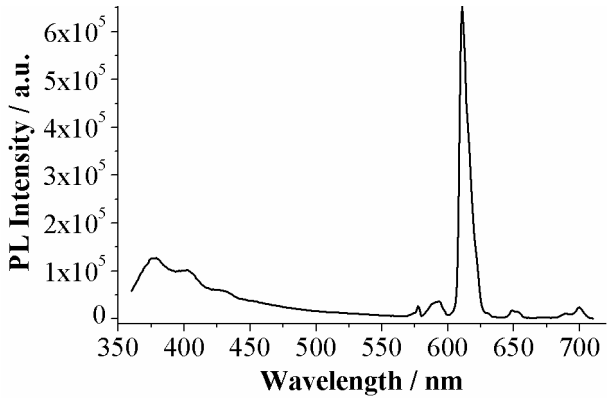

Fig. S3 PL spectrum of a thin film of CBP doped with $[EuZnL(tta)_2(\mu\text{-tfa})]$ (~10 wt %)

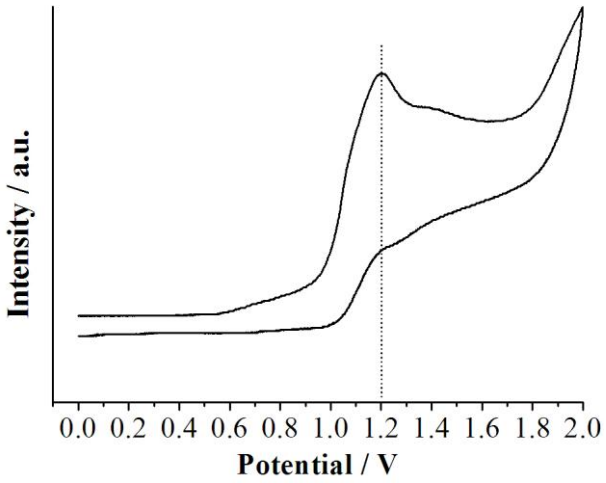

Fig. S4 Cyclic voltammograms of $[EuZnL(tta)_2(\mu\text{-tfa})]$
(0.1M tetrabutylammonium perchlorate ($n\text{-}Bu_4NClO_4$) as a supporting electrolyte)

Table S3 Electrochemical properties of the complex [EuZnL(tta)$_2$(μ-tfa)].
(The HOMO and LUMO data was calculated according to the equation reported by de Leeuw et al.[4])

complex	Voltage (Oxy. onset) [V], E_{HOMO} [eV]	E_{LUMO} [eV]
[EuZnL(tta)$_2$(μ-tfa)]	1.20, 5.80	3.40

Reference

[1] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.
[2] P. Nockemann, E. Beurer, K. Driesen, R. V. Deun, K. V. Hecke, L. V. Meervelt, K. Binnemans, *Chem. Commun.* **2005**, 4354.
[3] L. R. Melby, N. J. Rose, E. Abranmson, J. C. Caris, *J. Am. Chem. Soc.* **1964**, *86*, 5117.
[4] D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53.