Supporting Information

The Taji and Eight Trigrams Chemistry Philosophy of Chiral Iridium(III) Complexes with Triplex Stereogenic Centers

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1. Material and Measurements

The mass spectra were recorded by an electrospray ionization (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) and Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (autoflex TOF/TOF, Bruker Daltonics), High-resolution mass spectra were recorded on a micrOTOF-Q III instrument. ¹H NMR spectra were measured on a Bruker AM 400 spectrometer. Absorption spectra were measured on a UV-3100 spectrophotometer and photoluminescence spectra were obtained from a Hitachi F-4600 photoluminescence spectrophotometer. The emission spectra at 77K were measured on Hitachi F-4600 spectrophotometer. The luminescence quantum efficiencies were calculated by a comparison of the emission intensities (integrated areas) of a standard sample (fac- $Ir(ppy)_3$) the sample. The decay lifetimes were measured with and an Edinburgh Instruments FLS-980 fluorescence spectrometer.

The starting reactants and solvents were used as commercial grade without further purifications. All solvents were purified in our laboratory carefully and the reactions were performed under Argon.

2. Material and Syntheses

The cyclometalated and ancillary ligand were started from optically pure S and R isomers preparing according to the reported method.^{1,2}

First, IrCl₃ (0.45g 1.5 mmol) and *R*-pppy (0.8g 3 mmol) were dissolved in 2ethoxyethanol (15 ml) and water (5 ml) which was heating at 100 °C for 10 h and the Ir dimer was suspended in the solvent. The yellow solid precipitate was filtered and dried in vacuo. Then the yellow solid precipitate (0.5 g 0.3 mmol) and *S*-Kedp (0.15 g 0.65 mmol) in 2-ethoxyethanol (10 ml) was refluxed for another 10 h. The solvent was evaporated at low pressure and the crude product was purified by column chromatography (silica gel, ethyl acetate: petroleum ether 1:4 (v/v)) to get the luminous yellow solid which combined the racemic complexes (Δ/Λ)-(*R*-pppy)₂Ir(*S*edp). And other three couple racemic complexes were prepared in the same way.

The separations of isomers with chiral configuration were performed by chiral

HPLC. For (Λ/Δ) -(R-pppy)₂Ir(*S*-edp) a DAICEL CHIRALCEL OZ-H column (diameter 5 cm, length 25 cm) was employed as stationary phase and pure MeOH as eluent. The race was set as 60 ml min⁻¹ at 35 °C. For (Λ/Δ) -(S-pppy)₂Ir(*R*-edp) a DAICEL CHIRALPAK IC column (diameter 2.5 cm, length 25 cm) was employed as stationary phase and Hexane and IPA (70 :30,v/v) as eluent. The race was set as 15 ml min⁻¹ at 35 °C.



Scheme 1. Chemical structures and synthetic route of complexes (Δ/Λ) -(R-pppy)₂Ir(S-edp).



Fig. S1. The chiral HPLC separation reports for (Λ/Δ) -(R-pppy)₂Ir(*S*-edp) (left: mixture, middle: peak 1, right: peak2).



Fig. S2. The chiral HPLC separation reports for (Λ/Δ) -(S-pppy)₂Ir(*R*-edp) (left: mixture, middle: peak 1, right: peak2).

 (Δ/Λ) -(*R*-pppy)₂Ir(*S*-edp): Yield 60%. ESI-MS, Calculated: m/z 880.34 for $[M+H]^+$ (C₄₇H₄₉IrN₃O₂)⁺ found: m/z 880.25. HR-MS Calculated: 879.3376 for M $(C_{47}H_{48}IrN_3O_2)$, found: 879.3479. For Δ -(*R*-pppy)₂Ir(*S*-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.034. ¹H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.06 (s, 1H), 7.60 (d, J = 1.6 Hz, 2H), 7.55 (dd, J = 8.1, 1.9 Hz, 1H), 7.48 (t, J = 6.6 Hz, 2H), 7.06 (ddd, J = 8.6, 6.9, 1.8 Hz, 1H), 6.75 (dt, J = 12.0, 7.1 Hz, 2H), 6.61 (dt, J = 12.1, 7.3 Hz, 3H), 6.31 (t, J = 7.5 Hz, 2H), 6.17 (d, J = 7.1Hz, 1H), 4.05 (dt, J = 7.6, 3.8 Hz, 1H), 3.92 (t, J = 8.6 Hz, 1H), 3.18 (dd, J = 14.7, 12.0 Hz, 4H), 3.09 - 3.02 (m, 1H), 2.78 (t, J = 5.4 Hz, 1H), 2.63 (ddd, J = 12.5, 9.7, 5.3 Hz, 3H), 2.32 (ddd, J = 11.7, 7.3, 4.3 Hz, 2H), 1.39 (d, J = 3.5 Hz, 6H), 1.25 (s, 2H), 1.18 - 1.08 (m, 2H), 0.76 (d, J = 5.9 Hz, 6H), 0.35 (t, J = 7.3 Hz, 3H). For Λ -(*R*pppy)₂Ir(S-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.018. 1H NMR (400 MHz, CDCl3) & 8.70 (s, 1H), 7.88 (s, 1H), 7.69 (s, 1H), 7.54 (t, J = 8.7 Hz, 3H), 7.44 (d, J = 7.5 Hz, 1H), 6.98 (dd, J = 11.8, 4.9 Hz, 1H), 6.78 (t, J = 7.3 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 7.1 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 6.50 (d, J = 8.6 Hz, 1H), 6.24 (t, J = 7.3 Hz, 1H), 6.13 (d, J = 7.3 Hz, 1H), 4.28 (t, J = 8.8 Hz, 1H), 4.09 (dd, J = 8.6, 3.6 Hz, 1H), 3.93 - 3.83 (m, 1H), 3.31 - 3.833.18 (m, 2H), 3.14 – 2.99 (m, 2H), 2.85 (t, J = 5.4 Hz, 1H), 2.70 (s, 2H), 2.61 (t, J = 5.3 Hz, 1H), 2.31 (d, J = 26.5 Hz, 2H), 1.37 (d, J = 10.1 Hz, 8H), 0.67 – 0.49 (m, 5H), 0.29 (s, 3H), 0.23 (t, J = 7.4 Hz, 3H).

 (Λ/Δ) -(S-pppy)₂Ir(R-edp): Yield 50%. ESI-MS, Calculated: m/z 880.34 for

 $[M+H]^+$ (C₄₇H₄₉IrN₃O₂)⁺ found: m/z 880.17. HR-MS Calculated: 879.3376 for M $(C_{47}H_{48}IrN_3O_2)$, found: 879.3377. For Δ -(S-pppy)₂Ir(R-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 878.978. ¹H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.88 (s, 1H), 7.69 (s, 1H), 7.54 (dt, ^J = 7.9, 4.0 Hz, 3H), 7.44 (dd, J = 7.7, 1.0 Hz, 1H), 6.98 (ddd, J = 8.7, 6.8, 1.9 Hz, 1H), 6.81 - 6.74 (m, 2H),6.70 (td, *J* = 7.4, 1.3 Hz, 1H), 6.65 (td, *J* = 7.4, 1.3 Hz, 1H), 6.55 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.49 (dd, J = 8.6, 0.8 Hz, 1H), 6.22 (dt, J = 16.2, 4.6 Hz, 1H), 6.13 (dd, J = 7.5, 1.0 Hz, 1H), 4.29 (dd, J = 11.7, 6.0 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.87 (ddt, J = 9.9, 6.5, 3.4 Hz, 1H), 3.31 - 3.18 (m, 2H), 3.08 (dt, J = 40.7, 10.3 Hz, 2H), 2.85 (t, J = 5.4Hz, 1H), 2.75 - 2.66 (m, 2H), 2.61 (t, J = 5.4 Hz, 1H), 2.38 - 2.33 (m, 1H), 2.30 - 2.33 (m, 2H), 2.302.24 (m, 1H), 1.35 (dd, J = 14.9, 10.0 Hz, 8H), 0.65 (d, J = 8.7 Hz, 3H), 0.62 - 0.47 (m, 2H), 0.29 (s, 3H), 0.23 (t, J = 7.4 Hz, 3H). For Λ -(S-pppy)₂Ir(R-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.051. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.42 \text{ (s, 1H)}, 8.06 \text{ (s, 1H)}, 7.60 \text{ (s, 2H)}, 7.55 \text{ (d, } J = 8.0 \text{ Hz}, 1\text{H}),$ 7.48 (t, J = 7.3 Hz, 2H), 7.06 (t, J = 7.0 Hz, 1H), 6.82 – 6.70 (m, 2H), 6.61 (dt, J =22.6, 7.1 Hz, 3H), 6.32 (d, J = 6.7 Hz, 2H), 6.17 (d, J = 7.3 Hz, 1H), 4.12 – 4.00 (m, 1H), 3.92 (t, J = 8.5 Hz, 1H), 3.20 (dd, J = 23.7, 20.0 Hz, 4H), 3.06 (s, 1H), 2.78 (d, J= 5.0 Hz, 1H), 2.70 - 2.57 (m, 3H), 2.32 (s, 2H), 1.39 (d, J = 2.1 Hz, 6H), 1.25 (s, 2H), 1.14 (d, J = 8.5 Hz, 2H), 0.75 (t, J = 11.5 Hz, 6H), 0.35 (t, J = 7.0 Hz, 3H).

(Δ/Λ)-(*R*-pppy)₂Ir(*R*-edp): Yield 55%. ESI-MS, Calculated: m/z 880.34 for [M+H] + (C₄₇H₄₉IrN₃O₂)⁺ found: m/z 880.17. HR-MS Calculated: 879.3376 for M (C₄₇H₄₈IrN₃O₂), found: 879.3395. For Δ-(*R*-pppy)₂Ir(*R*-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.117. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.88 (s, 1H), 7.66 – 7.59 (m, 2H), 7.57 (s, 1H), 7.47 (dd, J =13.8, 7.6 Hz, 2H), 7.08 (ddd, J = 8.6, 6.8, 1.9 Hz, 1H), 6.77 (dd, J = 16.2, 7.6 Hz, 2H), 6.71 – 6.64 (m, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.30 (dd, J = 17.3, 7.3 Hz, 2H), 6.08 (d, J = 7.3 Hz, 1H), 4.17 – 4.10 (m, 1H), 3.96 – 3.86 (m, 1H), 3.33 – 3.04 (m, 5H), 2.80 (t, J = 5.4 Hz, 1H), 2.71 – 2.60 (m, 3H), 2.36 – 2.27 (m, 2H), 1.43 (s, 3H), 1.40 (s, 3H), 1.26 (s, 2H), 0.82 (s, 3H), 0.80 (s, 3H), 0.66 – 0.51 (m, 2H), 0.18 (t, J = 7.4 Hz, 3H). For Λ -(*R*-pppy)₂Ir(*R*-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.018. ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 7.99 (s, 1H), 7.65 (s, 1H), 7.57 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.93 (ddd, *J* = 8.7, 6.9, 1.9 Hz, 1H), 6.82 – 6.75 (m, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.64 – 6.56 (m, 2H), 6.42 (d, *J* = 8.5 Hz, 1H), 6.28 (dd, *J* = 16.6, 7.3 Hz, 2H), 4.12 (dd, *J* = 8.4, 3.5 Hz, 1H), 3.74 (t, *J* = 8.6 Hz, 1H), 3.27 – 3.17 (m, 2H), 3.07 (dd, *J* = 32.6, 9.4 Hz, 2H), 2.97 – 2.92 (m, 1H), 2.82 (t, *J* = 5.5 Hz, 1H), 2.68 (td, *J* = 10.5, 5.5 Hz, 2H), 2.52 (t, *J* = 5.4 Hz, 1H), 2.35 (dd, *J* = 7.0, 4.3 Hz, 1H), 2.29 – 2.24 (m, 1H), 1.53 – 1.44 (m, 2H), 1.39 (s, 3H), 1.30 (s, 3H), 1.26 (s, 2H), 0.65 (s, 3H), 0.37 (t, *J* = 7.4 Hz, 3H), 0.25 (s, 3H).

 (Δ/Λ) -(S-pppy)₂Ir(S-edp): Yield 49%. ESI-MS, Calculated: m/z 880.34 for [M+H] + (C₄₇H₄₉IrN₃O₂)⁺ found: m/z 880.25. HR-MS Calculated: 879.3376 for M $(C_{47}H_{48}IrN_3O_2)$, found: 879.3382. For Δ -(S-pppy)₂Ir(S-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 879.093. ¹H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.00 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.57 (s, 1H), 7.51 (dd, J = 15.5, 7.3 Hz, 2H), 7.44 (dd, J = 8.0, 1.8 Hz, 1H), 6.93 (ddd, J = 8.7, 6.9, 1.9 Hz, 1H), 6.82 - 6.75 (m, 2H), 6.68 (td, J = 7.4, 1.1 Hz, 1H), 6.64 - 6.56 (m, 2H), 6.43 (t, J = 6.1 Hz, 1H), 6.34 - 6.22 (m, 2H), 4.12 (dd, J = 8.4, 3.5 Hz, 1H), 3.74 (t, J= 8.6 Hz, 1H), 3.29 - 3.15 (m, 2H), 3.07 (dd, J = 33.3, 10.3 Hz, 2H), 2.98 - 2.89 (m, 1H), 2.82 (t, J = 5.4 Hz, 1H), 2.73 – 2.63 (m, 2H), 2.52 (t, J = 5.4 Hz, 1H), 2.37 – 2.32 (m, 1H), 2.29 – 2.24 (m, 1H), 1.48 (ddd, J = 20.0, 9.7, 5.6 Hz, 2H), 1.38 (d, J = 7.5 Hz, 3H), 1.30 (s, 3H), 1.26 (d, J = 8.5 Hz, 2H), 0.65 (s, 3H), 0.36 (q, J = 7.0 Hz, 3H), 0.23 (d, J = 19.4 Hz, 3H). For Λ -(S-pppy)₂Ir(S-edp) MALDI-TOF-MS Calculated: 879.338 for M (C₄₇H₄₈IrN₃O₂), founded: 878.971. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.88 (s, 1H), 7.66 – 7.60 (m, 2H), 7.55 (d, J = 14.2 Hz, 1H), 7.47 (dd, J = 13.1, 7.8 Hz, 2H), 7.09 (t, J = 7.0 Hz, 1H), 6.77 (dd, J = 16.9, 7.8 Hz, 2H), 6.68 (dd, J = 11.5, 8.0 Hz, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.30 (dd, J = 15.8, 7.6 Hz, 2H), 6.08 (d, J = 7.5 Hz, 1H), 4.13 (d, J = 5.5 Hz, 1H), 3.91 (s, 1H), 3.31 - 3.06(m, 5H), 2.79 (d, J = 5.1 Hz, 1H), 2.66 (d, J = 5.6 Hz, 3H), 2.34 (s, 2H), 1.43 (s, 3H), 1.40 (s, 3H), 1.26 (s, 2H), 0.82 (s, 3H), 0.80 (s, 3H), 0.65 - 0.50 (m, 2H), 0.18 (t, J = 7.3 Hz, 3H).

3. 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 5×10^{-5} mol L⁻¹ under 298 K on a Shimadzu UV-3100 spectrometer and under 77K on a Hitachi F-4600 spectrophotometer.

Compound	λmax abs nm	Emission 298K		Emission 77K			
		λmax PL nm	FWHM nm	λmax PL nm	FWHM nm	Ф	τ μs
Δ -(<i>R</i> -pppy) ₂ Ir(<i>R</i> -edp)	262	516	58	521	76	0.51	1.61
Λ -(<i>R</i> -pppy) ₂ Ir(<i>R</i> -edp)	262	514	57	521	74	0.51	1.64
Δ -(S-pppy) ₂ Ir(S-edp)	262	514	57	520	74	0.47	1.67
Λ -(S-pppy) ₂ Ir(S-edp)	262	517	57	523	76	0.46	1.62
Δ -(<i>R</i> -pppy) ₂ Ir(<i>S</i> -edp)	262	515	57	523	77	0.46	1.63
Λ -(<i>R</i> -pppy) ₂ Ir(<i>S</i> -edp)	262	519	57	524	72	0.49	1.60
Δ -(S-pppy) ₂ Ir(R-edp)	262	519	57	522	73	0.51	1.66
Λ -(S-pppy) ₂ Ir(R-edp)	262	516	58	523	76	0.53	1.77

Table S1. The photophysical properties for all the isomers







Fig. S3. The lifetime curves of all the isomers in degassed solution at room temperature.

4. Theoretical Calculations

All the TD-DFT and DFT All the DFT and TD-DFT calculations were carried out using Gaussian 16 software package. The initial structures were created according to the GaussView 6. 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 Gaussview 6 software.



Fig. S4. Electronic cloud distribution of Λ -(R-pppy)₂Ir(S-edp) and Δ -(S-pppy)₂Ir(R-edp) (The first and forth picture refer to the LUMOs of Λ -(R-pppy)₂Ir(S-edp) and Δ -(S-pppy)₂Ir(R-edp); The second and third picture refer to the HOMOs of Λ -(R-pppy)₂Ir(S-edp) and Δ -(S-pppy)₂Ir(R-edp))



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

5. Electronic circular dichroism spectra and circular polarized luminescent spectra

The ECD and CPL spectra were measured in the same condition with UV-Vis absorption 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 200 nm min⁻¹ with 1 nm resolution and a respond time of 1.0 s. The unit of the ECD spectra is transformed from mdeg (θ) into $\Delta \epsilon$ by using the equation: $\Delta \epsilon$ (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 circularly polarized luminescence (CPL) spectra were measured on a Jasco CPL-300

spectrophotometer with 'Standard' sensitivity at 200 nm min⁻¹ scan speed with 1 nm resolution and respond time of 1s with 20 times circulation. The CPL signals were presented in ΔI and no corrections are applied on the CPL spectra.



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

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