

Supplementary Information

Dual emission from an iridium(III) complex/counter anion ion pair

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Peak	ν (F1) [ppm]
1	8.8872
2	8.8834
3	8.8647
4	8.8165
5	8.799
6	8.7934
7	8.7759
8	8.6115
9	8.61
10	8.5912
11	8.5897
12	8.2506
13	8.2471
14	8.2308
15	8.2272
16	8.2109
17	8.2073
18	7.5978
19	7.5957
20	7.5837
21	7.5816
22	7.5158
23	7.5125
24	7.5015
25	7.4967
26	7.493
27	7.4821
28	7.4788

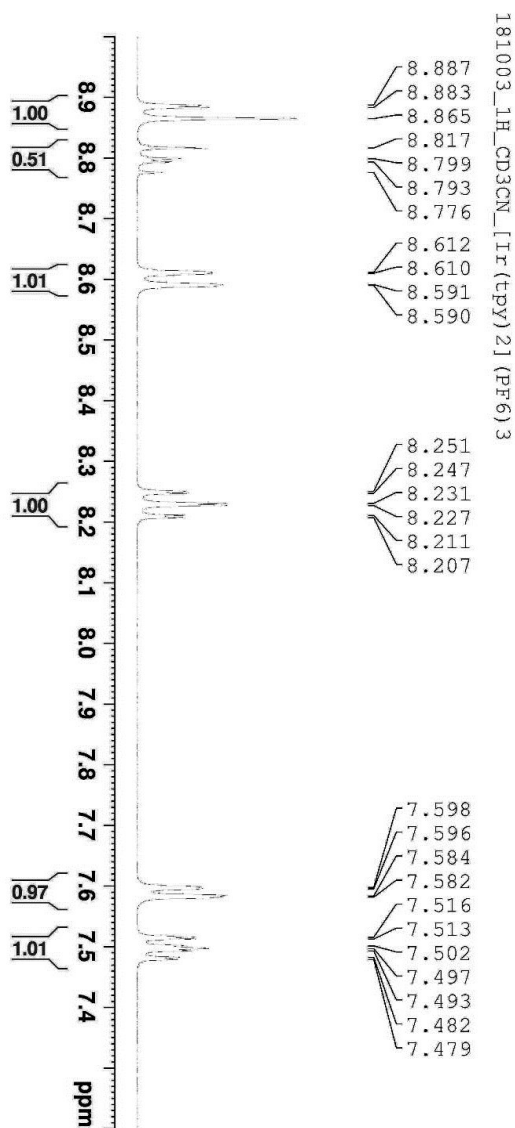


Figure S1. ^1H NMR of
 $[\text{Ir}(\text{tpy})_2](\text{PF}_6)_3$ in CD_3CN

^1H NMR(400 MHz, Acetonitrile- d_3);

δ 8.8784 (*d*, 4H, J = 8.24 Hz), 8.7962 (*t*, 2H, J =8.12 Hz) 8.6006 (*d*, 4H, J =8.12 Hz), 8.2290 (*t*, 4H, J =7.95. Hz), 7.5897 (*d*, 4H, J =5.64 Hz), 7.4972 (*t*, 4H, J =6.74 Hz)

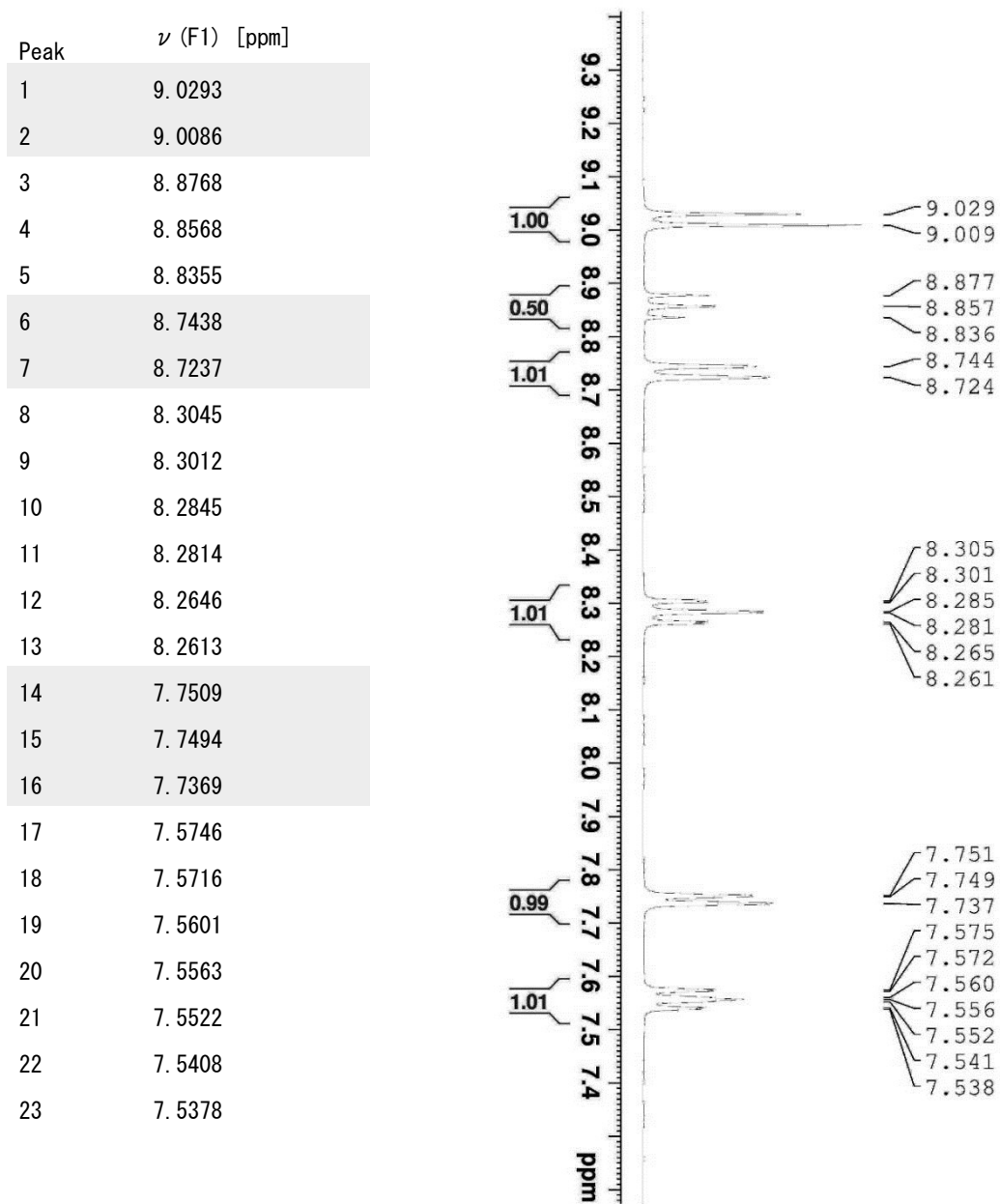


Figure S2. ^1H NMR of $[\text{Ir}(\text{tpy})_2]\text{Cl}_3$ in D_2O

^1H NMR(400 MHz, D_2O); δ 9.0190 (*d*, 4H, $J = 8.28$ Hz), 8.8564 (*t*, 2H, $J = 8.26$ Hz)
 8.7338 (*d*, 4H, $J = 8.04$ Hz), 8.2829 (*t*, 4H, $J = 7.98$ Hz), 7.7457 (*d*, 4H, $J = 5.30$ Hz),
 7.5562 (*t*, 4H, $J = 6.76$ Hz)

Peak	ν (F1) [ppm]
1	9.0107
2	8.9901
3	8.8625
4	8.8428
5	8.8211
6	8.725
7	8.7059
8	8.292
9	8.2884
10	8.272
11	8.2686
12	8.2521
13	8.2485
14	7.726
15	7.7137
16	7.5579
17	7.5546
18	7.5435
19	7.5389
20	7.5353
21	7.5242
22	7.521

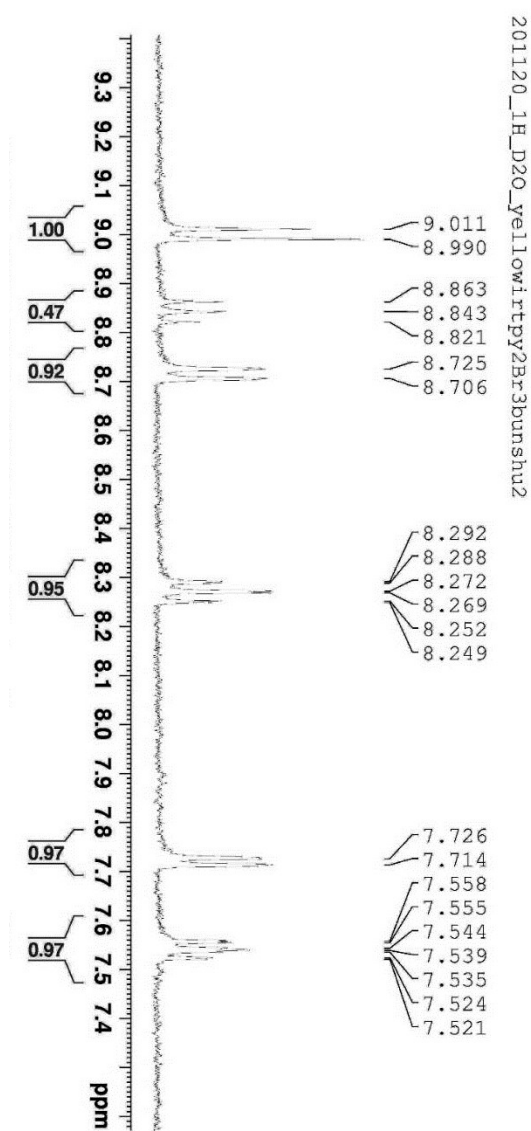


Figure S3. ^1H NMR of $[\text{Ir}(\text{tpy})_2]\text{Br}_3$ in D_2O

^1H NMR(400 MHz, D_2O); δ 9.0004 (*d*, 4H, $J = 8.24$ Hz), 8.8421 (*t*, 2H, $J = 8.28$ Hz), 8.7155 (*d*, 4H, $J = 7.64$ Hz), 8.2703 (*t*, 4H, $J = 7.98$ Hz), 7.7199 (*d*, 4H, $J = 4.92$ Hz), 7.5393 (*t*, 4H, $J = 6.73$ Hz)

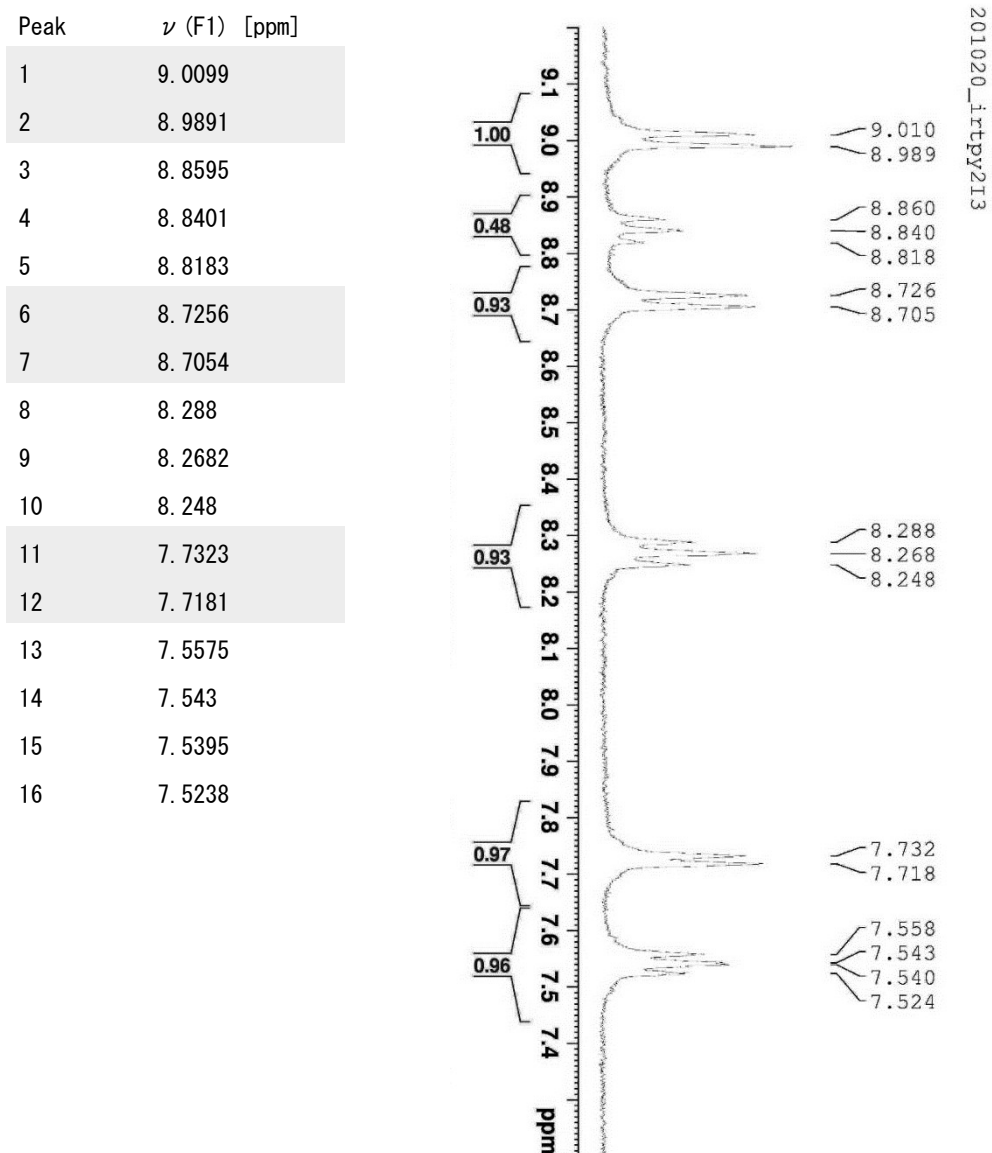


Figure S4. ^1H NMR of $[\text{Ir}(\text{tpy})_2]\text{I}_3$ in D_2O

^1H NMR(400 MHz, D_2O); δ 8.9995 (*d*, 4H, $J = 8.32$ Hz), 8.8393 (*t*, 2H, $J = 8.24$ Hz)
 8.7155 (*d*, 4H, $J = 8.08$ Hz), 8.2681 (*t*, 4H, $J = 8.00$ Hz), 7.7252 (*d*, 4H, $J = 5.68$ Hz),
 7.5410 (*t*, 4H, $J = 6.74$ Hz)

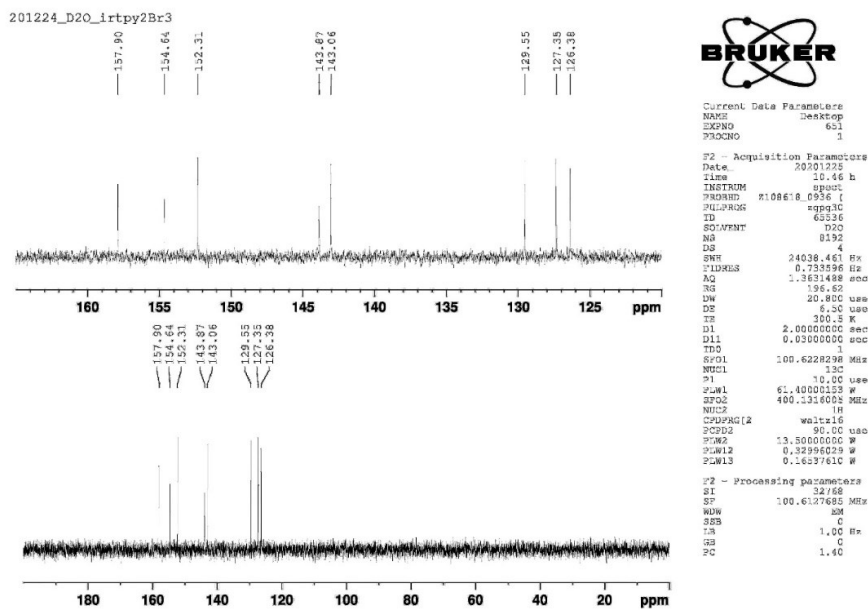


Figure S5. ^{13}C NMR of $[\text{Ir}(\text{tpy})_2]\text{Br}_3$ in D_2O

^{13}C NMR(400 MHz, D_2O); δ 157.9, 154.6, 152.3, 143.9, 143.1, 130.0, 127.4, 126.4

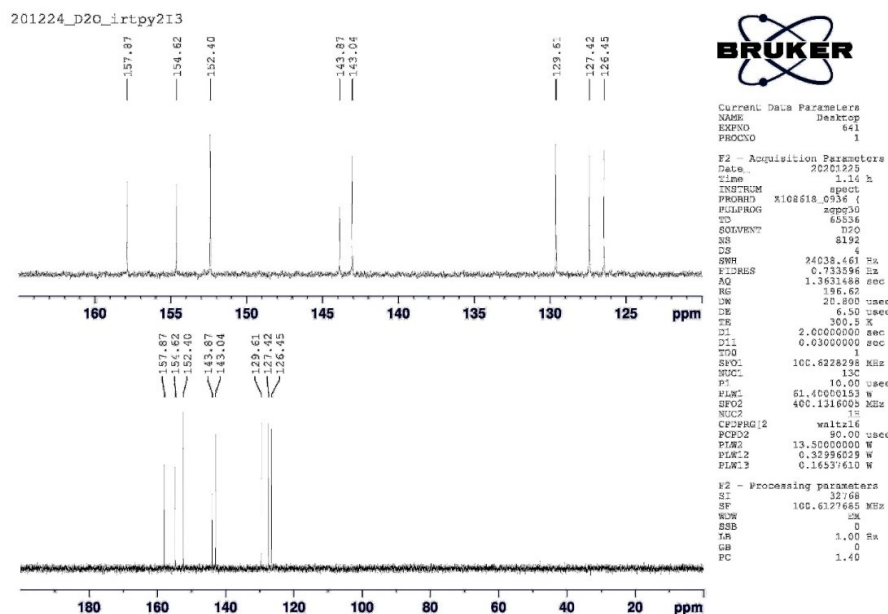


Figure S6. ^{13}C NMR of $[\text{Ir}(\text{tpy})_2]\text{I}_3$ in D_2O

^{13}C NMR(400 MHz, D_2O); δ 157.9, 154.6, 152.4, 143.9, 143.0, 129.6, 127.4, 126.5

The density functionals were evaluated by comparing the calculated and experimental absorption spectra. The TD-DFT calculation was performed at ω B97X/Jorge-DZP-DKH, B3LYP/Jorge-DZP-DKH, and PBE0/Jorge-DZP-DKH levels with zeroth order regular approximation (ZORA) and conductor-like polarizable continuum model (CPCM) to predict absorption spectra at the structure optimized at ω B97X/Jorge-DZP-DKH level, which are exhibited in Fig. S1. At ω B97X/Jorge-DZP-DKH level, the predicted spectrum in 200 - 300 nm is in good agreement with the experimental spectrum, while the spectra predicted at B3LYP/Jorge-DZP-DKH and PBE0/Jorge-DZP-DKH levels are inconsistent with the experimental result and show long tails in the lowest absorption bands. So we adopted the ω B97X/Jorge-DZP-DKH to the functional for DFT and TD-DFT calculations for $[\text{Ir}(\text{tpy})_2]^{3+}$ complex.

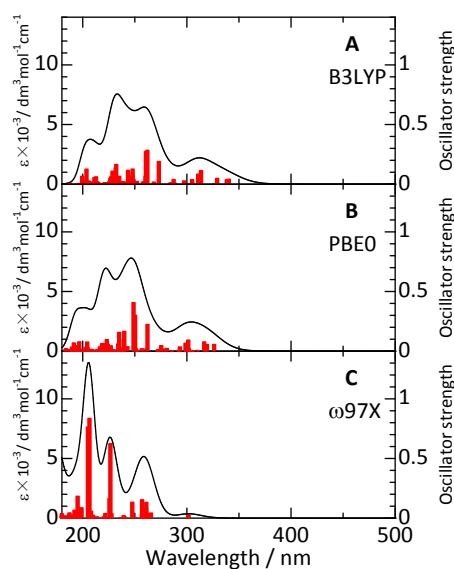


Figure S7. The absorption spectra predicted by TD-DFT calculation at the three density functionals of (a) B3LYP, (b) PBE0, and (c) ω B97X. Each spectrum is constructed with superposition of Gaussian functions⁶⁹ produced from oscillator strength at excitation energy.

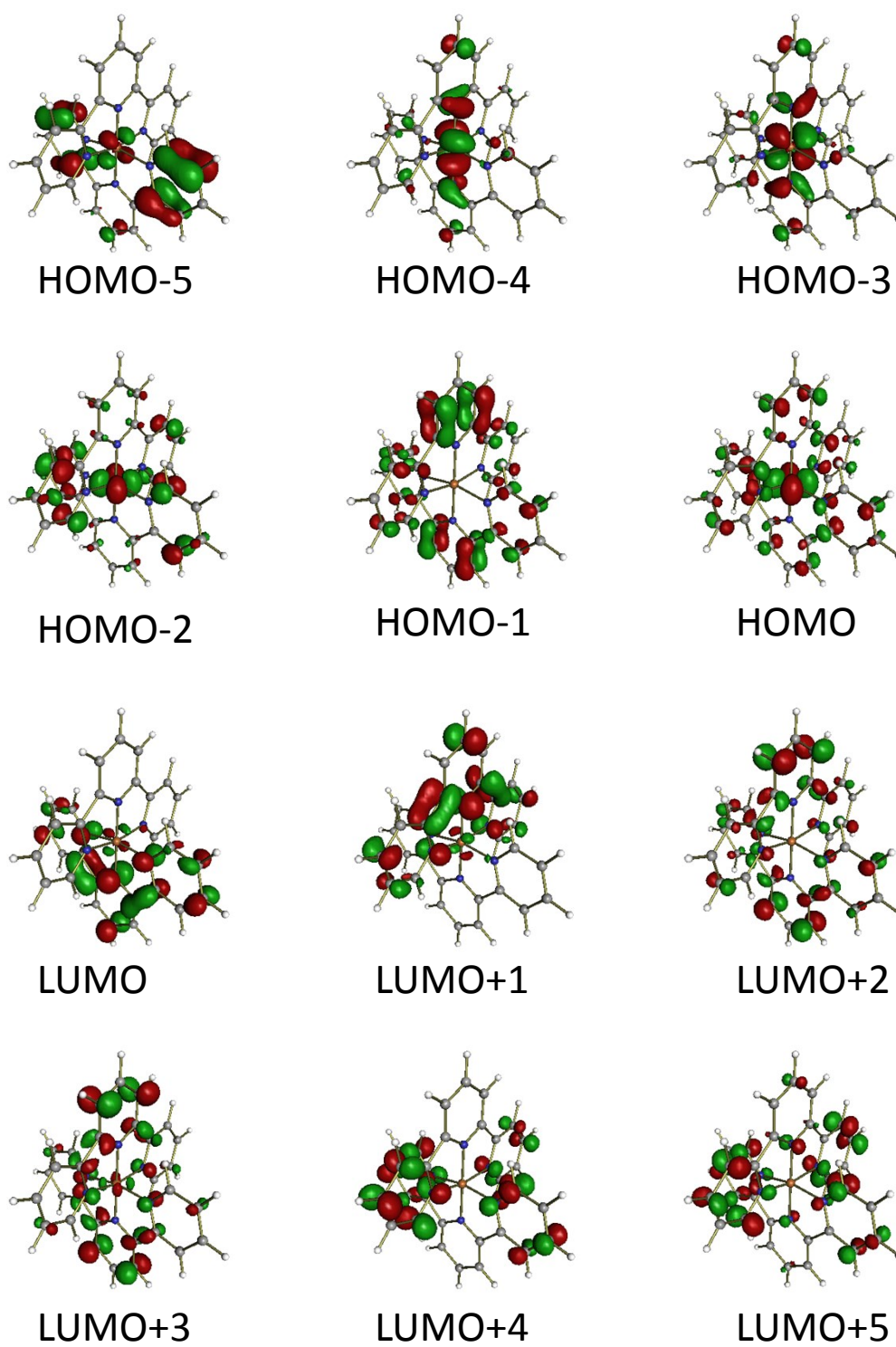


Figure S8. Molecular orbitals of $[\text{Ir}(\text{tpy})_2]^{3+}$.

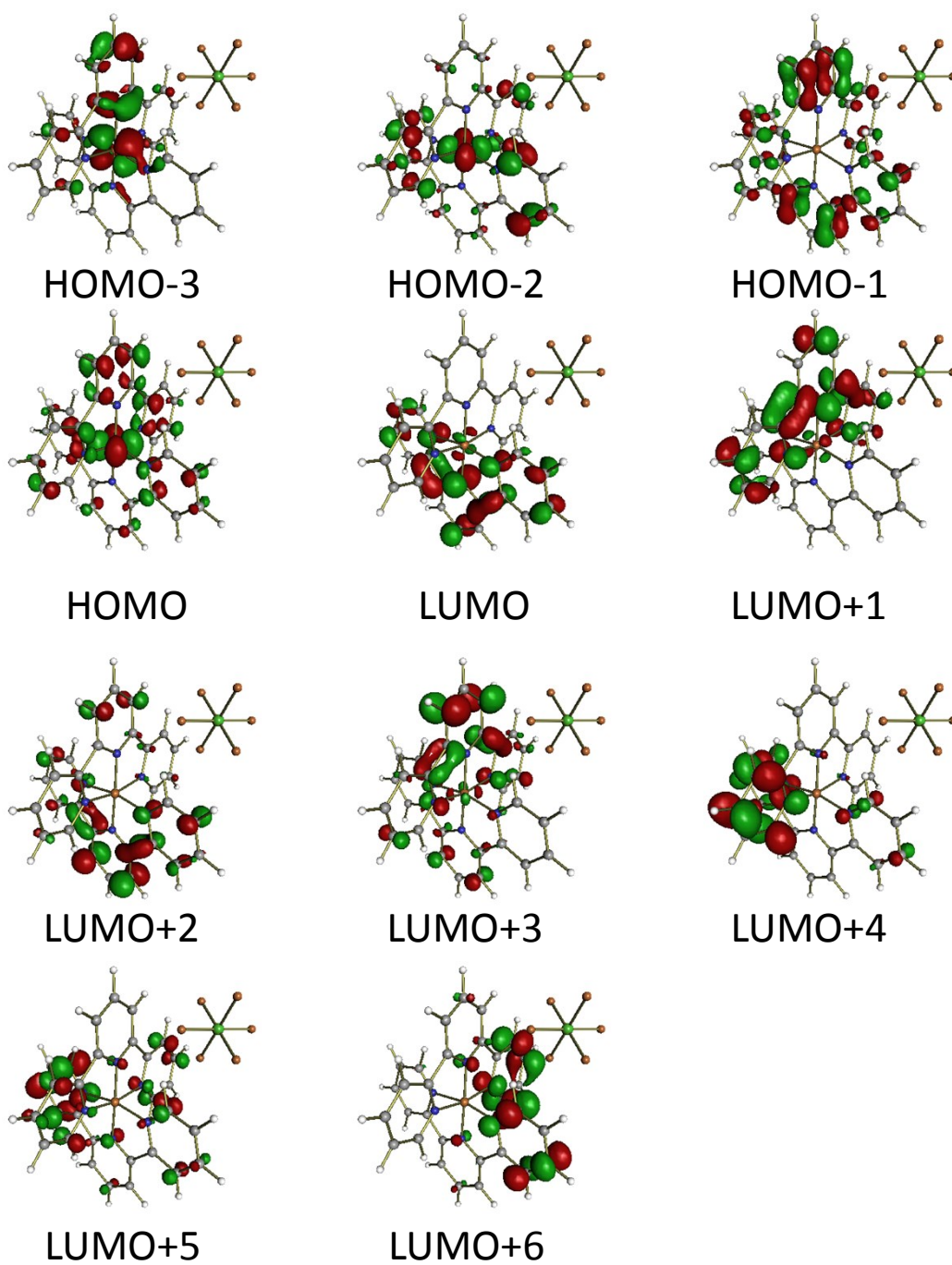


Figure S9. Molecular orbitals of $[\text{Ir}(\text{tpy})_2]^{3+}\text{PF}_6^-$.

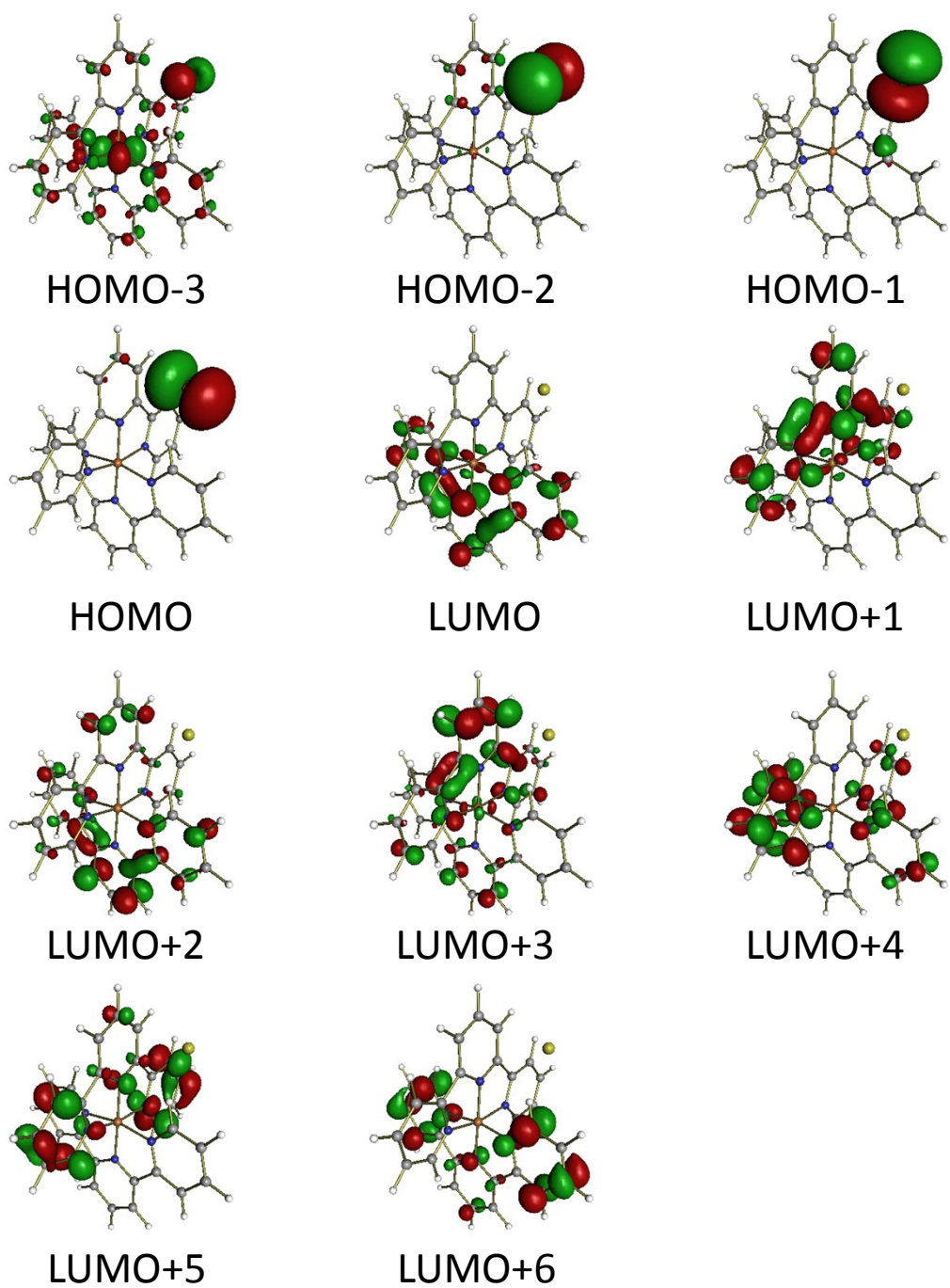


Figure S10. Molecular orbitals of $[\text{Ir}(\text{tpy})_2]^{3+}\text{Cl}^-$.

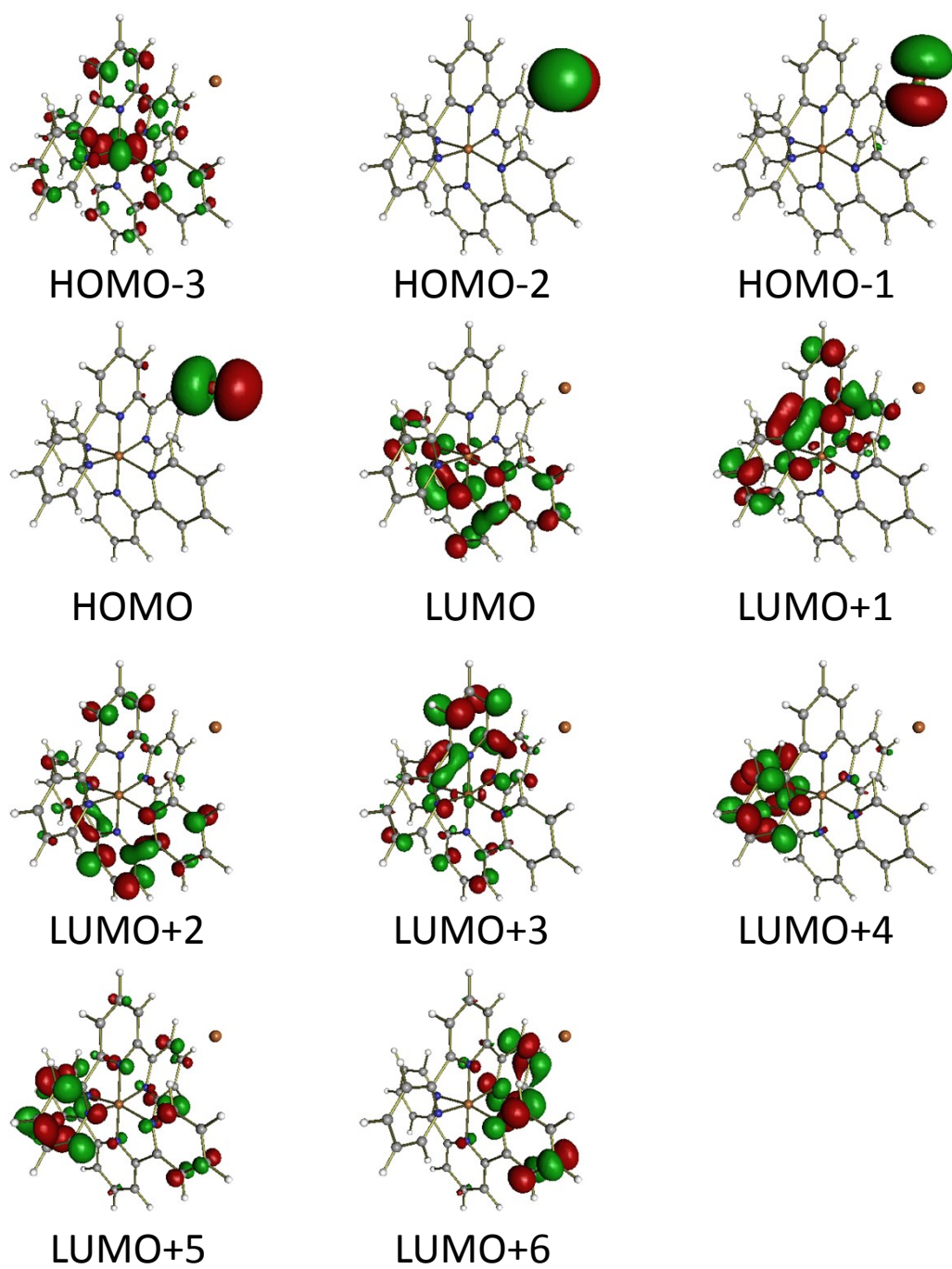


Figure S11. Molecular orbitals of $[\text{Ir}(\text{tpy})_2]^{3+}\text{Br}^-$.

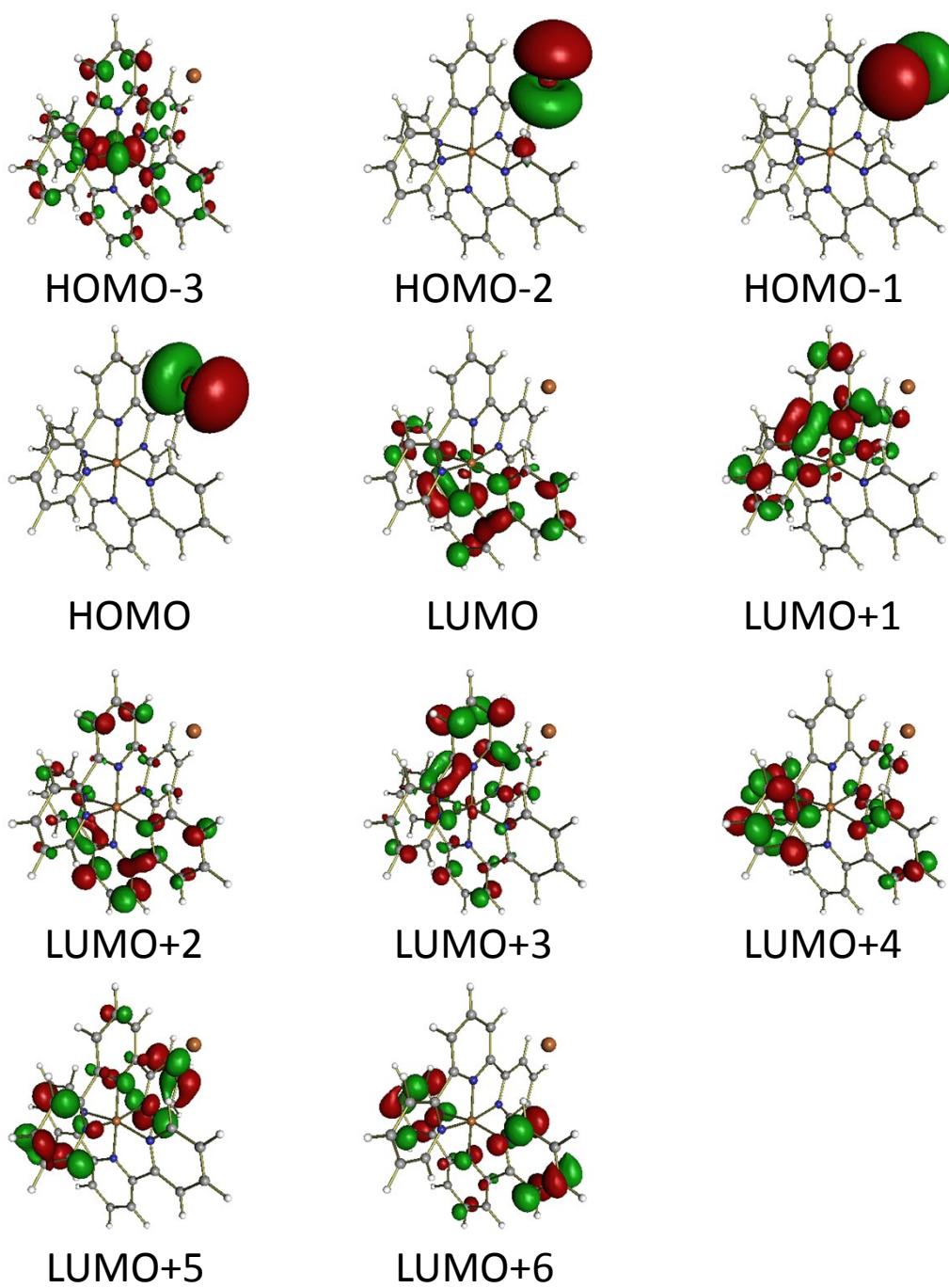


Figure S12. Molecular orbitals of $[\text{Ir}(\text{tpy})_2]^{3+}\text{I}^-$.

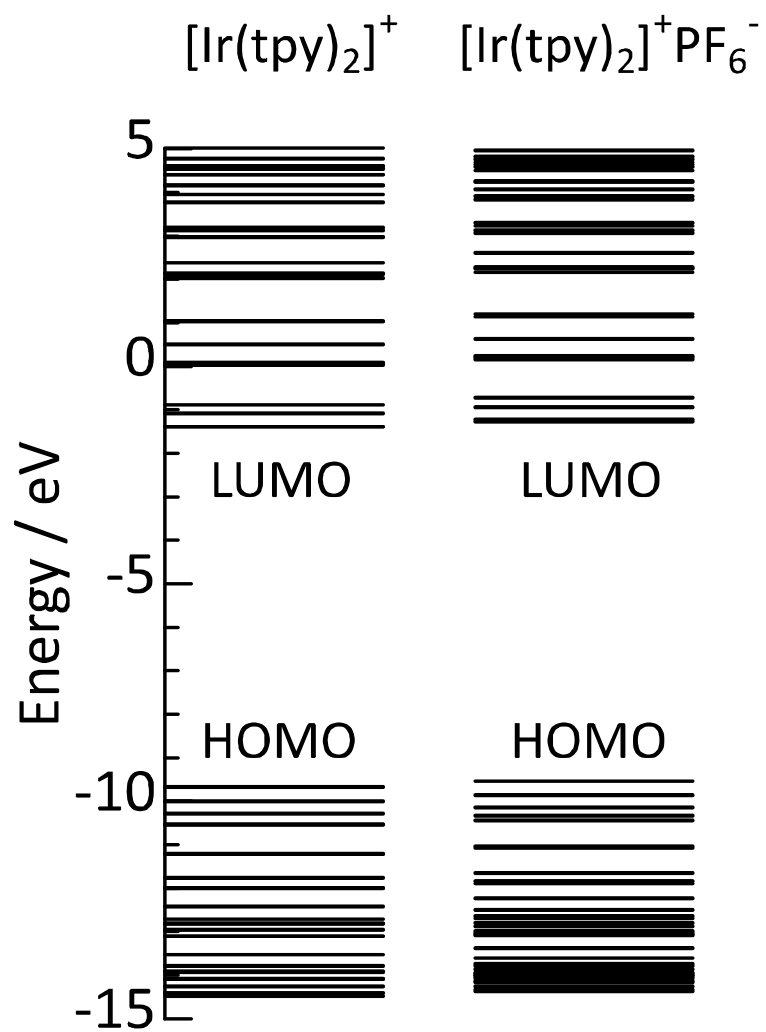


Figure S13. Molecular orbital energies of $[\text{Ir}(\text{tpy})_2]^{3+}$ (Left) and $[\text{Ir}(\text{tpy})_2]^{3+}\text{PF}_6^-$ (Right).

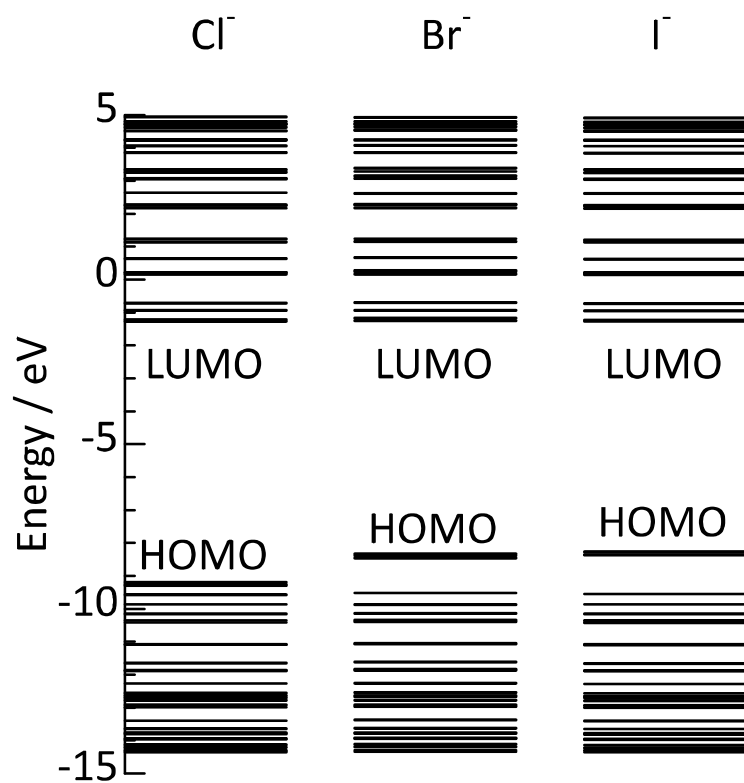


Figure S14. Molecular orbital energies of $[\text{Ir}(\text{tpy})_2]^{3+}\text{Cl}^-$ (Left), $[\text{Ir}(\text{tpy})_2]^{3+}\text{Br}^-$ (Middle) and $[\text{Ir}(\text{tpy})_2]^{3+}\text{I}^-$ (Right).

Table S1 SOC states of $[\text{Ir}(\text{tpy})_2]^{3+}$

State	Wavelength	Composition	f
1	365.357 nm	49%T ₁ , 44%T ₂ , 5%T ₄	1.7×10 ⁻⁸
2	365.245 nm	54%T ₁ , 45%T ₂	3.2×10 ⁻⁷
3	365.105 nm	67%T ₁ , 15%T ₂ , 18%T ₃	9.0×10 ⁻⁷
4	365.051 nm	16%T ₁ , 69%T ₂ , 8%T ₃ , 6%T ₄	1.1×10 ⁻⁶
5	364.848 nm	31%T ₁ , 37%T ₂ , 30%T ₃	3.4×10 ⁻⁸
6	364.559 nm	46%T ₁ , 51%T ₂ , 1%T ₄	2.0×10 ⁻⁵
7	364.266 nm	1%T ₁ , 2%T ₂ , 91%T ₃ , 3%T ₄	5.5×10 ⁻⁶
8	364.134 nm	8%T ₁ , 10%T ₂ , 80%T ₃ , 1%T ₄	2.4×10 ⁻⁶
9	364.039 nm	14%T ₁ , 15%T ₂ , 65%T ₃ , 7%T ₄	2.0×10 ⁻⁷
10	363.853 nm	1%T ₃ , 95%T ₄	6.2×10 ⁻⁶
11	363.773 nm	3%T ₁ , 5%T ₂ , 90%T ₄	1.8×10 ⁻⁷
12	363.755 nm	6%T ₁ , 6%T ₂ , 2%T ₃ , 85%T ₄	5.0×10 ⁻⁷
13	309.371 nm	43%T ₅ , 42%T ₆ , 14%T ₇	7.8×10 ⁻⁷
14	308.870 nm	51%T ₅ , 48%T ₆	7.0×10 ⁻⁶
15	308.836 nm	1%S ₁ , 82%T ₅ , 4%T ₆ , 6%T ₇ , 5%T ₈	1.8×10 ⁻⁴
16	308.799 nm	1%S ₂ , 3%T ₅ , 83%T ₆ , 4%T ₇ , 6%T ₈	1.8×10 ⁻⁴
17	308.080 nm	43%T ₅ , 46%T ₆ , 11%T ₈	3.3×10 ⁻⁶
18	307.679 nm	49%T ₅ , 51%T ₆	1.0×10 ⁻⁴
19	306.264 nm	2%S ₁ , 20%S ₂ , 67%T ₇ , 11%T ₈	0.0034
20	306.226 nm	22%S ₁ , 2%S ₂ , 62%T ₇ , 14%T ₈	0.0037
21	305.159 nm	7%T ₅ , 6%T ₆ , 86%T ₇	8.5×10 ⁻⁷
22	304.336 nm	8%S ₁ , 12%T ₅ , 25%T ₇ , 54%T ₈	0.0015
23	304.230 nm	7%S ₂ , 11%T ₆ , 20%T ₇ , 61%T ₈	0.0013
24	303.743 nm	3%T ₅ , 6%T ₆ , 89%T ₈	6.2×10 ⁻⁷
25	302.207 nm	67%S ₁ , 6%T ₇ , 26%T ₈	0.0177
26	302.151 nm	69%S ₂ , 8%T ₇ , 22%T ₈	0.0179
27	282.176 nm	100%T ₉	2.9×10 ⁻⁷
28	282.174 nm	100%T ₉	3.9×10 ⁻⁵
29	282.174 nm	100%T ₉	1.1×10 ⁻⁴
30	282.107 nm	100%T ₁₀	3.0×10 ⁻⁹
31	282.104 nm	100%T ₁₀	8.7×10 ⁻⁵
32	282.103 nm	100%T ₁₀	1.5×10 ⁻⁴
33	277.395 nm	100%T ₁₁	2.0×10 ⁻⁸
34	277.386 nm	100%T ₁₁	1.9×10 ⁻⁴
35	277.386 nm	100%T ₁₁	2.6×10 ⁻⁴
36	277.148 nm	100%T ₁₂	1.2×10 ⁻⁴
37	277.147 nm	100%T ₁₂	2.1×10 ⁻⁴
38	277.143 nm	100%T ₁₂	2.5×10 ⁻⁷
39	274.880 nm	90%T ₁₃ , 10%T ₁₄	3.6×10 ⁻⁷
40	274.873 nm	89%T ₁₃ , 11%T ₁₄	3.1×10 ⁻⁸
41	274.861 nm	100%T ₁₃	1.4×10 ⁻⁵

42	274.777 nm	100%T ₁₄	1.4×10 ⁻⁵
43	274.771 nm	10%T ₁₃ , 90%T ₁₄	1.1×10 ⁻⁶
44	274.764 nm	11%T ₁₃ , 89%T ₁₄	1.2×10 ⁻⁸
45	270.944 nm	76%T ₁₅ , 24%T ₁₆	1.7×10 ⁻⁶
46	270.913 nm	35%T ₁₅ , 65%T ₁₆	8.4×10 ⁻⁷
47	270.899 nm	64%T ₁₅ , 36%T ₁₆	2.0×10 ⁻⁷
48	270.896 nm	100%T ₁₅	2.5×10 ⁻⁵
49	270.879 nm	100%T ₁₆	2.2×10 ⁻⁵
50	270.870 nm	25%T ₁₅ , 75%T ₁₆	3.3×10 ⁻⁷

Table S2 SOC-free states of [Ir(tpy)₂]³⁺

State	Wavelength	Composition
S ₁	304.208 nm	HOMO-6→LUMO+1 1%, HOMO-6→LUMO+2 1%, HOMO-3→HOMO 1%, HOMO-2→HOMO 14%, HOMO-2→LUMO 1%, HOMO-1→HOMO 73%, HOMO-1→LUMO 2%
S ₂	304.075 nm	HOMO-7→LUMO+1 1%, HOMO-7→LUMO+2 1%, HOMO-3→LUMO 1%, HOMO-2→HOMO 1%, HOMO-2→LUMO 15%, HOMO-1→HOMO 2%, HOMO-1→LUMO 73%
S ₃	261.170 nm	HOMO-5→HOMO 22%, HOMO-5→LUMO 12%, HOMO-4→HOMO 12%, HOMO-4→LUMO 24%, HOMO-3→LUMO+1 4%, HOMO-2→LUMO+2 9%, HOMO-1→LUMO+1 6%, HOMO-1→LUMO+3 3%
S ₄	260.322 nm	HOMO-7→LUMO+2 1%, HOMO-7→LUMO+3 1%, HOMO-5→HOMO 3%, HOMO-5→LUMO 3%, HOMO-4→HOMO 6%, HOMO-3→LUMO 36%, HOMO-2→HOMO 3%, HOMO-2→LUMO 18%, HOMO-2→LUMO+1 3%, HOMO-1→LUMO 4%, HOMO-1→LUMO+2 6%, HOMO-1→LUMO+4 1%
S ₅	260.533 nm	HOMO-10→LUMO+1 1%, HOMO-10→LUMO+2 1%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+3 2%, HOMO-6→LUMO+6 1%, HOMO-3→HOMO 46%, HOMO-2→HOMO 26%, HOMO-2→LUMO 3%, HOMO-1→HOMO 4%, HOMO-1→LUMO+5 1%
S ₆	259.543 nm	HOMO-5→HOMO 3%, HOMO-5→LUMO 16%, HOMO-4→HOMO 13%, HOMO-4→LUMO 6%, HOMO-3→LUMO 11%, HOMO-2→LUMO 6%, HOMO-2→LUMO+1 10%, HOMO-1→LUMO 1%, HOMO-1→LUMO+2 18%, HOMO-1→LUMO+6 2%
S ₇	248.686 nm	HOMO-17→HOMO 2%, HOMO-16→LUMO 2%, HOMO-14→HOMO 1%, HOMO-13→LUMO 1%, HOMO-7→HOMO 3%, HOMO-6→LUMO 3%, HOMO-5→HOMO 33%, HOMO-5→LUMO 10%, HOMO-4→HOMO 10%, HOMO-4→LUMO 31%
S ₈	248.557 nm	HOMO-8→LUMO+2 1%, HOMO-3→LUMO+1 14%, HOMO-3→LUMO+3 2%, HOMO-2→LUMO+6 2%, HOMO-1→LUMO+1 66%
S ₉	247.277 nm	HOMO-17→HOMO 1%, HOMO-16→LUMO 1%, HOMO-14→HOMO 1%, HOMO-13→LUMO 1%, HOMO-7→HOMO 2%, HOMO-6→LUMO 2%, HOMO-5→HOMO 14%, HOMO-5→LUMO 28%, HOMO-4→HOMO 27%, HOMO-4→LUMO 14%
S ₁₀	240.466 nm	HOMO-12→LUMO 2%, HOMO-11→LUMO 2%, HOMO-7→LUMO+3 1%, HOMO-5→LUMO+1 18%, HOMO-5→LUMO+2 18%, HOMO-4→LUMO+1 16%, HOMO-4→LUMO+2 14%, HOMO-3→LUMO+7 2%, HOMO-2→LUMO+4 2%, HOMO-2→LUMO+5 2%, HOMO-2→LUMO+7 2%, HOMO-1→LUMO 1%, HOMO-1→LUMO+4 6%, HOMO-1→LUMO+5 4%
S ₁₁	240.447 nm	HOMO-12→HOMO 2%, HOMO-11→HOMO 2%, HOMO-6→LUMO+3 1%,

		HOMO-5→LUMO+1 16%, HOMO-5→LUMO+2 14%, HOMO-4→LUMO+1 19%, HOMO-4→LUMO+2 19%, HOMO-3→LUMO+8 2%, HOMO-2→LUMO+4 2%, HOMO-2→LUMO+5 2%, HOMO-2→LUMO+8 2%, HOMO-1→HOMO 1%, HOMO-1→LUMO+4 4%, HOMO-1→LUMO+5 6%
S ₁₂	237.155 nm	HOMO-10→HOMO 2%, HOMO-9→LUMO 2%, HOMO-8→LUMO+1 3%, HOMO-7→LUMO 5%, HOMO-7→LUMO+4 2%, HOMO-6→HOMO 5%, HOMO-6→LUMO+5 2%, HOMO-5→LUMO+4 1%, HOMO-4→LUMO+5 1%, HOMO-3→LUMO+2 23%, HOMO-2→LUMO+3 8%, HOMO-1→LUMO+2 30%, HOMO-1→LUMO+6 6%
S ₁₃	226.348 nm	HOMO-10→LUMO+4 1%, HOMO-9→LUMO+5 1%, HOMO-8→LUMO+6 1%, HOMO-7→HOMO 2%, HOMO-7→LUMO 9%, HOMO-6→HOMO 10%, HOMO-6→LUMO 2%, HOMO-5→HOMO 5%, HOMO-5→LUMO 3%, HOMO-4→HOMO 3%, HOMO-4→LUMO 5%, HOMO-3→LUMO+1 12%, HOMO-3→LUMO+3 1%, HOMO-2→LUMO+2 12%, HOMO-1→LUMO+1 6%, HOMO-1→LUMO+3 14%
S ₁₄	221.485 nm	HOMO-7→LUMO 10%, HOMO-6→HOMO 9%, HOMO-5→HOMO 4%, HOMO-5→LUMO 11%, HOMO-4→HOMO 10%, HOMO-4→LUMO 3%, HOMO-3→LUMO+2 6%, HOMO-2→LUMO+1 24%, HOMO-1→LUMO+2 12%
S ₁₅	226.192 nm	HOMO-8→LUMO 1%, HOMO-5→LUMO+1 2%, HOMO-4→LUMO+1 2%, HOMO-3→HOMO 1%, HOMO-3→LUMO 25%, HOMO-2→HOMO 2%, HOMO-2→LUMO 44%, HOMO-1→LUMO 13%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+5 2%
S ₁₆	226 nm	HOMO-8→HOMO 1%, HOMO-5→LUMO+1 1%, HOMO-4→LUMO+1 2%, HOMO-3→HOMO 26%, HOMO-3→LUMO 1%, HOMO-2→HOMO 44%, HOMO-2→LUMO 2%, HOMO-1→HOMO 13%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+5 2%
S ₁₇	214.225 nm	HOMO-16→LUMO+2 1%, HOMO-13→LUMO+1 1%, HOMO-13→LUMO+2 1%, HOMO-6→LUMO+2 3%, HOMO-5→LUMO+1 37%, HOMO-5→LUMO+2 1%, HOMO-5→LUMO+3 2%, HOMO-4→LUMO+1 3%, HOMO-4→LUMO+2 40%, HOMO-4→LUMO+6 3%
S ₁₈	214.213 nm	HOMO-17→LUMO+2 1%, HOMO-14→LUMO+1 1%, HOMO-14→LUMO+2 1%, HOMO-7→LUMO+2 3%, HOMO-5→LUMO+1 3%, HOMO-5→LUMO+2 40%, HOMO-5→LUMO+6 3%, HOMO-4→LUMO+1 36%, HOMO-4→LUMO+2 1%, HOMO-4→LUMO+3 2%
S ₁₉	209.795 nm	HOMO-18→LUMO+1 1%, HOMO-5→LUMO+5 1%, HOMO-4→LUMO+4 1%, HOMO-3→LUMO+1 23%, HOMO-2→LUMO+2 20%, HOMO-2→LUMO+6 3%, HOMO-1→LUMO+3 35%
S ₂₀	208.395 nm	HOMO-18→LUMO+2 2%, HOMO-12→LUMO+1 1%, HOMO-11→LUMO+2 1%, HOMO-10→HOMO 2%, HOMO-9→LUMO 2%, HOMO-8→LUMO+1 3%, HOMO-7→LUMO 7%, HOMO-6→HOMO 7%, HOMO-3→LUMO+2 8%, HOMO-2→LUMO+1 29%, HOMO-2→LUMO+3 4%, HOMO-1→LUMO+2 17%, HOMO-1→LUMO+6 6%
T ₁	366.314 nm	HOMO-7→LUMO+1 2%, HOMO-6→LUMO+1 1%, HOMO-6→LUMO+2 2%, HOMO-5→LUMO+1 1%, HOMO-4→LUMO+2 1%, HOMO-3→HOMO 1%, HOMO-2→HOMO 9%, HOMO-2→LUMO 16%, HOMO-2→LUMO+2 2%, HOMO-1→HOMO 35%, HOMO-1→LUMO 10%, HOMO-1→LUMO+1 2%
T ₂	366.271 nm	HOMO-7→LUMO+2 2%, HOMO-6→LUMO+1 3%, HOMO-5→LUMO+2 1%, HOMO-4→LUMO+1 1%, HOMO-3→LUMO 1%, HOMO-2→HOMO 18%, HOMO-2→LUMO 8%, HOMO-2→LUMO+1 1%, HOMO-1→HOMO 12%, HOMO-1→LUMO 33%, HOMO-1→LUMO+2 1%
T ₃	365.740 nm	HOMO-12→LUMO+9 1%, HOMO-11→LUMO+10 1%, HOMO-6→HOMO 3%, HOMO-6→LUMO+8 3%, HOMO-5→HOMO 8%, HOMO-4→HOMO 7%, HOMO-4→LUMO 3%, HOMO-3→LUMO+1 6%, HOMO-2→LUMO 1%, HOMO-2→LUMO+1 4%, HOMO-2→LUMO+2 21%, HOMO-1→HOMO 2%,

		HOMO-1→LUMO 1%, HOMO-1→LUMO+1 22%, HOMO-1→LUMO+2 4%
T ₄	365.309 nm	HOMO-12→LUMO+10 1%, HOMO-11→LUMO+9 1%, HOMO-7→LUMO 3%, HOMO-7→LUMO+7 2%, HOMO-5→LUMO 8%, HOMO-4→HOMO 3%, HOMO-4→LUMO 5%, HOMO-3→LUMO+2 5%, HOMO-2→LUMO 3%, HOMO-2→LUMO+1 24%, HOMO-2→LUMO+2 3%, HOMO-1→LUMO 5%, HOMO-1→LUMO+1 3%, HOMO-1→LUMO+2 20%
T ₅	309.127 nm	HOMO-10→LUMO+2 2%, HOMO-10→LUMO+6 1%, HOMO-9→LUMO+1 2%, HOMO-9→LUMO+3 2%, HOMO-8→LUMO 6%, HOMO-8→LUMO+4 1%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+3 1%, HOMO-4→LUMO+2 2%, HOMO-3→HOMO 15%, HOMO-3→LUMO 28%, HOMO-3→LUMO+5 2%, HOMO-2→LUMO 10%, HOMO-1→HOMO 4%, HOMO-1→LUMO 8%, HOMO-1→LUMO+5 1%
T ₆	309.098 nm	HOMO-10→LUMO+1 2%, HOMO-10→LUMO+3 2%, HOMO-9→LUMO+2 2%, HOMO-9→LUMO+6 1%, HOMO-8→HOMO 6%, HOMO-8→LUMO+5 1%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+3 1%, HOMO-3→HOMO 28%, HOMO-3→LUMO 15%, HOMO-3→LUMO+4 2%, HOMO-2→HOMO 11%, HOMO-1→HOMO 8%, HOMO-1→LUMO 4%, HOMO-1→LUMO+4 1%
T ₇	306.476 nm	HOMO-14→LUMO 1%, HOMO-10→LUMO+5 1%, HOMO-9→LUMO+4 1%, HOMO-8→LUMO+1 1%, HOMO-8→LUMO+3 2%, HOMO-7→LUMO 5%, HOMO-6→HOMO 4%, HOMO-5→HOMO 5%, HOMO-5→LUMO 20%, HOMO-5→LUMO+7 1%, HOMO-5→LUMO+8 1%, HOMO-4→HOMO 18%, HOMO-4→LUMO 7%, HOMO-4→LUMO+7 1%, HOMO-3→LUMO+6 2%, HOMO-2→LUMO+1 3%, HOMO-1→LUMO+2 11%
T ₈	305.030 nm	HOMO-13→HOMO 1%, HOMO-10→LUMO+4 1%, HOMO-9→LUMO+5 1%, HOMO-8→LUMO+2 1%, HOMO-7→HOMO 1%, HOMO-7→LUMO 4%, HOMO-6→HOMO 4%, HOMO-6→LUMO 1%, HOMO-5→HOMO 18%, HOMO-5→LUMO 8%, HOMO-5→LUMO+7 2%, HOMO-4→HOMO 10%, HOMO-4→LUMO 16%, HOMO-4→LUMO+8 2%, HOMO-3→LUMO+3 3%, HOMO-2→LUMO+2 2%, HOMO-1→LUMO+1 11%
T ₉	283.039 nm	HOMO-12→LUMO+2 2%, HOMO-12→LUMO+6 2%, HOMO-11→LUMO+1 2%, HOMO-11→LUMO+3 2%, HOMO-10→HOMO 2%, HOMO-10→LUMO 1%, HOMO-9→HOMO 1%, HOMO-7→HOMO 3%, HOMO-7→LUMO 6%, HOMO-7→LUMO+5 2%, HOMO-6→HOMO 14%, HOMO-6→LUMO 2%, HOMO-6→LUMO+4 3%, HOMO-6→LUMO+5 2%, HOMO-5→LUMO+5 5%, HOMO-4→LUMO+4 5%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+3 14%, HOMO-2→LUMO+6 9%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+3 2%
T ₁₀	282.961 nm	HOMO-12→LUMO+1 2%, HOMO-12→LUMO+3 2%, HOMO-11→LUMO+2 2%, HOMO-11→LUMO+6 1%, HOMO-10→HOMO 2%, HOMO-9→LUMO 4%, HOMO-8→LUMO+3 2%, HOMO-7→LUMO 16%, HOMO-7→LUMO+4 4%, HOMO-7→LUMO+5 1%, HOMO-6→HOMO 9%, HOMO-6→LUMO+5 2%, HOMO-5→LUMO+4 6%, HOMO-4→LUMO+5 5%, HOMO-3→LUMO+2 5%, HOMO-3→LUMO+6 10%, HOMO-2→LUMO+3 12%, HOMO-1→LUMO+2 1%
T ₁₁	278.194 nm	HOMO-12→LUMO+1 3%, HOMO-11→LUMO+2 4%, HOMO-10→HOMO 6%, HOMO-10→LUMO 1%, HOMO-9→LUMO 9%, HOMO-9→LUMO+4 1%, HOMO-8→LUMO+1 4%, HOMO-8→LUMO+3 4%, HOMO-7→LUMO 2%, HOMO-7→LUMO+4 2%, HOMO-6→HOMO 1%, HOMO-6→LUMO+5 1%, HOMO-5→LUMO 3%, HOMO-4→HOMO 2%, HOMO-4→LUMO 1%, HOMO-3→LUMO+2 15%, HOMO-2→LUMO+1 9%, HOMO-2→LUMO+3 4%, HOMO-2→LUMO+10 1%, HOMO-1→LUMO+2 2%, HOMO-1→LUMO+6 12%, HOMO-1→LUMO+9 2%
T ₁₂	277.962 nm	HOMO-12→LUMO+2 3%, HOMO-11→LUMO+1 4%, HOMO-10→HOMO 7%, HOMO-10→LUMO 4%, HOMO-10→LUMO+4 1%, HOMO-9→HOMO 5%, HOMO-9→LUMO 4%, HOMO-9→LUMO+5 1%, HOMO-8→LUMO+2 5%, HOMO-8→LUMO+6 3%, HOMO-5→HOMO 2%, HOMO-4→HOMO 1%,

		HOMO-4→LUMO 1%, HOMO-3→LUMO+1 15%, HOMO-3→LUMO+3 2%, HOMO-2→LUMO+2 7%, HOMO-2→LUMO+6 2%, HOMO-2→LUMO+9 1%, HOMO-1→LUMO+3 14%, HOMO-1→LUMO+10 2%
T ₁₃	275.696 nm	HOMO-12→HOMO 4%, HOMO-12→LUMO+5 1%, HOMO-11→HOMO 4%, HOMO-6→LUMO+3 12%, HOMO-6→LUMO+6 9%, HOMO-5→LUMO+3 3%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+3 3%, HOMO-4→LUMO+6 2%, HOMO-3→LUMO+4 5%, HOMO-3→LUMO+5 7%, HOMO-2→LUMO+4 9%, HOMO-2→LUMO+5 14%, HOMO-1→HOMO 2%, HOMO-1→LUMO+4 5%, HOMO-1→LUMO+5 7%
T ₁₄	275.612 nm	HOMO-12→LUMO 4%, HOMO-11→LUMO 5%, HOMO-7→LUMO+3 12%, HOMO-7→LUMO+6 9%, HOMO-5→LUMO+3 3%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+3 2%, HOMO-4→LUMO+6 2%, HOMO-3→LUMO+4 7%, HOMO-3→LUMO+5 5%, HOMO-2→LUMO+4 14%, HOMO-2→LUMO+5 9%, HOMO-1→LUMO 1%, HOMO-1→LUMO+4 7%, HOMO-1→LUMO+5 5%
T ₁₅	271.701 nm	HOMO-12→HOMO 1%, HOMO-12→LUMO 7%, HOMO-11→LUMO 10%, HOMO-11→LUMO+4 1%, HOMO-7→LUMO+1 8%, HOMO-7→LUMO+2 6%, HOMO-7→LUMO+9 2%, HOMO-7→LUMO+10 1%, HOMO-6→LUMO+1 2%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+2 3%, HOMO-4→LUMO+1 4%, HOMO-4→LUMO+2 1%, HOMO-3→LUMO+4 2%, HOMO-3→LUMO+7 5%, HOMO-2→LUMO 2%, HOMO-2→LUMO+7 13%, HOMO-1→LUMO 5%, HOMO-1→LUMO+7 8%
T ₁₆	271.684 nm	HOMO-12→HOMO 7%, HOMO-12→LUMO 1%, HOMO-11→HOMO 11%, HOMO-11→LUMO+5 1%, HOMO-7→LUMO+1 2%, HOMO-6→LUMO+1 8%, HOMO-6→LUMO+2 6%, HOMO-6→LUMO+9 2%, HOMO-6→LUMO+10 1%, HOMO-5→LUMO+1 4%, HOMO-5→LUMO+2 1%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+2 3%, HOMO-3→LUMO+5 1%, HOMO-3→LUMO+8 5%, HOMO-2→HOMO 2%, HOMO-2→LUMO+8 13%, HOMO-1→HOMO 5%, HOMO-1→LUMO+5 1%, HOMO-1→LUMO+8 8%
T ₁₇	261.888 nm	HOMO-12→LUMO+2 5%, HOMO-12→LUMO+6 2%, HOMO-11→LUMO+1 8%, HOMO-8→LUMO+2 1%, HOMO-7→LUMO 3%, HOMO-7→LUMO+4 2%, HOMO-7→LUMO+5 4%, HOMO-7→LUMO+7 2%, HOMO-6→HOMO 3%, HOMO-6→LUMO+4 4%, HOMO-6→LUMO+5 2%, HOMO-6→LUMO+8 2%, HOMO-5→LUMO+5 3%, HOMO-5→LUMO+7 1%, HOMO-4→LUMO+4 3%, HOMO-4→LUMO+8 1%, HOMO-3→LUMO+1 7%, HOMO-3→LUMO+3 6%, HOMO-3→LUMO+10 3%, HOMO-2→LUMO+2 1%, HOMO-2→LUMO+6 3%, HOMO-2→LUMO+9 6%, HOMO-1→LUMO+1 8%, HOMO-1→LUMO+3 1%, HOMO-1→LUMO+10 2%
T ₁₈	260.491 nm	HOMO-12→LUMO+1 8%, HOMO-12→LUMO+3 1%, HOMO-11→LUMO+2 7%, HOMO-11→LUMO+6 2%, HOMO-8→LUMO+1 1%, HOMO-7→LUMO 4%, HOMO-7→LUMO+4 5%, HOMO-7→LUMO+5 1%, HOMO-7→LUMO+7 2%, HOMO-6→HOMO 4%, HOMO-6→LUMO+5 5%, HOMO-6→LUMO+8 2%, HOMO-5→LUMO 1%, HOMO-5→LUMO+4 3%, HOMO-4→LUMO+5 3%, HOMO-4→LUMO+7 1%, HOMO-3→LUMO+2 1%, HOMO-3→LUMO+6 4%, HOMO-3→LUMO+9 4%, HOMO-2→LUMO+3 6%, HOMO-2→LUMO+10 7%, HOMO-1→LUMO+2 10%, HOMO-1→LUMO+6 1%, HOMO-1→LUMO+9 3%
T ₁₉	258.395 nm	HOMO-17→LUMO+1 2%, HOMO-17→LUMO+2 2%, HOMO-14→LUMO+1 2%, HOMO-14→LUMO+2 2%, HOMO-9→LUMO+1 2%, HOMO-9→LUMO+2 2%, HOMO-7→LUMO+1 7%, HOMO-7→LUMO+2 7%, HOMO-5→LUMO+1 16%, HOMO-5→LUMO+2 16%, HOMO-5→LUMO+9 1%, HOMO- 5→LUMO+10 1%, HOMO-4→LUMO+1 13%, HOMO-4→LUMO+2 14%
T ₂₀	258.306 nm	HOMO-16→LUMO+1 2%, HOMO-16→LUMO+2 2%, HOMO-13→LUMO+1 2%, HOMO-13→LUMO+2 2%, HOMO-10→LUMO+1 2%, HOMO- 10→LUMO+2 2%, HOMO-6→LUMO+1 8%, HOMO-6→LUMO+2 7%, HOMO- 5→LUMO+1 13%, HOMO-5→LUMO+2 13%, HOMO-4→LUMO+1 16%, HOMO-4→LUMO+2 16%, HOMO-4→LUMO+10 1%

Table S3 SOC state of $[\text{Ir}(\text{tpy})_2]^{3+} \cdot \text{PF}_6^-$

State	Wavelength	Composition	f
1	367.785 nm	92%T ₁ , 7%T ₂	1.3×10^{-7}
2	367.757 nm	93%T ₁ , 7%T ₂	4.7×10^{-6}
3	367.723 nm	99%T ₁	3.4×10^{-7}
4	366.884 nm	98%T ₂	1.1×10^{-6}
5	366.831 nm	6%T ₁ , 92%T ₂	7.2×10^{-8}
6	366.773 nm	6%T ₁ , 93%T ₂	1.2×10^{-5}
7	363.778 nm	97%T ₃ , 1%T ₄	8.7×10^{-6}
8	363.755 nm	98%T ₃	3.2×10^{-8}
9	363.751 nm	98%T ₃	7.5×10^{-7}
10	362.984 nm	98%T ₄	8.5×10^{-6}
11	362.958 nm	99%T ₄	1.2×10^{-7}
12	362.938 nm	97%T ₄	3.8×10^{-7}
13	310.364 nm	84%T ₅ , 6%T ₆ , 5%T ₇ , 4%T ₈	3.5×10^{-5}
14	310.218 nm	89%T ₅ , 4%T ₆ , 4%T ₈	4.9×10^{-5}
15	309.982 nm	95%T ₅ , 2%T ₇	2.9×10^{-5}
16	308.599 nm	59%T ₆ , 36%T ₇	6.9×10^{-5}
17	308.400 nm	10%T ₅ , 61%T ₆ , 26%T ₇	1.5×10^{-4}
18	308.079 nm	3%S ₁ , 3%S ₂ , 90%T ₆	7.1×10^{-4}
19	306.727 nm	4%T ₅ , 92%T ₇ , 2%T ₈	1.4×10^{-4}
20	306.149 nm	7%S ₁ , 3%S ₂ , 30%T ₆ , 39%T ₇ , 20%T ₈	0.0014
21	305.818 nm	31%T ₆ , 64%T ₇ , 3%T ₈	1.9×10^{-5}
22	305.126 nm	6%S ₁ , 5%S ₂ , 7%T ₆ , 22%T ₇ , 58%T ₈	0.0016
23	304.158 nm	6%T ₅ , 3%T ₇ , 89%T ₈	9.4×10^{-5}
24	304.076 nm	6%T ₅ , 5%T ₇ , 88%T ₈	8.0×10^{-5}
25	301.708 nm	63%S ₁ , 26%S ₂ , 6%T ₆ , 5%T ₈	0.0241
26	301.320 nm	19%S ₁ , 61%S ₂ , 18%T ₈	0.0216
27	283.862 nm	100%T ₉	1.7×10^{-6}
28	283.861 nm	100%T ₉	1.3×10^{-5}
29	283.860 nm	100%T ₉	8.8×10^{-5}
30	282.757 nm	100%T ₁₀	8.3×10^{-7}
31	282.757 nm	100%T ₁₀	3.7×10^{-6}
32	282.754 nm	100%T ₁₀	2.0×10^{-4}
33	277.306 nm	100%T ₁₁	1.8×10^{-5}
34	277.302 nm	100%T ₁₁	4.8×10^{-5}
35	277.299 nm	100%T ₁₁	5.1×10^{-4}
36	276.687 nm	99%T ₁₂	1.4×10^{-4}
37	276.686 nm	99%T ₁₂	1.2×10^{-4}
38	276.682 nm	100%T ₁₂	7.7×10^{-5}
39	276.281 nm	100%T ₁₃	4.5×10^{-5}
40	276.269 nm	99%T ₁₃	1.4×10^{-5}

41	276.265 nm	99%T ₁₃	2.5×10 ⁻⁶
42	274.461 nm	100%T ₁₄	2.3×10 ⁻⁵
43	274.455 nm	100%T ₁₄	1.3×10 ⁻⁵
44	274.449 nm	100%T ₁₄	1.5×10 ⁻⁶
45	271.318 nm	98%T ₁₅	9.3×10 ⁻⁵
46	271.285 nm	99%T ₁₅	3.4×10 ⁻⁵
47	271.272 nm	99%T ₁₅	5.6×10 ⁻⁶
48	270.806 nm	99%T ₁₆	6.4×10 ⁻⁵
49	270.791 nm	99%T ₁₆	1.6×10 ⁻⁵
50	270.788 nm	99%T ₁₆	4.9×10 ⁻⁵

Table S4 SOC-free states of [Ir(tpy)₂]³⁺·PF₆⁻

State	Wavelength	Composition
S ₁	303.172 nm	HOMO-7→LUMO+1 1%, HOMO-2→HOMO 15%, HOMO-2→LUMO 3%, HOMO-1→HOMO 38%, HOMO-1→LUMO 35%
S ₂	302.865 nm	HOMO-2→HOMO 6%, HOMO-2→LUMO 8%, HOMO-1→HOMO 31%, HOMO-1→LUMO 44%
S ₃	262.639 nm	HOMO-5→HOMO 8%, HOMO-5→LUMO 4%, HOMO-4→HOMO 3%, HOMO-4→LUMO 45%, HOMO-3→LUMO 6%, HOMO-3→LUMO+1 3%, HOMO-2→LUMO 4%, HOMO-2→LUMO+2 7%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 6%, HOMO-1→LUMO+3 1%
S ₄	262.045 nm	HOMO-10→LUMO+1 1%, HOMO-7→LUMO+1 1%, HOMO-5→HOMO 11%, HOMO-4→HOMO 2%, HOMO-4→LUMO 1%, HOMO-3→HOMO 33%, HOMO-2→HOMO 23%, HOMO-2→LUMO+1 2%, HOMO-1→HOMO 5%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 4%
S ₅	260.099 nm	HOMO-5→HOMO 21%, HOMO-4→HOMO 5%, HOMO-3→HOMO 11%, HOMO-3→LUMO 16%, HOMO-3→LUMO+1 2%, HOMO-2→HOMO 1%, HOMO-2→LUMO 14%, HOMO-2→LUMO+1 5%, HOMO-1→LUMO 1%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 4%, HOMO-1→LUMO+3 1%, HOMO-1→LUMO+6 1%
S ₆	258.490 nm	HOMO-6→LUMO+2 1%, HOMO-5→HOMO 9%, HOMO-4→HOMO 2%, HOMO-4→LUMO 12%, HOMO-3→HOMO 4%, HOMO-3→LUMO 24%, HOMO-2→HOMO 2%, HOMO-2→LUMO 13%, HOMO-2→LUMO+1 6%, HOMO-1→LUMO 1%, HOMO-1→LUMO+2 8%, HOMO-1→LUMO+6 1%
S ₇	255.359 nm	HOMO-16→HOMO 2%, HOMO-13→HOMO 4%, HOMO-6→HOMO 4%, HOMO-5→HOMO 12%, HOMO-5→LUMO 3%, HOMO-4→HOMO 70%
S ₈	248.382 nm	HOMO-10→HOMO 2%, HOMO-9→LUMO 1%, HOMO-5→HOMO 1%, HOMO-3→LUMO+1 14%, HOMO-3→LUMO+3 2%, HOMO-2→LUMO+6 2%, HOMO-1→LUMO+1 61%, HOMO-1→LUMO+2 2%
S ₉	250.154 nm	HOMO-17→LUMO 3%, HOMO-14→LUMO 2%, HOMO-7→LUMO 6%, HOMO-5→HOMO 1%, HOMO-5→LUMO 74%, HOMO-4→HOMO 1%, HOMO-4→LUMO 6%
S ₁₀	240.522 nm	HOMO-11→LUMO 2%, HOMO-5→LUMO+1 11%, HOMO-4→LUMO+1 9%, HOMO-4→LUMO+2 42%, HOMO-3→LUMO+2 1%, HOMO-3→LUMO+8 2%, HOMO-2→LUMO+4 2%, HOMO-2→LUMO+8 2%, HOMO-1→LUMO 1%, HOMO-1→LUMO+3 2%, HOMO-1→LUMO+4 1%, HOMO-1→LUMO+5 7%
S ₁₁	240.068 nm	HOMO-12→HOMO 2%, HOMO-11→HOMO 1%, HOMO-5→LUMO+1 33%, HOMO-5→LUMO+2 17%, HOMO-4→LUMO+1 14%, HOMO-3→LUMO+7 2%, HOMO-2→LUMO+4 1%, HOMO-2→LUMO+5 3%, HOMO-2→LUMO+7

		2%, HOMO-1→HOMO 1%, HOMO-1→LUMO+4 7%, HOMO-1→LUMO+5 1%
S ₁₂	236.746 nm	HOMO-9→LUMO 2%, HOMO-8→LUMO+1 2%, HOMO-7→HOMO 4%, HOMO-7→LUMO+4 2%, HOMO-6→LUMO 5%, HOMO-6→LUMO+5 1%, HOMO-4→LUMO+2 2%, HOMO-3→LUMO+2 20%, HOMO-2→LUMO+3 6%, HOMO-2→LUMO+5 1%, HOMO-1→LUMO+2 29%, HOMO-1→LUMO+6 5%
S ₁₃	226.761 nm	HOMO-10→LUMO+4 1%, HOMO-8→LUMO+6 1%, HOMO-7→HOMO 9%, HOMO-7→LUMO 2%, HOMO-6→HOMO 2%, HOMO-6→LUMO 10%, HOMO-5→HOMO 5%, HOMO-5→LUMO 1%, HOMO-4→HOMO 1%, HOMO- 4→LUMO 8%, HOMO-3→LUMO+1 11%, HOMO-2→LUMO+2 11%, HOMO- 1→LUMO+1 5%, HOMO-1→LUMO+2 1%, HOMO-1→LUMO+3 11%, HOMO- 1→LUMO+5 2%
S ₁₄	222.063 nm	HOMO-7→HOMO 10%, HOMO-6→LUMO 8%, HOMO-5→HOMO 14%, HOMO-4→LUMO 12%, HOMO-3→LUMO+2 5%, HOMO-2→LUMO+1 23%, HOMO-1→LUMO+2 13%
S ₁₅	227.158 nm	HOMO-8→HOMO 1%, HOMO-5→HOMO 2%, HOMO-5→LUMO+1 3%, HOMO-3→HOMO 24%, HOMO-2→HOMO 42%, HOMO-1→HOMO 17%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+5 1%
S ₁₆	220.054 nm	HOMO-13→LUMO+1 3%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 1%, HOMO-5→LUMO+1 7%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO+1 54%, HOMO-4→LUMO+2 16%, HOMO-4→LUMO+6 2%, HOMO-3→LUMO 1%, HOMO-2→LUMO 2%
S ₁₇	222.142 nm	HOMO-5→LUMO+2 1%, HOMO-4→LUMO+2 7%, HOMO-3→HOMO 1%, HOMO-3→LUMO 23%, HOMO-2→LUMO 46%, HOMO-1→LUMO 9%, HOMO-1→LUMO+3 2%, HOMO-1→LUMO+4 1%, HOMO-1→LUMO+5 1%
S ₁₈	214.105 nm	HOMO-17→LUMO+2 1%, HOMO-14→LUMO+2 1%, HOMO-7→LUMO+2 3%, HOMO-6→LUMO 1%, HOMO-5→LUMO+1 13%, HOMO-5→LUMO+2 34%, HOMO-5→LUMO+3 1%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+2 5%, HOMO-3→LUMO+1 5%, HOMO-3→LUMO+2 4%, HOMO-2→LUMO+1 1%, HOMO-2→LUMO+2 6%, HOMO-1→LUMO+2 1%, HOMO-1→LUMO+3 5%, HOMO-1→LUMO+5 2%
S ₁₉	210.533 nm	HOMO-10→HOMO 2%, HOMO-7→HOMO 4%, HOMO-5→LUMO+1 3%, HOMO-5→LUMO+2 3%, HOMO-3→HOMO 2%, HOMO-3→LUMO+1 14%, HOMO-2→LUMO+1 10%, HOMO-2→LUMO+2 8%, HOMO-2→LUMO+3 2%, HOMO-2→LUMO+4 1%, HOMO-2→LUMO+6 2%, HOMO-1→LUMO+1 1%, HOMO-1→LUMO+2 4%, HOMO-1→LUMO+3 18%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+5 2%, HOMO-1→LUMO+6 1%
S ₂₀	208.495 nm	HOMO-11→LUMO+2 1%, HOMO-9→LUMO 1%, HOMO-8→LUMO+1 1%, HOMO-7→HOMO 3%, HOMO-7→LUMO+2 1%, HOMO-6→LUMO 4%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+2 18%, HOMO-3→HOMO 2%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 5%, HOMO-2→LUMO+1 13%, HOMO-2→LUMO+2 6%, HOMO-2→LUMO+3 2%, HOMO-1→LUMO+1 1%, HOMO-1→LUMO+2 8%, HOMO-1→LUMO+3 4%, HOMO-1→LUMO+4 1%, HOMO-1→LUMO+5 4%, HOMO-1→LUMO+6 3%
T ₁	369.137 nm	HOMO-7→HOMO 2%, HOMO-7→LUMO+1 2%, HOMO-7→LUMO+7 2%, HOMO-5→HOMO 7%, HOMO-3→HOMO 1%, HOMO-3→LUMO+1 4%, HOMO-3→LUMO+2 1%, HOMO-2→HOMO 13%, HOMO-2→LUMO+1 15%, HOMO-2→LUMO+2 4%, HOMO-1→HOMO 17%, HOMO-1→LUMO 2%, HOMO-1→LUMO+1 10%, HOMO-1→LUMO+2 3%
T ₂	368.252 nm	HOMO-11→LUMO+8 2%, HOMO-6→LUMO 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 3%, HOMO-4→LUMO 4%, HOMO-2→LUMO 18%, HOMO-2→LUMO+2 4%, HOMO-1→LUMO 43%, HOMO-1→LUMO+1 3%, HOMO-1→LUMO+2 2%
T ₃	365.201 nm	HOMO-7→HOMO 2%, HOMO-7→LUMO+1 3%, HOMO-7→LUMO+2 1%, HOMO-7→LUMO+7 1%, HOMO-5→HOMO 8%, HOMO-5→LUMO+1 1%,

		HOMO-4→HOMO 1%, HOMO-3→LUMO+1 3%, HOMO-2→HOMO 20%, HOMO-2→LUMO+1 7%, HOMO-2→LUMO+2 6%, HOMO-1→HOMO 23%, HOMO-1→LUMO+1 7%
T ₄	364.420 nm	HOMO-6→LUMO 3%, HOMO-6→LUMO+2 1%, HOMO-6→LUMO+8 3%, HOMO-4→LUMO 13%, HOMO-3→LUMO+2 4%, HOMO-2→HOMO 1%, HOMO-2→LUMO 4%, HOMO-2→LUMO+1 10%, HOMO-2→LUMO+2 11%, HOMO-1→LUMO 9%, HOMO-1→LUMO+1 4%, HOMO-1→LUMO+2 21%
T ₅	310.633 nm	HOMO-10→LUMO+1 2%, HOMO-10→LUMO+2 1%, HOMO-10→LUMO+6 1%, HOMO-8→HOMO 5%, HOMO-5→HOMO 1%, HOMO-5→LUMO+1 3%, HOMO-4→LUMO 1%, HOMO-3→HOMO 38%, HOMO-3→LUMO 4%, HOMO-3→LUMO+1 1%, HOMO-3→LUMO+5 2%, HOMO-2→HOMO 7%, HOMO-1→HOMO 11%, HOMO-1→LUMO 1%
T ₆	308.429 nm	HOMO-13→LUMO 2%, HOMO-9→LUMO+8 1%, HOMO-6→LUMO 8%, HOMO-5→HOMO 2%, HOMO-5→LUMO 4%, HOMO-4→LUMO 45%, HOMO-4→LUMO+8 4%, HOMO-3→LUMO+6 1%, HOMO-2→LUMO+1 1%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 9%
T ₇	307.611 nm	HOMO-9→LUMO+2 3%, HOMO-9→LUMO+3 1%, HOMO-9→LUMO+6 1%, HOMO-8→LUMO 6%, HOMO-4→LUMO+2 2%, HOMO-4→LUMO+3 1%, HOMO-3→HOMO 5%, HOMO-3→LUMO 37%, HOMO-3→LUMO+4 2%, HOMO-2→LUMO 13%, HOMO-1→HOMO 2%, HOMO-1→LUMO 8%
T ₈	305.316 nm	HOMO-14→HOMO 2%, HOMO-10→LUMO+4 2%, HOMO-10→LUMO+7 1%, HOMO-7→HOMO 8%, HOMO-6→HOMO 1%, HOMO-5→HOMO 42%, HOMO-5→LUMO+7 3%, HOMO-4→HOMO 6%, HOMO-4→LUMO 1%, HOMO-3→LUMO+3 1%, HOMO-2→LUMO+1 2%, HOMO-2→LUMO+2 1%, HOMO-1→HOMO 1%, HOMO-1→LUMO+1 8%, HOMO-1→LUMO+2 1%
T ₉	284.748 nm	HOMO-11→LUMO+2 2%, HOMO-11→LUMO+3 1%, HOMO-9→LUMO 4%, HOMO-7→LUMO 3%, HOMO-6→LUMO 22%, HOMO-6→LUMO+3 1%, HOMO-6→LUMO+4 4%, HOMO-6→LUMO+5 4%, HOMO-4→LUMO+3 2%, HOMO-4→LUMO+4 4%, HOMO-4→LUMO+5 4%, HOMO-4→LUMO+8 1%, HOMO-3→LUMO+2 2%, HOMO-3→LUMO+3 5%, HOMO-3→LUMO+5 3%, HOMO-3→LUMO+6 4%, HOMO-2→LUMO+3 4%, HOMO-2→LUMO+5 3%, HOMO-2→LUMO+6 5%, HOMO-1→LUMO+3 2%, HOMO-1→LUMO+6 1%
T ₁₀	283.631 nm	HOMO-12→LUMO+1 2%, HOMO-12→LUMO+2 1%, HOMO-12→LUMO+3 1%, HOMO-11→LUMO+1 1%, HOMO-10→HOMO 4%, HOMO-7→HOMO 23%, HOMO-7→LUMO+4 5%, HOMO-7→LUMO+5 2%, HOMO-6→HOMO 3%, HOMO-5→LUMO+4 6%, HOMO-5→LUMO+5 3%, HOMO-5→LUMO+7 1%, HOMO-3→LUMO+1 1%, HOMO-3→LUMO+2 1%, HOMO-3→LUMO+3 5%, HOMO-3→LUMO+6 6%, HOMO-2→LUMO+3 6%, HOMO-2→LUMO+6 5%, HOMO-1→LUMO+1 1%
T ₁₁	278.107 nm	HOMO-12→LUMO+1 3%, HOMO-11→LUMO+2 2%, HOMO-10→HOMO 14%, HOMO-10→LUMO+4 1%, HOMO-9→HOMO 4%, HOMO-8→LUMO+1 4%, HOMO-8→LUMO+3 2%, HOMO-7→HOMO 1%, HOMO-7→LUMO+5 1%, HOMO-5→HOMO 5%, HOMO-3→LUMO+1 9%, HOMO-3→LUMO+2 8%, HOMO-2→LUMO+1 7%, HOMO-2→LUMO+3 2%, HOMO-2→LUMO+6 1%, HOMO-1→LUMO+3 2%, HOMO-1→LUMO+6 8%, HOMO-1→LUMO+9 2%
T ₁₂	277.497 nm	HOMO-12→LUMO+2 1%, HOMO-11→LUMO+1 2%, HOMO-11→LUMO+2 3%, HOMO-10→HOMO 1%, HOMO-10→LUMO 3%, HOMO-9→LUMO 13%, HOMO-8→LUMO+2 3%, HOMO-8→LUMO+6 2%, HOMO-6→LUMO 1%, HOMO-6→LUMO+3 3%, HOMO-4→LUMO 3%, HOMO-3→LUMO+1 6%, HOMO-3→LUMO+2 6%, HOMO-3→LUMO+4 1%, HOMO-3→LUMO+5 1%, HOMO-2→LUMO+2 6%, HOMO-2→LUMO+3 1%, HOMO-1→LUMO+3 10%, HOMO-1→LUMO+6 3%, HOMO-1→LUMO+10 2%
T ₁₃	277.110 nm	HOMO-12→LUMO 2%, HOMO-11→LUMO 6%, HOMO-9→LUMO 2%, HOMO-7→LUMO+3 1%, HOMO-6→LUMO+3 7%, HOMO-6→LUMO+5 3%,

		HOMO-6→LUMO+6 7%, HOMO-4→LUMO+3 4%, HOMO-4→LUMO+6 3%, HOMO-3→LUMO+2 1%, HOMO-3→LUMO+3 3%, HOMO-3→LUMO+4 3%, HOMO-3→LUMO+5 3%, HOMO-2→LUMO+3 3%, HOMO-2→LUMO+4 7%, HOMO-2→LUMO+5 7%, HOMO-1→LUMO 1%, HOMO-1→LUMO+3 1%, HOMO-1→LUMO+4 5%, HOMO-1→LUMO+5 9%
T ₁₄	275.288 nm	HOMO-12→HOMO 7%, HOMO-11→HOMO 4%, HOMO-7→LUMO+3 8%, HOMO-7→LUMO+4 1%, HOMO-7→LUMO+6 7%, HOMO-6→LUMO+3 1%, HOMO-5→LUMO+3 4%, HOMO-5→LUMO+6 4%, HOMO-3→LUMO+4 6%, HOMO-3→LUMO+5 5%, HOMO-2→LUMO+4 13%, HOMO-2→LUMO+5 10%, HOMO-1→HOMO 1%, HOMO-1→LUMO+4 7%, HOMO-1→LUMO+5 3%
T ₁₅	272.067 nm	HOMO-12→HOMO 6%, HOMO-12→LUMO 2%, HOMO-12→LUMO+5 1%, HOMO-11→HOMO 4%, HOMO-11→LUMO 4%, HOMO-11→LUMO+4 1%, HOMO-8→LUMO+5 1%, HOMO-7→LUMO+1 5%, HOMO-7→LUMO+2 4%, HOMO-7→LUMO+9 2%, HOMO-6→LUMO+1 5%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+10 1%, HOMO-5→LUMO+1 4%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO+1 3%, HOMO-3→LUMO+4 2%, HOMO-3→LUMO+7 4%, HOMO-2→HOMO 2%, HOMO-2→LUMO+7 7%, HOMO-2→LUMO+8 6%, HOMO-1→HOMO 4%, HOMO-1→LUMO 1%, HOMO-1→LUMO+7 6%, HOMO-1→LUMO+8 2%
T ₁₆	271.575 nm	HOMO-12→HOMO 3%, HOMO-12→LUMO 2%, HOMO-12→LUMO+4 1%, HOMO-11→LUMO 10%, HOMO-11→LUMO+5 2%, HOMO-7→LUMO+1 6%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 8%, HOMO-6→LUMO+9 2%, HOMO-5→LUMO+1 4%, HOMO-4→LUMO+2 5%, HOMO-3→LUMO+5 2%, HOMO-3→LUMO+7 1%, HOMO-3→LUMO+8 4%, HOMO-2→LUMO+7 7%, HOMO-2→LUMO+8 6%, HOMO-1→HOMO 1%, HOMO-1→LUMO 4%, HOMO-1→LUMO+8 9%
T ₁₇	262.466 nm	HOMO-12→LUMO+2 4%, HOMO-12→LUMO+6 1%, HOMO-11→LUMO+1 7%, HOMO-11→LUMO+2 2%, HOMO-9→LUMO 1%, HOMO-8→LUMO+2 2%, HOMO-7→HOMO 2%, HOMO-7→LUMO+5 3%, HOMO-7→LUMO+7 1%, HOMO-6→LUMO 4%, HOMO-6→LUMO+3 1%, HOMO-6→LUMO+4 4%, HOMO-6→LUMO+5 2%, HOMO-6→LUMO+8 2%, HOMO-5→LUMO+5 1%, HOMO-5→LUMO+7 1%, HOMO-4→LUMO 1%, HOMO-4→LUMO+4 2%, HOMO-4→LUMO+8 2%, HOMO-3→LUMO+1 6%, HOMO-3→LUMO+3 3%, HOMO-3→LUMO+5 1%, HOMO-3→LUMO+10 3%, HOMO-2→LUMO+6 3%, HOMO-2→LUMO+9 5%, HOMO-1→LUMO+1 7%, HOMO-1→LUMO+2 1%, HOMO-1→LUMO+3 1%, HOMO-1→LUMO+10 3%
T ₁₈	261.223 nm	HOMO-12→LUMO+1 8%, HOMO-11→LUMO+2 7%, HOMO-11→LUMO+6 2%, HOMO-8→LUMO+1 1%, HOMO-7→HOMO 4%, HOMO-7→LUMO+4 6%, HOMO-7→LUMO+5 1%, HOMO-7→LUMO+7 2%, HOMO-6→LUMO 3%, HOMO-6→LUMO+3 1%, HOMO-6→LUMO+5 4%, HOMO-6→LUMO+8 2%, HOMO-5→HOMO 1%, HOMO-5→LUMO+4 3%, HOMO-5→LUMO+7 2%, HOMO-4→LUMO+5 2%, HOMO-4→LUMO+8 1%, HOMO-3→LUMO+2 1%, HOMO-3→LUMO+6 4%, HOMO-3→LUMO+9 4%, HOMO-2→LUMO+3 4%, HOMO-2→LUMO+5 1%, HOMO-2→LUMO+10 6%, HOMO-1→LUMO+1 1%, HOMO-1→LUMO+2 8%, HOMO-1→LUMO+6 1%, HOMO-1→LUMO+9 3%
T ₁₉	259.415 nm	HOMO-16→LUMO+2 1%, HOMO-13→LUMO+1 1%, HOMO-13→LUMO+2 3%, HOMO-9→LUMO+1 1%, HOMO-9→LUMO+2 3%, HOMO-7→LUMO+2 1%, HOMO-6→LUMO+1 4%, HOMO-6→LUMO+2 9%, HOMO-5→LUMO+1 1%, HOMO-5→LUMO+2 4%, HOMO-4→HOMO 1%, HOMO-4→LUMO+1 14%, HOMO-4→LUMO+2 39%, HOMO-4→LUMO+9 1%, HOMO- 4→LUMO+10 3%
T ₂₀	257.504 nm	HOMO-17→LUMO+1 3%, HOMO-17→LUMO+2 1%, HOMO-14→LUMO+1 2%, HOMO-10→LUMO+1 3%, HOMO-10→LUMO+2 1%, HOMO- 7→LUMO+1 10%, HOMO-7→LUMO+2 3%, HOMO-6→LUMO+1 2%, HOMO- 5→LUMO+1 36%, HOMO-5→LUMO+2 13%, HOMO-5→LUMO+9 2%,

HOMO-5→LUMO+10 1%, HOMO-4→LUMO+1 5%, HOMO-4→LUMO+2 2%,
HOMO-3→HOMO 1%

Table S5 SOC states of $[\text{Ir}(\text{tpy})_2]^{3+}\cdot\text{Cl}^-$

State	Wavelength	Composition	f
1	368.509 nm	94%T ₁ , 5%T ₂	2.7×10 ⁻⁸
2	368.479 nm	95%T ₁ , 5%T ₂	6.8×10 ⁻⁶
3	368.445 nm	99%T ₁	7.1×10 ⁻⁷
4	367.373 nm	94%T ₂ , 6%T ₃	1.2×10 ⁻⁶
5	367.320 nm	5%T ₁ , 89%T ₂ , 5%T ₃	1.4×10 ⁻⁸
6	367.202 nm	5%T ₁ , 94%T ₂	1.4×10 ⁻⁵
7	365.655 nm	100%T ₃	1.1×10 ⁻⁵
8	365.551 nm	6%T ₂ , 94%T ₃	1.1×10 ⁻⁷
9	365.549 nm	6%T ₂ , 94%T ₃	4.6×10 ⁻⁷
10	363.605 nm	99%T ₄	1.1×10 ⁻⁵
11	363.593 nm	99%T ₄	2.4×10 ⁻⁷
12	363.568 nm	99%T ₄	1.1×10 ⁻⁸
13	350.040 nm	28%T ₃₂ , 70%T ₃₅	1.7×10 ⁻⁵
14	349.964 nm	28%T ₃₂ , 71%T ₃₅	2.6×10 ⁻⁶
15	348.351 nm	2%T ₂₃ , 96%T ₃₅	8.0×10 ⁻⁷
16	346.045 nm	33%T ₂₃ , 65%T ₃₂	6.8×10 ⁻⁶
17	345.343 nm	85%T ₂₃ , 8%T ₃₂ , 6%T ₃₅	7.1×10 ⁻⁶
18	345.216 nm	99%T ₂₃	2.5×10 ⁻⁶
19	344.613 nm	64%T ₂₃ , 34%T ₃₂	1.3×10 ⁻⁵
20	343.728 nm	71%T ₃₂ , 28%T ₃₅	5.2×10 ⁻⁶
21	343.474 nm	13%T ₂₃ , 63%T ₃₂ , 24%T ₃₅	4.0×10 ⁻⁷
22	328.600 nm	99%T ₂₆	2.1×10 ⁻⁷
23	328.577 nm	100%T ₂₆	5.8×10 ⁻⁶
24	328.576 nm	100%T ₂₆	3.2×10 ⁻⁵
25	314.507 nm	94%T ₅ , 2%T ₇	4.6×10 ⁻⁵
26	314.419 nm	2%S ₁ , 95%T ₅ , 2%T ₁₈	7.6×10 ⁻⁵
27	314.383 nm	96%T ₅ , 4%T ₇	1.7×10 ⁻⁶
28	311.387 nm	1%S ₁ , 88%T ₆ , 4%T ₈	1.5×10 ⁻⁴
29	311.261 nm	91%T ₆ , 6%T ₈	1.4×10 ⁻⁵
30	311.117 nm	91%T ₆ , 4%T ₇ , 3%T ₁₈	5.7×10 ⁻⁵
31	310.551 nm	4%T ₆ , 2%T ₇ , 91%T ₁₈ , 1%T ₂₄	7.6×10 ⁻⁵
32	310.291 nm	1%S ₁ , 2%T ₅ , 3%T ₆ , 91%T ₁₈	2.0×10 ⁻⁴
33	310.179 nm	1%T ₅ , 95%T ₁₈	1.4×10 ⁻⁴
34	307.905 nm	2%S ₂ , 90%T ₇ , 4%T ₈	4.4×10 ⁻⁴
35	307.644 nm	5%S ₂ , 82%T ₇ , 4%T ₈ , 4%T ₁₈	6.2×10 ⁻⁴
36	307.358 nm	2%T ₅ , 91%T ₇ , 2%T ₁₈	1.2×10 ⁻⁶
37	306.483 nm	19%S ₂ , 14%T ₇ , 66%T ₈	0.0027
38	305.261 nm	1%S ₁ , 6%T ₆ , 91%T ₈	4.0×10 ⁻⁴

39	305.231 nm	1% S_1 , 7% T_6 , 90% T_8	3.3×10^{-4}
40	303.975 nm	89% S_1 , 1% T_5 , 2% T_8 , 2% T_{18}	0.0268
41	302.831 nm	72% S_2 , 25% T_8	0.0177
42	298.626 nm	3% S_3 , 95% T_{24}	1.9×10^{-4}
43	298.398 nm	96% T_{24}	5.4×10^{-5}
44	298.038 nm	3% S_1 , 1% T_{18} , 95% T_{24}	0.0020
45	290.237 nm	95% S_3 , 3% T_{24}	0.0033
46	286.235 nm	2% T_{46} , 93% T_{47}	5.4×10^{-6}
47	286.204 nm	4% T_{46} , 95% T_{47}	3.4×10^{-5}
48	285.923 nm	7% T_9 , 91% T_{47}	2.8×10^{-7}
49	285.577 nm	65% T_9 , 31% T_{15} , 3% T_{47}	3.7×10^{-5}
50	285.567 nm	54% T_9 , 37% T_{15} , 8% T_{47}	1.4×10^{-6}

Table S6 SOC-free states of $[\text{Ir}(\text{tpy})_2]^{3+}\cdot\text{Cl}^-$

State	Wavelength	Composition
S_1	305.156 nm	HOMO-10 \rightarrow LUMO+2 2%, HOMO-5 \rightarrow LUMO 13%, HOMO-4 \rightarrow LUMO 50%, HOMO-2 \rightarrow LUMO 26%
S_2	304.660 nm	HOMO-9 \rightarrow LUMO+1 2%, HOMO-6 \rightarrow HOMO 1%, HOMO-5 \rightarrow HOMO 16%, HOMO-4 \rightarrow HOMO 66%, HOMO-2 \rightarrow HOMO 7%
S_3	291.368 nm	HOMO-8 \rightarrow HOMO 1%, HOMO-7 \rightarrow LUMO 12%, HOMO-5 \rightarrow LUMO+2 1%, HOMO-4 \rightarrow LUMO+2 1%, HOMO-2 \rightarrow LUMO+2 2%, HOMO-1 \rightarrow LUMO 69%, HOMO-1 \rightarrow LUMO+4 3%, HOMO-1 \rightarrow LUMO+8 4%
S_4	267.834 nm	HOMO-12 \rightarrow LUMO+2 1%, HOMO-6 \rightarrow LUMO 27%, HOMO-5 \rightarrow LUMO 8%, HOMO-4 \rightarrow LUMO 25%, HOMO-4 \rightarrow LUMO+4 1%, HOMO-2 \rightarrow LUMO 20%, HOMO-2 \rightarrow LUMO+8 1%, HOMO-1 \rightarrow LUMO+1 2%, HOMO-1 \rightarrow LUMO+2 5%
S_5	275.305 nm	HOMO-8 \rightarrow HOMO 4%, HOMO-7 \rightarrow LUMO 24%, HOMO-6 \rightarrow HOMO 2%, HOMO-6 \rightarrow LUMO+1 2%, HOMO-5 \rightarrow HOMO 1%, HOMO-5 \rightarrow LUMO+2 3%, HOMO-3 \rightarrow LUMO 40%, HOMO-3 \rightarrow LUMO+4 1%, HOMO-3 \rightarrow LUMO+8 2%, HOMO-2 \rightarrow LUMO+1 2%, HOMO-2 \rightarrow LUMO+2 4%, HOMO-1 \rightarrow LUMO 8%
S_6	262.351 nm	HOMO-13 \rightarrow LUMO+1 2%, HOMO-9 \rightarrow LUMO+1 1%, HOMO-9 \rightarrow LUMO+3 1%, HOMO-8 \rightarrow HOMO 20%, HOMO-6 \rightarrow HOMO 27%, HOMO-5 \rightarrow HOMO 24%, HOMO-5 \rightarrow LUMO+1 2%, HOMO-4 \rightarrow HOMO 3%, HOMO-4 \rightarrow LUMO+1 3%, HOMO-4 \rightarrow LUMO+2 2%
S_7	260.739 nm	HOMO-8 \rightarrow HOMO 31%, HOMO-7 \rightarrow LUMO 4%, HOMO-6 \rightarrow HOMO 15%, HOMO-6 \rightarrow LUMO+1 2%, HOMO-5 \rightarrow HOMO 6%, HOMO-5 \rightarrow LUMO+1 9%, HOMO-4 \rightarrow HOMO 2%, HOMO-4 \rightarrow LUMO+1 2%, HOMO-4 \rightarrow LUMO+2 7%, HOMO-4 \rightarrow LUMO+6 2%, HOMO-2 \rightarrow LUMO+2 7%
S_8	279.324 nm	HOMO-8 \rightarrow HOMO 1%, HOMO-7 \rightarrow LUMO 15%, HOMO-5 \rightarrow LUMO+2 2%, HOMO-3 \rightarrow LUMO 50%, HOMO-3 \rightarrow LUMO+4 2%, HOMO-3 \rightarrow LUMO+8 2%, HOMO-2 \rightarrow LUMO+1 2%, HOMO-2 \rightarrow LUMO+2 3%, HOMO-1 \rightarrow LUMO 12%
S_9	275.855 nm	HOMO-7 \rightarrow HOMO 7%, HOMO-7 \rightarrow LUMO+1 1%, HOMO-7 \rightarrow LUMO+2 4%, HOMO-4 \rightarrow LUMO+4 1%, HOMO-2 \rightarrow LUMO 8%, HOMO-1 \rightarrow LUMO+1 22%, HOMO-1 \rightarrow LUMO+2 45%, HOMO-1 \rightarrow LUMO+11 2%
S_{10}	257.461 nm	HOMO-19 \rightarrow HOMO 2%, HOMO-16 \rightarrow HOMO 3%, HOMO-10 \rightarrow HOMO 4%, HOMO-8 \rightarrow LUMO 1%, HOMO-7 \rightarrow HOMO 69%, HOMO-3 \rightarrow HOMO 3%, HOMO-2 \rightarrow LUMO 2%, HOMO-1 \rightarrow HOMO 5%, HOMO-1 \rightarrow LUMO+1 3%, HOMO-1 \rightarrow LUMO+2 3%
S_{11}	266.613 nm	HOMO-10 \rightarrow LUMO+2 1%, HOMO-10 \rightarrow LUMO+3 1%, HOMO-7 \rightarrow LUMO+2 2%, HOMO-6 \rightarrow LUMO 19%, HOMO-5 \rightarrow LUMO 19%, HOMO-4 \rightarrow LUMO 5%,

		HOMO-4→LUMO+4 1%, HOMO-2→LUMO 32%, HOMO-2→LUMO+4 5%, HOMO-2→LUMO+8 2%
S ₁₂	249.640 nm	HOMO-13→HOMO 2%, HOMO-12→LUMO 1%, HOMO-7→LUMO 2%, HOMO-6→LUMO+1 11%, HOMO-6→LUMO+3 2%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+1 45%, HOMO-2→LUMO+1 16%, HOMO-2→LUMO+2 5%
S ₁₃	250.498 nm	HOMO-20→LUMO 3%, HOMO-17→LUMO 3%, HOMO-9→LUMO 7%, HOMO-8→LUMO 82%
S ₁₄	274.201 nm	HOMO-7→LUMO+1 2%, HOMO-7→LUMO+2 6%, HOMO-3→LUMO+1 30%, HOMO-3→LUMO+2 54%, HOMO-3→LUMO+11 2%
S ₁₅	264.868 nm	HOMO-8→LUMO+1 1%, HOMO-7→LUMO 8%, HOMO-6→LUMO+1 2%, HOMO-4→LUMO+1 15%, HOMO-4→LUMO+2 7%, HOMO-2→LUMO+1 15%, HOMO-2→LUMO+2 41%, HOMO-2→LUMO+11 1%
S ₁₆	241.029 nm	HOMO-15→HOMO 2%, HOMO-14→HOMO 2%, HOMO-8→LUMO+1 46%, HOMO-8→LUMO+2 17%, HOMO-6→LUMO+7 2%, HOMO-5→LUMO+5 3%, HOMO-5→LUMO+7 2%, HOMO-4→LUMO+5 7%, HOMO-2→HOMO 1%, HOMO-2→LUMO+1 2%
S ₁₇	236.975 nm	HOMO-13→HOMO 1%, HOMO-12→LUMO 2%, HOMO-11→LUMO+1 2%, HOMO-10→LUMO 5%, HOMO-10→LUMO+4 3%, HOMO-9→HOMO 4%, HOMO-9→LUMO+5 2%, HOMO-7→LUMO+4 1%, HOMO-6→LUMO+2 19%, HOMO-5→LUMO+3 7%, HOMO-4→LUMO+2 33%, HOMO-4→LUMO+6 4%, HOMO-2→LUMO+6 1%
S ₁₈	240.263 nm	HOMO-14→LUMO 2%, HOMO-7→LUMO+1 14%, HOMO-7→LUMO+2 35%, HOMO-6→LUMO+8 1%, HOMO-5→LUMO 3%, HOMO-5→LUMO+4 2%, HOMO-5→LUMO+8 2%, HOMO-4→LUMO+4 5%, HOMO-3→LUMO+1 4%, HOMO-3→LUMO+2 6%, HOMO-2→LUMO 2%, HOMO-2→LUMO+4 1%, HOMO-1→LUMO+1 5%, HOMO-1→LUMO+2 7%
S ₁₉	275.393 nm	HOMO-7→HOMO 2%, HOMO-3→HOMO 64%, HOMO-3→LUMO+1 12%, HOMO-3→LUMO+2 4%, HOMO-3→LUMO+3 4%, HOMO-3→LUMO+5 5%, HOMO-3→LUMO+6 4%, HOMO-1→HOMO 1%
S ₂₀	274.282 nm	HOMO-7→HOMO 6%, HOMO-1→HOMO 66%, HOMO-1→LUMO+1 12%, HOMO-1→LUMO+2 4%, HOMO-1→LUMO+3 3%, HOMO-1→LUMO+5 3%, HOMO-1→LUMO+6 3%
T ₁	369.864 nm	HOMO-9→HOMO 2%, HOMO-9→LUMO+1 2%, HOMO-9→LUMO+7 2%, HOMO-8→HOMO 8%, HOMO-6→LUMO+1 3%, HOMO-5→HOMO 13%, HOMO-5→LUMO+1 13%, HOMO-5→LUMO+2 5%, HOMO-4→HOMO 19%, HOMO-4→LUMO+1 10%, HOMO-4→LUMO+2 3%, HOMO-2→HOMO 3%, HOMO-2→LUMO+1 2%
T ₂	368.676 nm	HOMO-14→LUMO+8 1%, HOMO-10→LUMO+1 2%, HOMO-10→LUMO+2 4%, HOMO-7→LUMO 2%, HOMO-7→LUMO+2 1%, HOMO-6→LUMO 2%, HOMO-5→LUMO 20%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO 30%, HOMO-4→LUMO+2 1%, HOMO-2→LUMO 18%, HOMO-2→LUMO+2 1%
T ₃	367.098 nm	HOMO-14→LUMO+11 1%, HOMO-10→LUMO 4%, HOMO-10→LUMO+8 3%, HOMO-7→LUMO 16%, HOMO-7→LUMO+4 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 4%, HOMO-5→LUMO 2%, HOMO-5→LUMO+1 6%, HOMO-5→LUMO+2 15%, HOMO-4→LUMO 3%, HOMO-4→LUMO+1 5%, HOMO-4→LUMO+2 9%, HOMO-2→LUMO 2%, HOMO-2→LUMO+1 4%, HOMO-2→LUMO+2 9%
T ₄	365.027 nm	HOMO-9→HOMO 3%, HOMO-9→LUMO+1 3%, HOMO-9→LUMO+2 1%, HOMO-9→LUMO+7 2%, HOMO-8→HOMO 10%, HOMO-8→LUMO+1 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 1%, HOMO-5→HOMO 17%, HOMO-5→LUMO+1 11%, HOMO-5→LUMO+2 3%, HOMO-4→HOMO 22%, HOMO-4→LUMO+1 5%, HOMO-4→LUMO+2 4%, HOMO-2→HOMO 1%
T ₅	315.013 nm	HOMO-16→LUMO 2%, HOMO-12→LUMO+4 2%, HOMO-12→LUMO+8 1%, HOMO-10→LUMO 8%, HOMO-10→LUMO+4 1%, HOMO-7→LUMO 39%,

		HOMO-7→LUMO+8 5%, HOMO-5→LUMO+1 1%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+2 6%, HOMO-2→LUMO+2 2%, HOMO-1→LUMO 16%, HOMO-1→LUMO+4 1%, HOMO-1→LUMO+8 2%
T ₆	311.754 nm	HOMO-13→LUMO+1 3%, HOMO-13→LUMO+2 1%, HOMO-13→LUMO+3 2%, HOMO-13→LUMO+6 1%, HOMO-11→HOMO 5%, HOMO-11→LUMO+5 1%, HOMO-8→HOMO 2%, HOMO-8→LUMO+1 3%, HOMO-8→LUMO+2 1%, HOMO-6→HOMO 39%, HOMO-6→LUMO+5 2%, HOMO-5→HOMO 10%, HOMO-4→HOMO 12%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+5 1%
T ₇	308.674 nm	HOMO-12→LUMO+1 1%, HOMO-12→LUMO+2 3%, HOMO-12→LUMO+3 3%, HOMO-12→LUMO+6 1%, HOMO-11→LUMO 6%, HOMO-11→LUMO+4 1%, HOMO-7→LUMO+2 3%, HOMO-7→LUMO+3 1%, HOMO-6→LUMO 40%, HOMO-6→LUMO+4 2%, HOMO-5→LUMO 9%, HOMO-4→LUMO 17%, HOMO-4→LUMO+4 1%
T ₈	306.396 nm	HOMO-17→HOMO 2%, HOMO-13→LUMO+5 2%, HOMO-13→LUMO+7 1%, HOMO-9→HOMO 9%, HOMO-9→LUMO+5 1%, HOMO-8→HOMO 49%, HOMO-8→LUMO+7 4%, HOMO-6→HOMO 2%, HOMO-5→LUMO+1 2%, HOMO-4→HOMO 2%, HOMO-4→LUMO+1 6%, HOMO-4→LUMO+2 2%
T ₉	286.239 nm	HOMO-15→LUMO+3 1%, HOMO-14→LUMO+2 1%, HOMO-14→LUMO+3 1%, HOMO-12→LUMO 7%, HOMO-12→LUMO+4 1%, HOMO-11→LUMO+2 1%, HOMO-11→LUMO+3 1%, HOMO-10→LUMO 16%, HOMO-10→LUMO+4 8%, HOMO-7→LUMO 4%, HOMO-7→LUMO+4 8%, HOMO-6→LUMO+2 4%, HOMO-6→LUMO+3 8%, HOMO-6→LUMO+6 5%, HOMO-5→LUMO+3 5%, HOMO-5→LUMO+6 3%, HOMO-4→LUMO+2 2%, HOMO-2→LUMO+3 1%, HOMO-1→LUMO 7%
T ₁₀	283.475 nm	HOMO-15→LUMO+1 2%, HOMO-15→LUMO+2 1%, HOMO-15→LUMO+3 1%, HOMO-14→LUMO+1 2%, HOMO-13→HOMO 5%, HOMO-9→HOMO 26%, HOMO-9→LUMO+5 7%, HOMO-8→LUMO+5 10%, HOMO-8→LUMO+7 2%, HOMO-6→LUMO+1 1%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+3 6%, HOMO-6→LUMO+6 5%, HOMO-5→LUMO+3 6%, HOMO-5→LUMO+6 6%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+3 1%
T ₁₁	280.251 nm	HOMO-15→LUMO+1 1%, HOMO-15→LUMO+2 2%, HOMO-14→LUMO+1 1%, HOMO-14→LUMO+2 5%, HOMO-12→LUMO 14%, HOMO-12→LUMO+4 2%, HOMO-11→LUMO+2 3%, HOMO-11→LUMO+3 2%, HOMO-11→LUMO+6 1%, HOMO-10→LUMO 8%, HOMO-10→LUMO+4 2%, HOMO-7→LUMO 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 8%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+2 2%, HOMO-5→LUMO+3 3%, HOMO-5→LUMO+11 1%, HOMO-4→LUMO+2 3%, HOMO-4→LUMO+3 6%, HOMO-4→LUMO+6 5%, HOMO-4→LUMO+11 1%, HOMO-2→LUMO+1 1%, HOMO-2→LUMO+2 2%, HOMO-2→LUMO+3 2%, HOMO-2→LUMO+6 2%, HOMO-2→LUMO+11 1%, HOMO-1→LUMO 3%
T ₁₂	278.228 nm	HOMO-15→LUMO+1 2%, HOMO-15→LUMO+2 1%, HOMO-14→LUMO+1 3%, HOMO-13→HOMO 18%, HOMO-13→LUMO+5 2%, HOMO-11→LUMO+1 3%, HOMO-11→LUMO+2 2%, HOMO-11→LUMO+3 2%, HOMO-11→LUMO+6 2%, HOMO-9→HOMO 2%, HOMO-9→LUMO+5 2%, HOMO-8→HOMO 5%, HOMO-6→LUMO+1 11%, HOMO-6→LUMO+2 4%, HOMO-5→LUMO+1 6%, HOMO-5→LUMO+2 2%, HOMO-5→LUMO+3 1%, HOMO-5→LUMO+6 1%, HOMO-5→LUMO+9 1%, HOMO-4→LUMO+3 6%, HOMO-4→LUMO+6 5%, HOMO-4→LUMO+9 1%
T ₁₃	278.001 nm	HOMO-15→LUMO 4%, HOMO-14→LUMO 8%, HOMO-14→LUMO+4 1%, HOMO-10→LUMO+2 2%, HOMO-10→LUMO+3 11%, HOMO-10→LUMO+6 7%, HOMO-7→LUMO+3 5%, HOMO-7→LUMO+6 3%, HOMO-6→LUMO+4 9%, HOMO-5→LUMO+4 16%, HOMO-5→LUMO+8 1%, HOMO-4→LUMO 3%, HOMO-4→LUMO+4 7%, HOMO-2→LUMO 3%, HOMO-2→LUMO+4 9%, HOMO-2→LUMO+8 2%

T ₁₄	275.006 nm	HOMO-15→HOMO 6%, HOMO-15→LUMO+5 1%, HOMO-14→HOMO 6%, HOMO-9→LUMO+3 11%, HOMO-9→LUMO+6 8%, HOMO-8→LUMO+3 5%, HOMO-8→LUMO+6 4%, HOMO-6→LUMO+5 10%, HOMO-5→LUMO+5 23%, HOMO-4→LUMO+5 9%, HOMO-4→LUMO+7 1%, HOMO-2→LUMO+5 1%
T ₁₅	285.890 nm	HOMO-19→LUMO+2 2%, HOMO-16→LUMO+2 2%, HOMO-14→LUMO 1%, HOMO-12→LUMO+2 2%, HOMO-7→LUMO+1 10%, HOMO-7→LUMO+2 22%, HOMO-2→LUMO 3%, HOMO-1→LUMO+1 14%, HOMO-1→LUMO+2 29%, HOMO-1→LUMO+11 2%
T ₁₆	273.936 nm	HOMO-15→LUMO 3%, HOMO-15→LUMO+4 2%, HOMO-14→LUMO 5%, HOMO-14→LUMO+4 2%, HOMO-10→LUMO+1 7%, HOMO-10→LUMO+2 12%, HOMO-10→LUMO+3 2%, HOMO-10→LUMO+6 2%, HOMO-10→LUMO+11 1%, HOMO-7→LUMO+3 1%, HOMO-7→LUMO+11 1%, HOMO-6→LUMO 2%, HOMO-6→LUMO+4 4%, HOMO-6→LUMO+8 4%, HOMO-5→LUMO+4 2%, HOMO-5→LUMO+8 8%, HOMO-4→LUMO 1%, HOMO-4→LUMO+8 3%, HOMO-2→LUMO 9%, HOMO-2→LUMO+8 6%, HOMO-1→LUMO+1 3%, HOMO-1→LUMO+2 6%
T ₁₇	272.498 nm	HOMO-15→HOMO 8%, HOMO-15→LUMO+5 2%, HOMO-14→HOMO 7%, HOMO-14→LUMO+5 1%, HOMO-13→LUMO+3 1%, HOMO-11→LUMO+5 1%, HOMO-9→LUMO+1 12%, HOMO-9→LUMO+2 3%, HOMO-9→LUMO+6 1%, HOMO-9→LUMO+9 3%, HOMO-8→LUMO+1 9%, HOMO-8→LUMO+2 2%, HOMO-8→LUMO+6 1%, HOMO-6→LUMO+5 3%, HOMO-6→LUMO+7 5%, HOMO-5→HOMO 2%, HOMO-5→LUMO+7 14%, HOMO-4→HOMO 5%, HOMO-4→LUMO+7 6%
T ₁₈	311.136 nm	HOMO-10→LUMO+4 4%, HOMO-7→LUMO 10%, HOMO-7→LUMO+4 4%, HOMO-6→LUMO+3 2%, HOMO-3→LUMO 28%, HOMO-3→LUMO+4 1%, HOMO-3→LUMO+8 1%, HOMO-2→LUMO+2 1%, HOMO-1→LUMO 28%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+8 2%
T ₁₉	263.078 nm	HOMO-15→LUMO+1 1%, HOMO-15→LUMO+2 3%, HOMO-15→LUMO+6 1%, HOMO-14→LUMO+1 6%, HOMO-13→LUMO+5 1%, HOMO-12→LUMO 1%, HOMO-11→LUMO+2 1%, HOMO-10→LUMO 3%, HOMO-10→LUMO+4 3%, HOMO-9→HOMO 4%, HOMO-9→LUMO+5 7%, HOMO-9→LUMO+7 2%, HOMO-8→HOMO 1%, HOMO-8→LUMO+5 4%, HOMO-8→LUMO+7 2%, HOMO-7→LUMO+8 1%, HOMO-6→LUMO+1 6%, HOMO-6→LUMO+3 3%, HOMO-6→LUMO+11 2%, HOMO-5→LUMO+6 3%, HOMO-5→LUMO+9 5%, HOMO-4→LUMO+1 6%, HOMO-4→LUMO+3 1%, HOMO-3→LUMO 6%, HOMO-1→LUMO 3%
T ₂₀	262.544 nm	HOMO-15→LUMO+1 6%, HOMO-14→LUMO+2 6%, HOMO-14→LUMO+6 1%, HOMO-12→LUMO 1%, HOMO-11→LUMO+1 1%, HOMO-10→LUMO 6%, HOMO-10→LUMO+4 7%, HOMO-10→LUMO+8 2%, HOMO-9→HOMO 2%, HOMO-9→LUMO+5 4%, HOMO-9→LUMO+7 2%, HOMO-8→LUMO+5 2%, HOMO-8→LUMO+7 1%, HOMO-7→LUMO+4 2%, HOMO-7→LUMO+8 2%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+6 3%, HOMO-6→LUMO+9 3%, HOMO-5→LUMO+3 5%, HOMO-5→LUMO+11 5%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+2 4%, HOMO-4→LUMO+6 1%, HOMO-4→LUMO+9 1%, HOMO-3→LUMO 7%, HOMO-2→LUMO+2 5%, HOMO-1→LUMO 2%

Table S7 SOC states of $[\text{Ir}(\text{tpy})_2]^{3+}\cdot\text{Br}^-$

State	Wavelength	Composition	f
1	448.970 nm	2% S_3 , 93% T_5 , 2% T_6	1.5×10^{-4}
2	448.221 nm	93% T_5 , 5% T_6	7.1×10^{-7}
3	447.169 nm	1% S_2 , 96% T_5	1.0×10^{-4}
4	401.552 nm	17% S_1 , 80% T_6	0.0033
5	399.524 nm	1% S_1 , 2% S_2 , 20% S_3 , 73% T_6	0.0022
6	395.421 nm	2% T_1 , 2% T_5 , 86% T_6 , 5% T_7	3.7×10^{-6}
7	381.964 nm	16% S_1 , 45% T_1 , 8% T_2 , 20% S_3 , 5% T_6 , 4% T_7	0.0012
8	379.600 nm	8% S_1 , 75% T_1 , 4% S_2 , 1% T_2 , 4% T_6 , 2% T_{20}	0.0015
9	378.387 nm	91% T_1 , 1% T_7 , 4% T_{20}	1.9×10^{-5}
10	377.598 nm	30% S_1 , 47% T_1 , 6% T_2 , 5% T_6 , 6% T_7 , 1% T_{20}	0.0057
11	375.498 nm	1% S_1 , 6% T_3 , 4% S_{11} , 86% T_{20}	2.9×10^{-4}
12	374.726 nm	2% S_1 , 10% T_1 , 4% S_2 , 24% T_2 , 8% S_3 , 4% T_3 , 2% T_6 , 42% T_{20}	7.2×10^{-4}
13	374.228 nm	9% T_1 , 10% T_2 , 2% S_3 , 5% T_3 , 69% T_{20}	1.8×10^{-4}
14	373.977 nm	2% S_1 , 4% T_1 , 1% S_2 , 19% T_2 , 3% S_3 , 63% T_{20}	0.0022
15	371.971 nm	3% S_1 , 90% T_2	0.0014
16	371.814 nm	7% S_1 , 1% S_2 , 85% T_2 , 1% T_6	0.0025
17	369.807 nm	2% T_2 , 95% T_3	5.9×10^{-5}
18	369.520 nm	3% T_2 , 1% S_3 , 86% T_3 , 4% T_{20}	6.4×10^{-5}
19	369.184 nm	1% S_2 , 2% T_2 , 1% S_3 , 83% T_3 , 9% T_{20}	7.4×10^{-5}
20	368.692 nm	3% T_1 , 12% S_2 , 32% T_2 , 16% S_3 , 16% T_3 , 1% T_6 , 12% T_7 , 2% T_{20}	8.3×10^{-4}
21	364.962 nm	100% T_4	2.5×10^{-5}
22	364.954 nm	99% T_4	2.8×10^{-6}
23	364.942 nm	99% T_4	6.3×10^{-6}
24	359.626 nm	2% S_1 , 3% T_1 , 46% S_2 , 6% T_2 , 17% S_3 , 3% T_5 , 11% T_6 , 8% T_7 , 1% T_{10}	0.0110
25	347.221 nm	5% T_6 , 88% T_7	5.0×10^{-5}
26	345.691 nm	6% S_1 , 2% S_3 , 4% T_6 , 80% T_7 , 2% T_{10}	0.0011
27	344.398 nm	14% S_2 , 2% S_3 , 70% T_7 , 5% T_{10}	2.8×10^{-4}
28	333.050 nm	1% T_8 , 5% S_9 , 73% S_{11} , 2% T_{12} , 3% T_{20} , 4% T_{21} , 1% T_{23}	0.0046
29	330.924 nm	66% S_9 , 3% T_{10} , 7% S_{11} , 11% T_{12}	0.0011
30	330.610 nm	49% T_{35} , 45% T_{39} , 2% T_{44}	1.6×10^{-4}
31	330.503 nm	52% T_{35} , 45% T_{39}	3.4×10^{-5}
32	327.959 nm	4% S_7 , 17% S_8 , 52% T_{10} , 3% T_{11} , 15% T_{12} , 2% T_{21}	0.0023
33	326.394 nm	2% S_1 , 4% S_8 , 5% S_9 , 69% T_{10} , 6% T_{11} , 1% T_{12}	1.7×10^{-4}
34	326.093 nm	3% S_2 , 3% S_5 , 4% S_8 , 74% T_{10} , 9% T_{12}	0.0051
35	324.982 nm	1% S_2 , 2% S_6 , 23% S_7 , 10% S_8 , 2% S_{10} , 27% T_{10} , 4% T_{11} , 5% T_{12} , 16% T_{21} , 2% T_{35}	0.0024
36	324.320 nm	2% S_8 , 92% T_{35}	9.3×10^{-5}
37	323.665 nm	1% S_6 , 5% S_7 , 11% S_8 , 2% T_8 , 2% S_9 , 14% S_{10} , 5% T_{10} , 28% T_{12} , 14% T_{21} , 1% T_{23} , 8% T_{39}	0.0031
38	323.328 nm	7% S_7 , 35% T_{12} , 17% T_{21} , 34% T_{39}	0.0068
39	322.929 nm	2% S_8 , 4% S_{10} , 5% T_{10} , 24% T_{12} , 8% T_{21} , 47% T_{39}	0.0011
40	322.660 nm	7% S_7 , 2% S_8 , 3% S_{10} , 10% T_{10} , 31% T_{12} , 34% T_{21} , 2% T_{39}	0.0025

41	321.369 nm	2% S_5 , 24% S_6 , 1% S_8 , 2% T_8 , 14% S_{10} , 3% T_{10} , 11% T_{12} , 35% T_{21}	0.0244
42	319.891 nm	6% S_6 , 23% S_7 , 17% S_8 , 1% S_9 , 6% S_{10} , 15% T_{12} , 5% T_{16} , 10% T_{21} , 7% T_{23} , 1% T_{25}	0.0507
43	318.543 nm	3% S_7 , 3% S_8 , 2% T_8 , 2% S_9 , 20% S_{10} , 34% T_{12} , 21% T_{16} , 2% T_{21}	0.0091
44	318.117 nm	3% T_{21} , 1% S_{23} , 36% T_{35} , 28% T_{39} , 23% T_{44}	8.1×10^{-4}
45	317.589 nm	1% S_6 , 36% T_{35} , 36% T_{39} , 17% T_{44}	3.3×10^{-4}
46	317.047 nm	4% S_7 , 2% T_8 , 5% S_{10} , 14% T_{12} , 19% T_{16} , 39% T_{21} , 2% T_{23} , 2% T_{35} , 2% T_{39} , 1% T_{44}	0.0123
47	316.245 nm	6% S_6 , 70% T_8 , 1% T_9 , 5% T_{16} , 7% T_{21} , 1% T_{23}	0.0017
48	316.001 nm	2% S_5 , 11% S_6 , 64% T_8 , 9% T_{16} , 5% T_{21} , 4% T_{23}	0.0024
49	315.607 nm	2% S_5 , 8% S_6 , 62% T_8 , 2% S_{10} , 9% T_{16} , 4% T_{21} , 5% T_{23}	0.0024
50	314.500 nm	5% S_6 , 65% T_8 , 3% S_{11} , 10% T_{16} , 8% T_{21}	6.4×10^{-4}

Table S8 SOC-free states of $[\text{Ir}(\text{tpy})_2]^{3+}\cdot\text{Br}^-$

State	Wavelength	Composition
S ₁	377.622 nm	HOMO-5→LUMO 1%, HOMO-4→LUMO 5%, HOMO-1→LUMO 62%, HOMO-1→LUMO+1 10%, HOMO-1→LUMO+2 16%
S ₂	360.429 nm	HOMO-5→LUMO 1%, HOMO-4→LUMO 10%, HOMO-3→LUMO 12%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 3%, HOMO-2→LUMO 48%, HOMO-2→LUMO+1 7%, HOMO-2→LUMO+2 9%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 3%
S ₃	377.380 nm	HOMO-3→LUMO 50%, HOMO-3→LUMO+1 8%, HOMO-3→LUMO+2 14%, HOMO-2→LUMO 17%, HOMO-2→LUMO+1 3%, HOMO-2→LUMO+2 3%
S ₄	304.483 nm	HOMO-10→LUMO+1 2%, HOMO-5→HOMO 18%, HOMO-4→HOMO 70%, HOMO-4→LUMO 1%
S ₅	309.622 nm	HOMO-5→LUMO 6%, HOMO-4→HOMO 2%, HOMO-4→LUMO 38%, HOMO-3→LUMO 3%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 3%, HOMO-2→LUMO 5%, HOMO-2→LUMO+1 3%, HOMO-2→LUMO+2 3%, HOMO-1→LUMO 2%, HOMO-1→LUMO+1 10%, HOMO-1→LUMO+2 17%
S ₆	313.255 nm	HOMO-6→LUMO 2%, HOMO-5→LUMO 2%, HOMO-4→LUMO 24%, HOMO-2→HOMO 3%, HOMO-2→LUMO+2 3%, HOMO-1→LUMO 24%, HOMO-1→LUMO+1 12%, HOMO-1→LUMO+2 19%, HOMO-1→LUMO+8 2%
S ₇	318.739 nm	HOMO-8→HOMO 2%, HOMO-6→HOMO 4%, HOMO-4→HOMO 2%, HOMO-2→HOMO 41%, HOMO-2→LUMO 6%, HOMO-2→LUMO+1 23%, HOMO-2→LUMO+2 1%, HOMO-2→LUMO+5 2%, HOMO-2→LUMO+6 2%, HOMO-1→HOMO 3%, HOMO-1→LUMO+1 2%
S ₈	317.761 nm	HOMO-7→LUMO 1%, HOMO-4→LUMO 1%, HOMO-3→LUMO 2%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 2%, HOMO-2→HOMO 6%, HOMO-2→LUMO 16%, HOMO-2→LUMO+1 10%, HOMO-2→LUMO+2 34%, HOMO-2→LUMO+8 2%, HOMO-1→HOMO 9%, HOMO-1→LUMO+1 2%
S ₉	325.693 nm	HOMO-3→LUMO 18%, HOMO-3→LUMO+1 17%, HOMO-3→LUMO+2 23%, HOMO-3→LUMO+8 2%, HOMO-1→HOMO 27%, HOMO-1→LUMO+1 6%, HOMO-1→LUMO+5 1%
S ₁₀	314.700 nm	HOMO-6→HOMO 2%, HOMO-5→HOMO 2%, HOMO-3→LUMO 7%, HOMO-3→LUMO+1 8%, HOMO-3→LUMO+2 9%, HOMO-2→HOMO 7%, HOMO-2→LUMO 2%, HOMO-2→LUMO+2 7%, HOMO-1→HOMO 33%, HOMO-1→LUMO 3%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 6%, HOMO-1→LUMO+5 2%
S ₁₁	331.093 nm	HOMO-3→HOMO 68%, HOMO-3→LUMO 2%, HOMO-3→LUMO+1 8%,

		HOMO-3→LUMO+2 10%, HOMO-3→LUMO+4 2%, HOMO-3→LUMO+5 4%, HOMO-3→LUMO+6 2%
S ₁₂	261.552 nm	HOMO-8→HOMO 37%, HOMO-8→LUMO 2%, HOMO-7→HOMO 10%, HOMO-7→LUMO 6%, HOMO-6→HOMO 8%, HOMO-6→LUMO+1 3%, HOMO-5→HOMO 6%, HOMO-5→LUMO+1 3%, HOMO-5→LUMO+2 4%, HOMO-4→LUMO+1 5%, HOMO-4→LUMO+2 2%, HOMO-4→LUMO+3 2%
S ₁₃	258.260 nm	HOMO-8→HOMO 2%, HOMO-8→LUMO 2%, HOMO-7→LUMO 23%, HOMO-6→LUMO 20%, HOMO-5→LUMO 14%, HOMO-5→LUMO+1 5%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO 2%, HOMO-4→LUMO+2 9%, HOMO-4→LUMO+5 1%, HOMO-4→LUMO+6 2%
S ₁₄	256.653 nm	HOMO-12→LUMO+2 1%, HOMO-9→LUMO+2 1%, HOMO-9→LUMO+3 1%, HOMO-8→LUMO 3%, HOMO-7→LUMO 24%, HOMO-6→HOMO 2%, HOMO-6→LUMO 20%, HOMO-5→LUMO 17%, HOMO-5→LUMO+1 1%, HOMO-5→LUMO+2 1%, HOMO-4→LUMO+2 5%, HOMO-4→LUMO+4 2%, HOMO-1→LUMO 2%
S ₁₅	259.024 nm	HOMO-13→LUMO+1 1%, HOMO-8→HOMO 4%, HOMO-7→HOMO 7%, HOMO-6→HOMO 28%, HOMO-6→LUMO 2%, HOMO-5→HOMO 14%, HOMO-5→LUMO+1 2%, HOMO-4→HOMO 3%, HOMO-4→LUMO+1 6%, HOMO-4→LUMO+2 2%, HOMO-2→HOMO 7%, HOMO-2→LUMO+1 4%, HOMO-2→LUMO+2 3%
S ₁₆	254.939 nm	HOMO-19→HOMO 3%, HOMO-16→HOMO 3%, HOMO-9→HOMO 5%, HOMO-8→HOMO 13%, HOMO-8→LUMO 2%, HOMO-7→HOMO 63%, HOMO-6→HOMO 1%, HOMO-4→LUMO+1 3%
S ₁₇	247.987 nm	HOMO-13→HOMO 1%, HOMO-12→LUMO 1%, HOMO-8→HOMO 5%, HOMO-6→LUMO+1 13%, HOMO-6→LUMO+3 2%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+1 54%, HOMO-4→LUMO+2 3%, HOMO-2→HOMO 2%
S ₁₈	249.806 nm	HOMO-20→LUMO 3%, HOMO-17→LUMO 2%, HOMO-10→LUMO 6%, HOMO-8→HOMO 2%, HOMO-8→LUMO 72%, HOMO-7→LUMO 9%
S ₁₉	242.403 nm	HOMO-15→HOMO 2%, HOMO-14→HOMO 1%, HOMO-8→LUMO+1 36%, HOMO-8→LUMO+2 14%, HOMO-7→LUMO+1 6%, HOMO-7→LUMO+2 2%, HOMO-6→LUMO+1 1%, HOMO-6→LUMO+7 2%, HOMO-5→LUMO+4 1%, HOMO-5→LUMO+5 1%, HOMO-5→LUMO+7 2%, HOMO-4→LUMO+3 1%, HOMO-4→LUMO+4 3%, HOMO-4→LUMO+5 4%, HOMO-2→HOMO 4%, HOMO-2→LUMO+1 2%, HOMO-2→LUMO+2 2%
S ₂₀	240.105 nm	HOMO-15→LUMO 1%, HOMO-14→LUMO 2%, HOMO-8→LUMO+1 3%, HOMO-8→LUMO+2 5%, HOMO-7→LUMO+1 16%, HOMO-7→LUMO+2 37%, HOMO-6→LUMO+8 1%, HOMO-5→LUMO 1%, HOMO-5→LUMO+4 2%, HOMO-5→LUMO+8 2%, HOMO-4→LUMO 1%, HOMO-4→LUMO+4 5%, HOMO-4→LUMO+5 3%, HOMO-1→LUMO+4 2%, HOMO-1→LUMO+5 3%, HOMO-1→LUMO+8 1%
T ₁	379.383 nm	HOMO-14→LUMO+8 1%, HOMO-9→LUMO+1 1%, HOMO-9→LUMO+2 3%, HOMO-7→LUMO 3%, HOMO-6→LUMO 1%, HOMO-5→LUMO 17%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO 31%, HOMO-4→LUMO+2 2%, HOMO-3→LUMO 1%, HOMO-2→LUMO 2%, HOMO-1→LUMO 18%
T ₂	373.168 nm	HOMO-14→LUMO+11 1%, HOMO-9→LUMO 3%, HOMO-9→LUMO+8 2%, HOMO-8→LUMO 1%, HOMO-7→LUMO 9%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 3%, HOMO-5→LUMO 2%, HOMO-5→LUMO+1 4%, HOMO-5→LUMO+2 15%, HOMO-4→LUMO 5%, HOMO-4→LUMO+1 8%, HOMO-4→LUMO+2 12%, HOMO-3→LUMO 1%, HOMO-3→LUMO+2 2%, HOMO-2→LUMO+2 1%, HOMO-1→LUMO 1%, HOMO-1→LUMO+1 4%, HOMO-1→LUMO+2 8%
T ₃	371.005 nm	HOMO-10→HOMO 3%, HOMO-10→LUMO+1 2%, HOMO-10→LUMO+7 2%, HOMO-8→HOMO 9%, HOMO-7→HOMO 1%, HOMO-6→HOMO 1%, HOMO- 6→LUMO+1 4%, HOMO-6→LUMO+2 2%, HOMO-5→HOMO 8%, HOMO-

		5→LUMO+1 17%, HOMO-5→LUMO+2 3%, HOMO-4→HOMO 13%, HOMO-4→LUMO+1 10%, HOMO-4→LUMO+2 6%, HOMO-2→HOMO 3%, HOMO-2→LUMO+1 2%
T ₄	366.274 nm	HOMO-10→HOMO 2%, HOMO-10→LUMO+1 4%, HOMO-10→LUMO+2 1%, HOMO-10→LUMO+7 1%, HOMO-8→HOMO 6%, HOMO-8→LUMO+1 1%, HOMO-7→HOMO 1%, HOMO-6→HOMO 1%, HOMO-6→LUMO+1 2%, HOMO-5→HOMO 22%, HOMO-5→LUMO+1 6%, HOMO-5→LUMO+2 2%, HOMO-4→HOMO 30%, HOMO-4→LUMO+1 4%, HOMO-4→LUMO+2 2%
T ₅	443.483 nm	HOMO-9→LUMO+2 1%, HOMO-4→LUMO 6%, HOMO-3→LUMO 3%, HOMO-3→LUMO+2 1%, HOMO-2→LUMO 5%, HOMO-2→LUMO+2 1%, HOMO-1→LUMO 41%, HOMO-1→LUMO+1 9%, HOMO-1→LUMO+2 16%
T ₆	394.536 nm	HOMO-9→LUMO 1%, HOMO-8→LUMO 2%, HOMO-7→LUMO 11%, HOMO-6→LUMO 2%, HOMO-5→LUMO 3%, HOMO-3→LUMO 2%, HOMO-2→LUMO 47%, HOMO-2→LUMO+1 7%, HOMO-2→LUMO+2 11%, HOMO-1→LUMO+2 1%
T ₇	350.806 nm	HOMO-12→LUMO+2 2%, HOMO-12→LUMO+3 1%, HOMO-11→LUMO 3%, HOMO-9→LUMO 2%, HOMO-7→LUMO 3%, HOMO-6→LUMO 11%, HOMO-4→LUMO 15%, HOMO-3→LUMO 32%, HOMO-3→LUMO+1 5%, HOMO-3→LUMO+2 8%, HOMO-1→LUMO 2%
T ₈	316.201 nm	HOMO-13→LUMO+1 2%, HOMO-13→LUMO+3 2%, HOMO-13→LUMO+6 1%, HOMO-11→HOMO 5%, HOMO-8→LUMO+1 2%, HOMO-6→HOMO 36%, HOMO-6→LUMO+4 1%, HOMO-6→LUMO+5 1%, HOMO-5→HOMO 5%, HOMO-4→HOMO 16%, HOMO-2→HOMO 10%, HOMO-2→LUMO+1 1%
T ₉	307.341 nm	HOMO-17→HOMO 2%, HOMO-13→LUMO+7 1%, HOMO-10→HOMO 9%, HOMO-8→HOMO 44%, HOMO-8→LUMO+7 4%, HOMO-7→HOMO 7%, HOMO-6→LUMO+6 1%, HOMO-5→LUMO+1 3%, HOMO-4→LUMO+1 7%, HOMO-4→LUMO+2 4%
T ₁₀	327.521 nm	HOMO-12→LUMO+2 1%, HOMO-11→LUMO 2%, HOMO-7→LUMO 6%, HOMO-7→LUMO+2 2%, HOMO-6→LUMO 20%, HOMO-5→LUMO 8%, HOMO-4→LUMO 4%, HOMO-3→LUMO 19%, HOMO-3→LUMO+1 4%, HOMO-3→LUMO+2 6%, HOMO-2→LUMO 3%, HOMO-2→LUMO+1 1%, HOMO-2→LUMO+2 2%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 3%
T ₁₁	310.645 nm	HOMO-16→LUMO 1%, HOMO-12→LUMO 2%, HOMO-12→LUMO+4 2%, HOMO-12→LUMO+8 1%, HOMO-11→LUMO+2 1%, HOMO-9→LUMO 6%, HOMO-8→LUMO 3%, HOMO-7→LUMO 21%, HOMO-7→LUMO+8 2%, HOMO-6→LUMO+3 1%, HOMO-6→LUMO+6 1%, HOMO-5→LUMO+2 1%, HOMO-4→LUMO+1 4%, HOMO-4→LUMO+2 9%, HOMO-3→LUMO 4%, HOMO-2→LUMO 9%, HOMO-2→LUMO+1 2%, HOMO-2→LUMO+2 2%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 3%
T ₁₂	319.550 nm	HOMO-15→LUMO 1%, HOMO-14→LUMO 2%, HOMO-14→LUMO+2 1%, HOMO-9→LUMO 6%, HOMO-9→LUMO+2 3%, HOMO-9→LUMO+3 1%, HOMO-8→LUMO 2%, HOMO-7→LUMO 9%, HOMO-6→LUMO 5%, HOMO-5→LUMO 4%, HOMO-5→LUMO+4 1%, HOMO-1→LUMO 15%, HOMO-1→LUMO+1 8%, HOMO-1→LUMO+2 13%, HOMO-1→LUMO+8 3%
T ₁₃	297.192 nm	HOMO-15→LUMO+1 2%, HOMO-14→LUMO+1 1%, HOMO-13→HOMO 3%, HOMO-10→HOMO 16%, HOMO-10→LUMO+4 2%, HOMO-10→LUMO+5 2%, HOMO-8→LUMO+3 1%, HOMO-8→LUMO+4 2%, HOMO-8→LUMO+5 2%, HOMO-6→HOMO 5%, HOMO-6→LUMO+3 3%, HOMO-6→LUMO+6 3%, HOMO-5→HOMO 2%, HOMO-5→LUMO+3 2%, HOMO-5→LUMO+5 1%, HOMO-5→LUMO+6 3%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+5 1%, HOMO-2→HOMO 13%, HOMO-2→LUMO+1 3%, HOMO-2→LUMO+2 1%, HOMO-2→LUMO+4 1%, HOMO-2→LUMO+5 4%, HOMO-2→LUMO+6 2%, HOMO-1→HOMO 2%
T ₁₄	292.399 nm	HOMO-12→LUMO 3%, HOMO-9→LUMO 13%, HOMO-9→LUMO+4 3%,

		HOMO-9→LUMO+5 4%, HOMO-9→LUMO+6 1%, HOMO-7→LUMO+4 3%, HOMO-7→LUMO+5 4%, HOMO-6→LUMO+2 1%, HOMO-6→LUMO+3 3%, HOMO-6→LUMO+5 3%, HOMO-6→LUMO+6 4%, HOMO-5→LUMO+2 1%, HOMO-5→LUMO+3 2%, HOMO-5→LUMO+5 5%, HOMO-5→LUMO+6 3%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 3%, HOMO-3→LUMO+5 2%, HOMO-2→LUMO 2%, HOMO-2→LUMO+1 6%, HOMO-2→LUMO+2 8%, HOMO-2→LUMO+5 1%
T ₁₅	283.838 nm	HOMO-14→LUMO+1 1%, HOMO-13→HOMO 12%, HOMO-11→LUMO+1 2%, HOMO-11→LUMO+3 2%, HOMO-10→LUMO+5 1%, HOMO- 10→LUMO+6 1%, HOMO-8→HOMO 2%, HOMO-6→LUMO+1 9%, HOMO- 6→LUMO+2 4%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+6 2%, HOMO- 4→LUMO+1 1%, HOMO-4→LUMO+3 3%, HOMO-4→LUMO+5 2%, HOMO- 4→LUMO+6 2%, HOMO-2→LUMO 6%, HOMO-2→LUMO+1 9%, HOMO- 2→LUMO+2 3%
T ₁₆	305.717 nm	HOMO-15→LUMO+1 1%, HOMO-13→HOMO 6%, HOMO-11→LUMO+1 1%, HOMO-9→LUMO+5 1%, HOMO-8→HOMO 2%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 4%, HOMO-6→LUMO+5 2%, HOMO-5→LUMO+1 4%, HOMO-5→LUMO+3 1%, HOMO-4→LUMO+6 3%, HOMO-3→LUMO 1%, HOMO-3→LUMO+1 2%, HOMO-3→LUMO+2 2%, HOMO-2→HOMO 1%, HOMO-2→LUMO 11%, HOMO-2→LUMO+1 9%, HOMO-2→LUMO+2 17%, HOMO-2→LUMO+8 1%
T ₁₇	282.375 nm	HOMO-14→LUMO+4 1%, HOMO-12→LUMO 3%, HOMO-9→LUMO 2%, HOMO-9→LUMO+1 1%, HOMO-9→LUMO+3 4%, HOMO-9→LUMO+4 2%, HOMO-9→LUMO+6 4%, HOMO-7→LUMO+3 3%, HOMO-7→LUMO+4 2%, HOMO-6→LUMO 1%, HOMO-6→LUMO+1 1%, HOMO-6→LUMO+2 1%, HOMO-6→LUMO+3 2%, HOMO-6→LUMO+4 6%, HOMO-5→LUMO+3 5%, HOMO-5→LUMO+4 3%, HOMO-5→LUMO+5 3%, HOMO-4→LUMO 2%, HOMO-4→LUMO+4 4%, HOMO-4→LUMO+5 1%, HOMO-3→LUMO 10%, HOMO-3→LUMO+1 3%, HOMO-3→LUMO+2 4%, HOMO-3→LUMO+8 1%
T ₁₈	278.574 nm	HOMO-15→HOMO 5%, HOMO-14→HOMO 4%, HOMO-10→HOMO 5%, HOMO-10→LUMO+3 9%, HOMO-10→LUMO+4 1%, HOMO-10→LUMO+6 4%, HOMO-8→LUMO+3 5%, HOMO-8→LUMO+6 1%, HOMO-6→HOMO 1%, HOMO-6→LUMO+3 6%, HOMO-6→LUMO+4 1%, HOMO-6→LUMO+5 2%, HOMO-5→LUMO+3 5%, HOMO-5→LUMO+4 8%, HOMO-5→LUMO+5 2%, HOMO-4→LUMO+3 4%, HOMO-4→LUMO+4 2%, HOMO-4→LUMO+5 3%, HOMO-4→LUMO+7 1%, HOMO-2→HOMO 2%, HOMO-2→LUMO+1 3%, HOMO-2→LUMO+5 1%, HOMO-1→HOMO 2%
T ₁₉	275.876 nm	HOMO-15→HOMO 2%, HOMO-14→HOMO 1%, HOMO-13→HOMO 1%, HOMO-12→LUMO 6%, HOMO-11→LUMO+2 2%, HOMO-11→LUMO+6 1%, HOMO-10→LUMO+1 3%, HOMO-10→LUMO+6 1%, HOMO-9→LUMO+4 2%, HOMO-8→LUMO+1 2%, HOMO-6→LUMO+1 4%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+5 3%, HOMO-6→LUMO+6 1%, HOMO-6→LUMO+7 2%, HOMO-5→HOMO 1%, HOMO-5→LUMO+2 4%, HOMO-5→LUMO+3 1%, HOMO-5→LUMO+4 1%, HOMO-5→LUMO+5 1%, HOMO-5→LUMO+7 4%, HOMO-4→HOMO 2%, HOMO-4→LUMO+3 3%, HOMO-4→LUMO+6 2%, HOMO-4→LUMO+7 2%, HOMO-2→HOMO 1%, HOMO-2→LUMO+2 3%, HOMO-2→LUMO+5 1%, HOMO-1→HOMO 3%, HOMO-1→LUMO+1 3%
T ₂₀	372.032 nm	HOMO-15→HOMO 2%, HOMO-14→HOMO 2%, HOMO-10→LUMO+1 2%, HOMO-5→LUMO+7 2%, HOMO-4→LUMO+7 2%, HOMO-2→LUMO+2 2%, HOMO-1→HOMO 56%, HOMO-1→LUMO+1 9%, HOMO-1→LUMO+2 3%, HOMO-1→LUMO+4 1%, HOMO-1→LUMO+5 3%, HOMO-1→LUMO+6 2%

Table S9 SOC orbit states of $[\text{Ir}(\text{tpy})_2]^{3+}\cdot\text{I}^-$

State	Wavelength	Composition	f
1	484.118 nm	52%T ₁₈ , 48%T ₂₃	2.6×10 ⁻⁶
2	484.102 nm	52%T ₁₈ , 48%T ₂₃	3.8×10 ⁻⁵
3	458.299 nm	3%S ₁₀ , 94%T ₁₈	1.4×10 ⁻⁷
4	456.392 nm	4%S ₉ , 94%T ₂₃	7.0×10 ⁻⁷
5	446.329 nm	30%T ₉ , 68%T ₁₅	5.0×10 ⁻⁵
6	446.158 nm	32%T ₉ , 67%T ₁₅	8.3×10 ⁻⁷
7	435.662 nm	6%S ₅ , 90%T ₁₅	1.1×10 ⁻⁵
8	424.355 nm	45%T ₁₈ , 48%T ₂₃ , 2%T ₂₆	7.4×10 ⁻⁵
9	423.399 nm	3%S ₁₁ , 46%T ₁₈ , 49%T ₂₃	9.5×10 ⁻⁴
10	417.289 nm	32%T ₅ , 3%S ₈ , 60%T ₉	3.1×10 ⁻⁶
11	416.219 nm	2%S ₁ , 3%S ₄ , 86%T ₅ , 3%T ₁₁	3.5×10 ⁻⁴
12	414.209 nm	1%S ₂ , 2%S ₅ , 90%T ₅ , 1%T ₉	2.2×10 ⁻⁴
13	414.002 nm	59%T ₅ , 2%S ₈ , 30%T ₉ , 2%T ₁₁	4.4×10 ⁻⁵
14	403.047 nm	6%S ₁ , 16%S ₇ , 54%T ₉ , 20%T ₁₅	0.0024
15	399.241 nm	74%S ₁ , 1%S ₇ , 5%T ₉ , 9%T ₁₁	9.4×10 ⁻⁴
16	397.704 nm	2%T ₅ , 59%T ₉ , 7%T ₁₃ , 25%T ₁₅	3.2×10 ⁻⁵
17	374.004 nm	25%T ₃₅ , 73%T ₃₆	2.7×10 ⁻⁶
18	373.850 nm	26%T ₃₅ , 72%T ₃₆	2.5×10 ⁻⁵
19	370.364 nm	81%T ₁ , 1%T ₂ , 3%T ₃ , 6%S ₄ , 6%T ₁₁	0.0011
20	370.139 nm	66%T ₁ , 3%T ₂ , 23%T ₃ , 2%S ₅ , 1%T ₁₁	1.5×10 ⁻⁵
21	369.537 nm	86%T ₁ , 2%T ₂ , 5%T ₃ , 1%S ₅	9.7×10 ⁻⁵
22	368.947 nm	89%T ₂ , 5%T ₃	4.9×10 ⁻⁶
23	368.885 nm	94%T ₂ , 3%T ₃	3.5×10 ⁻⁶
24	368.685 nm	2%T ₁ , 96%T ₂	3.1×10 ⁻⁵
25	368.190 nm	11%T ₁ , 4%T ₂ , 77%T ₃ , 4%S ₅	1.5×10 ⁻⁵
26	367.964 nm	13%T ₁ , 3%T ₂ , 78%T ₃ , 1%S ₅ , 1%S ₈	1.4×10 ⁻⁴
27	366.603 nm	12%T ₁ , 83%T ₃	1.1×10 ⁻⁴
28	365.696 nm	2%S ₂₂ , 93%T ₃₆	9.8×10 ⁻⁷
29	363.785 nm	99%T ₄	2.3×10 ⁻⁶
30	363.777 nm	99%T ₄	9.9×10 ⁻⁸
31	363.759 nm	99%T ₄	3.0×10 ⁻⁷
32	362.463 nm	12%T ₁ , 1%S ₃ , 2%T ₃ , 22%S ₄ , 1%T ₆ , 58%T ₁₁	0.0038
33	359.460 nm	3%T ₁ , 3%S ₅ , 1%T ₆ , 6%T ₇ , 10%T ₈ , 67%T ₁₁	8.5×10 ⁻⁵
34	358.761 nm	2%T ₁ , 7%T ₃ , 43%S ₅ , 4%T ₇ , 6%T ₈ , 19%T ₁₁ , 9%T ₁₃	0.0010
35	358.187 nm	2%S ₁ , 4%T ₃ , 3%S ₄ , 15%S ₅ , 5%T ₇ , 10%T ₈ , 48%T ₁₁ , 3%T ₁₂ , 4%T ₁₃	7.3×10 ⁻⁴
36	348.297 nm	3%S ₂₃ , 93%T ₃₅	7.9×10 ⁻⁷
37	344.853 nm	60%S ₈ , 33%T ₁₃	6.2×10 ⁻⁶
38	342.262 nm	45%S ₂ , 5%S ₆ , 10%T ₇ , 24%T ₈ , 1%T ₁₂ , 8%T ₁₃	0.0067
39	340.670 nm	58%T ₃₅ , 15%T ₃₆ , 4%T ₄₀ , 15%T ₄₁ , 6%T ₄₂	4.4×10 ⁻⁶
40	340.539 nm	81%S ₉ , 5%T ₂₅ , 9%T ₂₆	8.1×10 ⁻⁵
41	339.156 nm	1%S ₂₅ , 52%T ₃₅ , 14%T ₃₆ , 23%T ₄₁ , 8%T ₄₂	4.2×10 ⁻⁴

42	337.790 nm	80%S ₁₀ , 5%T ₂₅ , 9%T ₂₆	2.3×10 ⁻⁵
43	334.599 nm	31%S ₄ , 4%T ₅ , 22%T ₆ , 3%T ₇ , 4%T ₈ , 23%T ₁₁ , 6%T ₁₂	0.0055
44	330.851 nm	45%T ₆ , 12%S ₇ , 1%T ₇ , 18%T ₈ , 10%T ₁₁ , 4%T ₁₂	9.0×10 ⁻⁴
45	329.913 nm	54%T ₆ , 2%S ₇ , 4%T ₇ , 19%T ₈ , 10%T ₁₁ , 3%T ₁₂ , 2%T ₁₃	1.3×10 ⁻⁴
46	329.716 nm	1%S ₂₈ , 87%T ₄₁	2.8×10 ⁻⁵
47	329.391 nm	8%T ₃₅ , 6%T ₃₆ , 4%T ₄₀ , 72%T ₄₁ , 5%T ₄₂	1.9×10 ⁻⁴
48	327.484 nm	2%S ₂₅ , 17%T ₃₅ , 12%T ₃₆ , 61%T ₄₁ , 5%T ₄₂	3.8×10 ⁻⁴
49	326.655 nm	1%S ₂ , 23%T ₆ , 5%S ₇ , 8%T ₇ , 43%T ₈ , 12%T ₁₂	8.3×10 ⁻⁴
50	326.062 nm	2%S ₂ , 24%T ₆ , 15%T ₇ , 39%T ₈ , 16%T ₁₂	4.3×10 ⁻⁴

Table S10 SOC-free states of [Ir(tpy)₂]³⁺-I⁻

State	Wavelength	Composition
S ₁	385.460 nm	HOMO-3→LUMO 7%, HOMO-1→LUMO 83%, HOMO-1→LUMO+4 4%, HOMO-1→LUMO+8 4%
S ₂	328.652 nm	HOMO-5→LUMO 7%, HOMO-4→LUMO 28%, HOMO-2→LUMO 47%, HOMO-2→LUMO+4 1%, HOMO-2→LUMO+8 1%, HOMO-1→LUMO+1 3%, HOMO-1→LUMO+2 6%
S ₃	306.659 nm	HOMO-9→LUMO+1 1%, HOMO-5→HOMO 15%, HOMO-4→HOMO 55%, HOMO-3→LUMO 18%, HOMO-2→HOMO 1%, HOMO-1→LUMO 2%
S ₄	337.992 nm	HOMO-5→HOMO 4%, HOMO-4→HOMO 15%, HOMO-3→LUMO 66%, HOMO-3→LUMO+4 2%, HOMO-3→LUMO+8 2%, HOMO-1→LUMO 6%
S ₅	353.846 nm	HOMO-3→LUMO+1 1%, HOMO-3→LUMO+2 2%, HOMO-2→LUMO 14%, HOMO-1→LUMO+1 29%, HOMO-1→LUMO+2 47%, HOMO-1→LUMO+11 2%
S ₆	307.187 nm	HOMO-6→LUMO 2%, HOMO-5→LUMO 5%, HOMO-4→LUMO 50%, HOMO-3→LUMO+2 1%, HOMO-2→LUMO 29%, HOMO-2→LUMO+4 1%, HOMO-2→LUMO+8 1%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 3%
S ₇	336.430 nm	HOMO-2→LUMO+1 35%, HOMO-2→LUMO+2 57%, HOMO-2→LUMO+11 1%
S ₈	334.558 nm	HOMO-4→LUMO 1%, HOMO-3→LUMO+1 37%, HOMO-3→LUMO+2 53%, HOMO-3→LUMO+11 1%, HOMO-1→LUMO+1 2%, HOMO-1→LUMO+2 3%
S ₉	335.848 nm	HOMO-3→HOMO 68%, HOMO-3→LUMO+1 11%, HOMO-3→LUMO+2 5%, HOMO-3→LUMO+3 3%, HOMO-3→LUMO+5 4%, HOMO-3→LUMO+6 3%, HOMO-1→HOMO 1%
S ₁₀	332.771 nm	HOMO-7→HOMO 3%, HOMO-1→HOMO 73%, HOMO-1→LUMO+1 10%, HOMO-1→LUMO+2 4%, HOMO-1→LUMO+3 2%, HOMO-1→LUMO+5 3%, HOMO-1→LUMO+6 2%
S ₁₁	292.617 nm	HOMO-8→HOMO 13%, HOMO-7→LUMO 2%, HOMO-6→HOMO 5%, HOMO-6→LUMO+1 1%, HOMO-5→LUMO+1 2%, HOMO-5→LUMO+2 1%, HOMO-4→HOMO 2%, HOMO-2→HOMO 49%, HOMO-2→LUMO+1 9%, HOMO-2→LUMO+2 2%, HOMO-2→LUMO+3 2%, HOMO-2→LUMO+5 2%, HOMO-2→LUMO+6 2%
S ₁₂	262.391 nm	HOMO-13→LUMO+1 2%, HOMO-9→LUMO+1 1%, HOMO-9→LUMO+3 1%, HOMO-8→HOMO 17%, HOMO-6→HOMO 30%, HOMO-5→HOMO 24%, HOMO-5→LUMO+1 2%, HOMO-4→HOMO 4%, HOMO-4→LUMO+1 3%, HOMO-4→LUMO+2 3%, HOMO-4→LUMO+5 1%
S ₁₃	260.659 nm	HOMO-8→HOMO 5%, HOMO-7→LUMO 54%, HOMO-6→LUMO+1 3%, HOMO-5→LUMO+1 1%, HOMO-5→LUMO+2 6%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+2 7%, HOMO-4→LUMO+3 2%, HOMO-2→HOMO 5%,

		HOMO-2→LUMO+1 3%
S ₁₄	258.556 nm	HOMO-12→LUMO+1 1%, HOMO-12→LUMO+2 2%, HOMO-10→LUMO+2 2%, HOMO-10→LUMO+3 2%, HOMO-10→LUMO+6 1%, HOMO-6→LUMO 45%, HOMO-5→LUMO 28%, HOMO-4→LUMO 2%, HOMO-4→LUMO+4 3%
S ₁₅	261.351 nm	HOMO-8→HOMO 23%, HOMO-7→LUMO 6%, HOMO-6→HOMO 9%, HOMO-5→HOMO 5%, HOMO-5→LUMO+1 8%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+2 11%, HOMO-4→LUMO+6 2%, HOMO-2→HOMO 18%, HOMO-2→LUMO+2 2%
S ₁₆	254.852 nm	HOMO-19→HOMO 3%, HOMO-16→HOMO 3%, HOMO-10→HOMO 4%, HOMO-8→LUMO 3%, HOMO-7→HOMO 77%, HOMO-1→HOMO 1%, HOMO-1→LUMO+1 1%
S ₁₇	248.626 nm	HOMO-13→HOMO 2%, HOMO-12→LUMO 1%, HOMO-9→LUMO+5 1%, HOMO-8→HOMO 1%, HOMO-6→LUMO+1 13%, HOMO-6→LUMO+3 2%, HOMO-5→LUMO+6 2%, HOMO-4→LUMO+1 63%, HOMO-4→LUMO+2 1%
S ₁₈	250.416 nm	HOMO-20→LUMO 3%, HOMO-17→LUMO 2%, HOMO-9→LUMO 7%, HOMO-8→LUMO 80%, HOMO-7→HOMO 3%
S ₁₉	240.660 nm	HOMO-15→HOMO 2%, HOMO-14→HOMO 2%, HOMO-8→LUMO+1 45%, HOMO-8→LUMO+2 20%, HOMO-6→LUMO+7 2%, HOMO-5→LUMO+5 4%, HOMO-5→LUMO+7 2%, HOMO-4→HOMO 1%, HOMO-4→LUMO+5 8%
S ₂₀	239.852 nm	HOMO-15→LUMO 1%, HOMO-14→LUMO 2%, HOMO-7→LUMO+1 21%, HOMO-7→LUMO+2 44%, HOMO-6→LUMO+8 2%, HOMO-5→LUMO 1%, HOMO-5→LUMO+4 3%, HOMO-5→LUMO+8 2%, HOMO-4→LUMO 1%, HOMO-4→LUMO+4 9%
T ₁	370.269 nm	HOMO-14→LUMO+8 1%, HOMO-10→LUMO+1 2%, HOMO-10→LUMO+2 4%, HOMO-7→LUMO 2%, HOMO-7→LUMO+2 1%, HOMO-6→LUMO 1%, HOMO-5→LUMO 20%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO 41%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+2 2%, HOMO-2→LUMO 7%
T ₂	370.118 nm	HOMO-9→HOMO 2%, HOMO-9→LUMO+1 2%, HOMO-9→LUMO+7 2%, HOMO-8→HOMO 8%, HOMO-8→LUMO+1 1%, HOMO-6→HOMO 1%, HOMO-6→LUMO+1 3%, HOMO-5→HOMO 13%, HOMO-5→LUMO+1 12%, HOMO-5→LUMO+2 5%, HOMO-4→HOMO 21%, HOMO-4→LUMO+1 11%, HOMO-4→LUMO+2 3%
T ₃	368.583 nm	HOMO-10→LUMO 3%, HOMO-10→LUMO+8 3%, HOMO-7→LUMO 16%, HOMO-7→LUMO+4 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 4%, HOMO-5→LUMO 3%, HOMO-5→LUMO+1 7%, HOMO-5→LUMO+2 13%, HOMO-4→LUMO 6%, HOMO-4→LUMO+1 7%, HOMO-4→LUMO+2 14%, HOMO-2→LUMO 1%, HOMO-2→LUMO+1 2%, HOMO-2→LUMO+2 3%, HOMO-1→LUMO 2%
T ₄	365.101 nm	HOMO-9→HOMO 3%, HOMO-9→LUMO+1 3%, HOMO-9→LUMO+2 1%, HOMO-9→LUMO+7 2%, HOMO-8→HOMO 10%, HOMO-8→LUMO+1 1%, HOMO-6→LUMO+1 2%, HOMO-6→LUMO+2 1%, HOMO-5→HOMO 18%, HOMO-5→LUMO+1 11%, HOMO-5→LUMO+2 4%, HOMO-4→HOMO 22%, HOMO-4→LUMO+1 5%, HOMO-4→LUMO+2 4%
T ₅	405.826 nm	HOMO-10→LUMO 4%, HOMO-7→LUMO 7%, HOMO-7→LUMO+8 2%, HOMO-5→LUMO+2 2%, HOMO-4→LUMO+1 1%, HOMO-4→LUMO+2 3%, HOMO-1→LUMO 66%, HOMO-1→LUMO+4 3%, HOMO-1→LUMO+8 4%
T ₆	324.504 nm	HOMO-12→LUMO+2 2%, HOMO-12→LUMO+3 2%, HOMO-11→LUMO 4%, HOMO-7→LUMO 1%, HOMO-6→LUMO 24%, HOMO-6→LUMO+4 1%, HOMO-5→LUMO 4%, HOMO-4→LUMO 14%, HOMO-3→LUMO 2%, HOMO-2→LUMO 26%, HOMO-2→LUMO+8 1%
T ₇	323.424 nm	HOMO-13→LUMO+1 1%, HOMO-11→HOMO 2%, HOMO-8→HOMO 2%, HOMO-8→LUMO+1 1%, HOMO-7→LUMO 5%, HOMO-6→HOMO 20%, HOMO-6→LUMO 2%, HOMO-5→HOMO 5%, HOMO-4→HOMO 6%, HOMO-4→LUMO 1%, HOMO-4→LUMO+2 2%, HOMO-3→LUMO 31%, HOMO-

		3→LUMO+8 1%, HOMO-1→LUMO 1%
T ₈	328.616 nm	HOMO-13→LUMO+1 1%, HOMO-11→HOMO 2%, HOMO-8→LUMO+1 1%, HOMO-7→LUMO 5%, HOMO-6→HOMO 20%, HOMO-6→LUMO+5 1%, HOMO-5→HOMO 4%, HOMO-4→HOMO 6%, HOMO-4→LUMO+1 1%, HOMO-3→LUMO 36%, HOMO-3→LUMO+4 1%, HOMO-3→LUMO+8 1%, HOMO-1→LUMO 1%
T ₉	406.273 nm	HOMO-7→LUMO+1 2%, HOMO-7→LUMO+2 3%, HOMO-3→LUMO 1%, HOMO-1→LUMO+1 31%, HOMO-1→LUMO+2 51%, HOMO-1→LUMO+9 1%, HOMO-1→LUMO+11 2%
T ₁₀	306.297 nm	HOMO-17→HOMO 2%, HOMO-13→LUMO+5 2%, HOMO-13→LUMO+7 1%, HOMO-9→HOMO 9%, HOMO-9→LUMO+5 1%, HOMO-8→HOMO 49%, HOMO-8→LUMO+7 4%, HOMO-6→HOMO 2%, HOMO-5→LUMO+1 2%, HOMO-4→HOMO 2%, HOMO-4→LUMO+1 6%, HOMO-4→LUMO+2 3%
T ₁₁	352.535 nm	HOMO-11→LUMO 1%, HOMO-10→LUMO+1 1%, HOMO-10→LUMO+2 2%, HOMO-10→LUMO+3 1%, HOMO-7→LUMO+2 2%, HOMO-6→LUMO 16%, HOMO-5→LUMO 8%, HOMO-2→LUMO 52%, HOMO-2→LUMO+4 2%, HOMO-2→LUMO+8 2%
T ₁₂	314.968 nm	HOMO-12→LUMO 2%, HOMO-12→LUMO+4 2%, HOMO-11→LUMO+2 1%, HOMO-10→LUMO+4 2%, HOMO-7→LUMO 33%, HOMO-7→LUMO+8 1%, HOMO-6→LUMO+2 2%, HOMO-6→LUMO+3 3%, HOMO-6→LUMO+6 2%, HOMO-4→LUMO+1 2%, HOMO-4→LUMO+2 4%, HOMO-3→LUMO 19%, HOMO-2→LUMO+2 1%, HOMO-1→LUMO 13%
T ₁₃	323.469 nm	HOMO-15→LUMO+2 2%, HOMO-14→LUMO+1 1%, HOMO-14→LUMO+2 3%, HOMO-12→LUMO 2%, HOMO-10→LUMO 13%, HOMO-10→LUMO+4 1%, HOMO-4→LUMO+2 2%, HOMO-4→LUMO+3 4%, HOMO-4→LUMO+6 2%, HOMO-2→LUMO+1 20%, HOMO-2→LUMO+2 31%, HOMO-2→LUMO+11 1%
T ₁₄	284.059 nm	HOMO-15→LUMO+1 2%, HOMO-15→LUMO+3 1%, HOMO-14→LUMO+1 2%, HOMO-14→LUMO+2 1%, HOMO-13→HOMO 4%, HOMO-9→HOMO 26%, HOMO-9→LUMO+5 7%, HOMO-8→LUMO+5 10%, HOMO-8→LUMO+7 1%, HOMO-6→LUMO+3 6%, HOMO-6→LUMO+6 5%, HOMO-5→LUMO+3 7%, HOMO-5→LUMO+6 5%, HOMO-4→LUMO+1 2%, HOMO-2→HOMO 2%
T ₁₅	423.148 nm	HOMO-3→LUMO+1 38%, HOMO-3→LUMO+2 55%, HOMO-3→LUMO+11 1%
T ₁₆	283.566 nm	HOMO-14→LUMO+3 1%, HOMO-12→LUMO 7%, HOMO-11→LUMO+3 1%, HOMO-10→LUMO 17%, HOMO-10→LUMO+4 7%, HOMO-7→LUMO 3%, HOMO-7→LUMO+4 11%, HOMO-7→LUMO+8 2%, HOMO-6→LUMO+2 3%, HOMO-6→LUMO+3 7%, HOMO-6→LUMO+6 4%, HOMO-5→LUMO+3 5%, HOMO-5→LUMO+6 3%, HOMO-3→LUMO 1%, HOMO-2→LUMO+1 3%, HOMO-2→LUMO+2 6%, HOMO-1→LUMO 5%
T ₁₇	278.358 nm	HOMO-15→LUMO+1 2%, HOMO-14→LUMO+1 2%, HOMO-14→LUMO+2 1%, HOMO-13→HOMO 18%, HOMO-13→LUMO+5 3%, HOMO-11→LUMO+1 3%, HOMO-11→LUMO+2 1%, HOMO-11→LUMO+3 2%, HOMO-11→LUMO+6 1%, HOMO-9→LUMO+5 1%, HOMO-8→HOMO 5%, HOMO-6→LUMO+1 10%, HOMO-6→LUMO+2 6%, HOMO-6→LUMO+3 1%, HOMO-5→LUMO+1 6%, HOMO-5→LUMO+2 2%, HOMO-5→LUMO+3 1%, HOMO-5→LUMO+5 1%, HOMO-5→LUMO+6 1%, HOMO-4→LUMO+3 5%, HOMO-4→LUMO+6 6%, HOMO-4→LUMO+9 1%
T ₁₈	448.759 nm	HOMO-7→HOMO 1%, HOMO-3→HOMO 66%, HOMO-3→LUMO+1 10%, HOMO-3→LUMO+2 5%, HOMO-3→LUMO+3 4%, HOMO-3→LUMO+5 5%, HOMO-3→LUMO+6 3%, HOMO-1→HOMO 1%
T ₁₉	276.357 nm	HOMO-15→LUMO 1%, HOMO-15→LUMO+4 2%, HOMO-14→LUMO 2%, HOMO-14→LUMO+4 2%, HOMO-10→LUMO+3 13%, HOMO-10→LUMO+6

9%, HOMO-7→LUMO+1 1%, HOMO-7→LUMO+3 5%, HOMO-7→LUMO+6 4%, HOMO-6→LUMO+4 13%, HOMO-5→LUMO+4 19%, HOMO-4→LUMO 2%, HOMO-4→LUMO+4 12%, HOMO-2→LUMO 1%

T₂₀ 275.371 nm HOMO-15→HOMO 6%, HOMO-14→HOMO 6%, HOMO-9→LUMO+2 1%, HOMO-9→LUMO+3 10%, HOMO-9→LUMO+6 7%, HOMO-8→LUMO+3 5%, HOMO-8→LUMO+6 4%, HOMO-6→LUMO+5 9%, HOMO-5→LUMO+5 21%, HOMO-5→LUMO+7 1%, HOMO-4→LUMO+5 10%, HOMO-4→LUMO+7 1%, HOMO-2→HOMO 1%