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

DFT/TDDFT Investigation on the Electronic Structures and Photophysical Properties of Phosphorescent Ir(Ⅲ) Complexes with Conjugated/Non-conjugated Carbene Ligands

Yuqi Liu,[a] Xiaobo Sun,[b] Godefroid Gahungu,[c] Xiaochun Qu,[a] Ying Wang,[*,a] and Zhijian Wu[*,a]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022， People's Republic of China

[b] Department of Applied Chemistry, Qingdao Agricultural University, Qingdao 266109, P. R. China

[c] Université du Burundi, Faculté des Sciences, Département de Chimie, Unité de Chimie Théorique et Modélisation Moléculaire, BP. 2700 Bujumbura, Burundi.

*Corresponding authors. Email: ywang_2012@ciac.jl.cn(YW), zjwu@ciac.jl.cn (ZJW);*Tel: +86-431-85682801*

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Benchmark calculations for different density functionals

In order to find a method that would allow for reliable prediction of structure parameters, the ground-state geometries of **2b**, **3a** and **3b** were fully optimized at PBE0, B3LYP[17] and CAM-B3LYP[18] levels with the same basis set based on their single-crystal X-ray structures,[10] respectively. The partial key parameters of geometrical structures are tabulated in Table S1, along with the experimental values.

Generally, the calculated bond distances are elongated as compared with the corresponding X-ray data. This can be attributed to the crystal packing effect which is not taken into account in our calculation. Compared with the crystal data of **2b**, **3a** and **3b**, the Ir-N/Ir-C bond lengths calculated at B3LYP level are drastically overestimated, especially the Ir-N1 and Ir-N2 bond lengths deviating from the experimental values by ~0.110 and 0.070 Å, respectively. Therefore, the B3LYP functional is not reliable in predicting the structures of the herein studied Ir(III) complexes. The CAM-B3LYP functional gives better Ir-C bond lengths (deviation within 0.035 Å) than the B3LYP functional, however, the Ir-N1 and Ir-N2 bond lengths are still overestimated by ~0.070 and 0.050 Å respectively. However, the PBE0 functional performs much better than B3LYP and CAM-B3LYP in predicting the metal-related bond lengths. The Ir–C bond lengths calculated at PBE0 level are in quite good agreement with the experimental data (within 0.020 Å), and about 0.060 and 0.030 Å of deviation from the experimental values are revealed for the two Ir-N bond lenghts, respectively. Besides, the three functionals give an excellent accuracy in predicting the metal-related bond angles. Overall, the hybrid PBE0 functional predict more satisfactory bond length and bond angles (gives more satisfactory geometry parameters) for these Ir(III) complexes compared with B3LYP and CAM- B3LYP functionals. Therefore, we will discuss in detail the geometrical structures of the studied complexes obtained at PBE0 level.

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Table S1 Selected optimized bond length (in Å) and bond angles (in °) of **2b, 3a** and **3b** in ground-state at PBE0, B3LYP and CAM-B3LYP levels, respectively, along with the experimental data

	2b				**3a**				**3b**			
	PBE0	B3LYP	CAM-B3LYP	Exptl.[a]	PBE0	B3LYP	CAM-B3LYP	Exptl.[a]	PBE0	B3LYP	CAM-B3LYP	Exptl.[a]
Ir-C1	2.044	2.068	2.059	2.057	2.026	2.048	2.039	2.030	2.042	2.066	2.057	2.037
Ir-C2	2.038	2.059	2.051	2.041	2.027	2.045	2.038	2.027	2.038	2.059	2.051	2.024
Ir-C3	2.061	2.086	2.076	2.041	2.034	2.056	2.049	2.023	2.059	2.084	2.074	2.057
Ir-C4	2.037	2.056	2.046	2.042	2.021	2.038	2.030	2.023	2.040	2.060	2.050	2.025
Ir-N1	2.247	2.308	2.270	2.212	2.202	2.252	2.222	2.154	2.241	2.300	2.265	2.174
Ir-N2	2.165	2.200	2.178	2.129	2.128	2.162	2.142	2.103	2.175	2.213	2.187	2.137
C1-Ir-C2	87.8	87.9	87.8	87.2	78.9	78.8	78.9	79.2	87.6	87.8	87.6	86.9
C3-Ir-C4	86.9	87.0	86.9	86.3	78.8	78.7	78.8	78.6	86.6	86.7	86.6	86.3
N1-Ir-N2	75.0	74.1	74.7	75.5	75.7	75.0	75.4	76.3	74.9	73.9	74.6	75.8
C1-Ir-C3	175.1	175.7	175.4	174.4	169.7	170.2	169.8	168.7	174.7	175.2	175.0	173.8
C2-Ir-N2	171.2	170.7	171.2	171.1	169.5	169.1	169.5	170.8	170.9	170.3	170.8	170.3
C4-Ir-N1	175.8	175.0	175.4	174.7	173.6	173.1	173.5	175.1	176.0	175.3	175.6	177.5
C1-Ir-N1-N2	91.2	91.3	91.3	92.7	98.9	98.9	98.8	97.3	90.9	91.1	91.0	91.0
C4-Ir-C1-C2	-88.0	-88.4	-88.2	-89.5	-91.8	-91.9	-91.7	-88.0	-88.0	-88.3	-88.2	-87.7
N2-Ir-C3-C4	101.0	101.1	100.8	99.6	-87.5	98.5	-87.3	-90.7	-87.2	101.6	-87.0	-86.7

[a] Experimental data from Ref. [10]

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Table S2 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for the related ligands

	MO[a]	*E*	MO composition(%)[b]				Assign
			F-ph	NHC	$-CH_3$		
fpmb	L	-0.31	98	2	0		π*(F-ph)
	H	-3.43	9	89	2		π(NHC)
			2F-ph	NHC	$-CH_3$		
dfpmb	L	-0.18	90	10	0		π*(2F-ph)
	H	-3.29	8	89	2		π(NHC)
			F-ph	NHC	$-CH_3$	$-CH_2$	
fbmb	L	-0.19	98	1	0	1	π*(F-ph)
	H	-3.40	2	95	2	1	π(NHC)
			2F-ph	NHC	$-CH_3$	$-CH_2$	
dfbmb	L	-0.12	98	1	0	2	π*(2F-ph)
	H	-3.22	2	95	2	1	π(NHC)
			N3	py	$-CF_3$		
fptz	L	-1.67	31	69	0		π*(N3+py)
	H	-7.32	49	50	1		π(N3+py)
			N3	py	-tBu	$-CF_3$	
bptz	L	-1.48	33	66	2	0	π*(N3+py)
	H	-7.18	47	52	0	0	π(N3+py)

[a] H = HOMO; L= LUMO; [b] F-ph = 4-fluorophenyl; 2F-ph = 2,4-fluorophenyl; NHC = benzimidazolyl; N3 = triazolyl; py = pyridyl; -tBu = tert-butyl.

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Table S3 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **1a**

MO[a]	Energy	MO composition(%)					Assign
		Ir	fpmb1	fpmb2	fptz	$-CF_3$	
L+6	0.07	7	79	11	3	0	π*(fpmb)
L+4	-0.26	1	95	2	1	0	π*(fpmb1)
L+3	-0.75	5	1	93	1	0	π*(fpmb2)
L+2	-0.87	7	91	1	1	0	π*(fpmb1)
L+1	-1.04	1	1	1	97	0	π*(fptz)
L	-1.57	3	1	1	96	0	π*(fptz)
H	-5.52	27	17	54	2	0	d(Ir)+π(fpmb)
H-1	-5.91	11	50	36	3	0	d(Ir)+π(fpmb)
H-2	-6.23	29	11	22	37	1	d(Ir)+π(fpmb+fptz)
H-3	-6.30	16	33	44	6	0	d(Ir)+π(fpmb)
H-4	-6.57	34	49	8	10	0	d(Ir)+π(fpmb1)
H-5	-6.74	8	3	42	46	1	π(fpmb2+fptz)

[a] H = HOMO; L= LUMO.

Table S4 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **1b**

MO[a]	Energy	MO composition(%)					Assign
		Ir	fbmb1	fbmb2	fptz	$-CF_3$	
L+5	0.23	1	24	75	0	0	π*(fbmb)
L+4	0.13	7	85	6	1	0	π*(fbmb1)
L+3	-0.47	4	51	45	0	0	π*(fbmb)
L+2	-0.89	5	43	50	2	0	π*(fbmb)
L+1	-1.00	0	2	1	96	0	π*(fptz)
L	-1.56	2	1	1	96	0	π*(fptz)
H	-5.66	36	14	48	3	0	d(Ir)+π(fbmb)
H-1	-5.88	36	36	19	9	0	d(Ir)+π(fbmb)
H-2	-6.27	4	14	81	1	0	π(fbmb)
H-3	-6.34	12	41	34	13	0	d(Ir)+π(fbmb+fptz)
H-4	-6.40	35	17	13	35	1	d(Ir)+π(fbmb+fptz)
H-5	-6.69	8	67	19	6	0	π(fbmb)

[a] H = HOMO; L= LUMO.

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Table S5 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **2a**

MO[a]	Energy	MO composition(%)					Assign
		Ir	dfpmb1	dfpmb2	fptz	$-CF_3$	
L+5	-0.12	1	2	97	0	0	π*(dfpmb2)
L+4	-0.31	1	96	2	1	0	π*(dfpmb1)
L+3	-0.74	6	3	90	1	0	π*(dfpmb2)
L+2	-0.89	8	87	2	2	0	π*(dfpmb1)
L+1	-1.13	1	1	1	97	0	π*(fptz)
L	-1.67	3	1	1	96	0	π*(fptz)
H	-5.76	28	16	53	2	0	d(Ir)+π(dfpmb)
H-1	-6.08	15	38	44	4	0	d(Ir)+π(dfpmb)
H-2	-6.35	14	25	42	19	1	d(Ir)+π(dfpmb+fptz)
H-3	-6.36	21	31	22	24	1	d(Ir)+π(dfpmb+fptz)
H-4	-6.67	27	59	5	9	0	d(Ir)+π(dfpmb1)
H-5	-6.80	6	5	49	39	1	π(dfpmb2+fptz)

[a] H = HOMO; L= LUMO.

Table S6 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **2b**

MO[a]	Energy	MO composition(%)					Assign
		Ir	dfbmb1	dfbmb2	fptz	$-CF_3$	
L+5	0.15	2	90	7	0	0	π*(dfbmb1)
L+4	0.08	10	73	14	3	0	π*(dfbmb)
L+3	-0.55	4	46	50	0	0	π*(dfbmb)
L+2	-0.97	5	48	45	2	0	π*(dfbmb)
L+1	-1.1	0	2	1	96	0	π*(fptz)
L	-1.67	2	1	1	96	0	π*(fptz)
H	-5.88	38	14	45	3	0	d(Ir)+π(dfbmb)
H-1	-6.05	37	30	21	11	0	d(Ir)+π(dfbmb)
H-2	-6.27	2	10	88	1	0	π(dfbmb)
H-3	-6.52	33	13	4	49	1	d(Ir)+π(fptz)
H-4	-6.56	6	53	39	1	0	π(dfbmb)
H-5	-6.67	1	85	13	1	0	π(dfbmb)
H-9	-7.19	29	25	23	23	0	d(Ir)+π(dfbmb+fptz)

[a] H = HOMO; L= LUMO.

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Table S7 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **3a**

MO[a]	Energy	MO composition(%)					Assign
		Ir	fpmb1	fpmb2	bptz	CF3	
L+6	0.12	7	80	10	3	0	π*(fpmb)
L+4	-0.22	1	95	2	1	0	π*(fpmb1)
L+3	-0.70	5	1	92	1	0	π*(fpmb2)
L+2	-0.83	7	91	1	1	0	π*(fpmb1)
L+1	-0.87	1	2	1	96	0	π*(bptz)
L	-1.45	2	1	1	96	0	π*(bptz)
H	-5.47	27	17	54	2	0	d(Ir)+π(fpmb)
H-1	-5.86	12	48	36	3	0	d(Ir)+π(fpmb)
H-2	-6.16	27	10	21	40	1	d(Ir)+π(fpmb+bptz)
H-3	-6.25	16	34	44	5	0	d(Ir)+π(fpmb)
H-4	-6.51	33	46	8	13	0	d(Ir)+π(fpmb1)
H-5	-6.68	10	5	40	44	1	π(fpmb2+bptz)

[a] H = HOMO; L= LUMO.

Table S8 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **3b**

MO[a]	Energy	MO composition(%)					Assign
		Ir	fbmb1	fbmb2	bptz	CF3	
L+5	0.30	2	42	55	1	0	π*(fbmb)
L+4	0.18	3	81	15	1	0	π*(fbmb)
L+3	-0.44	4	47	50	0	0	π*(fbmb)
L+2	-0.86	5	47	45	3	0	π*(fbmb)
L+1	-0.93	0	3	2	95	0	π*(bptz)
L	-1.41	2	1	1	95	0	π*(bptz)
H	-5.60	35	15	48	2	0	d(Ir)+π(fbmb)
H-1	-5.84	37	33	20	10	0	d(Ir)+π(fbmb)
H-2	-6.22	6	7	82	4	0	π(fbmb2)
H-3	-6.32	30	12	17	40	1	d(Ir)+π(fbmb+bptz)
H-4	-6.37	11	47	37	5	0	d(Ir)+π(fbmb)
H-6	-6.66	19	14	37	29	0	d(Ir)+π(fbmb+bptz)

[a] H = HOMO; L= LUMO.

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Table S9 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **4a**

MO[a]	Energy	MO composition(%)					Assign
		Ir	dfpmb1	dfpmb2	bptz	CF3	
L+5	-0.08	1	2	97	0	0	π*(dfpmb2)
L+4	-0.27	1	95	2	1	0	π*(dfpmb1)
L+3	-0.70	6	3	90	1	0	π*(dfpmb2)
L+2	-0.85	8	87	3	2	0	π*(dfpmb1)
L+1	-1.04	1	1	1	97	0	π*(bptz)
L	-1.49	2	1	1	96	0	π*(bptz)
H	-5.71	28	17	53	2	0	d(Ir)+π(dfpmb)
H-1	-6.02	16	37	43	4	0	d(Ir)+π(dfpmb)
H-2	-6.28	19	5	36	39	1	d(Ir)+π(dfpmb2+bptz)
H-3	-6.31	16	51	27	6	0	d(Ir)+π(dfpmb)
H-4	-6.62	28	57	5	10	0	d(Ir)+π(dfpmb1)
H-5	-6.73	8	5	48	38	1	π(dfpmb2+bptz)

[a] H = HOMO; L= LUMO.

Table S10 Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **4b**

MO[a]	Energy	MO composition(%)					Assign
		Ir	dfbmb1	dfbmb2	bptz	CF3	
L+5	0.19	2	91	7	0	0	π*(dfbmb1)
L+4	0.14	9	73	15	3	0	π*(dfbmb)
L+3	-0.51	4	46	50	0	0	π*(dfbmb)
L+2	-0.93	5	48	45	2	0	π*(dfbmb)
L+1	-1.01	0	2	1	96	0	π*(bptz)
L	-1.49	2	1	1	95	0	π*(bptz)
H	-5.83	38	14	45	3	0	d(Ir)+π(dfbmb)
H-1	-5.99	38	30	20	12	0	d(Ir)+π(dfbmb)
H-2	-6.23	2	10	88	1	0	π(dfbmb)
H-3	-6.44	32	13	4	51	1	d(Ir)+π(bptz)
H-6	-6.75	19	18	40	23	0	d(Ir)+π(dfbmb+bptz)
H-9	-7.12	26	29	25	20	0	d(Ir)+π(dfbmb+bptz)

[a] H = HOMO; L= LUMO.

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Table S11 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution and transition characters for **1a-4a** in CH_2Cl_2 media, along with the experimental data for **3a**

	state	λ/E	*f*	Configuration[a]	Assignment	Exptl[b]
1a	S_1	373/3.32	0.0004	H→L(96%)	d(Ir)+π(fpmb)→π*(fptz)/MLCT/LLCT	
	S_2	329/3.77	0.0533	H-1→L(84%)	d(Ir)+π(fpmb)→π*(fptz)/MLCT/LLCT	
	S_7	298/4.15	0.0573	H-3→L(79%)	d(Ir)+π(fpmb)→π*(fptz)/MLCT/LLCT	
	S_{11}	277/4.48	0.1463	H-1→L+3(80%)	d(Ir)+π(fpmb)→π*(fpmb2)/MLCT/LLCT/IL	
	S_{17}	262/4.73	0.1614	H→L+6(33%)	d(Ir)+π(fpmb)→π*(fpmb)/MLCT/LLCT/IL	
				H-2→L+3(16%)	d(Ir)+π(fpmb+fptz)→π*(fpmb2)/MLCT/LLCT/IL	
2a	S_1	360/3.44	0.0007	H→L(96%)	d(Ir)+π(dfpmb)→π*(fptz)/MLCT/LLCT	
	S_2	325/3.82	0.0667	H-1→L(82%)	d(Ir)+π(dfpmb)→π*(fptz)/MLCT/LLCT	
	S_7	296/4.18	0.0311	H-3→L(45%)	d(Ir)+π(dfpmb+fptz)→π*(fptz)/MLCT/LLCT/IL	
	S_9	282/4.40	0.0617	H-1→L+2(60%)	d(Ir)+π(dfpmb)→π*(dfpmb1)/MLCT/LLCT/IL	
	S_{12}	272/4.56	0.1985	H-1→L+3(77%)	d(Ir)+π(dfpmb)→π*(dfpmb2)/MLCT/LLCT/IL	
	S_{24}	250/4.95	0.2435	H-3→L+3(37%)	d(Ir)+π(dfpmb+fptz)→π*(dfpmb2)/MLCT/LLCT/IL	
				H→L+5(27%)	d(Ir)+π(dfpmb)→π*(dfpmb2)/MLCT/LLCT/IL	
3a	S_1	367/3.38	0.0004	H→L(97%)	d(Ir)+π(fpmb)→π*(bptz)/MLCT/LLCT	356
	S_2	325/3.81	0.0808	H-1→L(83%)	d(Ir)+π(fpmb)→π*(bptz)/MLCT/LLCT	318
	S_7	295/4.20	0.0804	H-3→L(75%)	d(Ir)+π(fpmb)→π*(bptz)/MLCT/LLCT	298
	S_{10}	278/4.47	0.0826	H-1→L+3(55%)	d(Ir)+π(fpmb)→π*(fpmb2)/MLCT/LLCT/IL	
				H-1→L+1(21%)	d(Ir)+π(fpmb)→π*(bptz)/MLCT/LLCT	
	S_{12}	271/4.58	0.1207	H-5→L(65%)	π(fpmb2+bptz)→π*(bptz)/LLCT/IL	
	S_{16}	262/4.70	0.1420	H→L+6(31%)	d(Ir)+π(fpmb)→π*(fpmb)/MLCT/LLCT	
				H-2→L+3(21%)	d(Ir)+π(fpmb+bptz)→π*(fpmb2)/MLCT/LLCT/IL	
	S_{23}	252/4.93	0.1617	H-4→L+2(45%)	d(Ir)+π(fpmb1)→π*(fpmb1)/MLCT/IL	
4a	S_1	348/3.56	0.0007	H→L(96%)	d(Ir)+π(dfpmb)→π*(bptz)/MLCT/LLCT	
	S_2	316/3.92	0.0964	H-1→L(81%)	d(Ir)+π(dfpmb)→π*(bptz)/MLCT/LLCT	
	S_8	282/4.40	0.0790	H-1→L+2(61%)	d(Ir)+π(dfpmb)→π*(dfpmb1)/MLCT/LLCT/IL	
	S_{11}	272/4.55	0.1593	H-1→L+3(76%)	d(Ir)+π(dfpmb)→π*(dfpmb2)/MLCT/LLCT/IL	
	S_{14}	262/4.73	0.0972	H-2→L+1(62%)	d(Ir)+π(dfpmb2+bptz)→π*(bptz)/MLCT/LLCT/IL	
	S_{22}	251/4.94	0.2637	H-3→L+3(29%)	d(Ir)+π(dfpmb)→π*(dfpmb2)/MLCT/LLCT/IL	
				H-4→L+1(25%)	d(Ir)+π(dfpmb1)→π*(bptz)/MLCT/LLCT	

[a] H = HOMO; L= LUMO; [b] Experimental data from Ref. [10]

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Table S12 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution and transition characters for **1b**-**4b** in CH_2Cl_2 media, along with the experimental data for **2b** and **3b**

	state	λ/E	*f*	Configuration[a]	Assignment	Exptl[b]
1b	S_1	361/3.43	0.0004	H→L(95%)	d(Ir)+π(fbmb)→π*(fptz)/MLCT/LLCT	
	S_2	343/3.62	0.0581	H-1→L(94%)	d(Ir)+π(fbmb)→π*(fptz)/MLCT/LLCT	
	S_6	293/4.23	0.4525	H-1→L+2(62%)	d(Ir)+π(fbmb)→π*(fbmb)/MLCT/LLCT/IL	
				H-1→L+1(32%)	d(Ir)+π(fbmb)→π*(fptz)/MLCT/LLCT	
	S_{10}	278/4.46	0.0637	H-5→L(57%)	π(fbmb)→π*(fptz)/LLCT	
	S_{13}	267/4.64	0.0436	H-3→L+2(47%)	d(Ir)+π(fbmb+fptz)→π*(fbmb)/MLCT/LLCT/IL	
				H-3→L+1(27%)	d(Ir)+π(fbmb)→π*(fptz)/MLCT/LLCT	
	S_{18}	258/4.81	0.1814	H-2→L+2(55%)	π(fbmb)→π*(fbmb)/LLCT/IL	
2b	S_1	349/3.55	0.0002	H→L(93%)	d(Ir)+π(dfbmb)→π*(fptz)/MLCT/LLCT	363
	S_2	337/3.68	0.0601	H-1→L(92%)	d(Ir)+π(dfbmb)→π*(fptz)/MLCT/LLCT	316
	S_3	306/4.05	0.0284	H-3→L(82%)	d(Ir)+π(fptz)→π*(fptz)/MLCT/IL	
	S_6	289/4.30	0.5070	H-1→L+2(64%)	d(Ir)+π(dfbmb)→π*(dfbmb)/MLCT/LLCT/IL	293
				H-1→L+1(27%)	d(Ir)+π(dfbmb)→π*(fptz)/MLCT/LLCT	
	S_{10}	276/4.50	0.0291	H-4→L(37%)	π(dfbmb)→π*(fptz)/LLCT	
				H-5→L(27%)	π(dfbmb)→π*(fptz)/LLCT	
	S_{13}	264/4.69	0.0465	H-3→L+2(34%)	d(Ir)+π(fptz)→π*(dfbmb)/MLCT/LLCT	
				H-3→L+1(31%)	d(Ir)+π(fptz)→π*(fptz)/MLCT/IL	
	S_{20}	252/4.91	0.1489	H→L+4(25%)	d(Ir)+π(dfbmb)→π*(dfbmb)/MLCT/LLCT/IL	
				H-9→L(17%)	d(Ir)+π(dfbmb+fptz)→π*(fptz)/MLCT/LLCT/IL	
3b	S_1	350/3.54	0.0006	H→L(95%)	d(Ir)+π(fbmb)→π*(bptz)/MLCT/LLCT	363
	S_2	333/3.72	0.0791	H-1→L(94%)	d(Ir)+π(fbmb)→π*(bptz)/MLCT/LLCT	322
	S_6	294/4.22	0.4854	H-1→L+2(56%)	d(Ir)+π(fbmb)→π*(fbmb)/MLCT/LLCT/IL	298
				H-1→L+1(39%)	d(Ir)+π(fbmb)→π*(bptz)/MLCT/LLCT	
	S_9	274/4.52	0.0516	H-6→L(46%)	d(Ir)+π(fbmb+bptz)→π*(bptz)/MLCT/LLCT/IL	
	S_{14}	262/4.73	0.0911	H-2→L+1(28%)	π(fbmb2)→π*(bptz)/LLCT	
				H-6→L(23%)	d(Ir)+π(fbmb+bptz)→π*(bptz)/MLCT/LLCT/IL	
				H-2→L+2(21%)	π(fbmb2)→π*(fbmb)/LLCT	
	S_{19}	254/4.87	0.2156	H-3→L+2(42%)	d(Ir)+π(fbmb+bptz)→π*(fbmb)/MLCT/LLCT/IL	
				H-3→L+1(20%)	d(Ir)+π(fbmb+bptz)→π*(bptz)/MLCT/LLCT/IL	
4b	S_1	339/3.66	0.0002	H→L(92%)	d(Ir)+π(dfbmb)→π*(bptz)/MLCT/LLCT	
	S_2	328/3.78	0.0817	H-1→L(90%)	d(Ir)+π(dfbmb)→π*(bptz)/MLCT/LLCT	
	S_3	299/4.15	0.0296	H-3→L(79%)	d(Ir)+π(bptz)→π*(dfbmb)/MLCT/LLCT	
	S_5	289/4.29	0.4453	H-1→L+1(45%)	d(Ir)+π(dfbmb)→π*(dfbmb)/MLCT/LLCT/IL	
				H-1→L+2(37%)	d(Ir)+π(dfbmb)→π*(dfbmb)/MLCT/LLCT/IL	
	S_9	274/4.52	0.0611	H-6→L(41%)	d(Ir)+π(dfbmb+bptz)→π*(bptz)/MLCT/LLCT/IL	
	S_{12}	265/4.68	0.0568	H-3→L+2(36%)	d(Ir)+π(bptz)→π*(bptz)/MLCT/IL	
				H-3→L+1(33%)	d(Ir)+π(bptz)→π*(dfbmb)/MLCT/LLCT	
	S_{20}	250/4.96	0.1419	H-9→L(67%)	d(Ir)+π(dfbmb+bptz)→π*(dfbmb)/MLCT/LLCT/IL	

[a] H = HOMO; L= LUMO; [b] Experimental data from Ref. [10]

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Table S13 Calculated emission wavelengths (λ, in nm) for **2b**, **3a** and **3b** at PBE0, M06-2X, M05-2X, B3LYP, and CAM-B3LYP levels, respectively, together with the experimental values

	PBE0		M06-2X		M05-2X		B3LYP		CAM-B3LYP		Exptl[b]
	λ	Configuration[a]	λ	Configuration[a]	λ	Configuration[a]	λ	Configuration[a]	λ	Configuration[a]	
2b	521	H-2→L(50%)	451	H→L(49%)	473	H-2→L(40%)	513	H-2→L(48%)	524	H-2→L(53%)	458
		H→L(31%)		H-2→L(41%)		H→L(48%)		H→L(34%)		H→L(29%)	
3a	518	H-2→L(56%)	449	H-2→L(75%)	469	H-2→L(74%)	511	H-2→L(51%)	520	H-2→L(58%)	461
		H→L(15%)		H→L(8%)		H→L(6%)		H→L(24%)		H→L(7%)	
3b	510	H-2→L(53%)	442	H-2→L(51%)	461	H-2→L(51%)	503	H-2→L(49%)	512	H-2→L(58%)	460
		H→L(23%)		H→L(28%)		H→L(27%)		H→L(27%)		H->L(18%)	

[a] H = HOMO; L= LUMO; [b] Experimental data from Ref. [10]

TD-DFT was used to calculate the phosphorescent spectra in CH_2Cl_2 media on the basis of the lowest triplet state (T_1) geometries. In order to find a method that would allow for reliable prediction of emission properties, five different density functionals (PBE0, B3LYP, CAM-B3LYP, M05-2X[21] and M06-2X[22]) were performed on the emission properties of **2b**, **3a** and **3b**, respectively. The results are summarized in Table S13, together with the available experimental values. It shows that the PBE0, B3LYP and CAM-B3LYP significantly overestimate the emission wavelengths by >43 nm of **2b**, **3a** and **3b** compared with the corresponding experimental data. While the M06-2X functional gives improved results for **2b** (deviation of 7 nm) and relatively larger discrepancy from the experimental data by 12 and 18 nm for **3a** and **3b**, respectively. The best results are obtained at M05-2X level with smaller discrepancy of 8 and 1 nm **3a** and **3b**, and relatively larger deviation of 15 nm for **2b**, respectively. Overall, we would employ the M05-2X functional for further emission spectra calculations of all the studied complexes.

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Table S14 Frontier molecular orbital energies (eV) and compositions (%) of **1a**−**4a** and **1b**−**4b** in the excited states, respectively

	MO[a]	*E*	MO composition(%)				Assign
			Ir	fpmb1	fpmb2	fptz	
1a	L+11	1.33	56	21	14	8	d(Ir)+π*(fpmb)
	L	-1.85	3	1	1	95	π*(fptz)
	H-2	-6.08	20	2	16	62	d(Ir)+π(fpmb2+fptz)
			Ir	dfpmb1	dfpmb2	fptz	
2a	L+13	1.42	62	23	15	1	d(Ir)+π*(dfpmb)
	L	-1.93	3	1	1	95	π*(fptz)
	H-2	-6.19	12	2	24	61	d(Ir)+π(dfpmb2+fptz)
			Ir	fpmb1	fpmb2	bptz	
3a	L+11	1.36	53	22	13	11	d(Ir)+π*(fpmb)
	L	-1.75	3	1	1	95	π*(bptz)
	H-2	-6.00	17	2	16	65	d(Ir)+π(fpmb2+bptz)
			Ir	dfpmb1	dfpmb2	bptz	
4a	L+13	1.44	61	20	16	3	d(Ir)+π*(dfpmb)
	L	-1.77	3	1	1	95	π*(bptz)
	H-2	-6.10	8	5	33	54	π(dfpmb2+bptz)
			Ir	fbmb1	fbmb2	fptz	
1b	L+14	1.61	86	1	7	5	d(Ir)
	L	-1.84	2	1	1	95	π*(fptz)
	H	-5.64	35	16	43	6	d(Ir)+π(fbmb)
	H-2	-6.18	22	18	4	56	d(Ir)+π(fbmb1+fptz)
			Ir	dfbmb1	dfbmb2	fptz	
2b	L+14	1.54	86	1	6	6	d(Ir)
	L	-1.94	2	1	1	95	π*(fptz)
	H	-5.86	36	16	37	10	d(Ir)+π(dfbmb+fptz)
	H-2	-6.31	24	18	4	53	d(Ir)+π(dfbmb1+fptz)
			Ir	fbmb1	fbmb2	bptz	
3b	L+14	1.67	86	1	8	5	d(Ir)
	L	-1.69	2	1	1	95	π*(bptz)
	H	-5.58	34	17	42	7	d(Ir)+π(fbmb)
	H-2	-6.11	23	18	4	55	d(Ir)+π(fbmb1+bptz)
			Ir	dfbmb1	dfbmb2	bptz	
4b	L+14	1.58	86	1	6	6	d(Ir)
	L	-1.78	2	1	1	95	π(bptz)
	H	-5.80	36	17	34	13	d(Ir)+π(dfbmb+bptz)
	H-2	-6.22	2	11	82	5	π(dfbmb)
	H-3	-6.23	23	20	11	45	d(Ir)+π(dfbmb+bptz)

[a] H = HOMO; L= LUMO.

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Table S15: The xyz coordinates for the optimized structures for **2b** in the S_0 and T_1 states

2b	**S_0**			**T_1**		
Ir	-0.10459100	-0.20606600	-0.19415000	-0.08428300	-0.21196800	-0.18547200
N	-0.13901200	0.20511800	-2.40271700	-0.24351200	0.16319600	-2.35120600
N	0.81840300	1.73944500	-0.41705300	0.68842000	1.74648000	-0.39788600
N	1.36857400	2.66185200	0.37595200	1.23160700	2.67266300	0.36959900
N	1.42582300	3.42661400	-1.75033000	1.11014500	3.53800100	-1.74108100
N	2.72529600	-0.71989700	0.65889400	2.80211600	-0.58025400	0.57243500
N	2.40564500	-1.85888700	-1.15210700	2.47957700	-1.70462400	-1.24817100
N	-3.09037700	0.14463600	-0.50229400	-3.09355600	-0.05573500	-0.45166400
N	-2.34097500	1.69686100	0.80702300	-2.42174900	1.57371400	0.80586400
C	-0.59393000	-0.59762500	-3.37442300	-0.67277300	-0.62798100	-3.32287300
H	-0.97637200	-1.55994600	-3.04836900	-0.94972400	-1.63598800	-3.02379000
C	-0.58194200	-0.24795700	-4.71588900	-0.77469100	-0.25343900	-4.66437200
H	-0.96695600	-0.94200400	-5.45568600	-1.13659100	-0.97611900	-5.38754600
C	-0.07037200	0.99841400	-5.07913100	-0.39644700	1.07277600	-5.05935400
H	-0.04642100	1.30583600	-6.12068200	-0.46977900	1.38354200	-6.09601600
C	0.41033000	1.83582500	-4.08806000	0.06124500	1.91618600	-4.09523300
H	0.82789200	2.81476100	-4.29766600	0.37784600	2.93252000	-4.30911000
C	0.36390000	1.40880300	-2.75830900	0.14682200	1.47780700	-2.73383000
C	0.86549200	2.21716700	-1.67204900	0.62586900	2.26802100	-1.70541100
C	1.71603700	3.64393600	-0.46181100	1.45623500	3.71170700	-0.47708800
C	2.32547100	4.91743700	0.02772400	1.99177600	5.00652800	0.05835400
C	-0.00415700	-0.44958100	1.82583400	0.09801800	-0.43261300	1.83616600
C	-1.13000300	-0.82304600	2.58045800	-0.98743400	-0.84347800	2.63047500
H	-2.08358700	-1.02425500	2.10371600	-1.94807800	-1.08280400	2.18643500
C	-1.05334400	-0.96546800	3.95575300	-0.86158200	-0.97497200	4.00271600
C	0.12146600	-0.76609400	4.66284000	0.32766900	-0.72707300	4.66995100
H	0.17604900	-0.88063800	5.73851500	0.42164000	-0.83316400	5.74379400
C	1.23022300	-0.42369400	3.90986800	1.39736500	-0.34755800	3.88002800
C	1.20459100	-0.26268800	2.52601100	1.32119900	-0.19609800	2.49623400
C	2.47717200	0.11807600	1.82716500	2.56025100	0.22837200	1.76243100
H	2.44787500	1.16572000	1.51041300	2.49585100	1.28120200	1.46734900
H	3.32242200	-0.01305700	2.50324600	3.42803900	0.10900600	2.41176600
C	3.93287900	-1.33381100	0.37892900	4.03172300	-1.11849500	0.23562800
C	5.16878100	-1.32505300	1.01958500	5.28855300	-1.04777500	0.83030700
H	5.33941200	-0.75443500	1.92648800	5.46045500	-0.48341500	1.74091400
C	6.18599900	-2.07708400	0.44300700	6.32485300	-1.72865900	0.20209400
H	7.16427500	-2.09268300	0.91397600	7.31974000	-1.69487400	0.63580400
C	5.97879900	-2.81148100	-0.73320700	6.11553500	-2.45335400	-0.97989700
H	6.79954600	-3.38392100	-1.15489700	6.95151700	-2.96845300	-1.44350100
C	4.74480500	-2.81866200	-1.37398900	4.86077700	-2.52225600	-1.57440300
H	4.58993300	-3.38232500	-2.28860800	4.70526400	-3.07663200	-2.49444800
C	3.72753800	-2.06697200	-0.79393000	3.82385000	-1.84213900	-0.94256000

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C	1.78726700	-1.01963800	-0.27220300	1.85076600	-0.91708400	-0.33191300
C	1.79664200	-2.50357200	-2.29059800	1.86414500	-2.36065800	-2.37854000
H	0.72429100	-2.56385900	-2.12115200	0.81728000	-2.54241600	-2.14729000
H	2.18930100	-3.52086200	-2.37426700	2.35562400	-3.32452400	-2.53528100
H	2.00702800	-1.95728200	-3.21572000	1.95148300	-1.75490900	-3.28553200
C	-1.02989900	-2.01912200	-0.29169000	-0.89588700	-2.08636400	-0.24038800
C	-0.42649500	-3.18691400	0.21397900	-0.20025200	-3.20160700	0.26540900
H	0.53467000	-3.13911600	0.71531900	0.76976300	-3.08159300	0.73649700
C	-1.03942300	-4.42314400	0.10709800	-0.73084500	-4.47751800	0.19474200
C	-2.27969000	-4.59232700	-0.48993300	-1.97479000	-4.73709400	-0.36075300
H	-2.75608500	-5.56159700	-0.57196800	-2.38846200	-5.73678100	-0.41331000
C	-2.88620800	-3.44124600	-0.95559700	-2.67049000	-3.63726200	-0.82597400
C	-2.31446500	-2.17031200	-0.86869700	-2.18206000	-2.33004900	-0.77830100
C	-3.14130300	-1.01470900	-1.37294600	-3.09618500	-1.24440400	-1.28480900
H	-2.85520100	-0.69821000	-2.38304500	-2.86408400	-0.94468300	-2.31348500
H	-4.18514900	-1.32704100	-1.43069500	-4.11925800	-1.62363100	-1.29424800
C	-4.19713800	0.88811800	-0.12793100	-4.23611600	0.64040000	-0.09209900
C	-5.55098600	0.79585900	-0.43623700	-5.58467200	0.46457600	-0.38707500
H	-5.93917900	0.02821000	-1.09809700	-5.93388500	-0.34333900	-1.02207200
C	-6.39638200	1.73690300	0.14229800	-6.47651300	1.37705000	0.16658700
H	-7.45972300	1.69646400	-0.07416200	-7.53719800	1.27239700	-0.04104100
C	-5.90711700	2.73490300	0.99650400	-6.03739100	2.42847500	0.98315600
H	-6.59919900	3.45125600	1.42888900	-6.76477500	3.12144000	1.39519000
C	-4.55339200	2.82766500	1.30116800	-4.68912400	2.60489600	1.27428000
H	-4.17388700	3.60062600	1.96168400	-4.34898300	3.42203400	1.90233500
C	-3.70957500	1.88695100	0.71956800	-3.79903800	1.69074200	0.71964600
C	-1.95171400	0.63362200	0.05283100	-1.98207000	0.51192700	0.07841700
C	-1.51672200	2.50424300	1.68268300	-1.62925300	2.45467700	1.63888600
H	-0.49178800	2.14645800	1.66217300	-0.62628700	2.05282500	1.74930700
H	-1.90517200	2.43664000	2.70369400	-2.09878500	2.52420500	2.62464800
H	-1.53390600	3.54742900	1.35180300	-1.56911900	3.45212600	1.19201200
F	1.40088200	5.88714700	0.15698700	1.00288600	5.72849700	0.61429600
F	3.25504100	5.37106600	-0.82178200	2.54264600	5.74264500	-0.90576000
F	2.89975400	4.75337700	1.22572200	2.91257200	4.79218100	1.00566700
F	-2.15795100	-1.31137500	4.63663800	-1.92893000	-1.35775700	4.72154900
F	2.39485000	-0.23360200	4.56410900	2.57424100	-0.10926000	4.49549400
F	-0.41373500	-5.50650600	0.59102600	-0.02058200	-5.50871200	0.67488300
F	-4.10428400	-3.56473100	-1.52569300	-3.89342000	-3.85179400	-1.35580300

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Table S16: The xyz coordinates for the optimized structures for **3a** in the S_0 and T_1 states

3a	**S_0**			**T_1**		
Ir	-0.29365200	0.37864300	-0.10854300	-0.26642300	0.39978900	-0.07864400
N	-0.13725300	-1.18889400	1.32192300	-0.17857500	-1.12590100	1.34523200
N	-0.77426700	-1.54194100	2.43677100	-0.88046600	-1.48600700	2.40090400
N	0.85462800	-3.06315600	2.01343000	0.70175000	-3.10163200	2.03475100
N	1.37010900	-0.86401200	-0.84120000	1.35151600	-0.85686900	-0.81229700
N	1.49254300	2.66632300	-0.11128300	1.58708600	2.63652500	-0.09855900
N	1.72110600	1.78614900	1.86887100	1.82843300	1.73310500	1.86919600
N	-3.11563600	-0.16125300	-0.52670300	-3.09063000	-0.06920700	-0.55359600
N	-2.10252500	-1.57793800	-1.82957900	-2.08516000	-1.51639700	-1.83183000
C	-0.55653500	-3.43794300	4.02189300	-0.84458200	-3.43273100	3.94319700
C	-0.14520200	-2.66288600	2.81263000	-0.30838900	-2.65886000	2.77557500
C	0.82234900	-2.10322900	1.08628600	0.78196300	-2.12777900	1.09591700
C	1.67591200	-1.92895500	-0.06766400	1.59848500	-2.01100100	-0.01959800
C	2.74354500	-2.77906600	-0.36339500	2.64791000	-2.92767200	-0.35513000
H	2.91258700	-3.61186500	0.30912200	2.73583600	-3.80740400	0.27364000
C	3.54537000	-2.54095400	-1.47427900	3.49435900	-2.68764100	-1.39790900
C	3.21830800	-1.41684800	-2.25257000	3.26279900	-1.46232000	-2.13154400
H	3.79725200	-1.15440600	-3.13233500	3.89555300	-1.18248400	-2.96669200
C	2.14436200	-0.61674100	-1.90807500	2.20333200	-0.61787300	-1.79750500
H	1.86989200	0.25367400	-2.49688300	2.01721500	0.28573900	-2.37391500
C	4.72876500	-3.42783100	-1.84933100	4.62914700	-3.61289300	-1.81045400
C	4.50980200	-3.98818100	-3.26428500	4.40410700	-4.08021300	-3.25854100
H	3.59708400	-4.59254800	-3.31211100	3.46854600	-4.64429500	-3.34492400
H	5.35469200	-4.62651400	-3.54762100	5.22609100	-4.73116000	-3.58022400
H	4.42857700	-3.19244100	-4.01234900	4.35429200	-3.23764100	-3.95716900
C	4.89774200	-4.60120400	-0.88118900	4.71639700	-4.84631600	-0.90975400
H	5.75338600	-5.21087900	-1.19142500	5.54433800	-5.48550700	-1.23636100
H	4.01550200	-5.25111700	-0.86876200	3.79845000	-5.44376100	-0.95034000
H	5.08841400	-4.26169700	0.14304400	4.90050600	-4.57135800	0.13503000
C	6.01337000	-2.58298500	-1.82585500	5.96379800	-2.85303800	-1.72453200
H	5.96645300	-1.74796800	-2.53294000	5.97420600	-1.96695100	-2.36877500
H	6.87420000	-3.20434900	-2.09895000	6.79016800	-3.50211200	-2.03871800
H	6.19447900	-2.17051300	-0.82720100	6.15939500	-2.52377400	-0.69792600
C	-0.11280300	1.75160700	-1.58930700	-0.06491100	1.77702000	-1.55959000
C	-0.77458300	1.78227900	-2.82001900	-0.75290800	1.84047900	-2.77389200
H	-1.55336700	1.06301400	-3.05626800	-1.55047700	1.14101500	-3.00583900
C	-0.45648500	2.73902100	-3.77607100	-0.43335700	2.80380000	-3.72213200
C	0.52303000	3.69452000	-3.56934200	0.56855500	3.73687900	-3.51956500
H	0.74929300	4.42058400	-4.34253000	0.79300400	4.47118900	-4.28545000
C	1.19825800	3.69391000	-2.35017100	1.26804700	3.70454300	-2.31505800
H	1.97478500	4.42994900	-2.18733800	2.05615500	4.42827800	-2.15437000
C	0.87023000	2.74854500	-1.38563900	0.94440900	2.74758300	-1.36044600

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C	2.39755400	3.48049800	0.56179900	2.54998900	3.40133800	0.55336000
C	3.09595500	4.64394000	0.24073600	3.29897400	4.52827900	0.21646100
H	2.99686300	5.13711700	-0.71682200	3.20416600	5.02704700	-0.73849300
C	3.93878900	5.18116600	1.20873700	4.19398600	5.01730700	1.16258300
H	4.49077300	6.08730600	0.97735200	4.78674900	5.89375000	0.91827000
C	4.08999200	4.58766800	2.46680200	4.34849800	4.41126400	2.41427000
H	4.75954900	5.03579500	3.19463200	5.06055000	4.82047600	3.12443100
C	3.39147900	3.43264400	2.79915900	3.60239000	3.29122700	2.76154000
H	3.50118900	2.96632800	3.77310500	3.71855800	2.81331200	3.72903400
C	2.54770500	2.89946100	1.83254300	2.70639000	2.80622800	1.81676200
C	1.08278100	1.63405400	0.68832500	1.15617400	1.61861500	0.70532200
C	1.54262500	0.95460100	3.04160000	1.65375400	0.88512900	3.03043700
H	2.38240400	0.26198500	3.15818900	2.42938600	0.11353400	3.06893600
H	0.61610500	0.39110100	2.94304300	0.67283300	0.41478700	2.98222000
H	1.47717300	1.59498100	3.92554900	1.70959800	1.50084600	3.93192700
C	-1.83841600	1.37226100	0.73475600	-1.80267000	1.42029700	0.75138100
C	-1.77524200	2.44078600	1.63065500	-1.73012900	2.47586300	1.66186100
H	-0.82683100	2.86901100	1.93880400	-0.77608800	2.87653500	1.98987400
C	-2.93412700	2.99064300	2.16177500	-2.88571400	3.04153400	2.18242500
C	-4.19355800	2.52098800	1.83606500	-4.14929700	2.59907600	1.83168700
H	-5.07632900	2.97332900	2.27421400	-5.02909300	3.06167100	2.26518300
C	-4.28699300	1.46122100	0.93778500	-4.25202000	1.55386100	0.91782200
H	-5.26863700	1.08541200	0.68282800	-5.23710400	1.19651500	0.64966500
C	-3.12949100	0.91174200	0.40121900	-3.09741000	0.99026100	0.38909900
C	-4.12307000	-0.89525900	-1.14341000	-4.10252200	-0.76282100	-1.20930800
C	-5.51679800	-0.88612400	-1.09209900	-5.49588700	-0.69707300	-1.21136300
H	-6.07235600	-0.19975300	-0.46817500	-6.04669000	0.01295400	-0.60997900
C	-6.20063800	-1.80532400	-1.88143800	-6.18444200	-1.58428000	-2.03203100
H	-7.28612300	-1.81387600	-1.85214900	-7.26964100	-1.54843400	-2.04616500
C	-5.52925400	-2.71525400	-2.70538500	-5.51825500	-2.51669400	-2.83565600
H	-6.09898800	-3.41981000	-3.30361200	-6.09254000	-3.19442000	-3.45993000
C	-4.14063700	-2.73080100	-2.76551700	-4.13035200	-2.58599700	-2.84553000
H	-3.61083300	-3.43641300	-3.39787600	-3.60404100	-3.30514300	-3.46532300
C	-3.46090400	-1.81012900	-1.97788500	-3.44534200	-1.69673400	-2.02673600
C	-1.88303800	-0.58105700	-0.93997100	-1.86163700	-0.52947500	-0.93613800
C	-1.09193500	-2.33102800	-2.53260800	-1.07571000	-2.30233100	-2.50353600
H	-1.01844900	-3.34764600	-2.13185900	-1.11188500	-3.34124500	-2.16042000
H	-0.13667900	-1.82533900	-2.41682700	-0.09975100	-1.87935000	-2.27651200
H	-1.34532200	-2.38021600	-3.59613400	-1.24422400	-2.27210100	-3.58465100
F	-1.37995100	-2.73013300	4.80123200	-1.48744900	-2.63559000	4.80151100
F	-1.19147100	-4.57567400	3.68855000	-1.71016900	-4.37518000	3.53566100
F	0.50981200	-3.78929600	4.75828600	0.14080300	-4.05017500	4.60338000
F	-1.11665700	2.72879400	-4.94694100	-1.11641400	2.82543600	-4.87881100
F	-2.82460000	4.01706100	3.02320000	-2.77174500	4.05321700	3.05941700

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Table S17: The xyz coordinates for the optimized structures for **3b** in the S_0 and T_1 states

3b	**S_0**			**T_1**		
Ir	0.48598500	0.12434500	-0.17423000	-0.45500500	0.20985300	-0.17189900
N	-0.86098500	0.09999000	1.53320300	0.50395400	-0.62134600	1.52333100
N	-0.81018700	0.39890100	2.83446900	0.22846100	-0.84305500	2.79683800
N	-2.87645000	-0.38860400	2.36613700	2.36307200	-1.57644900	2.43743000
N	-1.47289400	-0.60263300	-0.98519300	1.47592300	-0.50489900	-0.97529700
N	-0.65013300	2.77583400	-1.45035300	-1.31826600	-2.52078900	-1.48008100
N	0.23741100	3.03209700	0.50634200	-2.22080400	-2.14254900	0.45061400
N	1.47220600	-2.35715200	1.40263300	0.51390700	2.71946200	1.37468500
N	1.30845900	-2.73035300	-0.72340100	0.84726700	2.87500500	-0.75930000
C	-2.39418400	0.22737900	4.72757900	1.46666700	-1.71311800	4.75033800
C	-2.03057500	0.09438100	3.28503100	1.36425700	-1.40290000	3.28664500
C	-2.09683400	-0.36427000	1.28242500	1.81501400	-1.09011500	1.29058500
C	-2.45551600	-0.74139200	-0.06651000	2.34105900	-1.04092500	0.01380800
C	-3.72863300	-1.19910000	-0.39656800	3.65645100	-1.50598000	-0.31586200
H	-4.44870700	-1.27741700	0.41175100	4.24206400	-1.90312900	0.50869200
C	-4.04412000	-1.53301800	-1.71256000	4.13858800	-1.45369100	-1.59402900
C	-3.01873900	-1.37021600	-2.65267600	3.23463900	-0.91639900	-2.57468800
H	-3.17041900	-1.59774600	-3.70150300	3.51322900	-0.84203400	-3.61879500
C	-1.77329100	-0.91016600	-2.25118900	1.95965500	-0.47596200	-2.20426300
H	-0.97176800	-0.77626100	-2.97203400	1.29161400	-0.08345400	-2.96772400
C	-5.43698800	-2.04223700	-2.07108600	5.54119500	-1.95260200	-1.94121700
C	-6.47547700	-0.97364200	-1.69235200	5.64222100	-3.45245700	-1.61991800
H	-6.44763800	-0.73871900	-0.62357400	5.45165400	-3.64922300	-0.55970800
H	-7.48375300	-1.33197600	-1.93055300	6.64563300	-3.82709800	-1.85759000
H	-6.30525500	-0.04390800	-2.24684700	4.91585200	-4.02909100	-2.20389500
C	-5.57266000	-2.34766600	-3.56459400	5.86990300	-1.75210000	-3.42365300
H	-5.40787900	-1.45610600	-4.18078900	5.18688700	-2.31205600	-4.07321300
H	-6.58549900	-2.70851800	-3.77330700	6.88482100	-2.11176200	-3.62650500
H	-4.87247400	-3.12675700	-3.88781100	5.83015400	-0.69467700	-3.71047300
C	-5.71549600	-3.33085400	-1.27951200	6.57981000	-1.18425500	-1.10849900
H	-4.98879900	-4.11181200	-1.52979600	6.53441200	-0.10972600	-1.31885300
H	-6.71662500	-3.70712900	-1.52005800	7.59205400	-1.53625400	-1.34315700
H	-5.67136400	-3.16284900	-0.19865600	6.41860500	-1.32239700	-0.03432000
C	-0.01766600	2.10190300	-0.44627300	-1.38105300	-1.60928300	-0.46985300
C	-0.81713400	4.11092400	-1.12302800	-2.09015200	-3.63324200	-1.19037300
C	-1.40730600	5.17183600	-1.80287700	-2.33009600	-4.81064500	-1.89213300
H	-1.86215000	5.04280800	-2.78002200	-1.87027300	-5.00591300	-2.85576400
C	-1.39855200	6.41080400	-1.17156500	-3.18141500	-5.73703400	-1.30058700
H	-1.85142000	7.26361100	-1.66839700	-3.39210600	-6.66948300	-1.81565500
C	-0.82201600	6.57923400	0.09501900	-3.76819300	-5.49404600	-0.05077000
H	-0.83749000	7.56040000	0.56008900	-4.42474600	-6.24238600	0.38291600
C	-0.23409600	5.51731500	0.77327100	-3.52523700	-4.31804900	0.64990300

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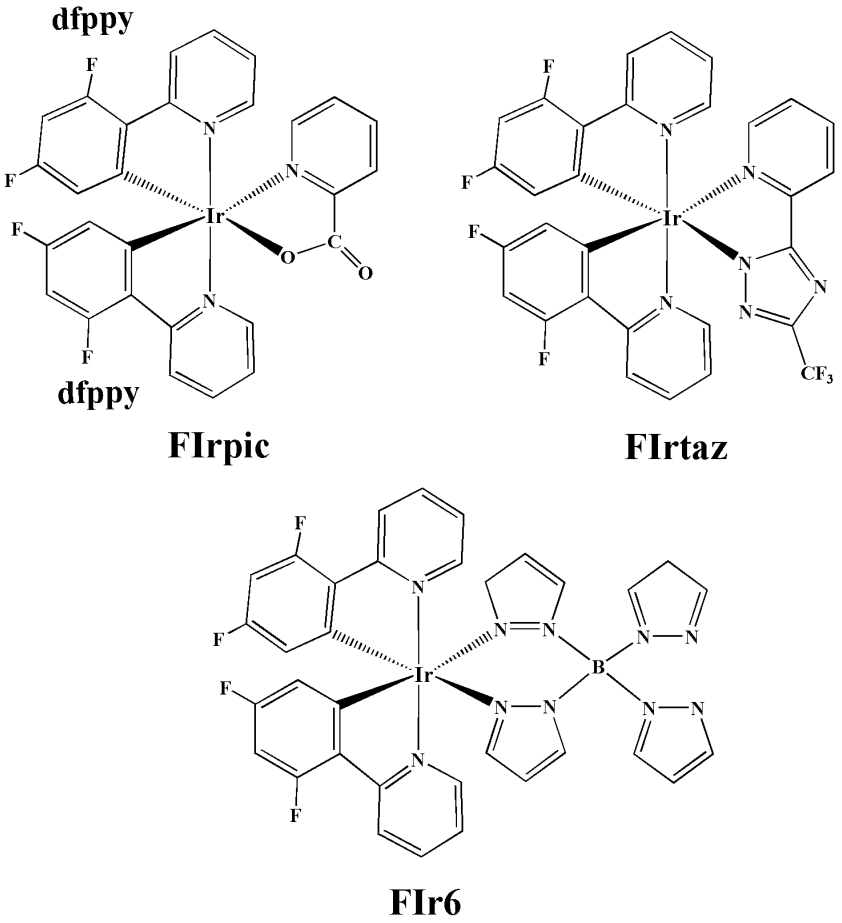
H	0.20238300	5.65600500	1.75693400	-3.97792800	-4.14301500	1.62033500
C	-0.24035900	4.27710800	0.14075100	-2.67540000	-3.38839500	0.05650100
C	0.96128600	2.74501800	1.74213000	-2.60999100	-1.46852400	1.68646900
H	0.29363200	2.19970000	2.41725200	-1.77887100	-1.53719000	2.39674000
H	1.19872700	3.70759400	2.20153200	-3.45468800	-2.02684400	2.09732600
C	2.22387000	1.96919800	1.48905600	-3.00691200	-0.03563900	1.46086700
C	2.20375300	0.80819400	0.68773100	-2.19708800	0.83031400	0.69515900
C	3.43491400	0.15595800	0.50667000	-2.66523400	2.14720400	0.54496300
H	3.51710900	-0.71863000	-0.13141100	-2.12715900	2.86627900	-0.06506000
C	4.58967800	0.61252000	1.12163600	-3.83420700	2.57233100	1.15382000
C	4.60568800	1.73918300	1.92678400	-4.61750400	1.72846000	1.92421700
H	5.52853900	2.07361300	2.38870700	-5.53165000	2.09055800	2.38257800
C	3.40341500	2.41640400	2.08921300	-4.18886600	0.41394400	2.05614600
H	3.38257900	3.31577900	2.70232700	-4.79033300	-0.28043200	2.64022600
C	-1.07127600	2.22379600	-2.71580600	-0.59440700	-2.37154800	-2.72100500
H	-0.45627800	1.35413100	-2.93672600	-0.48526300	-1.31042700	-2.93124100
H	-0.90695500	2.96849700	-3.49965800	-1.17798300	-2.82619900	-3.52620000
H	-2.13036400	1.94719400	-2.69579000	0.38863500	-2.84929500	-2.66719200
C	1.10862800	-1.77908600	0.22539100	0.36663600	2.04706100	0.20123500
C	1.88670200	-3.66232200	1.20229200	1.10232500	3.95438400	1.16146600
C	2.34333600	-4.63501200	2.08570200	1.45462100	4.97746000	2.03580600
H	2.42808400	-4.44083300	3.15007200	1.28650000	4.89530300	3.10482300
C	2.68550400	-5.86971400	1.54455800	2.03764000	6.11090900	1.47962600
H	3.04571000	-6.65624900	2.20087200	2.32829800	6.93157200	2.12857300
C	2.57360700	-6.11963100	0.16997800	2.26067000	6.21419800	0.09967500
H	2.84813300	-7.09643200	-0.21710400	2.72148800	7.11315200	-0.29874500
C	2.11770900	-5.14491500	-0.71181400	1.90778300	5.18973700	-0.77259200
H	2.03235900	-5.35046200	-1.77420900	2.09046900	5.27767600	-1.83884300
C	1.77945400	-3.90846800	-0.17014000	1.32035600	4.05770200	-0.21577700
C	1.06715800	-2.51686000	-2.13961500	0.85244600	2.56126000	-2.17812800
H	-0.01173600	-2.60576400	-2.31565600	1.71953400	1.92114400	-2.38052000
H	1.53869400	-3.34856800	-2.66958600	1.02948600	3.50262800	-2.70491100
C	1.63685900	-1.21617400	-2.65329100	-0.44255500	1.96101000	-2.66953900
C	1.50793600	-0.00346300	-1.93254100	-1.14692500	0.97600400	-1.93530400
C	2.14422400	1.11625900	-2.50155000	-2.37428200	0.55969300	-2.48535300
H	2.14026600	2.07235100	-1.98693900	-3.00329300	-0.15001800	-1.95674400
C	2.80517700	1.04149100	-3.71582100	-2.82856900	1.04209200	-3.70040500
C	2.89972800	-0.13876900	-4.43648000	-2.11928500	1.97891700	-4.43629700
H	3.43225900	-0.16758300	-5.38109100	-2.50615900	2.34498700	-5.38137600
C	2.31727500	-1.26721200	-3.87568700	-0.92902100	2.44072000	-3.89147200
H	2.40341300	-2.21748900	-4.40063800	-0.36715900	3.20300900	-4.42906200
C	1.53314800	-1.73023700	2.70669800	0.07010700	2.29740000	2.68750600
H	2.55633900	-1.79743800	3.08941400	-0.50501100	3.10926000	3.14282000
H	0.84821500	-2.23532800	3.39498200	0.92859000	2.05614300	3.32221500

H	1.24580100	-0.68619900	2.62802400	-0.56438300	1.42056500	2.59584500
F	-3.64777100	0.67480900	4.87676500	2.43767700	-2.59139000	4.99808600
F	-2.31992200	-0.95554000	5.36636900	1.73375500	-0.59609000	5.45022500
F	-1.57271300	1.07312400	5.36206000	0.31633300	-2.21275300	5.21971200
F	5.73733200	-0.06198000	0.92356700	-4.22427600	3.84889900	0.98614100
F	3.37670800	2.15186700	-4.21333800	-3.99861000	0.59024000	-4.18271400



Scheme S1. Schematic structures of FIrpic, Fir6 and FIrtaz.

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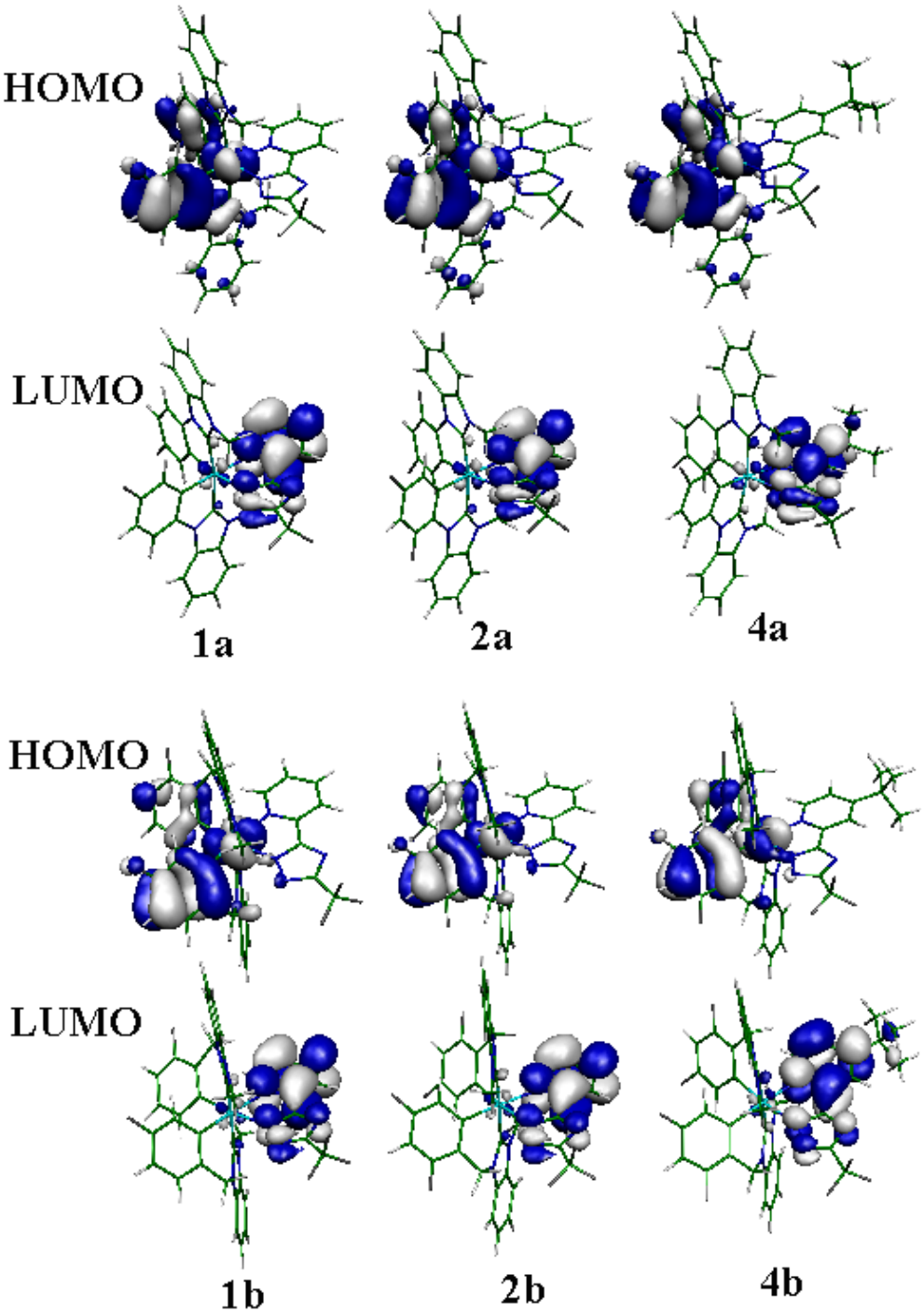

Figure S1. Calculated HOMO and LUMO surfaces for the studied complexes obtained from DFT calculations at their S_0 optimized geometries.