Supporting information

DFT/TD-DFT Study on the Electronic Structures and Optoelectronic Properties of Several Blue-emitting Iridium(III) Complexes

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Table S1. Frontier molecular orbital compositions (%) and energies (eV) in the ground state for $(dfppy)_2Ir(pyN2)$.

MO	Energy	Composition				Assign
		Ir	dfppy	dfppy'	pyN2	
L+9	0.75	4.3	91.5	3.2	1.1	π*(dfppy)
L+8	0.58	41.3	25.1	31.2	2.4	d*(Ir)+π*(dfppy)
L+7	0.35	11.2	5.6	81.4	1.8	d*(Ir)+π*(dfppy)
L+6	-0.01	7.5	82.4	7.4	2.7	π*(dfppy)
L+5	-0.95	1.2	0.7	83.3	14.8	π*(dfppy/pyN2)
L+4	-1.03	1.5	64.5	3.6	30.4	π*(dfppy/pyN2)
L+3	-1.20	1.1	33.1	11.6	54.1	π*(dfppy/pyN2)
L+2	-1.54	4	1.6	90.5	3.9	π*(dfppy)
L+1	-1.63	3.4	10.4	2.6	83.6	π*(pyN2/dfppy)
L	-1.72	3.1	83.3	2.7	10.9	π*(dfppy/pyN2)
Gap				3.85 eV		
H	-5.57	38.7	19.7	38.9	2.7	d(Ir)+π(dfppy)
H-1	-5.85	32.4	4.1	8.9	54.7	d(Ir)+π(pyN2)
H-2	-6.06	10.6	4.4	33.1	51.9	d(Ir)+π(dfppy/pyN2)
H-3	-6.18	10.4	6.6	52.6	30.4	d(Ir)+π(dfppy/pyN2)
H-4	-6.26	15.6	65.5	15.3	3.6	d(Ir)+π(dfppy)
H-5	-6.49	39.9	29.8	20.5	9.7	d(Ir)+π(dfppy)
H-6	-6.60	16.4	59.7	18.9	5.1	d(Ir)+π(dfppy)
H-7	-6.89	3.5	12.8	7.5	76.2	π(pyN2)
H-8	-7.14	27.3	2.6	11.4	58.7	d(Ir)+π(pyN2)
H-9	-7.80	33.0	34.3	29.1	3.5	d(Ir)+π(dfppy)

Table S2. Frontier molecular orbital compositions (%) and energies (eV) in the ground state for (dfppy)Ir(pyN2)$_2$.

MO	Energy	Composition				Assign
		Ir	dfppy	pyN2	pyN2'	
L+9	0.81	3.6	1.1	94.5	0.7	π*(pyN2)
L+8	0.53	44.1	23.4	15.3	17.2	d*(Ir)
L+7	0.25	4.2	92.5	1.4	1.9	π*(dfppy)
L+6	0.14	54.4	20.8	4.6	20.3	d*(Ir)
L+5	-0.97	1.2	94.5	4.2	0.1	π*(dfppy)
L+4	-1.22	0.8	2.0	29.6	67.6	π*(pyN2)
L+3	-1.34	0.6	3.3	65.7	30.4	π*(pyN2)
L+2	-1.58	3.3	94.2	1.0	1.4	π*(dfppy)
L+1	-1.80	4.5	0.8	68.6	26.2	π*(pyN2)
L	-1.87	2.1	1.1	28.0	68.7	π*(pyN2)
Gap				3.87 eV		
H	-5.74	34.2	43.8	2.2	19.7	d(Ir)+π(dfppy/pyN2)
H-1	-6.07	27.3	21.5	42.9	8.3	d(Ir)+π(pyN2/dfppy)
H-2	-6.21	5	57.6	29.3	8.0	π(dfppy/pyN2)
H-3	-6.31	7.4	16.6	1.2	74.9	π(pyN2/dfppy)
H-4	-6.41	15.4	8.0	71.0	5.6	d(Ir)+π(pyN2)
H-5	-6.67	18.9	35.5	6.3	39.3	d(Ir)+π(dfppy/pyN2)
H-6	-6.85	49.9	13.4	7.4	29.4	d(Ir)+π(pyN2)
H-7	-7.33	2.9	3.3	65.5	28.4	π(pyN2)
H-8	-7.51	21.1	19.9	38.8	20.2	d(Ir)+π(pyN2/dfppy)
H-9	-7.66	7.2	7.1	36.1	49.6	π(pyN2)

Table S3. Frontier molecular orbital compositions (%) and energies (eV) in the ground state for $(fpmb)_2Ir(pyN3)$.

MO	Energy	Composition				Assign
		Ir	fpmb	fpmb'	pyN3	
L+9	0.43	2.9	2.5	94.3	0.4	π*(fpmb)
L+8	0.25	4.3	46.3	48.8	0.7	π*(fpmb)
L+7	0.20	3.2	59.7	36.6	0.5	π*(fpmb)
L+6	-0.10	8.7	76.8	11.1	3.4	π*(fpmb)
L+5	-0.23	0.9	2.7	96.3	0.1	π*(fpmb)
L+4	-0.40	1.3	95.6	2.3	0.8	π*(fpmb)
L+3	-0.89	5.5	1.0	92.7	0.9	π*(fpmb)
L+2	-1.02	7.3	90.5	0.8	1.4	π*(fpmb)
L+1	-1.16	0.7	0.9	0.5	97.9	π*(pyN3)
L	-1.69	2.5	0.5	0.7	96.3	π*(pyN3)
Gap				3.59 eV		
H	-5.28	29.1	18.0	51.0	1.8	d(Ir)+π(fpmb)
H-1	-5.67	11.9	47.2	38.3	2.7	d(Ir)+π(fpmb)
H-2	-5.96	30.5	12.5	21.2	35.8	d(Ir)+π(pyN3/fpmb)
H-3	-6.03	16.5	32.6	43.1	7.8	d(Ir)+π(fpmb)
H-4	-6.29	36.4	47.0	7.6	9.0	d(Ir)+π(fpmb)
H-5	-6.45	8.8	3.1	37.3	50.7	π(pyN3/fpmb)
H-6	-6.55	3.2	60.3	33.3	3.3	π(fpmb)
H-7	-6.93	9.1	8.0	47.5	35.4	π(fpmb/pyN3)
H-8	-7.03	1.7	15.1	75.1	8.1	π(fpmb)
H-9	-7.13	11.1	47.2	19.1	22.6	d(Ir)+π(fpmb/pyN3)

Table S4. Selected calculated wavelength (nm) /energies (eV), oscillator strength (*f*), major contribution, and transition characters of $(dfppy)_2Ir(pyN2)$.

State	λ/E	*f*	Configuration	Nature
S_1	383/3.23	0.041	H→L (0.68)	MLCT/IL/LLCT [d(Ir)+π(dfppy)→π*(dfppy)]
S_5	337/3.67	0.077	H-1→L+1 (0.55)	MLCT/LLCT [d(Ir)+π(pyN2)→π*(dfppy)]
			H-1→L+2 (0.37)	MLCT/IL [d(Ir)+π(pyN2)→π*(pyN2)]
S_{18}	294/4.21	0.152	H-5→L (0.47)	MLCT/IL [d(Ir)+π(dfppy)→π*(dfppy)]
			H-4→L (0.21)	MLCT/IL/LLCT [d(Ir)+π(dfppy)→π*(dfppy)]
			H-1→L+4 (0.21)	MLCT/LLCT [d(Ir)+π(pyN2)→π*(dfppy)]
S_{23}	284/4.37	0.090	H-6→L (0.33)	IL/MLCT/LLCT [π(dfppy)+d(Ir)→π*(dfppy)]
			H-1→L+4 (0.43)	MLCT/LLCT [d(Ir)+π(pyN2)→π*(dfppy)]
S_{27}	276/4.50	0.088	H-2→L+3 (0.52)	MLCT/LLCT/IL[d(Ir)+π(pyN2)→π*(dfppy/pyN2)]
S_{30}	268/4.63	0.151	H-4→L+3 (0.37)	MLCT/IL/LLCT[d(Ir)+π(dfppy)→π*(dfppy/pyN2)]
			H-3→L+3 (0.33)	MLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)]
			H-2→L+4 (0.27)	MLCT/LLCT [d(Ir)+π(pyN2)→π*(dfppy)]
S_{32}	264/4.70	0.139	H-2→L+5 (0.52)	MLCT/IL/LLCT [d(Ir)+π(pyN2)→π*(pyN2/dfppy)]
S_{34}	260/4.77	0.109	H-4→L+4 (0.32)	MLCT/IL [d(Ir)+π(dfppy)→π*(dfppy)]
			H-3→L+4 (0.31)	MLCT/IL/LLCT [d(Ir)+π(dfppy/pyN2)→π*(dfppy)]

Table S5. Selected calculated wavelength (nm) /energies (eV), oscillator strength (*f*), major contribution, and transition characters of (dfppy)Ir(pyN2)$_2$ as well as the corresponding experimental data[14].

State	λ/E	*f*	Configuration	Nature	Exp.[14]
S_1	368/3.37	0.039	H→L(68%)	MLCT/IL/LLCT [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	356
S_5	329/3.76	0.075	H-1→L+1(64%)	MLCT/LLCT/IL [d(Ir)+π(pyN2)→π*(dfppy/pyN2)]	326
S_7	312/3.97	0.068	H-2→L (64%)	MLCT/LLCT/IL [π(dfppy/pyN2)+d(Ir)→π*(pyN2)]	311
S_{14}	297/4.18	0.079	H-3→L+1(58%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)]	299
S_{16}	295/4.21	0.091	H-3→L+2(56%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)]	
S_{18}	291/4.26	0.081	H-4→L+2(44%)	IL/MLCT [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)	
			H→L+5(39%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)]	
S_{19}	289/4.30	0.075	H-5→L(45%)	MLCT [d(Ir)→π*(pyN2)]	
			H-4→L+1(25%)	IL/MLCT [d(Ir)+π(dfppy/pyN2)→π*(dfppy/pyN2)]	
S_{23}	278/4.47	0.125	H-1→L+4(45%)	MLCT/IL/LLCT [d(Ir)+π(pyN2)→π*(pyN2)]	
			H-5→L+1(29%)	MLCT [d(Ir)→π*(dfppy/pyN2)]	
S_{27}	268/4.63	0.111	H-2→L+3(54%)	IL/LLCT/MLCT [π(dfppy/pyN2)+d(Ir)→π*(pyN2)]	264
S_{31}	262/4.73	0.119	H-4→L+3(49%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	
			H-3→L+3(31%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	
S_{32}	262/4.74	0.097	H-2→L+4(32%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	
			H-2→L+5(29%)	IL/LLCT/MLCT [π(dfppy/pyN2)+d(Ir)→π*(pyN2)]	
			H-4→L+3(29%)	MLCT/LLCT/IL [π(dfppy/pyN2)+d(Ir)→π*(dfppy/pyN2)]	
S_{34}	258/4.80	0.177	H-3→L+4(39%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	
			H-2→L+5(34%)	MLCT/LLCT/IL [π(dfppy/pyN2)+d(Ir)→π*(dfppy/pyN2)]	
S_{35}	258/4.81	0.089	H-3→L+4(38%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	
			H-2→L+5(38%)	MLCT/LLCT/IL [π(dfppy/pyN2)+d(Ir)→π*(dfppy/pyN2)]	
S_{36}	256/4.84	0.089	H-4→L+4(61%)	MLCT/LLCT/IL [d(Ir)+π(dfppy/pyN2)→π*(pyN2)]	

Table S6. Selected calculated wavelength (nm) /energies (eV), oscillator strength (*f*), major contribution, and transition characters of $(fpmb)_2Ir(pyN3)$ as well as the corresponding experimental data[17].

State	λ/E	*f*	Configuration	Nature	Exp.[17]
S_1	399/3.11	0.000	H→L(0.70)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	
S_2	348/3.57	0.036	H-1→L(0.68)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	356
S_{11}	289/4.29	0.120	H-1→L+3(0.66)	MLCT/IL/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	298
S_{12}	286/4.34	0.074	H-5→L(0.55)	IL/LLCT [π(pyN3/fpmb)→π*(pyN3)]	
			H-2→L+1(0.34)	MLCT/IL/LLCT[d(Ir)+π(pyN3/fpmb)→π*(pyN3)]	
S_{18}	274/4.52	0.081	H→L+6(0.46)	MLCT/IL/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{19}	273/4.55	0.262	H-3→L+2(0.33)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	
			H-2→L+3(0.30)	MLCT/LLCT/IL[d(Ir)+π(pyN3/fpmb)→π*(fpmb)]	
			H→L+6 (0.37)	MLCT/IL/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{22}	267/4.65	0.103	H-3→L+3(0.55)	MLCT/IL [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{23}	264/4.69	0.102	H-4→L+1(0.52)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	
			H-4→L+2(0.28)	MLCT/IL [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{24}	264/4.70	0.127	H-4→L+1(0.30)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	
			H-4→L+2(0.47)	MLCT/IL [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{28}	255/4.86	0.089	H-1→L+4(0.51)	MLCT/IL/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	
S_{30}	250/4.95	0.072	H-8→L(0.30)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	
			H-7→L(0.29)	MLCT/LLCT/IL[d(Ir)+π(fpmb/pyN3)→π*(pyN3)]	
			H-5→L+1(0.34)	IL/LLCT [π(pyN3/fpmb)→π*(pyN3)]	
S_{31}	250/4.97	0.095	H-8→L(0.29)	MLCT/LLCT [d(Ir)+π(fpmb)→π*(pyN3)]	
			H-1→L+5(0.31)	MLCT/IL/LLCT [d(Ir)+π(fpmb)→π*(fpmb)]	