Supporting Information

Iridium(III) phosphorescent complexes with dual stereogenic centers: single crystal, electronic circular dichroism evidence and circularly polarized luminescence property

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1. Material and Syntheses

The mass spectra were recorded by an electrospray ionization mass spectrometer (LCQ fleet, Thermo Fisher Scientific). High-resolution mass spectra were recorded on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS instrument. ¹H NMR spectra were measured on a Bruker AM 300 spectrometer.

All the starting reactants and solvents were used as commercial grade without further purifications. The main ligand dfppy was synthesized according to our former researches by a modified Suzuki cross coupling reaction from 2,4-diflorophenyl boronic acid and 2-bromopyridine.¹ The chloro-bridged dimer complex was synthesized by reacting 2.2 *equiv* of dfppy and 1.0 *equiv* of IrCl₃ in 2-ethoxyethanol at 120 °C for 12 h. The resulting suspension was poured into excess water and the formed yellow solid was isolated by filtering and used in the following reactions with further purifications. The Schiff base ancillary ligands chty-*S* and chty-*R* were prepared according to the reported method.² 1.0 *equiv* of 2-hydroxybenzaldehyde and 1.0 *equiv* of (*R*/*S*)-(±)-1-phenylethylamine were stirred in THF with the presence of 10 *equiv* of anhydrous sodium sulfate. The resulting white solid was isolated by filtering and washed by aether. The formed ancillary ligands were used without further purifications.

General synthesis of racemic complexes: The chloro-bridged dimer complexes (0.5 mmol, 0.57 g), corresponding ancillary ligand (0.88 mmol, 0.20 g) and potassium carbonate (10 mmol, 1.4 g) were added to 50 ml 2-ethoxyethanol and heated at 120 °C for 12 h. The solvent was removed under vacuum and the raw mixture was extracted by 200 ml CH₂Cl₂. Flash column chromatography (silicon, eluent : ethyl ether/hexane = 1:1 v/v) was performed and the final product was crystalized by slow diffusing of iso-hexane into CH₂Cl₂ solutions. The racemic complexes (Λ/Δ)-(dfppy)₂Ir(chty-*R*) or (Λ/Δ)-(dfppy)₂Ir(chty-*S*) were obtained as yellow cubic crystals.

The separations of isomers with chiral configuration were performed by chiral synthetic HPLC methods. For (Λ/Δ) -(dfppy)₂Ir(chty-*R*), a DAICEL CHIRALPAK IC column (diameter 5 cm, length 25 cm) was employed as stationary phase and a mixture of hexane and CH₂Cl₂ (1:1, v/v) as eluent. The race was set as 60 ml min⁻¹ at 35 °C. For (Λ/Δ) -(dfppy)₂Ir(chty-*S*), a DAICEL CHIRALPAK AD column (diameter 2.5 cm, length 25 cm) was employed as stationary phase and methonal as eluent. The race was set as 20 ml min⁻¹ at 28 °C.

(Λ/Δ)-(dfppy)₂Ir(chty-*R*): Yield: 45% (0.36 g). ESI-MS Calcd: *m*/*z* 798.2 for [M+H]⁺ (C₃₇H₂₇F₄IrN₃O)⁺, found: *m*/*z* 798.3. HR-MS Calcd: *m*/*z* 798.1719 for [M+H]⁺ (C₃₇H₂₇F₄IrN₃O)⁺, found: *m*/*z* 798.1722. For Λ-Ir-*R*, Anal. Calcd. for C₃₇H₂₆F₄IrN₃O: C 55.77, N 5.27, H 3.29; found: C 55.52, N 5.48, H 3.55. ¹H NMR (300 MHz, CDCl₃) δ 8.97 (dd, *J* = 5.8, 0.9 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.17 – 8.14 (m, 1H), 8.12 (s, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.34 (dt, *J* = 6.0, 5.1 Hz, 3H), 7.25 – 7.05 (m, 4H), 6.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.80 – 6.71 (m, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.45 – 6.28 (m, 3H), 5.87 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.60 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.64 (q, *J* = 6.9 Hz, 1H), 1.47 (s, 3H). For Δ-Ir-*R*, Anal. Calcd. for C₃₇H₂₆F₄IrN₃O: C 55.77, N 5.27, H 3.29; found: C 55.60, N 5.51, H 3.57. ¹H NMR (300 MHz, CDCl₃) δ 8.81 (dd, *J* = 5.8, 0.9 Hz, 1H), 8.52 – 8.44 (m, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.12 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.74 (t, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.09 (m, 1H), 7.04 (ddd, *J* = 12.1, 9.1, 4.4 Hz, 3H), 6.93 (t, *J* = 8.6, 2.3 Hz, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 5.83 (dd, *J* = 8.8, 2.3 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.46 – 6.24 (m, 5H), 5.83 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.47 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.16 – 7.09 (m, 1H), 7.04 (ddd, *J* = 12.1, 9.1, 4.4 Hz, 3H), 6.93 (t, *J* = 8.6, 2.3 Hz, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 5.47 (Hz, 3H).

(Λ/Δ)-(dfppy)₂Ir(chty-*S*): Yield: 48% (0.38 g). ESI-MS Calcd: *m*/*z* 798.2 for $[M+H]^+$ (C₃₇H₂₇F₄IrN₃O)⁺, found: *m*/*z* 798.3. HR-MS Calcd: *m*/*z* 798.1719 for $[M+H]^+$ (C₃₇H₂₇F₄IrN₃O)⁺, found: *m*/*z* 798.1720. For Λ-Ir-*S*, Anal. Calcd. for C₃₇H₂₆F₄IrN₃O: C 55.77, N 5.27, H 3.29; found: C 55.49, N 5.57, H 3.52. ¹H NMR (300 MHz, CDCl₃) δ 8.81 (dd, *J* = 5.7, 0.9 Hz, 1H), 8.48 (d, *J* = 5.0 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.12 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.21 (ddd, *J* = 8.7, 6.9, 1.9 Hz, 1H), 7.16 – 6.98 (m, 4H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.46 – 6.25 (m, 5H), 5.83 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.47 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 1.52 (d, *J* = 7.0 Hz, 3H). For Δ-Ir-*S*, Anal. Calcd. for C₃₇H₂₆F₄IrN₃O: C 55.77, N 5.27, H 3.29; found: C 55.45, N 5.60, H 3.59. ¹H NMR (300 MHz, CDCl₃) δ 8.97 (dd, *J* = 5.8, 0.9 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.16 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.21 – 7.13 (m, 3H), 6.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.76 (ddd, *J* = 7.3, 5.9, 1.3 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.41 – 6.28 (m, 3H), 5.88 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.61 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.64 (q, *J* = 7.0 Hz, 1H), 1.58 (s, 3H).



Scheme S1. The synthetic routes of the racemic complexes. (i) $IrCl_3$, 2-Ethoxyethanol, 120 °C, overnight; (ii) K_2CO_3 , 2-Ethoxyethanol, 120 °C, 12 h.



Fig. S1. The chiral HPLC separation reports for (Λ/Δ) -(dfppy)₂Ir(chty-*R*) (left: mixture, middle: peak 1, right: peak 2). The tiny peak followed the second peak at 7.8 min maybe optically inactive impurity which did not influence the *ee* value and can be removed by recrystallization.



Fig. S2. The chiral HPLC separation reports for (Λ/Δ) -(dfppy)₂Ir(chty-*S*) (left: mixture, middle: peak 1, right: peak 2).

2. Steady state photophysical measurements

The UV-Vis absorption spectra of all the isolated isomers were measured in CH_2Cl_2 solutions at a concentration of 1×10^{-5} mol L⁻¹ under 298 K on a Shimadzu UV-3100 spectrometer. The emission spectra at 298 K and 77K were measured in 5×10^{-5} mol L⁻¹ DCM solutions on a Hitachi F-4600 spectrophotometer.

Common d	2 ^{max}	- M-11	Emission 298K		Emission 77K	
Compound	nabs nm	E M · CM ·	λ_{PL}^{max} nm	FWHM nm		FWHM nm
Λ -(dfppy) ₂ Ir(chty- <i>R</i>)	248	51 300	572	104	520	81
Δ -(dfppy) ₂ Ir(chty- <i>R</i>)	248	52 200	579	107	535	89
Λ -(dfppy) ₂ Ir(chty-S)	248	48 900	577	112	537	89
Δ -(dfppy) ₂ Ir(chty-S)	248	53 100	571	103	532	92

Table S1 The photophysical properties for all the isomers

3. Single crystal measurements and data

Single crystal samples that suitable for the X-ray diffraction measurements were obtained by the slow diffusion of iso-hexane into the CH₂Cl₂ solutions of each isomer. A Siemens SMART CCD diffractometer (Bruker Daltonic Inc.) was used to collect the crystallographic data at room temperature using graphite-monochromated Mo K α radiation (λ =0.71073 Å). The crystal cell parameters were retrieved with SMART software and refined using SAINT on all observed reflections.³ Absorption corrections were performed using SADABS supplied by Bruker.⁴ The SHELXTL software package was used to calculate and determine the structure.⁵ Initial atomic positions were located using Patterson method and the structures of the complexes were resolved anisotropically by the least-squares method. The hydrogen atoms were fixed in the calculated positions and refined as riding atoms with uniform U_{iso} values.

Complex	Λ -(dfppy) ₂ Ir(chty- <i>R</i>)	Δ -(dfppy) ₂ Ir(chty- <i>R</i>)	Λ -(dfppy) ₂ Ir(chty-S)	Δ -(dfppy) ₂ Ir(chty-S)
Formula	C37H26N3OF4Ir	C ₃₇ H ₂₆ N ₃ OF ₄ Ir	C ₃₇ H ₂₆ N ₃ OF ₄ Ir	C ₃₇ H ₂₆ N ₃ OF ₄ Ir
Formula	796.81	796.81	796.81	796.81
weight				
Crystal	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
system				

Table S2. The single crystal diffraction data and refinement parameters

Space	$P2_{1}2_{1}2_{1}$	$P2_1$	$P2_1$	$P2_{1}2_{1}2_{1}$
group				
<i>a</i> [Å]	9.8067(9)	10.0391(13)	10.1586(4)	9.696(4)
<i>b</i> [Å]	12.3224(11)	16.249(2)	16.4188(7)	12.172(5)
<i>c</i> [Å]	27.064(2)	18.799(2)	18.9530(8)	26.736(12)
α [deg]	90.00	90.00	90.00	90.00
β [deg]	90.00	99.547(2)	99.3820(10)	90.00
γ [deg]	90.00	90.00	90.00	90.00
Volume	3270.4(5)	3024.1(7)	3118.9(2)	3155(2)
Ζ	4	4	4	4
R_I	0.0328	0.0505	0.0200	0.0536
wR_2	0.0812	0.0967	0.0486	0.1493
GoF	1.041	0.996	0.890	1.088
Flack	0.017(10)	-0.001(8)	0.011(4)	0.00
index				
CCDC	1033812	1033811	1033814	1033813
No.				
$\sum_{R_{I}} \left F_{O} - F_{C} / F_{O} \right wR2 = \left[\sum_{w} w(F_{O} - F_{C})^{2} / \sum_{w} w(F_{O})^{2} \right]^{1/2}$				

 Table S3. The selected bond lengths and bond angles of the four isomers

Complex	Λ -(dfppy) ₂ Ir(chty- <i>R</i>)	Δ -(dfppy) ₂ Ir(chty- <i>R</i>)	Λ -(dfppy) ₂ Ir(chty-S)	Δ -(dfppy) ₂ Ir(chty-S)	
Bond length $[Å]$					
Ir-N1	2.053(5)	2.052(8)	2.051(3)	2.063(9)	
Ir-N2	2.045(5)	2.023(9)	2.045(3)	2.034(9)	
Ir-N3	2.183(5)	2.155(6)	2.158(3)	2.185(10)	
Ir-C1	2.004(6)	2.019(9)	2.019(4)	1.979(13)	
Ir-C2	1.999(6)	2.012(9)	1.989(4)	1.987(12)	
Ir-O1	2.130(4)	2.120(6)	2.123(3)	2.127(8)	
Bond Ang	le [deg]				
N1-Ir-	173.3(2)	174.3(3)	174.72(14)	173.6(4)	
N2					
C1-Ir-C2	89.1(3)	89.0(3)	88.03(16)	88.1(5)	
N1-Ir-C1	81.1(2)	81.2(4)	79.80(17)	81.0(4)	
N2-Ir-C2	79.8(2)	81.3(4)	80.53(16)	79.5(4)	
O1-Ir-	87.93(17)	88.3(3)	88.1(1)	88.4(3)	
N3					
N1-Ir-	93.35(19)	94.9(3)	97.17(13)	93.1(4)	
N3					
N2-Ir-	93.7(2)	94.3(3)	94.57(13)	94.0(4)	
01					



Fig. S3. The intermolecular π - π stacking diagrams of Λ -(dfppy)₂Ir(chty-*R*) (left) and Δ -(dfppy)₂Ir(chty-*S*) (right).

4. Theoretical Calculations

All the DFT and TD-DFT calculations were carried out using Gaussian 09 software package.⁶ The initial structures were created according to the single crystal results. The ground state geometry optimizations with frequent calculations for all the complexes were performed using B3LYP exchange-correlation functional. On the basis of the optimized structures, vertical transition energy calculations were carried out with M062x functional. For all the calculations, a combination of basis sets, Lanl2dz for iridium and 6-31G(d,p) for the others, were employed and the solvent effect are considered by C-PCM model in CH₂Cl₂. The simulated ECD spectra were visualized by GaussSum software.









Fig. S5 The simulated ECD spectra (black) and the corresponding experimental data (red).

5. Electronic circular dichroism spectra and circular polarized luminescent spectra

The electronic circular dichroism (ECD) spectra were measured on a Jasco J-810 circular dichroism spectrometer with 'standard' sensitivity. The scan speed was set as 100 nm min⁻¹ with 0.5 nm resolution and a respond time of 1.0 s. The unit of the ECD spectra is transformed from mdeg (θ) into $\Delta \varepsilon$ by using the equation: $\Delta \varepsilon$ (L mol⁻¹ cm⁻¹)=ellipticity (mdeg)/[32980×*b* (cm)×*c* (mol L⁻¹)], where *b* is the length of the light path and *c* is the concentration of the samples. The magnitude of circular polarization in the ground state is defined as $g_{CD}=2\times(\varepsilon_L-\varepsilon_R) / (\varepsilon_L+\varepsilon_R)$, where ε_L and ε_R represent the extinction coefficients for left and right circularly polarized light. Experimentally, the anisotropy factors *g*CD is calculated as $\Delta \varepsilon/\varepsilon=[ellipticity/(32980)]/total absorbance. The circularly polarized luminescence (CPL) spectra wre measured on a Jasco CPL-200 spectrophotometer with 'Standard' sensitivity at 50 nm min⁻¹ scan speed with 0.5 nm resolution and respond time of 8 s. The CPL signals are presented in <math>\Delta I$ and no corrections are applied on the CPL 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 $g_{PL}=2\times(I_L-I_R)/(I_L+I_R)$. Experimentally, the value of is calculated as $\Delta I/I = [ellipticity/(32980)/In10)]/unpolarised PL intensity.⁷$



Fig. S6 The CPL spectra depicted along ΔI (left) and g_{LUM} (right) as the function of the wavelength.

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