

Columnar Iridium(III) Metallomesogens Based on Polycatenar Pyridyltetrazolate with Ambipolar Carrier Mobility Behavior

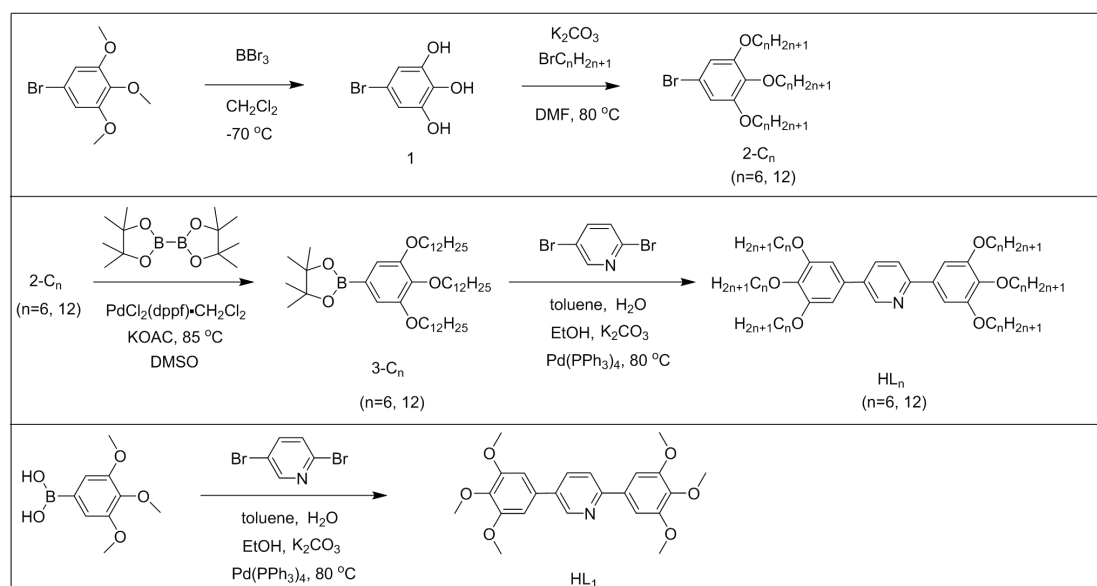
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Table of contents:

1. Synthetic Procedures and Characterization.....	2
2. ¹ H NMR and ¹³ C NMR spectra of all complexes.....	12
3. The crystallographic data, selected bond lengths and angles of Ir-A3.....	19
4. Photophysical data of iridium(III) complexes.....	20
5. Cyclic voltammetry (CV) of complex Ir-B3.....	22
6. Polarized optical micrographs of Ir-C1.....	22
7. DSC curves of iridium(III) complexes.....	23
8. Computed excitation energies and oscillator strengths for complex Ir-A3.....	27
9. DSC data of all complexes.....	28

1. Synthetic Procedures and Characterization



Scheme S1. Synthetic route for cyclometalated ligands.

1-Bromo-3,4,5-trihydroxybenzene (1)

To a stirred solution of 1-bromo-3,4,5-trimethoxybenzene (3.00 g, 12.10 mmol) in dry CH_2Cl_2 (25.00 mL) was added dropwise BBr_3 (10.02 g, 40.08 mmol) at $-70\text{ }^\circ\text{C}$. The mixture was allowed to warm up to room temperature (RT) and stirred overnight. The reaction mixture was then added dropwise a large amount of ice-water, and then extracted with ethyl acetate. The combined organic layers were washed with water three times, and dried over anhydrous MgSO_4 . After filtration and evaporation, the product was recrystallized from ethyl acetate/hexane, and dried under vacuum to afford **1** as an off-white solid (yield = 2.40 g, 97%). This product was used in the next reaction directly without further purification.

1-Bromo-3,4,5-tridodecyloxybenzene (2-C₁₂)

A mixture of **1** (2.00 g, 9.80 mmol), 1-bromododecane (8.02 g, 32.20 mmol), and K_2CO_3 (8.11 g, 58.80 mmol) in dry *N,N*-Dimethylformamide (DMF, 50.00 mL) was vigorously stirred for 36 h at $80\text{ }^\circ\text{C}$. After cooling to RT, the reaction mixture was poured into a large amount of water, and then extracted with CH_2Cl_2 . The combined organic layers were washed with water, and dried over anhydrous MgSO_4 . After filtration and evaporation, the product was purified by silica gel column chromatography (petroleum ether (PE)/ethyl acetate = 10:1, v/v), and dried under vacuum to give 2-C₁₂ as a white solid (yield = 6.78 g, 98%). ^1H NMR (400MHz, CDCl_3): δ 6.67 (s, 2H), 3.97 – 3.87 (m, 6H), 1.83 – 1.68 (m, 6H), 1.45 (d, J = 6.0 Hz, 6H), 1.28 (d, J = 14.7 Hz, 48H), 0.88 (t, J = 6.8 Hz, 9H).

5-bromo-1,2,3-tris(hexyloxy)benzene (2-C₆)

It was synthesised according to the preparation procedure of 2-C₁₂. A colorless oil of 2-C₆ was obtained in 89% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.67 (s, 2H), 3.92 (t,

$J = 6.5$ Hz, 6H), 1.83 – 1.69 (m, 6H), 1.52 – 1.44 (m, 6H), 1.36 – 1.30 (m, 12H), 0.90 (t, $J = 7.0$ Hz, 9H).

4,4,5,5-tetramethyl-2-(3,4,5-tris(dodecyloxy)phenyl)-1,3,2-dioxaborolane (3-C₁₂)

A mixture of 2-C₁₂ (2.00 g, 2.82 mmol), bis(pinacolato)diboron (0.79 g, 3.10 mmol), potassium acetate (0.83 g, 8.47 mmol), [1,1'-bis(diphenylphosphino)-ferrocene]dichloropalladium complex with dichloromethane (1:1) (0.087 g, 0.11 mmol), and dimethyl sulfoxide (DMSO, 60 mL) was stirred at 85 °C for 24 h under nitrogen atmosphere. The resulting mixture was cooled to RT, poured into ice-water (150 mL) and then extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water and dried over anhydrous MgSO₄ and filtrated. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / ethyl acetate (6:1) as the eluent to give 3-C₁₂ as a gray waxy solid (yield = 1.50 g, 70 %). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 2H), 4.03 – 3.95 (m, 6H), 1.84 – 1.69 (m, 6H), 1.45 (dd, $J = 14.7$, 7.2 Hz, 6H), 1.33 (s, 12H), 1.26 (s, 48H), 0.88 (t, $J = 6.8$ Hz, 9H).

4,4,5,5-tetramethyl-2-(3,4,5-tris(hexyloxy)phenyl)-1,3,2-dioxaborolane (3-C₆)

It was synthesised according to the preparation procedure of 3-C₁₂. A colorless oil of 3-C₆ was obtained in 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.01 (s, 2H), 4.01 (dt, $J = 13.1$, 6.6 Hz, 6H), 1.85 – 1.70 (m, 6H), 1.53 – 1.44 (m, 6H), 1.38 – 1.30 (m, 24H), 0.91 (t, $J = 1.7$ Hz, 9H).

2,5-bis(3,4,5-tris(dodecyloxy)phenyl)pyridine (HL₁₂)

To a mixture of 3-C₁₂ (3.00 g, 3.96 mmol), 2,5-dibromopyridine (0.47 g, 1.98 mmol), potassium carbonate (1.1 g, 7.97 mmol) and tetrakis(triphenylphosphine) palladium (0.23 g, 0.20 mmol) was added a degassed mixture of toluene (30 mL), ethanol (15 mL) and water (15 mL). The mixture was refluxed for 24 h under the protection of nitrogen. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / CH₂Cl₂ (2:1) as the eluent to give a white solid (1.32 g, 50 %). ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, $J = 2.2$ Hz, 1H), 7.86 (dd, $J = 8.3$, 2.3 Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 1H), 7.25 (s, 2H), 6.77 (s, 2H), 4.12 – 3.98 (m, 12H), 1.80 (ddd, $J = 20.6$, 12.9, 6.5 Hz, 12H), 1.48 (dd, $J = 13.7$, 6.5 Hz, 12H), 1.29 (d, $J = 21.4$ Hz, 96H), 0.88 (dd, $J = 7.3$, 6.2 Hz, 18H).

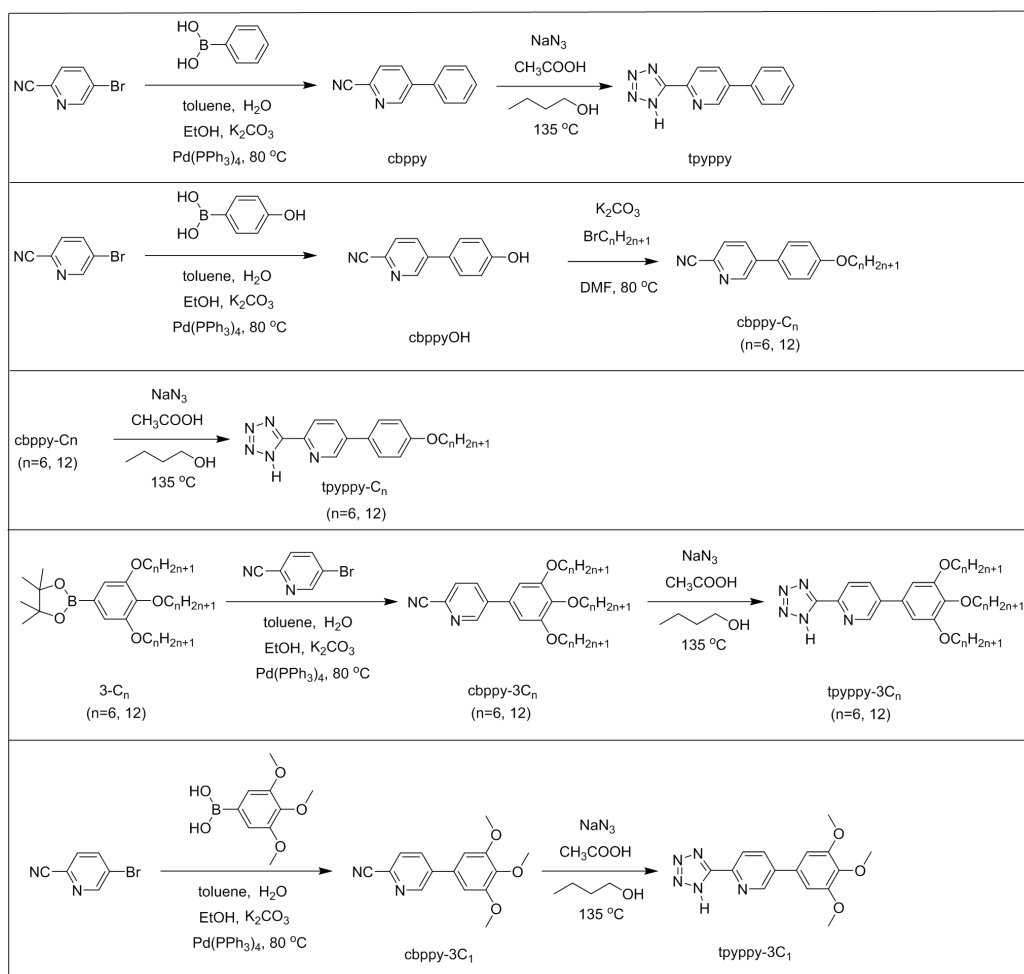
2,5-bis(3,4,5-tris(hexyloxy)phenyl)pyridine (HL₆)

It was synthesised according to the preparation procedure of HL₁₂. A white waxy solid of HL₆ was obtained in 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, $J = 2.0$ Hz, 1H), 7.86 (dd, $J = 8.3$, 2.3 Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 1H), 7.25 (s, 2H), 6.78 (s, 2H), 4.13 – 3.98 (m, 12H), 1.89 – 1.73 (m, 12H), 1.55 – 1.44 (m, 12H), 1.41 – 1.23 (m, 24H), 0.91 (t, $J = 7.0$ Hz, 18H).

2,5-bis(3,4,5-trimethoxyphenyl)pyridine (HL₁)

To a mixture of (3,4,5-trimethoxyphenyl)boronic acid (3.00 g, 14.15 mmol), 2,5-dibromopyridine (1.67 g, 7.00 mmol), potassium carbonate (5.86 g, 42.45 mmol) and tetrakis(triphenylphosphine) palladium (0.82 g, 0.71 mmol) was added a degassed mixture of toluene (30 mL), ethanol (15 mL) and water (15 mL). The mixture was

refluxed for 24 h under the protection of nitrogen. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE/CH₂Cl₂/ethyl acetate (2:1:1) as the eluent to give a white powder (1.97 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.87 (d, J = 1.9 Hz, 1H), 7.89 (dd, J = 8.3, 2.3 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.28 (s, 2H), 6.79 (s, 2H), 3.97 (s, 6H), 3.93 (s, 6H), 3.90 (d, J = 2.6 Hz, 6H).



Scheme S2. Synthetic route for ancillary ligands.

cbppy

To a mixture of 5-bromopicolonitrile (1.00 g, 5.46 mmol), phenylboronic acid (0.80 g, 6.55 mmol), potassium carbonate (2.26 g, 16.38 mmol) and tetrakis(triphenylphosphine) palladium (500 mg) was added a degassed mixture of tetrahydrofuran (THF, 40 mL) and water (20 mL). The mixture was refluxed for 18 h under the protection of argon. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / ethyl acetate (2:1) as the eluent to give a white solid (0.85 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 8.97 - 8.91 (m, 1H), 8.01 (dd, J = 8.1, 2.2 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H),

7.60 (d, $J = 7.9$ Hz, 2H), 7.56 – 7.45 (m, 3H).

tpyppy

cbppy(0.50 g, 2.78 mmol), NaN_3 (0.54 g, 8.34mmol), acetic acid (0.53 g, 8.83 mmol) and n-butyl alcohol (30 mL) were added into a 100 mL round-bottom flask. The mixture was refluxed for 4 days under the protection of argon. After cooled to RT, adjusting its pH to 2-3, the suspension was filtered, and washed with CH_2Cl_2 (3×5mL) and water (3×5mL). Then a white solid of tpyppy was obtained (0.49 g, 80%). The product was used directly to the next step of no further purification. ^1H NMR (400 MHz, DMSO-d_6) δ : 9.06 (s, 1H), 8.32 (d, $J = 8.2$ Hz, 1H), 8.24 (d, $J = 8.2$ Hz, 1H), 7.80 (d, $J = 7.4$ Hz, 2H), 7.53-7.46 (m, 2H), 7.43 (t, $J = 7.3$ Hz, 1H).

cbppyOH

To a mixture of 5-bromopicolonitrile (1.00 g, 5.46 mmol), 4-Hydroxyphenylboronic acid(0.90 g, 6.55mmol), potassium carbonate (2.00 g 14.49 mmol) and tetrakis(triphenylphosphine) palladium (500 mg) was added a degassed mixture of THF (40 mL) and water (20mL). The mixture was refluxed for 18 h under the protection of argon. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (3 × 50mL). The combined organic layer was dried over anhydrous MgSO_4 and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / ethyl acetate (1:1) as the eluent to give a white solid (0.92 g, 86%). ^1H NMR (400 MHz, CDCl_3) δ : 8.90 (d, $J = 1.5$ Hz, 1H), 7.95 (dd, $J = 8.1, 2.3$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.51 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 2H).

cbppy-C₆

cbppyOH (0.50g, 2.55 mmol) was added to a solution of 1-bromohexane (0.51g, 3.09mmol) and K_2CO_3 (1.06 g, 7.68mmol) in DMF (50 mL), and was stirred vigorously for 24 h at 80 °C under a argon atmosphere. The mixture was cooled to RT and filtrated. The filtrate was evaporated to remove the solvent and then poured into 100 mL of water and was extracted with CH_2Cl_2 (3 × 50 mL). The mixed organic layer was washed with water and brine, dried over MgSO_4 and filtered. The filtrate was evaporated and the residue was purified by dry a flash silica gel column using PE / ethyl acetate (7:1) as eluent to gain cbppy-C₆ as a white solid (0.57 g, 80%). ^1H NMR (400 MHz, CDCl_3) δ : 8.91 (d, $J = 1.7$ Hz, 1H), 7.96 (dd, $J = 8.1, 2.3$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.54 (dd, $J = 9.3, 2.4$ Hz, 2H), 7.02 (t, $J = 5.9$ Hz, 2H), 4.01 (t, $J = 6.6$ Hz, 2H), 1.86 - 1.74 (m, 2H), 1.53 - 1.29 (m, 6H), 0.91 (t, $J = 7.0$ Hz, 3H).

tpyppy-C₆

It was synthesised according to the preparation procedure of tpyppy. A white solid of tpyppy-C₆ was obtained in 68% yield. ^1H NMR (400 MHz, DMSO-d_6) δ : 8.76 (s, 1H), 7.99 (s, 2H), 7.61 (d, $J = 7.8$ Hz, 2H), 7.00 (d, $J = 7.9$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 1.74-1.63 (m, 2H), 1.32-1.25 (m, 6H), 0.83 (t, $J = 6.6$ Hz, 3H).

cbppy-C₁₂

It was synthesised according to the preparation procedure of cbppy-C₆. A white solid of cbppy-C₁₂ was obtained in 88% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.92 (s, 1H), 7.96 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.73 (t, $J = 8.4$ Hz, 1H), 7.54 (t, $J = 7.1$ Hz, 2H),

7.02 (t, $J = 8.7$ Hz, 2H), 4.00 (d, $J = 6.6$ Hz, 2H), 1.87 – 1.75 (m, 2H), 1.52 - 1.19 (m, 18H), 0.88 (t, $J = 6.7$ Hz, 3H).

tpyppy- C_{12}

It was synthesised according to the preparation procedure of tpyppy. A white solid of tpyppy- C_{12} was obtained in 62% yield. 1H NMR (400 MHz, DMSO- d_6) δ : 8.76 (s, 1H), 7.98 (s, 2H), 7.62 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 2H), 3.95 (t, $J = 6.4$ Hz, 2H), 1.65 (m, 2H), 1.36-1.18 (m, 17H), 0.88 (t, $J = 6.6$ Hz, 3H).

cbppy- $3C_6$

To a mixture of 5-bromopicolinonitrile (1.00 g, 5.46 mmol), 3- C_6 (3.04 g, 6.02 mmol), potassium carbonate (2.26 g, 16.38 mmol) and tetrakis(triphenylphosphine) palladium (500 mg) was added a degassed mixture of toluene (20 mL), water (10 mL) and ethanol (10 mL). The mixture was refluxed for 18 h under the protection of argon. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / ethyl acetate (10:1) as the eluent to give a white solid (1.39 g, 53%). 1H NMR (400 MHz, $CDCl_3$) δ : 8.89 (s, 1H), 7.94 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 1H), 6.73 (s, 2H), 4.09 – 3.96 (m, 6H), 1.79 (ddd, $J = 27.1, 14.5, 6.9$ Hz, 6H), 1.47 (dd, $J = 14.4, 7.3$ Hz, 6H), 1.29 (d, $J = 22.0$ Hz, 12H), 0.88 (t, $J = 6.6$ Hz, 9H).

tpyppy- $3C_6$

It was synthesised according to the preparation procedure of tpyppy. A white solid of tpyppy- $3C_6$ was obtained in 50% yield. 1H NMR (400 MHz, DMSO- d_6) δ : 8.73 (s, 1H), 7.95 (s, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 3.91 (t, $J = 6.5$ Hz, 6H), 1.82 – 1.71 (m, 6H), 1.53 – 1.42 (m, 6H), 1.35 – 1.31 (m, 12H), 0.90 (t, $J = 7.0$ Hz, 9H).

cbppy- $3C_{12}$

It was synthesised according to the preparation procedure of cbppy- $3C_6$. A white solid of cbppy- $3C_{12}$ was obtained in 58% yield. 1H NMR (400 MHz, $CDCl_3$) δ : 8.92 – 8.85 (m, 1H), 7.97 – 7.91 (m, 1H), 7.75 – 7.70 (m, 1H), 6.73 (s, 2H), 4.07 – 3.96 (m, 6H), 1.88 – 1.72 (m, 6H), 1.54 – 1.44 (m, 6H), 1.37 – 1.22 (m, 48H), 0.88 (t, $J = 5.2$ Hz, 9H).

tpyppy- $3C_{12}$

It was synthesised according to the preparation procedure of tpyppy. A white solid of tpyppy- $3C_{12}$ was obtained in 60% yield. 1H NMR (400 MHz, DMSO- d_6) δ : 8.75 (s, 1H), 7.99 (s, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 4.04 – 3.95 (m, 6H), 1.86 – 1.73 (m, 6H), 1.52 – 1.47 (m, 6H), 1.35 – 1.22 (m, 48H), 0.89 (t, $J = 5.2$ Hz, 9H).

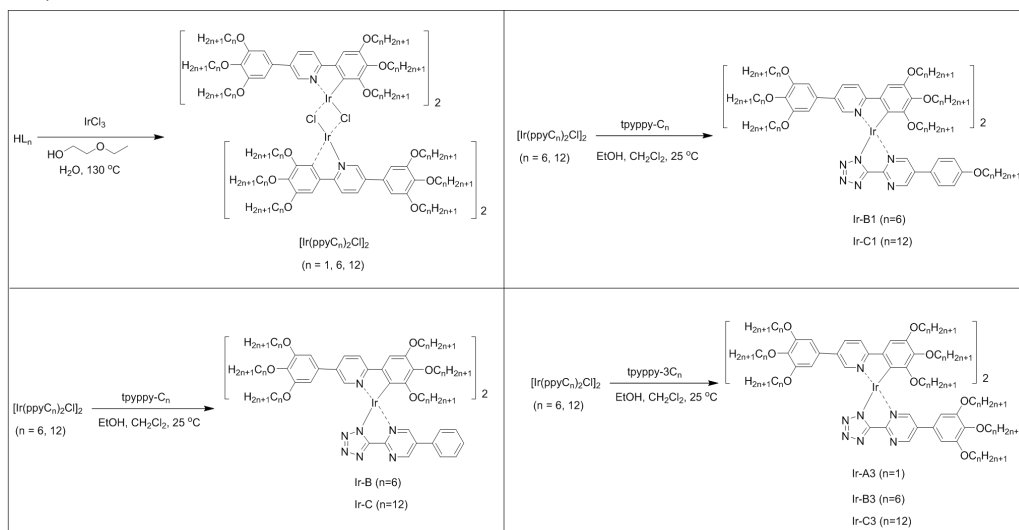
cbppy- $3C_1$

To a mixture of 5-bromopicolinonitrile (1.00 g, 5.46 mmol), (3,4,5-trimethoxyphenyl)boronic acid (1.16 g, 5.47 mmol), potassium carbonate (2.26 g, 16.38 mmol) and tetrakis(triphenylphosphine) palladium (0.32 mg) was added a degassed mixture of toluene (20 mL), water (10 mL) and ethanol (10 mL). The mixture was refluxed for 18 h under the protection of argon. After cooled to RT, the mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was

evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / ethyl acetate (10:1) as the eluent to give a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.91 (d, J = 1.5 Hz, 1H), 7.97 (dd, J = 8.1, 2.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 6.76 (s, 2H), 3.94 (s, 6H), 3.91 (s, 3H).

tpyppy-3C₁

It was synthesised according to the preparation procedure of tpyppy. A white solid of tpyppy-3C₁ was obtained in 82% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 8.42 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.12 (s, 2H), 3.91 (s, 6H), 3.73 (s, 3H).



Scheme S3. Synthetic route for iridium(III) complexes.

Ir-A3

To a mixture of IrCl_3 (0.25 g, 0.85 mmol) and water (2.50 mL) was added a solution of HL_1 (0.70 g, 1.70 mmol) and 2-ethoxyethanol (10.00 mL). The mixture was stirred under inert gas atmosphere at 130 °C for 24 h. After cooled to RT, the colored precipitate was filtered off and was washed with water (10 mL) and ethanol (10 mL) to gain $[\text{Ir}(\text{ppyC}_1)_2\text{Cl}]_2$ dimmers as a red solid (0.60 g, 0.29 mmol) directly used in the following process. A mixture of $[\text{Ir}(\text{ppyC}_1)_2\text{Cl}]_2$ (0.60 g, 0.29 mmol), and tpyppy-3C₁ (0.27 g, 0.86 mmol) were stirred in CH_2Cl_2 (10 mL) and ethanol (3 mL) under argon atmosphere at RT of overnight. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the mixed organic layer was dried over anhydrous MgSO_4 and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using ethyl acetate as eluent to gain Ir-A3 as an orange solid (0.23 g, 30%).

^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 1.7 Hz, 1H), 8.09 (dd, J = 8.3, 2.2 Hz, 1H), 7.79 – 7.66 (m, 5H), 7.58 (s, 1H), 7.16 (d, J = 11.5 Hz, 2H), 6.50 (s, 2H), 6.40 (s, 2H), 6.28 (s, 2H), 3.89 (d, J = 1.2 Hz, 6H), 3.87 (s, 6H), 3.85 (s, 3H), 3.82 (s, 9H), 3.81 – 3.79 (m, 6H), 3.79 (s, 3H), 3.65 (s, 6H), 2.97 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 167.24, 166.07, 163.64, 159.30, 159.27, 154.03, 153.77, 153.57, 149.87, 149.80, 148.08, 147.92, 147.61, 146.79, 140.51, 139.79, 137.85, 135.36, 134.34, 133.81, 133.73, 133.44, 133.26, 131.98, 130.76, 129.77,

127.81, 122.42, 118.14, 117.83, 104.87, 104.78, 103.48, 103.25, 103.13, 61.02, 60.92, 60.79, 60.73, 60.57, 60.48, 56.41, 56.25, 56.23, 56.17, 55.89.

Elemental analysis calcd. for $C_{61}H_{62}IrN_7O_{15}$: C 55.28, H 4.72, N 7.40; found: C 54.87, H 4.65, N 7.33.

Ir-B3

It was synthesised according to the preparation procedure of Ir-A3. A red solid of Ir-B3 was obtained in 28% yield.

1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 1.2 Hz, 1H), 7.97 (dd, J = 8.3, 1.9 Hz, 1H), 7.76 (d, J = 1.4 Hz, 1H), 7.68 – 7.55 (m, 5H), 7.16 (s, 1H), 7.12 (s, 1H), 6.46 (s, 2H), 6.32 (s, 2H), 6.19 (s, 2H), 4.03 – 3.84 (m, 22H), 3.72 (t, J = 6.2 Hz, 4H), 3.33 (dd, J = 14.1, 8.9 Hz, 1H), 3.23 (dd, J = 14.4, 8.5 Hz, 1H), 2.70 (d, J = 3.9 Hz, 2H), 1.76 (dddd, J = 25.3, 20.0, 15.9, 7.9 Hz, 30H), 1.50 (s, 15H), 1.41 – 0.96 (m, 75H), 0.95 – 0.82 (m, 45H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.89, 165.57, 163.43, 159.19, 158.88, 153.94, 153.59, 153.42, 149.71, 149.60, 148.16, 147.91, 147.25, 146.67, 144.43, 143.29, 140.40, 139.83, 139.44, 138.52, 138.15, 137.98, 135.28, 134.66, 134.09, 133.75, 133.22, 131.52, 130.53, 129.66, 128.52, 121.99, 118.12, 117.65, 106.95, 105.54, 104.65, 104.57, 73.95, 73.59, 73.49, 73.47, 73.25, 73.07, 70.00, 69.29, 68.94, 68.81, 31.97, 31.94, 31.80, 31.75, 31.73, 31.66, 31.57, 30.46, 30.41, 30.29, 30.24, 30.22, 29.76, 29.60, 29.52, 29.41, 29.35, 26.01, 25.95, 25.92, 25.86, 25.80, 25.74, 25.72, 25.49, 25.43, 22.71, 22.68, 22.65, 22.64, 22.63, 22.60, 14.08, 14.06, 14.05, 14.02, 14.01.

Elemental analysis calcd. for $C_{136}H_{212}IrN_7O_{15}$: C 68.71, H 8.99, N 4.12; found: C 68.61, H 8.86, N 4.06.

Ir-C3

It was synthesised according to the preparation procedure of Ir-A3. A red solid of Ir-C3 was obtained in 33% yield.

1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.3 Hz, 1H), 8.09 (s, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.76 (s, 1H), 7.66 – 7.48 (m, 5H), 7.13 (d, J = 15.9 Hz, 2H), 6.46 (s, 2H), 6.32 (s, 2H), 6.19 (s, 2H), 4.05 – 3.83 (m, 22H), 3.70 (s, 4H), 3.27 (d, J = 36.6 Hz, 2H), 2.70 (s, 2H), 1.80 (d, J = 8.3 Hz, 26H), 1.47 (d, J = 15.0 Hz, 18H), 1.24 (d, J = 10.1 Hz, 256H), 0.88 (dd, J = 8.0, 5.5 Hz, 45H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 165.54, 163.41, 159.17, 158.87, 153.96, 153.60, 153.43, 149.71, 149.62, 148.21, 147.88, 147.23, 146.67, 144.45, 143.31, 140.41, 139.83, 139.47, 138.56, 138.16, 137.95, 135.26, 134.66, 134.04, 133.79, 133.18, 131.47, 130.90, 130.52, 129.63, 128.82, 128.55, 122.07, 118.11, 117.66, 106.95, 105.53, 104.59, 73.97, 73.61, 73.51, 73.28, 73.08, 70.02, 69.31, 68.95, 68.83, 31.98, 31.95, 30.35, 30.33, 29.88, 29.82, 29.79, 29.77, 29.75, 29.71, 29.64, 29.57, 29.53, 29.51, 29.48, 29.43, 29.41, 26.42, 26.33, 26.27, 26.20, 26.13, 22.71, 14.12.

Elemental analysis calcd. for $C_{226}H_{392}IrN_7O_{15}$: C 74.58, H 10.86, N 2.69; found: C 74.49, H 10.73, N 2.58.

Ir-B1

To a mixture of $IrCl_3$ (0.25 g, 0.85 mmol) and water (2.50 mL) was added a solution of HL_6 (1.00 g, 1.20 mmol) and 2-ethoxyethanol (10.00 mL). The mixture

was stirred under inert gas atmosphere at 130°C for 24 h. After cooled to RT, the colored precipitate was filtered off and was washed with water (10 mL) and ethanol (10 mL) to gain $[\text{Ir}(\text{ppyC}_6)_2\text{Cl}]_2$ dimmers as a red solid (0.80 g, 0.21mmol) directly used in the following process. A mixture of $[\text{Ir}(\text{ppyC}_6)_2\text{Cl}]_2$ (0.80 g, 0.21mmol), and tpyppy- C_6 (0.20 g, 0.63 mmol) were stirred in CH_2Cl_2 (10 mL) and ethanol (3mL) under argon atmosphere at RT of overnight. The mixture was extracted with CH_2Cl_2 (3×50 mL) and the mixed organic layer was dried over anhydrous MgSO_4 and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using ethyl acetate as eluent to gain Ir-B1 as a red solid (0.25 g, 27%).

^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 4.5 Hz, 2H), 7.78 (d, J = 1.8 Hz, 1H), 7.63 (ddd, J = 27.3, 16.9, 5.9 Hz, 5H), 7.23 (d, J = 8.8 Hz, 2H), 7.18 (s, 1H), 7.12 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.33 (s, 2H), 6.20 (s, 2H), 4.08 – 3.84 (m, 18H), 3.68 (t, J = 6.3 Hz, 4H), 3.34 (d, J = 5.9 Hz, 1H), 3.24 (d, J = 6.0 Hz, 1H), 2.71 (dd, J = 15.7, 6.8 Hz, 2H), 1.91 – 1.59 (m, 26H), 1.54 – 1.21 (m, 72H), 1.11 (d, J = 6.5 Hz, 6H), 0.94 – 0.82 (m, 39H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.93, 165.53, 163.52, 160.23, 159.24, 159.01, 153.58, 153.44, 149.75, 149.60, 148.33, 147.52, 146.89, 146.69, 144.40, 143.32, 140.60, 139.80, 138.52, 138.08, 137.57, 134.81, 134.02, 133.79, 133.73, 133.10, 131.54, 130.57, 128.77, 127.40, 126.88, 122.19, 118.09, 117.64, 115.29, 106.79, 105.56, 104.61, 104.44, 74.13, 73.59, 73.48, 73.45, 73.08, 69.81, 69.29, 68.86, 68.17, 31.95, 31.87, 31.80, 31.79, 31.75, 31.72, 31.66, 31.57, 30.41, 30.40, 30.22, 29.66, 29.61, 29.42, 29.32, 29.13, 26.00, 25.95, 25.89, 25.84, 25.81, 25.72, 25.70, 25.68, 25.46, 25.43, 22.68, 22.64, 22.61, 22.58, 14.08, 14.06, 14.02.

Elemental analysis calcd. for $\text{C}_{124}\text{H}_{188}\text{IrN}_7\text{O}_{13}$: C 68.41, H 8.70, N 4.50; found: C 68.35, H 8.64, N 4.45.

Ir-C1

It was synthesised according to the preparation procedure of Ir-B1. A red solid of Ir-C1 was obtained in 33% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, J = 8.1 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.78 (d, J = 1.7 Hz, 1H), 7.70 – 7.49 (m, 5H), 7.23 (d, J = 8.8 Hz, 2H), 7.17 (s, 1H), 7.12 (s, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.33 (s, 2H), 6.20 (s, 2H), 4.12 – 3.83 (m, 18H), 3.67 (td, J = 6.0, 2.5 Hz, 4H), 3.28 (dd, J = 37.1, 6.1 Hz, 2H), 2.80 – 2.65 (m, 2H), 1.93 – 0.93 (m, 260H), 0.88 (dd, J = 8.0, 5.5 Hz, 39H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.93, 165.51, 163.51, 160.23, 159.25, 159.01, 153.59, 153.45, 149.75, 149.61, 148.37, 147.53, 146.88, 146.71, 144.45, 143.35, 140.61, 139.80, 138.57, 138.10, 137.53, 134.86, 133.82, 133.11, 131.54, 130.57, 128.78, 127.38, 126.89, 122.21, 118.07, 117.63, 115.29, 106.87, 105.59, 104.64, 104.44, 74.12, 73.61, 73.50, 73.46, 73.08, 69.89, 69.32, 68.88, 68.22, 31.97, 31.96, 31.94, 30.52, 30.32, 29.85, 29.81, 29.76, 29.73, 29.70, 29.66, 29.64, 29.57, 29.51, 29.48, 29.46, 29.41, 29.40, 29.37, 29.24, 26.39, 26.33, 26.24, 26.20, 26.12, 26.10, 26.08, 25.82, 25.80, 22.69, 14.11.

Elemental analysis calcd. for $\text{C}_{202}\text{H}_{344}\text{IrN}_7\text{O}_{13}$: C 74.17, H 10.60, N 3.00; found: C 74.06, H 10.52, N 2.97.

Ir-B

To a mixture of IrCl_3 (0.25 g, 0.85 mmol) and water (2.50 mL) was added a solution of HL_6 (1.00 g, 1.20 mmol) and 2-ethoxyethanol (10.00 mL). The mixture was stirred under inert gas atmosphere at 130 °C for 24 h. After cooled to RT, the colored precipitate was filtered off and was washed with water (10 mL) and ethanol (10 mL) to gain $[\text{Ir}(\text{ppyC}_6)_2\text{Cl}]_2$ dimmers as a red solid (0.80 g, 0.21mmol) directly used in the following process. A mixture of $[\text{Ir}(\text{ppyC}_6)_2\text{Cl}]_2$ (0.80 g, 0.21mmol), and tpyppy (0.14 g, 0.63 mmol) were stirred in CH_2Cl_2 (10 mL) and ethanol (3mL) under argon atmosphere at RT of overnight. The mixture was extracted with CH_2Cl_2 (3×50 mL) and the mixed organic layer was dried over anhydrous MgSO_4 and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using ethyl acetate as eluent to gain Ir-B as a red solid (0.31g, 35%).

^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 9.0 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.79 (d, J = 1.5 Hz, 1H), 7.70 – 7.54 (m, 5H), 7.42 – 7.36 (m, 3H), 7.32 (d, J = 1.4 Hz, 2H), 7.19 (s, 1H), 7.13 (s, 1H), 6.33 (s, 2H), 6.20 (s, 2H), 4.12 – 3.84 (m, 16H), 3.68 (t, J = 6.2 Hz, 4H), 3.34 (d, J = 5.9 Hz, 1H), 3.25 (d, J = 6.1 Hz, 1H), 2.80 – 2.62 (m, 2H), 1.69 (ddd, J = 29.4, 17.1, 6.7 Hz, 22H), 1.55 – 1.21 (m, 61H), 1.11 (d, J = 6.6 Hz, 4H), 1.05 – 0.81 (m, 40H), 0.78 (d, J = 3.1 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.91, 165.52, 163.44, 159.24, 159.01, 153.59, 153.44, 149.80, 149.63, 148.43, 148.32, 147.52, 146.71, 144.42, 143.30, 140.55, 139.78, 138.49, 138.08, 137.82, 135.68, 134.96, 134.63, 134.12, 133.81, 133.18, 131.57, 130.56, 129.40, 129.29, 128.64, 126.28, 122.21, 118.12, 117.67, 106.77, 105.51, 104.57, 104.48, 74.15, 73.56, 73.49, 73.45, 73.08, 69.75, 69.27, 68.85, 68.78, 31.96, 31.88, 31.81, 31.76, 31.72, 31.69, 31.66, 31.54, 30.42, 30.38, 30.21, 29.65, 29.62, 29.60, 29.42, 29.29, 25.96, 25.86, 25.81, 25.73, 25.70, 25.47, 25.44, 22.69, 22.65, 22.62, 14.07, 14.03.

Elemental analysis calcd. for $\text{C}_{118}\text{H}_{176}\text{IrN}_7\text{O}_{12}$: C 68.24, H 8.54, N 4.72; found: C 68.17, H 8.37, N 4.63.

Ir-C

It was synthesised according to the preparation procedure of Ir-B. A red solid of Ir-C was obtained in 30% yield.

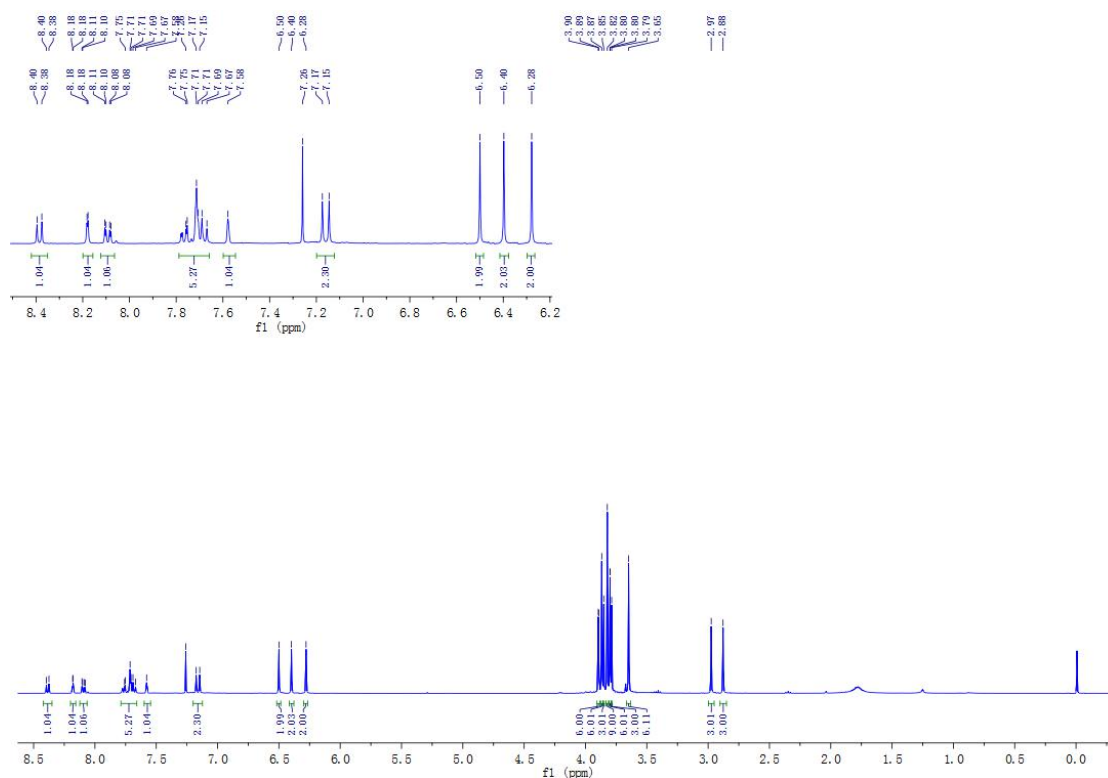
^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.78 (s, 1H), 7.67 – 7.51 (m, 5H), 7.38 (d, J = 4.7 Hz, 3H), 7.31 (d, J = 3.8 Hz, 2H), 7.18 (s, 1H), 7.12 (s, 1H), 6.33 (s, 2H), 6.20 (s, 2H), 4.11 – 3.83 (m, 16H), 3.68 (d, J = 4.6 Hz, 4H), 3.37 – 3.19 (m, 2H), 2.71 (dd, J = 16.3, 6.8 Hz, 2H), 1.80 (d, J = 6.9 Hz, 9H), 1.63 (dt, J = 13.9, 11.0 Hz, 18H), 1.48 (dd, J = 13.8, 5.5 Hz, 11H), 1.34 (d, J = 61.1 Hz, 202H), 0.88 (t, J = 6.6 Hz, 36H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.92, 165.52, 163.42, 159.26, 159.00, 153.61, 153.45, 149.81, 149.64, 148.47, 148.35, 147.49, 146.74, 144.49, 143.36, 140.57, 139.77, 138.60, 138.15, 137.76, 135.66, 134.99, 134.69, 134.10, 133.82, 133.17, 131.57, 130.53, 129.39, 129.24, 128.65, 126.26, 122.22, 118.08, 117.64, 106.86, 105.58, 104.64, 104.54, 74.14, 73.59, 73.50, 73.46, 73.08, 69.83, 69.33, 68.90, 31.97,

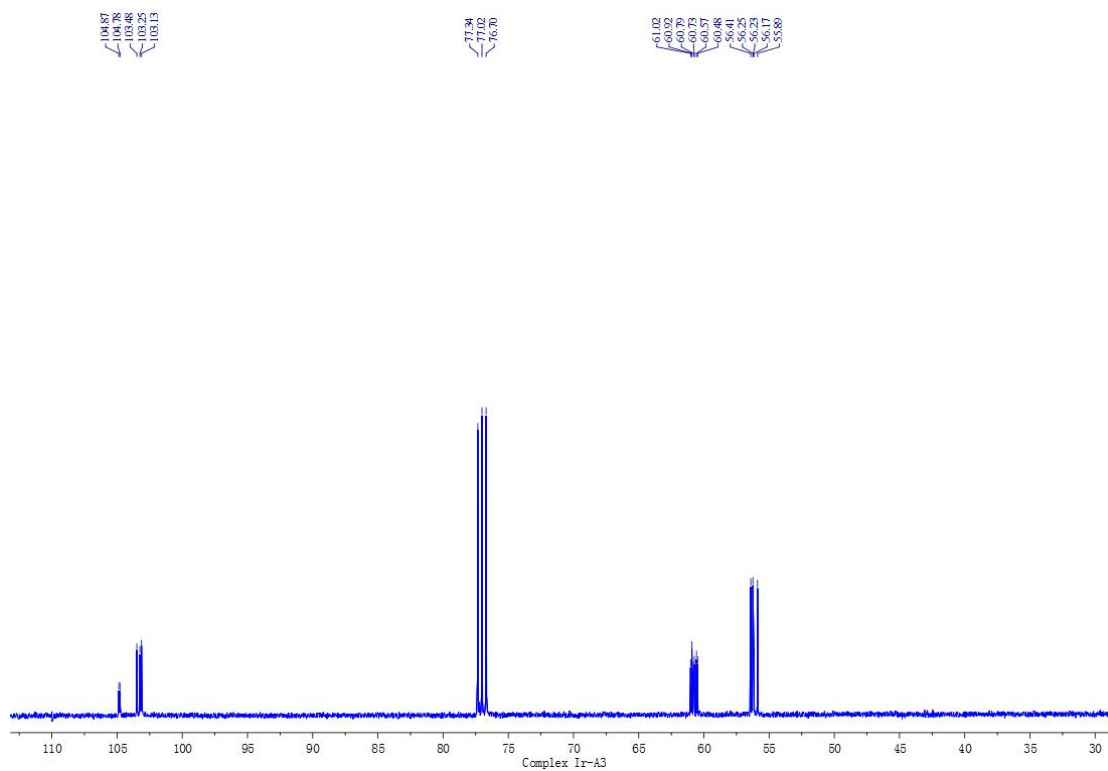
31.93, 30.52, 30.49, 30.33, 29.85, 29.74, 29.70, 29.68, 29.63, 29.60, 29.57, 29.52, 29.45, 29.38, 26.33, 26.28, 26.24, 26.20, 26.12, 26.10, 25.82, 22.69, 14.11.

Elemental analysis calcd. for $C_{190}H_{320}IrN_7O_{12}$: C 73.93, H 10.45, N 3.18; found: C 73.85, H 10.34, N 3.16.

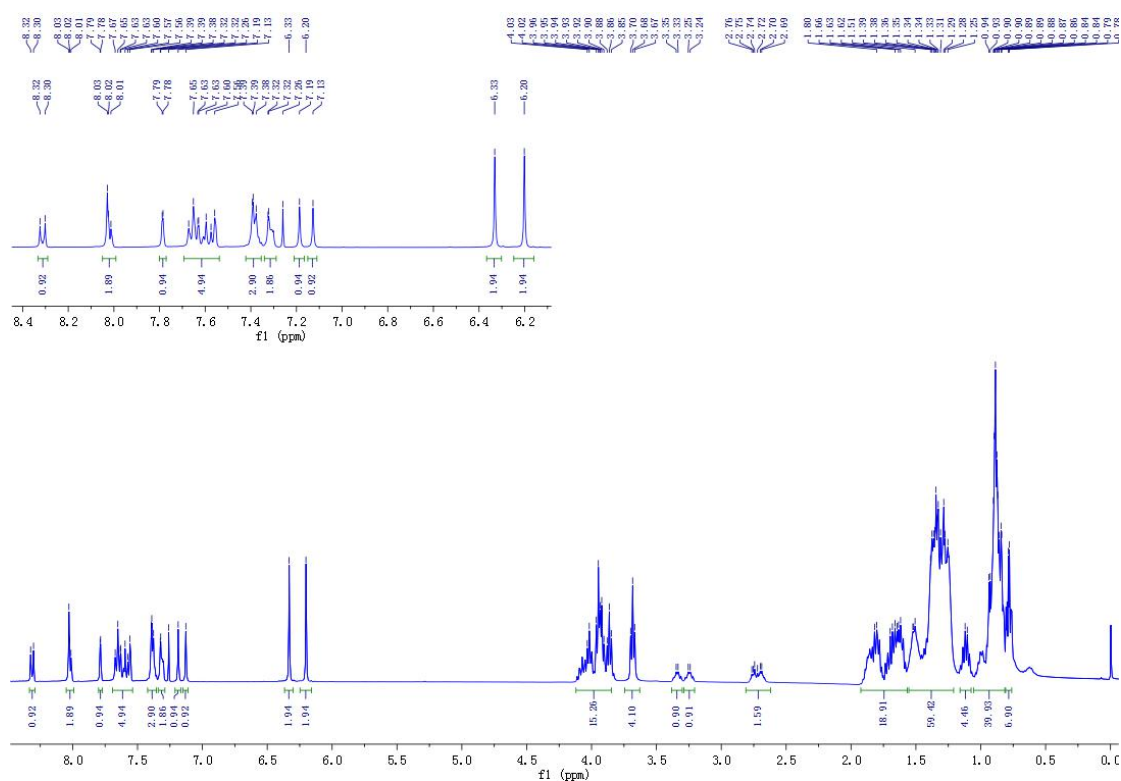
2. ^1H NMR and ^{13}C NMR spectra of all complexes



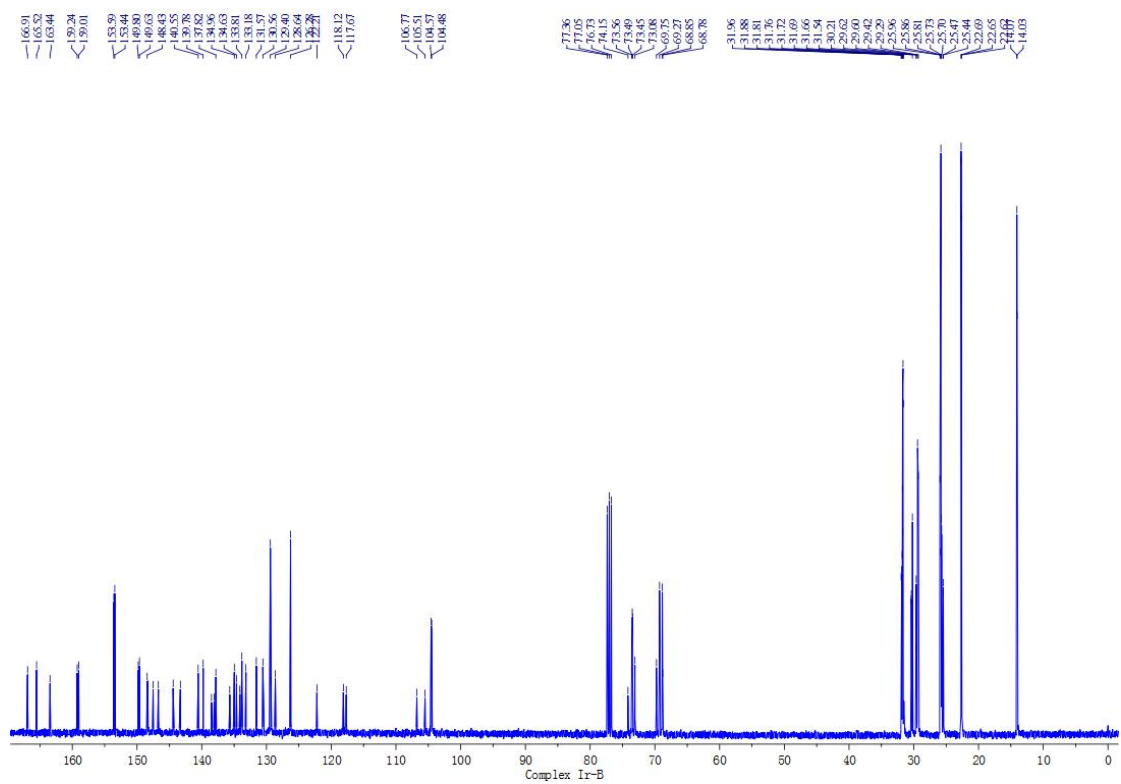
^1H NMR (400 MHz, CDCl_3) spectrum of complex Ir-A3.



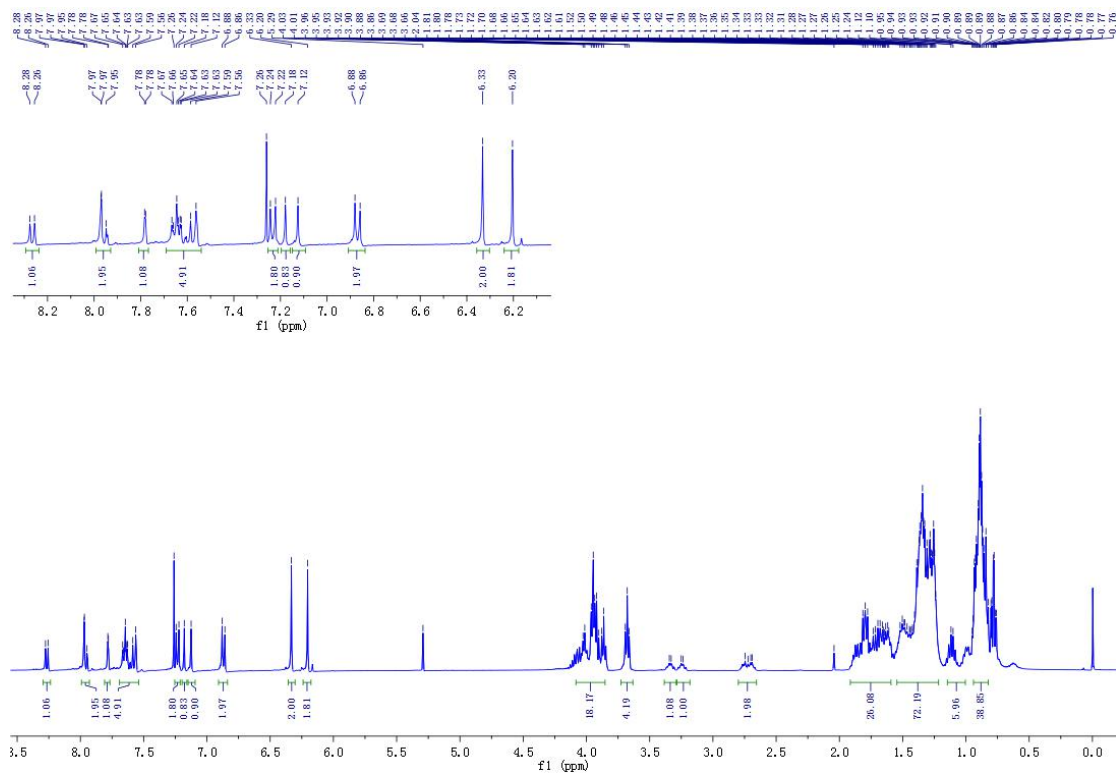
^{13}C NMR (100 MHz, CDCl_3) spectrum of complex Ir-A3.



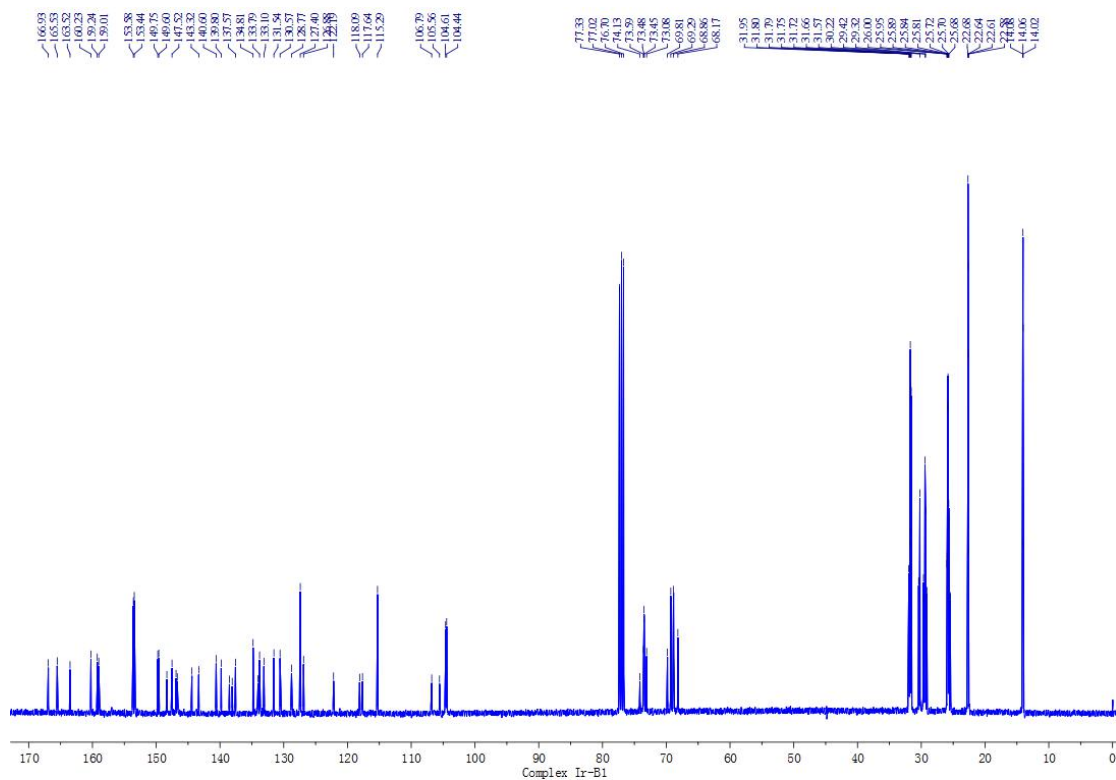
¹H NMR (400 MHz, CDCl₃) spectrum of complex Ir-B.



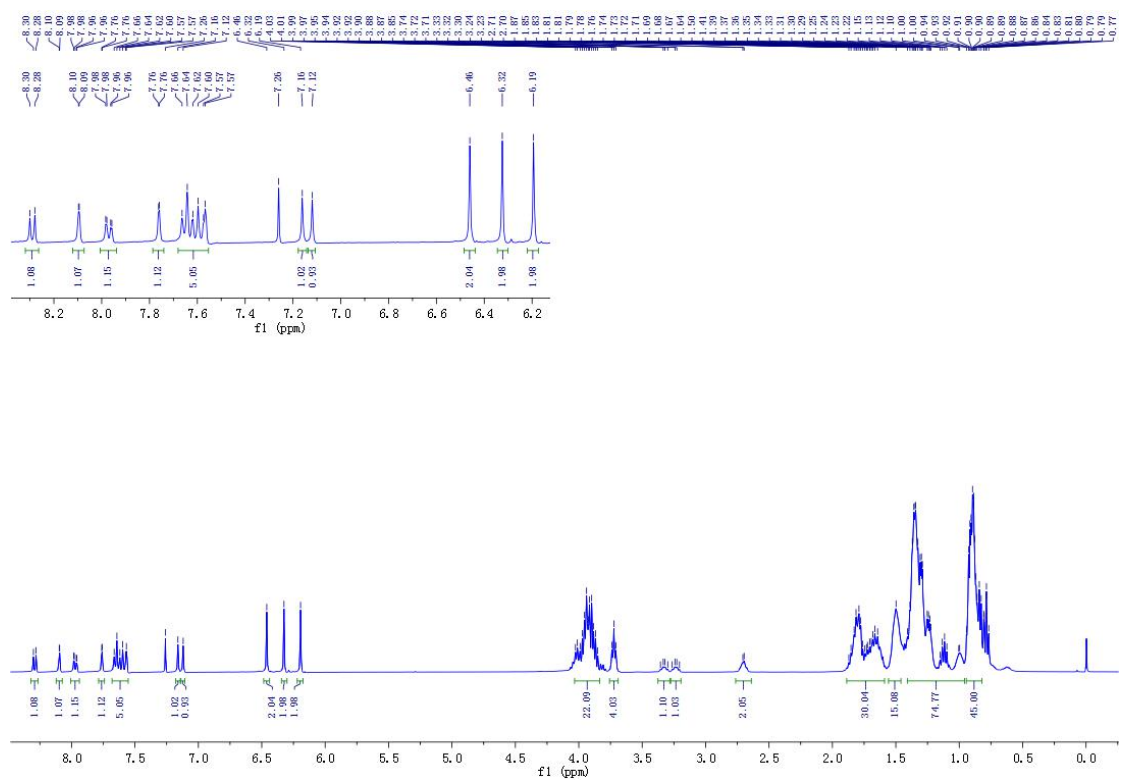
¹³C NMR (100 MHz, CDCl₃) spectrum of complex Ir-B.



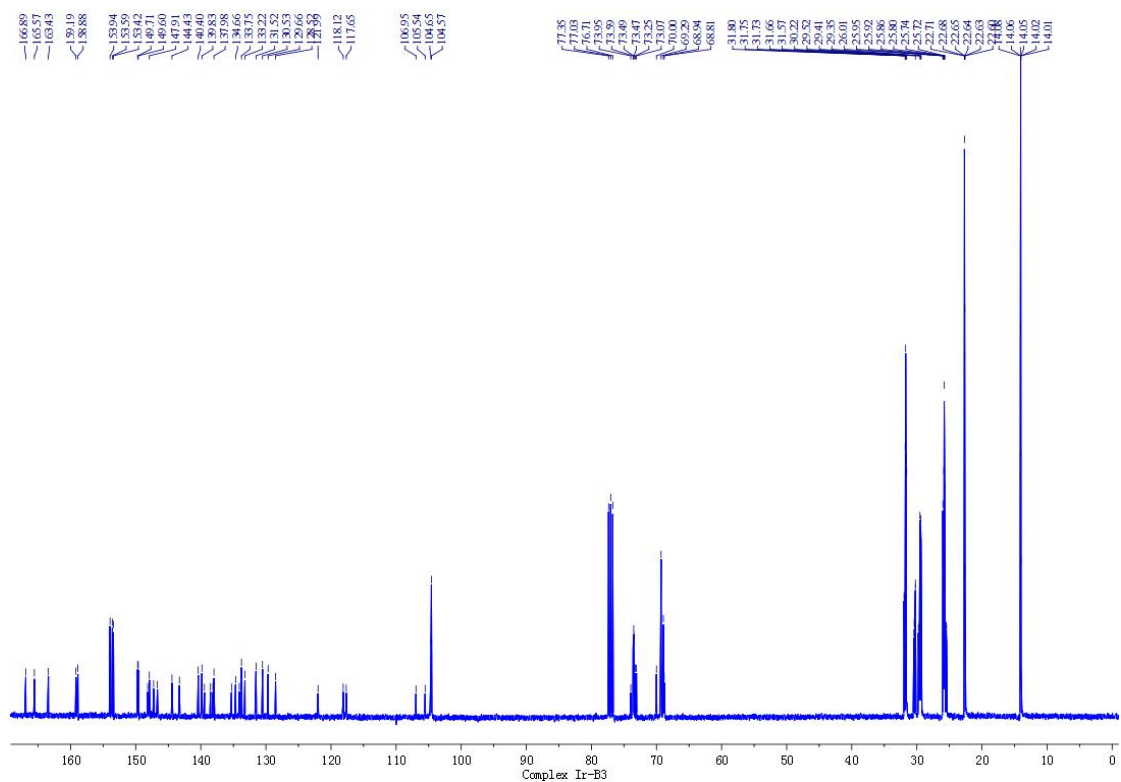
¹H NMR (400 MHz, CDCl₃) spectrum of complex Ir-B1.



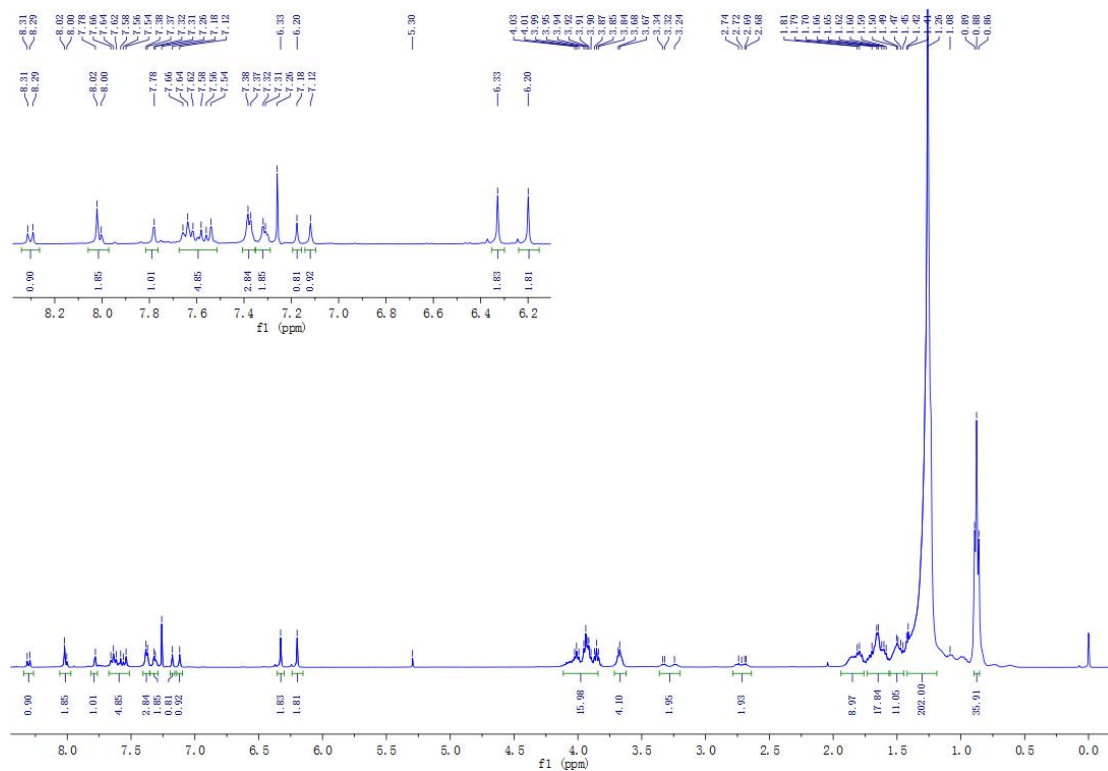
¹³C NMR (100 MHz, CDCl₃) spectrum of complex Ir-B1.



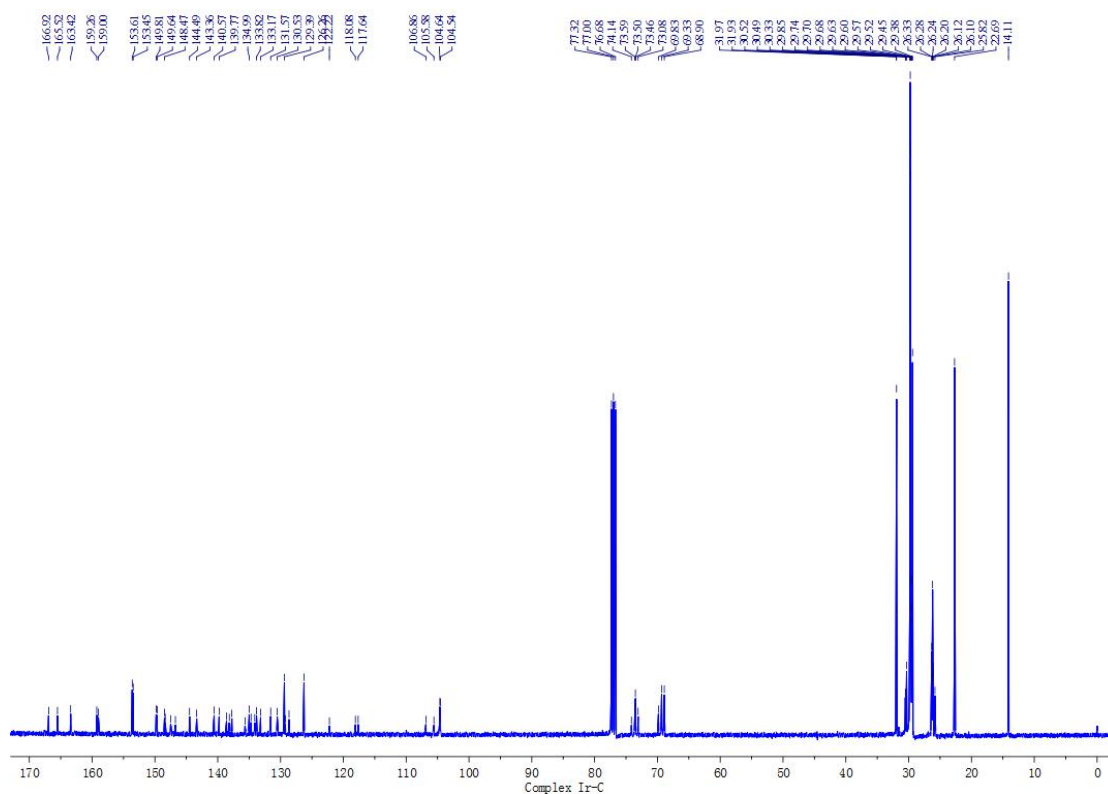
¹H NMR (400 MHz, CDCl₃) spectrum of complex Ir-B3.



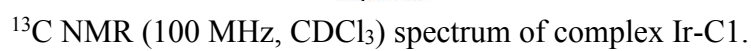
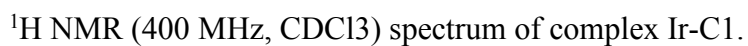
¹³C NMR (100 MHz, CDCl₃) spectrum of complex Ir-B3.

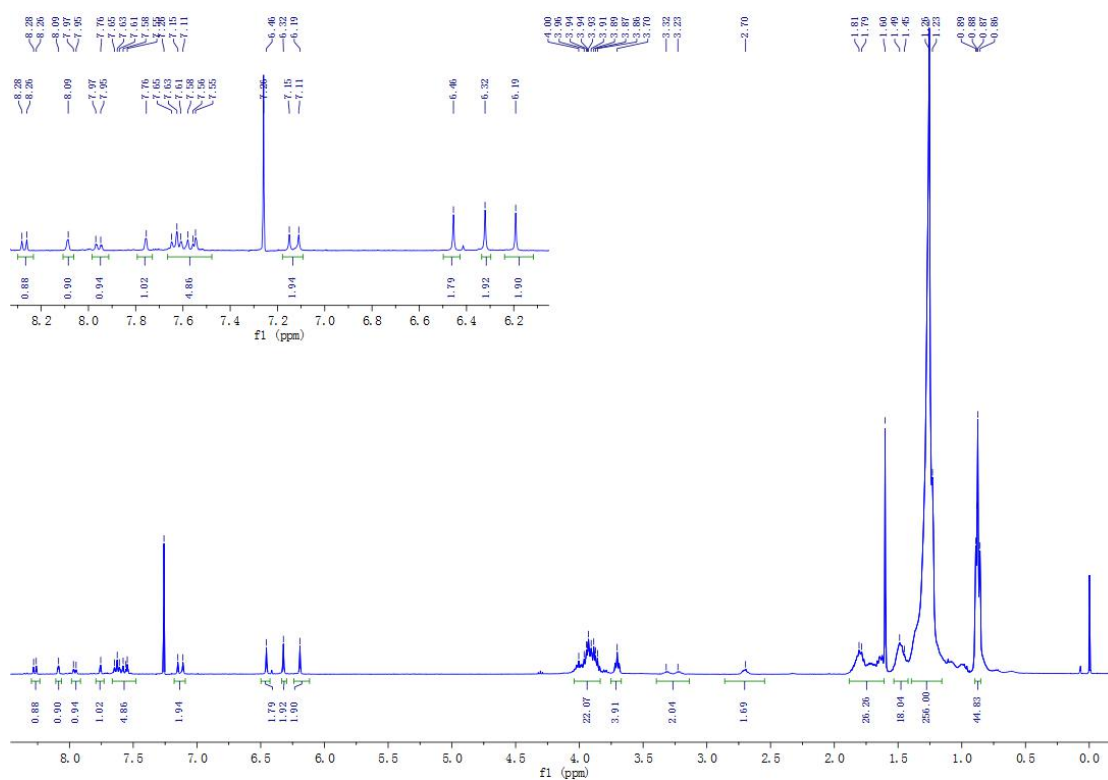


^1H NMR (400 MHz, CDCl_3) spectrum of complex Ir-C.

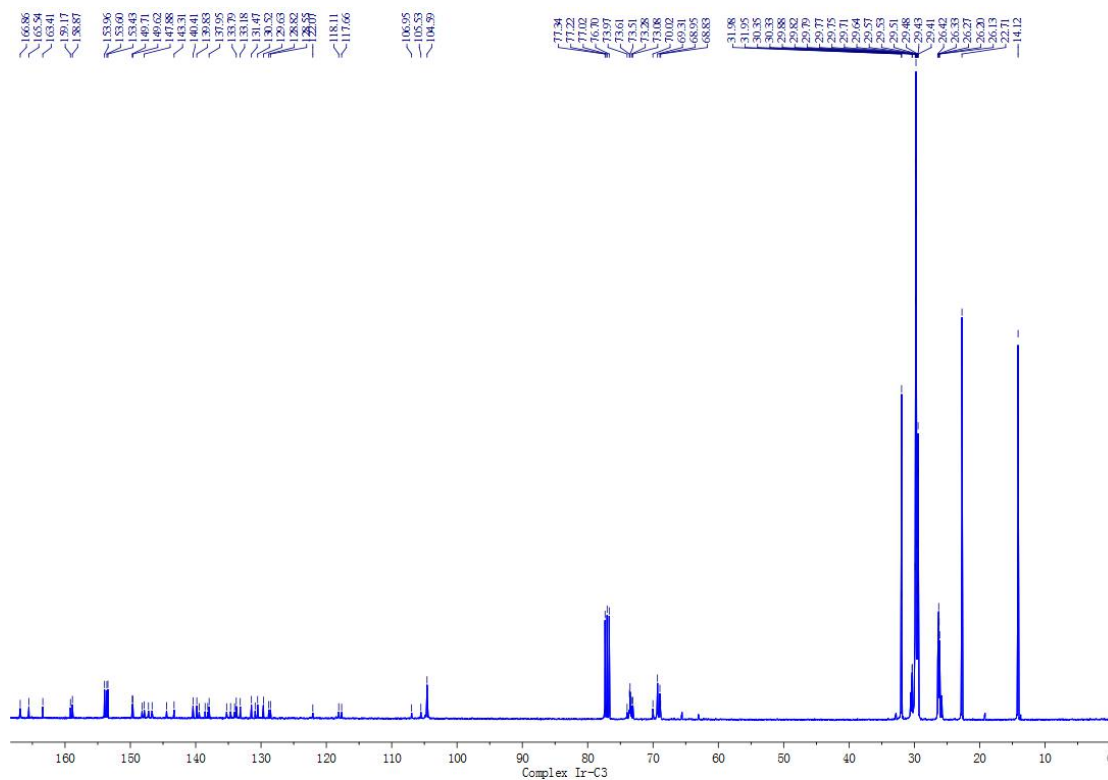


^{13}C NMR (100 MHz, CDCl_3) spectrum of complex Ir-C.





¹H NMR (400 MHz, CDCl₃) spectrum of complex Ir-C3.



¹³C NMR (100 MHz, CDCl₃) spectrum of complex Ir-C3.

3. The crystallographic data, selected bond lengths and angles of Ir-A3.

Table S1. The detailed crystallographic data of complex Ir-A3.	
Empirical formula	C ₆₁ H ₆₂ IrN ₇ O ₁₅
Formula weight	1325.37
Temperature/K	150
Crystal system	triclinic
Space group	P $\bar{1}$
a/Å	14.7045(4)
b/Å	14.9110(5)
c/Å	17.8440(6)
α /°	79.706(3)
β /°	78.030(3)
γ /°	81.738(3)
Volume/Å ³	3742.6(2)
Z	2
ρ_{calc} /g/cm ³	1.176
μ /mm ⁻¹	3.938
F(000)	1348.0
Crystal size/mm ³	0.7 × 0.4 × 0.15
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/	8.168 to 130.172
Index ranges	-11 ≤ h ≤ 17, -17 ≤ k ≤ 17, -19 ≤ l ≤ 20
Reflections collected	38444
Independent reflections	12744 [R _{int} = 0.0602, R _{sigma} = 0.0498]
Data/restraints/parameters	12744/0/772
Goodness-of-fit on F ²	1.039
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0498, wR ₂ = 0.1343
Final R indexes [all data]	R ₁ = 0.0522, wR ₂ = 0.1377
Largest diff. peak/hole / e Å ⁻³	3.12/-1.45

Table S2. Selected bond lengths and angles of complex Ir-A3.					
	lengths (Å) ^a	lengths (Å) ^b		angles (°) ^a	angles (°) ^b
Ir01-C01C	2.039(4)	2.0358	C00U-Ir01-C01C	90.56(17)	90.4197
Ir01-C00U	2.049(4)	2.0505	N00M-Ir01-N00N	94.38(14)	93.0017
Ir01-N00H	2.056(3)	2.0743	N00L-Ir01-N00N	85.87(15)	89.7447
Ir01-N00N	2.064(3)	2.0682	N00L-Ir01-N00H	92.71(15)	91.0424
Ir01-N00M	2.183(3)	2.2083	N00H-Ir01-C00U	79.34(17)	79.7396
Ir01-N00L	2.125(3)	2.1608	N00L-Ir01-C01C	97.76(14)	102.6064
^a Data from single crystals structure of Ir-A3. ^b Data from computational investigation of Ir-A3.					

4. Photophysical data of iridium(III) complexes.

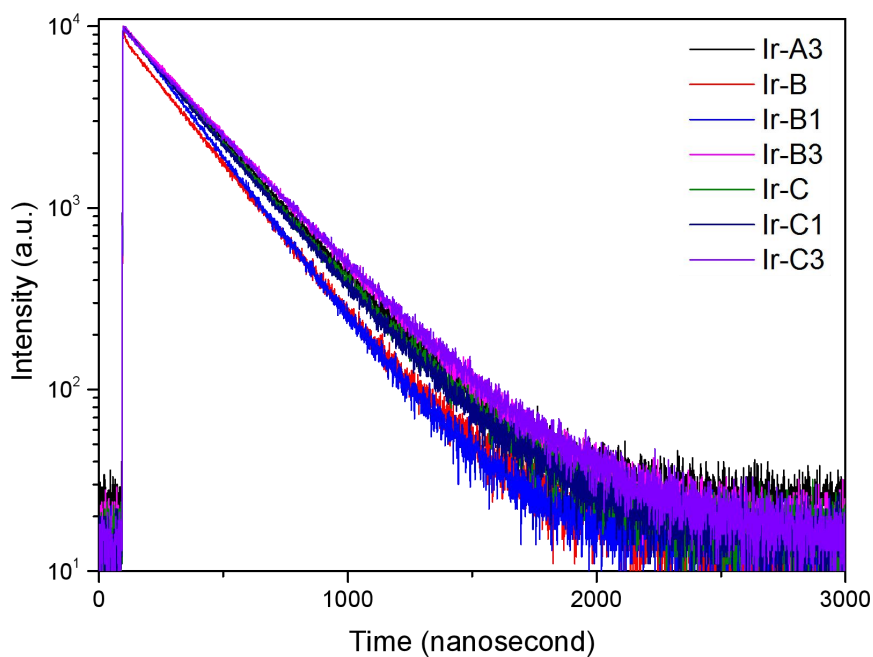


Figure S1. Phosphorescence decays of the complexes measured in CH₂Cl₂ at 25 °C under argon.

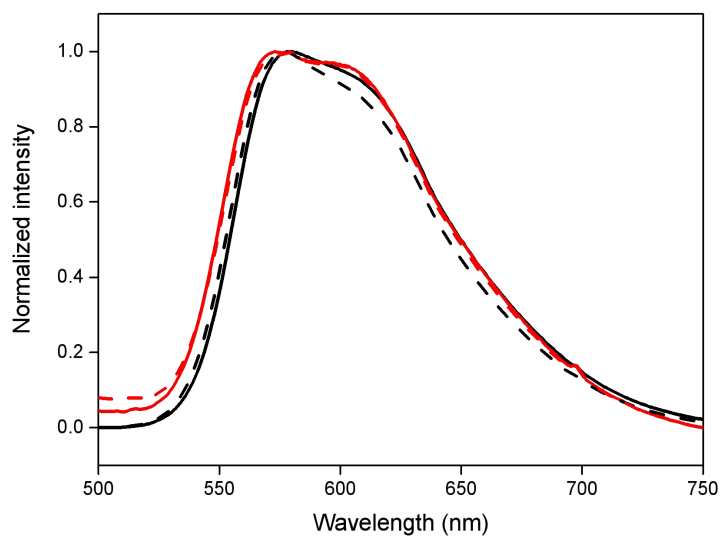


Figure S2. The normalized photoluminescence spectra of complexes Ir-C1 (black) and Ir-C3 (red) in the state of amorphous (solid) and liquid crystalline (dash).

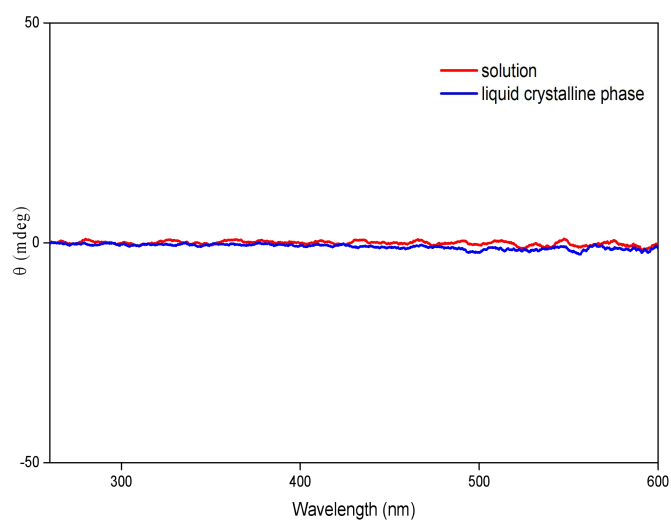


Figure S3. The CD spectra in CH_2Cl_2 solution (red) and in liquid crystalline phase (blue) at room temperature.

5. Cyclic voltammetry (CV) of complex Ir-B3.

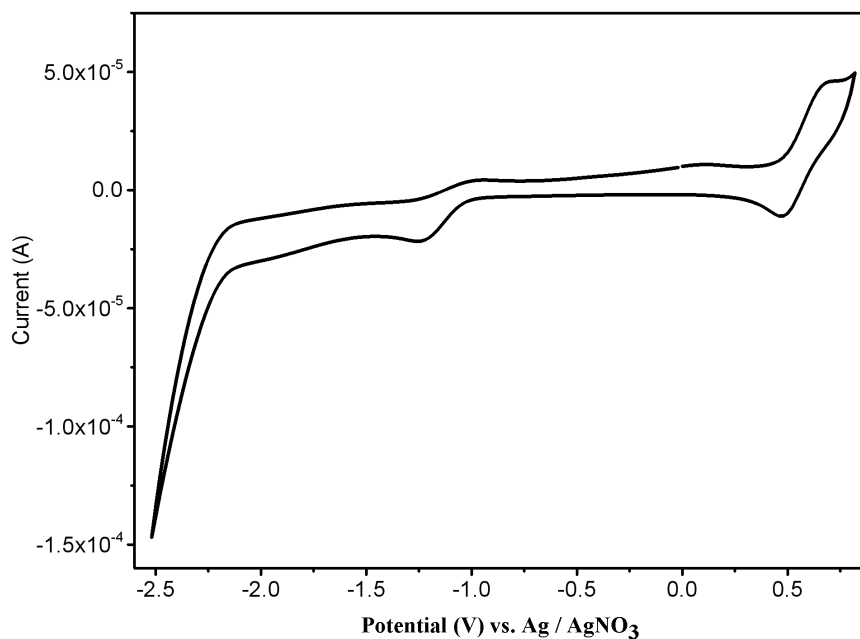


Figure S4. Cyclic voltammetry (CV) of complex Ir-B3. CV data were measured in degassed CH_2Cl_2 solution ($M = 1.0 \times 10^{-3} \text{ mol/L}$) with Pt wire, Ag/AgNO₃ electrode and Glassy carbon as counter, reference, and working electrodes, respectively. The scan rate was 100 mV/s, and ferrocene was used as a reference.

6. Polarized optical micrographs of Ir-C1

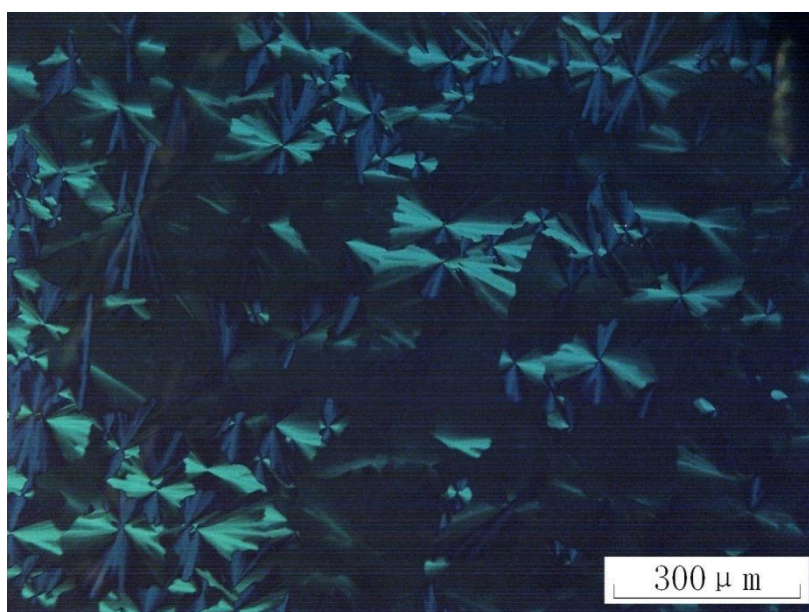
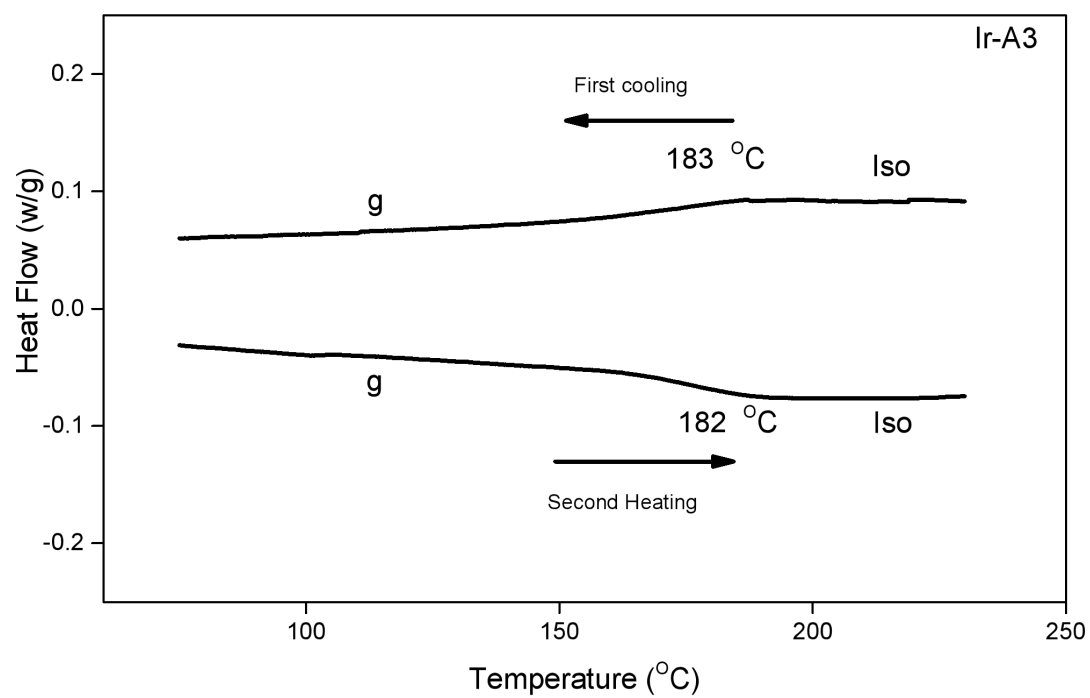
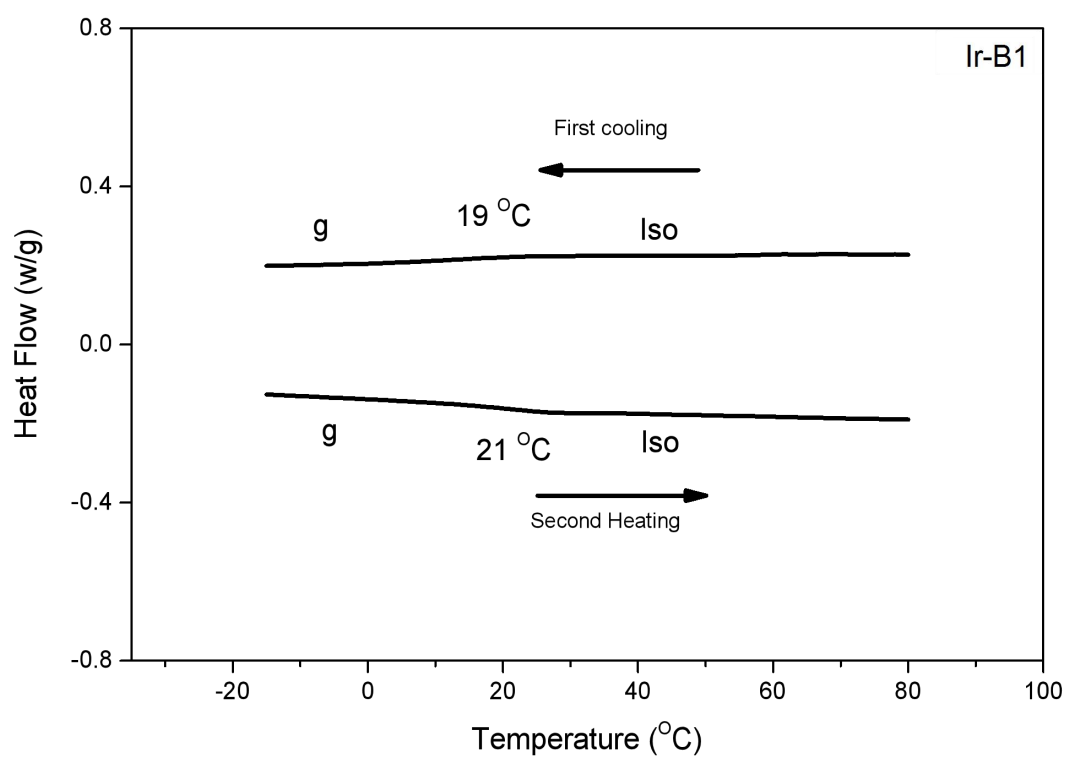
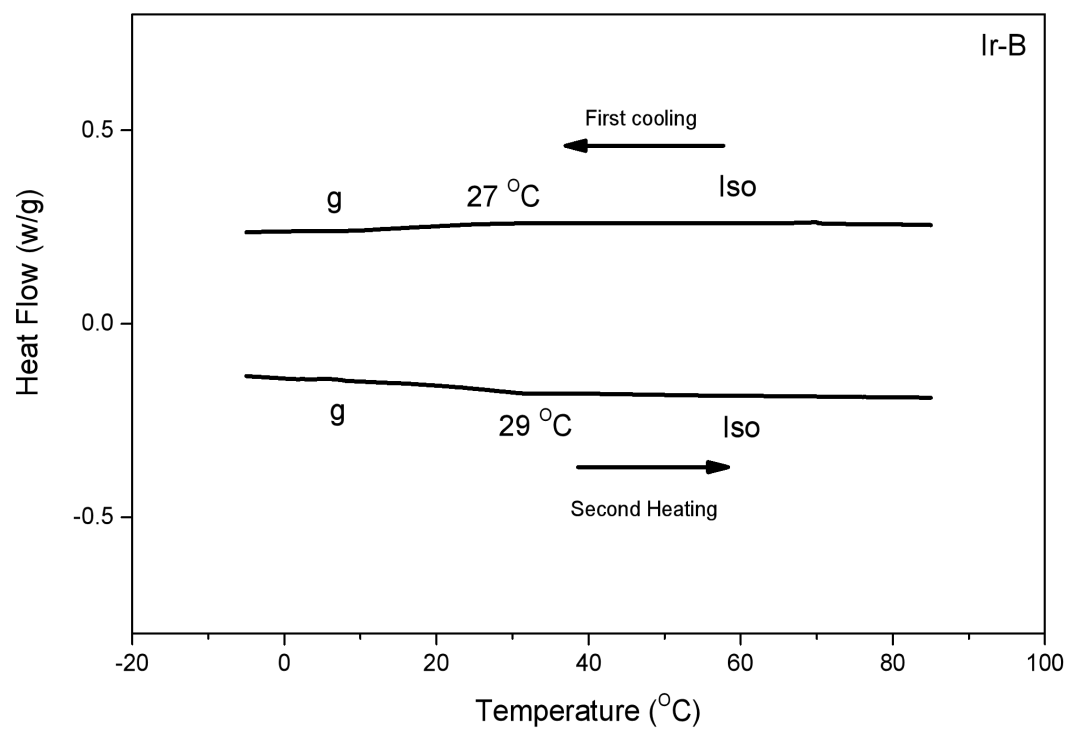


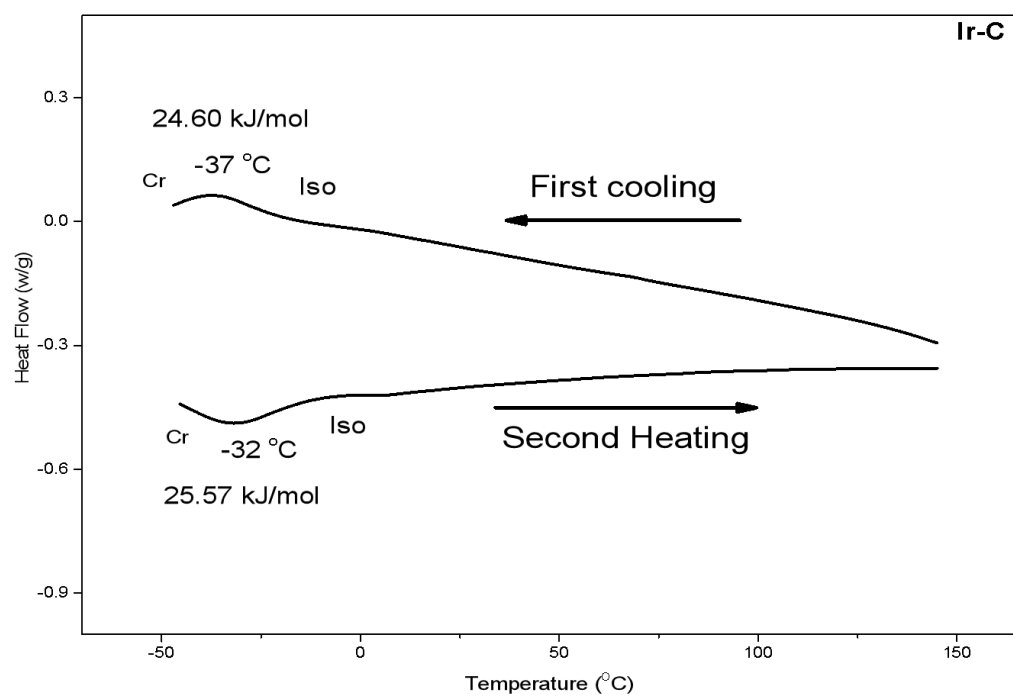
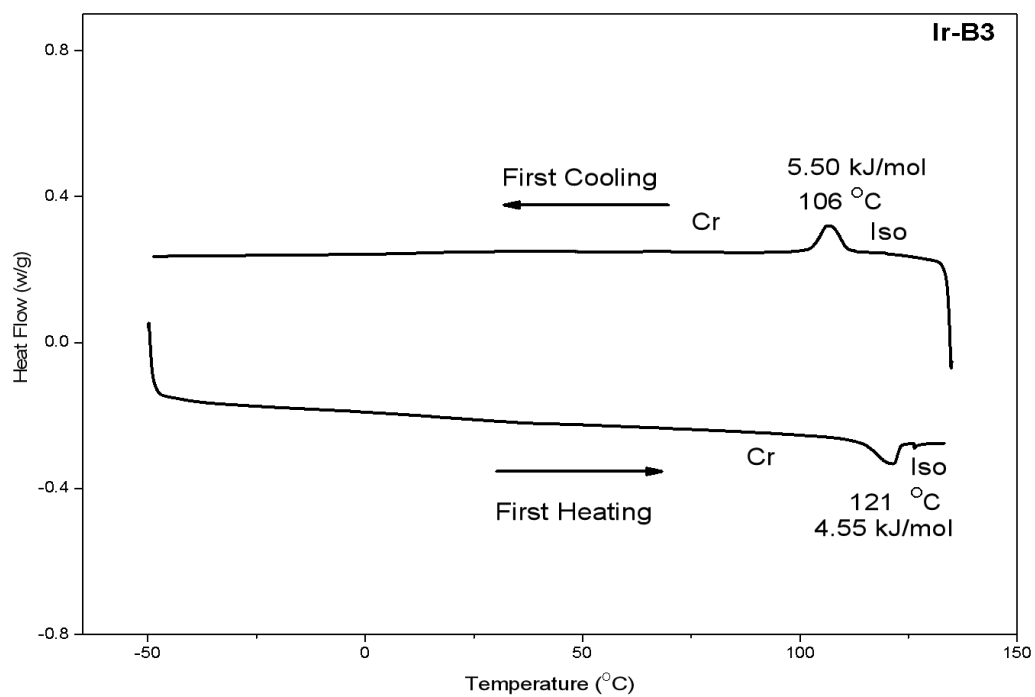
Figure S5. Polarized optical micrographs (on cooling) of Ir-C1, 102 °C.

Table S3. The photoluminescence data of complexes Ir-C1 and Ir-C3 in amorphous and liquid crystalline states at room temperature ($\lambda_{\text{ex}} = 425 \text{ nm}$).		
complex	LC (nm)	A (nm)
Ir-C1	578	579
Ir-C3	579	578
LC and A are liquid crystalline phase and amorphous state, respectively.		

7. DSC curves of iridium(III) complexes







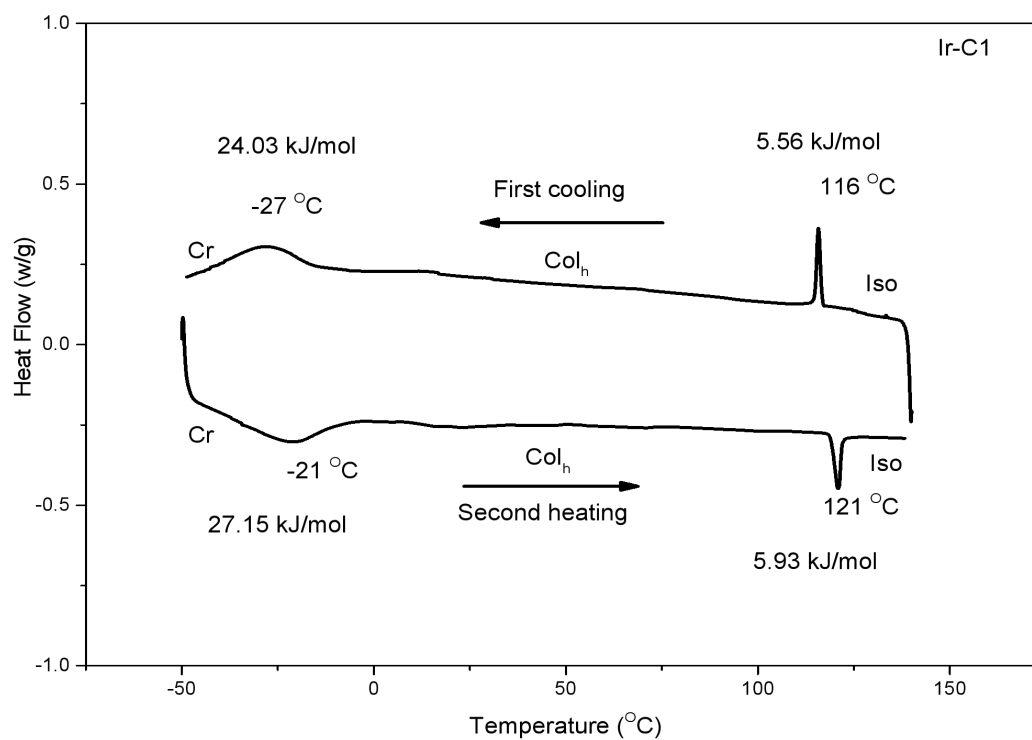


Figure S6. DSC spectra of iridium(III) complexes at the scan rate of 10 °C/min under the protection of nitrogen.

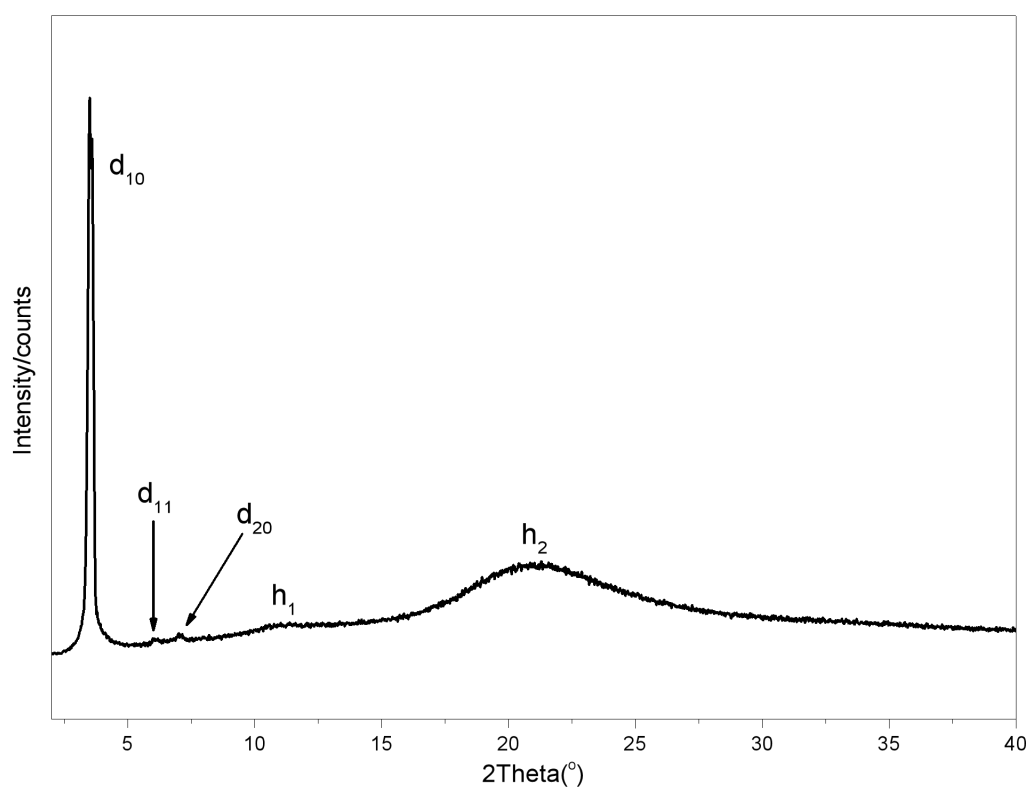


Figure S7. The powder XRD patterns of Ir-C1 at room temperature.

8. Computed excitation energies and oscillator strengths for complex Ir-A3

Table S4. Computed Excitation Energies and Oscillator Strengths for the $S_0 \rightarrow S_n$ Transitions of the Complex Ir-A3.^a

$\lambda(\text{nm})$	E(eV)	f	transitions
463.2	2.68	0.0048	S1 HOMO \rightarrow LUMO(+98%)
428.6	2.89	0.1445	HOMO \rightarrow LUMO+1(+96%)
358.1	3.46	0.2189	HOMO-1 \rightarrow LUMO+1(+83%) HOMO-1 \rightarrow LUMO+2(6%)
351.2	3.53	0.0913	HOMO-2 \rightarrow LUMO+1(+54%) HOMO-3 \rightarrow LUMO+1(12%)
			HOMO-2 \rightarrow LUMO+2(11%) HOMO-3 \rightarrow LUMO+2(+6%)
342.3	3.62	0.2865	HOMO-2 \rightarrow LUMO+2(+55%) HOMO-2 \rightarrow LUMO+1(+24%)
			HOMO-3 \rightarrow LUMO+2(10%)
336.3	3.69	0.1034	HOMO-3 \rightarrow LUMO+1(+63%) HOMO-2 \rightarrow LUMO+1(+9%)
			HOMO-2 \rightarrow LUMO+2(8%)
334.2	3.71	0.0666	HOMO-3 \rightarrow LUMO+2(+46%) HOMO-1 \rightarrow LUMO+3(19%)
			HOMO-2 \rightarrow LUMO+2(+12%) HOMO-3 \rightarrow LUMO+2(+7%)
331.2	3.74	0.0704	HOMO-6 \rightarrow LUMO(+31%) HOMO-7 \rightarrow LUMO(15%)
			HOMO-1 \rightarrow LUMO+3(9%) HOMO-3 \rightarrow LUMO+2(9%)
			HOMO-5 \rightarrow LUMO(+9%) HOMO-8 \rightarrow LUMO(6%)
323.6	3.83	0.065	HOMO-2 \rightarrow LUMO+3(+46%) HOMO-5 \rightarrow LUMO+2(+19%)
320.9	3.86	0.0684	HOMO-5 \rightarrow LUMO+2(+33%) HOMO-2 \rightarrow LUMO+3(23%)
			HOMO-6 \rightarrow LUMO(+10%) HOMO-1 \rightarrow LUMO+5(+8%)
			HOMO-7 \rightarrow LUMO+2(+7%)
318.5	3.89	0.1906	HOMO-7 \rightarrow LUMO(+55%) HOMO-6 \rightarrow LUMO(+27%)
			HOMO-2 \rightarrow LUMO+3(+5%)
317.3	3.91	0.1933	HOMO-8 \rightarrow LUMO(+71%) HOMO-6 \rightarrow LUMO(+6%)
310.9	3.99	0.0642	HOMO-2 \rightarrow LUMO+4(+19%) HOMO-1 \rightarrow LUMO+5(16%)
			HOMO-8 \rightarrow LUMO+2(9%) HOMO-1 \rightarrow LUMO+4(+9%)
			HOMO-6 \rightarrow LUMO+1(+8%) HOMO-2 \rightarrow LUMO+3(7%)
			HOMO-7 \rightarrow LUMO+2(5%)
308.9	4.01	0.1788	HOMO-6 \rightarrow LUMO+2(+31%) HOMO-1 \rightarrow LUMO+5(+30%)
			HOMO-6 \rightarrow LUMO+1(12%) HOMO-8 \rightarrow LUMO+2(8%)
			HOMO-3 \rightarrow L+2(+6%)
306.7	4.04	0.0637	HOMO-1 \rightarrow LUMO+4(+40%) HOMO-5 \rightarrow LUMO+3(11%)
			HOMO-6 \rightarrow LUMO+1(9%) HOMO-5 \rightarrow LUMO+2(8%)
299.9	4.13	0.1941	HOMO-5 \rightarrow LUMO+3(+28%) HOMO-2 \rightarrow LUMO+5(19%)
			HOMO-6 \rightarrow LUMO+1(15%) HOMO-2 \rightarrow LUMO+4(+11%)
			HOMO-3 \rightarrow LUMO+5(+8%)
298.1	4.16	0.1276	HOMO-7 \rightarrow LUMO+1(+24%) HOMO-2 \rightarrow LUMO+5(19%)
			HOMO-8 \rightarrow LUMO+1(+12%) HOMO-6 \rightarrow LUMO+1(+10%)

^aExcept for S1 transitions, only calculated excitation with $f \geq 0.06$ are listed.

9. DSC data of all complexes.

Table S5. DSC data of all complexes.			
Com	Heating process		
	Transition	Tem (°C)	$\Delta H(\text{KJ}\cdot\text{mol}^{-1})$
Ir-A3	g-Iso	182	—
Ir-B	g-Iso	29	—
Ir-B1	g-Iso	21	—
Ir-B3	Cr-Iso	121	4.55
Ir-C	Cr-Iso	-32	25.57
Ir-C1	Cr-Col _h	-21	27.15
	Col _h -Iso	121	5.93
Ir-C3	Cr-Col _h	-9	52.24
	Col _h -Iso	97	5.77
Com = compounds; Tem = temperature; g = glass state; Iso = isotropic liquid; Cr = crystal phase. Data from the second heating process of DSC (Figure S6 and Figure 7 , 10 °C/min).			