Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supporting Information:

Highly Photo-, and Electroluminescent 1,3-Diketonate Eu(III) Complexes With Spiro-Fluorene-Xanthphos Dioxide Ligand. Synthesis and Properties.

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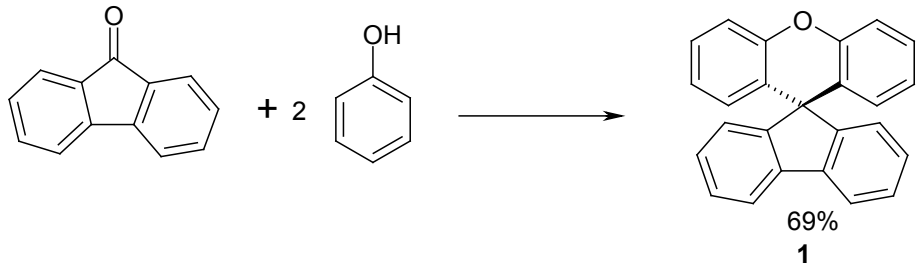
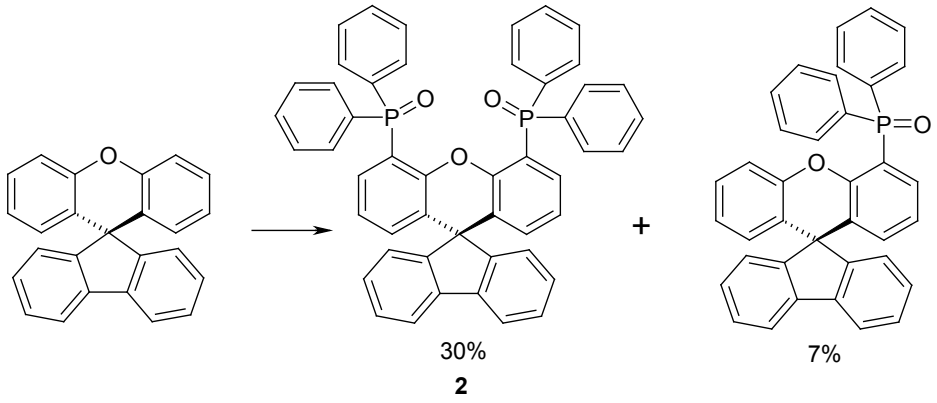


Scheme S1: Spiro-fluorene-xanthene (1) synthesis: $MeSO_3H$, 1,2-dichlorobenzene, 24h, 150^0C



Scheme S2: Spiro-fluorene-xanthene diphosphine oxide (2) synthesis: 1) n-BuLi, TMEDA, hexane, 1h, reflux, Ar; 2) Ph_2PCl, 12h, 0^0C to r.t.; 3) 30% H_2O_2, 1,4-dioxane, 2h, r.t.

Synthetic and analytical data of novel compounds

All conventional chemicals were purchased from Aldrich, and were used as received. THF was distilled over $LiAlH_4$ prior to use.

3.2. Synthesis

3.2.1. *Spiro[fluorene-9,9'-xanthene]* (**1**)**.** A mixture of fluorenone (0.3 g, 1.667 mmol, 1 equiv) and methanesulfonic acid ($MeSO_3H$, d =1.48 g/mL, 0.43 mL, 6.668 mmol, 4 equiv) in dichlorobenzene was added to phenol (1.567 g, 16.67 mmol, 10 eq) at 100°C during 1h. The mixture was heated at 150°C under argon for 24 h. The reaction mixture was then slowly added into water (25 mL) and extracted with dichloromethane. The combined extracts were

dried over $MgSO_4$, filtered, evaporated, and purified by column chromatography (hexane:ethyl acetate, 10:1) to afford colorless solid SFX (0.382 g, 69%). M.p.: 212-213°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ= 7.87 (d, J= 7.6 Hz, 2H), 7.45 (ddd, J = 7.6 Hz, J = 6.4 Hz, J = 2.2 Hz, 2H), 7.32-7.20 (m, 8H), 6.85 (ddd, J= 7.1 Hz, J= 2.3 Hz, 2H), 6.51 (m, 1H), 6.47 (d, J = 1.3 Hz, 1H).

3.2.2. *4',5'-Bis-(diphenyl-phosphinoyl)-spiro[fluorene-9,9'-xanthene]* (**2**). At room temp. *n*-butyllithium (7.3 mL, 18.361 mmol, 3.2 eq) in *n*-hexane was added within 40 min. to a solution of SFX (1.905 g, 5.738 mmol) and of TMEDA (2.134 g, 2.77 mL, 18.361 mmol, 3.2 eq) in hexane. The mixture was heated at reflux for 1 h and then cooled to 0°C after what a solution of Ph_2PCl (2.87 g, 2.4 mL, 18.361 mL, 3.2 eq) in hexane (10 mL) was added within 1 h. After stirring at room temp. for 12 h the mixture was cooled to 0°C and obtained precipitate was filtered off and washed with hexane and water. A 30% aqueous H_2O_2 solution (2 mL) was added to the solution of obtained products mixture in 1,4-dioxane. After stirring for 2 h, the reaction was worked up with CH_2Cl_2 and water. After drying over Na_2SO_4 and filtering the solvent was evaporated and the residue was purified by column chromatography (hexane:acetone, 1:1) to afford colorless solids of diphenylhosphine oxide derivative (0.181 g, 7%). M.p.: 238-240°C and bis-diphenylhosphine oxide derivative (1.241 g, 30%). M.p.: 305-306°C. Diphenylhosphine oxide of SFX: ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 6.37-6.42 (m, 2H); 6.62-6.78 (m, 2H); 6.84-8.00 (m, 21H). MS (EI, 70 eV): m/z (%)= 532,1 (M+, 100), 331 (M+(-$POPh_2$), 15,62). Bis-diphenylhosphine oxide of SFX: ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 7.80 (d, J= 7.7 Hz, 2H), 7,57-7.18 (m, 26H), 6.95-6.85 (m, 2H), 6.70 (ddd, J= 7.7 Hz, J= 1.9 Hz, 2H), 6.60 (d, J= 7.7 Hz, 2H), 1.88 (bs, 2xH_2O, 4H). ^{31}P NMR (400 MHz, $CDCl_3$, ppm): δ= 29.16. Elemental anal. (%): calcd. for $C_{49}H_{34}O_3P_2$ + 2xH_2O: C, 76.55; H, 4.98; found C, 76.45; H, 4.99. MS (EI, 70 eV): m/z (%)= 732 (M+, 93), 731 (M-1, 100), 655 (M+(-Ph), 25), 639(M+(-Ph,-O),32).

3.2.3. *Complex 4',5'-bis-(diphenyl-phosphinoyl)-spiro[fluorene-9,9'-xanthene] with tris-(thenoyltrifluoroacetonate) europium(III)* (**3**). Equimolar solution of $Eu(tta)_3$ (0.164 g, 0.2 mmol) and bis-diphenylhosphine oxide (0.146 g, 0.2 mmol) in chloroform was stirred at reflux for 24 h. The product was obtained as a light orange powder at daylight (0.233 g, 75%) after solvent evaporation and recrystallization from chloroform-hexane mixture. M.p.: 238-240°C. ^{31}P NMR (400 MHz, $CDCl_3$, ppm): δ= -86.04. Elemental anal. (%): calcd. for $C_{73}H_{46}O_9P_2F_9S_3Eu$ + H_2O: C, 55.98; H, 3.09; found C, 55.97; H, 3.19. MS (TOF MS FD+ 26.7, 9 kV): m/z (%)= 2059.1 ($Eu(tta)_2$ + 2×phosphine oxide), 1327 (M- tta).

3.2.4. *Complex 4',5'-bis-(diphenyl-phosphinoyl)-spiro[fluorene-9,9'-xanthene] with tris-(hexafluoroacetylacetonate) europium(III)* (**4**). Complex 4 was synthesized using the same reaction and workup procedure as that of 3 but employing $Eu(hfac)_3$ and yielded 0.105 g (35%) as a light yellow powder. M.p.: 255-256°C. ^{31}P NMR (400 MHz, $CDCl_3$, ppm): δ= -109.67. Elemental anal. (%): calcd. for $C_{64}H_{37}O_9P_2Eu$ + H_2O: C, 50.44; H, 2.58; found C, 50.53; H, 2.51. MS (TOF MS): m/z (%)= 1711.4 (M+ 1+ hfac), 1487.4 (M- F).

3.2.5. *Complex 4',5'-bis-(diphenyl-phosphinoyl)-spiro[fluorene-9,9'-xanthene] with tris-(naphthoiltrifluoroacetonate) europium(III)* (**5**). Complex 5 was synthesized using the same reaction and workup procedure as that of 3 but employing $Eu(nta)_3$ and yielded 0.165 g (49%) as a light yellow powder. M.p.: 244-245°C. ^{31}P NMR (400 MHz, $CDCl_3$, ppm): δ= -79.50. Elemental anal. (%): calcd. for $C_{91}H_{60}O_{10}P_2Eu$ + H_2O: C, 64.36; H, 3.56; found C, 64.01; H, 3.36. MS (TOF MS): m/z (%)= 1415 (M- nta).

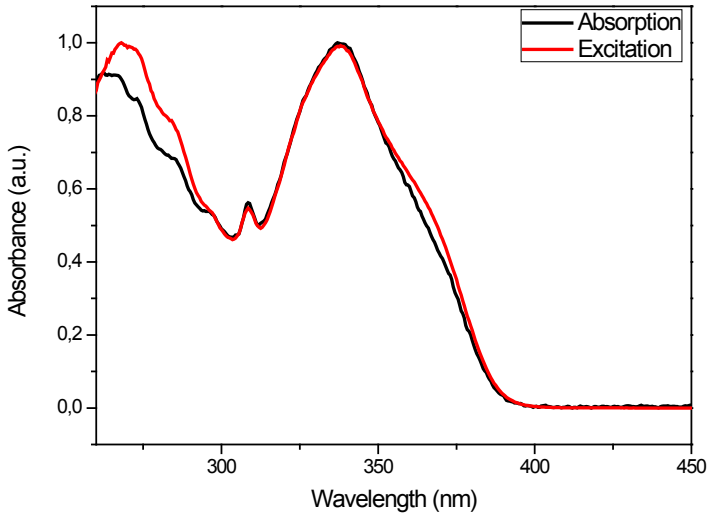


Figure S2: Absorption and excitation spectra of $Eu(tta)_3SFXPO$

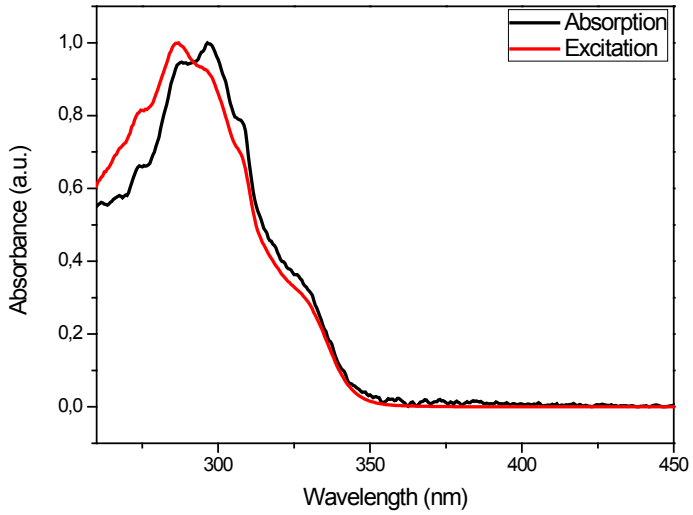


Figure S3: Absorption and excitation spectra of $Eu(hfac)_3SFXPO$

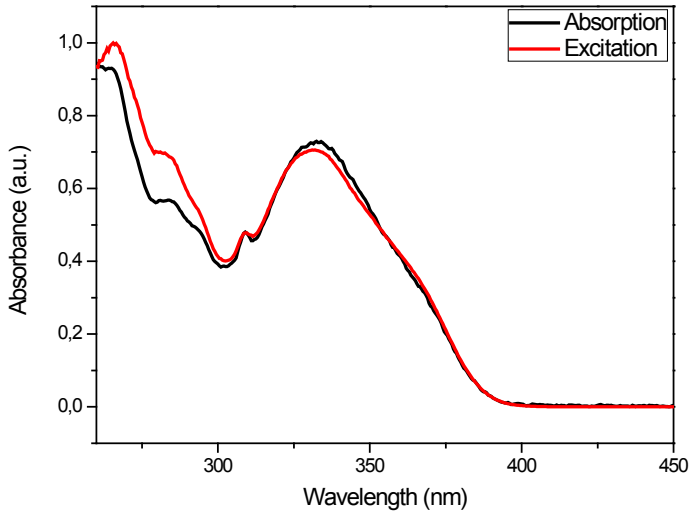


Figure S4: Absorption and excitation spectra of $Eu(nta)_3SFXPO$

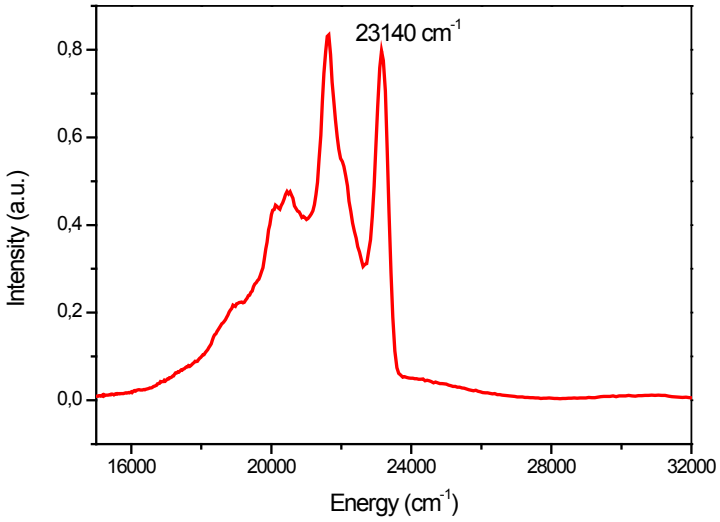


Figure S5: Phosphorescence spectrum of SFXPO in 2-methyltetrahydrofuran at 77 K

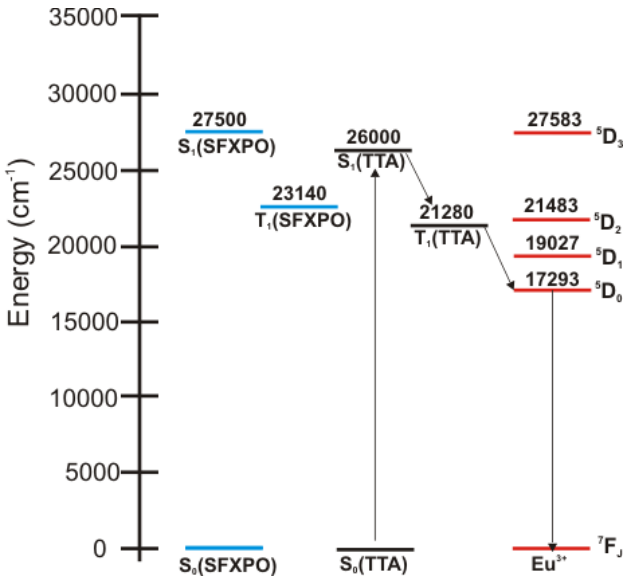


Figure S6: Energy levels for SFXPO, tta ligands and Eu(III)

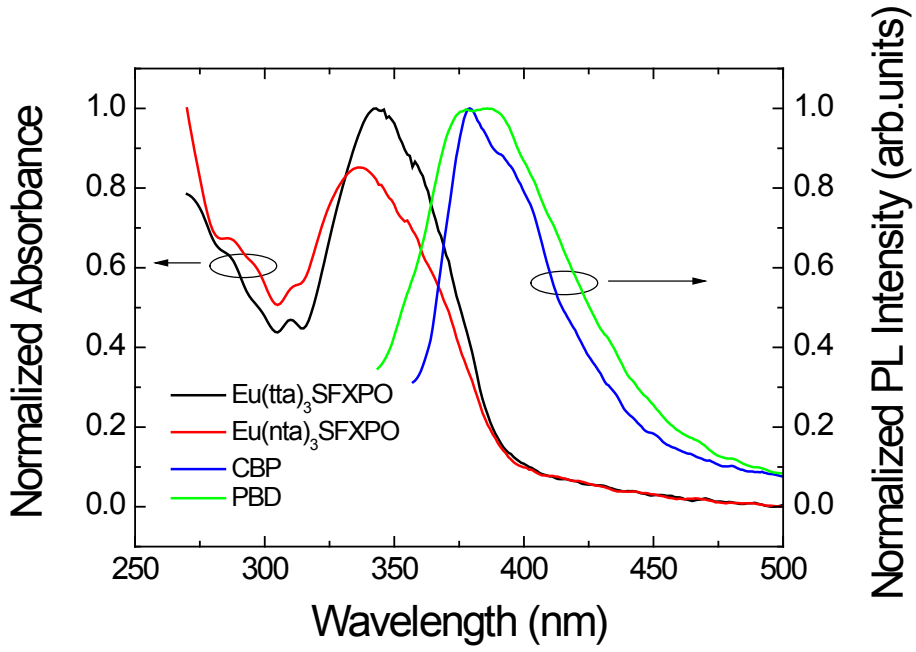


Figure S7: Absorption spectra of Eu(III) complexes and emission of host materials.

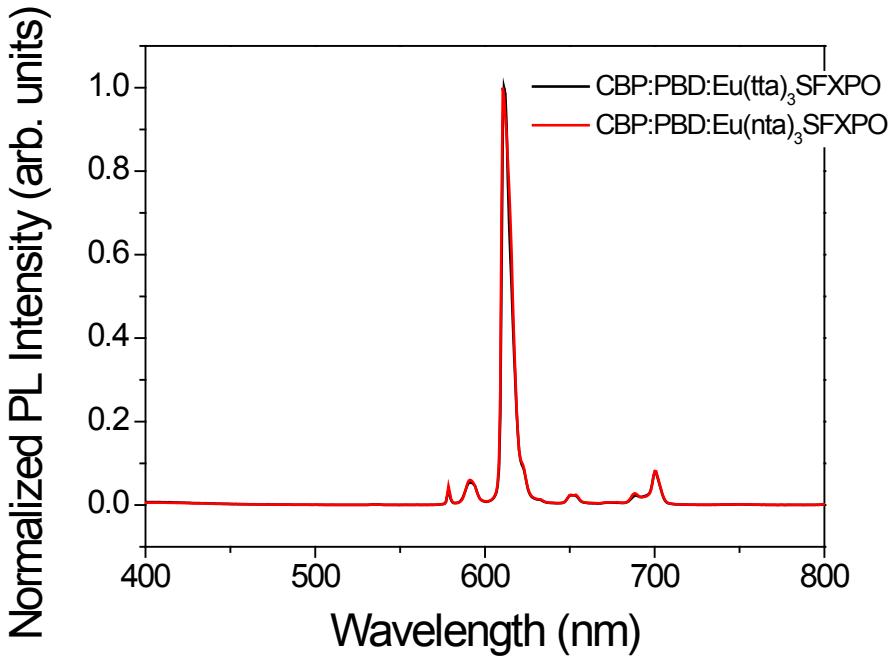


Figure S8: Photoluminescence spectra of the Eu(III) complexes in blend: CBP and PBD.

Table S1: photoluminescent properties of ternary complexes in neat complexes and their blends with CBP:PBD

		$Eu(tta)_3SFXPO$			$Eu(nta)_3SFXPO$		
	CBP:PBD ratio (wt %)	PLQY (%)	ABS	Ex Wavelength (nm)	PLQY (%)	ABS	Ex Wavelength (nm)
Neat Eu	N/A	71.3	0.238	380	64	0.218	380
CBP:PBD:Eu	100:0	76.6	0.726	325	80.4	0.742	325
CBP:PBD:Eu	70:30	78.6	0.762	325	82.7	0.776	325
CBP:PBD:Eu	50:50	80.8	0.763	325	84.8	0.764	325
CBP:PBD:Eu	30:70	81.4	0.798	325	84.2	0.781	325
CBP:PBD:Eu	0:100	84.6	0.791	325	86.2	0.766	325

All PLQY values are tested under N_2 environment.
Samples are dissolved in DCM with a concentration of 10mg/ml. Spincoating rate: 2500rpm, 60s, 50 ramp.
Europium complex is always 5 weight %.