Synthesis, Characterization and DFT/TD-DFT Calculations of Highly Phosphorescent Blue Light-Emitting Anionic Iridium Complexes

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Table S1. Optimized geometrical parameters of complexes **1**-**5**.

Parameter	1 (X-ray) S_0	1 S_0	1 T_1	2 S_0	2 T_1	3 S_0	3 T_1	4 S_0	4 T_1	5 S_0	5 T_1
Ir-N$_{(ppy)}$	2.061(4) 2.063(4)	2.046	2.056	2.045	2.060	2.048	2.060	2.050	2.056	2.052	2.065
Ir-C$_{(ppy)}$	2.055(5) 2.059(5)	2.051	2.031	2.051	2.027	2.050	2.040	2.048	2.041	2.068	2.040
Ir-C$_{(CN)}$	2.066(5) 2.079(5)	2.060	2.076	2.057	2.077	2.056	2.056	2.054	2.058	2.046	2.057
C$_{(ppy)}$-C$_{(ppy)}$	1.457(7) 1.463(6)	1.451	1.436	1.456	1.437	1.450	1.434	1.455	1.432	1.457	1.435
<N$_{(ppy)}$-Ir-C$_{(ppy)}$	79.85(17) 79.41(17)	79.6	80.8	79.3	80.8	79.7	80.6	79.4	80.5	78.9	80.0
<N$_{(ppy)}$-Ir-N$_{(ppy)}$	170.01(14)	171.9	173.1	171.3	173.2	171.8	172.6	171.5	172.2	174.5	175.8
<C$_{(ppy)}$-Ir-C$_{(ppy)}$	86.63(17)	91.7	92.4	91.7	95.0	91.7	91.4	91.9	91.3	91.6	96.6
<C$_{(CN)}$-Ir-C$_{(CN)}$	89.92(19)	89.7	88.1	88.5	85.3	89.0	89.1	89.0	88.9	89.8	84.9

DFT results vs. electrochemical data

In complex **2**, the para-substitution of pyridine by dimethylamino group leads to a destabilization of both the HOMOs and LUMOs. Compared to the **1** reference, the **2** HOMO is destabilized by 0.215 eV while the LUMO is destabilized by 0.317 eV, as a result of the increase donation from the dimethylamino-substituted ppy. The net effect is a small opening of the HOMO-LUMO gap, which increases from 3.889 to 3.990 eV. The calculated HOMO/LUMO shifts quantitatively correlate with the experimental redox potentials, showing an upshift of the oxidation and reduction potentials of 0.220 and 0.310 V, respectively. In complex **3**, the presence of fluorine substituents in 2,4 positions of phenyl rings does stabilizes the anionic complex resulting into an overall stabilization of all the HOMOs and LUMOs with respect to the orbitals of complex **1**. In particular, the HOMO (LUMO) is stabilized by 0.479 (0.306) eV, which is consistent with the

experimental trend of oxidation/reduction potentials. The calculated HOMO-LUMO gap is 4.062 eV, i.e. 0.173 eV larger than in **1**, which stems from the different stabilization of the HOMO and LUMO. The HOMOs of complexes **4** and **5** result stabilized with respect to both those of **1** and **2**, which have no fluorine substituents. Indeed, the electron distribution of the first HOMOs resembles to that of complex **2** HOMOs, a part that the **2** HOMO corresponds to HOMO-2 in both **4** and **5**, therefore resulting particularly stabilized by the presence of F atoms.

The two LUMOs of **4** and **5** complexes are destabilized with respect to the LUMO of complex **1**, as a result of the electron donating and electron withdrawing effect of the dimethylamino and fluoride ligands, respectively. Interestingly, the LUMO+2/LUMO+3 and LUMO+4/LUMO+5 couples, which are essentially localized on the pyridine and phenyl groups, respectively, feel differently the effect of the substituents. Indeed, in both **4** and **5**, the LUMO+2 and LUMO+3 are destabilized with respect to the same couple of orbitals of **1**, and lie at similar energies as the LUMO+2 and LUMO+3 of **2**. Complex **4** shows the largest HOMO-LUMO gap among the investigated species (4.137 eV) as a results of the concomitant HOMO stabilization and LUMO destabilization. In the isomeric complex **5**, the HOMO-LUMO gap is calculated to be 4.060 eV, the decreased value compared to that of **4** being related to smaller HOMO (LUMO) stabilization (destabilization). For **4**, our calculated molecular orbitals are consistent with experimental redox potentials, showing a down-shift (up-shift) of the oxidation (reduction) potentials compared to **1**. We notice, moreover, that comparing **4** and **5**, our calculations confirm the experimental trend of redox potentials, even though for complex **5**, compared to **1**, our calculations would predict an anodic shift of the oxidation potential, while experimentally a slight cathodic shift is observed. The only difference which can justify the electrochemical behavior of **4** and **5** complexes comes from the charge density distribution of LUMO and LUMO+1 of the two complexes. In complex **2**, the LUMO/LUMO+1 couple shows electron charge distribution in both the meta and ortho positions of phenyl ring. When hydrogen atoms are replaced by fluorides, together to the main stabilization effect on the LUMO/LUMO+1 due to the electron attractor
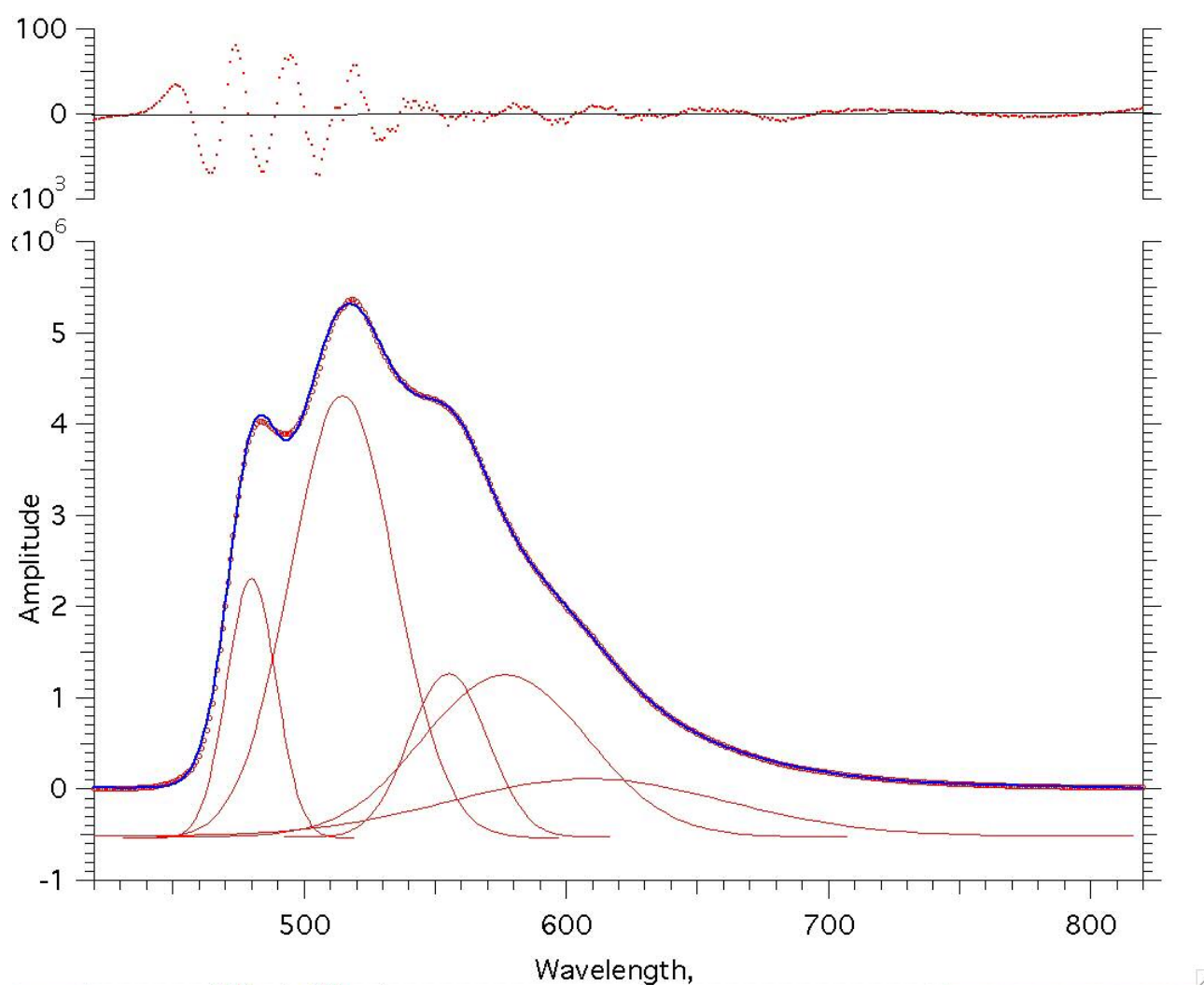
Figure SI-1. Emission spectra of complex 4 fitted with using a multigaussion Igor pro.