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Electronic Supplementary Information

Modular chiral Eu(III) complexes for efficient circularly polarized OLEDs

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Compound preparation

Eu1 was prepared following the procedure reported in ref[S1]. **Eu2** and **Eu3** were prepared as described in ref[S2]. Their identity and chemical purity was confirmed by comparison with literature data ref[S1,S2].

Spectral data

Electronic absorption spectra were carried out by a Perkin-Elmer Lambda 900 UV-VIS-NIR Spectrometer. ECD spectra were recorded with a Jasco J-1500 spectropolarimeter. Steady-state and time-resolved photoluminescence spectra were recorded on a modified Jobin-Yvon Horiba Fluorolog spectrofluorimeter. The PL quantum yields (PLQY) were obtained using a homemade integration sphere following the procedure already reported [S3]. PLQY of solution were measured in degassed Toluene. Films were deposited in inert atmosphere from degassed solutions, and the PLQY measurements were performed in air.

CP-PL and CP-EL spectra were obtained by selecting left and right CP components with a quarter wave plate and a linear polarizer placed in front of the CCD detector, as previously described [S4,S5]. Triplet levels were determined from the phosphorescence spectra in CH_2Cl_2 frozen solution of the corresponding Gd(III) complexes.

Electrochemistry

HPLC grade dichloromethane (Sigma Aldrich) was stored under Ar over 3 Å molecular sieves. $[^{n}Bu_4N][PF_6]$ (Fluka, electrochemical grade) and Cp_2Fe (Fluka) were used without further purification. Cyclic voltammetry measurements were performed at room temperature with a PalmSens4 instrument interfaced to a computer employing PSTrace5 electrochemical software. The experiments were carried out under Ar using 0.2 M $[^{n}Bu_4N][PF_6]$ in CH_2Cl_2 as the supporting electrolyte. The working and the counter electrode consisted of a Pt disk and a Pt gauze, respectively. A quasi-reference Pt electrode was employed as a reference. The three-electrode home-built cell was pre-dried by heating under vacuum and filled with argon. The Schlenk-type construction of the cell maintained anhydrous and anaerobic conditions. The solution of supporting electrolyte was introduced into the cell and the CV of the solvent was recorded. The analyte was then added and voltammograms were performed (0.1 V/s); then a small amount of ferrocene was added and the voltammograms repeated. Potentials were determined by placing $E_{1/2}$ for the Cp_2Fe^+/Cp_2Fe couple equal to +0.0 V. HOMO/LUMO levels were calculated by taking into account the optical gap (E_g^{opt}).

CP-OLED fabrication

For the manufacturing of the devices ITO was used as anode. After sequential cleaning of the ITO-coated glass of 2.5 cm x 2.5 cm in acetone and isopropanol in a sonicator for ten minutes in each solvent at 50 ºC, it was treated with a nitrogen plasma. PEDOT: PSS Clevios VPI 4083 was spin-coated to a 35 nm thickness. Solutions of the different emitters with the selected host matrix (PMMA, CBP and OXD-7) in $CHCl_3$ or toluene at a total concentration of 15 mg/mL were spin-coated on top of the glass or glass/ITO substrate (ITO: indium thin oxide). The TPBI electron transport/hole blocking layer (30 nm) was deposited using an Organic Molecular Beam Epitaxy (OMBE) system.

Finally, 1.5 nm of LiF and 6-to110 nm of Al were thermo-sublimated inside the high vacuum evaporator to achieve a transparent or mirror cathode. Photons emitted in forward direction through the glass substrate were collected by a calibrated photodiode. Current Density-Luminance-voltage curves are recorded by Keithley 2602 apparatus. Luminance of the OLEDs were measured by means of Konica-Minolta LS-150 luminance meter.

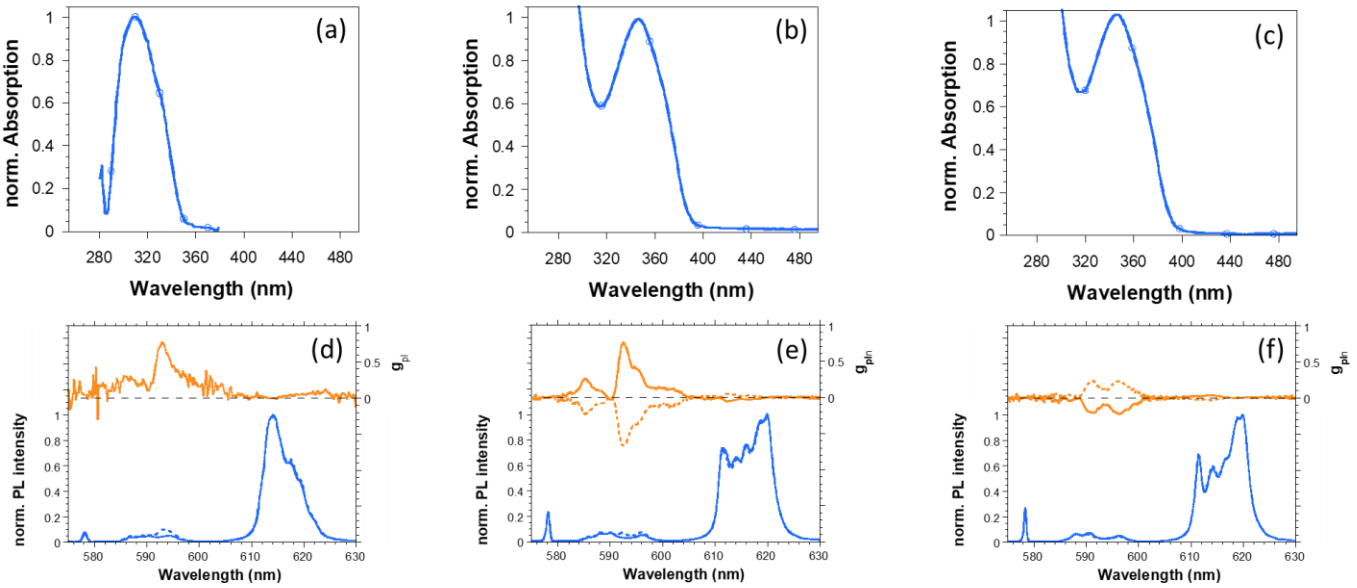


Figure S1. Absorption, CP-PL and g_{pl} of **Eu1** (a,d), **Eu2** (b,e), **Eu3** (c,f) complexes in toluene solutions. The g_{pl} of both enantiomers is reported (orange lines, continuous for *(S,S)*, dashed for *(R,R)* enantiomers).

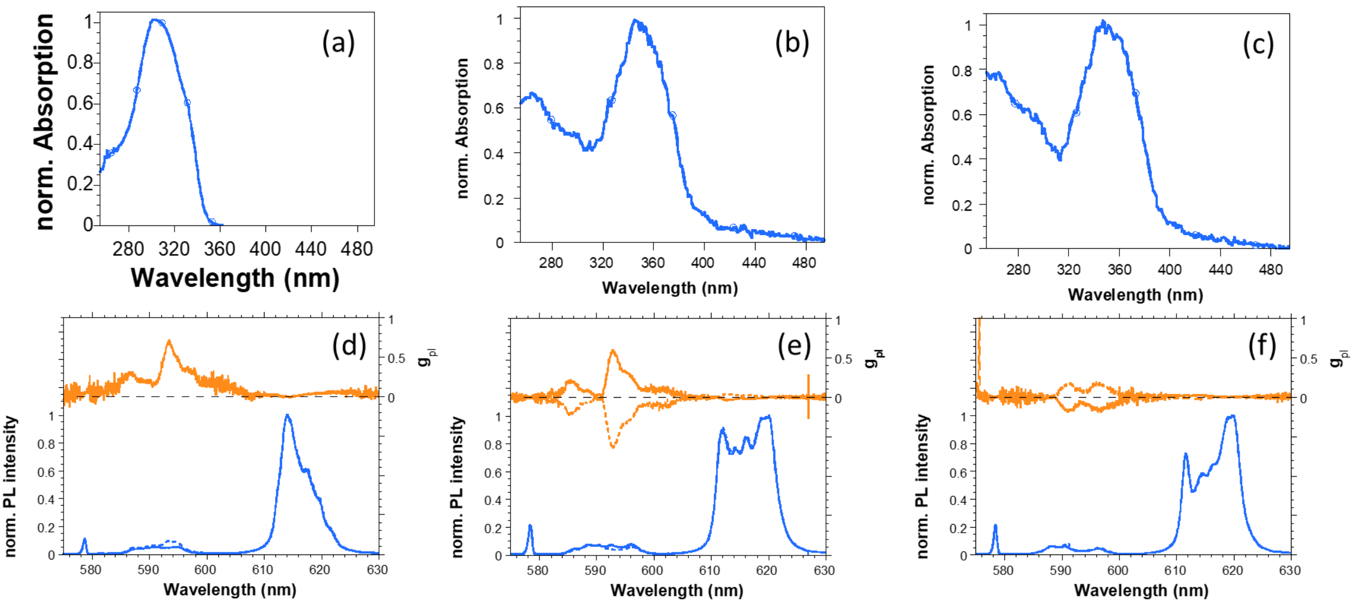


Figure S2. Absorption, CP-PL and g_{pl} of **Eu1** (a,d), **Eu2** (b,e), **Eu3** (c,f) complexes dispersed in PMMA films. The g_{pl} of both enantiomers is reported (orange lines, continuous for *(S,S)*, dashed for *(R,R)* enantiomers).

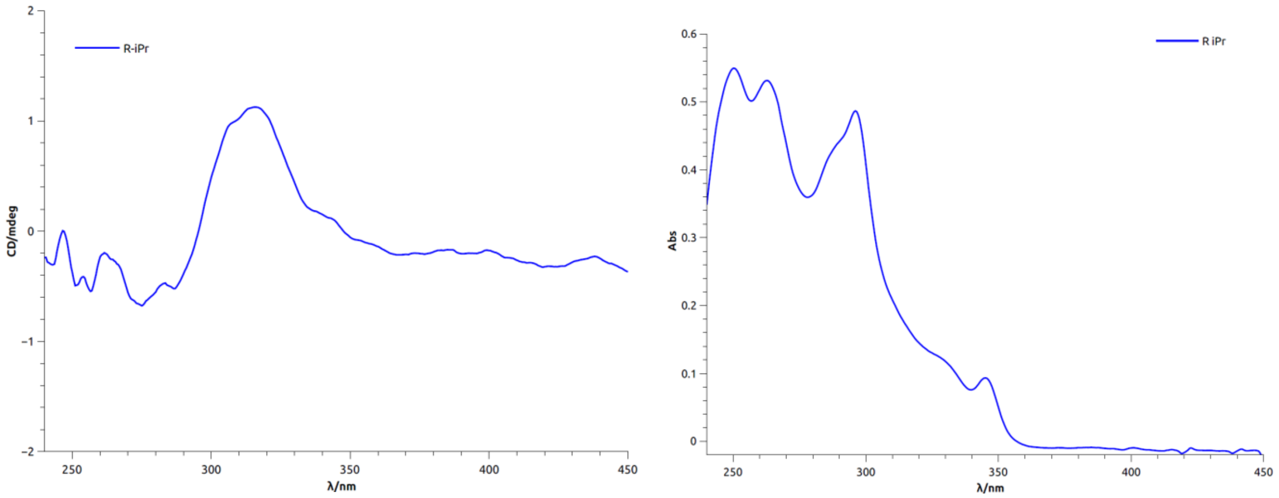


Figure S3. ECD (left) and Absorbance (right) spectrum of PVK:OXD7:**Eu1** films (blue for *(R,R)* enantiomer).

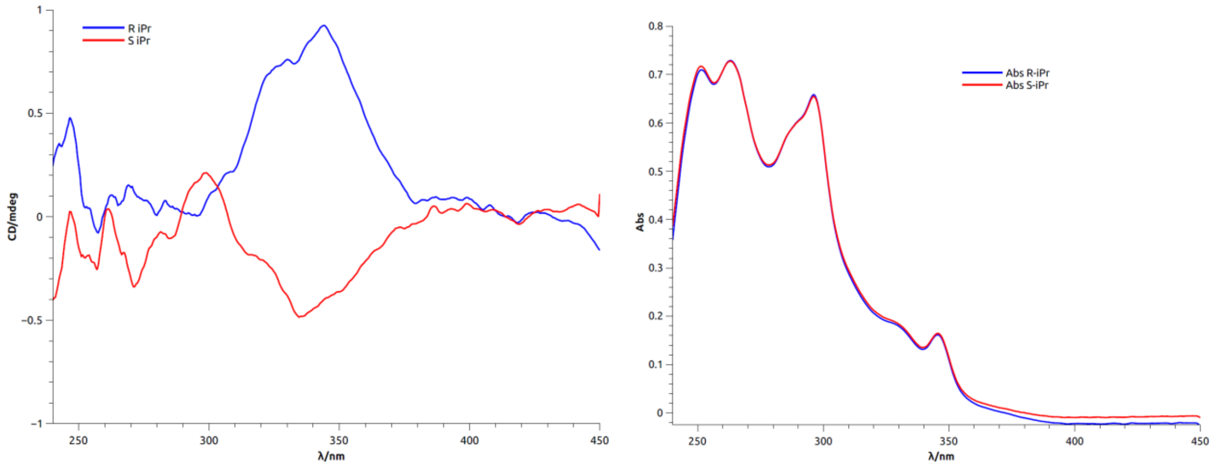


Figure S4. ECD (left) and Absorbance (right) spectrum of PVK:OXD7:**Eu2** films (blue for *(R,R)* and red for *(S,S)* enantiomer).

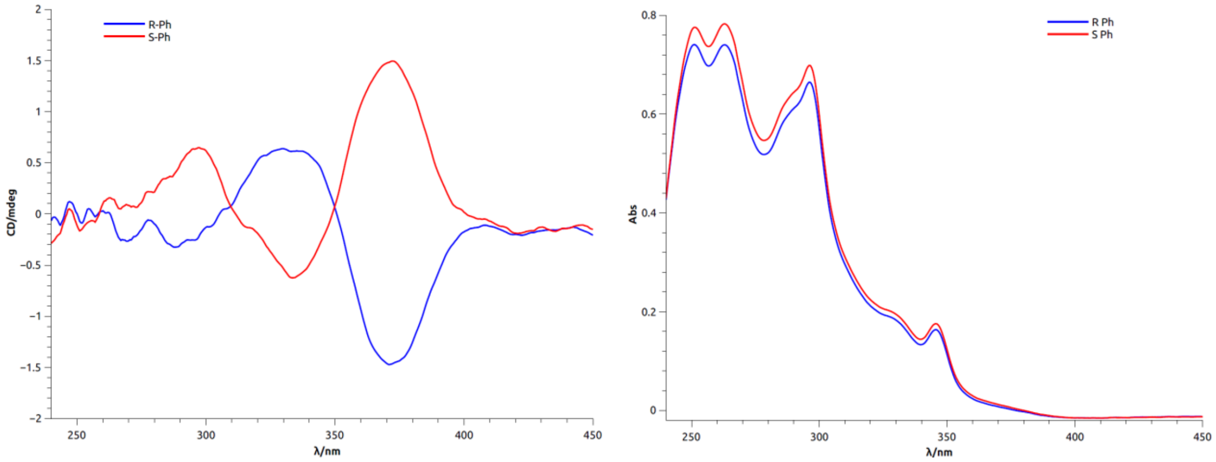


Figure S5. ECD (left) and Absorbance (right) spectrum of PVK:OXD7:**Eu3** films (blue for *(R,R)* and red for *(S,S)* enantiomer).

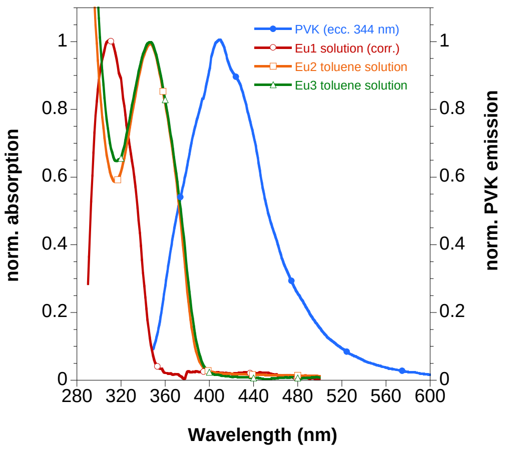


Figure S6. Spectral overlap analysis for FRET evaluation.

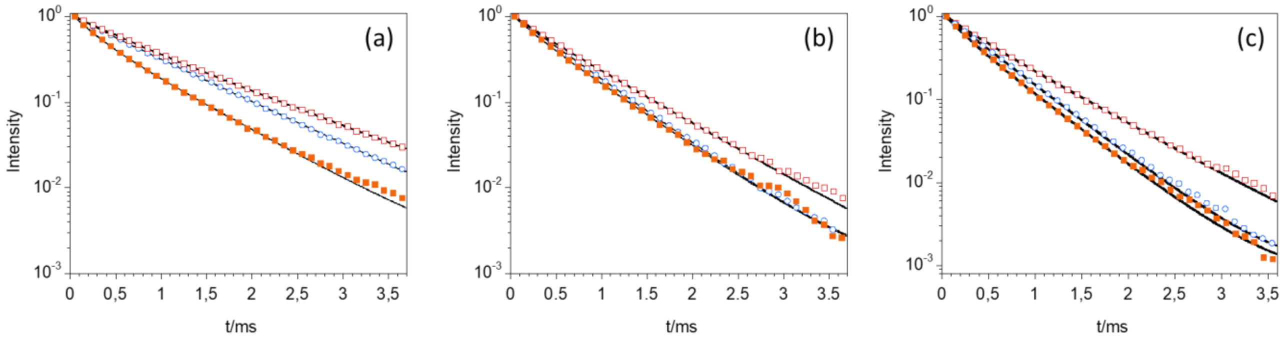


Figure S7. TrPL of **Eu1** (a), **Eu2** (b), **Eu3** (c) complexes in toluene solutions (O, blue), PMMA (☐, orange) and PVK:OXD7 blends (■, orange) with exponential fits (solid lines) with fitting parameters: a) Solution, biexponential fit (0.10) 0.336 ms; (0.90) 0.890 ms, Adj. R-Square=0.99997; PMMA film, biexponential fit (0.70) 1.125 ms; (0.30) 0.595 ms, Adj. R-Square=0.99996; PVK:OXD7 film, bi-exponential fit (0.38) 0.244 ms; (0.62) 0.741ms, Adj. R-Square=0.99992. b) Solution, monexponential fit 0.574 ms, Adj. R-Square=0.99993; PMMA film, biexponential fit (0.14) 0.237

ms; (0.86) 0.713 ms, Adj. R-Square=0.99994, PVK:OXD7 film, biexponential fit (0.78) 0.600 ms; (0.22) 0.227 ms, Adj. R-Square=0.99994. c) Solution, monexponential fit 0.508 ms, Adj. R-Square=0.99988; PMMA film, biexponential fit (0.80) 0.707 ms; (0.20) 0.307 ms, Adj. R-Square=0.99989; PVK:OXD7 film, biexponential fit (0.72) 0.509 ms; (0.28) 0.196 ms; Adj. R-Square=0.99998.

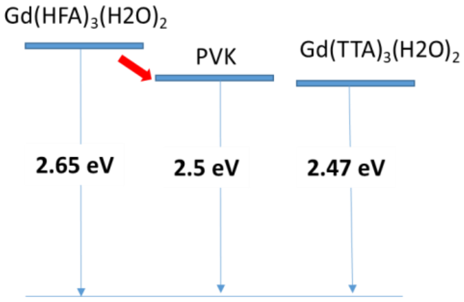
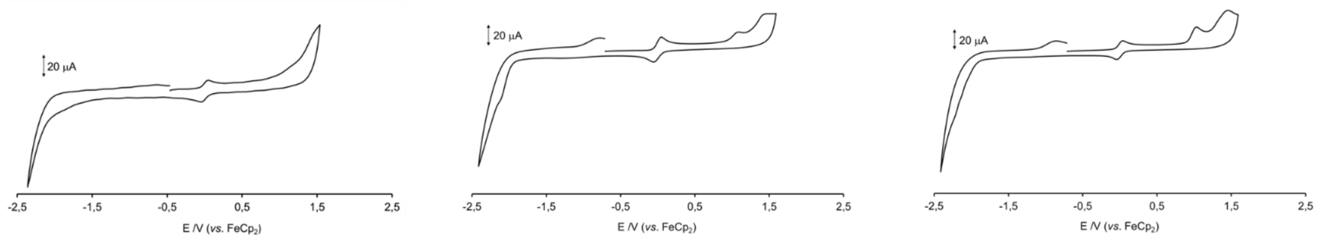


Figure S8. Energy level diagram showing the triplet energy level of the HFA- [S6] and TTA-based complexes [S7].



(a) (b) (c)

Figure S9. (a) Cyclic voltammetry at a platinum electrode in 0.2 M $[N^nBu_4][PF_6]/CH_2Cl_2$ solution containing $FeCp_2$ (scan rate of 100 mV s^{-1}) of (a) **Eu1**; (b) **Eu2**; (c) **Eu3**.

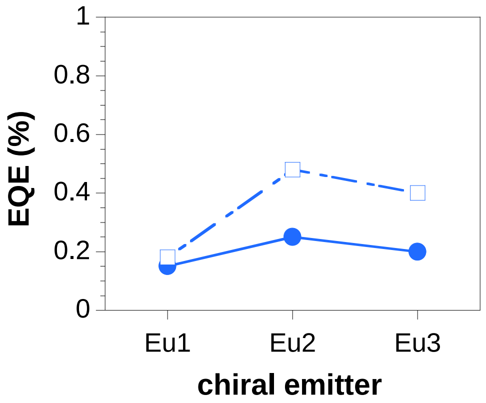


Figure S10. EQE of devices with transparent (●) and reflective cathode (☐) for **Eu1-3** based CP-OLEDs.

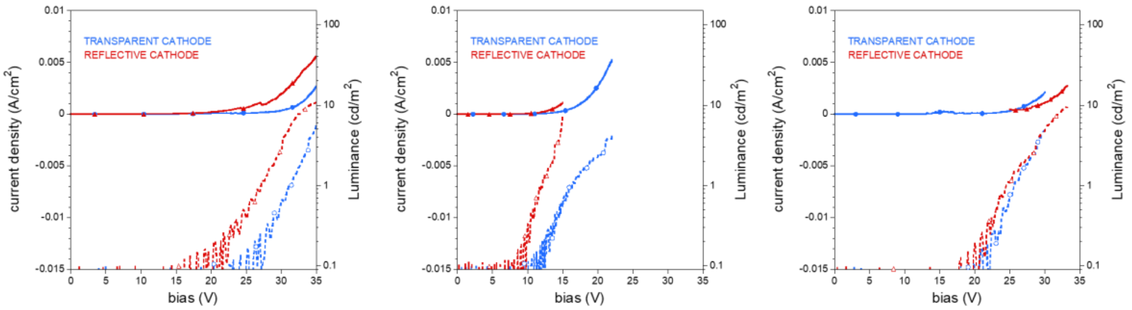


Figure S11. JLV characteristics for **Eu1-3** based CP-OLEDs with transparent (red lines) and reflective cathode (blue lines).

References

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