Supporting Information for:

# Iridium(III) complexes containing a *N*-heterocyclic carbene ligand: an experimental and theoretical study of structural, spectroscopic, electrochemical and electrogenerated chemiluminescence properties

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## NMR spectroscopy

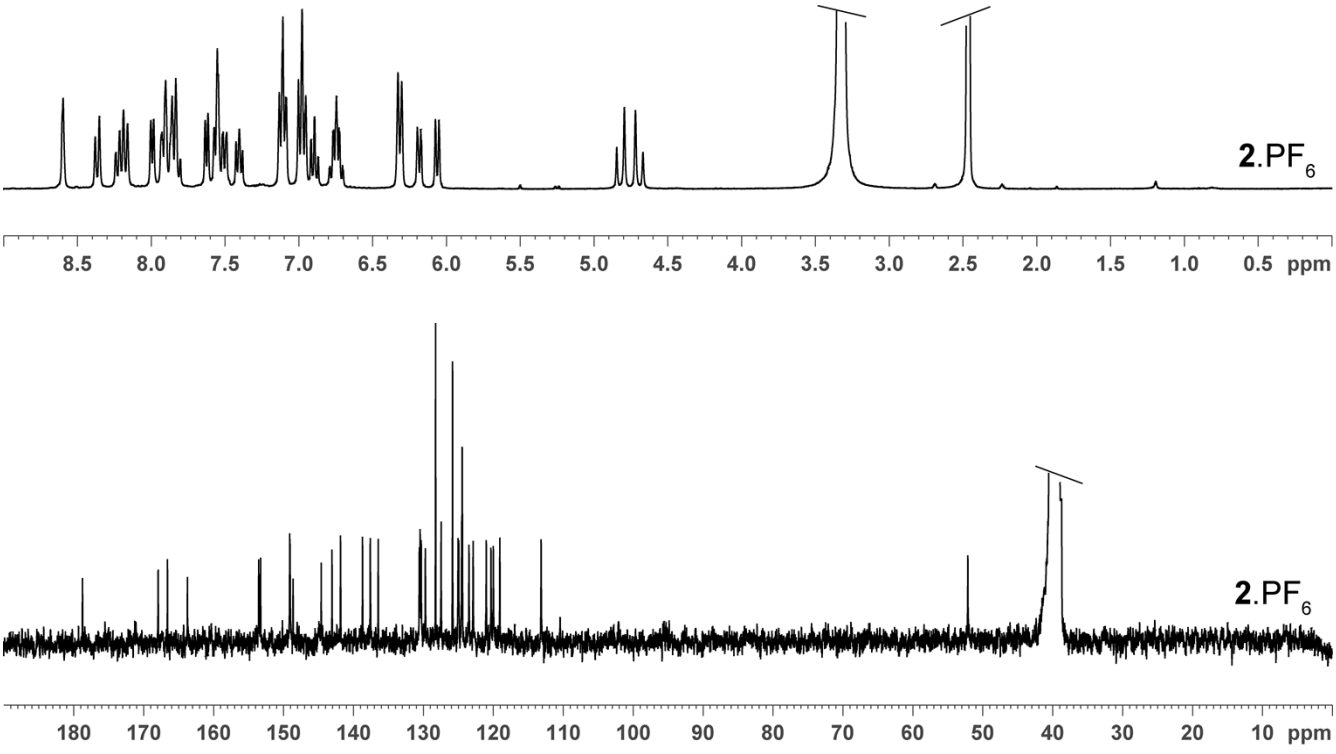



**Figure S1.** $^{1}$H NMR spectra (upper) and $^{13}$C NMR spectra (lower) for the Ir(III) complex (a) **2**.$PF_6$.

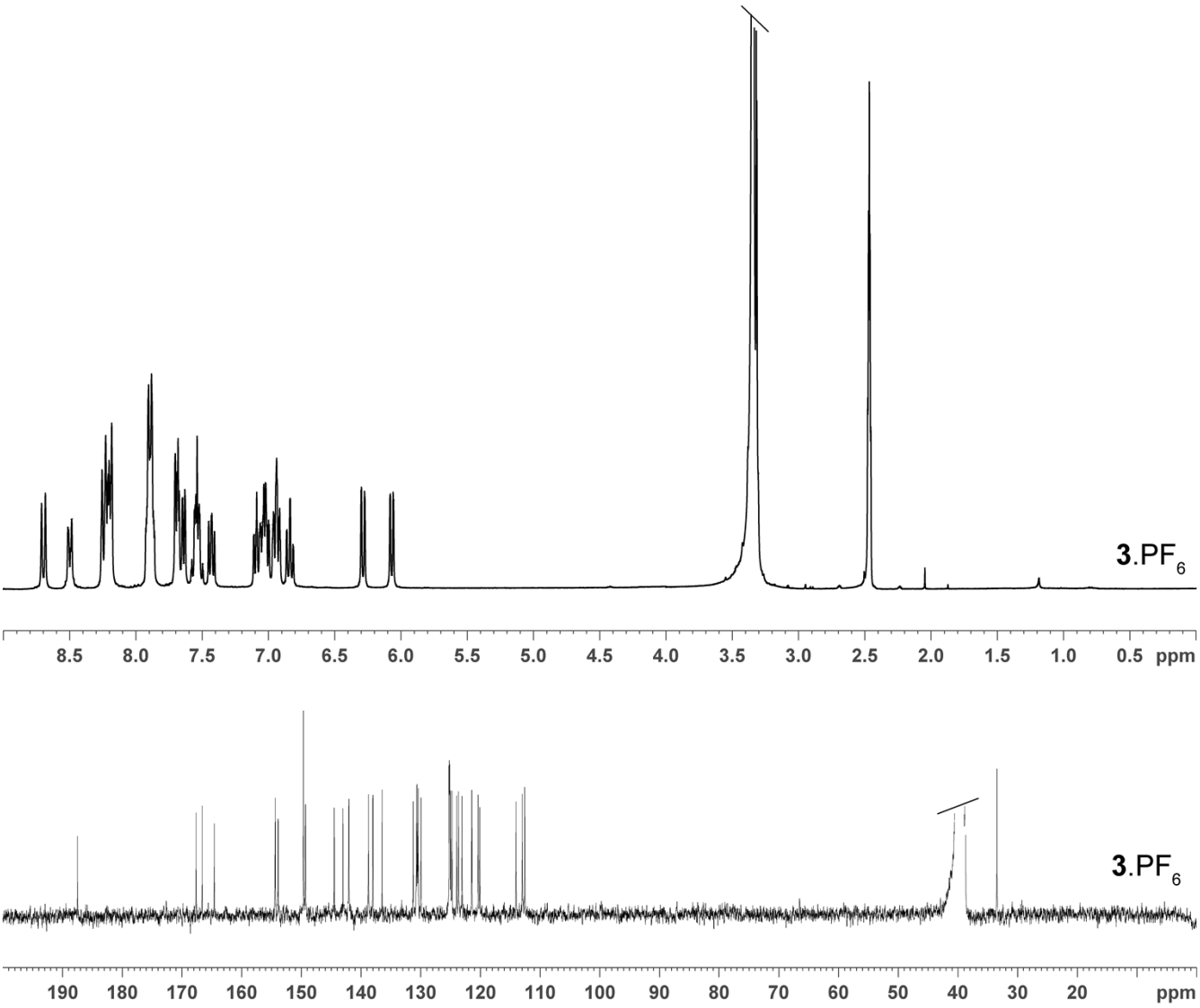



**Figure S2.** $^{1}$H NMR spectra (upper) and $^{13}$C NMR spectra (lower) for the Ir(III) complex (a) **3**.$PF_6$.

**X-Ray Crystallography**

**Details:**

**1**.$PF_6$: Solved in the orthorhombic space group *Pbca* using direct methods. The asymmetric unit contains the title compound.

**3**.$PF_6$: Solved using Direct method in the monoclinic space group $P2_1/n$. The asymmetric unit contains the title compound and one co-crystallised methanol molecule. Disorder was identified in the position of the hydroxyl group of the methanol molecule, with the hydroxyl group occupying two crystallographically independent positions that could be located from the additional residual electron

density. Refinement of the site occupancy factors for the disordered atoms gave the value 0.46 and 0.34 respectively. There was no obvious hydrogen bond acceptor for the hydroxyl group and no hydrogen was placed on the oxygen atom of this molecule.

**4**.$PF_6$: Solved using Direct method in the monoclinic space group $P2_1/c$. The asymmetric unit contains the title compound. Disorder was observed in the phenyl ring of the benzyl substituent on the NHC ligand (C15 - C19), with these atoms are occupying two crystallographically independent positions that could be located from the additional residual electron density. AFIX constraints were applied to give the two disordered components of the phenyl ring a regular hexagonal shape and refinement of the site occupancy factors for the disordered atoms gave the value 0.75 and 0.25, respectively.

**Theoretical Studies**

**Table S1**. Fragment MO populations from Mulliken population analysis for $\mathbf{1}^+$ (mPW1PW91/SDD,tzvp//mPW1PW91/SDD,6-31+G(d) with acetonitrile PCM-SCRF).

| Orbital | MO composition (%) | | | |
|---|---|---|---|---|
| | Ir | ppy 1 | ppy 2 | carbene |
| LUMO+3 | 2 | 14 | 22 | 62 |
| LUMO+2 | 3 | 74 | 18 | 6 |
| LUMO+1 | 3 | 3 | 30 | 65 |
| LUMO | 4 | 21 | 48 | 28 |
| HOMO | 33 | 40 | 23 | 4 |
| HOMO-1 | 16 | 28 | 47 | 9 |
| HOMO-2 | 41 | 16 | 20 | 23 |
| HOMO-3 | 26 | 32 | 35 | 7 |

**Table S2**. Fragment MO populations from Mulliken population analysis for $\mathbf{2}^+$ (mPW1PW91/SDD,tzvp//mPW1PW91/SDD,6-31+G(d) with acetonitrile PCM-SCRF).

| Orbital | MO composition (%) | | | |
|---|---|---|---|---|
| | Ir | ppy 1 | ppy 2 | carbene |
| LUMO+3 | 2 | 13 | 22 | 63 |
| LUMO+2 | 3 | 74 | 17 | 6 |
| LUMO+1 | 2 | 3 | 35 | 60 |
| LUMO | 4 | 21 | 43 | 33 |
| HOMO | 33 | 40 | 23 | 4 |
| HOMO-1 | 12 | 29 | 52 | 6 |
| HOMO-2 | 44 | 16 | 14 | 26 |
| HOMO-3 | 24 | 32 | 37 | 8 |

**Table S3**. Fragment MO populations from Mulliken population analysis for $\mathbf{3}^{+}$ (mPW1PW91/SDD,tzvp//mPW1PW91/SDD,6-31+G(d) with acetonitrile PCM-SCRF).

| Orbital | MO composition (%) | | | |
|---|---|---|---|---|
| | Ir | ppy 1 | ppy 2 | carbene |
| LUMO+3 | 3 | 11 | 22 | 64 |
| LUMO+2 | 3 | 72 | 20 | 6 |
| LUMO+1 | 3 | 3 | 18 | 76 |
| LUMO | 4 | 24 | 57 | 16 |
| HOMO | 32 | 41 | 23 | 5 |
| HOMO-1 | 7 | 29 | 61 | 2 |
| HOMO-2 | 43 | 18 | 6 | 33 |
| HOMO-3 | 21 | 31 | 38 | 10 |

**Table S4**. Fragment MO populations from Mulliken population analysis for $\mathbf{4}^{+}$ (mPW1PW91/SDD,tzvp//mPW1PW91/SDD,6-31+G(d) with acetonitrile PCM-SCRF).

| Orbital | MO composition (%) | | | |
|---|---|---|---|---|
| | Ir | ppy 1 | ppy 2 | carbene |
| LUMO+3 | 3 | 10 | 21 | 67 |
| LUMO+2 | 3 | 68 | 26 | 3 |
| LUMO+1 | 3 | 3 | 12 | 81 |
| LUMO | 4 | 27 | 57 | 13 |
| HOMO | 31 | 41 | 23 | 5 |
| HOMO-1 | 7 | 30 | 59 | 3 |
| HOMO-2 | 42 | 18 | 6 | 33 |
| HOMO-3 | 17 | 31 | 40 | 12 |

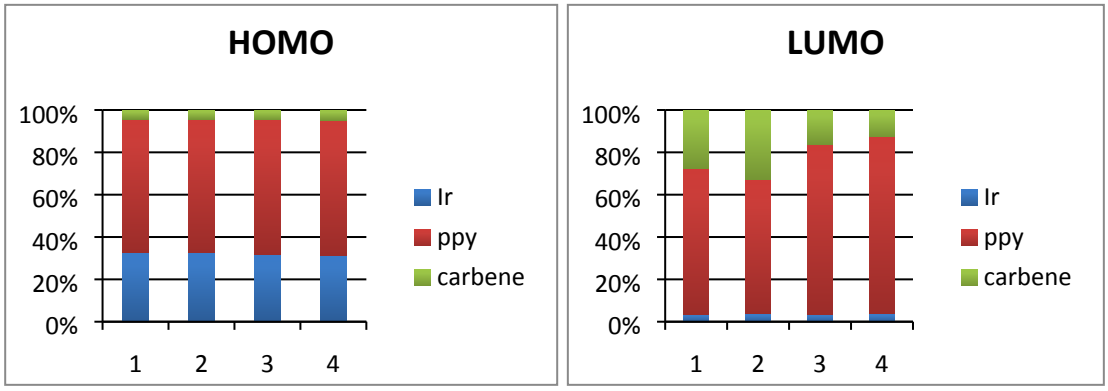
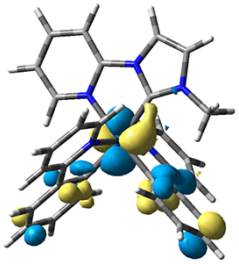
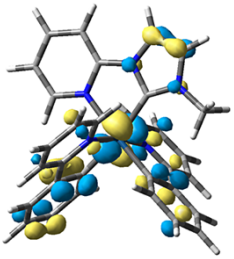


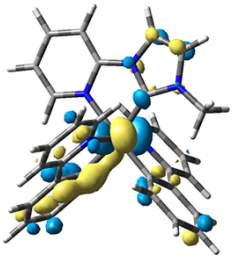

**Figure S3**. Fragment contributions to the HOMO and LUMO of complexes $\mathbf{1}^{2+}$ - $\mathbf{4}^{2+}$ (mPW1PW91/SDD,TZVP in acetonitrile PCM-SCRF). ppy = phenylpyridine, ligand = non-phenylpyridine ligand.



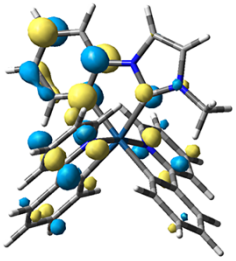
HOMO



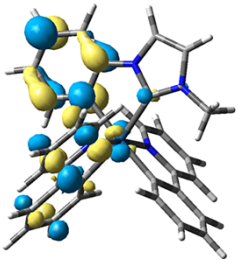
HOMO-1



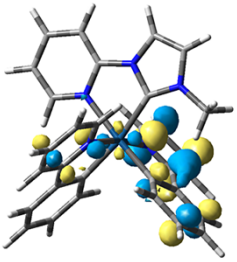
HOMO-2



LUMO

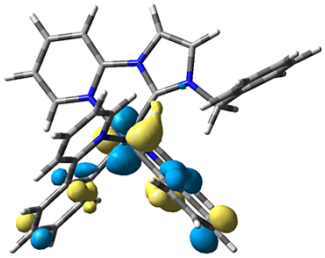


LUMO+1

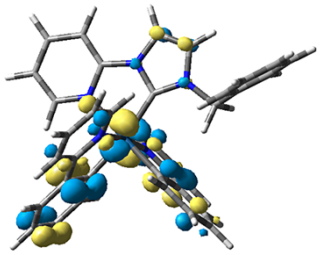


LUMO+2

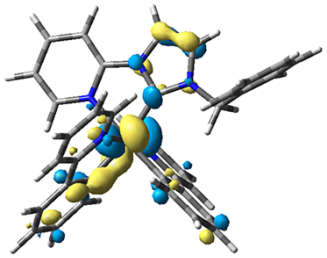
**Figure S4**. Frontier molecular orbitals of $\mathbf{1}^{+}$ (B3LYP/SDD,TZVP with acetonitrile PCM-SCRF at mPW1PW91/SDD,TZVP geometry).



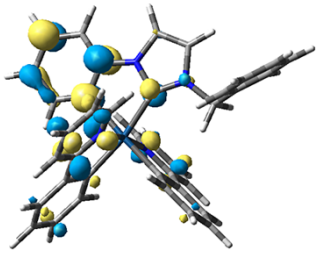
HOMO



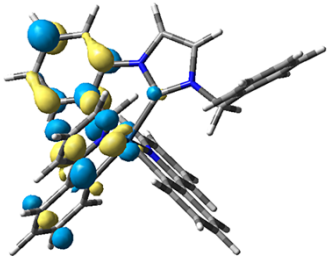
HOMO-1



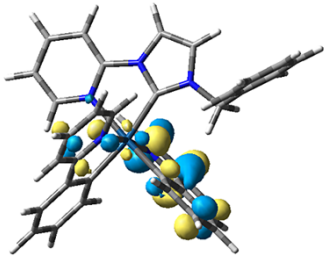
HOMO-2



LUMO

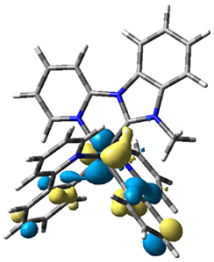


LUMO+1

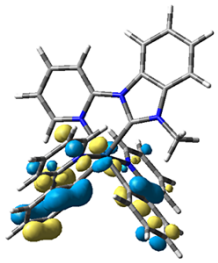


LUMO+2

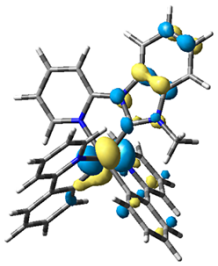
**Figure S5**. Frontier molecular orbitals of $\mathbf{2}^{+}$ (B3LYP/SDD,TZVP with acetonitrile PCM-SCRF at mPW1PW91/SDD,TZVP geometry).



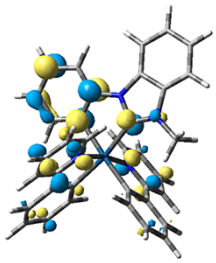
HOMO



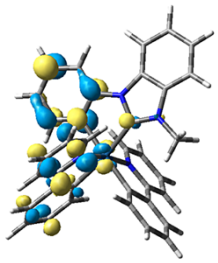
HOMO-1



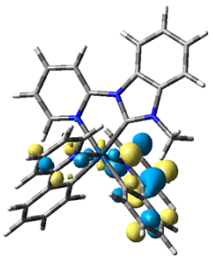
HOMO-2



LUMO

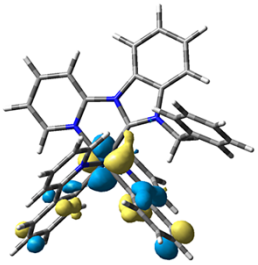


LUMO+1

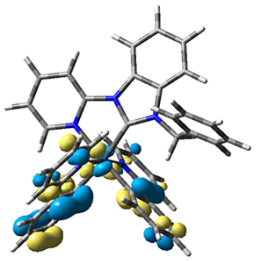


LUMO+2

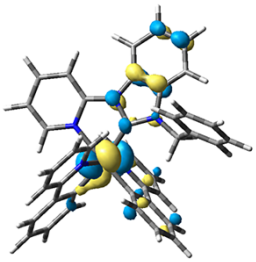
**Figure S6**. Frontier molecular orbitals of $\mathbf{3}^{+}$ (B3LYP/SDD,TZVP with acetonitrile PCM-SCRF at mPW1PW91/SDD,TZVP geometry).



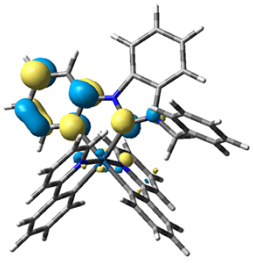
HOMO



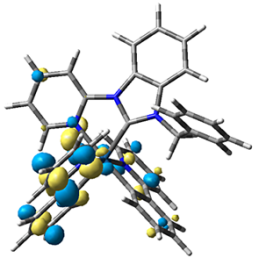
HOMO-1



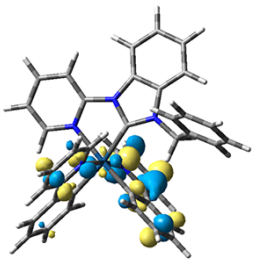
HOMO-2



LUMO

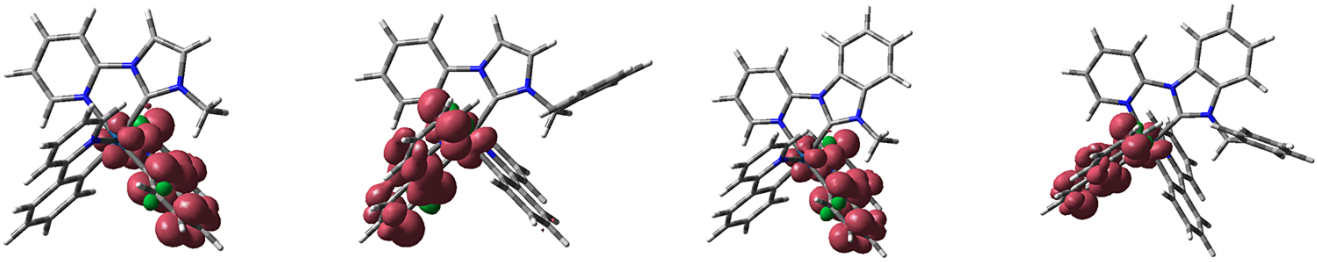


LUMO+1



LUMO+2

**Figure S7**. Frontier molecular orbitals of $\mathbf{4}^{+}$ (B3LYP/SDD,TZVP with acetonitrile PCM-SCRF at mPW1PW91/SDD,TZVP geometry).



**1**$^{+}$ **2**$^{+}$ **3**$^{+}$ **4**$^{+}$

**Figure S8**. Triplet-state spin density for **1**$^{+}$-**4**$^{+}$ (B3LYP/SDD,TZVP with acetonitrile PCM-SCRF at mPW1PW91/SDD,TZVP geometry).

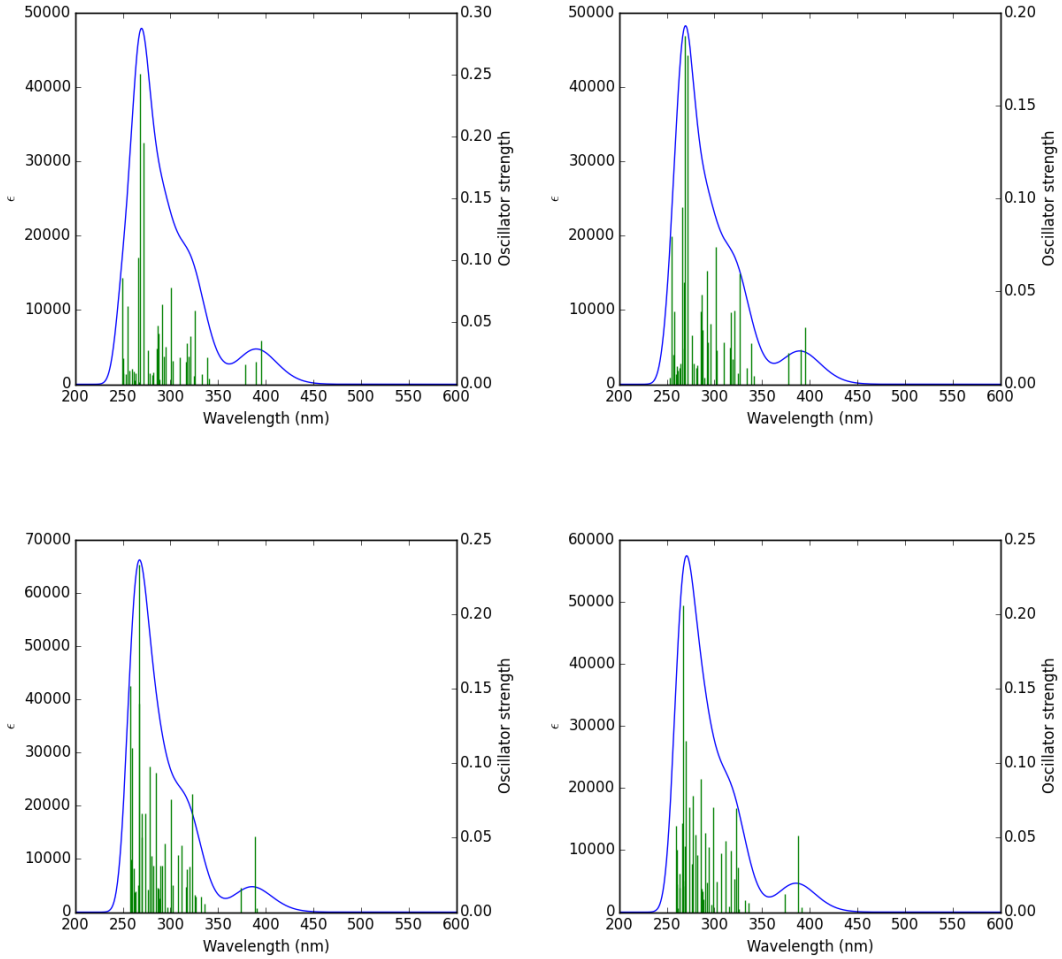



**Figure S9**. Calculated UV-Vis spectra for **1**$^{+}$ - **4**$^{+}$ (B3LYP/def2-SVP//mPW1PW91/SDD,TZVP in acetonitrile PCM-SCRF). TD-DFT with 40 singlet and triplet states.

**Table S5**. Selected singlet states for complexes $\mathbf{1}^{+}$-$\mathbf{4}^{+}$ calculated from TD-DFT (B3LYP/def2-SVP//mPW1PW91/SDD,6-31+G(D) with acetonitrile SCRF-PCM).

| Compound | State | λ (nm) | f | Dominant excitation | Nature | Assignment |
|---|---|---|---|---|---|---|
| $\mathbf{1}^{+}$ | S1 | 395.2 | 0.036 | H→L (96%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC, LLCT |
| | S2 | 390.1 | 0.018 | H→L+1 (95%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT, LLCT |
| | S3 | 378.1 | 0.016 | H→L+2 (97%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT, LC |
| | S27 | 271.9 | 0.195 | H-1→L+5 (32%), H-4→L+2 (20%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT, LC |
| | S28 | 268.3 | 0.251 | H-2→L+5 (25%), H-1→L+5 (17%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT |
| | S30 | 266.1 | 0.103 | H-3→L+4 (51%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S36 | 255.1 | 0.063 | H→L+6 (44%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT |
| | S40 | 249.4 | 0.086 | H-7→L (41%), H-4→L+5 (15%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT |
| $\mathbf{2}^{+}$ | S1 | 395.5 | 0.031 | H→L (97%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC, LLCT |
| | S2 | 390.4 | 0.019 | H→L+1 (96%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC, LLCT |
| | S3 | 377.6 | 0.017 | H→L+2 (97%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT, LC |
| | S27 | 271.9 | 0.177 | H-1→L+5 (25%), H-4→L+2 (19%) | $\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | LC, LLCT |
| | S28 | 269.2 | 0.188 | H→L+6 (23%), H-1→L+5 (18%), H-2→L+5 (17%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S31 | 266.4 | 0.095 | H-3→L+4 (43%), | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S40 | 254.9 | 0.080 | H→L+8 (39%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| $\mathbf{3}^{+}$ | S1 | 390.2 | 0.003 | H→L (74%), H→L+1 (23%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT, LC |
| | S2 | 388.9 | 0.051 | H→L+1 (74%), H→L (24%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT, LC, LLCT |
| | S3 | 374.1 | 0.016 | H→L+2 (97%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | MLCT, LC |
| | S8 | 323.2 | 0.080 | H-1→L+5 (59%) | $\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | LC |
| | S31 | 267.5 | 0.233 | H-1→L+5 (25%), H-3→L+4 (19%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC, LLCT |
| | S32 | 266.8 | 0.140 | H-3→L+4 (34%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S38 | 259.9 | 0.110 | H-2→L+6 (27%), H-5→L+3 (25%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S40 | 258.2 | 0.152 | H-5→L+3 (39%), H-2→L+6 (27%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| $\mathbf{4}^{+}$ | S1 | 391.3 | 0.003 | H→L (62%), H→L+1 (35%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC |
| | S2 | 387.9 | 0.052 | H→L+1 (62%), H→L (36%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{ppy} + \pi^{*}_{carbene}$ | MLCT, LC |
| | S3 | 373.6 | 0.012 | H→L+2 (97%) | $\pi_{ppy} \rightarrow \pi^{*}_{ppy}$ | LC |
| | S28 | 273.9 | 0.071 | H-3→L+3 (41%), H-6→L (21%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | LLCT |
| | S29 | 269.6 | 0.115 | H-6→L+1 (39%), H-1→L+5 (19%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |
| | S32 | 267.3 | 0.206 | H-6→L+1 (28%), H-1→L+5 (25%) | $d_{\pi}(Ir)+\pi_{ppy} \rightarrow \pi^{*}_{carbene}$ | MLCT |

**Table S6**. Crystallographic data for Ir(III) complexes **1**·$PF_6$, **3**·$PF_6$, and **4**·$PF_6$

| **Identification code** | **1**·$PF_6$ | **3**·$PF_6$ | **4**·$PF_6$ |
|---|---|---|---|
| **Empirical formula** | $C_{31}H_{25}N_5F_6PIr$ | $C_{36}H_{30}N_5F_6PIrO$ | $C_{41}H_{31}N_5F_6PIr$ |
| **Formula weight** | 804.73 | 885.82 | 930.88 |
| **Temperature/K** | 173.2 | 173.2 | 173.2 |
| **Crystal system** | orthorhombic | monoclinic | monoclinic |
| **Space group** | Pbca | P21/n | P21/c |
| **a/Å** | 10.9927(3) | 13.818(3) | 12.14380(14) |
| **b/Å** | 16.3330(5) | 13.881(3) | 15.66023(14) |
| **c/Å** | 31.7659(10) | 17.586(4) | 19.33573(19) |
| **α/°** | 90 | 90 | 90 |
| **β/°** | 90 | 101.65(3) | 101.3280(11) |
| **γ/°** | 90 | 90 | 90 |
| **Volume/Å$^3$** | 5703.4(3) | 3303.5(12) | 3605.53(6) |
| **Z** | 8 | 4 | 4 |
| **$\rho_{calc}$mg/mm$^3$** | 1.874 | 1.781 | 1.715 |
| **m/mm$^{-1}$** | 4.81 | 4.163 | 3.817 |
| **F(000)** | 3136 | 1740 | 1832 |
| **Crystal size/mm$^3$** | 0.08 × 0.04 × 0.03 | 0.06 × 0.05 × 0.05 | 0.1 × 0.1 × 0.04 |
| **Wavelength / Å** | Mo-Kα 0.71073 | Mo-Kα 0.71073 | Mo-Kα 0.71073 |
| **θ range collected** | 4.98 to 52.04° | 5.86 to 52.04° | 4.94 to 52.04° |
| **Index ranges** | -9 ≤ h ≤ 13, -20 ≤ k ≤ 19, -39 ≤ l ≤ 37 | -16 ≤ h ≤ 17, -17 ≤ k ≤ 17, -15 ≤ l ≤ 21 | -14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23 |
| **Reflections collected** | 21889 | 24187 | 61518 |
| **Independent reflections** | 5615[R(int) = 0.0476] | 6505[R(int) = 0.0258] | 7102[R(int) = 0.0328] |
| **Data/restraints/parameters** | 5615/0/398 | 6505/0/456 | 7102/18/503 |
| **Goodness-of-fit on $F_2$** | 1.04 | 1.095 | 1.079 |
| **Final R indexes [I>2σ(I)]** | $R_1$ = 0.0365, $wR_2$ = 0.0614 | $R_1$ = 0.0320, $wR_2$ = 0.0703 | $R_1$ = 0.0189, $wR_2$ = 0.0422 |
| **Final R indexes [all data]** | $R_1$ = 0.0647, $wR_2$ = 0.0707 | $R_1$ = 0.0378, $wR_2$ = 0.0728 | $R_1$ = 0.0224, $wR_2$ = 0.0438 |
| **Largest diff. peak/hole/e Å$^{-3}$** | 1.03/-0.86 | 2.91/-1.21 | 0.72/-0.41 |

**Table S7** Absorbance data for Ir(III) complexes **1-4** in $CH_3CN$ at room temperature.

| Complex | λ / nm | ε / $M^{-1}$ $cm^{-1}$ | |
|---|---|---|---|
| **1** | 218 | 51930 | sh |
| | 255 | 54640 | |
| | 266 | 51440 | |
| | 308 | 21320 | sh |
| | 379 | 7110 | |
| | | | |
| **2** | 219 | 53640 | sh |
| | 254 | 49150 | |
| | 266 | 46570 | |
| | 310 | 18480 | sh |
| | 378 | 5980 | |
| | | | |
| **3** | 250 | 65950 | |
| | 268 | 61950 | |
| | 285 | 45310 | sh |
| | 316 | 22510 | sh |
| | 376 | 8050 | |
| | | | |
| **4** | 251 | 65060 | |
| | 268 | 62130 | |
| | 285 | 46760 | sh |
| | 317 | 21450 | sh |
| | 375 | 6650 | |