Electronic Supplementary Material (ESI) for Dalton Transactions.

Room Temperature Blue Phosphorescence; A Combined Experimental and Theoretical Study on the Bis-tridentate Ir(III) Metal Complexes

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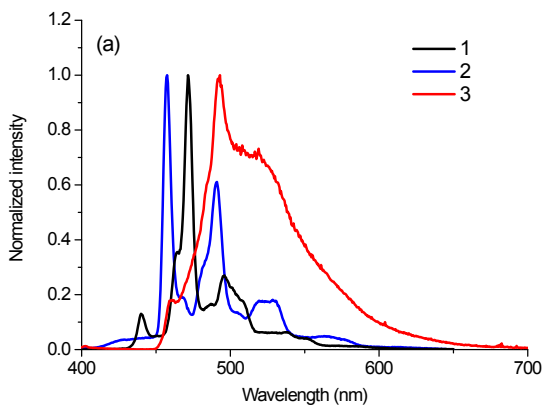
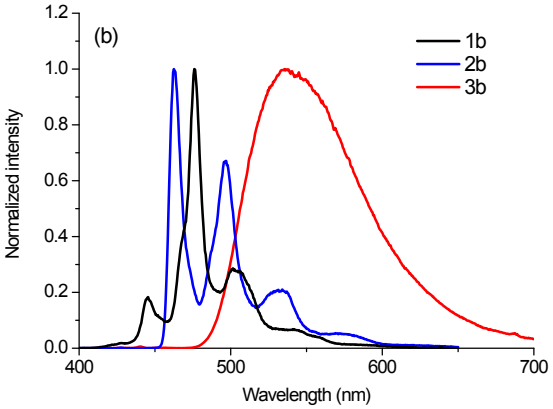
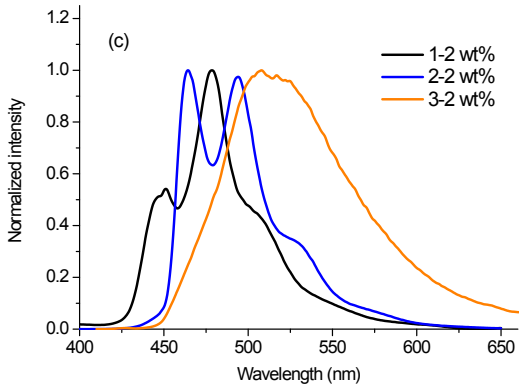






2wt.% in PMMA	em λ_{max} (nm)	em Φ (%)
1	453, 478, 509 (sh)	4.7
2	465, 494, 530 (sh)	91
3	516	75

Figure S1. Emission spectra of Ir(III) metal complexes (a) **1**–**3** (b) **1b**–**3b** in Me-THF matrix at 77 K (c) 2 wt.% of **1**–**3** in PMMA at RT and emission QY.

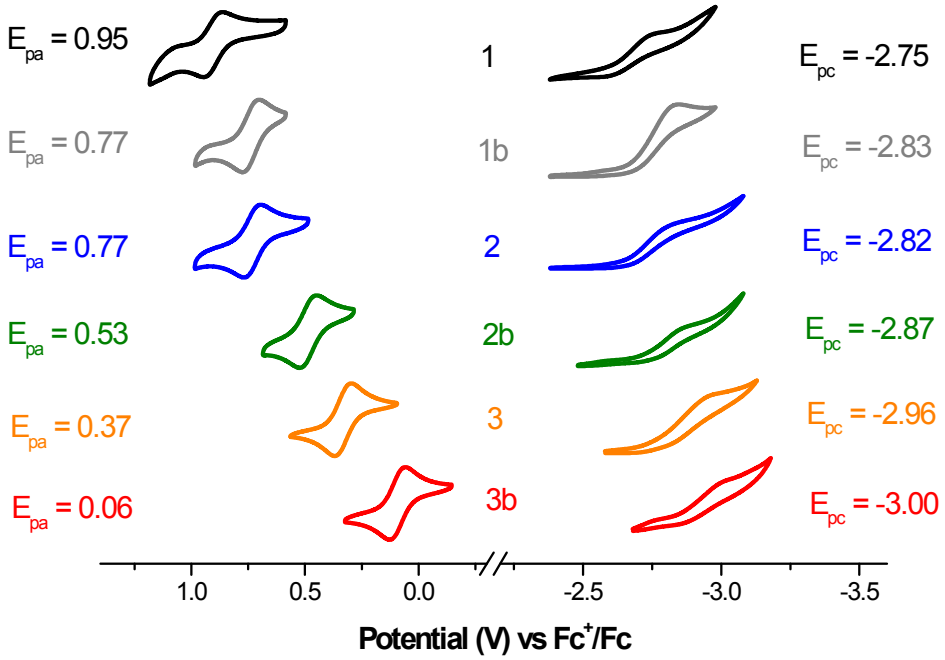


Figure S2. Cyclic voltammograms of Ir(III) metal complexes **1**/**1b**–**3**/**3b**.

Table S1. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **1** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	424.4	0	HOMO→LUMO+1(38%) HOMO-2→LUMO+1(35%) HOMO-3→LUMO(13%) HOMO-5→LUMO(6%)	18.20%
T_2	408.5	0	HOMO→LUMO(81%) HOMO-2→LUMO(14%)	22.31%
S_1	377.4	0.0099	HOMO→LUMO (98%)	26.91%
T_3	371.8	0	HOMO-1→LUMO+3(51%) HOMO-4→LUMO+2(16%) HOMO→LUMO+2(12%) HOMO-2→LUMO+2(6%)	14.64%
T_4	368.3	0	HOMO-3→LUMO(61%) HOMO→LUMO+1(32%)	34.87%
T_5	361.4	0	HOMO-2→LUMO(62%) HOMO-3→LUMO+1(12%) HOMO→LUMO(12%) HOMO-4→LUMO(8%)	8.87%
S_2	338.2	0.0001	HOMO→LUMO(81%) HOMO-2→LUMO(14%)	22.31%
S_3	331.9	0.0234	HOMO-1→LUMO+3(51%) HOMO-4→LUMO+2(16%) HOMO→LUMO+2(12%) HOMO-2→LUMO+2(6%)	14.64%
S_4	316.8	0.0817	HOMO-3→LUMO(61%) HOMO→LUMO+1(32%)	34.87%
S_5	309.6	0.1787	HOMO-2→LUMO(62%) HOMO-3→LUMO+1(12%) HOMO→LUMO(12%) HOMO-4→LUMO(8%)	8.87%

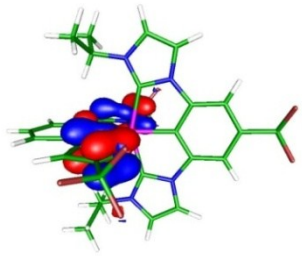
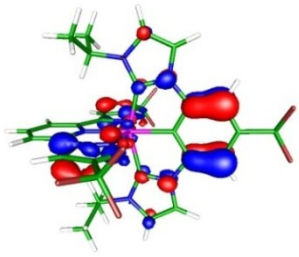
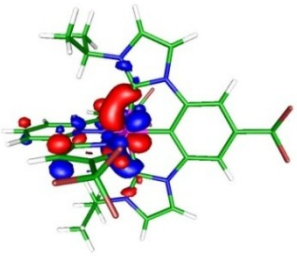
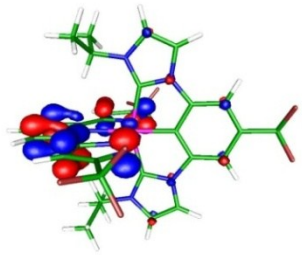
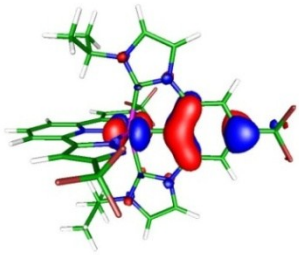
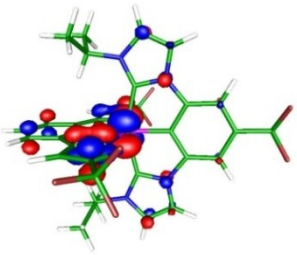
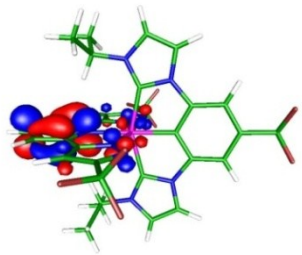
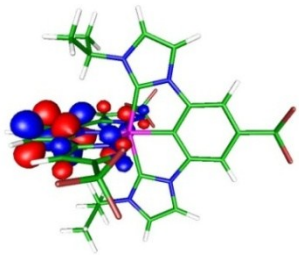
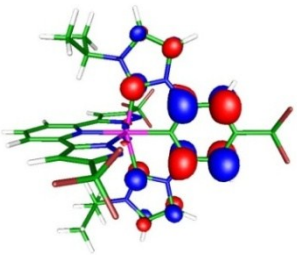
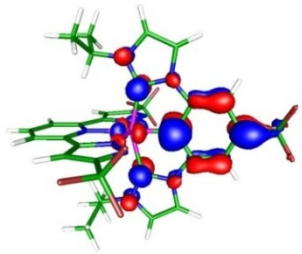
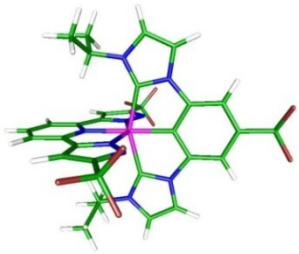
 HOMO-5 (-6.66 eV)	 HOMO-4 (-6.54 eV)	 HOMO-3 (-6.18 eV)
 HOMO-2 (-6.13 eV)	 HOMO-1 (-5.92 eV)	 HOMO (-5.63 eV)
 LUMO (-2.34 eV)	 LUMO+1 (-1.28 eV)	 LUMO+2 (-0.81 eV)
 LUMO+3 (-0.72 eV)	 optimized structure	

Figure S3. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **1**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S2. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **1b** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	426.1	0	HOMO-2→LUMO+1(36%) HOMO→LUMO+1(25%) HOMO-3→LUMO(15%) HOMO-1→LUMO+1(7%) HOMO-6→LUMO(6%)	15.59%
T_2	410.4	0	HOMO→LUMO(64%) HOMO-1→LUMO(17%) HOMO-2→LUMO(16%)	19.89%
S_1	382.4	0.0067	HOMO→LUMO(81%) HOMO-1→LUMO(16%)	24.58%
T_3	374.4	0	HOMO-3→LUMO(60%) HOMO→LUMO+1(26%) HOMO-1→LUMO+1(6%)	35.04%
T_4	373.2	0	HOMO-1→LUMO+3(30%) HOMO→LUMO+2(20%) HOMO-4→LUMO+2(14%) HOMO-2→LUMO+2(10%) HOMO→LUMO+3(8%) HOMO-1→LUMO+6(7%)	10.20%
T_5	370.1	0	HOMO-1→LUMO(74%) HOMO→LUMO(23%)	22.17%
S_2	366.9	0.0001	HOMO-1→LUMO(82%) HOMO→LUMO(16%)	22.10%
S_3	338.5	0.0166	HOMO→LUMO+1(82%) HOMO-3→LUMO(13%)	29.88%
S_4	334.8	0.0009	HOMO-1→LUMO+1(92%) HOMO→LUMO+1(6%)	25.21%
S_5	320.1	0.0565	HOMO-2→LUMO(70%) HOMO-3→LUMO+1(25%)	9.55%

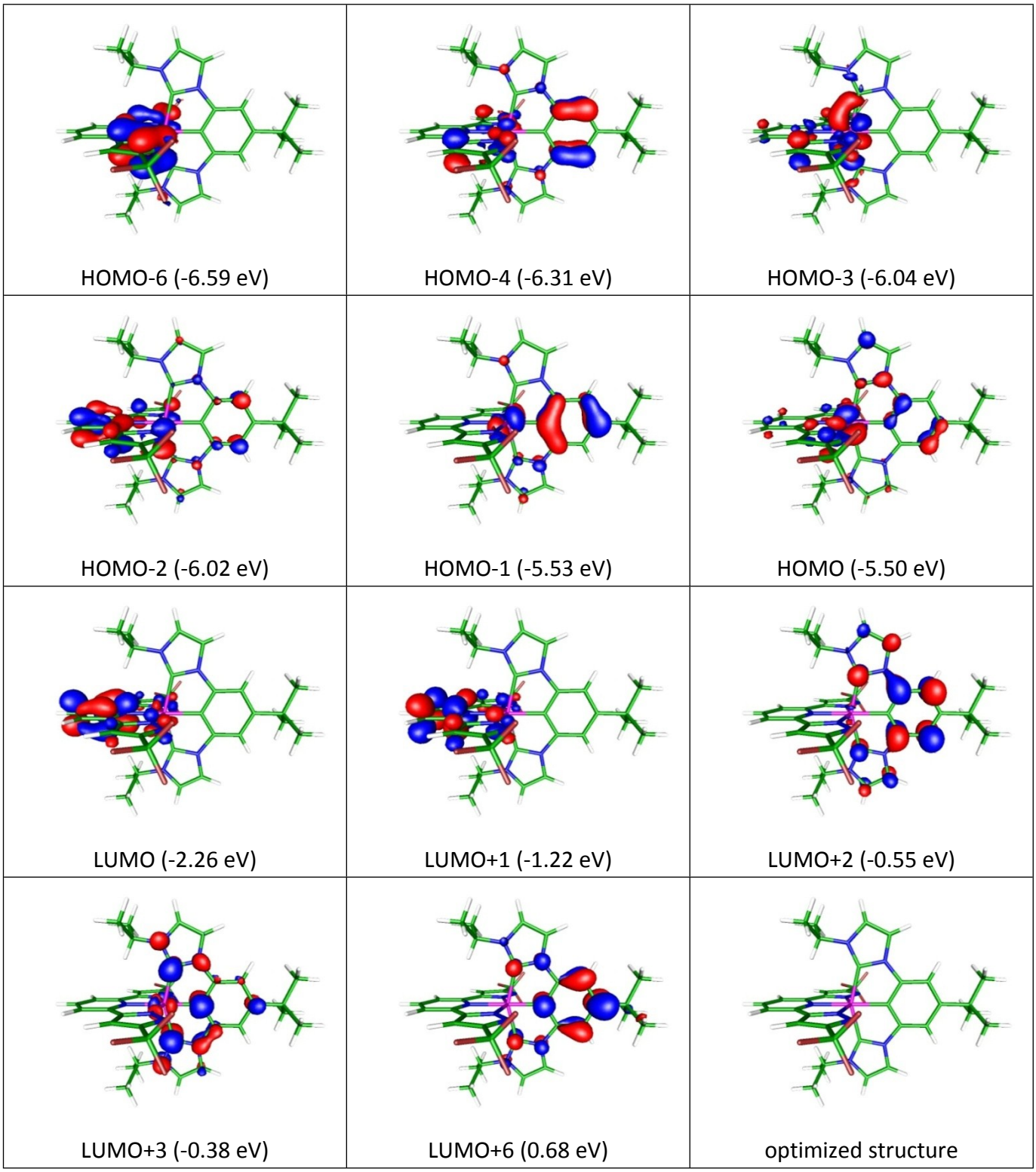


Figure S4. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **1b**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S3. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **2** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	435	0	HOMO→LUMO(28%) HOMO→LUMO+1(22%) HOMO-3→LUMO(13%) HOMO-2→LUMO+1(13%) HOMO-6→LUMO(8%) HOMO-3→LUMO+1(7%)	22.44%
T_2	411	0	HOMO→LUMO(51%) HOMO→LUMO+1(19%) HOMO-2→LUMO(11%) HOMO-2→LUMO+1(10%)	26.09%
S_1	381.3	0.0175	HOMO→LUMO(95%)	27.19%
T_3	376.4	0	HOMO-1→LUMO+3(60%) HOMO-4→LUMO+2(10%) HOMO→LUMO+2(8%)	18.13%
T_4	370.1	0	HOMO-2→LUMO(43%) HOMO→LUMO+1(28%) HOMO-3→LUMO(16%)	23.02%
T_5	363.6	0	HOMO-1→LUMO(96%)	33.67%
S_2	358.9	0.0001	HOMO-1→LUMO(97%)	34.02%
S_3	337	0.0189	HOMO→LUMO+1(75%) HOMO-2→LUMO(19%)	28.02%
S_4	326.2	0.0001	HOMO-1→LUMO+1(97%)	36.16%
S_5	321.4	0.142	HOMO-2→LUMO(68%) HOMO→LUMO+1(16%) HOMO-3→LUMO+1(11%)	24.97%

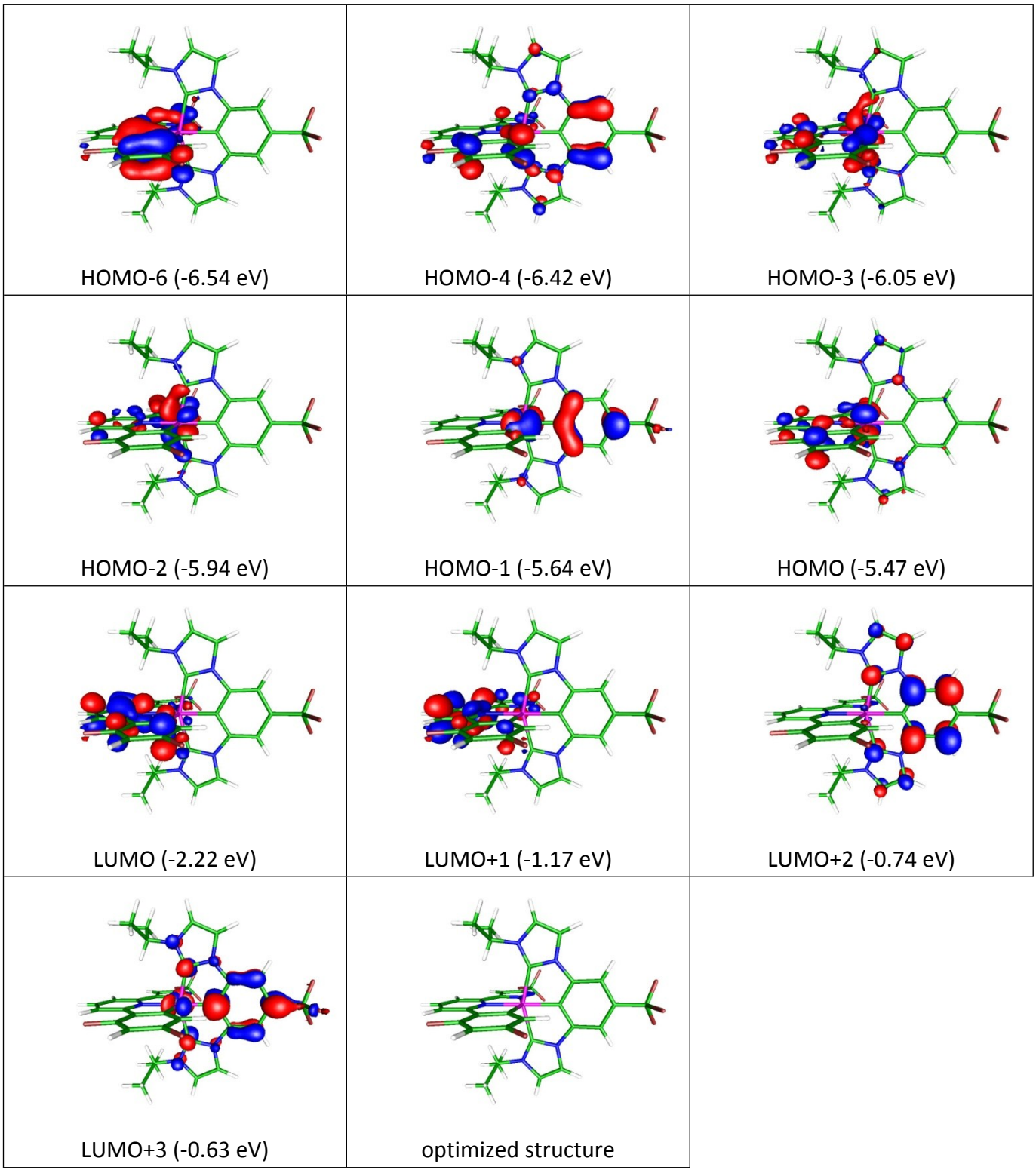


Figure S5. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **2**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S4. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **2b** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	437.2	0	HOMO-1→LUMO(28%) HOMO-1→LUMO+1(18%) HOMO-3→LUMO(14%) HOMO-2→LUMO+1(10%) HOMO-3→LUMO+1(10%) HOMO-6→LUMO(8%)	20.30%
T_2	413.1	0	HOMO-1→LUMO(47%) HOMO-1→LUMO+1(18%) HOMO-2→LUMO(12%) HOMO-2→LUMO+1(8%) HOMO-3→LUMO+1(6%)	27.63%
T_3	390.6	0	HOMO→LUMO(92%)	26.34%
S_1	387.5	0.0097	HOMO-1→LUMO(55%) HOMO→LUMO(41%)	28.17%
S_2	385.2	0.0036	HOMO→LUMO(57%) HOMO-1→LUMO(40%)	28.27%
T_4	377.5	0	HOMO-2→LUMO(31%) HOMO→LUMO+3(18%) HOMO-1→LUMO+1(18%) HOMO-3→LUMO(6%)	19.98%
T_5	376.6	0	HOMO→LUMO+3(26%) HOMO-2→LUMO(20%) HOMO-1→LUMO+1(10%) HOMO-4→LUMO+2(7%) HOMO-1→LUMO+2(7%) HOMO→LUMO+2(5%)	18.37%
S_3	349.9	0.0004	HOMO→LUMO+1(97%)	29.95%
S_4	343.5	0.0124	HOMO-1→LUMO+1(76%) HOMO-2→LUMO(20%)	31.26%
S_5	326.4	0.1381	HOMO-2→LUMO(67%) HOMO-1→LUMO+1(16%) HOMO-3→LUMO+1(9%)	32.33%

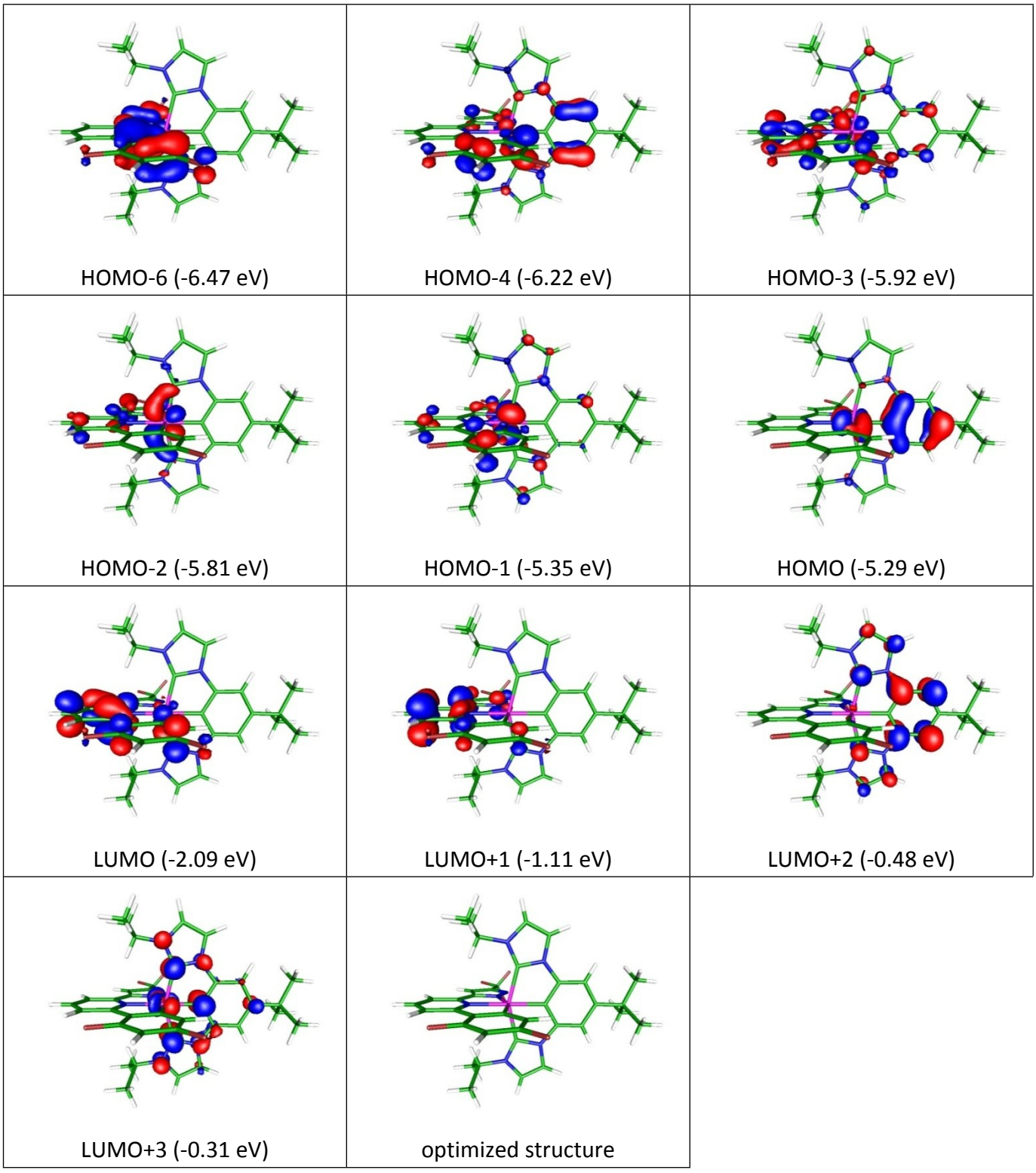


Figure S6. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **2b**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S5. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **3** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	437.3	0	HOMO-1→LUMO+1(44%) HOMO-3→LUMO+1(29%) HOMO-2→LUMO(10%) HOMO-6→LUMO(7%)	20.06%
T_2	421.8	0	HOMO-1→LUMO(81%) HOMO-3→LUMO(12%)	24.29%
T_3	409.8	0	HOMO→LUMO(98%)	31.76%
S_1	400.6	0.0001	HOMO→LUMO(99%)	32.09%
S_2	387.7	0.0122	HOMO-1→LUMO(98%)	29.34%
T_4	374.7	0.	HOMO-2→LUMO(37%) HOMO→LUMO+3(31%) HOMO-1→LUMO+1(12%)	29.90%
T_5	373.4	0	HOMO-2→LUMO(33%) HOMO→LUMO+3(28%) HOMO-1→LUMO+1(11%) HOMO-1→LUMO+2(7%) HOMO-4→LUMO+3(5%)	28.72%
S_3	367.8	0.0001	HOMO→LUMO+1(99%)	35.41%
S_4	345.4	0.0364	HOMO-1→LUMO+1(89%) HOMO-2→LUMO(8%)	33.33%
S_5	322.8	0.0765	HOMO→LUMO+2(97%)	33.42%

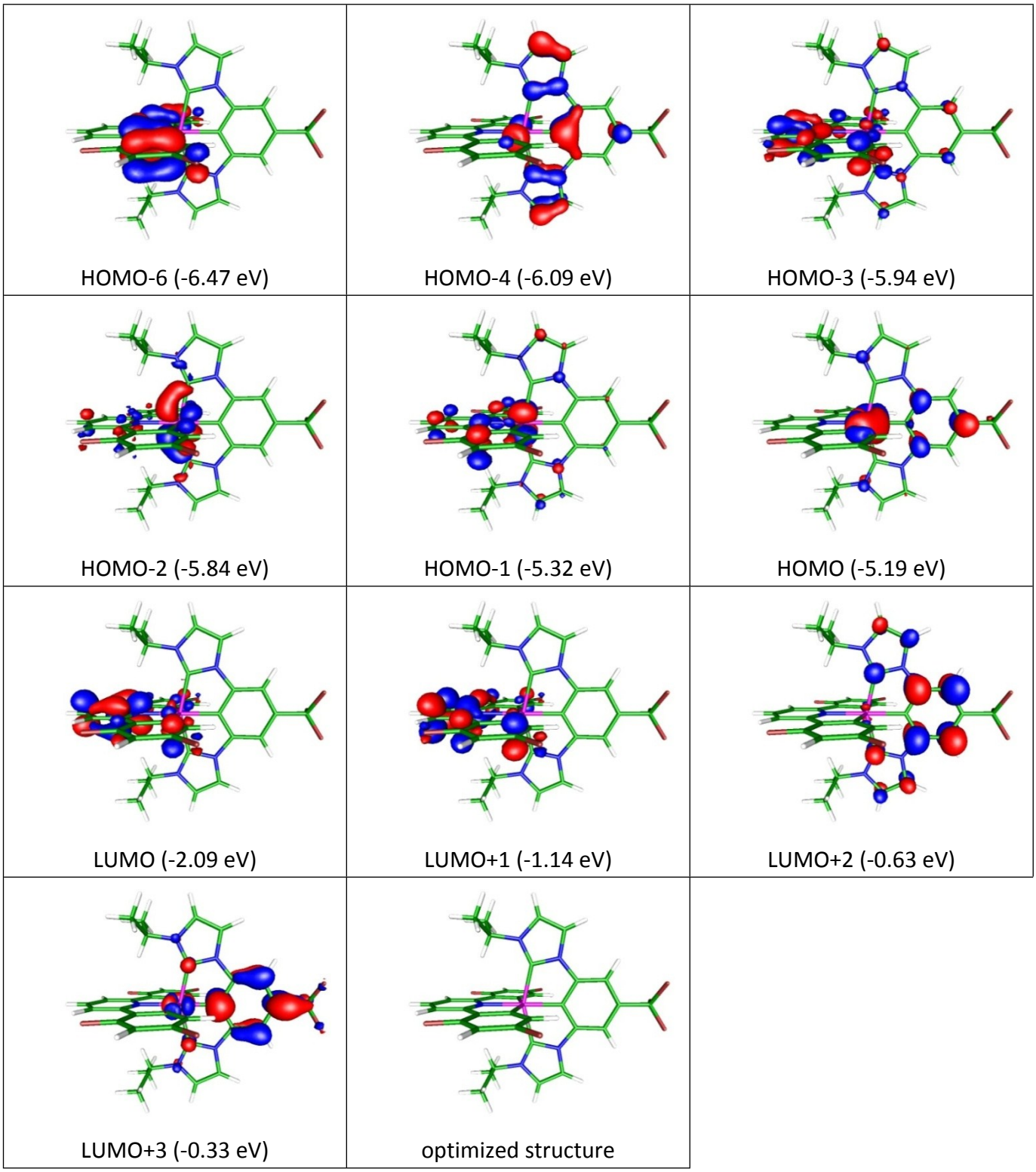


Figure S7. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **3**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S6. The calculated wavelengths, transition probabilities and charge transfer character of the optical transitions for Ir(III) complex **3b** in CH_2Cl_2.

State	λ (nm)	*f*	Assignments	MLCT
T_1	439.6	0	HOMO-1→LUMO+1(41%) HOMO-3→LUMO+1(27%) HOMO-2→LUMO(12%) HOMO-6→LUMO(7%)	19.77%
T_2	435	0	HOMO→LUMO(97%)	29.44%
S_1	425.6	0.0001	HOMO→LUMO(99%)	30.05%
T_3	424.5	0	HOMO-1→LUMO(81%) HOMO-3→LUMO(12%)	24.60%
T_4	394.4	0	HOMO→LUMO+1(98%)	33.21%
S_2	393.8	0.0088	HOMO-1→LUMO(98%)	30.18%
S_3	390.4	0.0001	HOMO→LUMO+1(99%)	33.55%
T_5	382.5	0	HOMO-2→LUMO(71%) HOMO-1→LUMO+1(25%)	42.92%
S_4	352.8	0.0269	HOMO-1→LUMO+1(89%) HOMO-2→LUMO(9%)	34.92%
S_5	325.9	0.1876	HOMO-2→LUMO(85%) HOMO-1→LUMO+1(7%)	43.51%

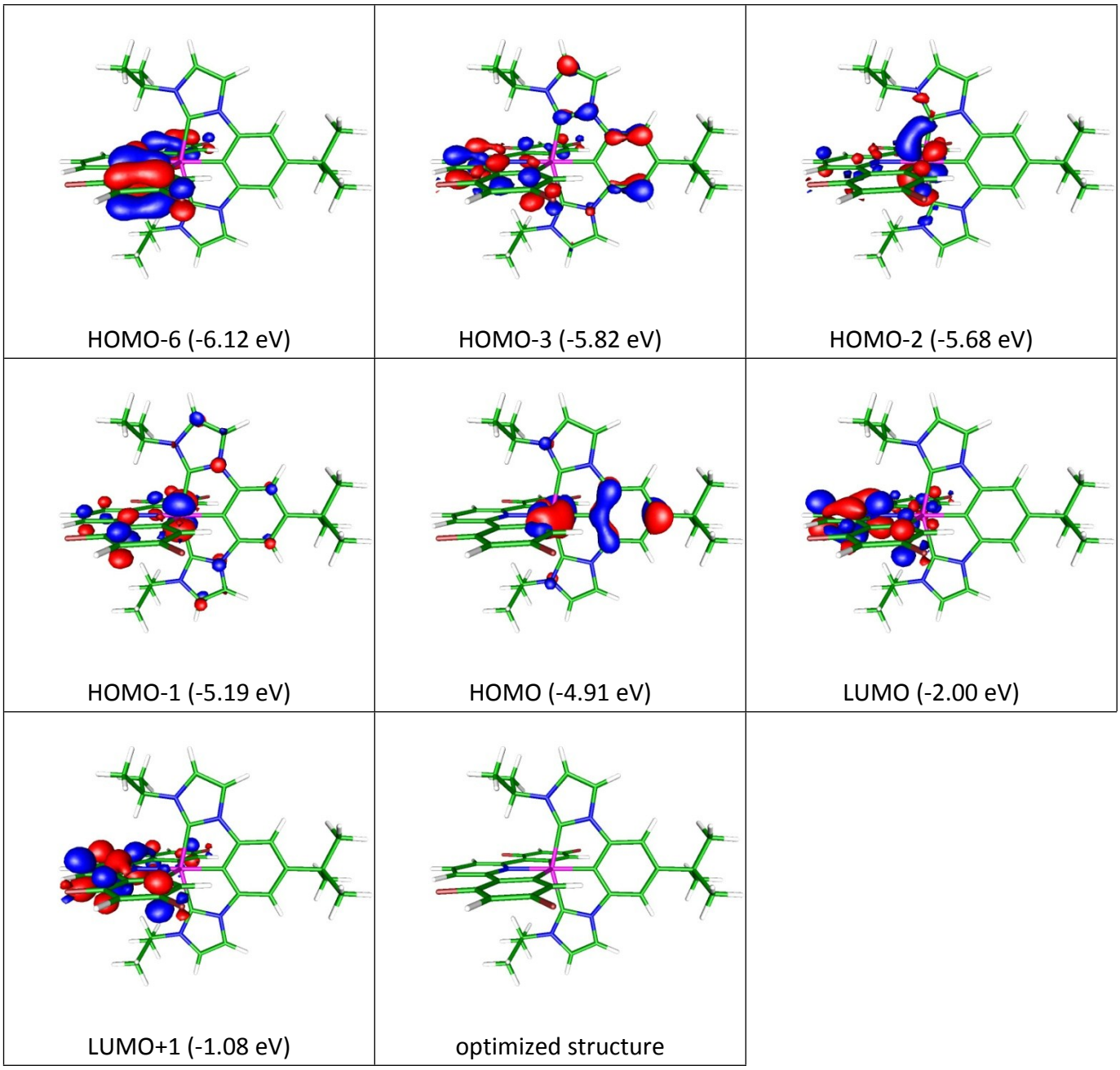


Figure S8. Frontier molecular orbitals pertinent to the optical transitions for Ir(III) complex **3b**. For the clarity of viewing, the optimized structure with no involvement of frontier orbitals is shown at the last figure.

Table S7. Photophysical properties of complexes **2**/**2b**,**3**/**3b** in various solvent systems.[a]

	solvent	abs λ/nm (ε × 10^{-3} M^{-1} cm^{-1})	em λ_{max} (nm)	em Φ (%)	τ_{obs} (μs)
3	CH_2Cl_2	306 (17.4), 339 (19.1), 414 (0.8)	536	70	2.84
	$C_6H_5CH_3$	307 (19.6), 340 (20.4), 440 (0.9)	530	78	3.12
	C_6H_{12}	307 (21.5), 340 (23.0), 443 (0.7)	505	85	2.91
3b	CH_2Cl_2	307 (19.7), 344 (20.5), 406 (1.6)	567	49	2.46
	$C_6H_5CH_3$	307 (17.2), 347 (17.1), 405 (1.3)	555	78	2.97
	C_6H_{12}	307 (17.1), 346 (16.5), 404 (2.0)	542	59	2.77
2	CH_2Cl_2	297 (21.4), 323 (21.6), 406 (1.0)	463, 495, 529 (sh)	95	4.67
	$C_6H_5CH_3$	301 (18.7), 324 (19.6), 418 (1.1)	467, 498, 534 (sh)	100	3.55
2b	CH_2Cl_2	302 (23.8), 325 (23.5), 433 (1.2)	472, 502, 541 (sh)	75	2.58
	$C_6H_5CH_3$	305 (22.9), 327 (22.4), 435 (1.1)	474, 507, 543 (sh)	100	2.48

[a] All samples have an approx. conc. of 10^{-5} M in various solvent systems. Coumarin C153 (Φ ~ 58%) were used as the standard for PL measurements.