Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Deep-blue emitting charged bis-cyclometallated iridium(III) complex for light-emitting electrochemical cells

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1. Blue-emitting complexes for LECs from literature

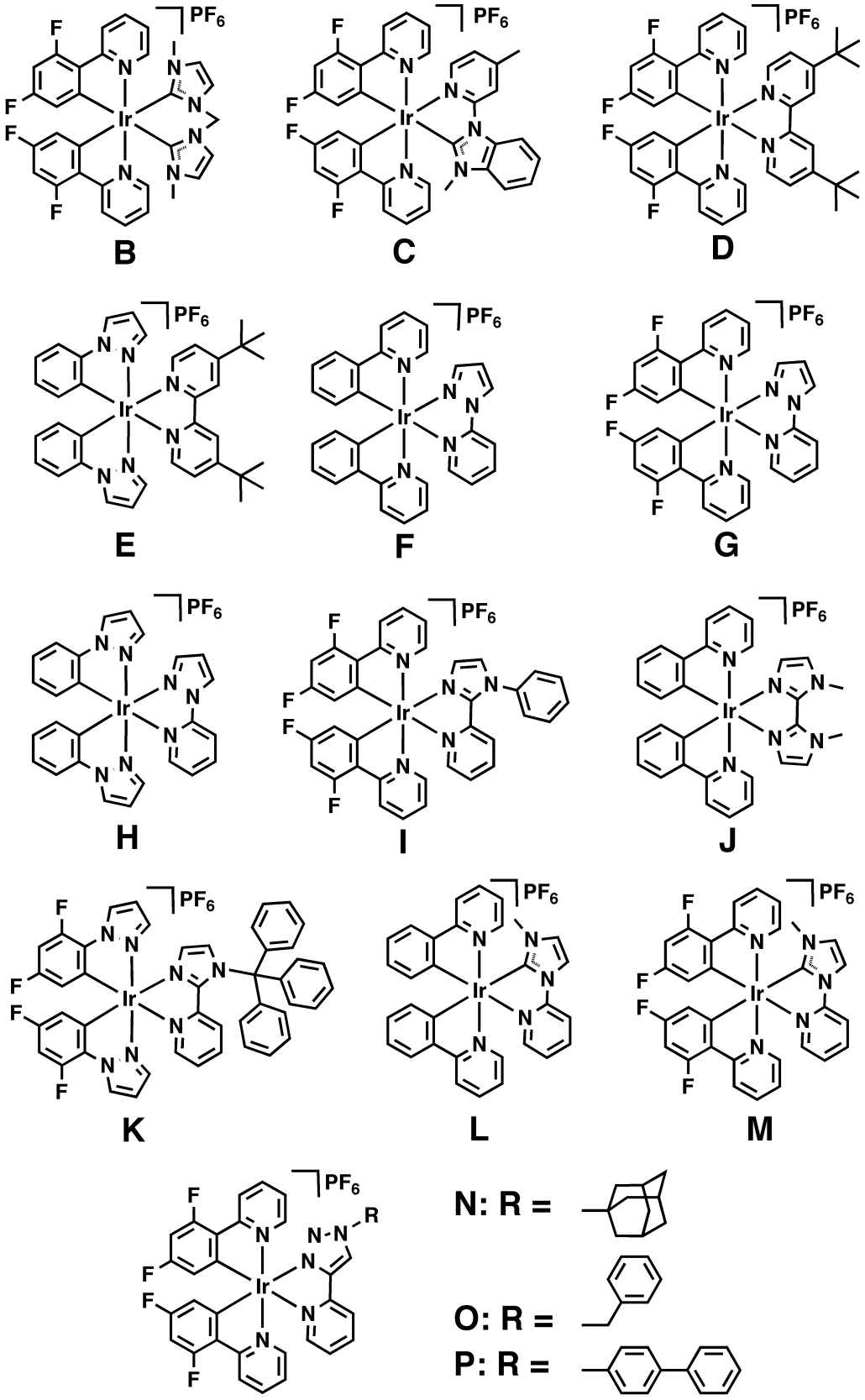

Figure S1. Blue-emitting charged iridium(III) complexes reported in the literature.[1-10]

Table S1. Summary of device characteristics for LECs comprising charged blue-emitting iridium(III) complexes.

	t_{on} min	L_{max} cd m^{-2}	$\eta_{C,max}$ cd A^{-1}	EQE %	λ_{EL} nm	CIE *x, y*	Note	Ref.
B	4.5[a]	21.6	0.73		488	0.27, 0.43	CVM	1
B'	5.3[a]	24	0.37		456	0.20, 0.34	CVM	1
C		≈20	0.001		512	0.27, 0.49	CVM	2
D	0.09[b]	970	9.7	2.83	490	0.29, 0.51	Pulsed	3
E	30[c]	1700		4.6	492	0.20, 0.41	CVM No IL	4
F	432[a]	52	0.96	0.36	486	0.27, 0.50	CVM, 5 V	5
F	24[a]	37.3	0.05	1.7	514	0.31, 0.54	CVM, 5 V	6
G	426[a]	39	0.65	0.28	460	0.20, 0.28	CVM	5
H	12[a]	1.2	0.1	0.1	493	0.25, 0.39	CVM	6
I	222[a] 18.5[c]	39	8.4	3.4	497	0.25, 0.46	CVM	7
J	174[a] 3.0[c]	68	0.4	0.14	524	0.35, 0.54	CVM	7
K	29[a] 4.5[c]	14.5	18.3	7.6	474	0.22, 0.41	CVM	8
L		5249	5.2		506	0.22, 0.46	OLED	9
M		748	0.85		483	0.23, 0.35	OLED	9
N	4[a]	19.4			460		CVM	10
O	2[a]	31.4			456		CVM	10
P	5.2[a]	32.1			456		CVM	10

[a] Time required to reach the maximum brightness. [b] Time needed to reach 100 cd m^{-2}. [c] Time required to reach 1.0 cd m^{-2}. **Note:** standard architecture: ITO/PEDOT:PSS/complex:IL/Al. No IL: no ionic liquid added; OLED: use an OLED-type architecture; CVM: Constant Voltage Mode; Pulsed: pulsed current driving mode with an average current density of 100 A m^{-2}.

2. Theoretical Calculations

Table S2. Selected bond distances (in Å) and bond angles (in deg.) calculated for complex **1** in the singlet ground state (S_0) and in the lowest-energy triplet states T_1 and T_2. X-ray values are included for comparison.

	Exp.[b]	S_0[c]	T_1[d]	T_2[d]
Ir(1)–N(1)[a]	2.057(6)	2.103	2.112	2.070
Ir(1)–N(4)	2.074(6)	2.093	2.055	2.099
Ir(1)–C(10)	2.047(8)	2.050	2.054	2.050
Ir(1)–C(11)	2.059(7)	2.058	2.058	2.059
Ir(1)–C(29)	2.111(8)	2.169	2.170	2.172
Ir(1)–C(35)	2.133(7)	2.161	2.164	2.159
N(1)–Ir(1)–N(4)	171.0(2)	170.5	170.5	171.0
C(10)–Ir(1)–C(29)	173.8(3)	175.1	176.2	175.0
C(11)–Ir(1)–C(35)	173.8(3)	174.8	175.0	174.5
C(29)–Ir(1)–C(35)	84.1(3)	84.5	84.4	84.6
C(10)–Ir(1)–C(11)	83.1(3)	85.4	85.6	85.6
C(10)–Ir(1)–C(35)	100.5(3)	97.4	96.8	97.8
C(11)–Ir(1)–C(29)	92.8(3)	93.0	93.5	92.3

[a] Atom numbering from Figure 1. [b] X-ray values from Figure 1. [c] DFT optimized structure. [d] TD-DFT optimized structure. All calculations performed at the B3LYP/(6-31G**+LANL2DZ) level in the presence of the solvent (acetonitrile).

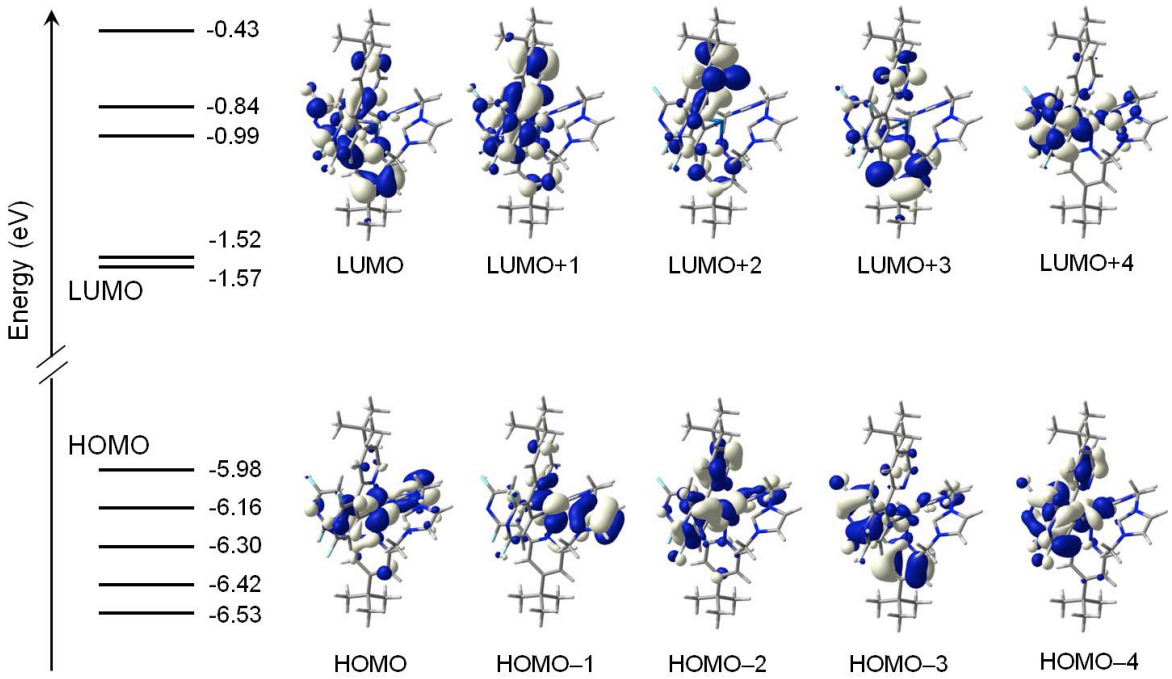

Figure S2. Electron density contours (0.03 e bohr^{-3}) and energy values (in eV) calculated for the highest occupied (HOMO–4 to HOMO) and lowest unoccupied (LUMO to LUMO+4) molecular orbitals of complex **1** in the presence of the solvent (acetonitrile).

Table S3: Lowest triplet excited states calculated at the TD-DFT B3LYP(6-31G**+LANL2DZ) level in acetonitrile for complex **1**. 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

Excited state	E (eV)	Monoexcitations	Nature[a]	Description[b]
T_1	3.06	H–3 → L (0.26)	$d_\pi(Ir) + \pi_{C\hat{}N} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LC
		H → L (0.31)	$d_\pi(Ir) + \pi_{:C\hat{}C:} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LLCT
T_2	3.11	H–2 → L+1 (0.23)	$d_\pi(Ir) + \pi_{C\hat{}N} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LC
		H–1 → L+1 (0.16)	$d_\pi(Ir) + \pi_{:C\hat{}C:} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LLCT
T_3	3.55	H–1 → L+1 (0.22)	$d_\pi(Ir) + \pi_{:C\hat{}C:} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LLCT
		H → L+1 (0.33)	$d_\pi(Ir) + \pi_{:C\hat{}C:} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LLCT
T_4	3.64	H–3 → L (0.30)	$d_\pi(Ir) + \pi_{C\hat{}N} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LC
		H–2 → L (0.16)	$d_\pi(Ir) + \pi_{C\hat{}N} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LC
T_5	3.70	H → L (0.37)	$d_\pi(Ir) + \pi_{:C\hat{}C:} \rightarrow \pi^*_{C\hat{}N}$	^{3}MLCT/^{3}LLCT

[a] $\pi_{C\hat{}N}$ and $\pi_{:C\hat{}C:}$ denote π orbitals of the 2',6'-difluoro-2,3'-bipyridine cyclometalating C^N ligands and of the bis-imidazolium carbene-type ancillary ligand, respectively. [b] MLCT: metal-to-ligand charge transfer, LLCT: ligand-to-ligand charge transfer, LC: ligand-centered.

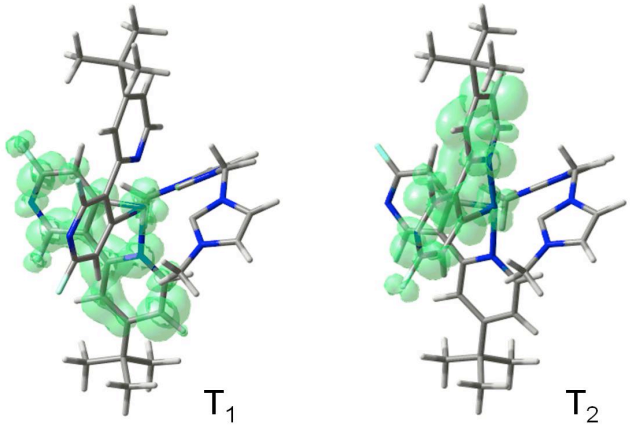

Figure S3. Unpaired-electron spin-density contours (0.005 e bohr^{-3}) computed for the T_1 and T_2 states of complex **1** at the TD-DFT optimized geometries. The spin density is fully concentrated on one of the C^N ligands wit a small contribution from the iridium core (0.13 and 0.08 e in the T_1 and T_2 states, respectively).

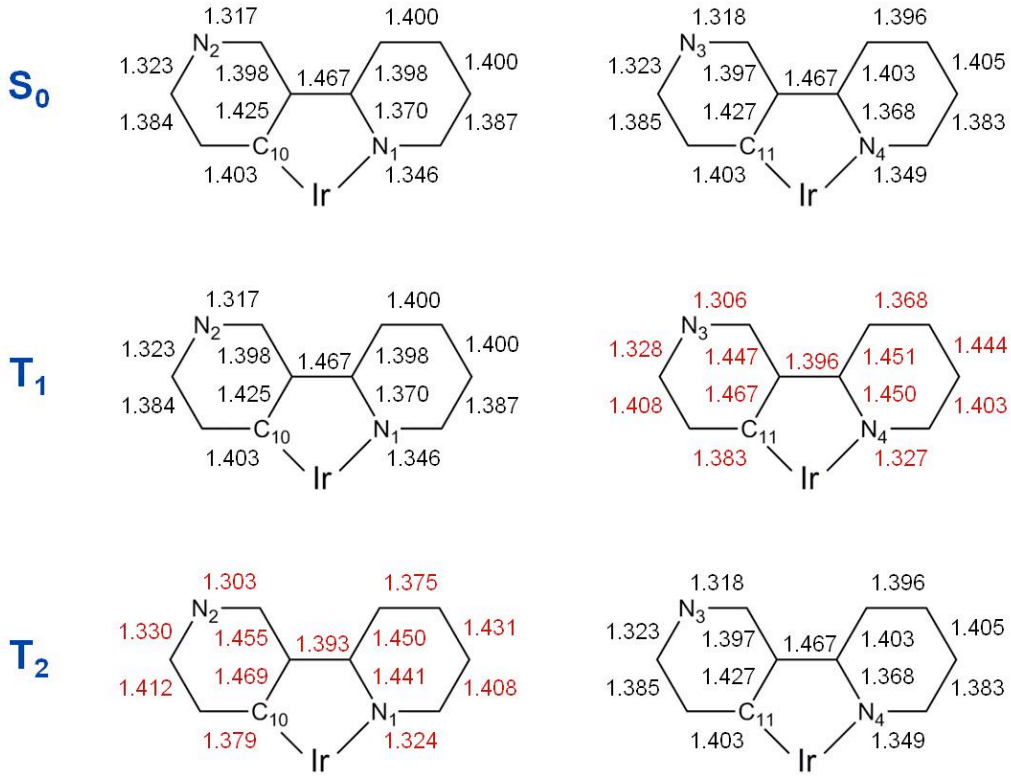

Figure S4. Optimized bond lengths (in Å) calculated for the two 2',6'-difluoro-2,3'-bipyridine C^N ligands of complex **1** in the singlet ground state (S_0, DFT optimization) and in the lowest-energy triplet states (T_1 and T_2, TD-DFT optimizations). The bond lengths of the ligand that modifies its geometry with respect to S_0 are marked in red. The fluorine substituents and the *tert*-butyl group have been omitted for clarity.

3. References for Supporting Information section

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