Supporting Information

Tuning the photophysical properties of cationic iridium(III) complexes containing cyclometallated 1-(2,4-difluorophenyl)-1*H*-pyrazole through functionalized 2,2'-bipyridine ligands: blue but not blue enough

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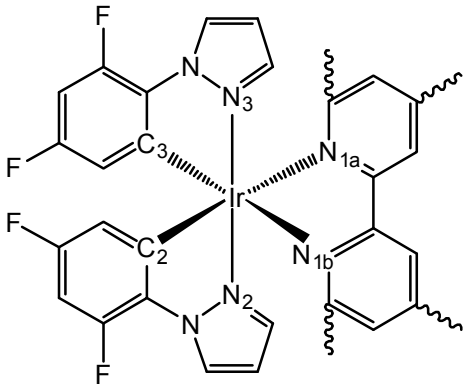
1. Theoretical Calculations

Table S1 summarizes the geometrical parameters calculated for the coordination sphere of the iridium metal in complexes $[Ir(dfppz)_2(N^N)]^+$ (N^N = **1**–**4**). Calculations were performed at the B3LYP/(6-31G**+LANL2DZ) level in the presence of the solvent (acetonitrile). The geometry of the lowest-energy triplet T_1 was optimized using the spin-unrestricted UB3LYP approach.

Table S1. Selected bond distances (in Å) and bond angles (in deg.) calculated for $[Ir(dfppz)_2(N^N)]^+$ (N^N = **1**–**4**) in the singlet ground state (S_0) and in the lowest-energy triplet state T_1.[a]



	N^N = **1**[b]		N^N = **2**[b]		N^N = **3**		N^N = **4**	
	S_0	T_1	S_0	T_1	S_0	T_1	S_0	T_1
$Ir–N_{1a}$	2.319	2.240	2.313	2.231	2.308	2.249	2.183	2.147
$Ir–N_{1b}$	2.184	2.183	2.180	2.169	2.307	2.254	2.183	2.147
$Ir–N_2$	2.062	2.065	2.061	2.057	2.053	2.054	2.052	2.050
$Ir–N_3$	2.050	2.049	2.049	2.053	2.049	2.051	2.052	2.050
$Ir–C_2$	2.022	2.030	2.022	2.031	2.031	2.032	2.035	2.044
$Ir–C_3$	2.042	2.002	2.043	2.009	2.033	2.034	2.035	2.044
$N_{1a}–Ir–N_{1b}$	74.86	75.75	74.68	75.83	75.26	76.53	75.28	77.22
$C_2–Ir–N_2$	79.65	79.48	79.71	79.70	79.55	79.72	79.73	79.67
$C_3–Ir–N_3$	79.47	80.04	79.54	79.88	79.60	79.63	79.73	79.67

[a] All calculations performed at the B3LYP/(6-31G**+LANL2DZ) level in the presence of the solvent (acetonitrile). [b] The phenyl substituent is attached to the pyridine ring containing N_{1a} and π-stacks with the phenyl ring containing C_3.

Figure S1 displays the molecular orbital distribution calculated at the B3LYP/(6-31G**+LANL2DZ) level for the $[Ir(dfppz)_2(\mathbf{4})]^+$ cation in the presence of the solvent (acetonitrile). The HOMO–1 and HOMO–2 (–5.75 eV) correspond to almost degenerate combinations of Ir-(t_{2g}) and π orbitals of the 4,4'-dimethylamino-2,2'-bipyridine ligand and lie very close in energy to the HOMO (–5.70 eV).

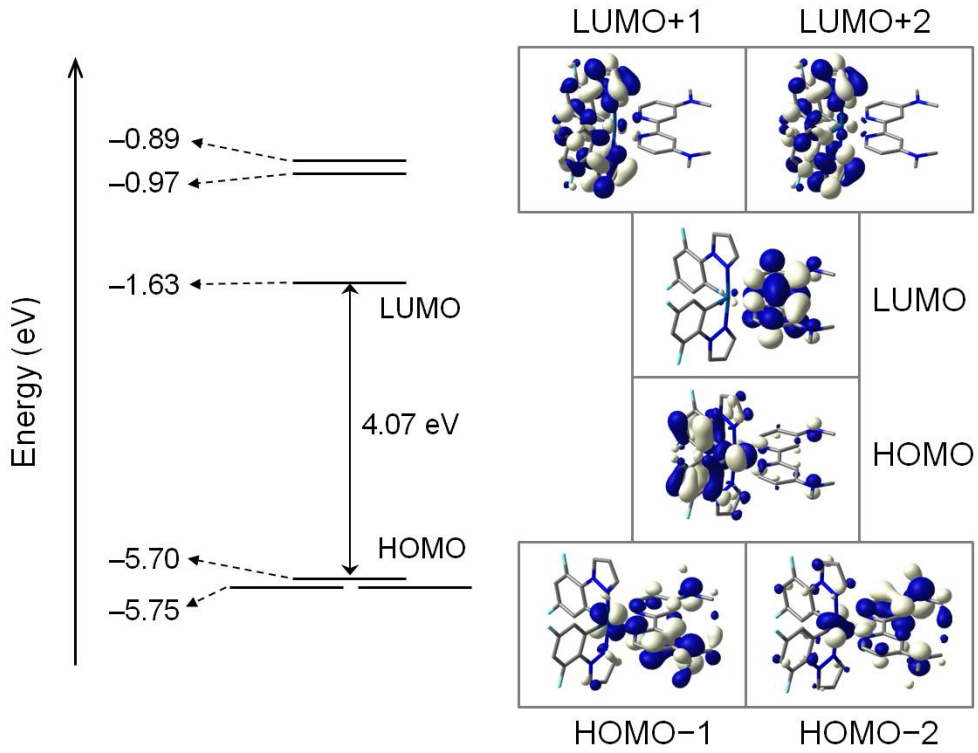


Figure S1. Electron density contours (0.03 e $bohr^{-3}$) and energy values (in eV) calculated for the highest occupied (HOMO–2 to HOMO) and lowest unoccupied (LUMO to LUMO+2) molecular orbitals of $[Ir(dfppz)_2(\mathbf{4})]^+$.

Table S2 summarizes the lowest triplet excited states calculated at the TD-DFT B3LYP(6-31G**+LANL2DZ) level in acetonitrile for complexes $[Ir(dfppz)_2(N^N)]^+$ (N^N = **1**–**4**). The lowest triplet T_1 of complexes with N^N = **1**–**3** mainly results from the HOMO → LUMO excitation that implies an electron transfer from the Ir-dfppz environment, where the HOMO is localized, to the bpy ligand, where the LUMO resides. The T_1 state therefore has a mixed ^{3}MLCT/^{3}LLCT character. For complex $[Ir(dfppz)_2(\mathbf{4})]^+$, the T_1 and T_2 states are very close in energy and mostly originate from the HOMO–2 → LUMO and HOMO–1 → LUMO excitations, respectively, that involve the ancillary ligand with some

contribution from the metal. These states therefore have a predominant ^{3}LC character. The lowest triplets of complexes with N^N = **1**–**3** are highly multiconfigurational and their electronic nature results from many monoexcitations with low relative weights (see Table S2).

Table S2: Lowest triplet excited states calculated at the TD-DFT B3LYP(6-31G**+LANL2DZ) level in acetonitrile for $[Ir(dfppz)_2(N^N)]^+$ (N^N = **1**–**4**). Vertical excitation energies (*E*), dominant monoexcitations with contributions (within parentheses) greater than 0.15%, nature of the electronic transition and description of the excited state are summarized.

N^N	Excited state	*E* (eV)	Monoexcitations	Nature[a]	Description[b]
1	T_1	2.91	H → L (0.65)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_2	3.09	H → L (0.28)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_3	3.29	H → L+4 (0.18)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}MLCT/^{3}LC
	T_4	3.31	H–2 → L (0.52)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
2	T_1	2.95	H → L (0.51)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_2	3.13	H–5 → L (0.17)	$d_\pi(Ir) + \pi_{C^N} + \pi_{N^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
			H → L (0.39)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_3	3.30	H → L+2 (0.26)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N} + \pi^*_{C^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
			H → L+4 (0.16)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N} + \pi^*_{C^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
	T_4	3.33	H–1 → L+3 (0.16)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N} + \pi^*_{C^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
			H → L+3 (0.15)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N} + \pi^*_{C^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
3	T_1	2.98	H → L (0.58)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_2	3.17	H–5 → L (0.27)	$d_\pi(Ir) + \pi_{N^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LC
			H → L (0.17)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_3	3.28	H–1 → L (0.19)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
			H → L+4 (0.22)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}MLCT/^{3}LC
			H → L+5 (0.20)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{C^N} + \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT/^{3}LC
	T_4	3.36	H–2 → L (0.64)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
4	T_1	2.91	H–2 → L (0.70)	$d_\pi(Ir) + \pi_{N^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LC
			H → L (0.17)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT
	T_2	2.94	H–1 → L (0.85)	$d_\pi(Ir) + \pi_{N^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LC
	T_3	3.30	H–8 → L (0.59)	$\pi_{N^N} \rightarrow \pi^*_{N^N}$	^{3}LC
	T_4	3.32	H–3 → L+2 (0.26)	$\pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}LC
			H → L+1 (0.38)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}MLCT/^{3}LC
	T_5	3.34	H–3 → L+1 (0.33)	$\pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}LC
			H → L+2 (0.31)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{C^N}$	^{3}MLCT/^{3}LC
	T_6	3.43	H → L (0.80)	$d_\pi(Ir) + \pi_{C^N} \rightarrow \pi^*_{N^N}$	^{3}MLCT/^{3}LLCT

[a] π_{C^N} and π_{N^N} denote π orbitals of the dfppz cyclometallating C^N ligands and of the bpy-based ancillary ligand, respectively. [b] MLCT: metal-to-ligand charge transfer, LLCT: ligand-to-ligand charge transfer, LC: ligand-centered.