Supporting Information

Carborane tuning photophysical properties of phosphorescent iridium(III) complexes

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I. Experimental details

I.1 Materials and methods

Unless noted, all reagents or solvents were obtained from commercial suppliers and used without further purification. All air and moisture sensitive reactions were carried out under an argon atmosphere. Dry DME and pyridine were obtained by refluxing and distilling over CaH_2 under nitrogen. Dry THF was distilled from sodium/benzophenone. 1-(4-Bromophenyl)-o-carborane,[S1a] 1-(4-Bromophenyl)-m-carborane,[S1b] 1-(4-Bromophenyl)-p-carborane,[S1b] 2-(6-phenyl-1,3,6,2-dioxazaborocan-2-yl)pyridine (**Py**),[S2] Ir(ppy)$_2$acac (complex **1**)[S3] and [Ir(ppy)$_2$phen]PF$_6$ (complex **2**)[S4] were synthesized according to literature procesures. The ^{1}H, ^{13}C and ^{11}B NMR spectra were measured at room temperature by using a Bruker 500 MHz spectrometer. $CDCl_3$ was used as deuterated reagent unless specified. Mass spectra were measured with a Bruker Daltonics Autoflex II^{TM} MALDI TOF MS spectrometer, Micromass GC-TOF for EI-MS (70 eV) or a ESI-MS (LCQ Fleet, Thermo Fisher Scientific). Electrochemical measurements were performed with an IM6ex (Zahner). Phosphorescence spectral measurements were carried out by using a Hitachi F-4600 fluorescence spectrophotometer. Electronic absorption spectra were recorded with Shimadzu UV-2550 spectrophotometers. Phosphorescence lifetimes were determined by an Edinburgh instrument laser impulse fluorometer with picosecond time resolution. Elemental analyses for C, H, and N were performed on a Vario MICRO elemental analyzer.

I.2 Quantum yields determination

Phosphorescence spectroscopic studies were performed on a Hitachi F-4600 fluorescence spectrophotometer and Shimadzu UV-2550 spectrophotometers. The slit width was 2.5 nm for excitation and 5.0 nm for emission. *Fac*-(Ir(ppy)$_3$ in degassed CH_2Cl_2 ($\Phi_P = 0.40$)[S5] under Ar was used as the standard for the phosphorescent quantum yield calculation according to the absorption of the test sample. The spectroscopic grade solvents and a 1 cm quartz cuvette were used. Dilute solutions (10^{-6} M) were used to minimize the reabsorption effects. The quantum yields of phosphorescence were measured three times for each complex and averaged. Quantum yields were determined using the following equation:

$$Yu=Ys*Fu/Fs*As/Au*Gu^2/Gs^2$$

Ys is the reported quantum yield of *fac*-(Ir(ppy)$_3$. Fu is the area under the emission spectra of the measured compound. Fs is the area under the emission spectra of the standard. As is the absorbance at the excitation wavelength of the measured compound. Au is the absorbance at the excitation wavelength of the standard. Gu is the refractive index of the solvent used. Gs is the refractive index of the solvent of the standard. Molar extinction coefficients were obtained from the slope of a graph of absorbance *vs* concentration for each complex with five different concentrations (10^{-6} M).

I.3 Electrochemical determination

Cyclic Volta metric experiments were carried out with an IM6ex (Zahner) using three electrode cell assemblies. All measurements were carried out in a one-compartment cell under Argon, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag$^+$ reference electrode with a scan rate of 100 mV s^{-1}. The supporting electrolyte was a 0.10 mol L^{-1} acetonitrile solution of tetrabutyl-ammonium hexafluorophosphate (Bu_4NPF_6). Each oxidation potential was calibrated with ferrocene as a reference.

I.4 X-ray structure determination

The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-2θ scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000. All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Mercury. CCDC 919799, 919800, 919801 and 919802 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

I.5 Quantum chemical calculations

The geometries of all iridium(III) complexes were optimized using the density functional theory (DFT) method. The electronic transition energies including electron correlation effects were computed by the time dependent density functional theory (TD-DFT) method using the B3LYP functional (TD-B3LYP). The LANL2DZ basis set was used to treat the iridium atom, whilst the 6-31G(d) basis set was used to treat all other atoms. All calculations described here were performed by using the Gaussian 03 program.[S6]

I.6 Synthetic section

o-ppy: A mixture of Py (0.089 g, 0.17 mmol), 1-(4-Bromophenyl)-o-carborane (0.03 g, 0.1 mmol), $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol), K_2CO_3 (27.6 mg, 0.2 mmol, 2 equiv), CuI (7.6 mg, 0.04 mmol, 0.4 equiv), and THF (8 mL) was refluxed for 24 h under argon. After cooling down to r.t., the mixture was quenched with sat.aq EDTA (40 mL). The resulting mixture was extracted with CH_2Cl_2 (3×50 mL) and the combined organic layers were dried (Mg_2SO_4). Removal of the solvents in vacuo gave a residue, which was subjected to column chromatography on silica gel. Elution with CH_2Cl_2 to give white solid 23.8 mg, 80 %. ^{1}H NMR: 8.71(d, 1H), 7.97 (d, 2H), 7.78 (t, 1H), 7.72 (d, 1H), 7.59 (d, 2H), 7.29 (d, 1H), 4.02 (s, 1H, carborane), 3.21–1.73 (br, 10H, B−H). ^{13}C NMR: 155.5, 149.7, 140.6, 137.1, 134.1, 127.9, 127.2, 122.9, 120.5, 76.1, 59.7. ^{11}B NMR: 1.2 (2B), −1.0 (1B), −5.7 (3B), −7.6 (2B), −8.0 (1B), −9.6 (1B). IR(KBr): (ν cm^{-1}) 2595 (B–H). $C_{13}H_{19}B_{10}N$ calcd: C, 52.34; N, 4.69; H, 6.37. Found: C, 52.06; N, 4.86; H, 6.25. EI-MS (*m/z*): 298.3 (M$^+$, 80%).

m-ppy was synthesized by the same proceture as o-ppy. White solid. 25.3 mg, 85 %. ^{1}H NMR: 8.69 (d, 1H), 7.89 (d, 2H), 7.76 (t, 1H), 7.65 (d, 1H), 7.53 (d, 2H), 7.25 (d, 1H), 3.10 (s, 1H, carborane), 3.29–1.71 (br, 10H, B−H). ^{13}C NMR: 156.3, 149.9, 139.9, 136.9, 135.8, 128.4, 126.9, 122.6, 120.6, 78.2, 55.2. ^{11}B NMR: −0.8 (2B), −5.5 (1B), −7.2 (3B), −10.1 (2B), −11.9 (2B). IR(KBr): (ν cm^{-1}) 2605 (B−H). $C_{13}H_{19}B_{10}N$ calcd: C, 52.34; N, 4.69; H, 6.37. Found: C, 52.10; N, 4.78; H, 6.28. EI-MS (*m/z*): 298.3 (M$^+$, 60%).

p-ppy was also synthesized by the same proceture as o-ppy. White solid. 23.8 mg, 80 %. ^{1}H NMR: 8.67(d, 1H), 7.95 (d, 2H), 7.73 (t, 1H), 7.65 (d, 1H), 7.31 (d, 2H), 7.23 (q, 1H), 2.82 (s, 1H, carborane), 3.17–1.73 (br, 10H, B−H). ^{13}C NMR: 156.4, 149.6, 139.3, 137.4, 136.6, 127.4, 126.5, 122.3, 120.4, 86.0, 59.7. ^{11}B NMR: −9.0 (5B), −11.6 (5B). IR(KBr): (ν cm^{-1}) 2610 (B−H). $C_{13}H_{19}B_{10}N$ calcd: C, 52.34; N, 4.69; H, 6.37. Found: C, 51.97; N, 4.82; H, 6.22. EI-MS (*m/z*): 298.2 (M$^+$, 44%).

[(o-ppy)$_2$Ir(μ-Cl)]$_2$: $IrCl_3·2H_2O$ (0.071 g, 0.2 mmol) and o-ppy (0.149 g, 0.5 mmol) were dissolved in 2-ethoxyethanol (6 mL) and water (2 mL), and then refluxed for 24 h. The solution was cooled to room temperature, and the resulting precipitate was collected by filtration and washed with water and ethanol. The washed product was dried under vacuum to give yellow solid 213 mg, 65 %. ^{1}H NMR: 9.25 (d, 4H), 7.94 (m, 8H), 7.43 (d, 4H), 6.99 (t, 4H), 6.89 (d, 4H), 5.98 (s, 4H), 3.53 (s, 4H, carborane), 2.77–1.61 (br, 40H, B−H). ^{11}B NMR: 0.9 (8B), −0.8 (4B), −6.1 (12B), −7.9 (16B). IR(KBr): (ν cm^{-1}) 2590 (B–H). $C_{52}H_{72}B_{40}N_4Cl_2Ir_2$ calcd: C, 38.04; N, 3.41; H, 4.38. Found: C, 37.75; N, 3.56; H, 4.25.

[(m-ppy)$_2$Ir(μ-Cl)]$_2$ was synthesized by the same proceture as [(o-ppy)$_2$Ir(μ-Cl)]$_2$. Yellow solid. 206 mg, 63 %. ^{1}H NMR: 9.27 (d, 4H), 7.88 (d, 4H), 7.84 (d, 4H), 7.34 (d, 4H), 6.90 (t, 4H), 6.85 (d, 4H), 5.88 (s, 4H), 2.84 (s, 4H, carborane), 2.76–1.69 (br, 40H, B−H). ^{11}B NMR: −1.0 (12B), −7.7 (12B), −10.6 (8B), −12.3 (8B). IR(KBr): (ν cm^{-1}) 2603 (B−H). $C_{52}H_{72}B_{40}N_4Cl_2Ir_2$ calcd: C, 38.04; N, 3.41; H, 4.38. Found: C, 37.80; N, 3.59; H, 4.28.

[(p-ppy)$_2$Ir(μ-Cl)]$_2$ was also synthesized by the same proceture as [(o-ppy)$_2$Ir(μ-Cl)]$_2$. Yellow solid. 196 mg, 60 %. ^{1}H NMR: 9.21 (d, 4H), 7.82 (m, 8H), 7.25 (d, 4H), 6.89 (t, 4H), 6.61 (d, 4H), 5.63 (d, 4H), 2.62 (s, 4H, carborane), 2.58–1.58 (br, 40H, B−H). ^{11}B NMR: −9.3 (20B), −12.1 (20B). IR(KBr): (ν cm^{-1}) 2610 (B–H). $C_{52}H_{72}B_{40}N_4Cl_2Ir_2$ calcd: C, 38.04; N, 3.41; H, 4.38. Found: C, 37.66; N, 3.61; H, 4.30.

o-1: [(o-ppy)$_2$Ir(μ-Cl)]$_2$ (0.328 g, 0.2 mmol), acetylacetone (0.1 mL, 1 mmol) and Na_2CO_3 (0.106 g, 1.0 mmol) were dissolved in 2-ethoxyethanol (12 ml). The mixture was kept at 120 ^{o}C under argon for 12 h. After cooling to room temperature, water was added, then the mixture was extracted with CH_2Cl_2 (3×20 mL) and the combined organic layers were dried (Mg_2SO_4). Removal of the solvents in vacuo gave a residue, which was subjected to column chromatography on silica gel. Elution with CH_2Cl_2/petroleum ether 2:1 (v/v) gave **o-1** as yellow solid. 62 mg, 35 %. ^1H NMR: 8.52 (d, 2H), 7.88 (m, 4H), 7.42 (d, 2H), 7.31 (t, 2H), 6.90 (d, 2H), 6.21 (s, 2H), 5.27 (s, 1H, CH), 3.64 (s, 2H, carborane), 1.83(s, 6H, 2Me), 2.87–1.62 (br, 20H, B−H). ^{13}C NMR: 184.9, 167.1, 148.4, 147.1, 146.6, 137.5, 132.5, 131.7, 123.2, 122.5, 120.5, 119.1, 100.7, 83.8, 60.4, 28.6. ^{11}B NMR: 0.9 (4B), −1.2 (2B), −6.2 (6B), −7.7 (4B), −8.4 (2B), −9.8 (2B). IR(KBr): (ν cm^{-1}) 2592 (B–H). $C_{31}H_{43}B_{20}N_2O_2Ir$ calcd: C, 42.03; N, 3.16; H, 4.85. Found: C, 41.65; N, 3.04; H, 4.69. MALDI-TOF: (*m/z*) 884.9 (M^+).

m-1 was synthesized by the same proceture as **o-1**. Yellow solid. 71 mg, 40 %. ^1H NMR: 8.51 (d, 2H), 7.82 (m, 4H), 7.35 (d, 2H), 7.24 (t, 2H), 6.84 (d, 2H), 6.13 (s, 2H), 5.24 (s, 1H, CH), 2.88 (s, 2H, carborane), 1.81(s, 6H, 2Me), 2.77–1.63 (br, 20H, B−H). ^{13}C NMR: 184.7, 167.7, 148.2, 146.8, 145.5, 137.1, 134.5, 131.8, 123.2, 121.9, 120.6, 118.7, 100.7, 79.0, 54.5, 28.6. ^{11}B NMR: −1.1 (2B), −5.7 (2B), −7.7 (8B), −10.6 (4B), −12.2 (4B). IR(KBr): (ν cm^{-1}) 2607 (B–H). $C_{31}H_{43}B_{20}N_2O_2Ir$ calcd: C, 42.03; N, 3.16; H, 4.85. Found: C, 41.72; N, 3.27; H, 4.95. MALDI-TOF: (*m/z*) 884.9 (M^+).

p-1 was synthesized by the same proceture as **o-1**. Yellow solid. 74 mg 42 %. ^1H NMR: 8.46 (d, 2H), 7.80 (d, 4H), 7.26 (s, 2H), 7.23 (t, 2H), 6.62 (d, 2H), 5.89 (s, 2H), 5.21 (s, 1H, CH), 2.65 (s, 2H, carborane), 1.79(s, 6H, 2Me), 2.61–1.62 (br, 20H, B−H). ^{13}C NMR: 184.6, 167.7, 148.2, 146.3, 144.9, 136.9, 136.0, 130.7, 122.7, 121.8, 119.5, 118.6, 100.4, 87.1, 59.3, 28.6. ^{11}B NMR: −9.3 (10B), −12.1 (10B). IR(KBr): (ν cm^{-1}) 2613 (B–H). $C_{31}H_{43}B_{20}N_2O_2Ir$ calcd: C, 42.03; N, 3.16; H, 4.85. Found: C, 41.70; N, 3.24; H, 4.93. MALDI-TOF: (*m/z*) 884.9 (M^+).

o-2: $[(o\text{-}ppy)_2Ir(\mu\text{-}Cl)]_2$ (0.082 g, 0.05 mmol) and 1,10-phenanthroline hydrate (0.02 g, 0.1 mmol) were dissolved in methaol (5 ml) and CH_2Cl_2 (5 ml). The mixture was refluxed under argon, After 4 h, the solution was cooled to room temperature, and then a 10-fold excess of potassium hexafluoro-phosphate was added. The suspension was stirred for 2 h, and then filtered to remove insoluble inorganic salts. The resulting solution was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with elution by CH_2Cl_2/aceton 15:1 (v/v) to give **o-2** as yellow solid. 36 mg, 65 %. ^1H NMR (CD_3CN): 8.73 (d, 2H), 8.26 (s, 2H), 8.21 (d, 2H), 8.12 (d, 2H), 7.88 (m, 4H), 7.79 (d, 2H), 7.49 (d, 2H), 7.24 (d, 2H), 7.02 (t, 2H), 6.44 (d, 2H), 4.49 (s, 2H, carborane), 2.93–1.63 (br, 20H, B−H). ^{13}C NMR (CD_3CN): 165.8, 151.3, 149.8, 149.3, 146.6, 146.3, 138.8, 138.7, 134.1, 131.6, 130.2, 128.2, 126.7, 124.6, 124.4, 121.5, 120.7, 76.7, 60.8. ^{11}B NMR (CD_3CN): 0.1 (4B), −1.6 (2B), −6.3 (6B), −8.0 (6B), −9.8 (2B). IR(KBr): (ν cm^{-1}) 2588 (B–H). $C_{38}H_{44}B_{20}N_4F_6PIr$ calcd: C, 41.04; N, 5.04; H, 3.96. Found: C, 40.69; N, 4.91; H, 4.07. ESI-MS: (*m/z*) 965.9 (M-PF_6, 100%), 145 (PF_6, 100%).

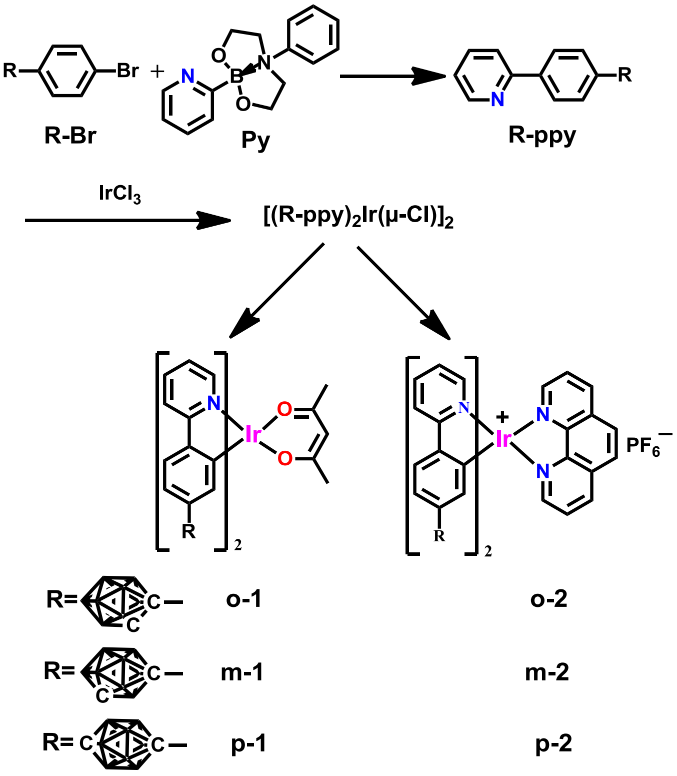
m-2 was sythesized by the same proceture as o-2. Yellow solid. 39 mg, 70 %. ^1H NMR (CD_3CN): 8.71

(d, 2H), 8.26 (s, 2H), 8.19 (d, 2H), 8.08 (d, 2H), 7.87 (m, 4H), 7.72 (d, 2H), 7.47 (d, 2H), 7.20(d, 2H), 6.98(t, 2H), 6.36(d, 2H), 3.43(s, 2H, carborane), 3.03–1.52 (br, 20H, B−H). ^{13}C NMR (CD_3CN): 166.2, 151.2, 149.6, 149.3, 146.7, 145.2, 138.7, 138.6, 136.1, 131.6, 130.3, 128.2, 126.7, 124.4, 123.9, 122.2, 120.4, 78.4, 55.8. ^{11}B NMR (CD_3CN): −1.2 (2B), −5.3 (2B), −7.7 (8B), −10.3 (4B), −11.9 (4B). IR(KBr): (ν cm^{-1}) 2600 (B–H). $C_{38}H_{44}B_{20}N_4F_6PIr$ calcd: C, 41.04; N, 5.04; H, 3.96. Found: C, 40.78; N, 5.12; H, 4.10. ESI-MS: (*m/z*) 965.9 (M-PF_6, 100%), 144.9 (PF_6, 100%).

p-2 was sythesized by the same proceture as o-2. Yellow solid. 38 mg, 68 %. ^{1}H NMR (CD_3CN): 8.69 (d, 2H), 8.24 (s, 2H), 8.12 (d, 2H), 8.04 (d, 2H), 7.86 (m, 4H), 7.63 (d, 2H), 7.43 (d, 2H), 6.97(m, 4H), 6.12(s, 2H), 3.14(s, 2H, carborane), 2.81–1.62 (br, 20H, B−H). ^{13}C NMR (CD_3CN): 166.2, 151.1, 149.6, 148.9, 146.7, 144.8, 138.6, 138.5, 137.6, 131.5, 129.4, 128.2, 126.7, 124.2, 123.8, 121.3, 120.2, 86.1, 60.4. ^{11}B NMR (CD_3CN): −9.3 (10B), −11.9 (10B). IR(KBr): (ν cm^{-1}) 2609 (B–H). $C_{38}H_{44}B_{20}N_4F_6PIr$ calcd: C, 41.04; N, 5.04; H, 3.96. Found: C, 40.80; N, 4.93; H, 3.88. ESI-MS: (*m/z*) 965.9 (M-PF_6, 100%), 144.9 (PF_6, 100%).

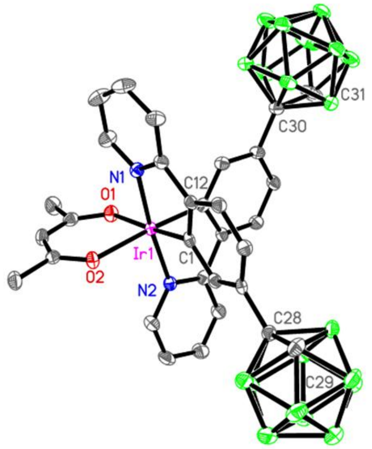
II Supplementary data

II.1

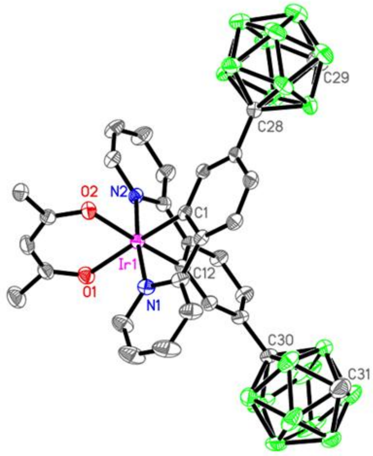


Scheme S1. Synthetic procedures for iridium(III) complexes containing carboranes

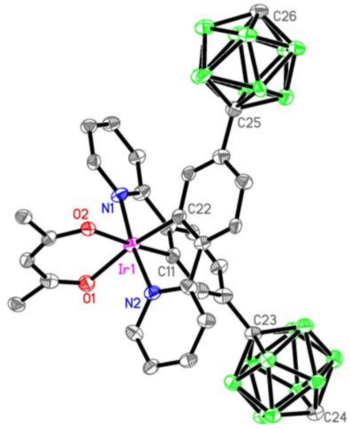
II.2



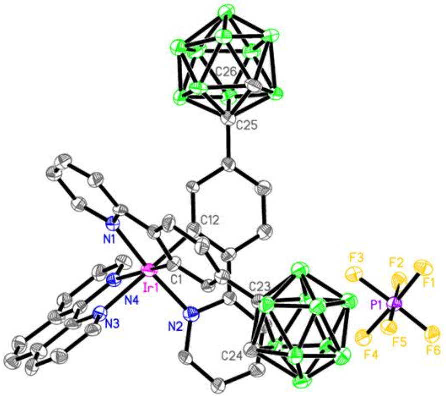
Crystal structure of **o-1**, selected bond lengths (Å): Ir(1)−N(1) 2.037(2), Ir(1)−N(2) 2.035(2), Ir(1)−O(1) 2.1352(18), Ir(1)−O(2) 2.1312(18), Ir(1)−C(1) 1.981(3), Ir(1)−C(12) 1.987(3), C(28)−C(29) 1.652(4), C(30)−C(31) 1.646(4).



Crystal structure of **m-1**, selected bond lengths (Å): Ir(1)−N(1) 2.035(3), Ir(1)−N(2) 2.039(3), Ir(1)−O(1) 2.142(3), Ir(1)−O(2) 2.132(3), Ir(1)−C(1) 1.980(4), Ir(1)−C(12) 1.981(5).



Crystal structure of **p-1**, selected bond lengths (Å): Ir(1)−N(1) 2.008(5), Ir(1)−N(2) 2.001(5), Ir(1)−O(1) 2.118(4), Ir(1)−O(2) 2.104(3), Ir(1)−C(11) 2.012(6), Ir(1)−C(22) 1.955(7).



Crystal structure of **o-2**, selected bond lengths (Å): Ir(1)−N(1) 1.984(5), Ir(1)−N(2) 2.007(5), Ir(1)−N(3) 2.161(5), Ir(1)−N(4) 2.144(5), Ir(1)−C(1) 2.003(6), Ir(1)−C(12) 2.026(6), C(23)−C(24) 1.687(8), C(25)−C(26) 1.681(9).

Figure S1. Crystal structures of **o-1**, **m-1**, **p-1** and **o-2**; ellipsoids show 30% probability levels, and the hydrogen atoms have been omitted for clarity.

II.3

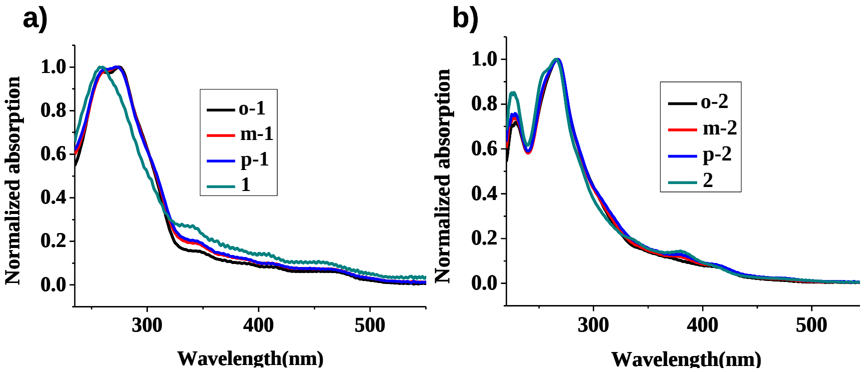


Figure S2. The absorption spectra of **a**) neutral complexes for **o-1**, **m-1**, **p-1** and **1** and **b**) cationic complexes for **o-2**, **m-2**, **p-2** and **2** in degassed CH_2Cl_2 at room temperature

II.4

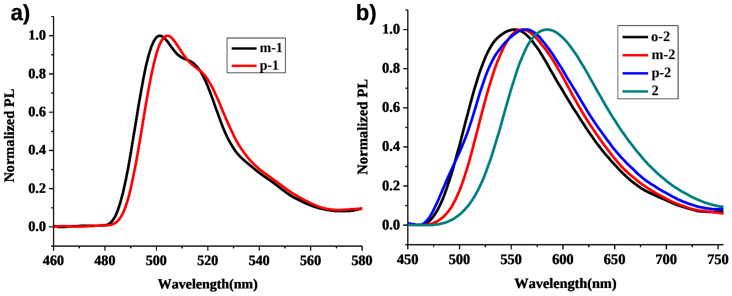
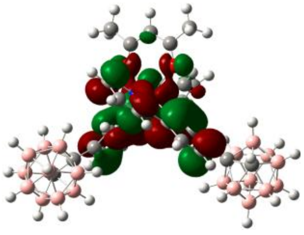
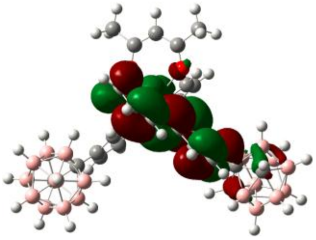
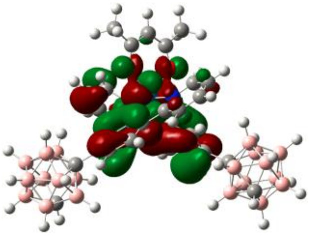
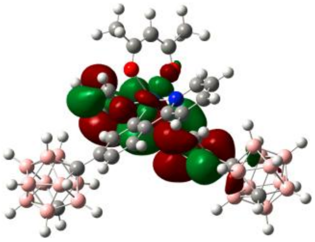
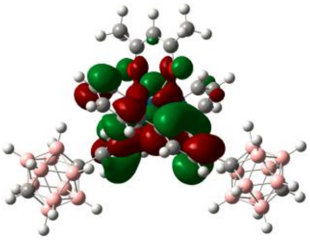
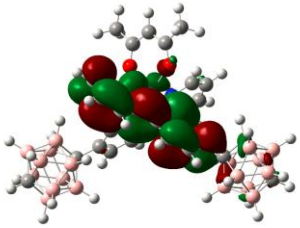
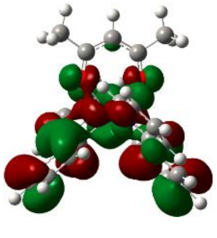
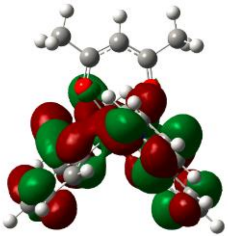


Figure S3. PL spectra of **a**) **m-1**, **p-1** and **b**) **o-2**, **m-2**, **p-2** , **2** in solid at room temperature

II.5

complexes	**HOMO**	**LUMO**
o-1	 -5.42ev	 -1.89ev
m-1	 -5.21ev	 -1.70ev
p-1	 -5.09ev	 -1.60ev
1	 -4.80ev	 -1.27ev

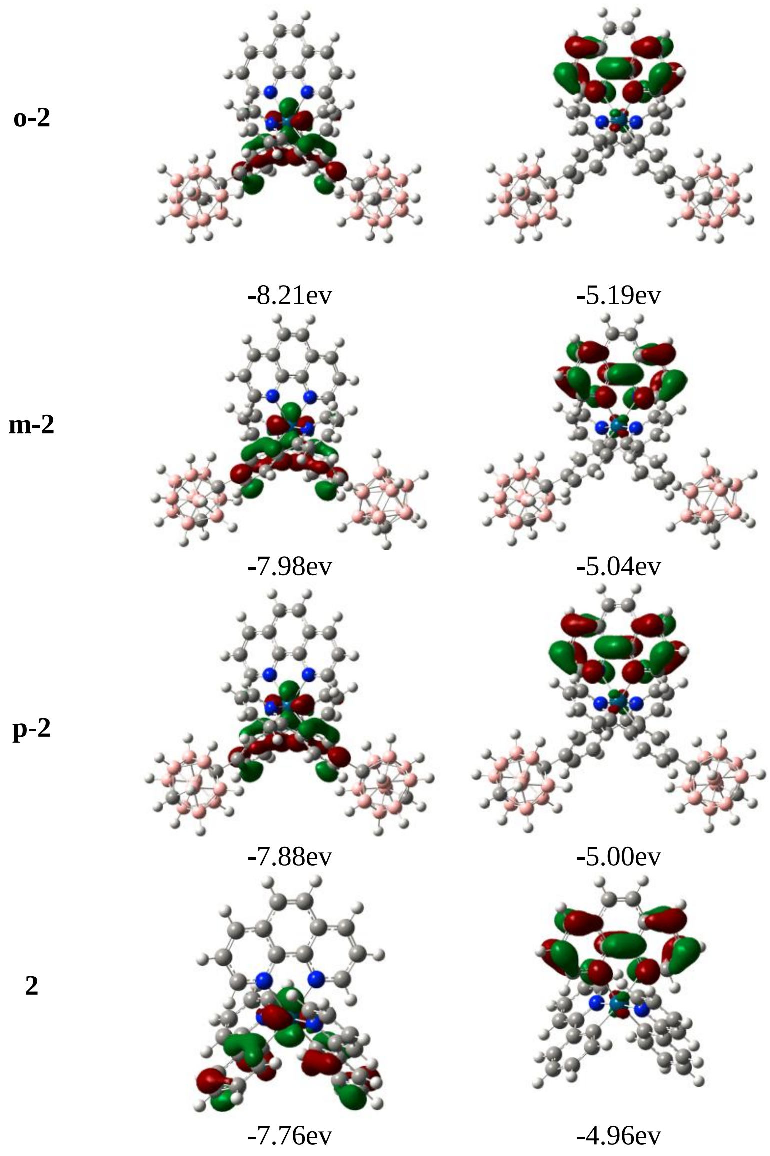


Figure S4. Calculated HOMO and LUMO of iridium(III) complexes

II.6

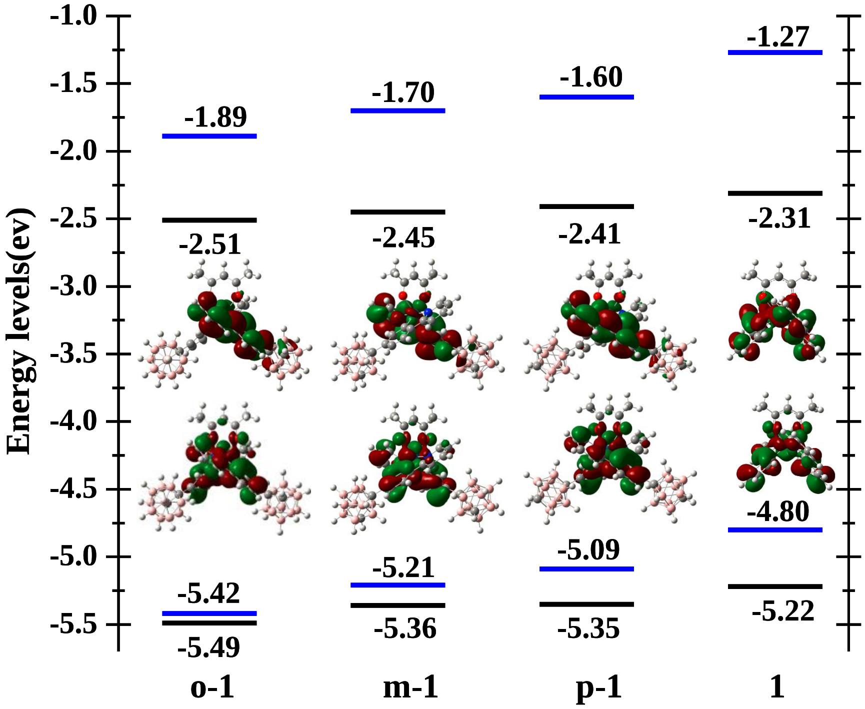


Figure S5 Calculated HOMO/LUMO molecular orbitals and comparison with the experimental energy levels. black (experimental) and blue (calculated).

II.7

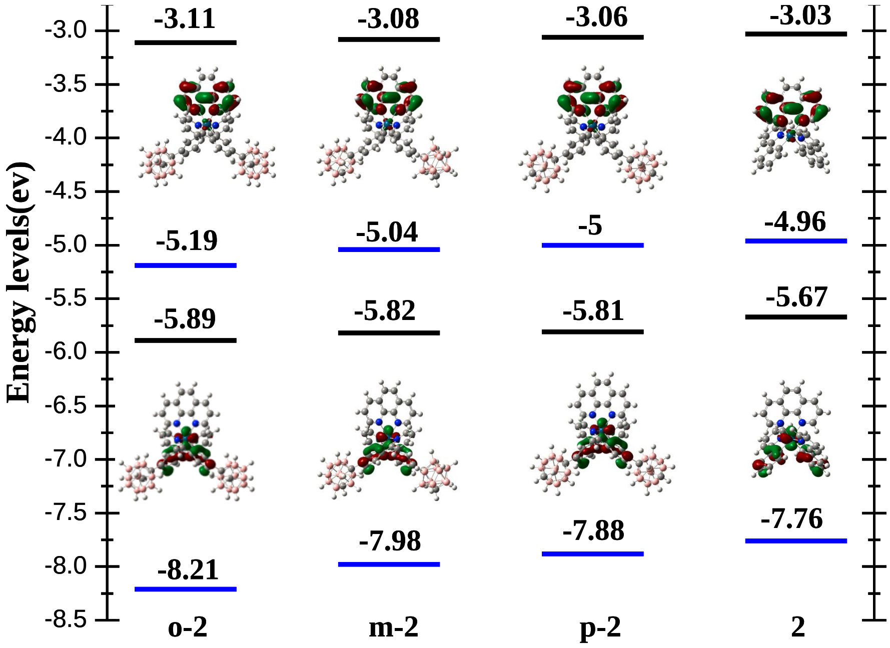


Figure S6. Calculated HOMO/LUMO molecular orbitals and comparison with the experimental energy levels: experimental data are shown in black, while calculated ones are in blue.

II.8

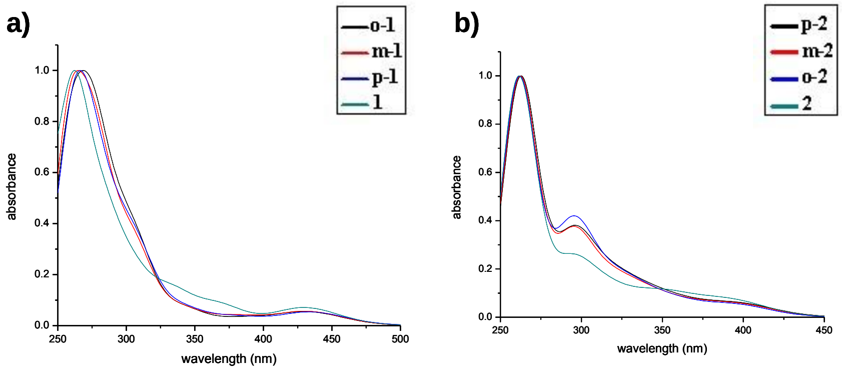


Figure S7. Calculated absorption spectra of **a**) neutral complexes for **o-1**, **m-1**, **p-1** and **1** and **b**) cationic complexes for **o-2**, **m-2**, **p-2** and **2** in CH_2Cl_2

II.9

Table S1. Crystallographic Data for for **o-1**, **m-1**, **p-1** and **o-2**

Compound	**o-1**	**m-1**	**p-1**	**o-2**
chemical formula	$C_{31}H_{43}B_{20}IrN_2O_2$, $CHCl_3$	$C_{31}H_{43}B_{20}IrN_2O_2$, $CHCl_3$	$2(C_{31}H_{43}B_{20}IrN_2O_2)$, $2(CHCl_3)$,H_2O	$2(C_{38}H_{44}B_{20}IrN_4)$, $2(F_6P)$,$7(CH_2Cl_2)$
formula weight	1003.46	1003.46	2024.94	2814.81
crystal size (mm)	0.13 ×0.16 × 0.20	0.13 ×0.16 ×0.20	0.22 ×0.24 ×0.28	0.12 ×0.15 ×0.20
temperature (K)	293	296	291	123
radiation	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	P2(1)/c	P2(1)/n	P2(1)/c	P-1
a(Å)	14.1326(3)	14.4291(15)	17.2631(15)	15.627(4)
b(Å)	15.3504(4)	15.2895(16)	15.3262(13)	15.656(4)
c(Å)	22.2269(4)	20.778(2)	19.1351(16)	27.437(7)
α(°)	90	90	90	100.030(4)
β(°)	114.6320(10)	103.871(2)	113.219(3)	90.447(4)
γ(°)	90	90	90	96.384(5)
V($Å^3$)	4383.15(17)	4450.2(8)	4652.7(7)	6567(3)
Z	4	4	2	2
ρ(calc) (g/cm^3)	1.521	1.498	1.445	1.423
F (000)	1976	1976	1996	2772
absorp.coeff. (mm^{-1})	3.264	3.215	3.076	2.393
θ range (deg)	1.6 to 26.0	1.7 to 26.0	1.3 to 26.0	0.8 to 26.0
reflns collected	26531 (R_{int} = 0.021)	26425 (R_{int} = 0.033)	37239 (R_{int} = 0.082)	52606 (R_{int} = 0.020)
indep. reflns	8617	8733	9144	25583
Refns obs. [$I > 2\sigma(I)$]	7751	7241	6605	17556
data/restr/paras	8617/0/543	8733/0/571	9144/0/597	25583/0/1477

GOF	1.08	1.04	1.01	0.96
R_1/wR_2 [$I > 2\sigma(I)$]	0.0208/0.0524	0.0298/0.0757	0.0510/0.0989	0.0497/0.1234
R_1/wR_2 (all data)	0.0247/0.0536	0.0398/0.0793	0.0717/0.1031	0.0660/0.1269
larg peak and hole(e/Å^3)	0.86/–0.81	0.77/–0.76	1.83/–1.35	1.35/–0.57

II.10

Table S2. Absorption of iridium(III) complexes in degassed CH_2Cl_2 solution at 298K.

complexes	**λ_{abs} /nm ($\varepsilon \times 10^{-3}$/$M^{-1}cm^{-1}$)**
o-1	259(42.1), 276(41.6), 350(5.5), 390(3.5), 414(2.6), 475(1.7), 501(0.5)
m-1	260(36.3),274(37.1), 349(5.3), 390(3.1), 415(2.5), 474(1.4), 500(0.4)
p-1	261(37.6), 274(37.2), 349(5.4), 390(3.0), 415(2.4), 474(1.3), 500(0.4)
1	258(46.8), 339(8.1), 408(3.3), 460(2.3), 493(0.5)
o-2	228(54.9), 266(76.5), 411(5.8), 473(0.9), 524(0.4)
m-2	228(52.7), 267(72.2), 380(8.7), 411(5.7), 479(1.1), 525(0.5)
p-2	227(51.4), 267(72.1), 380(8.5), 411(5.6), 479(1.3), 525(0.5)
2	226(57.5), 265(67.8), 379(9.5), 408(5.3), 479(1.1), 523(0.3)

II.11

Table S3. Absorption of iridium(III) complexes in CH_2Cl_2 solution from TD-DFT calculations.

Complex	states	λ (nm)	E (eV)	oscillator	main configurations (CI coeff)	assignment
o-1	S_1	433	2.86	0.0596	HOMO→LUMO (0.96)	MLCT/ILCT
m-1	S_1	433	2.86	0.0604	HOMO→LUMO (0.96)	MLCT/ILCT
p-1	S_1	435	2.85	0.0597	HOMO→LUMO (0.96)	MLCT/ILCT
1	S_1	431	2.88	0.0561	HOMO→LUMO (0.97)	MLCT/ILCT
o-2	S_1	452	2.74	0.0002	HOMO→LUMO (0.70)	MLCT/LLCT
	S_3	397	3.13	0.0770	HOMO→LUMO+2 (0.69)	MLCT/ILCT
m-2	S_1	464	2.67	0.0002	HOMO→LUMO (0.70)	MLCT/LLCT
	S_3	399	3.11	0.0761	HOMO→LUMO+2 (0.70)	MLCT/ILCT
p-2	S_1	471	2.63	0.0002	HOMO→LUMO (0.70)	MLCT/LLCT
	S_3	400	3.10	0.0763	HOMO→LUMO+2 (0.70)	MLCT/ILCT
2	S_1	493	2.52	0.0003	HOMO→LUMO (0.70)	MLCT/LLCT

	S_3	398	3.11	0.0649	HOMO→LUMO+2 (0.70)	MLCT/ILCT

II.12

Table S4. Calculated phosphorescent emission of iridium(III) complexes in CH_2Cl_2 solution with the TD-DFT method.

complex	state	λ(nm)/E(eV)	major configuration	character
o-1	T_1	593/2.09	HOMO→LUMO (0.82) HOMO-2→LUMO (0.10)	^{3}MLCT/^{3}ILCT ^{3}MLCT
	T_3	488/2.54	HOMO→LUMO+1 (0.63) HOMO-3→LUMO+1 (0.18)	^{3}MLCT/^{3}ILCT ^{3}ILCT
m-1	T_1	586/2.11	HOMO→LUMO (0.82) HOMO-2→LUMO (0.12)	^{3}MLCT/^{3}ILCT ^{3}MLCT
	T_2	488/2.54	HOMO→LUMO+1 (0.64) HOMO-3→LUMO+1 (0.16)	^{3}MLCT/^{3}ILCT ^{3}ILCT
p-1	T_1	588/2.11	HOMO→LUMO (0.82) HOMO-2→LUMO (0.11)	^{3}MLCT/^{3}ILCT ^{3}MLCT
	T_2	491/2.52	HOMO→LUMO+1 (0.63) HOMO-3→LUMO+1 (0.16)	^{3}MLCT/^{3}ILCT ^{3}ILCT
1	T_1	545/2.27	HOMO→LUMO (0.90)	^{3}MLCT/^{3}ILCT
	T_2	512/2.42	HOMO→LUMO+1 (0.65) HOMO-3→LUMO (0.22)	^{3}MLCT/^{3}ILCT ^{3}ILCT
o-2	T_1	563/2.20	HOMO→LUMO (0.70)	^{3}MLCT/^{3}LLCT
	T_3	476/2.60	HOMO→LUMO+2 (0.55)	^{3}MLCT/^{3}ILCT
m-2	T_1	582/2.13	HOMO→LUMO (0.70)	^{3}MLCT/^{3}LLCT

	T_3	478/2.59	HOMO-2→LUMO (0.35) HOMO-7→LUMO (0.31)	^{3}MLCT/^{3}LLCT ^{3}ILCT
p-2	T_1	587/2.11	HOMO→LUMO (0.70)	^{3}MLCT/^{3}LLCT
	T_3	479/2.59	HOMO-2→LUMO (0.35) HOMO-7→LUMO (0.30) HOMO-4→LUMO (0.30)	^{3}MLCT/^{3}LLCT ^{3}ILCT ^{3}MLCT
2	T_1	621/2.00	HOMO→LUMO (0.70)	^{3}MLCT/^{3}LLCT
	T_3	484/2.56	HOMO-2→LUMO (0.37) HOMO-4→LUMO (0.32)	^{3}MLCT/^{3}LLCT ^{3}MLCT

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