Electronic Supporting Information:

Highly Photo-, and Electroluminescent 1,3-Diketonate Eu(III) Complexes With Spiro-

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![Scheme S1: Spiro-fluorene-xanthene (1) synthesis: MeSO3H, 1,2-dichlorobenzene, 24h, 150°C](image)

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Synthetic and analytical data of novel compounds

All conventional chemicals were purchased from Aldrich, and were used as received. THF was distilled over LiAlH4 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 (MeSO3H, 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\textsubscript{4}, filtered, evaporated, and purified by column chromato- 
graphy (hexane:ethyl acetate, 10:1) to afford colorless solid SFX (0.382 g, 69%). M.p.: 212- 
213°C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{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] \textsuperscript{(2)}. At room temp. \textit{n}-
butyllithium (7.3 mL, 18.361 mmol, 3.2 eq) in \textit{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\textsubscript{2}PCl (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\textsubscript{2}O\textsubscript{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\textsubscript{2}Cl\textsubscript{2} and water. After drying over Na\textsubscript{2}SO\textsubscript{4} and 
filtering the solvent was evaporated and the residue was purified by column chromato-
graphy (hexane:acetone, 1:1) to afford colorless solids of diphenylphosphine oxide derivative (0.181 g, 
7%). M.p.: 238-240°C and bis-diphenylphosphine oxide derivative (1.241 g, 30%). M.p.: 305-
306°C. Diphenylphosphine oxide of SFX: \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{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\textsubscript{2}), 15,62). Bis-diphenylphosphine oxide of SFX: \textsuperscript{1}H NMR (200 MHz, 
CDCl\textsubscript{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\textsubscript{2}O, 4H). \textsuperscript{31}P NMR (400 MHz, 
CDCl\textsubscript{3}, ppm): δ = 29.16. Elemental anal. (%): calcd. for C\textsubscript{49}H\textsubscript{34}O\textsubscript{3}P\textsubscript{2} + 2xH\textsubscript{2}O: 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)\textsubscript{3} (0.164 g, 0.2 
mol) and bis-diphenylphosphine 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. \textsuperscript{31}P NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ = -86.04. Elemental anal. (%): calcd. for 
C\textsubscript{73}H\textsubscript{46}O\textsubscript{9}P\textsubscript{2}F\textsubscript{9}S\textsubscript{3}Eu + H\textsubscript{2}O: 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)\textsubscript{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) \textsuperscript{(4)}. Complex 4 was synthesized using the same 
reaction and workup procedure as that of 3 but employing Eu(hfac)\textsubscript{3} and yielded 0.105 g 
(35%) as a light yellow powder. M.p.: 255-256°C. \textsuperscript{31}P NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ = 
-109.67. Elemental anal. (%): calcd. for C\textsubscript{64}H\textsubscript{37}O\textsubscript{9}P\textsubscript{2}Eu + H\textsubscript{2}O: 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) \textsuperscript{(5)}. Complex 5 was synthesized using the same 
reaction and workup procedure as that of 3 but employing Eu(nta)\textsubscript{3} and yielded 0.165 g (49%) 
as a light yellow powder. M.p.: 244-245°C. \textsuperscript{31}P NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ = -79.50. 
Elemental anal. (%): calcd. for C\textsubscript{91}H\textsubscript{60}O\textsubscript{10}P\textsubscript{2}Eu + H\textsubscript{2}O: 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)$_3$SFXPO

**Figure S3:** Absorption and excitation spectra of Eu(hfac)$_3$SFXPO
Figure S4: Absorption and excitation spectra of Eu(NTA)$_3$SFXPO

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

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All PLQY values are tested under N₂ environment. Samples are dissolved in DCM with a concentration of 10mg/ml. Spincoating rate: 2500rpm, 60s, 50 ramp. Europium complex is always 5 weight %.