Electronic Supporting Information Available

Circularly polarized (CP) white organic light-emitting diodes (WOLED) based on chiral organo-Sm³⁺ complex

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Supporting information

Materials and methods

High performance liquid chromatography (HPLC)-grade CH_2Cl_2 for spectrum determination was purchased from Fisher Scientific and purified over solvent columns. Other solvents in the present work were used from the commercial source and stored over 3 Å activated molecule sieves. The complex precursor [Ln(tta)$_3$(H$_2$O)$_2$] (**Htta** = 2-thenoyltrifluoroactone; Ln = La or Sm) was synthesized according to a well-established procedure.[1] Other chemicals including PVK (poly(N-vinylcarbazole); weight-average molecular weight M_w = 90000 g/mol), OXD7 (1,3-*bis*(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene), PEDOT:PSS(poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)), PBD (2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole), TPBi (1,3,5-tris(2-N-phenylbenzimidazolyl)benzene) and BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), were commercial products of reagent grade and were used without further purification. All manipulations of air and water sensitive compounds were carried out under dry N_2 using the

standard Schlenk line techniques. Elemental analyses (EA) were performed on a Perkin-Elmer 240C elemental analyzer. Fourier Transform Infrared (FT-IR) spectra were recorded using PerkinElmer Frontier in the region 4000-400 cm^{-1}. ^{1}H NMR spectra were recorded on a JEOL EX 400 spectrometer with $SiMe_4$ as internal standard in $CDCl_3$ at room temperature. Electro-spray ionization mass spectrometry (ESI-MS) was performed on a Finnigan LCQ^{DECA} XP HPLC-MS$_n$ mass spectrometer with a mass to charge (m/z) range of 4000 using a standard electro-spray ion source and CH_2Cl_2 as solvent. Electronic absorption spectra in the UV/visible region were recorded with a Cary 300 UV spectrophotometer. The specific rotation was determined by ATAGO polarimeter (SAC-I; 589/882 nm). The CD (circular dichroism) spectra were transformed from mdeg (ϑ) into $\Delta\varepsilon$ by using the equation,

$$\Delta\varepsilon \text{ (L/mol·cm)} = \text{ellipticity (mdeg)}/[32980 \times b \text{ (cm)} \times c \text{ (mol/L)}]$$

where b is the length of the light path and c is the concentration of the sample.Visible emission and excitation spectra were collected by a combined fluorescence lifetime and steady-state spectrometer (FLS-980, Edinburgh) with a 450 W Xe lamp. Excited-state decay times were obtained by the same spectrometer but with a μF900 Xe lamp. The luminescent absolute quantum yield (Φ_{PL}) was measured by the same spectrometer using an integrating sphere. The circularly polarized (CP) photoluminescence/electroluminescence (PL/EL) spectra were measured on a Jasco CPL-200 spectrophotometer with the "Standard" sensitivity at a 50 nm/min scan speed with 0.5 nm resolution and the respond time of 8 s. The CP PL/EL signals were presented in ΔI and no corrections were applied on the CP PL/EL spectra $\Delta I = I_L - I_R$, where I_L and I_R indicate the output signals of left and right circularly polarized light. The magnitude of circular polarization in the excited state is defined as $|g_{PL}|$

or $|g_{EL}| = 2 \times (I_L - I_R)/(I_L + I_R)$. Experimentally, the value of is calculated as $\Delta I/I$ = [ellipticity/(32980/ln10)]/unpolarized PL/EL intensity.[2] Thermal properties were characterized using thermogravimetric (TG) analyses on a NETZSCH TG 209 instrument under flowing nitrogen at a heating rate of 10 °C/min.

Synthesis of the chiral ancillary ligand D-Phen (D-Phen = 2-(+)-menthol-1,10-phenanthroline)

The chiral ancillary ligand **D-Phen** was synthesized from an improved procedure as the literature.[3] To a stirred solution containing KH (0.160 g, 4 mmol) in absolute DMSO (30 mL), (+)-menthol (0.624 g, 4 mmol) was added, and the resultant mixture was reacted under an N_2 atmosphere at 80 °C for 3 h. Subsequently, 5-chloro-1,10-phenanthroline (0.856 g, 4 mmol) was added, and the resulting mixture was further reacted under an N_2 atmosphereat 95 °C for another 24 h. During the procedure, the reaction extent was *in situ* checked to completeness by TLC (thin layer chromatography). After the reaction was complete, the mixture was cooled down to room temperature and poured into cold water (250 mL). And the reaction products were extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with D. I. water (100 mL), and then dried with anhydrous Na_2SO_4 to get a black oily crude product. The oily crude product was further purified with flash-column chromatography on aluminum oxide (Al_2O_3; n-Hexane/EtOAc, v/v = 2:1), giving rise to the white powder product as desired. Yield: 0.962 g (72%). Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.00; H, 7.84; N, 8.38%. Found: C, 78.91; H, 7.92; N, 8.31%. FT-IR (KBr, cm^{-1}): 2919 (w), 2359 (w), 1618 (m), 1610 (m), 1561 (m), 1507 (w), 1484 (w), 1451 (m), 1420 (s), 1309 (m), 1277 (s),

1257 (s), 1217 (m), 1150 (m), 1119 (s), 1094 (m), 1075 (m), 1032 (w), 984 (w), 967 (w), 898 (w), 858 (m), 808 (w), 764 (vs), 742 (vs), 773 (w), 609 (w), 417 (w), 410 (w). ^{1}H NMR (CDCl$_3$, 400 MHz): δ(ppm) 9.17 (m, 1H, -Phen), 8.98 (m, 1H, -Phen), 8.68 (m, 1H, -Phen), 8.09 (m, 1H, -Phen), 7.61 (m, 1H, -Phen), 7.52 (m, 1H, -Phen), 6.95 (s, 1H, -Phen), 4.41 (m, 1H, -C*-H (1S) of Ch), 2.37 (d, 1H, -C*-H (2R) of Ch), 2.23 (m, 1H, -C*-H (5S) of Ch), 1.81 (m, 2H, -CH$_2$ of Ch), 1.71 (m, 2H, -CH$_2$ of Ch), 1.25 (m, 2H, -CH$_2$ of Ch), 1.18 (d, 1H, -CH(CH$_3$)$_2$), 0.97 (s, 3H, -CH$_3$), 0.95 (s, 3H, -CH$_3$), 0.78 (d, 3H, -CH$_3$). $[\alpha]_D^{25}$ = 56.0±0.1° (in THF; c = 0.05 g/ml).

Synthesis of the chiral organo-Sm^{3+} complex [Sm(tta)$_3$(D-Phen)]

To a stirred solution of **D-Phen** (67 mg, 0.2 mmol) in absolute MeOH (10 ml), another solution of the synthesized precursor [Sm(tta)$_3$(H$_2$O)$_2$] (170 mg, 0.2 mmol) in absolute MeOH (10 ml) was added, and the final mixture was further refluxed for 5 h. After cooling to room temperature, the yellow solution was filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature, and the pale-yellow microcrystalline product was obtained in a few weeks. For **[Sm(tta)$_3$(D-Phen)]**: Yield: 0.154 g (67%). Anal. Calcd for C$_{46}$H$_{38}$N$_2$O$_7$S$_3$F$_9$Sm: C, 48.11; H, 3.34; N, 2.44%. Found: C, 48.02; H, 3.39; N, 2.34%. FT-IR (KBr, cm^{-1}): 2928 (w), 1685 (w), 1622 (w), 1597 (s), 1537 (m), 1504 (w), 1462 (w), 1433 (w), 1354 (w), 1302 (s), 1246 (w), 1232 (s), 1191 (s), 1134 (vs), 1100 (w), 1084 (w), 1058 (w), 1034 (w), 1012 (w), 982 (w), 932 (w), 840 (w), 782 (m), 737 (m), 716 (m), 682 (m), 642 (s), 598 (w), 584 (w), 524 (w), 458 (w), 420 (w). ESI-MS (MeCN, m/z): 1149.35 (100%), [M-H]$^+$.

Synthesis of the chiral organo-La^{3+} complex [La(tta)$_3$(D-Phen)]

The synthesis of the chiral complex **[La(tta)₃(D-Phen)]**was adopted in the same way as the chiral complex **[Sm(tta)₃(D-Phen)]**except that the complex precursor [La(tta)$_3$(H$_2$O)$_2$] (158 mg, 0.2 mmol) instead of [Sm(tta)$_3$(H$_2$O)$_2$] (170 mg, 0.2 mmol) was used. For **[La(tta)₃(D-Phen)]**: Yield: 0.156 g (69%). Anal. Calcd for C$_{46}$H$_{38}$N$_2$O$_7$S$_3$F$_9$La: C, 48.60; H, 3.37; N, 2.46%. Found: C, 48.52; H, 3.42; N, 2.44%. FT-IR (KBr, cm^{-1}): 2930 (w), 2357 (w), 1682 (w), 1621 (w), 1598 (s), 1536 (m), 1506 (w), 1461 (w), 1434 (w), 1354 (w), 1304 (s), 1245 (w), 1228 (s), 1184 (s), 1134 (vs), 1100 (w), 1083 (w), 1058 (w), 1033 (w), 1014 (w), 981 (w), 932 (w), 840 (w), 783 (m), 735 (m), 714 (m), 679 (m), 641 (s), 580 (w), 519(w), 490 (w), 460 (w), 418 (w).^{1}H NMR (400 MHz, CDCl$_3$):δ(ppm) 9.57 (m, 1H, -Phen), 9.33 (m, 1H, -Phen), 8.76 (m, 1H, -Phen), 8.17 (m, 1H, -Phen), 7.76 (m, 1H, -Phen), 7.66 (m, 1H, -Phen), 7.54 (d, 3H, -Th), 7.45 (d, 3H, -Th), 6.99 (t, 3H, -Th), 6.93 (s, 1H, -Ph), 6.14 (s, 3H, -HC=C of *β*-diketonate), 4.38 (m, 1H, -C*-H (1S) of Ch), 2.28 (m, 1H, -C*-H (2R) of Ch), 2.16 (m, 1H, -C*-H (5S) of Ch), 1.81 (m, 2H, Ch), 1.75 (m, 2H, Ch), 1.58 (s, 1H, Ch), 1.25 (m, 2H, Ch), 0.96 (d, 3H, -CH$_3$), 0.94 (d, 3H, -CH$_3$), 0.75 (d, 3H, -CH$_3$). ESI-MS (MeCN, *m/z*): 1137.08 (100%), [M-H]$^+$.

Electronic structure calculations

To gain further insight into the photophysical behaviors ofthe chiral complex **[Sm(tta)₃(D-Phen)]**, time-dependent density functional theory (TD-DFT) calculations of the corresponding *anti*-magnetic while isostructural **[La(tta)₃(D-Phen)]** complex were carried out for simplification. The molecular structure was optimized at the ground state (S$_0$) in the gas phase. DFT calculations were conducted with the popular B3LYP functional theory. The 6-31G(d,p) basis set was applied for C, H, N, O, S, Fatoms, while effective core potentials

employed for La atom were based on a LanL2DZ basis set.[4-5] The excited states' energies of the chiral La(III)-complex were computed by TD-DFT based on all the ground-state (S_0) geometries. All calculations were carried out with Gaussian 09, Revision D.01 software package.[6] The electron density diagrams of molecular orbitals were obtained with the ChemOffice 2010 graphics program.

Cyclic voltammetry (CV) measurement

CV measurement was performed on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional three-electrode cell using an $Ag/AgNO_3$ (0.1 M) reference electrode, Pt carbon working electrode of 2 mm in diameter, and a platinum wire counter electrode. CV of the sample was performed in nitrogen-saturated dichloromethane containing 0.1 M Bu_4NPF_6 as supporting electrolyte. The CV was measured at a scan rate of 100 $mV \cdot s^{-1}$. The HOMO and the LUMO energy levels of each complexare calculated according to the following equations,[7] $E_{HOMO} = -(E_{ox}^{on} + 4.8)$ eV, $E_{LUMO} = -(E_{red}^{on} + 4.8)$ eV, and where E_{ox}^{on} is the recorded onset oxidation potential of the complex, and E_{red}^{on} is the recorded onset reduction potential of the complex. The HOMO and LUMO energy levels for the other used materials were obtained from the literatures.[8]

CP-WOLED fabrication and testing

The CP-WOLED was fabricated on ITO (Indium tin oxide) coated glass substrates with a sheet resistance of 20 Ω per square. Patterned ITO coated glass substrates were washed with acetone, detergent, D. I. water and isopropanol in an ultrasonic bath. After being exposed

under oxygen plasma for 20 min, PEDOT:PSS from water solution was spin-coated (at 2000 rpm) on the substrate and followed by drying in a vacuum oven at 140 °C for 20 min, giving a film of 40 nm thickness. The chlorobenzene solution (20 mg/mL) of the mixture of PVK, PBD and **[Sm(tta)₃(D-Phen)]** in 65:30:5 weight ratios as the emitting layer (EML) was prepared under an N_2 atmosphere and spin-coated (at 4000 rpm) on the PEDOT:PSS layer with a thickness of 80 nm. The TPBi layer (30 nm) and the following BCP layer (10 nm) were thermally deposited onto the EML, respectively. Finally, a thin layer (1 nm) of LiF followed by 100 nm thickness Al capping layer was deposited onto the substrate under vacuum of 5×10^{-6} Pa. The typical active area of the four devices is 9 mm^2. Current density (J)-voltage (V)-luminance (L) was collected using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The electroluminescent spectra were measured by a PR655 spectrometer. The eternal quantum efficiency (η_{EQE}) values were determined by a Si photodiode with calibration in an integration sphere (IS080, Labsphere).

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Table S1. Frontier orbital energy and electron density distribution for the chiral complex **[La(tta)$_3$(D-Phen)]** on the basis of its optimized S$_0$ geometry

Orbital	Contribution of metal d_π orbitals and π orbitals of ligand to MOs (%)				
	La	Htta-1	Htta-2	Htta-3	D-phen
LUMO+2	0.31	5.10	8.09	0.11	86.37
LUMO+1	2.28	33.60	45.47	5.96	12.67
LUMO	2.63	1.51	0.78	0.41	94.64
HOMO	0.33	12.16	32.47	53.96	1.06
HOMO-1	0.88	50.03	12.54	36.06	0.47
HOMO-2	1.88	36.65	53.02	7.88	0.55

Table S2. Calculated orbital transition analyses for the chiral complex **[La(tta)₃(D-Phen)]** by TD-DFT calculations with the IFCT (inter-fragment charge transfer) analyses at the B3LYP level

State	λ (nm)	E (eV)	Oscillator (f)	transition (contrib.) (%)		Assignment (%)	
$S_0 \rightarrow S_1$	388	3.194	0.011	H-1→L (7.6);	H→L (89.6)	^{1}ILCT: 1.69	^{1}MLCT: 0.49
						^{1}LLCT: 95.19	^{1}LMCT: 2.61
$S_0 \rightarrow S_2$	381	3.251	0.004	H-2→L (3.79);	H-1→L (88.4);	^{1}ILCT: 1.63	^{1}MLCT: 0.68
				H→L (6.14)		^{1}LLCT: 95.07	^{1}LMCT: 2.61
$S_0 \rightarrow S_3$	363	3.407	0.004	H-2→L (90.4);	H-1→L (2.56);	^{1}ILCT: 1.26	^{1}MLCT: 1.75
				H→L (3.2)		^{1}LLCT: 94.4	^{1}LMCT: 2.58
$S_0 \rightarrow T_1$	505	2.453	0.000	H-2→L+1 (14.5);	H-2→L+2 (2.5);		
				H-2→L+3 (23.2);	H-1→L+4 (2.6);	^{3}ILCT: 75.83	^{3}MLCT: 0.97
				H→L+1 (11.7);	H→L+1 (23.1);	^{3}LLCT: 21.31	^{3}LMCT: 1.88
				H→L+2 (3.5);	H→L+3 (8.9)		

Table S3. The g_{PL} values of the chiral complex **[Sm(tta)₃(D-Phen)]** checked upon photo-excitation.

| Transition	Wavelength (nm)	g_{PL}
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	560 nm	+0.009
$^4G_{5/2}{}^6 \rightarrow H_{7/2}$	595 nm	-0.005
$^4G_{5/2} \rightarrow {}^6H_{9/2}$	643 nm	-5.92×10^{-4}
$^4G_{5/2} \rightarrow {}^6H_{11/2}$	711 nm	-8.80×10^{-4}

Table S4. CIE (Commission International De L'Eclairage) coordinates, CCTs (correlated color temperatures) and CRI (color render indices) of the **[Sm(tta)₃(D-Phen)]**-doped CP-WOLED upon different applied bias voltages

| Voltage (V)	CIE coordinate x,y	CCT (K)	CRI	Color
7.0	0.268, 0.203	2625	96	White
8.0	0.272, 0.206	2625	96	White
9.0	0.277, 0.211	2625	96	White
10.0	0.285, 0.211	2631	96	White
11.0	0.288, 0.222	2631	97	White
12.0	0.290, 0.224	2631	97	White
13.0	0.297, 0.224	2625	96	White

Table S5. The g_{EL} values of the **[Sm(tta)₃(D-Phen)]**-doped CP-WOLED checked upon electricity-driving.

| Transition	Wavelength (nm)	g_{EL}
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	560 nm	+0.011
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	595 nm	-0.004
$^4G_{5/2}{}^6 \rightarrow H_{9/2}$	643 nm	-5.98×10^{-4}
$^4G_{5/2}{}^6 \rightarrow H_{11/2}$	711 nm	-0.002

Scheme S1. Synthetic scheme of the chiral ancillary ligand **D-Phen** and its two chiral organo-Ln^{3+} complexes **[Sm(tta)$_3$(D-Phen)]** and **[La(tta)$_3$(D-Phen)]**.
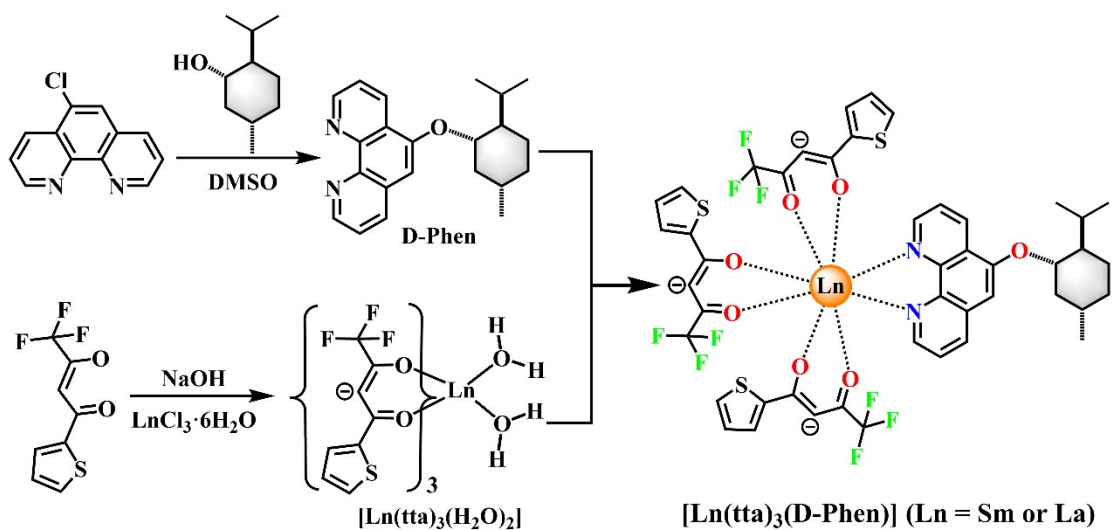
Figure S1. TG (thermogravimetric) curves ofthetwo chiral organo-Ln³⁺ complexes
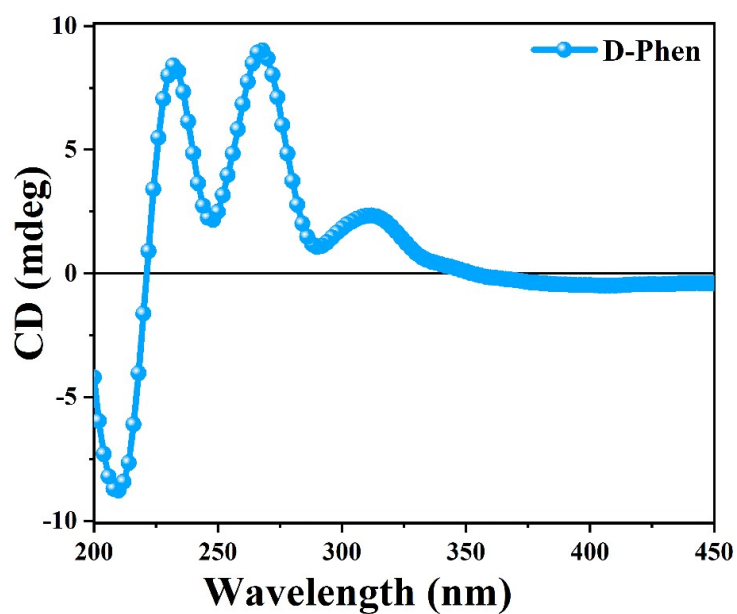
[Sm(tta)₃(D-Phen)] and [La(tta)₃(D-Phen)].
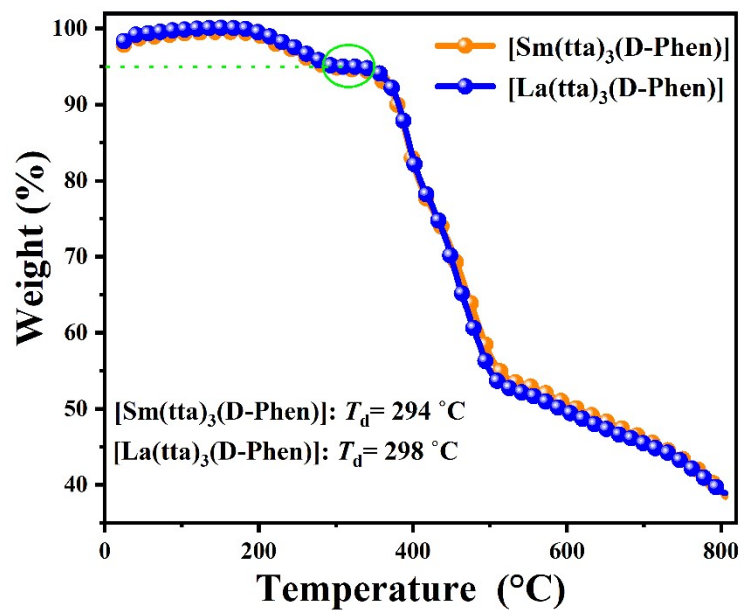
Figure S2. UV-visible absorption spectra of the chiral ancillary ligand **D-Phen** and the **Htta** ligand in degassed CH_2Cl_2 solution at room temperature.
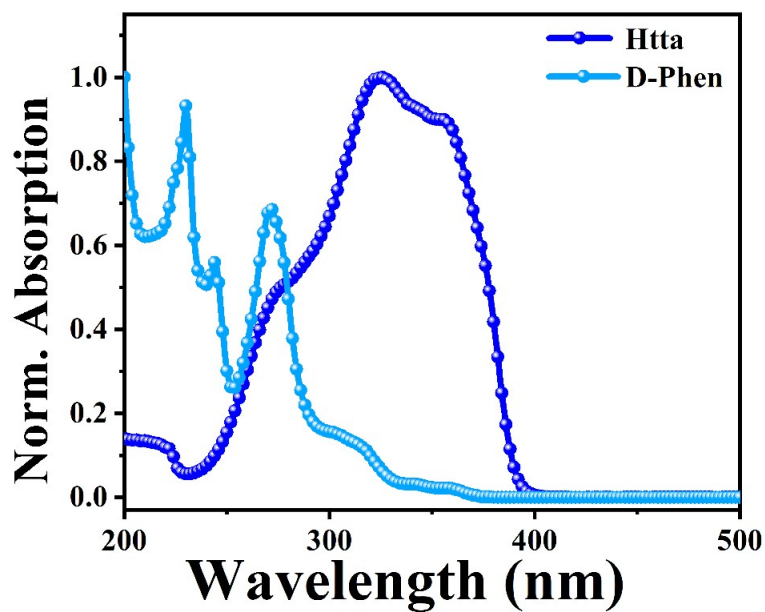
Figure S3. Energy levels and the possible energy transfer for the effective sensitization of Sm^{3+}-centered high-purity orange-light or the electroluminescent white-light from the chiral complex [**Sm(tta)₃(D-Phen)**].
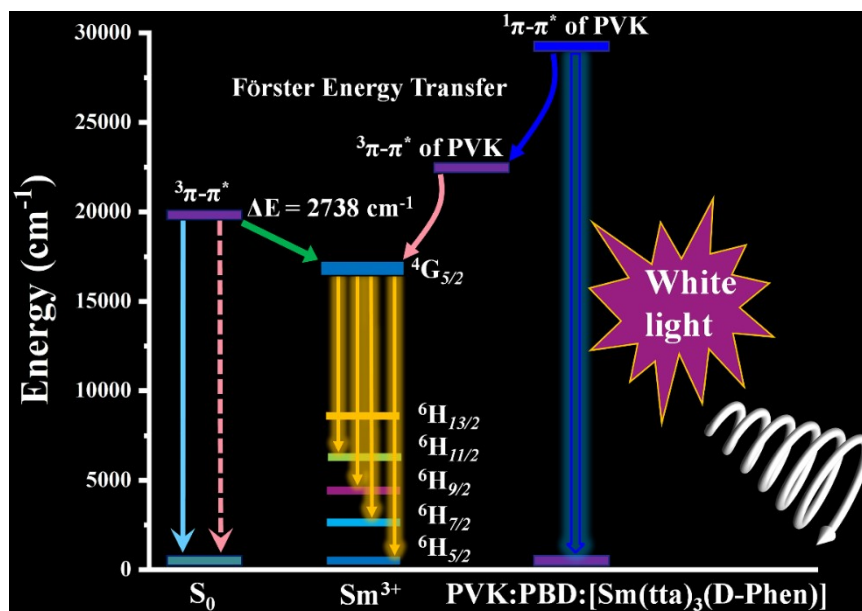
Figure S4. CD spectrum of the chiral ancillary ligand **D-Phen** in degassed CH_2Cl_2 solution at room temperature.

Figure S5. CV (cyclic voltammetry) curve of the chiral complex **[Sm(tta)₃(D-Phen)]** recorded

versus Fc⁺/Fc in degassed MeCN solution at room temperature under a N₂ atmosphere (scan

rate = 100 mV/s).