Supplementary Information for:

Tuning the Electrochemiluminescent properties of Iridium Complexes of N-Heterocyclic Carbene Ligands

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X ray crystallography

X-ray Crystallography. Single crystals of the Ir(III) complexes **1**, **3**, **5**, and **6** suitable for X-ray diffraction studies were grown by slow diffusion of ethyl acetate into acetonitrile solutions of each compound at ambient temperature. Crystallographic data for all structures determined are given in Tables 1 and S1. For all samples, crystals were removed from the crystallisation vial and immediately coated with paratone oil on a glass slide. A suitable crystal was mounted in Paratone oil on a glass fibre and cooled rapidly to 173 K in a stream of cold N2 using an Oxford low temperature device. Diffraction data were measured using an Oxford Gemini diffractometer mounted with Mo-Kα $\lambda = 0.71073$ Å and Cu-Kα $\lambda = 1.54184$. Data were reduced and corrected for absorption using the CrysAlis Pro program. The SHELXL2013-2 program was used to solve the structures with Direct Methods, with refinement by the Full-Matrix Least-Squares refinement techniques on F2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically and refined using the riding model. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. All calculations were carried out using the program Olex2. Images were generated by using ORTEP-3. Further XRD details are provided in the Supporting Information. CCDC 1869253-1869256 contains 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/data_request/cif.

Table S1. Crystallographic data for all structures **1**, **2**, **5**, and **6**.

Compound	**1**	**3**	**5**	**6**
Empirical formula	$C_{34}H_{24}N_5F_4Ir$	$C_{34}H_{25}F_4IrN_4O_2$	$C_{32}H_{19}N_4F_6Ir$	$C_{36}H_{29}N_5F_4IrCl$
Formula weight	770.78	789.78	765.71	835.29
Temperature/K	173	173	173	173
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	*P*-1	*P*-1	$P2_1/n$	*P*-1
a/Å	9.8986(3)	10.3830(3)	10.84307(11)	9.0031(3)
b/Å	11.6908(4)	10.6683(3)	15.66542(16)	12.7459(4)
c/Å	13.1739(4)	13.4176(4)	15.57142(16)	15.4060(5)
α/°	71.971(3)	76.274(2)	90	104.264(3)
β/°	89.258(2)	82.985(2)	92.5122(9)	105.973(3)
γ/°	88.706(3)	84.990(2)	90	98.494(2)
Volume/Å3	1449.28(8)	1430.37(7)	2642.44(5)	1602.56(9)
Z	2	2	4	2
ρcalcmg/mm$_3$	1.766	1.834	1.925	1.731
m/mm^{-1}	9.429	4.734	10.44	4.307
F(000)	752	772	1480	820
Crystal size/mm3	0.15 × 0.15 × 0.04	0.08 × 0.04 × 0.04	0.1 × 0.08 × 0.05	0.1 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection	7.056 to 147.464°	6.286 to 52.74	8.01 to 147.702°	5.77 to 52.738°
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -16 ≤ l ≤ 11	-12 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16	-8 ≤ h ≤ 13, -19 ≤ k ≤ 18, -19 ≤ l ≤ 19	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	9129	11588	17700	14873
Independent reflections	5672 [R_{int} = 0.0346, R_{sigma} = 0.0290]	5844 [R_{int} = 0.0181, R_{sigma} = 0.0280]	5281 [R_{int} = 0.0209, R_{sigma} = 0.0172]	6542 [R_{int} = 0.0255, R_{sigma} = 0.0347]
Data/restraints/parameters	5672/0/399	5844/0/409	5281/0/389	6542/0/428
Goodness-of-fit on F^2	1.054	1.075	1.16	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1270	R_1 = 0.0204, wR_2 = 0.0498	R_1 = 0.0205, wR_2 = 0.0506	R_1 = 0.0209, wR_2 = 0.0473
Final R indexes [all data]	R_1 = 0.0480, wR_2 = 0.1279	R_1 = 0.0233, wR_2 = 0.0515	R_1 = 0.0212, wR_2 = 0.0509	R_1 = 0.0244, wR_2 = 0.0492
Largest diff. peak/hole / e Å^{-3}	3.29/-2.19	0.89/-0.82	0.74/-1.13	0.85/-0.71

Details:

1: Solved using direct methods in the triclinic space group *P-1*. The asymmetric unit contains one molecule of the title compound.

3: Solved using direct methods in the triclinic space group *P-1*. The asymmetric unit contains one molecule of the title compound. Disorder was identified in the positions of fluorine atoms: F1 and F3. Attempts to model this disorder using two different closely spaced positions for each of these F atoms were unsatisfactory with the site occupancy for one component refining to unreasonably low levels. As a result, disorder in the positions of these atoms was not modelled. Three level B Checkcif alerts result from the disorder associated with these F atoms: Hirshfeld Test Diff for F1 - C12 ..10.7 su, Hirshfeld Test Diff for F3 - C23 .. 9.0 su and Short Inter HL..HL Contact F1 .. F3 . 2.42 Ang.

5: Solved using direct methods in the monoclinic space group $P2_1/n$. The asymmetric unit contains one molecule of the title compound.

6: Solved using direct methods in the triclinic space group *P-1*. The asymmetric unit contains one molecule of the title compound and one molecule of acetonitrile as a solvent of crystallisation.

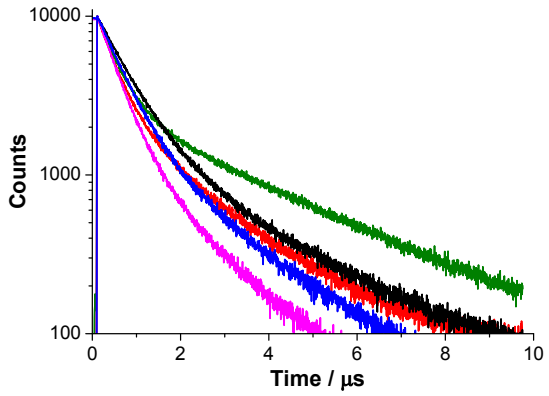

Figure S1. Photoluminescence decay profiles for dilute solutions of complexes 1 (red) **2** (green) **3** (black) **4** (pink) and **5** (blue) in de-aerated acetonitrile

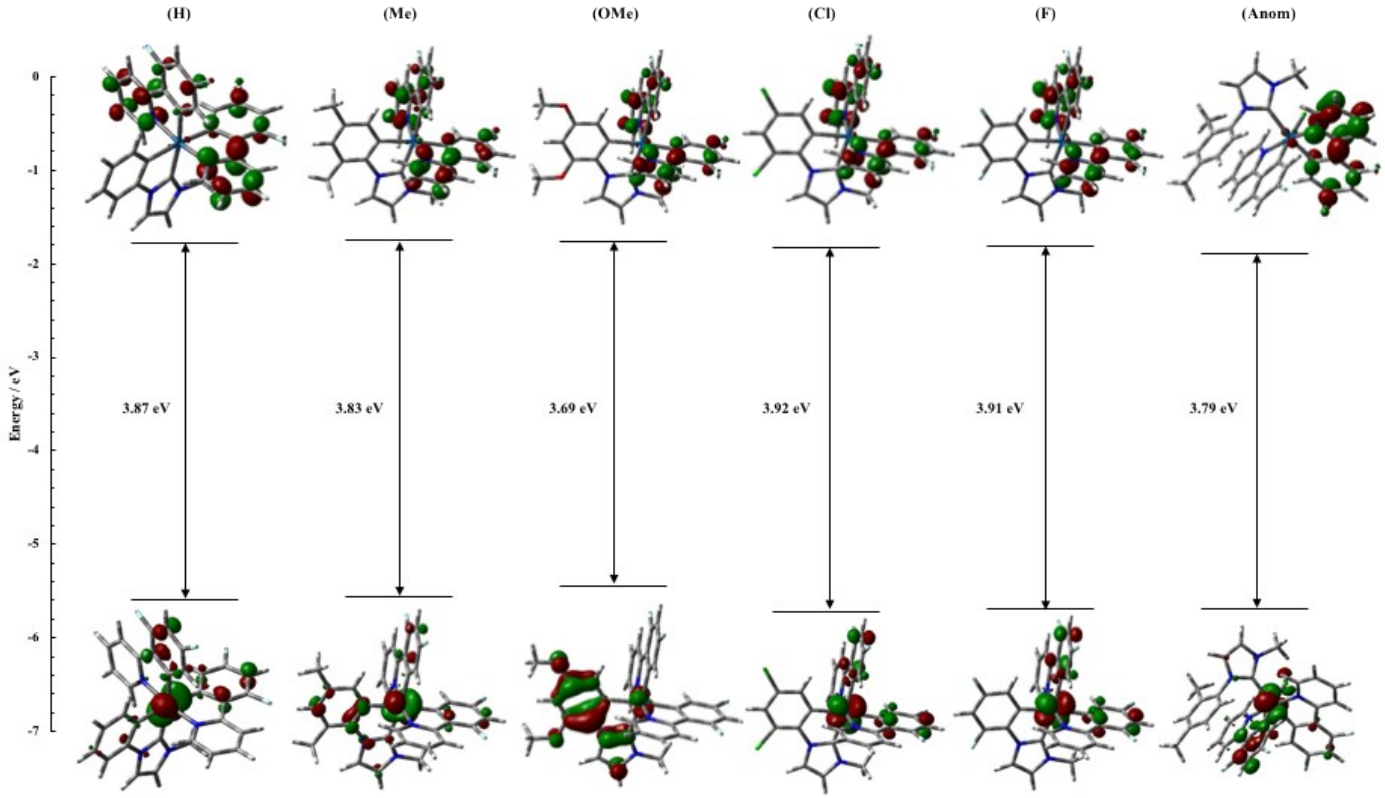

Figure S2. B3LYP/def2-TZVP//B3LYP/def2-SVP calculated molecular orbital energy HOMO–LUMO gaps and surface plots of the HOMO and LUMO for compounds **1**–**5**. Acetonitrile solvent correction included with single-pint SCRF. Units of eV.

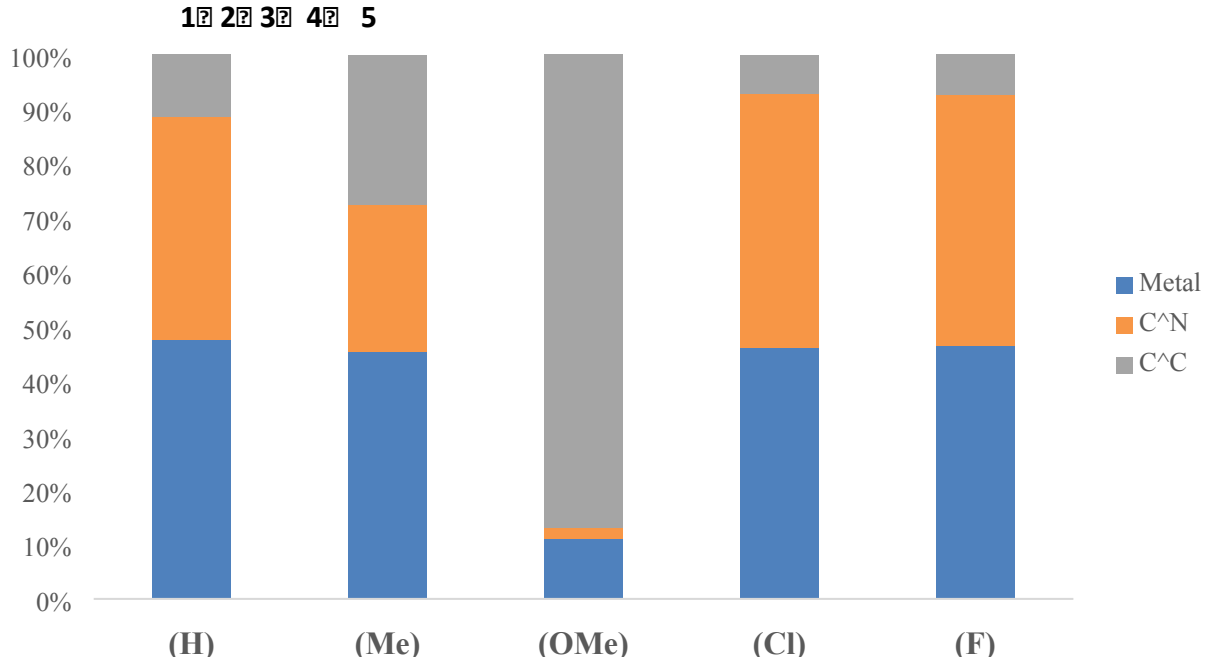

Figure S3. Percentage contribution to the HOMO from the metal centre and ligands (C^C and C^N ligands) of complexes 1-5 (B3LYP/def2-TZVP calculations).

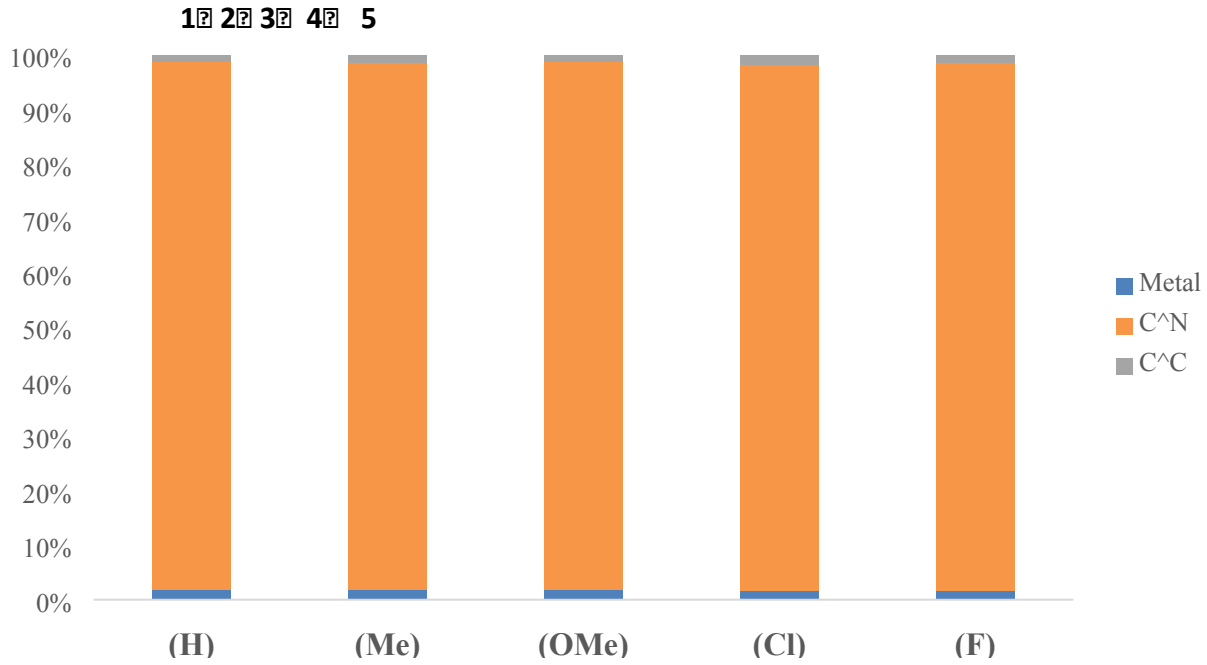

Figure S4. Percentage contribution to the LUMO from the metal centre and ligands (C^C and C^N ligands) of complexes 1-5 (B3LYP/def2-TZVP calculations).