Electronic Supplementary Information

New phosphorescent iridium(III) dipyrrinato complexes: synthesis, emission properties and their deep red to near-infrared OLEDs

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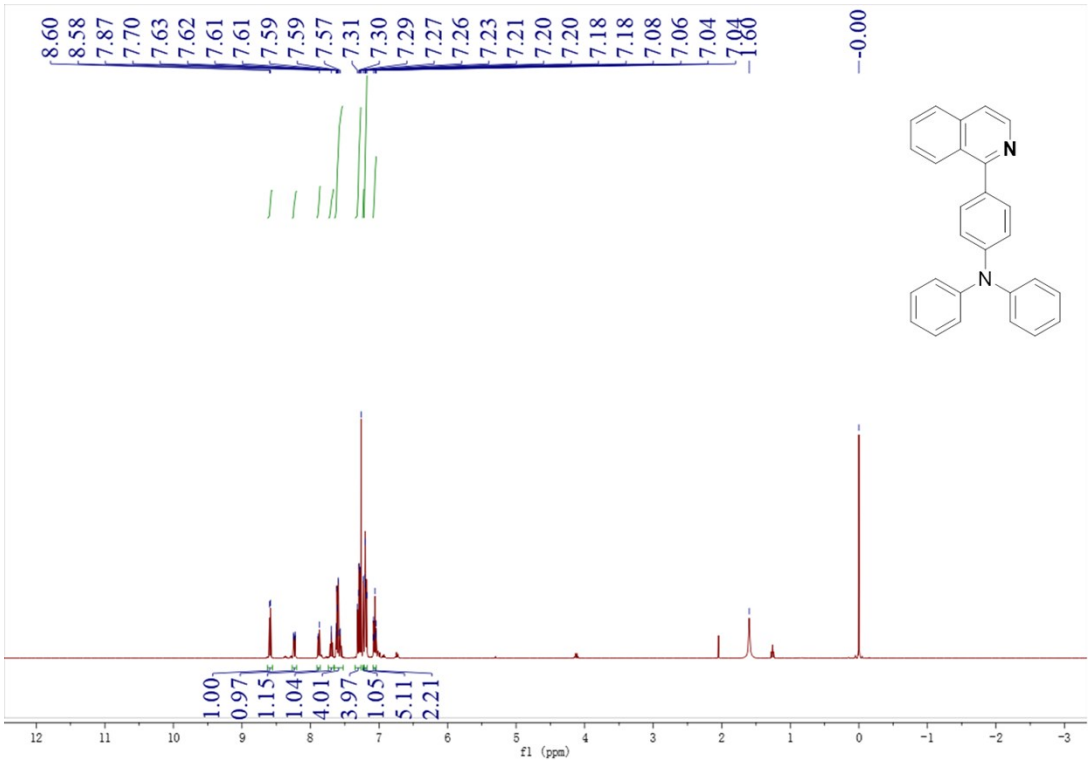


Figure S1. ^{1}H NMR spectrum of **piq-dpa** ligand in $CDCl_3$

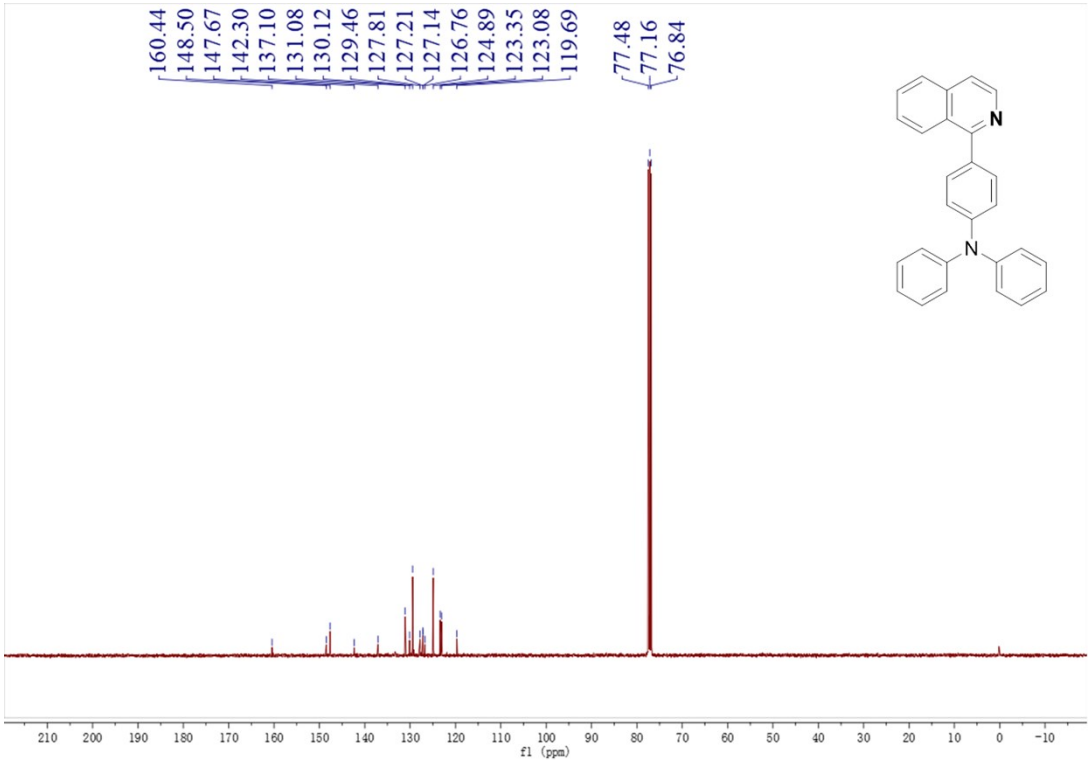


Figure S2. ^{13}C NMR spectrum of **piq-dpa** ligand in $CDCl_3$

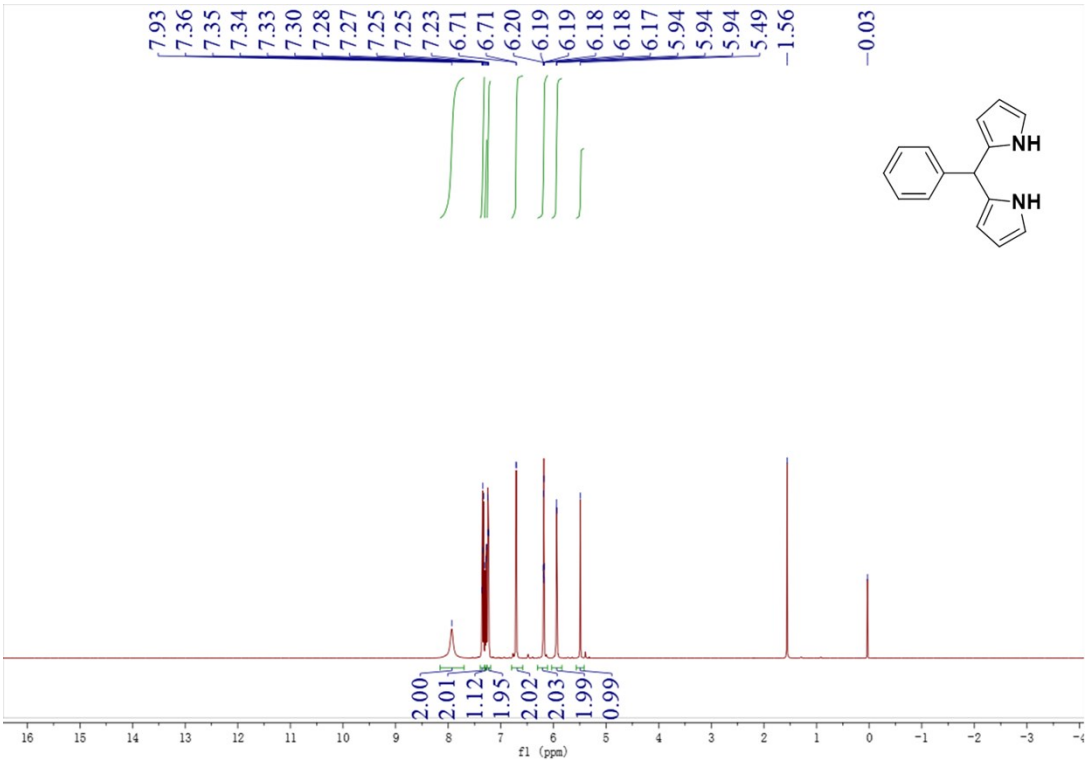


Figure S3. ^{1}H NMR spectrum of **5-phenyldipyrromethane** in $CDCl_3$

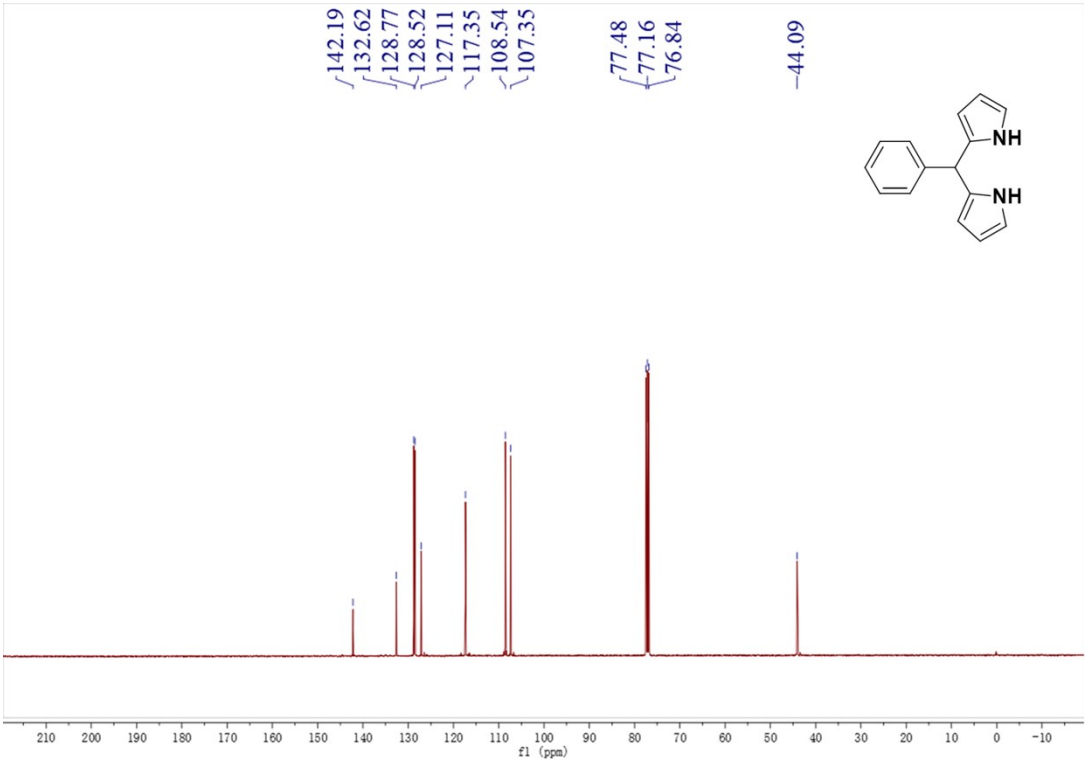


Figure S4. ^{13}C NMR spectrum of **5-phenyldipyrromethane** in $CDCl_3$

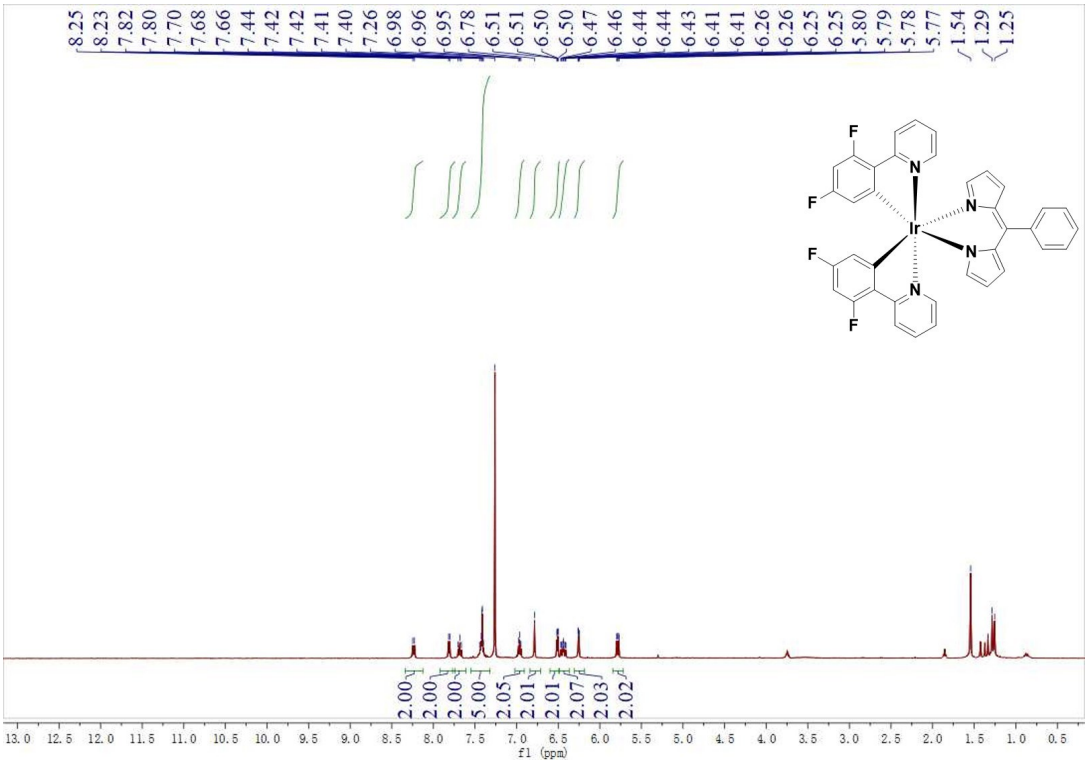


Figure S5. ^{1}H NMR spectrum of **Ir1** in $CDCl_3$

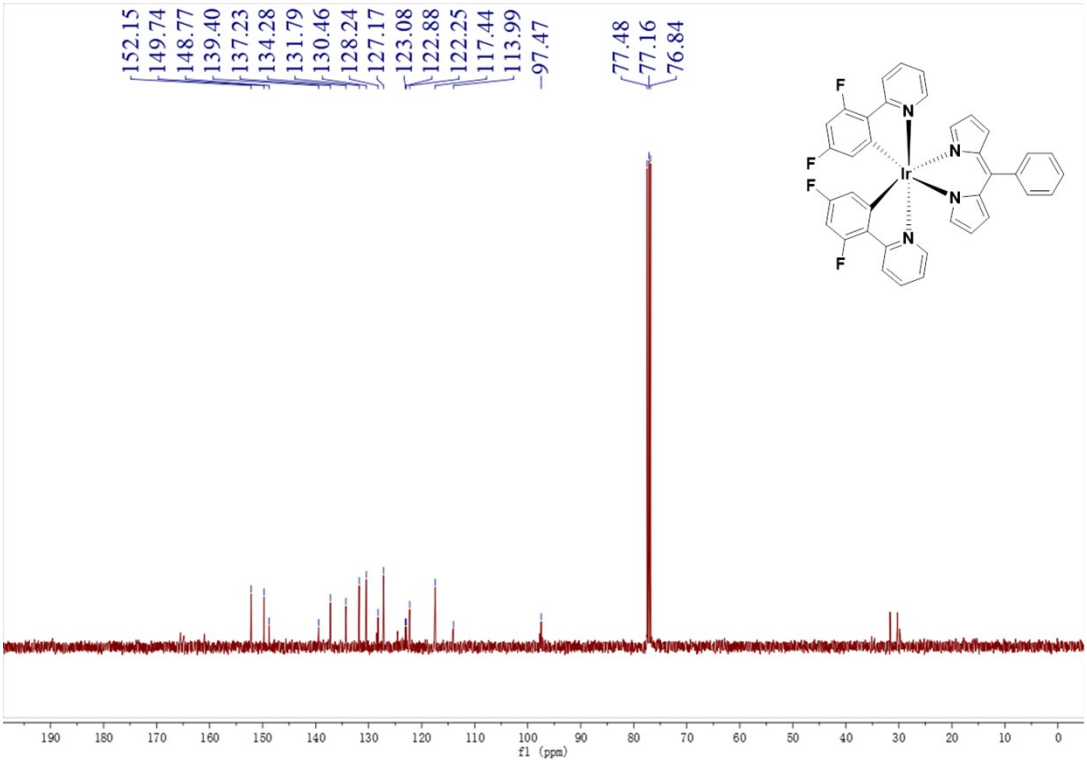


Figure S6. ^{13}C NMR spectrum of **Ir1** in $CDCl_3$

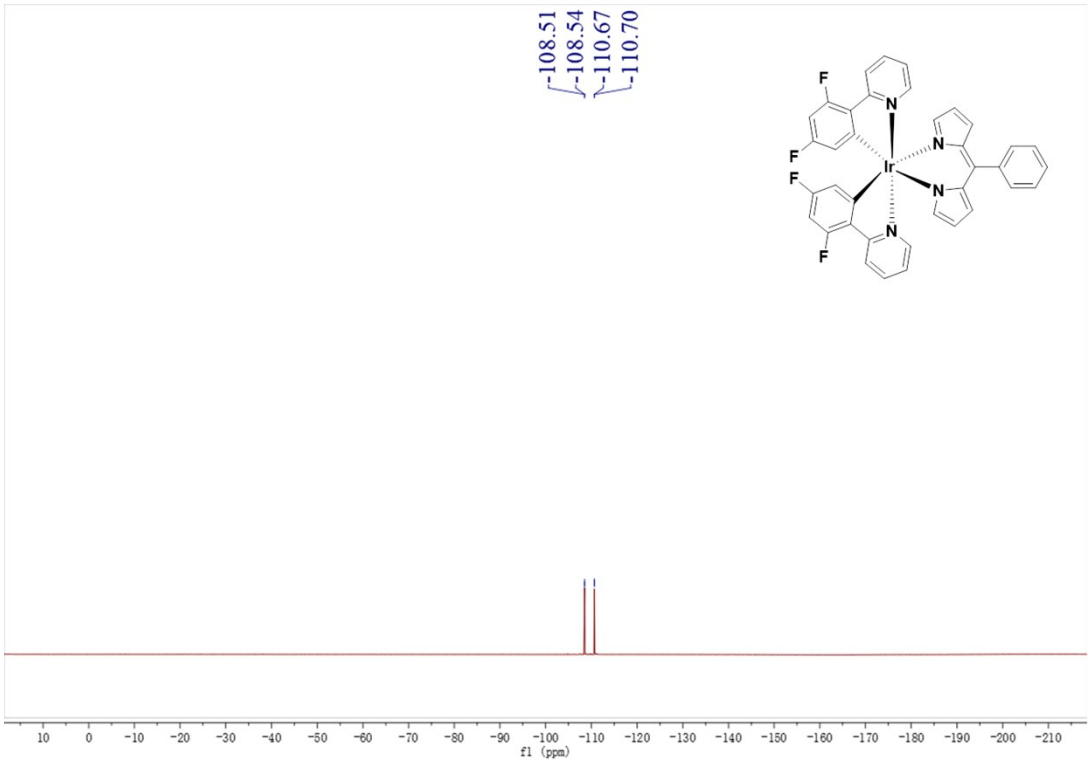


Figure S7. ^{19}F NMR spectrum of **Ir1** in $CDCl_3$

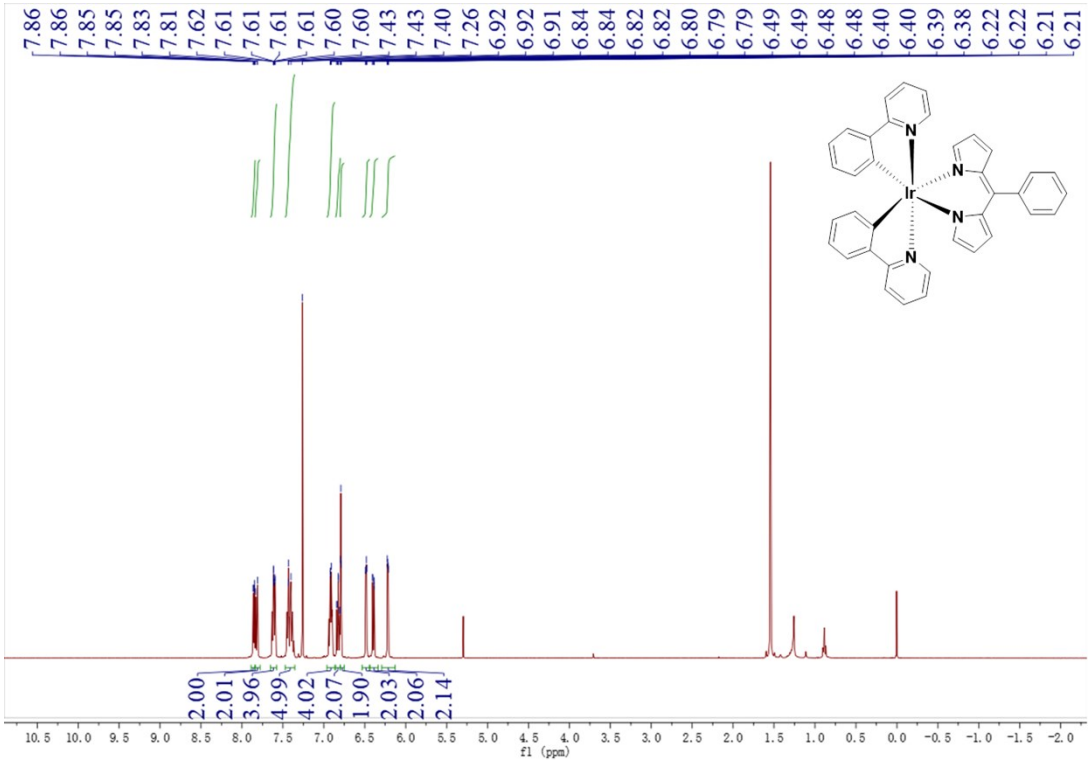


Figure S8. ^{1}H NMR spectrum of **Ir2** in $CDCl_3$

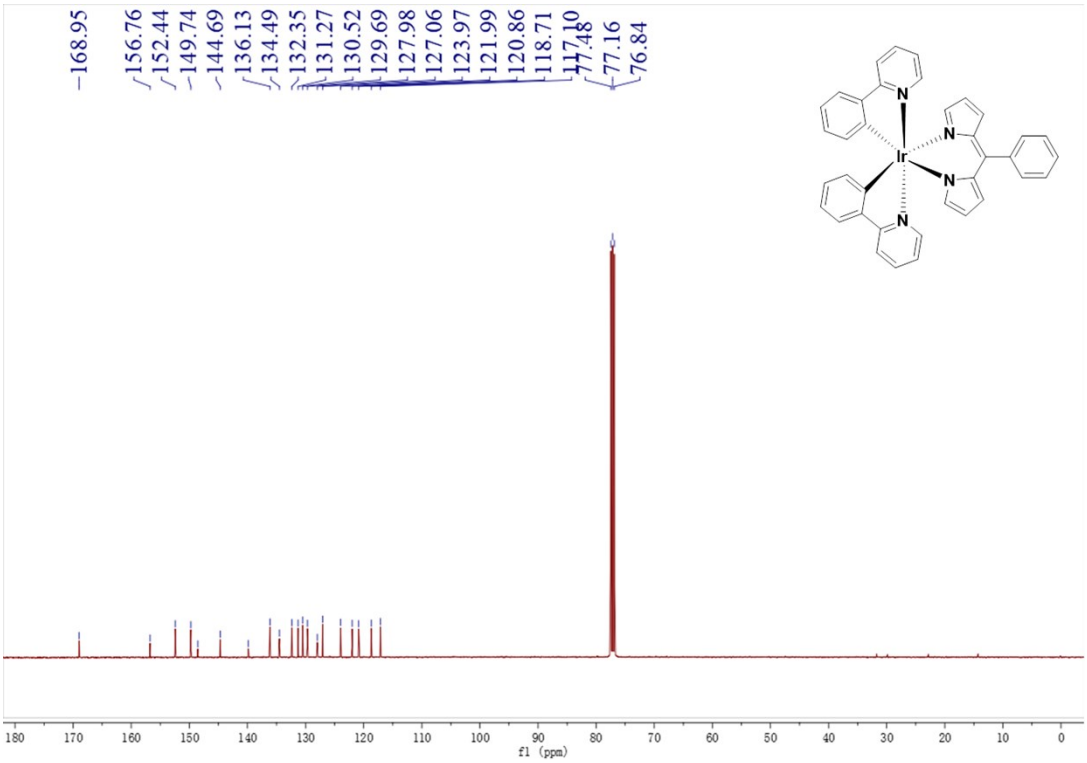


Figure S9. ^{13}C NMR spectrum of **Ir2** in $CDCl_3$

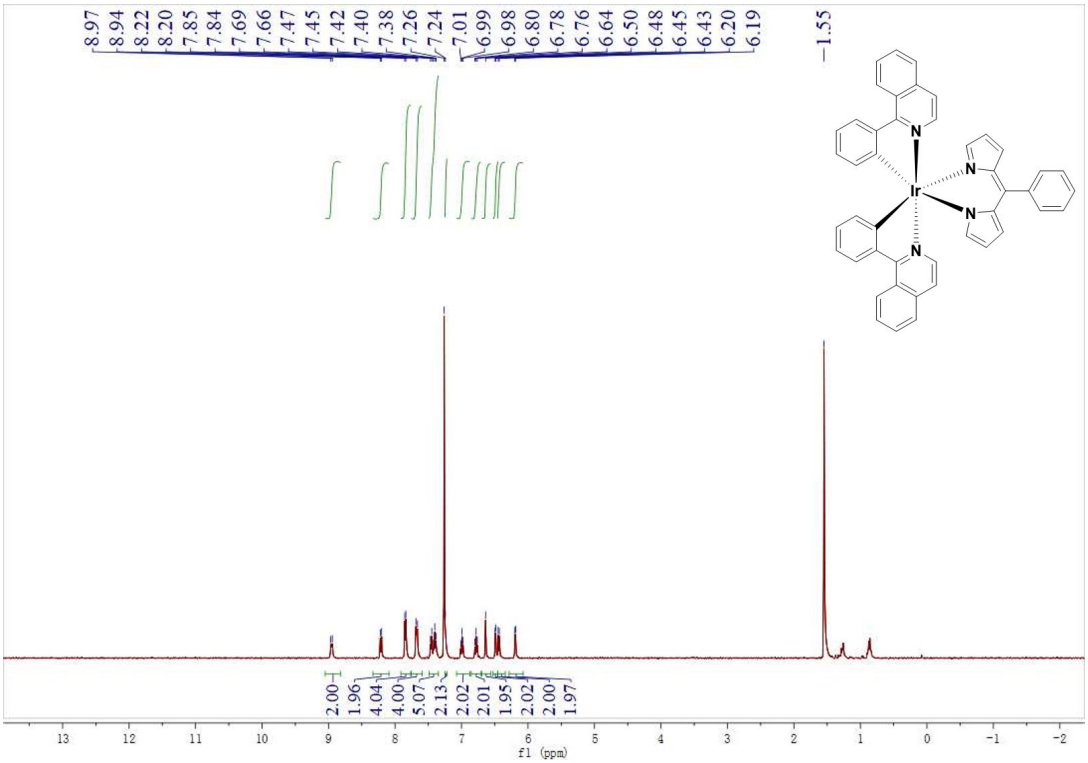


Figure S10. ^{1}H NMR spectrum of **Ir3** in $CDCl_3$

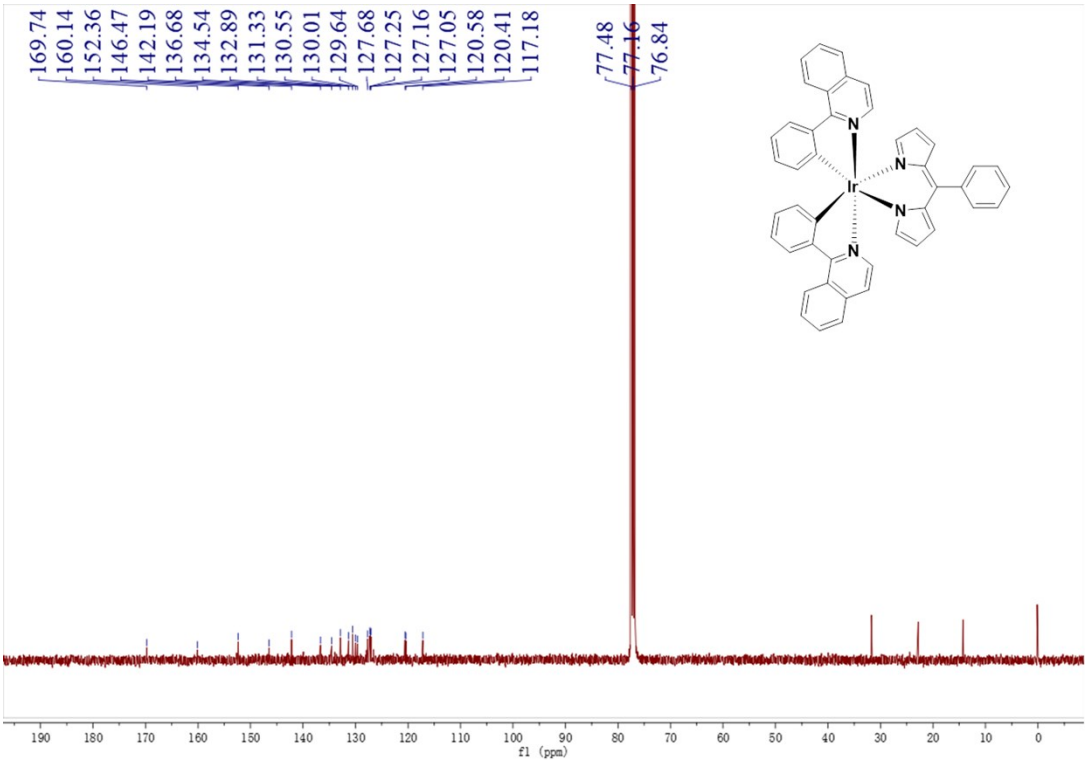


Figure S11. ^{13}C NMR spectrum of **Ir3** in $CDCl_3$

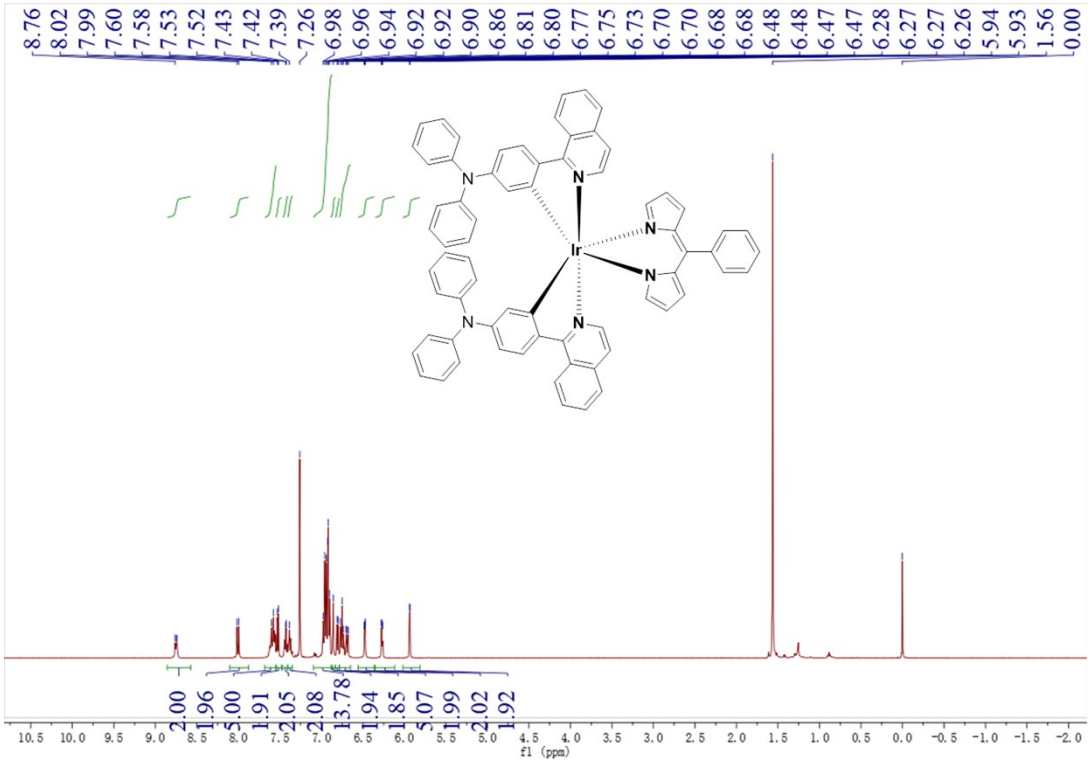


Figure S12. ^{1}H NMR spectrum of **Ir4** in $CDCl_3$

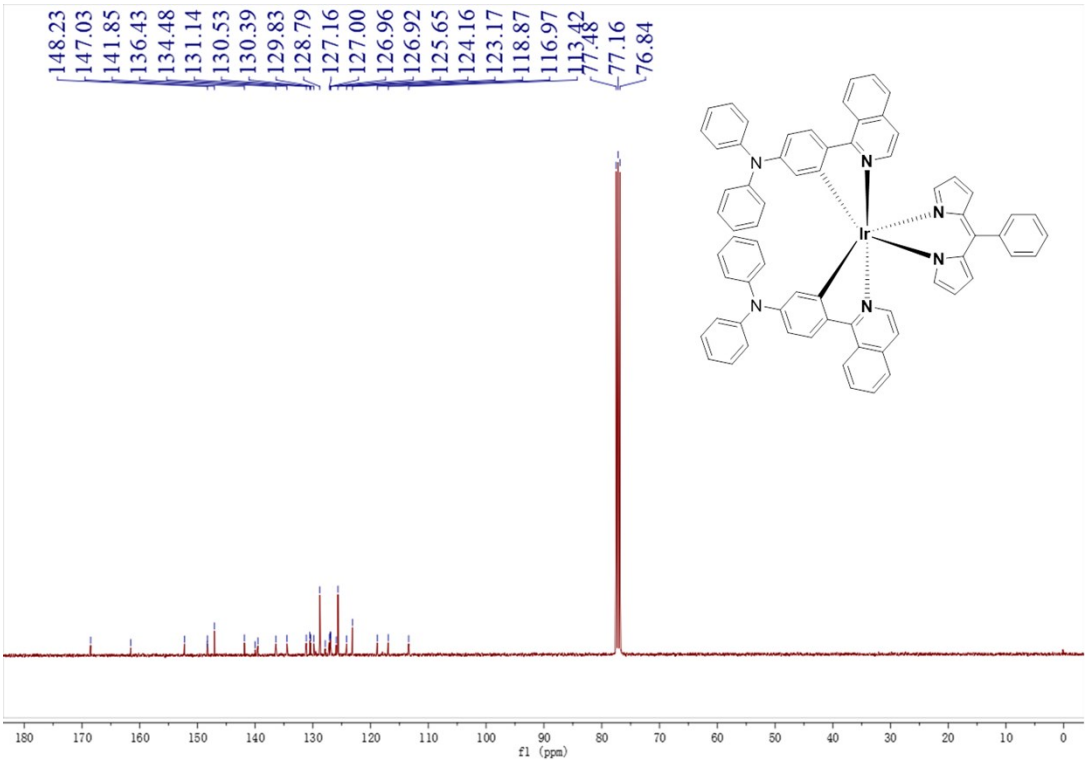


Figure S13. ^{13}C NMR spectrum of **Ir4** in $CDCl_3$

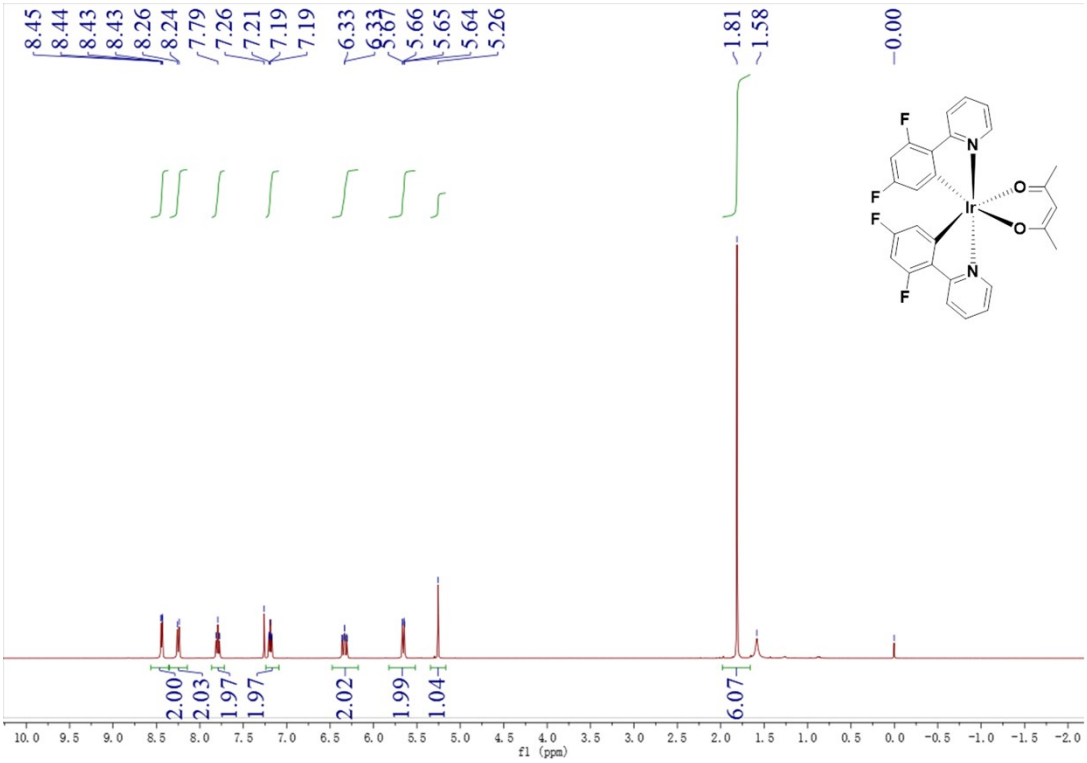


Figure S14. ^{1}H NMR spectrum of **Ir5** in $CDCl_3$

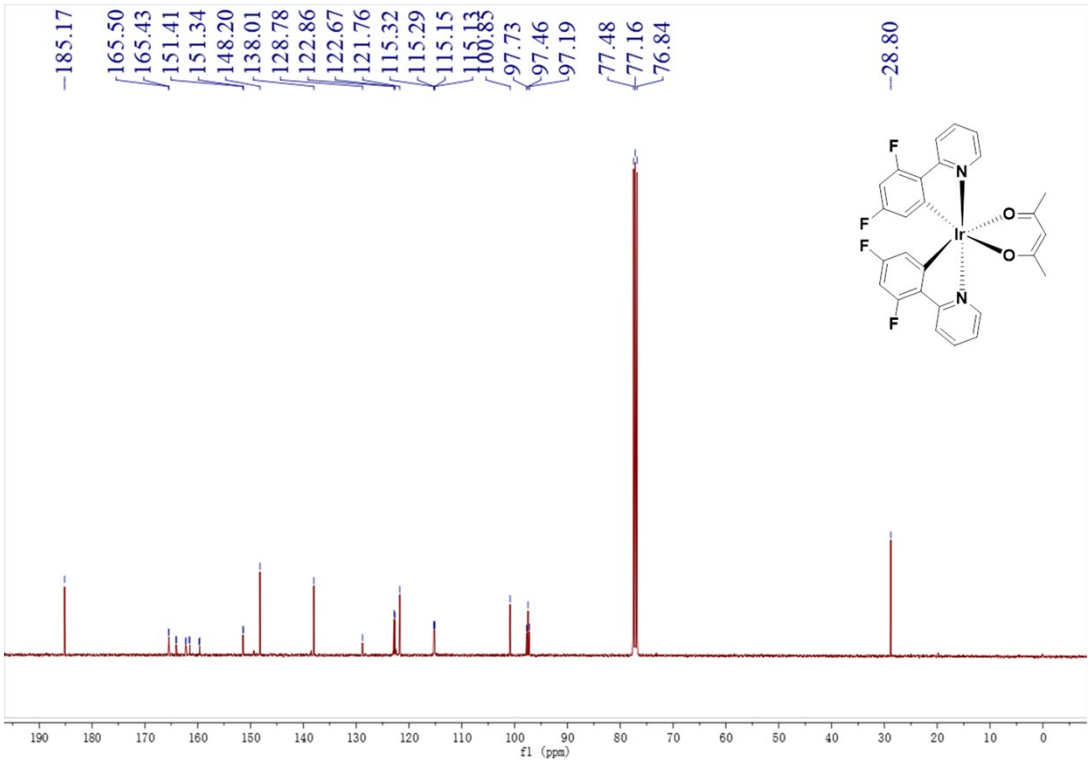


Figure S15. ^{13}C NMR spectrum of **Ir5** in $CDCl_3$

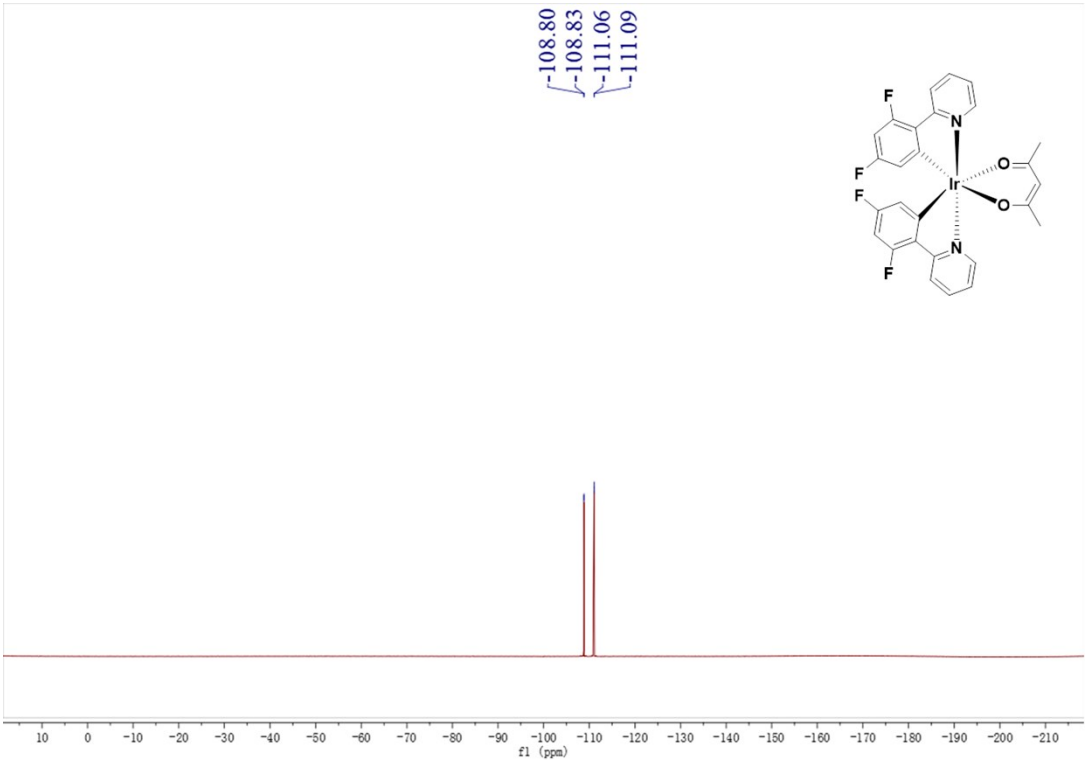


Figure S16. ^{19}F NMR spectrum of **Ir5** in $CDCl_3$

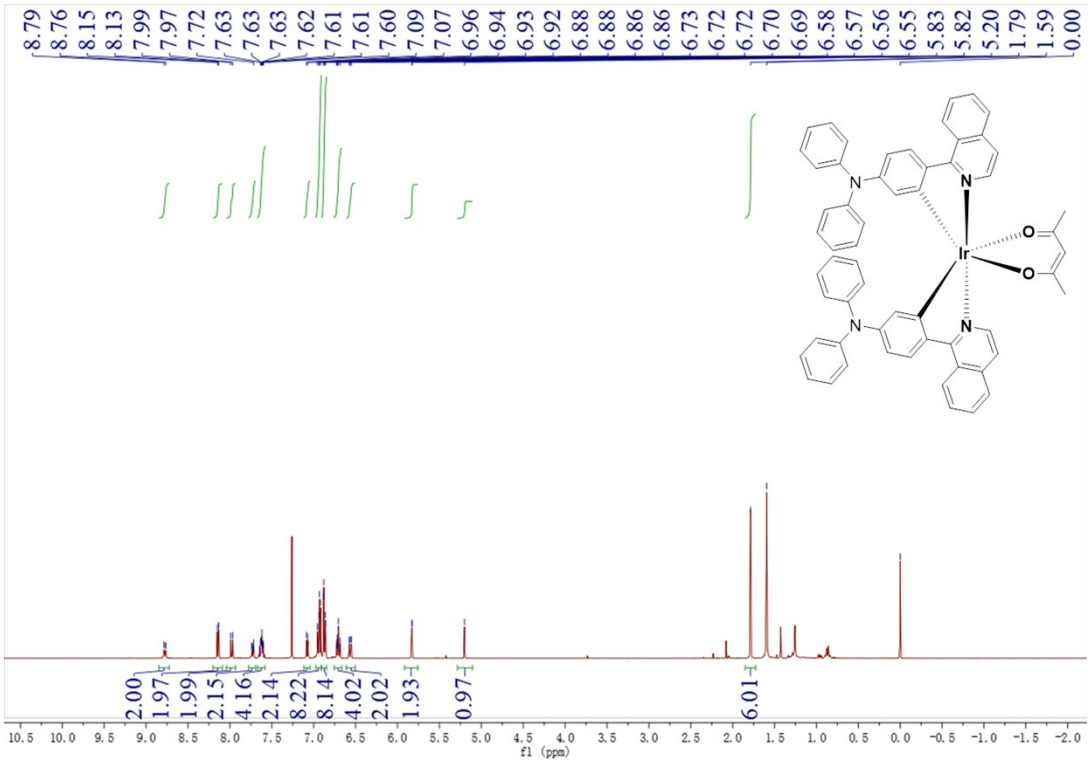


Figure S17. ^{1}H NMR spectrum of **Ir8** in $CDCl_3$

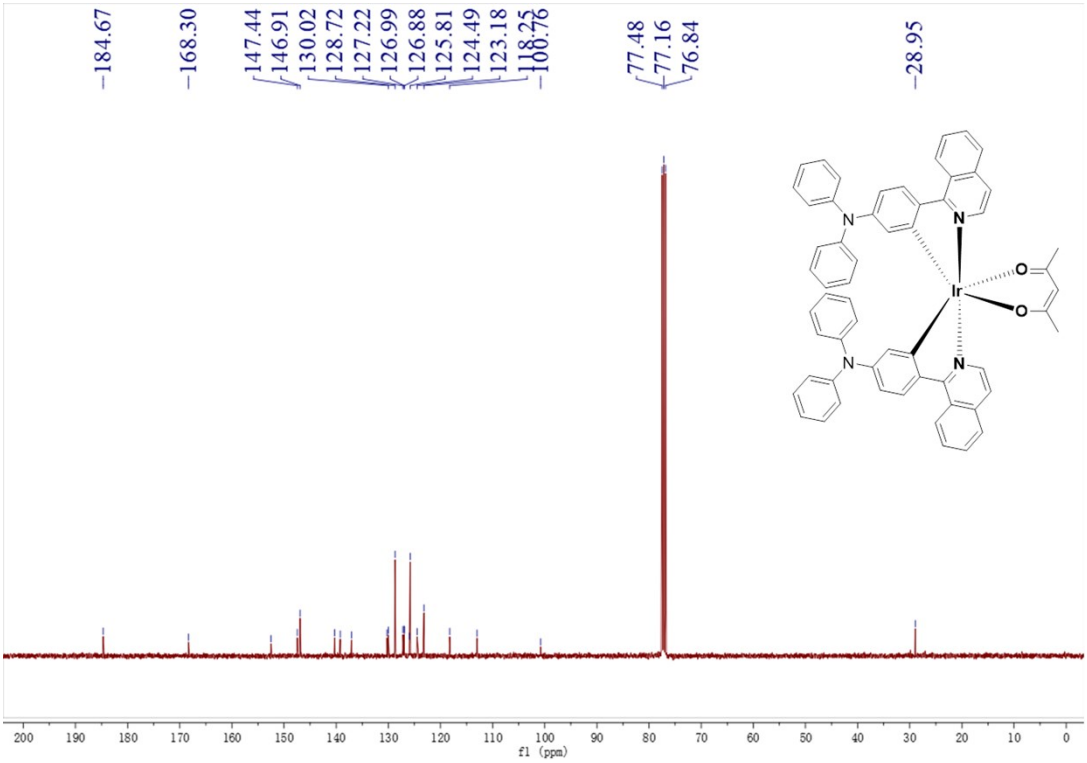


Figure S18. ^{13}C NMR spectrum of **Ir8** in $CDCl_3$

Table S1. The bond lengths and angles of **Ir2**, **Ir3**, **Ir6** and **Ir7**.

Iridium(Ⅲ) complex	Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Ir(ppy)$_2$(pdp) (Ir2)	Ir1	N2	2.122(7)	N2	Ir1	N3	86.6(3)
	Ir1	N3	2.145(8)	N1	Ir1	N2	88.8(3)
	Ir1	N1	2.056(7)	N1	Ir1	N3	97.0(3)
	Ir1	N4	2.031(8)	N4	Ir1	N2	95.5(3)
	Ir1	C13	2.022(10)	N4	Ir1	N3	88.6(3)
	Ir1	C1	2.018(9)	N4	Ir1	N1	173.2(3)
				C13	Ir1	N2	91.6(3)
				C13	Ir1	N3	177.3(3)
				C13	Ir1	N1	81.1(3)
				C13	Ir1	N4	93.5(3)
				C1	Ir1	N2	175.8(3)
				C1	Ir1	N3	92.6(3)
				C1	Ir1	N1	95.4(3)
				C1	Ir1	N4	80.3(3)
Ir(piq)$_2$(pdp) (Ir3)	Ir1	N2	2.139(4)	N2^1	Ir1	N2	87.2(2)
	Ir1	N2^1	2.139(4)	N1^1	Ir1	N2^1	95.77(19)
	Ir1	N1	2.049(5)	N1	Ir1	N2	95.77(19)
	Ir1	N1^1	2.049(5)	N1^1	Ir1	N2	90.58(18)
	Ir1	C11^1	2.013(5)	N1	Ir1	N2^1	90.58(18)
	Ir1	C11	2.012(5)	N1	Ir1	N1^1	171.2(3)
	^{1}1-X, +Y, 3/2-Z			C11	Ir1	N2^1	91.1(2)
				C11	Ir1	N2	175.5(2)
				C11^1	Ir1	N2^1	175.5(2)
				C11^1	Ir1	N2	91.1(2)
				C11^1	Ir1	N1^1	80.1(2)
				C11^1	Ir1	N1	93.7(2)
				C11	Ir1	N1^1	93.7(2)
				C11	Ir1	N1	80.1(2)
				C11	Ir1	C11^1	90.9(3)
Ir(ppy)$_2$(acac) (Ir6)	Ir1	N1	2.010(9)	N1	Ir1	N1^1	176.3(4)
	Ir1	N1^1	2.010(9)	N1	Ir1	C11	81.7(4)
	Ir1	C11	2.003(10)	N1^1	Ir1	C11	95.8(4)
	Ir1	C11^1	2.003(9)	N1	Ir1	C11^1	95.8(4)
	Ir1	O1	2.146(6)	N1^1	Ir1	C11^1	81.7(4)
	Ir1	O1^1	2.146(6)	C11	Ir1	C11^1	95.2(5)
	^{1}1-X, +Y, 3/2-Z			N1	Ir1	O1	94.5(3)
				N1^1	Ir1	O1	88.1(3)
				C11	Ir1	O1	175.6(3)
				C11^1	Ir1	O1	87.5(3)
				N1	Ir1	O1^1	88.1(3)
				N1^1	Ir1	O1^1	94.5(3)
				C11	Ir1	O1^1	87.5(3)
				C11^1	Ir1	O1^1	175.6(3)
				O1	Ir1	O1^1	90.0(3)

Ir(piq)$_2$(acac) (Ir7)	Ir1	O1	2.166(4)	O1	Ir1	O2	86.76(17)
	Ir1	O2	2.167(4)	N2	Ir1	O1	87.86(16)
	Ir1	N2	2.038(4)	N2	Ir1	O2	95.82(16)
	Ir1	N1	2.034(4)	N1	Ir1	O1	96.63(16)
	Ir1	C11	1.971(5)	N1	Ir1	O2	88.48(16)
	Ir1	C16	1.978(6)	N1	Ir1	N2	173.97(19)
				C11	Ir1	O1	175.91(17)
				C11	Ir1	O2	90.87(19)
				C11	Ir1	N2	95.71(19)
				C11	Ir1	N1	79.96(19)
				C11	Ir1	C16	91.6(2)
				C16	Ir1	O1	91.0(2)
				C16	Ir1	O2	175.32(18)
				C16	Ir1	N2	80.0(2)
				C16	Ir1	N1	95.9(2)

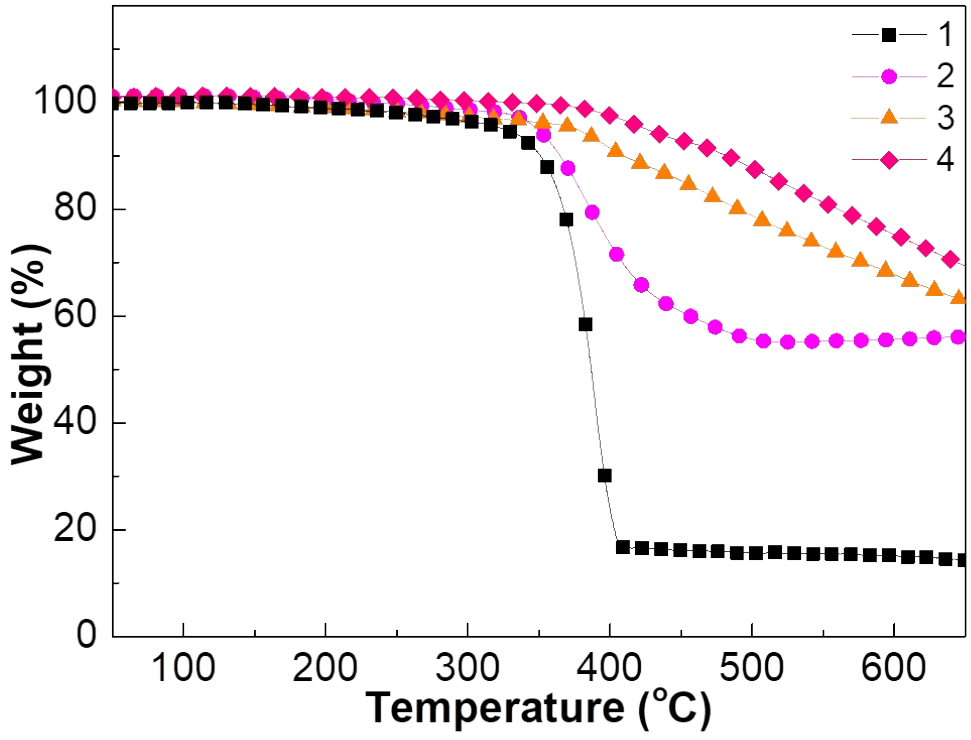


Figure S19. The thermogravimetric curves of four iridium(Ⅲ) dipyrrinato complexes **Ir1-Ir4**.

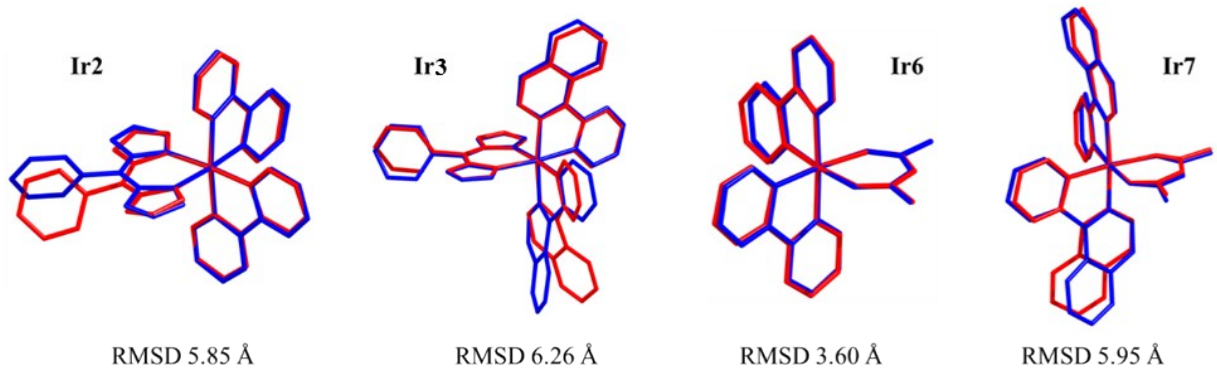


Figure S20. Stacking of crystal structure (red) and optimised geometry (blue) of **Ir2**, **Ir3**, **Ir6** and **Ir7**. RMSD (Root-Mean-Square Deviation of atomic positions).

1. $Ir(dfppy)_2(pdp)$ (Ir1)

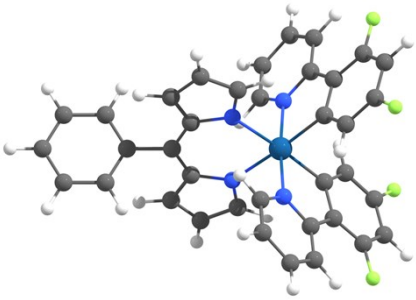
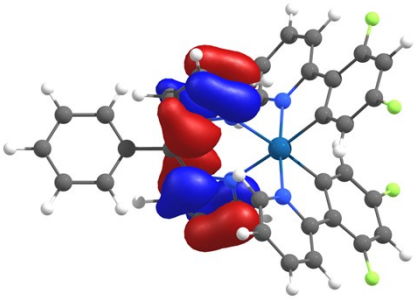
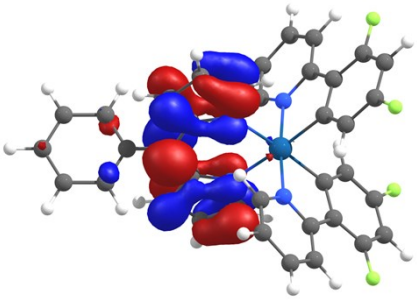


Figure S21. Optimized structure of **Ir1** in the ground state.



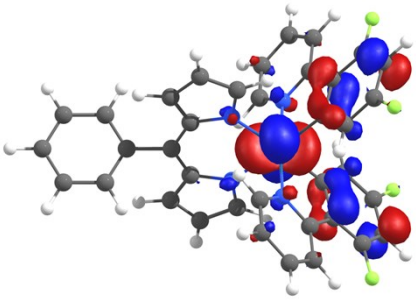
HOMO

(-5.40 eV)



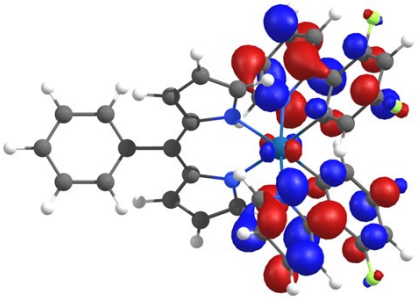
LUMO

(-2.15 eV)



HOMO-1

(-5.60 eV)



LUMO+1

(-1.57 eV)

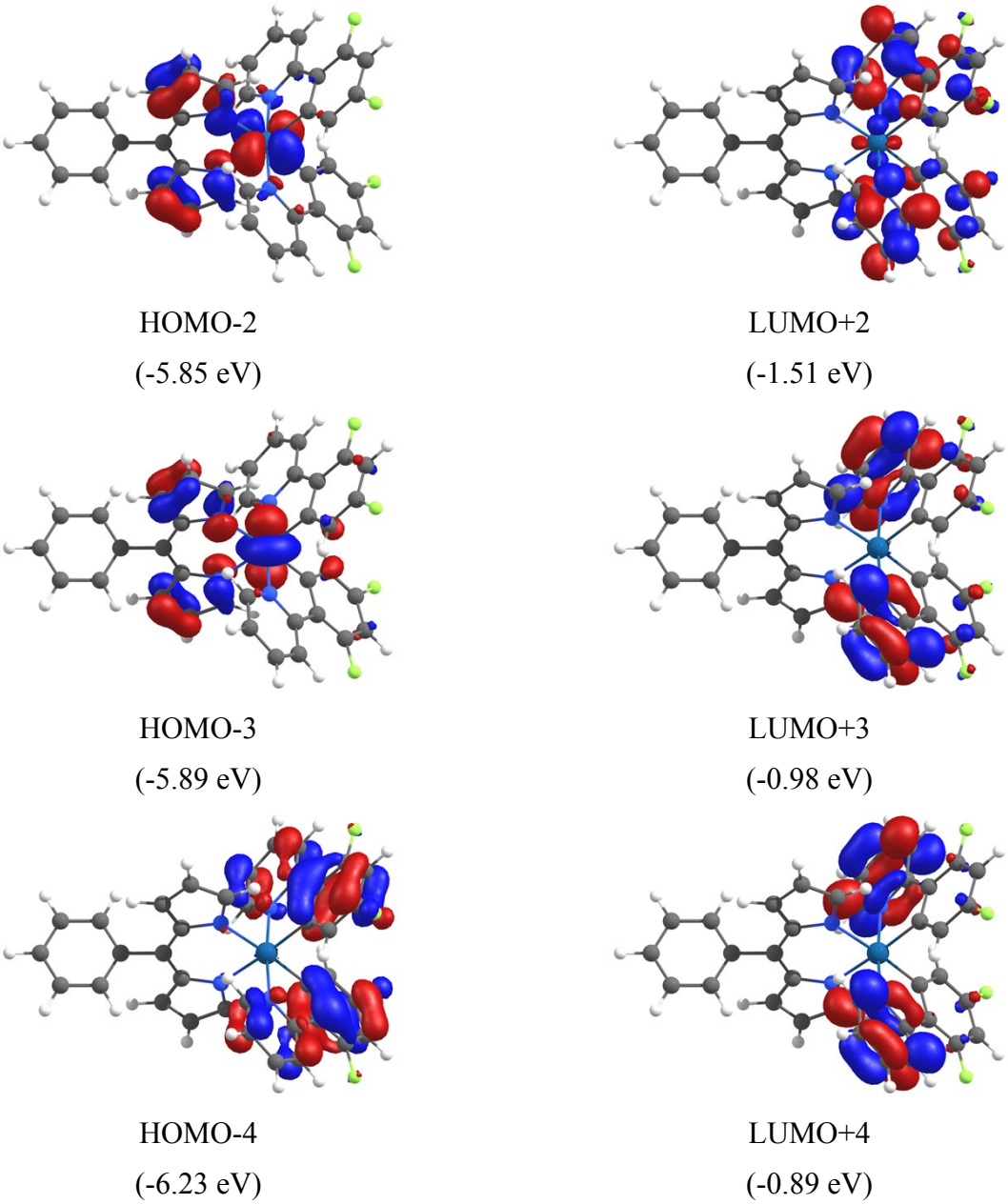


Figure S22. Representations of the frontier MOs of **Ir1** in the ground state.

Table S2. Atomic contributions of the frontier MOs of **Ir1**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-6.23	-5.89	-5.85	-5.60	-5.40	-2.15	-1.57	-1.51	-0.98	-0.89
Ir (%)	1.48	51.11	51.39	51.02	1.28	3.58	3.45	1.48	5.20	6.10
dfppy (%)	94.81	18.74	17.60	41.51	1.73	4.76	94.53	94.81	92.70	90.32
pdp (%)	3.71	30.15	31.01	7.47	96.99	91.66	2.02	3.71	2.10	3.58

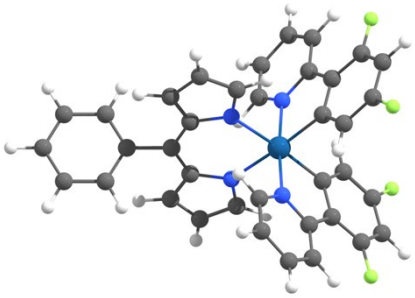
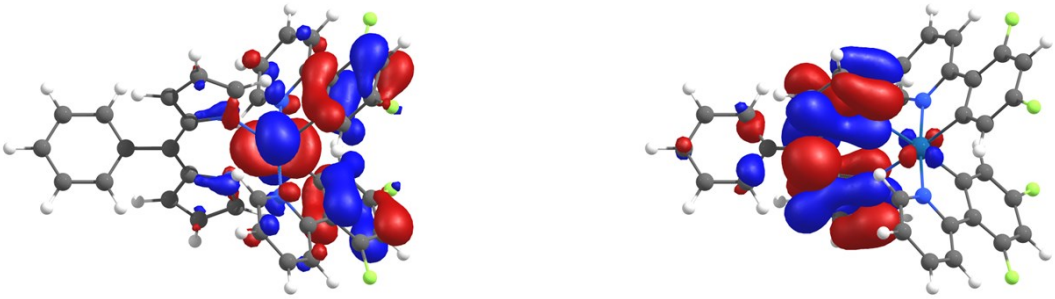


Figure S23. Optimized structure of **Ir1** in the triplet state.



LSOMO (-5.58 eV)

HSOMO (-3.53 eV)

Figure S24. Representation of the frontier MOs of **Ir1** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 1.89\ eV = 656\ nm$

Table S3. Atomic contributions of the frontier MOs of **Ir1** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-5.58	-3.53
Ir (%)	51.92	3.39
dfppy (%)	40.84	3.85
pdp (%)	7.24	92.76

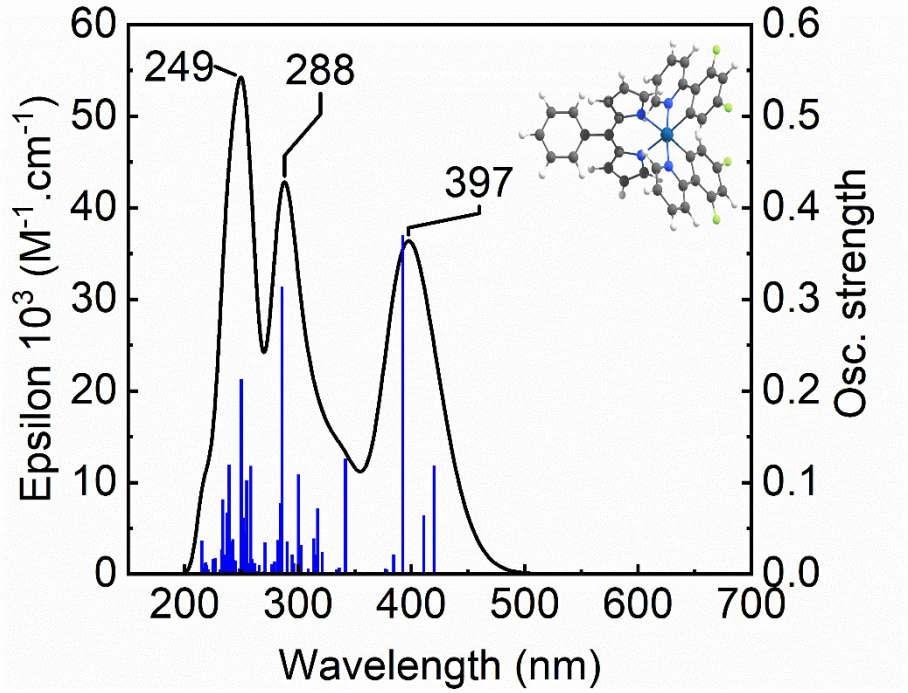


Figure S25. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir1** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S4. First 100 calculated spin-allowed electronic transitions of **Ir1**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	449.34834	2E-4	H-1→LUMO (97%)
2	419.9722	0.1184	H-3→LUMO (61%), HOMO→LUMO (37%)
3	410.80214	0.0638	H-2→LUMO (98%)
4	392.44197	0.3700	H-3→LUMO (36%), HOMO→LUMO (61%)
5	384.32794	0.0212	H-1→L+1 (64%), HOMO→L+1 (33%)
6	378.17353	0.0052	H-1→L+1 (32%), HOMO→L+1 (66%)
7	376.74859	0.0059	H-1→L+2 (53%), HOMO→L+2 (44%)
8	371.63297	0	H-1→L+2 (42%), HOMO→L+2 (56%)
9	350.04007	0.0029	H-3→L+1 (36%), H-2→L+2 (61%)
10	349.84253	0.0029	H-3→L+2 (12%), H-2→L+1 (82%)
11	348.36806	0.0016	H-4→LUMO (97%)
12	341.65778	0.1260	H-3→L+1 (61%), H-2→L+2 (36%)
13	336.14628	0.0069	H-5→LUMO (99%)
14	333.91019	0.0050	H-3→L+2 (80%), H-2→L+1 (11%)
15	321.15265	0.0243	HOMO→L+3 (93%)

16	317.0789	0.0715	H-7→LUMO (42%), H-6→LUMO (55%)
17	315.89939	0.0213	H-1→L+3 (88%)
18	315.40918	4E-4	HOMO→L+4 (96%)
19	313.749	0.0388	H-7→LUMO (54%), H-6→LUMO (41%)
20	308.77171	0.0062	H-1→L+4 (83%)
21	308.34169	2E-4	H-8→LUMO (99%)
22	302.74013	0.0318	H-4→L+1 (62%), H-2→L+3 (22%)
23	300.02951	0.1087	H-4→L+2 (59%), H-3→L+3 (16%), H-2→L+4 (14%)
24	295.98977	0.0114	H-9→LUMO (89%)
25	295.62278	0.0101	H-10→LUMO (99%)
26	295.35517	3E-4	H-5→L+2 (15%), H-4→L+1 (14%), H-2→L+3 (54%)
27	294.54825	0.0210	H-5→L+1 (63%), H-4→L+2 (17%), H-2→L+4 (14%)
28	293.05142	0.0022	H-3→L+3 (65%), H-2→L+4 (30%)
29	290.19121	0.0357	H-5→L+2 (50%), H-3→L+4 (38%)
30	285.80957	0.3140	H-5→L+1 (27%), H-4→L+2 (12%), H-3→L+3 (15%), H-2→L+4 (38%)
31	284.0612	0.0775	H-5→L+2 (27%), H-3→L+4 (51%)
32	282.27624	0.0370	H-6→L+1 (87%)
33	279.1808	0.0140	H-6→L+2 (91%)
34	276.63311	0.0107	HOMO→L+5 (99%)
35	270.63694	0.0348	HOMO→L+6 (96%)
36	269.64223	0.0029	H-11→LUMO (91%)
37	265.85512	0.0010	H-12→LUMO (89%)
38	265.72976	0.0100	H-8→L+1 (62%), H-4→L+4 (13%)
39	265.46804	9E-4	H-9→L+1 (12%), H-8→L+2 (13%), H-4→L+3 (30%), H-1→L+9 (15%)
40	264.48268	0.0034	H-8→L+2 (14%), H-4→L+3 (20%), H-3→L+9 (18%), H-1→L+9 (30%)
41	261.42112	0.0121	H-2→L+8 (17%), H-2→L+9 (61%)
42	259.19679	0.0162	H-9→L+1 (10%), H-8→L+2 (50%), H-4→L+3 (23%)
43	258.19282	0.1179	H-9→L+2 (21%), H-8→L+1 (19%), H-5→L+3 (20%), H-4→L+4 (24%)
44	257.35676	0.0010	H-7→L+1 (93%)
45	256.06517	0.0070	H-9→L+1 (50%), H-5→L+4 (21%), H-4→L+3 (13%)
46	255.95416	0.0122	H-5→L+3 (47%), H-4→L+4 (38%)
47	254.61904	0.1027	H-9→L+2 (19%), H-7→L+2 (32%), H-1→L+7 (24%)
48	254.24311	0.0448	H-7→L+2 (64%), H-1→L+7 (10%)
49	252.08237	0.0180	HOMO→L+7 (77%)
50	251.54026	0.0616	H-9→L+2 (16%), H-1→L+5 (69%)
51	250.5693	0.0305	H-9→L+1 (17%), H-5→L+4 (70%)
52	249.88249	0.2126	H-9→L+2 (19%), H-5→L+3 (11%), H-1→L+5 (10%), H-1→L+7 (34%)

53	249.53045	0.0154	HOMO→L+8 (77%)
54	248.38567	0.0047	H-1→L+6 (79%)
55	247.90393	0.0059	H-3→L+9 (28%), H-1→L+6 (14%), H-1→L+9 (25%), HOMO→L+8 (10%)
56	246.94603	1E-4	H-6→L+3 (83%)
57	246.63164	0.0013	H-14→LUMO (91%)
58	244.30864	0.0143	H-2→L+5 (86%)
59	244.13546	0.0036	H-10→L+1 (87%), H-8→L+1 (11%)
60	243.1301	0.0153	H-6→L+4 (83%)
61	242.36965	0.0379	H-10→L+2 (10%), H-3→L+8 (15%), H-1→L+8 (33%)
62	241.56686	0.0204	H-3→L+5 (74%), H-3→L+7 (12%)
63	241.39284	0.0046	H-11→L+1 (11%), H-2→L+7 (59%)
64	241.20031	0.0097	H-10→L+2 (69%), H-1→L+8 (11%)
65	240.90973	0.0185	H-2→L+6 (67%)
66	240.47052	0.002	H-12→L+1 (31%), H-11→L+2 (22%), H-2→L+6 (29%)
67	240.03755	2E-4	H-12→L+2 (17%), H-11→L+1 (49%), H-2→L+7 (19%)
68	239.57835	0.0358	H-3→L+5 (12%), H-3→L+7 (57%)
69	239.14397	0.1194	H-13→LUMO (55%), H-3→L+6 (30%)
70	237.34029	0.0669	H-13→LUMO (27%), H-3→L+6 (64%)
71	235.99405	0.0094	HOMO→L+9 (91%)
72	235.93567	0.0210	H-3→L+7 (13%), H-2→L+8 (55%), H-2→L+9 (14%)
73	233.57107	0.0211	H-15→LUMO (11%), H-11→L+2 (17%), H-8→L+3 (55%)
74	233.44793	0.0818	H-12→L+2 (21%), H-3→L+8 (40%)
75	233.23713	0.0099	H-12→L+1 (37%), H-11→L+2 (38%), H-8→L+3 (17%)
76	232.97855	0.0028	H-15→LUMO (86%), H-8→L+3 (10%)
77	232.28453	0.0266	H-12→L+2 (45%), H-11→L+1 (17%), H-3→L+8 (15%)
78	230.82286	0.0052	H-16→LUMO (91%)
79	229.80889	8E-4	H-8→L+4 (72%)
80	229.68543	1E-4	H-7→L+3 (94%)
81	228.03788	0.0014	H-9→L+3 (82%)
82	226.79897	0.0112	H-10→L+5 (15%), H-7→L+4 (18%), H-7→L+6 (26%), H-1→L+12 (15%)
83	226.76993	0.0176	H-7→L+6 (14%), H-1→L+11 (12%), H-1→L+12 (36%)
84	226.2733	1E-4	H-9→L+4 (21%), H-7→L+4 (49%)
85	226.02992	0.0069	H-14→L+1 (33%), H-9→L+4 (23%), H-7→L+4 (25%)
86	224.95544	0.0165	H-14→L+2 (32%), H-4→L+7 (23%), H-1→L+10 (22%)
87	224.6416	0.0100	H-14→L+1 (22%), H-9→L+4 (43%)
88	220.61637	0.0048	H-13→L+1 (20%), HOMO→L+10 (63%)
89	220.24015	0.0033	H-14→L+2 (13%), H-13→L+1 (41%), H-4→L+5 (33%)
90	220.13457	2E-4	H-13→L+1 (20%), H-4→L+5 (62%)
91	219.29356	0.0098	H-14→L+2 (23%), H-13→L+1 (14%), H-1→L+10 (17%), HOMO→L+10 (24%)

92	219.21214	4E-4	H-10→L+3 (85%), H-8→L+3 (11%)
93	218.45125	0.0129	H-14→L+1 (11%), H-4→L+6 (58%)
94	218.17064	7E-4	H-13→L+2 (80%), HOMO→L+11 (12%)
95	217.9099	0.0118	H-14→L+1 (10%), H-4→L+6 (38%), H-1→L+11 (11%)
96	217.26456	0.0071	HOMO→L+11 (74%)
97	216.17735	0.0026	H-10→L+4 (78%), H-8→L+4 (12%)
98	215.44109	0.0010	H-5→L+5 (95%)
99	214.90336	0.0367	H-15→L+1 (27%), H-1→L+11 (25%)
100	214.81772	0.0305	H-4→L+7 (17%), H-1→L+10 (20%)

2. $Ir(ppy)_2(pdp)$ (Ir2)

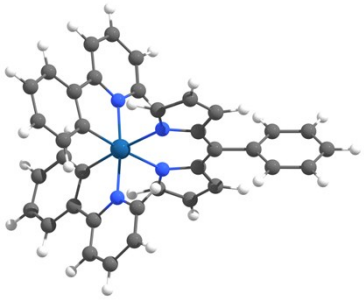
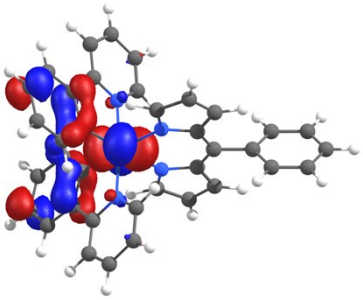
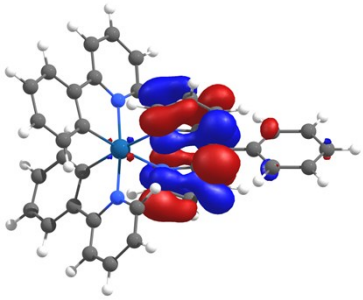


Figure S26. Optimized structure of **Ir2** in the ground state



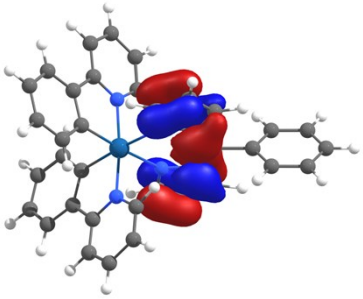
HOMO

(-5.28 eV)



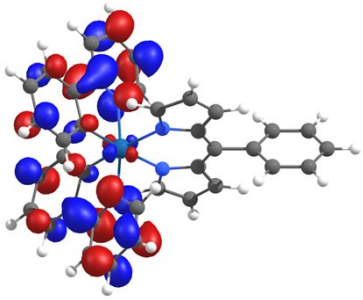
LUMO

(-2.06 eV)



HOMO-1

(-5.31 eV)



LUMO+1

(-1.47 eV)

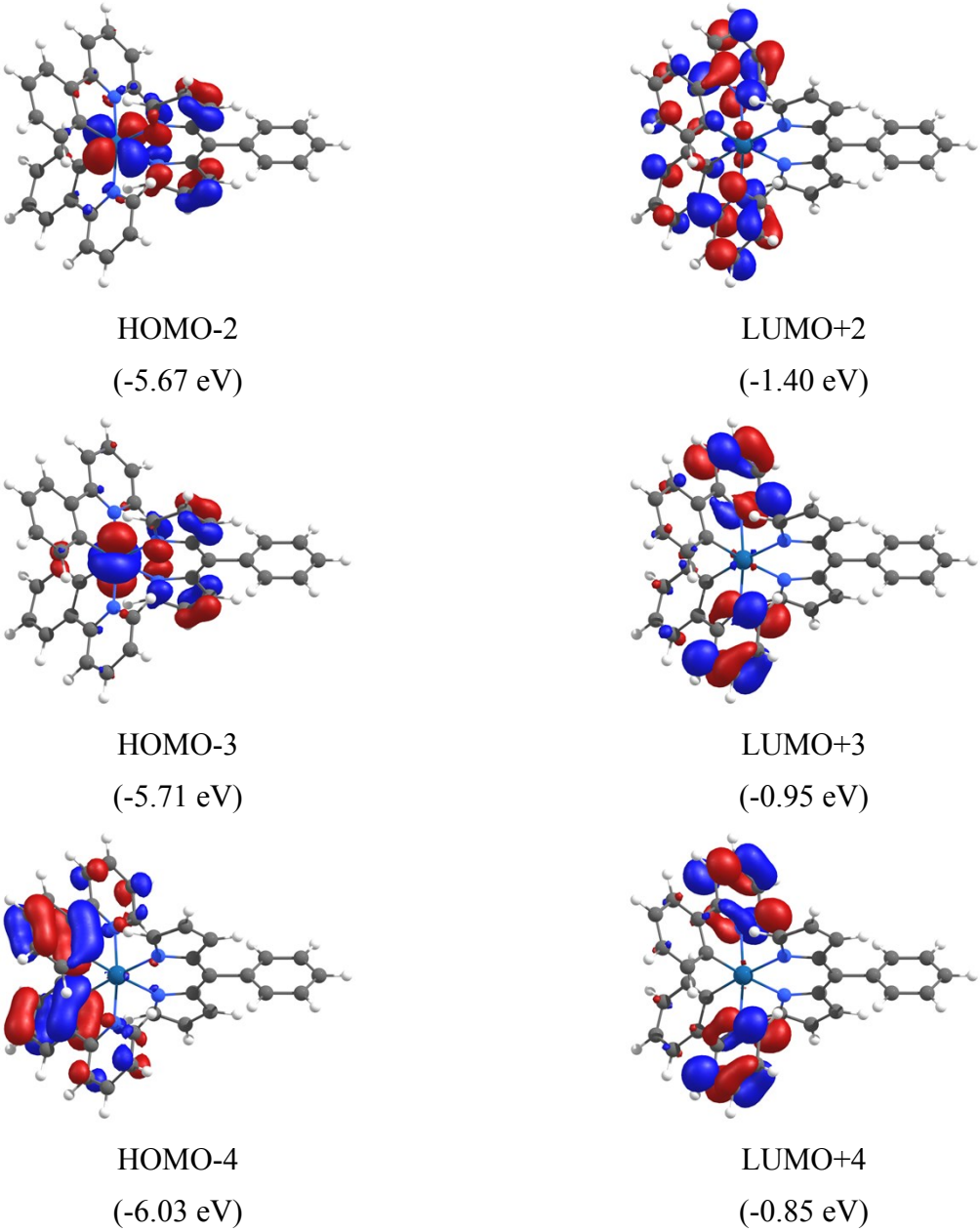


Figure S27. Representation of the frontier MOs of **Ir2** in the ground state.

Table S5. Atomic contributions of the frontier MOs of **Ir2**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-6.03	-5.71	-5.67	-5.31	-5.28	-2.06	-1.47	-1.40	-0.95	-0.85
Ir (%)	1.73	57.20	55.58	4.47	49.27	4.02	3.22	4.81	3.54	6.36
ppy (%)	95.67	19.11	18.48	2.64	42.07	5.71	94.24	93.35	94.38	89.88
pdp (%)	2.60	23.69	25.95	92.88	8.66	90.27	2.54	1.84	2.09	3.76

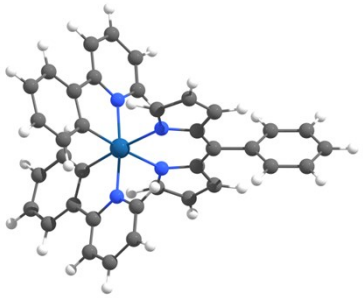


Figure S28. Optimized structure of **Ir2** in the triplet state.

LSOMO (-5.29 eV)

HSOMO (-3.44 eV)

Figure S29. Representation of the frontier MOs of **Ir2** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 1.89\ eV = 656\ nm$

Table S6. Atomic contributions of the frontier MOs of **Ir2** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-5.29	-3.44
Ir (%)	52.57	3.46
ppy (%)	41.86	3.63
pdp (%)	5.57	92.90

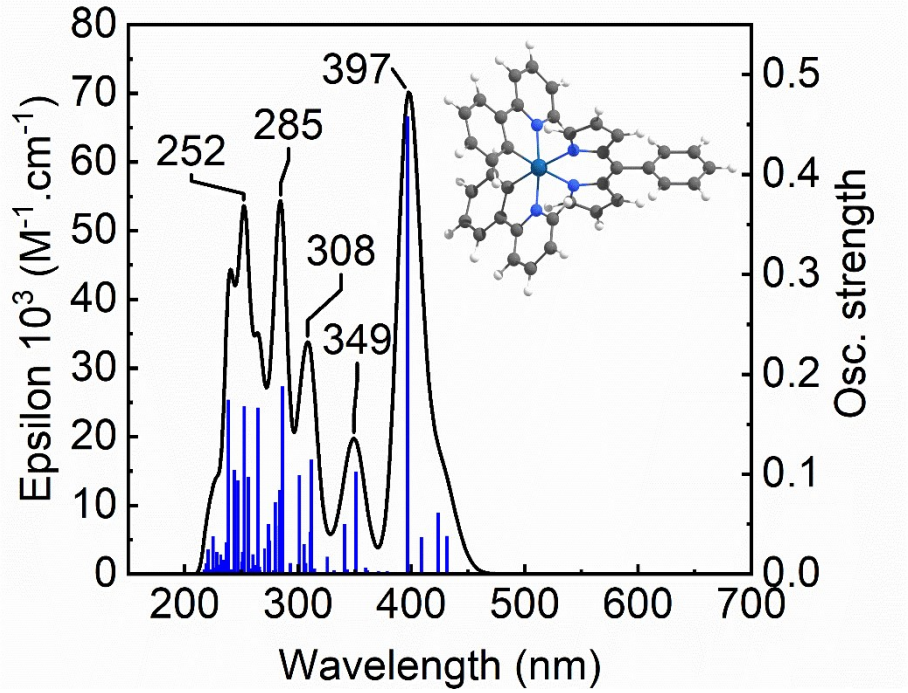


Figure S30. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir2** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S7. First 100 calculated spin-allowed electronic transitions of **Ir2**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	489.1667	4E-4	HOMO→LUMO (98%)
2	431.17438	0.0383	H-3→LUMO (83%), H-1→LUMO (15%)
3	423.48667	0.0615	H-2→LUMO (98%)
4	408.73011	0.0370	HOMO→L+1 (96%)
5	398.03587	0.0033	HOMO→L+2 (96%)
6	396.73672	0.4582	H-3→LUMO (15%), H-1→LUMO (83%)
7	378.312	0.0033	H-1→L+1 (99%)
8	370.7883	0.0032	H-1→L+2 (99%)
9	361.09096	0.0038	H-4→LUMO (94%)
10	359.68724	0.0064	H-3→L+1 (50%), H-2→L+2 (47%)
11	359.49952	0.0016	H-3→L+2 (13%), H-2→L+1 (79%)
12	350.96157	0.1025	H-3→L+1 (46%), H-2→L+2 (49%)
13	343.28486	0.0048	H-3→L+2 (76%), H-2→L+1 (10%)
14	340.925	0.0503	HOMO→L+3 (94%)
15	331.47309	0.0041	H-5→LUMO (97%)

16	330.74799	9E-4	HOMO→L+4 (90%)
17	325.83688	0.0173	H-1→L+3 (97%)
18	322.58988	0.0018	H-6→LUMO (95%)
19	318.56165	1E-4	H-1→L+4 (99%)
20	314.26593	0.0053	H-4→L+1 (75%), H-2→L+3 (18%)
21	311.54938	0.1145	H-8→LUMO (93%)
22	311.15063	0.0046	H-7→LUMO (95%)
23	310.50386	0.0425	H-4→L+2 (55%), H-3→L+3 (32%)
24	306.58801	0.0112	H-4→L+1 (13%), H-2→L+3 (70%)
25	305.16932	0.0298	H-4→L+2 (15%), H-3→L+3 (58%), H-2→L+4 (25%)
26	301.01287	0.0057	H-9→LUMO (91%)
27	300.99826	0.0989	H-4→L+2 (22%), H-2→L+4 (59%)
28	297.70258	0.0000	H-3→L+4 (79%)
29	293.09298	0.0111	H-10→LUMO (99%)
30	286.20543	0.1879	H-5→L+1 (84%)
31	283.5869	0.0843	H-5→L+2 (78%), H-4→L+3 (12%)
32	283.37949	0.0483	H-6→L+1 (81%)
33	280.08266	0.001	H-11→LUMO (92%)
34	280.04471	0.0043	H-1→L+5 (86%)
35	279.74773	0.0718	H-6→L+2 (76%)
36	278.0351	0.0041	H-12→LUMO (96%)
37	274.38023	0.0330	H-5→L+2 (10%), H-4→L+3 (68%)
38	274.01638	0.0504	H-1→L+6 (96%)
39	270.28884	0.0256	H-7→L+1 (30%), H-4→L+4 (55%)
40	266.24333	0.0041	HOMO→L+5 (97%)
41	265.58177	0.0075	H-3→L+9 (17%), HOMO→L+9 (36%), HOMO→L+10 (11%)
42	264.6577	0.1667	H-7→L+1 (58%), H-4→L+4 (31%)
43	262.76188	0.0018	HOMO→L+6 (93%)
44	262.556	0.0087	H-7→L+2 (71%)
45	260.29054	8E-4	H-9→L+1 (62%)
46	260.18676	0.0197	H-9→L+2 (21%), H-2→L+8 (12%), H-2→L+9 (36%)
47	258.49427	0.0058	H-9→L+2 (24%), H-5→L+3 (38%), H-2→L+9 (15%)
48	255.98058	0.0971	H-9→L+2 (21%), H-5→L+3 (22%), HOMO→L+7 (37%)
49	254.29004	0.0000	H-8→L+1 (94%)
50	252.54449	0.1678	H-13→LUMO (10%), H-9→L+2 (10%), H-5→L+3 (26%), HOMO→L+7 (32%)
51	251.96966	0.0016	H-6→L+3 (73%)
52	251.74455	0.0197	H-13→LUMO (84%)
53	251.27007	0.0105	H-6→L+3 (14%), H-5→L+4 (21%), H-2→L+5 (31%)
54	250.89889	0.0223	H-11→L+1 (14%), H-5→L+4 (33%), H-2→L+5 (30%)
55	250.8329	0.0039	H-12→L+1 (21%), H-11→L+2 (11%), H-8→L+2 (55%)

56	250.30119	0.0126	H-12→L+1 (32%), H-11→L+2 (10%), H-9→L+2 (13%), H-8→L+2 (32%)
57	250.12446	0.0110	H-11→L+1 (12%), H-5→L+4 (15%), H-3→L+9 (16%), H-2→L+5 (17%)
58	249.65103	0.0026	H-12→L+2 (10%), H-11→L+1 (21%), H-5→L+4 (13%), H-3→L+9 (10%), H-2→L+5 (14%), HOMO→L+9 (10%)
59	248.55996	7E-4	H-3→L+5 (96%)
60	247.37962	0.0029	H-2→L+6 (97%)
61	247.01491	0.0934	H-6→L+4 (84%)
62	245.2219	0.0011	H-3→L+6 (97%)
63	243.60781	0.1044	H-12→L+2 (12%), HOMO→L+8 (55%), HOMO→L+9 (13%)
64	241.94398	3E-4	H-11→L+2 (28%), H-10→L+1 (16%), H-1→L+7 (44%)
65	241.81657	0.0014	H-11→L+2 (26%), H-1→L+7 (54%)
66	241.50099	0.0044	H-12→L+2 (45%), H-11→L+1 (29%)
67	240.58717	0.0048	H-12→L+1 (16%), H-11→L+2 (13%), H-10→L+1 (68%)
68	240.12587	0.0032	H-1→L+8 (94%)
69	238.53665	0.0217	H-7→L+3 (86%)
70	238.46783	0.1745	H-14→LUMO (85%)
71	237.44483	1E-4	H-10→L+2 (88%)
72	236.73304	0.0028	H-2→L+7 (89%)
73	236.45763	0.0313	H-3→L+7 (67%), H-2→L+8 (17%)
74	234.22411	0.0142	H-9→L+3 (24%), H-7→L+4 (58%)
75	233.3864	0.0000	H-9→L+3 (55%), H-7→L+4 (33%)
76	233.12311	0.0056	H-15→LUMO (18%), H-13→L+1 (11%), H-3→L+7 (12%), H-2→L+8 (37%)
77	232.8123	2E-4	H-15→LUMO (81%)
78	231.62493	0.0192	H-3→L+8 (72%)
79	230.2784	0.0040	H-16→LUMO (77%), H-8→L+3 (16%)
80	230.25274	0.0076	H-13→L+1 (18%), H-9→L+4 (59%)
81	230.1758	3E-4	H-16→LUMO (17%), H-8→L+3 (73%)
82	228.69827	0.0094	H-1→L+9 (78%), H-1→L+10 (13%)
83	228.62236	0.0041	H-13→L+1 (15%), H-9→L+4 (20%), HOMO→L+11 (19%), HOMO→L+13 (28%)
84	228.01691	0.0220	H-13→L+1 (36%), H-2→L+8 (13%), HOMO→L+11 (14%)
85	227.9205	4E-4	H-13→L+2 (32%), H-4→L+5 (10%), H-4→L+7 (11%), HOMO→L+10 (27%)
86	226.94427	1E-4	H-10→L+5 (33%), H-8→L+6 (46%)
87	226.5379	0.0016	H-4→L+5 (88%)
88	225.99696	0.0063	H-8→L+4 (85%)
89	224.85753	0.0378	H-13→L+2 (47%), HOMO→L+10 (34%)
90	224.62125	1E-4	H-4→L+6 (95%)
91	222.32139	0.0050	H-12→L+3 (56%), H-11→L+3 (20%)

92	222.22177	0.0014	H-12→L+3 (19%), H-12→L+4 (10%), H-11→L+3 (62%)
93	220.47122	0.0250	HOMO→L+11 (39%), HOMO→L+13 (37%)
94	219.66655	0.0024	H-14→L+1 (73%), H-1→L+10 (22%)
95	219.27029	0.0012	H-10→L+3 (86%)
96	218.70944	0.0105	H-14→L+1 (23%), H-1→L+9 (11%), H-1→L+10 (63%)
97	217.11998	0.0046	H-12→L+4 (60%), H-11→L+3 (12%), H-10→L+4 (20%)
98	217.00977	0.0012	H-14→L+2 (78%), H-1→L+11 (10%)
99	216.74421	0.0022	H-12→L+3 (14%), H-11→L+4 (74%)
100	216.05303	0.0023	H-1→L+11 (83%)

3. $Ir(piq)_2(pdp)$ (Ir3)

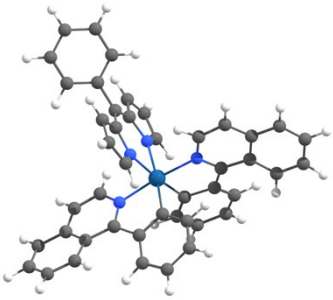
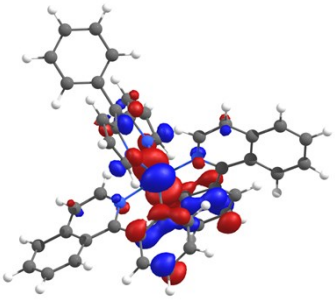
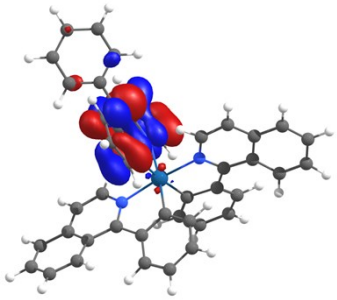


Figure S31. Optimized structure of **Ir3** in the ground state.



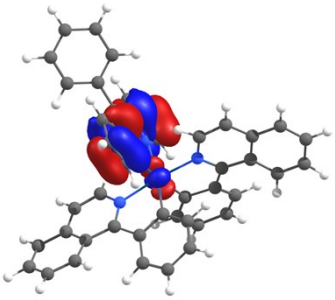
HOMO

(-5.26 eV)



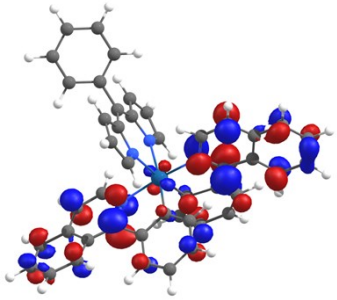
LUMO

(-2.07 eV)



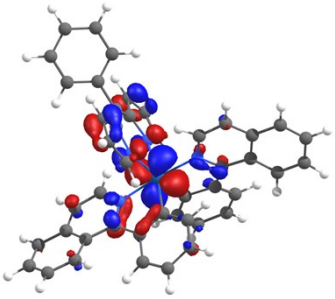
HOMO-1

(-5.32eV)



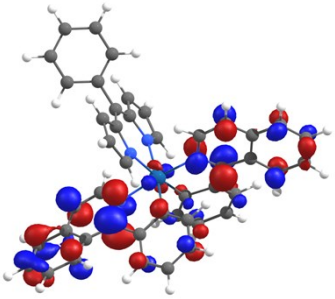
LUMO+1

(-1.98 eV)



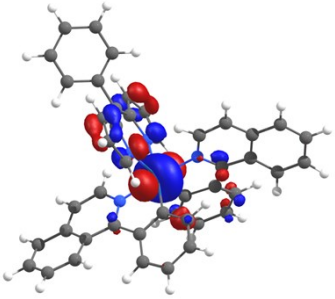
HOMO-2

(-5.61 eV)



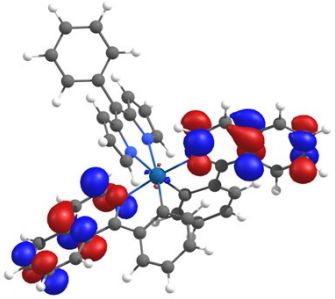
LUMO+2

(-1.91 eV)



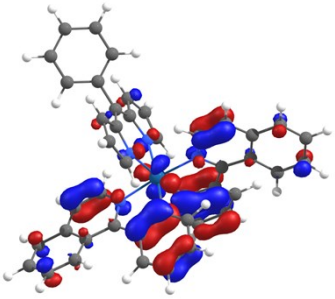
HOMO-3

(-5.68 eV)



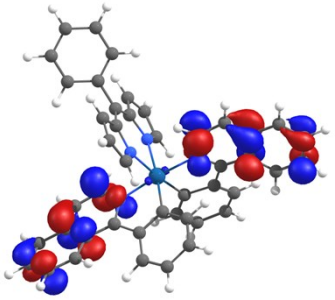
LUMO+3

(-0.93 eV)



HOMO-4

(-5.92 eV)



LUMO+4

(-0.90 eV)

Figure S32. Representation of the frontier MOs of **Ir3** in the ground state.

Table S8. Atomic contributions of the frontier MOs of **Ir3**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-5.92	-5.68	-5.61	-5.32	-5.26	-2.07	-1.98	-1.91	-0.93	-0.90
Ir (%)	9.78	51.19	48.56	8.39	42.01	3.39	4.00	4.50	2.61	4.38
piq (%)	82.15	28.74	32.94	6.98	42.17	7.34	92.76	93.52	95.38	93.04
pdp (%)	8.06	20.07	18.50	84.64	15.82	89.27	3.24	1.97	2.01	2.57

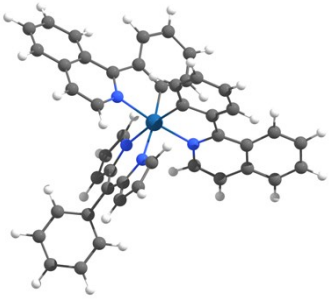
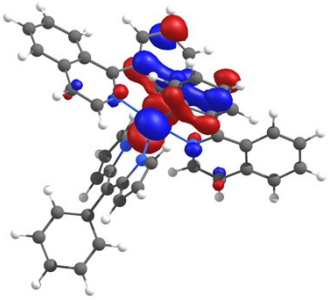
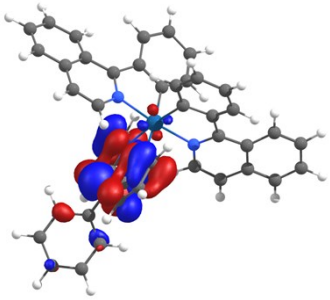


Figure S33. Optimized structure of **Ir3** in the triplet state.



LSOMO

(-5.27 eV)



HSOMO

(-3.57 eV)

Figure S34. Representation of the frontier MOs of **Ir3** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 1.90\ eV = 653\ nm$

Table S9. Atomic contributions of the frontier MOs of **Ir3** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-5.27	-3.57
Ir (%)	49.70	3.51
piq (%)	44.68	3.75
pdp (%)	5.61	92.74

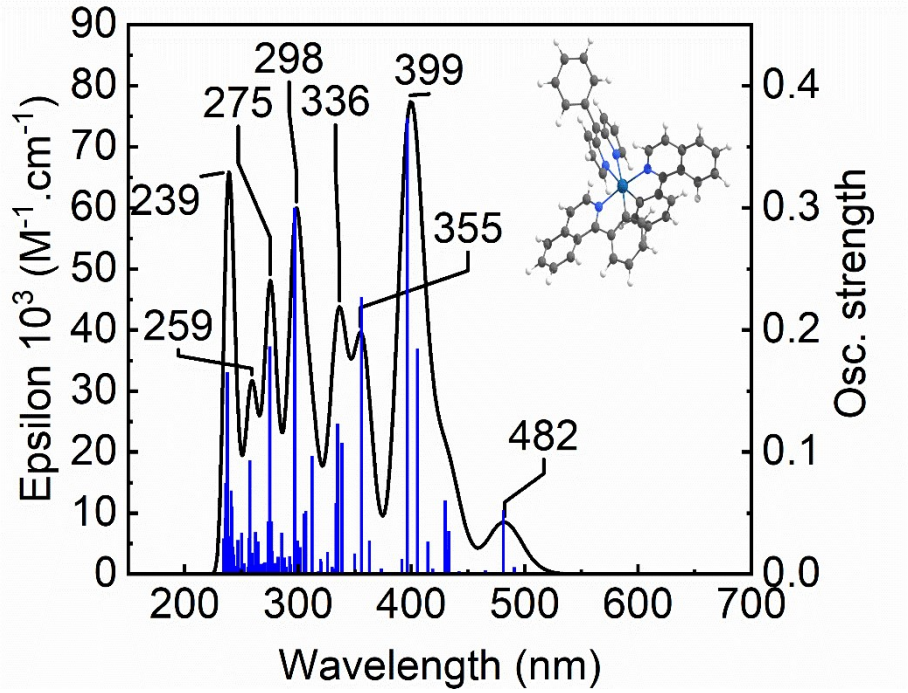


Figure S35. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir3** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S10. First 100 calculated spin-allowed electronic transitions of **Ir3**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	490.6573	0.0055	H-1→LUMO (17%), HOMO→LUMO (77%)
2	481.11833	0.0524	HOMO→L+1 (83%)
3	464.96978	0.0032	HOMO→L+2 (88%)
4	441.9011	0.0024	H-1→L+1 (88%), HOMO→L+1 (10%)
5	432.92082	0.0354	H-3→LUMO (66%), H-1→LUMO (12%), H-1→L+2 (13%)
6	430.71004	0.0199	H-3→LUMO (12%), H-2→LUMO (26%), H-1→L+2 (54%)
7	429.72478	0.0603	H-2→LUMO (65%), H-1→L+2 (21%)
8	418.75234	0.0043	H-3→L+1 (13%), H-2→L+1 (64%), H-2→L+2 (11%)
9	414.62125	0.0264	H-3→L+1 (41%), H-2→L+1 (18%), H-2→L+2 (28%)
10	405.20359	0.1849	H-3→L+1 (39%), H-2→L+2 (54%)
11	396.25489	0.3733	H-3→LUMO (15%), H-1→LUMO (65%), HOMO→LUMO (13%)
12	391.59911	0.0123	H-3→L+2 (81%)
13	373.33391	0.0047	H-4→LUMO (97%)
14	362.79208	0.0272	H-4→L+1 (93%)
15	355.8061	0.2271	H-4→L+2 (92%)

16	349.86227	0.0170	H-5→LUMO (98%)
17	338.79165	0.1077	H-5→L+1 (84%)
18	334.76669	0.1230	HOMO→L+3 (80%)
19	333.4791	0.0583	H-5→L+2 (74%), HOMO→L+4 (10%)
20	331.17205	0.0041	H-5→L+2 (14%), HOMO→L+4 (76%)
21	329.83292	0.0061	H-6→LUMO (96%)
22	325.85401	0.0179	H-6→L+1 (83%)
23	320.48025	0.0104	H-1→L+3 (82%)
24	319.60455	0.0124	H-6→L+2 (87%)
25	318.01419	0.0027	H-1→L+4 (83%)
26	312.12193	0.0966	H-8→LUMO (80%), H-7→LUMO (14%)
27	311.90207	0.0146	H-8→LUMO (14%), H-7→LUMO (81%)
28	306.6866	0.0516	H-2→L+3 (52%), H-2→L+4 (23%)
29	305.38731	0.0494	H-7→L+1 (15%), H-2→L+3 (24%), H-2→L+4 (46%)
30	301.69407	0.0221	H-3→L+3 (75%)
31	301.30548	0.0073	H-9→LUMO (87%)
32	299.10304	0.0276	H-3→L+3 (11%), H-3→L+4 (59%)
33	297.05351	0.3000	H-7→L+1 (59%), H-2→L+4 (16%)
34	293.55793	0.0078	H-11→LUMO (91%)
35	292.49833	0.0145	H-7→L+2 (41%), H-3→L+4 (20%)
36	289.45275	0.0059	H-9→L+1 (58%), H-7→L+2 (26%)
37	287.65967	0.0135	H-10→L+1 (29%), H-9→L+2 (39%)
38	285.52655	0.0337	H-12→L+2 (10%), H-10→L+1 (29%), H-9→L+2 (32%), HOMO→L+5 (12%)
39	284.96218	0.0016	H-12→L+1 (12%), H-10→LUMO (39%), H-10→L+2 (13%), H-8→L+1 (17%)
40	284.1263	0.0015	H-13→LUMO (12%), H-10→LUMO (30%), H-8→L+1 (33%)
41	282.51423	0.0127	H-13→LUMO (12%), H-10→L+2 (12%), H-8→L+1 (20%), HOMO→L+5 (32%)
42	282.27624	0.0141	H-10→L+1 (10%), H-8→L+1 (23%), HOMO→L+5 (36%)
43	281.5455	0.0024	H-13→LUMO (60%), H-10→LUMO (18%)
44	279.52698	0.0091	H-1→L+7 (73%), HOMO→L+7 (24%)
45	278.8982	9E-4	H-8→L+2 (43%), HOMO→L+6 (41%)
46	278.75398	0.0010	H-8→L+2 (49%), HOMO→L+6 (30%)
47	277.57448	0.0023	H-12→LUMO (73%)
48	276.62694	0.0185	H-13→L+1 (28%), H-4→L+3 (39%)
49	276.3926	0.0429	H-13→L+1 (23%), H-13→L+2 (12%), H-4→L+3 (16%), H-4→L+4 (18%)
50	274.91561	0.1864	H-9→L+2 (13%), H-4→L+4 (50%)
51	273.71392	0.0429	H-1→L+8 (68%), HOMO→L+8 (25%)
52	272.50471	0.0011	H-14→L+1 (10%), H-12→L+1 (36%), H-10→L+2 (24%)
53	272.36104	6E-4	H-14→LUMO (84%)

54	271.22898	8E-4	H-1→L+5 (88%)
55	270.48343	0.0098	H-14→L+1 (35%), H-13→L+2 (15%), H-12→L+1 (18%), H-10→L+2 (10%)
56	269.50742	0.0085	H-12→L+2 (72%), H-10→L+1 (11%)
57	268.49191	0.0012	H-1→L+6 (85%)
58	267.31677	0.0058	H-13→L+2 (13%), H-11→L+1 (55%)
59	266.8967	0.0084	H-11→L+1 (12%), HOMO→L+7 (19%), HOMO→L+9 (10%), HOMO→L+11 (15%)
60	266.30051	0.0018	H-13→L+2 (10%), H-11→L+1 (13%), HOMO→L+7 (28%)
61	266.1576	0.0023	H-14→L+1 (12%), H-13→L+2 (14%), HOMO→L+7 (24%)
62	264.81032	0.0266	H-5→L+3 (49%)
63	264.42628	0.0077	H-5→L+4 (36%), H-2→L+5 (15%)
64	263.07968	0.0175	H-11→L+2 (45%)
65	262.94578	8E-4	H-11→L+2 (10%), H-1→L+8 (23%), HOMO→L+8 (62%)
66	262.39486	0.0342	H-11→L+2 (26%), H-2→L+6 (16%), HOMO→L+9 (10%)
67	260.96991	0.0073	H-5→L+4 (16%), H-2→L+5 (48%)
68	259.37573	0.0171	H-14→L+1 (15%), H-14→L+2 (60%)
69	257.77411	0.0129	H-3→L+5 (56%)
70	257.39416	0.0929	H-3→L+5 (25%), HOMO→L+9 (35%)
71	256.94076	0.0297	H-3→L+6 (10%), H-2→L+6 (43%), H-2→L+11 (16%)
72	255.90133	0.006	H-3→L+6 (72%)
73	253.77995	0.0013	H-6→L+3 (66%), H-6→L+4 (12%), H-5→L+4 (12%)
74	252.19005	0.0088	H-2→L+7 (91%)
75	252.01576	0.0052	H-6→L+3 (13%), H-6→L+4 (66%)
76	250.15474	0.0338	H-3→L+11 (33%), HOMO→L+10 (26%)
77	248.96424	0.0048	H-2→L+8 (92%)
78	248.54003	0.0010	H-3→L+7 (91%)
79	247.70087	0.0020	H-18→LUMO (20%), H-15→LUMO (59%)
80	246.96571	0.0278	HOMO→L+10 (28%), HOMO→L+11 (20%)
81	246.59731	0.0016	H-1→L+9 (85%), HOMO→L+9 (10%)
82	245.37235	4E-4	H-18→L+1 (12%), H-3→L+8 (64%)
83	245.15887	0.0011	H-18→L+1 (26%), H-17→L+1 (11%), H-15→L+1 (16%), H-3→L+8 (26%)
84	244.58818	0.0066	H-4→L+5 (70%)
85	243.50733	0.0064	H-4→L+6 (22%), H-2→L+9 (34%)
86	242.8634	0.0161	H-18→LUMO (33%), H-15→LUMO (17%), H-4→L+6 (20%)
87	242.42178	0.0192	H-4→L+6 (16%), H-1→L+10 (44%)
88	242.14717	0.0225	H-18→LUMO (11%), H-2→L+9 (11%), H-1→L+10 (37%)
89	241.97231	0.0054	H-17→LUMO (45%), H-16→LUMO (33%)
90	241.65632	0.0550	H-15→L+1 (10%), H-15→L+2 (24%)
91	241.00807	0.0181	H-3→L+9 (28%)
92	240.83018	0.0684	--

93	240.60118	0.0313	H-18→L+2 (19%), H-3→L+9 (17%)
94	239.0241	0.0034	H-18→L+1 (13%), H-17→L+1 (19%), H-16→L+1 (52%)
95	237.37664	0.1655	H-18→LUMO (16%), H-17→LUMO (30%), H-16→LUMO (32%)
96	236.17836	0.0745	H-16→L+2 (21%), H-7→L+3 (21%), H-2→L+10 (15%)
97	235.91322	0.0459	H-16→L+2 (44%), H-2→L+10 (10%)
98	235.26412	0.0057	H-7→L+3 (65%), H-2→L+10 (13%)
99	234.35694	0.0040	H-18→L+1 (13%), H-17→L+1 (16%), H-7→L+4 (31%)
100	234.10029	0.0291	H-7→L+4 (31%), H-3→L+10 (23%)

4. Ir(piq-dpa)$_2$(pdp) (Ir4)

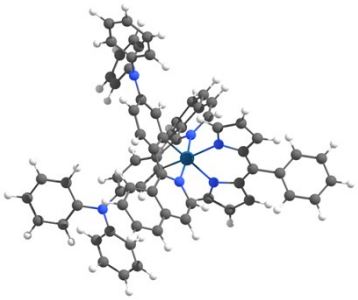
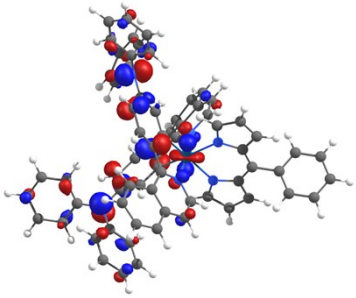
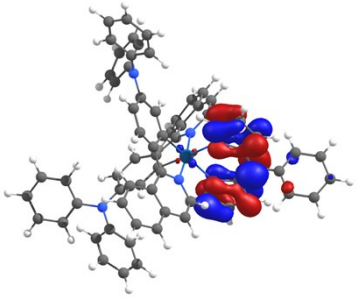


Figure S36. Optimized structure of **Ir4** in the ground state.



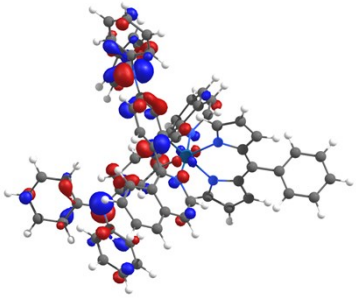
HOMO

(-4.93 eV)



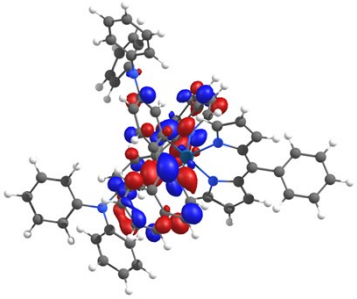
LUMO

(-2.05 eV)



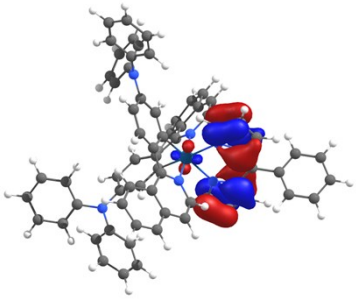
HOMO-1

(-4.98 eV)



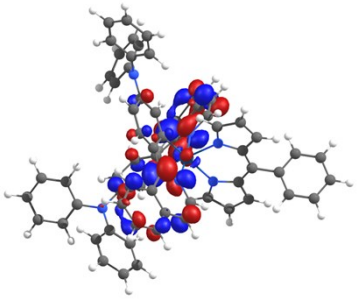
LUMO+1

(-1.92 eV)



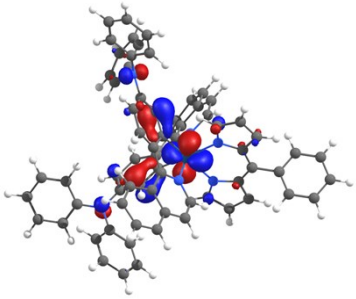
HOMO-2

(-5.29 eV)



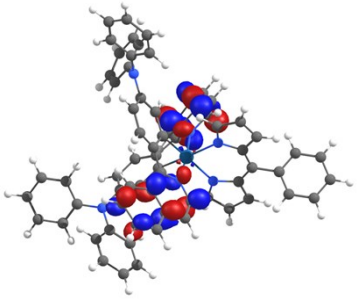
LUMO+2

(-1.85 eV)



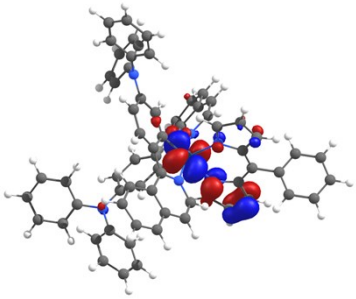
HOMO-3

(-5.38 eV)



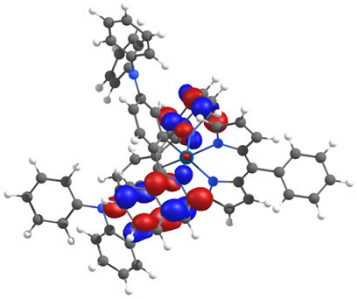
LUMO+3

(-0.88 eV)



HOMO-4

(-5.64 eV)



LUMO+4

(-0.84 eV)

Figure S37. Representation of the frontier MOs of **Ir4** in the ground state.

Table S11. Atomic contributions of the frontier MOs of **Ir4**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-5.64	-5.38	-5.29	-4.98	-4.93	-2.05	-1.92	-1.85	-0.88	-0.84
Ir (%)	52.65	43.41	4.93	2.94	8.16	3.94	3.24	3.93	4.81	4.83
Piq-dpa (%)	23.08	46.20	4.13	96.41	90.27	5.90	94.40	93.85	93.55	92.83
pdp (%)	24.27	10.39	90.94	0.65	1.57	90.15	2.36	2.22	1.64	2.34

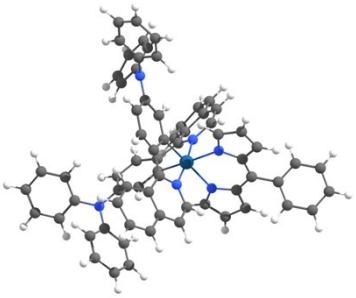


Figure S38. Optimized structure of **Ir4** in the triplet state.

LSOMO (-4.93 eV)

HSOMO (-3.41 eV)

Figure S39. Representation of the frontier MOs of **Ir4** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 1.89\ eV = 656\ nm$

Table S12. Atomic contributions of the frontier MOs of **Ir4** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-4.93	-3.41
Ir (%)	9.11	3.56
Piq-dpa (%)	89.32	3.62
pdp (%)	1.57	92.82

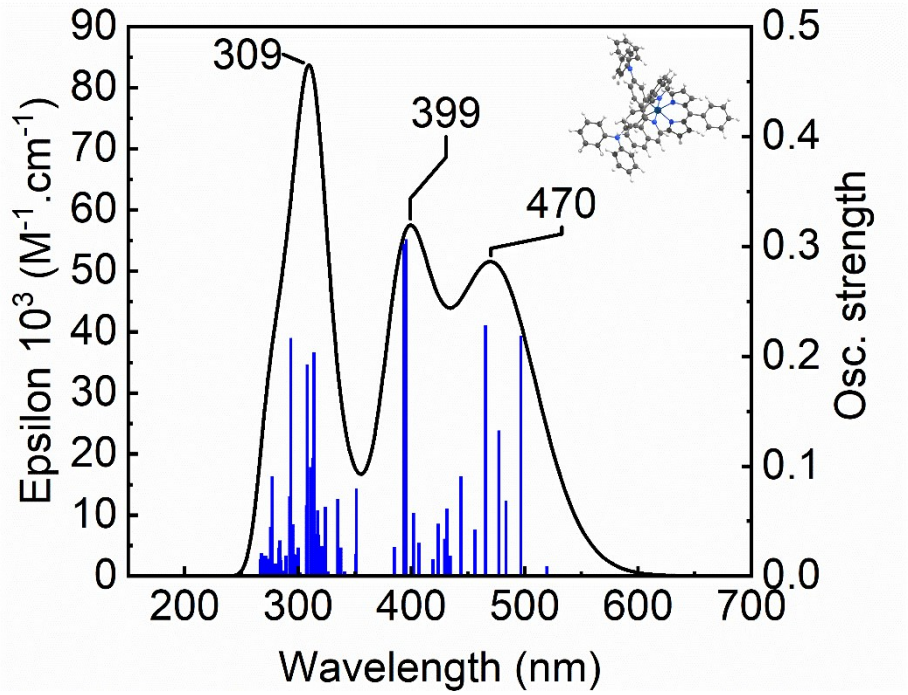


Figure S40. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir4** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S13. First 100 calculated spin-allowed electronic transitions of **Ir4**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	519.4143	0.0091	HOMO→LUMO (86%)
2	496.57238	0.2188	HOMO→L+1 (89%)
3	494.47313	0.0016	H-1→LUMO (97%)
4	483.33149	0.0686	HOMO→L+2 (90%)
5	477.11919	0.1324	H-1→L+1 (96%)
6	465.28387	0.2283	H-1→L+2 (94%)
7	455.97511	0.0421	H-3→LUMO (70%), H-2→LUMO (13%), HOMO→LUMO (12%)
8	443.62456	0.0907	H-3→L+1 (51%), H-2→L+1 (35%)
9	434.27038	0.0184	H-3→L+1 (23%), H-2→L+1 (40%)
10	431.23437	0.0615	H-3→L+1 (10%), H-3→L+2 (31%), H-2→L+1 (14%), H-2→L+2 (28%)
11	429.26356	0.0340	H-5→LUMO (53%), H-4→LUMO (11%), H-2→L+2 (10%)
12	423.3999	0.0476	H-4→LUMO (25%), H-3→L+2 (24%), H-2→L+2 (41%)
13	419.0354	0.0155	H-5→LUMO (17%), H-4→LUMO (43%), H-3→L+2 (22%)
14	406.53221	0.0300	H-5→L+1 (13%), H-4→L+1 (66%), H-4→L+2 (13%)
15	401.69834	0.0572	H-5→L+1 (61%), H-5→L+2 (10%), H-4→L+1 (17%)
16	395.23173	0.3064	H-4→L+2 (54%), H-2→LUMO (24%)

17	393.28848	0.3023	H-5→L+1 (16%), H-4→L+2 (24%), H-2→LUMO (38%)
18	384.76924	0.0263	H-5→L+2 (81%)
19	351.30963	0.0798	H-6→LUMO (11%), HOMO→L+3 (79%)
20	350.62411	0.0203	H-6→LUMO (85%), HOMO→L+3 (10%)
21	346.49878	5E-4	H-1→L+3 (18%), HOMO→L+4 (70%)
22	341.41317	0.002	H-1→L+3 (74%), HOMO→L+4 (19%)
23	340.84064	0.0042	H-6→L+1 (84%)
24	337.61081	0.0261	H-1→L+4 (80%)
25	336.81289	0.0030	H-7→LUMO (93%)
26	335.00187	0.0705	H-6→L+2 (83%)
27	326.23127	0.004	H-8→LUMO (91%)
28	323.96382	0.0631	H-7→L+1 (79%)
29	320.94482	0.0276	H-8→L+1 (37%), H-7→L+2 (31%)
30	320.1575	0.0051	H-3→L+3 (15%), H-2→L+3 (74%)
31	318.03866	0.0372	H-1→L+5 (13%), HOMO→L+5 (27%), HOMO→L+6 (12%)
32	317.09512	0.0596	H-7→L+2 (16%), H-1→L+5 (10%), H-1→L+6 (13%), HOMO→L+6 (25%)
33	316.69015	0.0056	H-2→L+4 (69%)
34	315.345	0.0383	H-3→L+3 (55%), H-2→L+3 (13%)
35	314.52902	0.0327	H-8→L+1 (28%), H-7→L+2 (33%)
36	313.95557	0.2035	H-1→L+6 (10%), H-1→L+8 (12%), H-1→L+10 (10%), HOMO→L+7 (33%), HOMO→L+9 (11%)
37	313.2971	0.1077	H-8→L+1 (12%), H-1→L+7 (18%), H-1→L+9 (14%), HOMO→L+8 (12%), HOMO→L+10 (21%)
38	311.77658	0.0026	H-3→L+4 (79%), H-2→L+4 (11%)
39	311.45547	0.0526	H-10→LUMO (25%), H-9→LUMO (29%), H-8→L+2 (28%)
40	310.97894	0.0271	H-9→LUMO (61%), H-8→L+2 (20%)
41	310.86978	0.0991	H-10→LUMO (61%), H-8→L+2 (22%)
42	308.01996	0.1924	H-1→L+10 (16%), HOMO→L+7 (23%), HOMO→L+9 (29%)
43	307.10441	0.0641	H-1→L+7 (17%), H-1→L+9 (12%), HOMO→L+8 (32%), HOMO→L+10 (19%)
44	301.67938	0.0031	H-13→LUMO (52%), H-11→LUMO (34%)
45	300.06581	0.0261	H-4→L+3 (28%), H-1→L+5 (18%), H-1→L+8 (11%), HOMO→L+5 (10%)
46	299.74662	0.0092	H-4→L+3 (47%), H-1→L+5 (10%)
47	298.26836	0.0191	H-9→L+1 (12%), H-4→L+4 (18%), H-1→L+6 (18%), HOMO→L+6 (10%)
48	297.99595	0.0029	H-9→L+1 (12%), H-4→L+4 (39%), H-1→L+6 (11%), H-1→L+8 (11%)
49	297.35273	0.0058	H-5→L+3 (65%), H-4→L+4 (14%)
50	295.84851	0.0197	H-1→L+5 (20%), H-1→L+8 (14%), HOMO→L+5 (17%), HOMO→L+7 (15%)
51	295.69328	0.0114	H-1→L+6 (17%), H-1→L+7 (26%), HOMO→L+6 (20%)

52	295.09507	0.0474	H-9→L+1 (14%), H-5→L+3 (10%), H-5→L+4 (40%)
53	293.52318	0.2166	H-16→LUMO (13%), H-9→L+1 (33%), H-5→L+4 (17%), H-4→L+4 (17%)
54	293.01679	0.0012	H-1→L+10 (31%), HOMO→L+9 (21%), HOMO→L+10 (12%)
55	292.80227	0.0045	H-1→L+9 (29%), HOMO→L+10 (21%)
56	292.56735	0.0728	H-16→LUMO (68%)
57	289.17596	0.0187	H-9→L+2 (35%), H-5→L+4 (26%)
58	286.06676	0.0046	H-13→L+1 (20%), H-11→L+1 (37%), H-9→L+2 (29%)
59	284.43918	0.0146	H-12→LUMO (15%), H-12→L+1 (15%), H-1→L+14 (23%), HOMO→L+14 (27%)
60	284.23703	0.0168	H-1→L+13 (26%), HOMO→L+13 (26%)
61	283.62582	0.0323	H-13→L+2 (31%), H-11→L+2 (27%)
62	283.06247	0.0257	H-12→LUMO (34%)
63	282.16703	0.0040	H-2→L+11 (25%), HOMO→L+11 (52%)
64	281.89117	0.0000	H-13→LUMO (13%), H-11→LUMO (23%)
65	281.78866	0.0045	H-11→LUMO (15%), H-3→L+7 (12%)
66	281.30915	0.0021	H-21→LUMO (45%), H-12→LUMO (25%)
67	280.99674	0.0039	H-10→L+1 (12%), H-3→L+8 (25%), H-2→L+8 (10%)
68	280.03838	0.0113	H-12→L+1 (36%)
69	279.79192	0.0022	H-10→L+1 (53%)
70	279.1368	1E-4	H-2→L+11 (57%), HOMO→L+11 (36%)
71	278.32845	0.011	HOMO→L+12 (84%)
72	278.19106	0.0013	H-13→L+1 (34%), H-11→L+1 (18%), H-10→L+1 (15%)
73	276.99156	0.0039	H-12→L+2 (19%), H-2→L+6 (18%), H-2→L+7 (14%)
74	276.93588	0.0909	H-3→L+5 (15%), H-3→L+7 (10%), H-3→L+9 (19%), H-2→L+5 (13%)
75	276.62076	0.0032	H-12→L+2 (19%), H-11→L+2 (10%), H-2→L+5 (10%)
76	276.22634	0.0089	H-10→L+2 (22%), H-3→L+5 (15%)
77	276.12791	0.0032	H-1→L+11 (79%)
78	275.96811	0.0016	H-22→LUMO (26%), H-15→LUMO (13%), H-14→LUMO (18%)
79	275.44698	0.0446	H-3→L+6 (40%), H-2→L+6 (11%), H-2→L+8 (15%)
80	275.09861	0.0025	H-3→L+8 (23%), H-2→L+6 (11%), H-2→L+8 (20%)
81	274.5078	0.0045	H-13→L+2 (12%), H-10→L+2 (33%), H-3→L+9 (11%)
82	273.94373	0.0157	H-13→L+2 (18%), H-11→L+2 (11%), H-3→L+7 (10%), H-3→L+9 (16%)
83	273.73809	0.0129	H-2→L+12 (52%), H-1→L+12 (25%)
84	273.41815	0.0048	H-2→L+12 (20%), H-1→L+12 (74%)
85	273.20125	0.0100	H-21→L+1 (25%), H-17→L+1 (14%), H-12→L+2 (11%)
86	272.52268	0.0056	H-3→L+5 (21%), H-2→L+5 (38%)
87	272.14582	0.0028	H-15→LUMO (12%), H-14→LUMO (36%)
88	271.81171	0.0012	H-3→L+10 (14%), H-2→L+6 (18%), H-2→L+9 (12%), H-2→L+10 (21%)

89	271.28833	0.0106	H-15→L+1 (16%), H-14→L+1 (27%)
90	271.20525	0.0183	H-3→L+10 (26%), H-2→L+6 (19%), H-2→L+8 (10%)
91	270.41263	0.0016	H-17→LUMO (46%), H-14→LUMO (13%)
92	270.21815	0.0182	H-17→LUMO (11%), H-15→L+1 (24%)
93	269.72435	0.0050	H-3→L+9 (14%), H-2→L+7 (15%), H-2→L+9 (39%)
94	269.48985	5E-4	H-15→L+1 (10%), H-14→L+1 (13%)
95	268.67227	0.0027	H-3→L+10 (12%), H-2→L+10 (28%)
96	268.38148	0.0029	H-14→L+1 (10%)
97	267.85386	0.0099	H-15→LUMO (11%)
98	267.58793	0.0040	H-18→LUMO (40%), H-15→LUMO (17%)
99	267.55329	0.0209	H-18→LUMO (26%), H-15→LUMO (11%)
100	266.83352	0.0151	H-18→L+1 (10%)

5. Ir(dfppy)$_2$(acac) (Ir5)

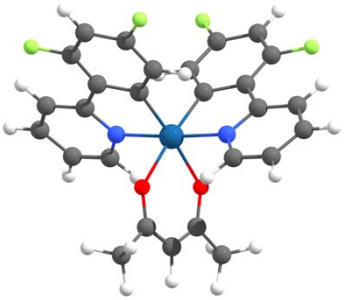
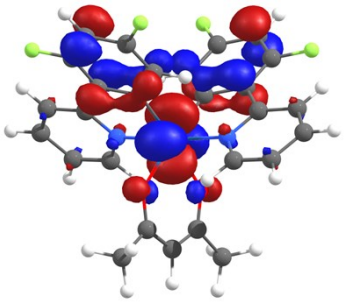
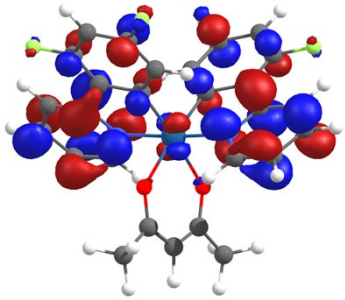


Figure S41. Optimized structure of **Ir5** in the ground state.



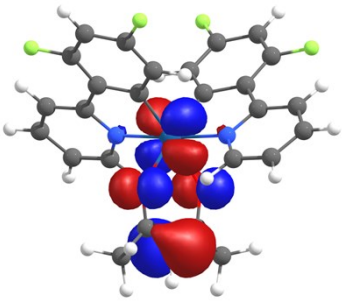
HOMO

(-5.49 eV)



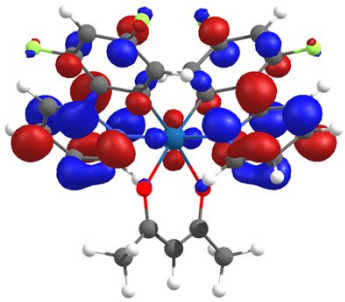
LUMO

(-1.59 eV)



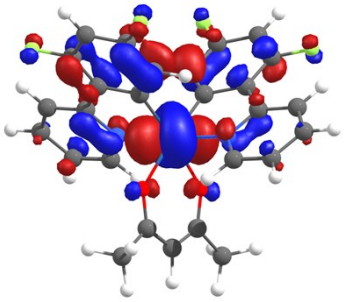
HOMO-1

(-5.75 eV)



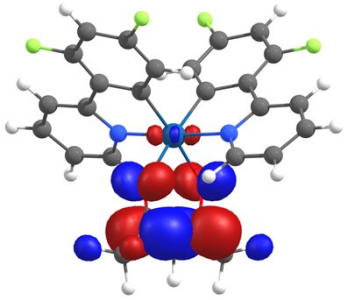
LUMO+1

(-1.56 eV)



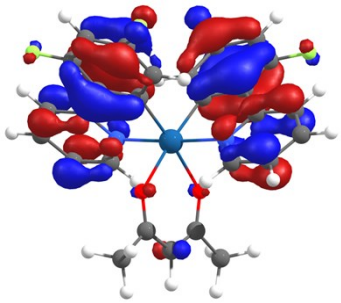
HOMO-2

(-6.24 eV)



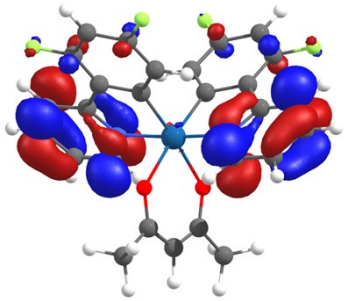
LUMO+2

(-1.08 eV)



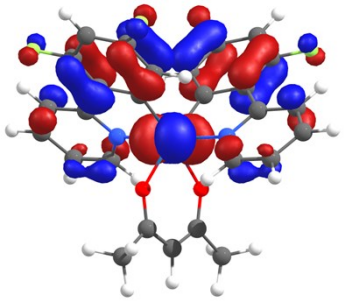
HOMO-3

(-6.24 eV)



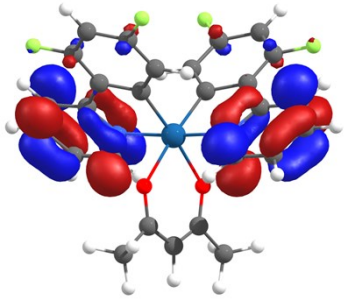
LUMO+3

(-1.00 eV)



HOMO-4

(-6.42 eV)



LUMO+4

(-0.92 eV)

Figure S42. Representation of the frontier MOs of **Ir5** in the ground state.

Table S14. Atomic contributions of the frontier MOs of **Ir5**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-6.42	-6.24	-6.24	-5.75	-5.49	-1.59	-1.56	-1.08	-1.00	-0.92
Ir (%)	33.45	1.05	50.38	36.35	51.24	4.35	4.27	4.84	3.41	6.56
dfppy (%)	64.18	92.12	42.38	11.71	41.20	84.88	82.93	5.07	91.85	88.71
acac (%)	2.36	6.84	7.25	51.94	7.56	10.77	12.80	90.09	4.74	4.73

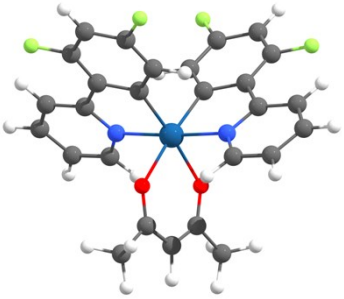
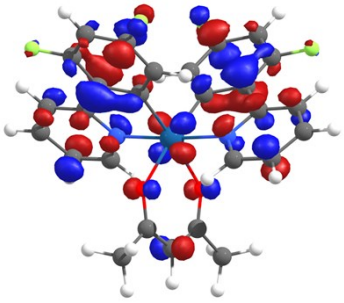
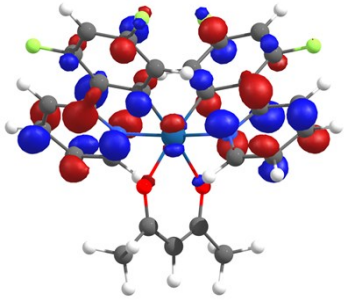


Figure S43. Optimized structure of **Ir5** in the triplet state.



LSOMO

(-6.06 eV)



HSOMO

(-2.48 eV)

Figure S44. Representation of the frontier MOs of **Ir5** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 2.99\ eV = 415\ nm$

Table S15. Atomic contributions of the frontier MOs of **Ir5** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-6.06	-2.48
Ir (%)	9.15	5.96
dfppy (%)	79.64	91.09
acac (%)	11.21	2.95

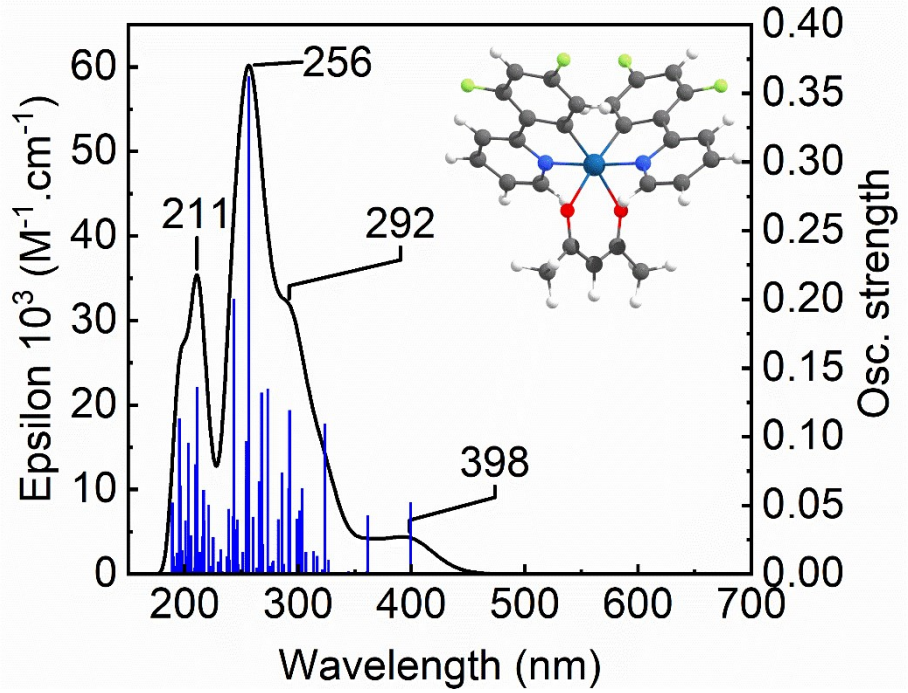


Figure S45. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir5** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S16. First 100 calculated spin-allowed electronic transitions of **Ir5**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	399.27925	0.0525	HOMO→LUMO (97%)
2	390.31699	0.0010	HOMO→L+1 (96%)
3	361.51211	0.0428	H-1→L+1 (95%)
4	360.27254	0.0024	H-1→LUMO (94%)
5	344.16154	0.0024	HOMO→L+2 (98%)
6	326.91943	0.0101	HOMO→L+3 (92%)
7	323.51579	0.1095	H-4→LUMO (11%), H-2→LUMO (74%)
8	321.1277	0.0032	H-2→L+1 (30%), HOMO→L+4 (60%)
9	316.86011	0.0132	H-2→L+1 (48%), HOMO→L+4 (37%)
10	313.50307	0.0169	H-1→L+2 (84%)
11	306.85359	0.0162	H-3→LUMO (24%), H-1→L+3 (68%)
12	303.63724	0.0624	H-3→L+1 (46%), H-1→L+4 (45%)
13	300.96173	0.0463	H-3→LUMO (71%), H-1→L+3 (23%)
14	298.81469	0.04	H-3→L+1 (47%), H-1→L+4 (41%)
15	292.33971	0.1193	H-4→LUMO (66%), H-2→LUMO (10%)

16	291.43265	0.0626	H-4→L+1 (73%), H-2→L+1 (13%)
17	287.49958	0.0075	H-5→LUMO (83%)
18	285.56601	0.0740	H-5→L+1 (81%)
19	282.34052	0.0399	H-4→L+2 (10%), H-2→L+2 (74%)
20	277.79215	0.0096	H-6→LUMO (76%)
21	277.20212	0.0087	H-6→L+1 (63%), H-2→L+3 (18%)
22	275.40415	0.0060	H-7→L+2 (62%), H-5→L+2 (30%)
23	273.04482	0.1350	H-6→L+1 (15%), H-2→L+3 (46%), HOMO→L+5 (19%)
24	268.57915	0.0220	H-3→L+2 (60%), HOMO→L+5 (21%)
25	268.20151	0.0136	H-7→LUMO (13%), H-2→L+4 (57%)
26	267.68037	0.1320	H-3→L+2 (32%), HOMO→L+5 (21%)
27	265.75255	0.0130	H-1→L+6 (28%), H-1→L+7 (34%)
28	265.33737	0.0673	H-7→LUMO (27%), H-2→L+4 (10%), HOMO→L+6 (17%), HOMO→L+7 (21%)
29	263.33112	0.0022	H-7→LUMO (38%), H-7→L+1 (21%), HOMO→L+7 (19%)
30	263.30875	0.0047	H-7→LUMO (12%), H-7→L+1 (66%)
31	261.39907	9E-4	H-4→L+2 (46%), H-3→L+3 (36%)
32	260.08305	0.0418	H-4→L+2 (35%), H-3→L+3 (32%)
33	256.29278	0.3625	H-3→L+4 (81%)
34	254.44137	0.0967	H-4→L+3 (78%), H-2→L+3 (13%)
35	253.8319	0.0689	H-4→L+4 (10%), H-1→L+5 (45%)
36	251.25989	0.0162	H-4→L+4 (69%), H-2→L+4 (12%)
37	250.03871	0.0000	H-5→L+3 (90%)
38	246.88702	0.0070	H-5→L+4 (89%)
39	246.29359	0.0395	H-4→L+7 (12%), H-2→L+7 (30%), H-1→L+5 (29%)
40	245.35292	0.0327	H-7→L+2 (27%), H-5→L+2 (43%)
41	243.13486	0.2004	HOMO→L+5 (19%), HOMO→L+9 (28%), HOMO→L+10 (22%)
42	242.79681	0.0251	H-6→L+3 (66%), HOMO→L+7 (12%)
43	242.66851	0.0419	H-6→L+2 (81%)
44	239.59224	0.0103	H-2→L+5 (24%), H-1→L+6 (38%), H-1→L+7 (15%)
45	238.79852	0.0474	H-8→L+1 (12%), H-6→L+3 (24%), HOMO→L+6 (28%), HOMO→L+7 (20%)
46	238.74794	0.0194	H-6→L+4 (84%)
47	237.27216	0.0129	H-8→LUMO (80%)
48	236.37648	1E-4	H-8→L+1 (70%)
49	232.82979	0.0020	H-7→L+3 (89%)
50	231.75915	0.0180	H-2→L+5 (39%), H-1→L+6 (16%), H-1→L+7 (16%)
51	229.91543	0.0025	H-7→L+4 (87%)
52	229.40494	0.0092	H-9→L+2 (12%), H-8→L+2 (67%)
53	227.82417	3E-4	H-9→L+1 (13%), H-3→L+5 (15%), HOMO→L+8 (42%)
54	225.03302	0.0270	H-9→LUMO (46%), HOMO→L+9 (11%)

55	224.91056	0.0012	H-2→L+7 (15%), H-1→L+9 (28%), H-1→L+10 (24%)
56	222.57283	0.0018	H-9→L+1 (41%), H-2→L+6 (18%), HOMO→L+8 (13%)
57	222.01485	0.0061	H-9→L+1 (28%), H-2→L+6 (35%)
58	221.10422	0.0504	H-9→LUMO (31%), HOMO→L+9 (14%), HOMO→L+10 (21%)
59	216.89209	0.0386	H-3→L+5 (52%), HOMO→L+8 (21%)
60	216.48309	0.061	H-11→L+1 (14%), H-10→LUMO (25%), H-3→L+6 (17%), H-1→L+8 (10%)
61	215.7823	0.0273	H-4→L+5 (27%), H-3→L+6 (43%)
62	214.32383	0.0091	H-11→LUMO (21%), H-10→L+1 (28%), H-4→L+6 (20%)
63	212.94711	0.0159	H-4→L+5 (12%), H-2→L+9 (11%), H-1→L+8 (49%)
64	212.04391	0.0072	H-8→L+3 (17%), H-2→L+9 (17%), H-2→L+10 (17%), H-1→L+8 (19%)
65	210.63895	0.1361	H-6→L+5 (14%), H-5→L+5 (69%)
66	210.38518	0.0551	H-10→LUMO (23%), H-8→L+3 (38%)
67	209.74454	0.0130	H-8→L+4 (10%), H-4→L+6 (34%)
68	209.42568	0.0799	H-8→L+3 (20%), H-4→L+5 (16%)
69	208.99148	0.0131	H-11→L+1 (15%), H-6→L+6 (11%), H-5→L+6 (36%)
70	208.7522	0.0000	H-11→LUMO (44%), H-10→L+1 (42%)
71	208.12145	0.0043	H-11→L+1 (55%), H-10→LUMO (15%)
72	207.64046	0.0022	H-8→L+4 (26%), H-1→L+9 (25%), H-1→L+10 (25%)
73	207.52576	9E-4	H-8→L+4 (38%), H-1→L+9 (16%), H-1→L+10 (13%)
74	207.15822	1E-4	H-9→L+2 (67%), H-8→L+2 (15%)
75	205.13939	0.0281	H-3→L+7 (74%)
76	202.97992	0.0955	H-7→L+5 (23%), H-6→L+5 (40%), H-5→L+5 (11%)
77	200.96963	0.0032	H-4→L+7 (49%), H-2→L+7 (16%)
78	200.75811	0.0127	H-9→L+3 (48%), H-6→L+6 (12%)
79	200.43356	0.0391	H-9→L+3 (25%), H-5→L+6 (23%)
80	199.82947	0.0018	H-14→LUMO (70%)
81	199.2162	0.0037	H-14→L+1 (72%)
82	198.43503	3E-4	H-9→L+4 (64%)
83	198.15911	6E-4	H-4→L+8 (13%), H-2→L+8 (74%)
84	197.96927	0.0176	H-6→L+6 (27%), H-5→L+7 (56%)
85	196.87531	0.0138	H-7→L+5 (60%), H-6→L+5 (12%), H-3→L+9 (11%)
86	196.00694	0.0646	H-12→LUMO (24%), H-11→L+4 (10%), H-10→L+3 (31%), H-3→L+8 (13%)
87	195.60494	0.0068	H-3→L+9 (35%), H-3→L+10 (20%)
88	195.05411	0.1131	H-7→L+6 (59%), H-3→L+8 (11%)
89	194.90999	1E-4	H-10→L+2 (89%)
90	194.61933	0.0038	H-11→L+3 (19%), H-10→L+4 (20%), H-3→L+10 (19%)
91	194.33868	0.0022	H-2→L+9 (34%), H-2→L+10 (37%)
92	193.95259	7E-4	H-11→L+2 (98%)
93	192.95048	0.0157	H-6→L+7 (33%), H-4→L+9 (15%), H-3→L+8 (11%)

94	192.50709	0.0024	H-15→LUMO (11%), H-4→L+9 (17%), H-4→L+10 (21%), H-2→L+9 (11%)
95	192.1729	6E-4	H-13→LUMO (39%), H-12→L+1 (48%)
96	192.04193	0.0058	H-13→L+1 (42%), H-12→LUMO (25%)
97	190.35542	0.0000	H-16→LUMO (50%), H-15→L+1 (21%)
98	190.28822	0.0127	H-16→L+1 (28%), H-15→LUMO (37%)
99	189.3322	0.0260	H-5→L+9 (44%), H-5→L+10 (19%)
100	188.79596	0.0520	H-10→L+3 (24%), H-3→L+8 (19%)

6. $Ir(ppy)_2(acac)$ (Ir6)

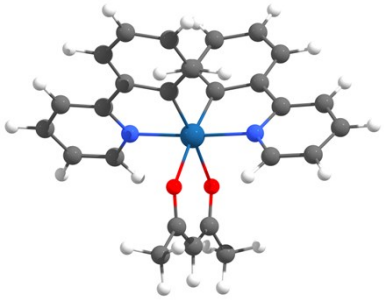
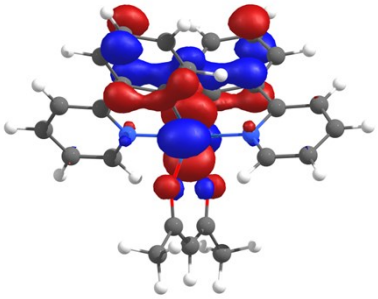
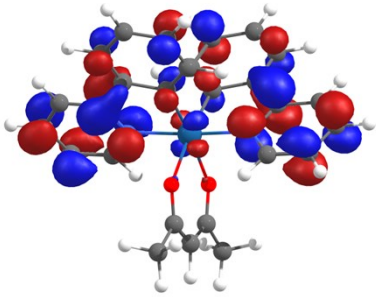


Figure S46. Optimized structure of **Ir6** in the ground state.



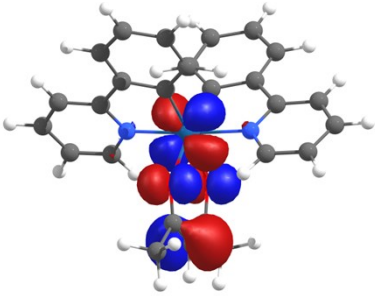
HOMO

(-5.17 eV)



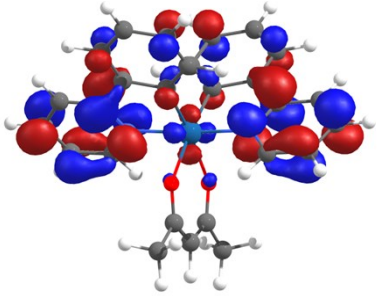
LUMO

(-1.50 eV)



HOMO-1

(-5.58eV)



LUMO+1

(-1.46 eV)

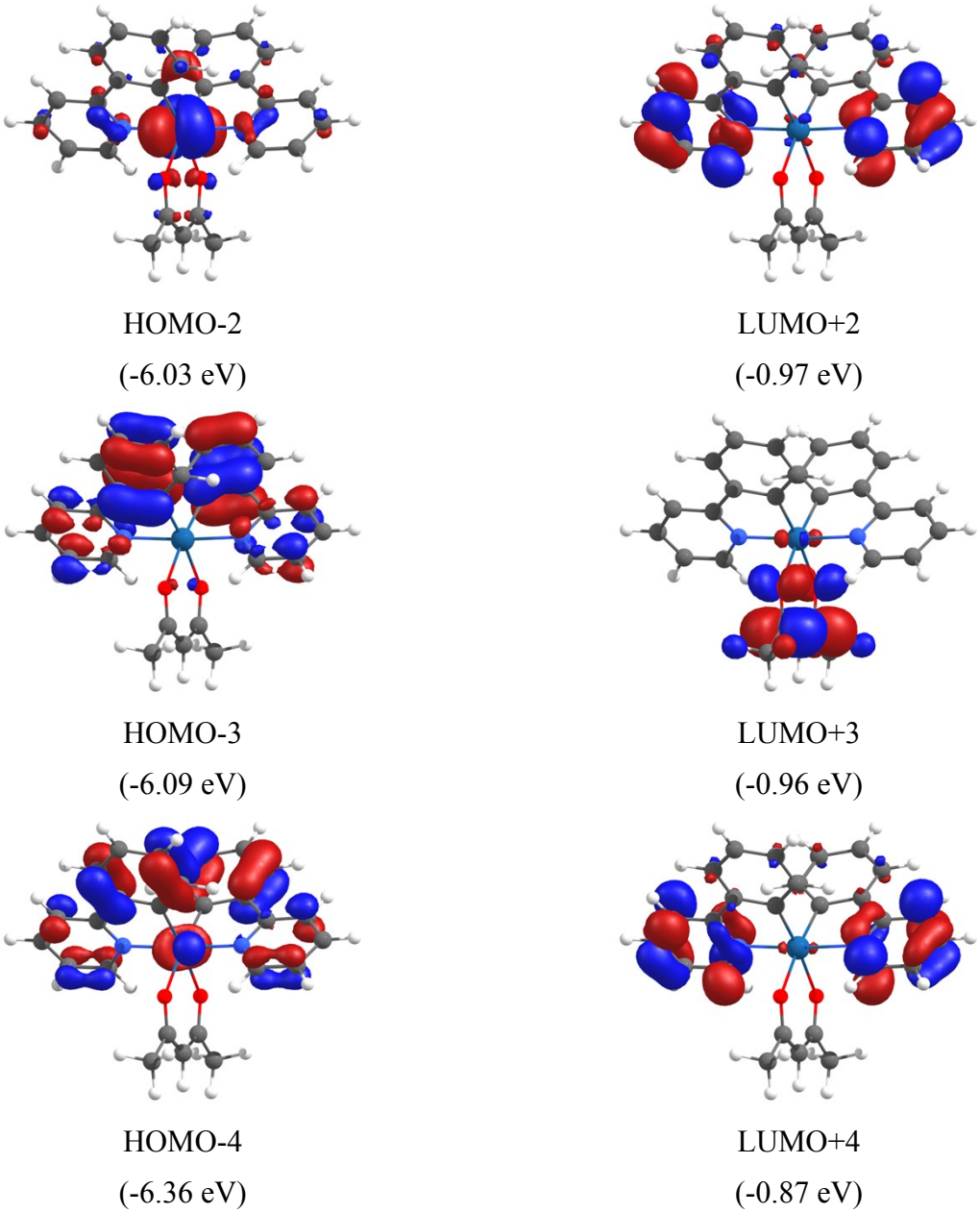


Figure S47. Representation of the frontier MOs of **Ir6** in the ground state.

Table S17. Atomic contributions of the frontier MOs of **Ir6**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-6.36	-6.09	-6.03	-5.58	-5.17	-1.50	-1.46	-0.97	-0.96	-0.87
Ir (%)	12.60	1.41	68.37	41.11	52.20	12.60	4.25	3.53	4.61	6.71
ppy (%)	85.27	92.52	25.07	12.52	40.73	85.27	83.08	90.80	6.89	86.91
acac (%)	2.13	6.07	6.56	46.37	7.07	2.13	12.67	5.67	88.50	6.38

Figure S48. Optimized structure of **Ir6** in the triplet state.

LSOMO
(-5.93 eV)

HSOMO
(-2.38 eV)

Figure S49. Representation of the frontier MOs of **Ir6** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 2.76\ eV = 449\ nm$

Table S18. Atomic contributions of the frontier MOs of **Ir6** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-5.93	-2.38
Ir (%)	12.43	5.49
ppy (%)	72.45	92.03
acac (%)	15.12	2.48

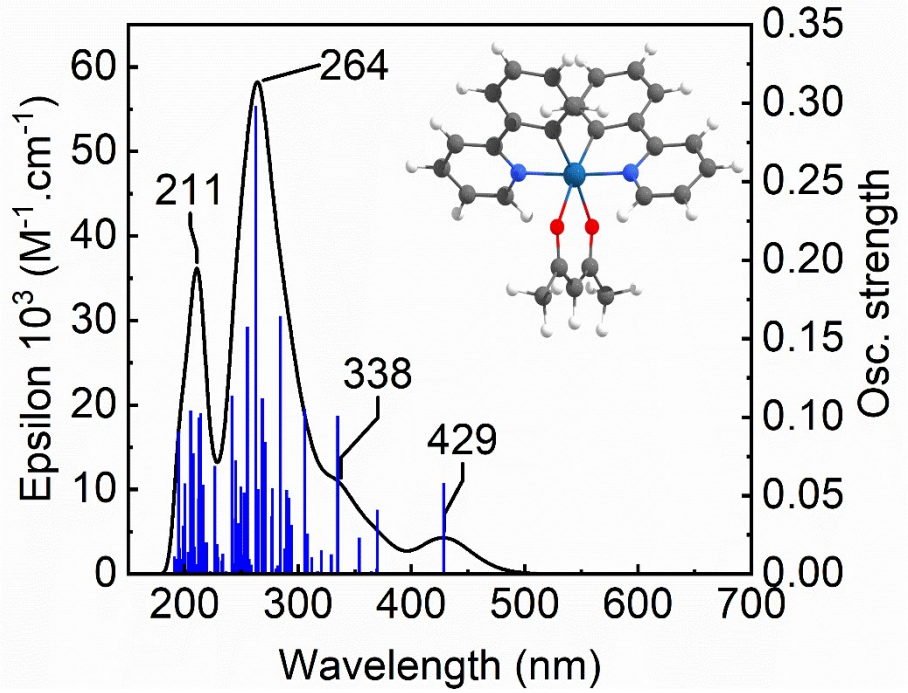


Figure S50. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir6** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S19. First 100 calculated spin-allowed electronic transitions of **Ir6**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	499.93626	5E-4	HOMO→LUMO (98%)
2	433.84489	0.0273	H-3→LUMO (87%), H-1→LUMO (12%)
3	427.44326	0.0611	H-2→LUMO (98%)
4	414.42723	0.0397	HOMO→L+1 (96%)
5	402.86	0.0027	HOMO→L+2 (95%)
6	397.57638	0.4669	H-3→LUMO (12%), H-1→LUMO (86%)
7	376.67991	0.0040	H-1→L+1 (98%)
8	368.98959	0.0036	H-1→L+2 (99%)
9	366.83885	0.0011	H-4→LUMO (99%)
10	361.40673	0.0069	H-3→L+1 (50%), H-2→L+2 (47%)
11	361.16459	0.0019	H-3→L+2 (13%), H-2→L+1 (83%)
12	352.11778	0.1303	H-3→L+1 (47%), H-2→L+2 (50%)
13	344.06603	0.0033	H-3→L+2 (78%), H-2→L+1 (11%)
14	334.17118	0.0426	HOMO→L+3 (95%)
15	333.21023	0.0047	H-5→LUMO (98%)
16	325.59729	0.0038	HOMO→L+4 (91%)
17	324.51498	0.0027	H-6→LUMO (95%)
18	316.38306	0.0061	H-4→L+1 (87%)
19	315.8672	0.0035	H-7→LUMO (41%), H-1→L+3 (57%)
20	314.44925	0.013	H-7→LUMO (56%), H-1→L+3 (42%)
21	311.62769	0.1092	H-4→L+2 (86%)
22	310.91655	0.125	H-8→LUMO (91%)
23	309.63537	5E-4	H-1→L+4 (99%)
24	304.19597	0.005	H-9→LUMO (90%)
25	300.28384	9E-4	H-2→L+3 (85%)
26	298.78589	0.0197	H-3→L+3 (86%)
27	296.7691	0.0292	H-5→L+1 (13%), H-2→L+4 (79%)
28	293.00986	0.0032	H-3→L+4 (78%)
29	292.77461	0.0113	H-10→LUMO (99%)
30	285.68445	0.1866	H-5→L+1 (76%), H-2→L+4 (10%)
31	283.64529	0	H-6→L+1 (57%), H-5→L+2 (41%)
32	282.55929	0.0108	H-11→LUMO (90%)
33	281.64144	0.1448	H-6→L+1 (25%), H-5→L+2 (37%), H-3→L+4 (13%)
34	280.56435	0.0093	H-1→L+5 (96%)
35	279.7351	0.033	H-12→LUMO (53%), H-6→L+2 (37%)
36	279.27513	0.0705	H-12→LUMO (42%), H-6→L+2 (45%)
37	274.64766	0.0386	H-1→L+6 (98%)

38	271.0748	0.0075	H-7→L+2 (12%), H-4→L+3 (70%)
39	269.99454	0.0097	H-7→L+1 (25%), HOMO→L+5 (60%)
40	269.73022	0.0028	H-7→L+1 (45%), H-4→L+4 (11%), HOMO→L+5 (37%)
41	266.39778	5E-4	HOMO→L+6 (98%)
42	264.40372	0.0148	H-9→L+1 (15%), H-3→L+10 (13%), HOMO→L+8 (10%), HOMO→L+10 (31%)
43	263.81299	0.1602	H-7→L+1 (23%), H-4→L+4 (65%)
44	263.54943	0.0072	H-7→L+2 (76%), H-4→L+3 (10%)
45	260.60787	0	H-9→L+1 (53%), HOMO→L+10 (10%)
46	259.50059	0.06	H-9→L+2 (53%), H-2→L+10 (11%)
47	258.17132	0.1686	HOMO→L+7 (67%)
48	256.68011	0.002	H-9→L+2 (15%), H-2→L+8 (11%), H-2→L+9 (11%), H-2→L+10 (36%)
49	254.90695	0.0058	H-13→LUMO (93%)
50	253.38577	0	H-8→L+1 (86%)
51	252.48792	0.0168	H-2→L+5 (95%)
52	251.18354	0.0026	H-12→L+1 (55%), H-11→L+2 (26%)
53	251.08689	0.0027	H-12→L+2 (24%), H-11→L+1 (57%)
54	249.8976	4E-4	H-3→L+5 (93%)
55	249.65606	0.0181	H-8→L+2 (73%), H-5→L+3 (14%)
56	249.03925	0.0462	H-5→L+3 (26%), H-2→L+6 (57%)
57	248.93925	0.0953	H-5→L+3 (40%), H-2→L+6 (41%)
58	248.43047	0.0186	H-3→L+10 (36%), HOMO→L+8 (17%), HOMO→L+10 (13%)
59	247.13308	0.0019	H-6→L+3 (39%), H-5→L+4 (14%), HOMO→L+8 (10%)
60	246.55317	5E-4	H-3→L+6 (95%)
61	245.65919	0.019	H-5→L+4 (74%)
62	245.20735	0.0623	H-6→L+3 (40%), HOMO→L+8 (34%)
63	243.65089	0.0063	H-1→L+7 (91%)
64	242.83961	0.0436	H-12→L+1 (10%), H-11→L+2 (23%), H-6→L+4 (54%)
65	242.23706	2E-4	H-12→L+2 (55%), H-11→L+1 (28%)
66	242.22759	0.0435	H-12→L+1 (16%), H-11→L+2 (41%), H-6→L+4 (28%)
67	241.17685	0.0562	H-16→LUMO (50%), H-14→LUMO (42%)
68	240.60585	0.0027	H-15→LUMO (95%)
69	239.85644	1E-4	H-2→L+7 (59%), H-1→L+8 (32%)
70	239.76367	0.0044	H-10→L+1 (85%)
71	239.02871	0.0273	H-3→L+7 (72%)
72	238.90896	0.0043	H-2→L+7 (31%), H-1→L+8 (65%)
73	237.29032	0.1298	H-16→LUMO (45%), H-14→LUMO (44%)
74	236.3855	2E-4	H-10→L+2 (93%)
75	234.86748	0.0121	H-13→L+1 (11%), H-7→L+3 (69%)
76	233.9501	0.0034	H-7→L+3 (21%), H-2→L+8 (38%), HOMO→L+11 (11%)

77	232.71617	0.0113	H-3→L+8 (72%), HOMO→L+9 (11%)
78	232.04543	0.0106	H-13→L+2 (19%), H-9→L+3 (12%), H-7→L+4 (39%), HOMO→L+9 (10%)
79	230.52673	0.0076	H-13→L+1 (53%), HOMO→L+13 (14%)
80	230.29551	3E-4	H-9→L+3 (14%), H-7→L+4 (51%)
81	230.0178	0.0096	H-2→L+8 (22%), HOMO→L+11 (35%), HOMO→L+13 (12%)
82	229.40069	0.0015	H-9→L+3 (22%), H-4→L+5 (68%)
83	228.58443	3E-4	H-9→L+3 (29%), H-4→L+5 (26%)
84	227.46889	1E-4	H-8→L+6 (10%), H-4→L+6 (78%)
85	226.68701	7E-4	H-10→L+5 (29%), H-8→L+6 (36%), H-4→L+6 (21%)
86	226.35179	0.0194	H-9→L+4 (72%), H-8→L+4 (12%)
87	226.24853	0.0469	H-13→L+2 (54%), HOMO→L+9 (20%)
88	225.86933	0.007	H-1→L+9 (37%), H-1→L+10 (59%)
89	224.67417	1E-4	H-9→L+3 (13%), H-8→L+3 (84%)
90	221.43593	0.0052	H-8→L+4 (70%)
91	221.40034	0.0206	H-8→L+4 (15%), HOMO→L+11 (21%), HOMO→L+13 (41%)
92	219.52264	0.003	H-14→L+1 (28%), H-1→L+9 (42%), H-1→L+10 (28%)
93	218.99531	0.0052	H-14→L+1 (57%), H-1→L+9 (17%)
94	218.54367	0.0126	H-15→L+1 (22%), H-12→L+3 (34%)
95	218.43201	0.0014	H-12→L+4 (12%), H-11→L+3 (78%)
96	217.61539	0.0405	H-15→L+1 (15%), H-12→L+3 (37%), H-11→L+4 (11%)
97	217.07436	0.006	H-18→LUMO (17%), H-16→L+1 (28%), H-15→L+2 (15%)
98	216.85036	5E-4	H-14→L+2 (24%), H-1→L+11 (72%)
99	216.5398	5E-4	H-5→L+5 (92%)
100	216.29803	0.0038	H-17→LUMO (91%)

7. $Ir(piq)_2(acac)$ (Ir7)

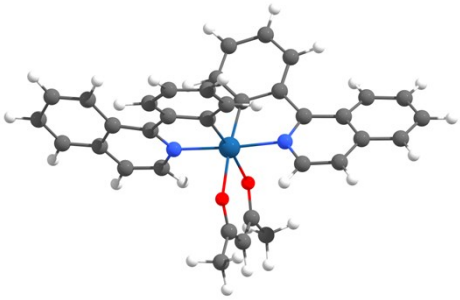
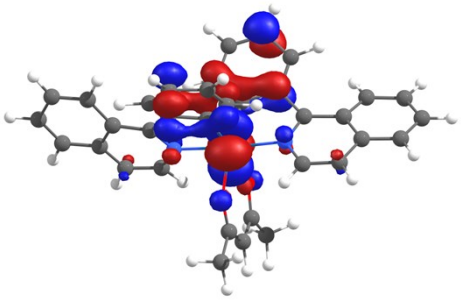
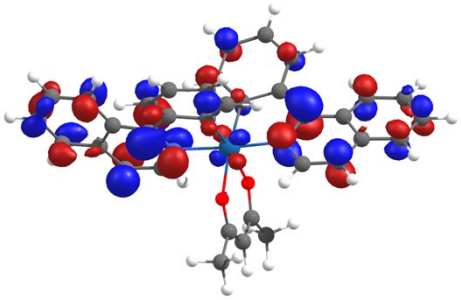


Figure S51. Optimized structure of **Ir7** in the ground state.



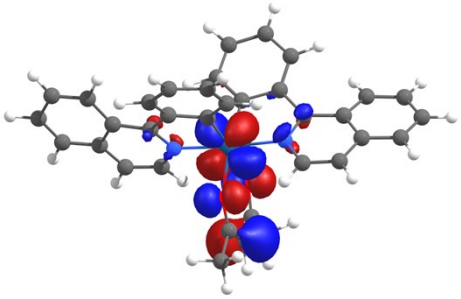
HOMO

(-5.17 eV)



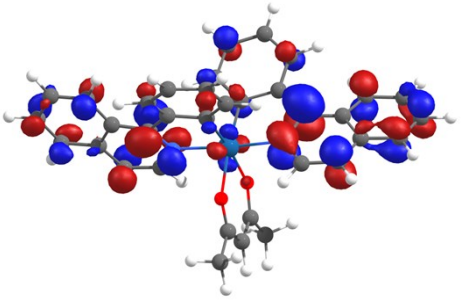
LUMO

(-2.00 eV)



HOMO-1

(-5.56 eV)



LUMO+1

(-1.95 eV)

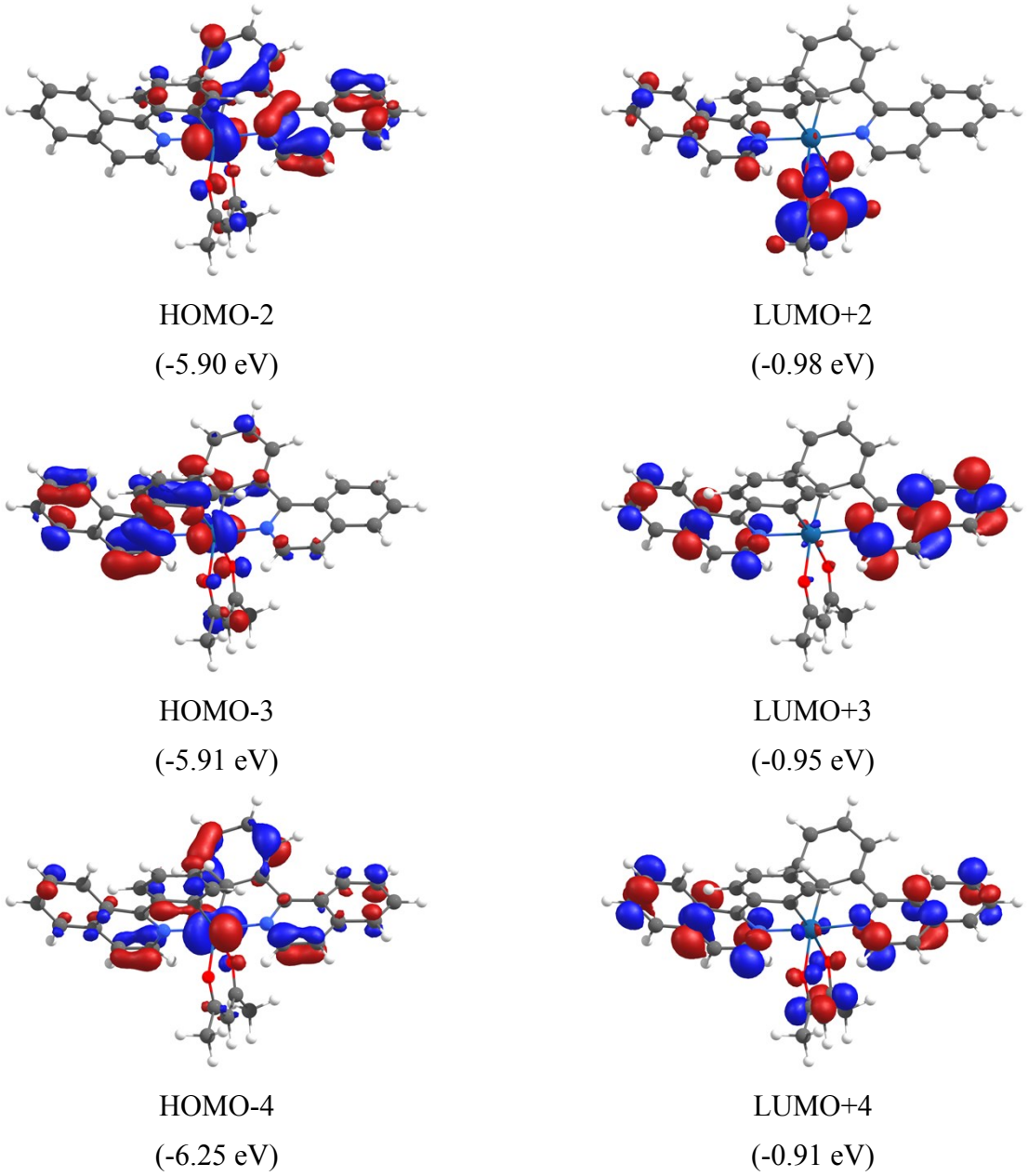


Figure S52. Representation of the frontier MOs of **Ir7** in the ground state.

Table S20. Atomic contributions of the frontier MOs of **Ir7**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-6.25	-5.91	-5.90	-5.56	-5.17	-2.00	-1.95	-0.98	-0.95	-0.91
Ir (%)	33.01	24.56	27.43	41.55	49.36	4.72	4.02	3.45	3.58	5.95
piq (%)	61.44	66.24	63.22	21.31	45.08	94.34	94.61	27.37	91.22	74.10
acac (%)	5.55	9.21	9.35	37.14	5.56	0.95	1.37	69.18	5.21	19.95

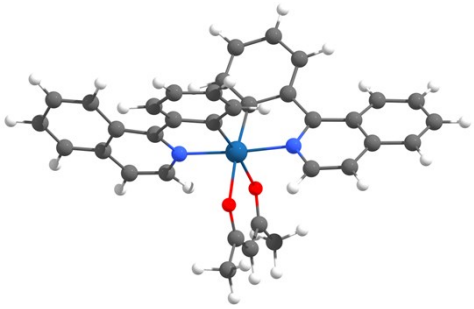
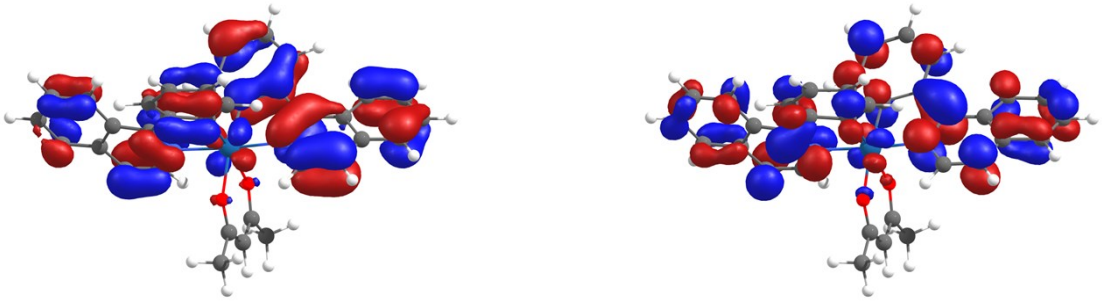


Figure S53. Optimized structure of **Ir7** in the triplet state.



LSOMO
(-5.69 eV)

HSOMO
(-2.82 eV)

Figure S54. Molecular orbitals of **Ir7** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 2.33\ eV = 532\ nm$

Table S21. Atomic contributions of the frontier MOs of **Ir7** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-5.69	-2.82
Ir (%)	38.60	4.94
piq (%)	56.47	93.68
acac (%)	4.92	1.38

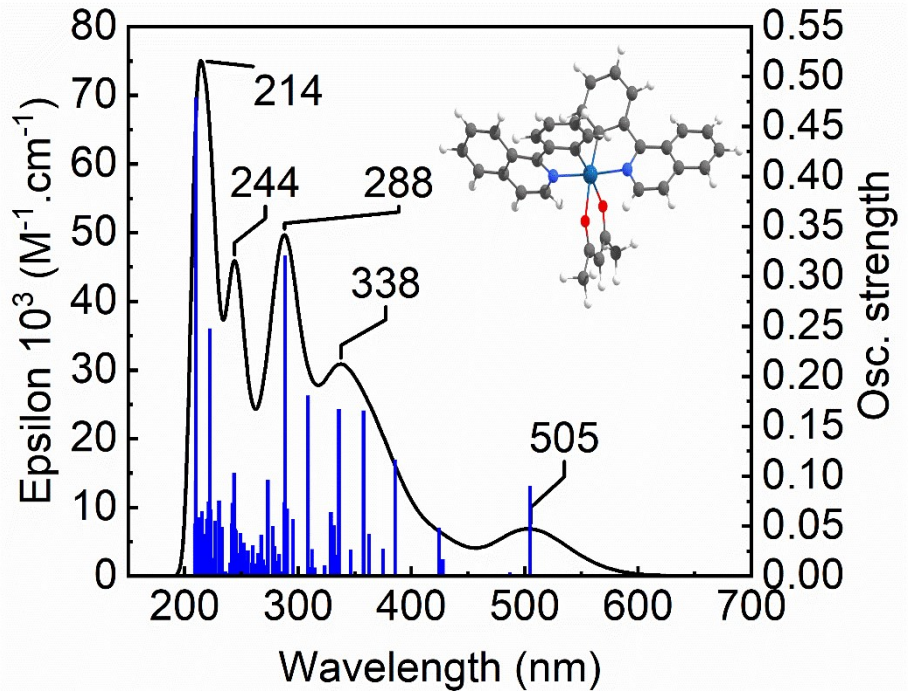


Figure S55. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir7** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S22. First 100 calculated spin-allowed electronic transitions of **Ir7**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	504.63671	0.0905	HOMO→LUMO (98%)
2	486.84255	0.004	HOMO→L+1 (97%)
3	427.57593	0.0171	H-1→LUMO (80%), H-1→L+1 (14%)
4	424.54524	0.0485	H-1→LUMO (14%), H-1→L+1 (81%)
5	385.41513	0.1164	H-3→LUMO (24%), H-2→LUMO (59%)
6	374.83506	0.0274	H-3→L+1 (25%), H-2→L+1 (59%)
7	363.96358	0.0013	HOMO→L+2 (83%), HOMO→L+4 (13%)
8	362.70717	0.042	H-3→LUMO (67%), H-2→LUMO (28%)
9	357.58138	0.1659	H-3→L+1 (65%), H-2→L+1 (30%)
10	346.30521	0.0263	HOMO→L+3 (93%)
11	342.76289	6E-4	HOMO→L+2 (12%), HOMO→L+4 (82%)
12	335.9459	0.167	H-4→LUMO (84%)
13	333.22814	0.0212	H-5→LUMO (16%), H-4→L+1 (66%)
14	331.48195	0.0506	H-5→LUMO (74%), H-4→L+1 (16%)
15	328.87054	0.0641	H-5→L+1 (80%)

16	323.37235	0.0106	H-1→L+2 (72%)
17	314.68868	0.0084	H-6→LUMO (65%), H-1→L+3 (20%)
18	312.07479	0.0269	H-6→L+1 (43%), H-1→L+3 (12%), H-1→L+4 (31%)
19	309.60444	0.009	H-6→LUMO (20%), H-1→L+3 (55%)
20	308.75633	0.1807	H-6→L+1 (35%), H-1→L+4 (49%)
21	300.80839	0.001	H-7→LUMO (89%)
22	296.66968	0.0013	H-7→L+1 (89%)
23	295.60163	0.057	H-3→L+2 (24%), H-2→L+2 (58%)
24	290.19121	0.0675	HOMO→L+5 (85%)
25	288.4024	0.3211	H-3→L+3 (14%), H-2→L+3 (43%)
26	287.68637	0.074	H-2→L+3 (10%), HOMO→L+6 (57%)
27	286.60901	0.0015	H-9→L+1 (14%), H-8→LUMO (62%)
28	284.96218	0.0042	H-9→LUMO (17%), H-8→L+1 (30%), H-2→L+4 (11%)
29	283.36006	0.0225	H-8→L+1 (12%), H-2→L+4 (26%), HOMO→L+6 (16%)
30	282.37267	0.0152	H-3→L+2 (44%), H-2→L+2 (18%)
31	279.38211	0.0298	H-7→L+2 (33%), H-5→L+2 (14%), H-3→L+2 (10%)
32	278.2535	0.0046	H-3→L+3 (49%), H-2→L+3 (13%), H-2→L+4 (13%)
33	277.51856	0.0504	H-7→L+2 (12%), H-3→L+4 (40%), H-2→L+4 (20%)
34	273.20125	0.0967	HOMO→L+7 (64%)
35	272.7505	0.0043	H-9→LUMO (55%), H-8→L+1 (31%)
36	271.41899	0.0111	H-9→L+1 (66%), H-8→LUMO (14%)
37	269.32593	0.0164	HOMO→L+8 (30%), HOMO→L+9 (31%)
38	267.33407	0.0416	H-1→L+5 (17%), H-1→L+6 (17%), H-1→L+8 (15%), H-1→L+9 (16%)
39	265.35441	0.0049	H-4→L+2 (58%)
40	264.62946	0.0076	H-10→LUMO (61%)
41	264.17274	0.0231	H-10→LUMO (12%), H-1→L+5 (50%), H-1→L+6 (17%)
42	261.58106	0.0123	H-10→L+1 (58%), H-4→L+3 (17%)
43	261.24485	0.0036	H-10→L+1 (25%), H-4→L+3 (42%)
44	259.97398	0.031	H-4→L+4 (21%), H-1→L+6 (30%), H-1→L+8 (10%), H-1→L+9 (10%)
45	259.32148	0.0133	H-4→L+3 (10%), H-4→L+4 (25%), H-1→L+6 (16%)
46	257.26064	0.0027	H-5→L+2 (15%), H-5→L+3 (37%), H-5→L+4 (19%), H-4→L+4 (16%)
47	255.6586	0.0257	H-5→L+3 (30%), H-5→L+4 (40%)
48	254.59289	0.015	H-1→L+7 (42%)
49	251.89288	0.0332	H-7→L+2 (21%), H-5→L+2 (37%), H-5→L+4 (14%)
50	249.48526	0.0202	H-13→LUMO (34%), H-12→LUMO (15%)
51	248.93425	0.0431	H-3→L+5 (17%), H-2→L+5 (44%)
52	248.44042	0.0119	H-13→LUMO (15%), HOMO→L+8 (17%), HOMO→L+9 (12%)
53	247.60194	0.0157	H-2→L+6 (32%), H-1→L+7 (15%)
54	246.51395	0.023	H-13→L+1 (45%), H-12→L+1 (21%)

55	245.39663	0.0244	H-6→L+3 (17%)
56	244.999	0.0456	H-11→LUMO (10%), H-6→L+2 (45%)
57	244.26051	0.0471	H-6→L+2 (11%), H-6→L+3 (13%), H-6→L+4 (24%)
58	243.44039	0.1035	H-3→L+5 (25%)
59	242.99667	0.0242	H-6→L+3 (17%), H-3→L+5 (15%), H-2→L+5 (25%)
60	242.48341	0.0443	H-6→L+3 (15%)
61	241.85431	0.0733	H-3→L+6 (27%)
62	241.70343	0.0296	H-6→L+3 (18%), H-3→L+6 (10%)
63	241.25663	0.0528	H-11→LUMO (10%), H-6→L+4 (40%)
64	239.7544	0.0137	H-3→L+7 (14%), H-2→L+7 (20%), H-1→L+8 (16%)
65	237.02721	0.0032	H-7→L+3 (91%)
66	236.50273	2E-4	H-13→LUMO (10%), H-12→LUMO (37%), H-11→L+1 (36%)
67	236.16487	0.002	H-13→L+1 (14%), H-12→L+1 (26%), H-11→LUMO (25%), H-7→L+4 (11%)
68	235.70243	0.0045	H-7→L+2 (13%), H-7→L+4 (68%)
69	232.96104	0.013	H-10→L+2 (53%), H-10→L+4 (10%)
70	232.80356	0.0493	H-10→L+2 (13%), H-2→L+7 (14%), H-1→L+8 (18%), H-1→L+9 (16%)
71	231.0164	0.0015	H-5→L+5 (12%), H-4→L+6 (26%), H-3→L+7 (19%)
72	230.22281	0.0758	H-4→L+5 (45%)
73	228.33185	0.0018	H-5→L+5 (14%), H-4→L+6 (33%)
74	227.0066	0.0029	H-8→L+2 (66%)
75	226.64971	0.0554	H-8→L+2 (10%), H-5→L+6 (44%)
76	224.6986	0.018	H-5→L+5 (36%), H-2→L+8 (12%), HOMO→L+10 (14%)
77	224.5155	0.0072	H-2→L+8 (20%), H-2→L+9 (10%), HOMO→L+10 (10%)
78	223.2019	0.0114	H-9→L+2 (78%)
79	222.92098	0.0666	H-1→L+10 (17%), H-1→L+12 (17%)
80	221.88771	0.248	H-8→L+3 (37%)
81	221.15155	0.0018	H-8→L+4 (29%), H-5→L+6 (14%), HOMO→L+11 (12%)
82	220.93087	0.0745	H-8→L+4 (15%), H-3→L+8 (11%), HOMO→L+11 (13%)
83	220.44378	0.0579	H-9→L+3 (18%), H-5→L+5 (10%), HOMO→L+10 (13%)
84	219.95883	0.0275	H-9→L+3 (18%), H-9→L+4 (15%), H-6→L+5 (16%)
85	219.42552	0.0574	H-9→L+4 (23%)
86	219.0727	0.0225	H-18→LUMO (19%), H-16→LUMO (62%)
87	218.04019	0.0419	H-16→L+1 (14%), H-3→L+8 (15%), HOMO→L+11 (15%), HOMO→L+12 (11%)
88	217.29883	0.0149	H-18→L+1 (14%), H-16→L+1 (40%), H-3→L+8 (11%)
89	215.23165	0.0646	H-15→LUMO (10%), H-6→L+5 (15%), H-6→L+6 (18%)
90	214.92571	0.0275	H-15→LUMO (11%), H-14→L+1 (15%), H-6→L+5 (16%), H-6→L+6 (17%)
91	214.73958	0.0156	H-14→LUMO (20%), H-10→L+3 (13%), H-4→L+7 (12%)
92	213.68111	0.0057	H-10→L+3 (37%)

93	212.97637	0.0069	H-18→LUMO (32%)
94	212.65856	0.0163	H-10→L+2 (11%), H-10→L+3 (21%), H-10→L+4 (34%)
95	212.00402	0.0588	H-18→L+1 (14%)
96	211.83378	0.0128	H-10→L+4 (17%), H-5→L+7 (21%)
97	211.47607	0.0437	H-18→L+1 (16%), H-5→L+7 (14%)
98	209.57436	0.4791	H-14→LUMO (10%), H-6→L+6 (13%), H-4→L+7 (13%)
99	209.35142	0.0957	H-5→L+7 (15%), H-4→L+8 (29%)
100	208.59415	0.0524	H-7→L+5 (53%)

8. Ir(piq-dpa)$_2$(acac) (Ir8)

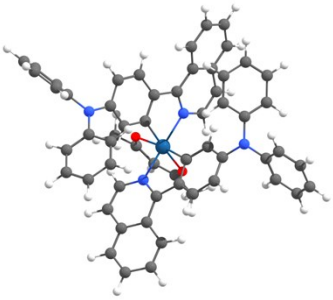
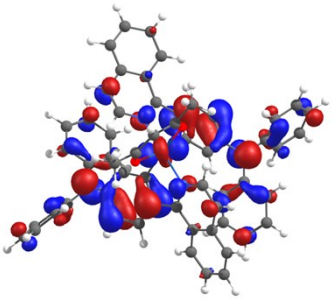
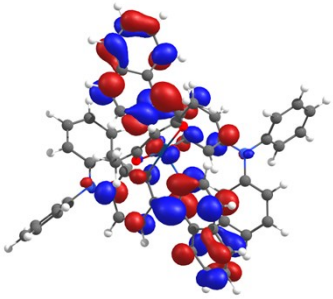


Figure S56. Optimized structure of **Ir8** in the ground state.



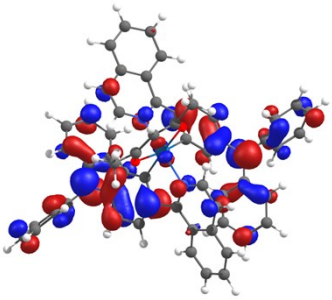
HOMO

(-4.94 eV)



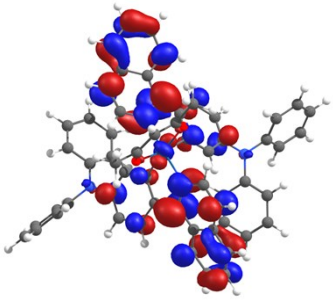
LUMO

(-1.93 eV)



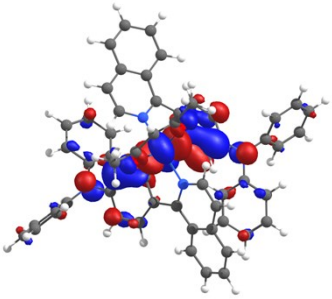
HOMO-1

(-4.99 eV)



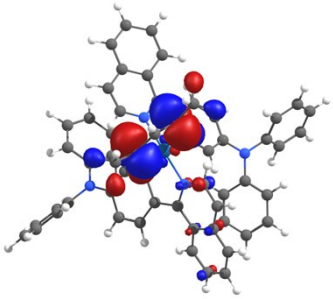
LUMO+1

(-1.90 eV)



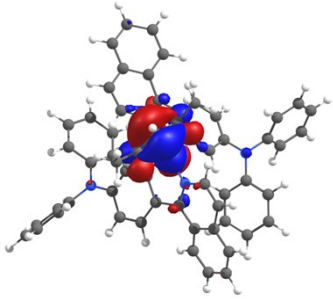
HOMO-2

(-5.26 eV)



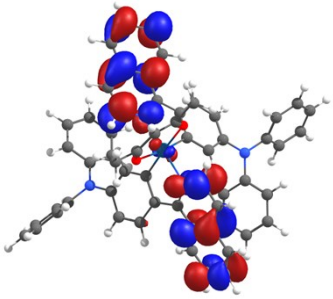
LUMO+2

(-0.95 eV)



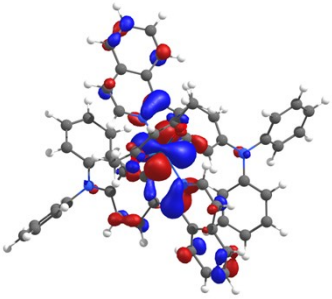
HOMO-3

(-5.56 eV)



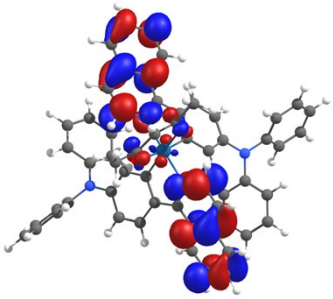
LUMO+3

(-0.89 eV)



HOMO-4

(-5.95 eV)



LUMO+4

(-0.86 eV)

Figure S57. Representation of the frontier MOs of **Ir8** in the ground state.

Table S23. Atomic contributions of the frontier MOs of **Ir8**.

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-5.95	-5.56	-5.26	-4.99	-4.94	-1.93	-1.90	-0.95	-0.89	-0.86
Ir (%)	58.05	40.73	44.20	2.09	9.71	4.55	3.80	4.33	3.43	5.43
piq-dpa (%)	37.77	17.96	49.51	97.52	89.66	94.53	94.99	10.57	95.24	88.37
acac (%)	4.19	41.31	6.30	0.39	0.63	0.92	1.20	85.11	1.33	6.20

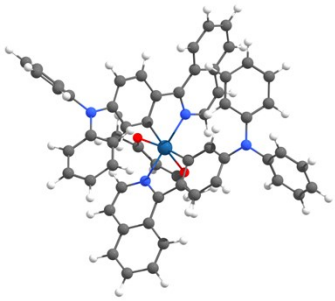
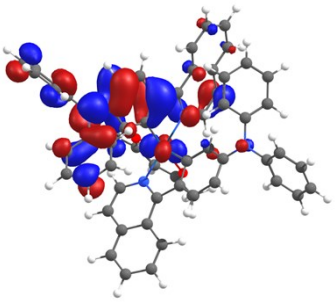
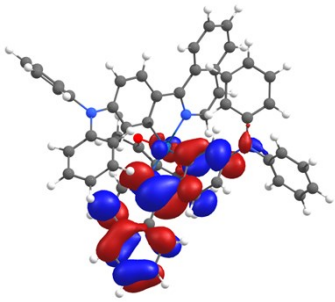


Figure S58. Optimized structure of **Ir8** in the triplet state.



LSOMO

(-4.98 eV)



HSOMO

(-2.88 eV)

Figure S59. Representation of the frontier MOs of **Ir8** in the triplet state.

Phosphorescence position : $E_{triplet} - E_{singlet} = 2.15\ eV = 577\ nm$

Table S24. Atomic contributions of the frontier MOs of **Ir8** in the triplet state.

Fragment	LSOMO	HSOMO
Energy (eV)	-4.98	-2.88
Ir (%)	6.53	4.28
piq-dpa (%)	92.83	94.77
acac (%)	0.64	0.96

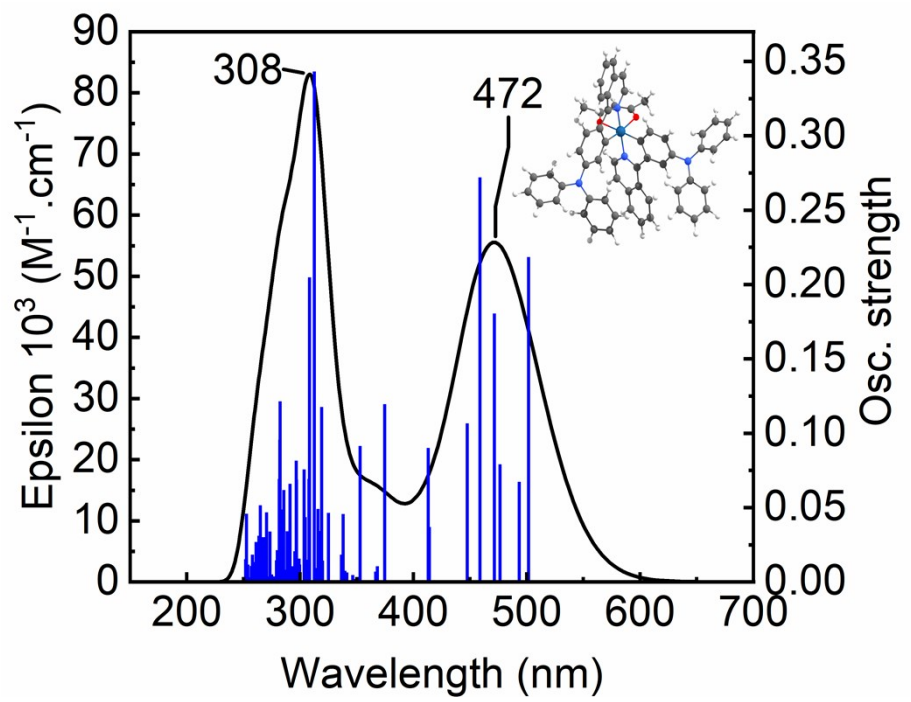


Figure S60. Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of **Ir8** *vs* their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S25. First 100 calculated spin-allowed electronic transitions of **Ir8**.

Transition No.	λ (nm)	Oscillator Strength	Major contributions (% ; - means no major contribution)
1	563.35966	0.2184	H-2→LUMO (22%), HOMO→LUMO (76%)
2	521.13906	0.0672	H-2→L+1 (14%), HOMO→L+1 (83%)
3	499.87579	0.079	H-1→LUMO (84%)
4	470.43898	0.1804	H-1→LUMO (10%), H-1→L+1 (83%)
5	440.91107	0.272	H-2→LUMO (72%), HOMO→LUMO (20%)
6	429.62054	0.1065	H-2→L+1 (81%), HOMO→L+1 (13%)
7	415.56626	0.0369	H-3→LUMO (67%), H-3→L+1 (27%)
8	411.64777	0.09	H-3→LUMO (27%), H-3→L+1 (67%)
9	386.84616	0.1194	H-4→LUMO (84%)
10	382.04232	0.0105	H-4→L+1 (82%)
11	373.16537	0.0069	H-2→L+2 (35%), HOMO→L+2 (60%)
12	369.35234	0.0914	HOMO→L+3 (83%)
13	362.03993	0.002	HOMO→L+4 (71%)

14	352.36797	0.0046	H-1→L+2 (93%)
15	348.69138	0.0064	H-1→L+3 (78%)
16	346.46973	0.0075	H-5→LUMO (92%)
17	340.97187	0.0024	H-2→L+2 (53%), HOMO→L+2 (28%)
18	337.44541	0.0456	H-1→L+4 (81%)
19	331.26053	0.0183	H-5→L+1 (92%)
20	328.73974	0.0012	H-2→L+3 (82%)
21	326.01681	0.0011	H-7→LUMO (55%), H-6→LUMO (26%)
22	321.66090	0.0463	H-7→L+1 (55%), H-6→L+1 (25%)
23	320.48025	0.0002	H-2→L+4 (79%)
24	318.38168	0.0142	H-6→LUMO (12%), H-3→L+2 (59%)
25	317.11945	0.1176	H-7→LUMO (18%), H-6→LUMO (38%), H-3→L+2 (16%)
26	316.57694	0.0247	H-7→L+1 (16%), H-6→L+1 (43%)
27	316.29428	0.0342	H-7→L+1 (11%), H-1→L+6 (18%), HOMO→L+5 (41%)
28	314.68069	0.049	H-1→L+5 (35%), HOMO→L+6 (32%)
29	313.79665	0.0094	H-1→L+9 (30%), HOMO→L+6 (16%), HOMO→L+7 (16%), HOMO→L+10 (12%)
30	312.98865	0.3432	H-1→L+6 (11%), H-1→L+7 (11%), H-1→L+10 (11%), HOMO→L+8 (11%), HOMO→L+9 (32%)
31	311.43982	0.2047	H-1→L+8 (18%), HOMO→L+7 (28%), HOMO→L+8 (29%)
32	311.19749	0.0692	H-3→L+3 (17%), H-1→L+7 (23%), HOMO→L+7 (19%), HOMO→L+8 (13%), HOMO→L+10 (11%)
33	309.56579	0.0149	H-8→LUMO (10%), H-3→L+3 (50%)
34	307.47760	0.0115	H-8→LUMO (55%), H-8→L+1 (13%)
35	305.62067	0.0436	H-3→L+3 (11%), H-3→L+4 (67%)
36	305.08672	0.0756	H-8→L+1 (62%), H-3→L+4 (12%)
37	304.31543	0.0116	H-1→L+6 (32%), H-1→L+8 (11%), HOMO→L+5 (13%)
38	303.25847	0.0156	H-1→L+5 (17%), H-1→L+7 (32%), HOMO→L+6 (18%)
39	302.31936	0.0688	H-9→LUMO (33%), H-1→L+8 (10%), H-1→L+10 (10%), HOMO→L+5 (10%)
40	300.42936	0.0815	H-9→LUMO (44%), H-1→L+10 (10%)
41	297.99595	0.0205	H-1→L+5 (22%), HOMO→L+6 (17%), HOMO→L+10 (17%)
42	297.53112	0.0104	H-9→L+1 (83%)
43	294.12899	0.0065	H-1→L+8 (21%), H-1→L+10 (20%), HOMO→L+8 (14%), HOMO→L+9 (16%)
44	292.00234	0.0087	H-1→L+9 (37%), HOMO→L+9 (21%), HOMO→L+10 (18%)
45	288.57022	0.066	H-4→L+2 (78%)
46	288.44266	0.034	H-2→L+7 (66%)
47	287.23316	0.0083	H-2→L+6 (30%), H-2→L+8 (33%)
48	287.14668	0.0617	H-2→L+5 (54%)
49	285.57916	0.0486	H-10→LUMO (26%), H-1→L+11 (24%), HOMO→L+11 (21%)
50	284.96873	0.0157	H-11→LUMO (11%), H-10→LUMO (11%), H-1→L+12 (24%),

			HOMO→L+12 (23%)
51	284.02216	0.1214	H-10→LUMO (12%), H-10→L+1 (10%), H-4→L+3 (29%)
52	282.62370	0.0956	H-4→L+3 (37%)
53	280.88852	0.0692	H-4→L+3 (18%), H-2→L+6 (34%), H-2→L+8 (23%)
54	279.99411	0.0107	H-10→L+1 (21%), H-4→L+4 (13%), H-2→L+10 (14%)
55	279.59632	0.0213	H-11→LUMO (13%), H-2→L+9 (41%)
56	276.68250	0.0133	H-11→LUMO (15%), H-10→L+1 (14%), H-2→L+9 (10%), H-2→L+10 (12%)
57	276.21403	0.0144	H-9→L+2 (60%), H-7→L+2 (19%)
58	275.31853	0.0018	H-11→LUMO (38%)
59	275.01318	0.0037	H-11→L+1 (63%)
60	273.96189	0.0049	H-4→L+4 (31%), H-2→L+10 (41%)
61	273.63539	0.0339	H-14→LUMO (10%), H-12→LUMO (23%), H-10→LUMO (15%), HOMO→L+13 (12%)
62	273.14708	0.0036	H-14→L+1 (10%), H-12→L+1 (14%), H-10→L+1 (14%)
63	273.00274	0.0036	H-12→LUMO (23%), HOMO→L+13 (11%)
64	272.21752	0.0468	H-5→L+4 (15%), HOMO→L+13 (13%)
65	271.96673	0.0068	H-13→LUMO (19%), H-12→L+1 (12%), H-3→L+7 (15%)
66	271.59141	0.0199	H-14→LUMO (36%), H-12→LUMO (24%)
67	271.21712	0.0068	H-13→LUMO (10%), H-5→L+3 (11%)
68	270.58968	0.013	H-13→L+1 (11%), H-5→L+2 (35%)
69	270.34777	0.0078	H-13→LUMO (30%)
70	269.84763	0.0301	H-14→L+1 (13%), H-12→L+1 (24%), H-5→L+2 (24%)
71	268.69556	0.0116	H-13→L+1 (17%), H-5→L+4 (15%)
72	268.13191	0.0011	H-14→L+1 (11%), H-13→L+1 (10%), H-5→L+3 (10%), H-3→L+7 (21%)
73	267.24187	0.0068	H-3→L+7 (14%), H-3→L+9 (11%)
74	266.98291	0.0078	H-3→L+5 (37%)
75	265.87792	0.0515	H-13→L+1 (16%), H-5→L+4 (13%), H-3→L+8 (11%)
76	265.50783	0.0083	H-15→LUMO (38%)
77	264.84992	0.0035	H-1→L+11 (33%), HOMO→L+11 (37%)
78	264.51654	0.031	H-15→L+1 (15%)
79	264.03772	0.0138	H-15→L+1 (15%), H-1→L+12 (17%), HOMO→L+12 (16%)
80	263.54383	0.0164	H-15→L+1 (12%), H-14→L+1 (11%), H-1→L+13 (17%)
81	263.34231	0.0269	H-2→L+13 (23%), H-1→L+14 (14%)
82	261.92368	0.0058	H-17→LUMO (24%), H-16→LUMO (31%), H-15→LUMO (15%), H-15→L+1 (13%)
83	260.95892	0.0134	H-3→L+6 (63%), H-3→L+8 (22%)
84	260.41081	0.0022	H-18→LUMO (11%), H-17→LUMO (50%), H-16→LUMO (18%)
85	258.90992	0.0013	H-18→L+1 (13%), H-17→L+1 (15%), H-16→L+1 (32%)
86	258.72082	0.0003	H-3→L+5 (14%), H-3→L+8 (16%), H-3→L+9 (53%)
87	258.41346	0.0182	H-18→LUMO (19%), H-17→L+1 (41%), H-16→LUMO (11%), H-

			15→L+1 (11%)
88	258.27350	0.0012	H-18→LUMO (14%), H-17→L+1 (20%), H-16→LUMO (21%), H-16→L+1 (22%)
89	257.92426	0.0106	H-7→L+2 (18%), H-6→L+2 (65%)
90	257.22862	0.0015	H-1→L+15 (15%), HOMO→L+14 (29%)
91	256.28218	0.0031	H-18→L+1 (40%), H-16→L+1 (22%)
92	255.35320	0.0009	H-3→L+10 (26%), HOMO→L+14 (25%)
93	254.98559	0.0005	H-7→L+3 (29%), H-6→L+3 (12%)
94	254.65041	0.0116	H-6→L+3 (11%), HOMO→L+16 (16%)
95	253.20466	0.0006	H-6→L+3 (17%), HOMO→L+15 (10%)
96	253.01347	0.003	H-1→L+14 (26%)
97	252.58051	0.0027	H-2→L+11 (67%)
98	252.34917	0.0458	H-2→L+12 (48%)
99	251.65769	0.0011	H-7→L+4 (38%), H-6→L+4 (19%)
100	250.74159	0.0152	H-2→L+12 (18%)

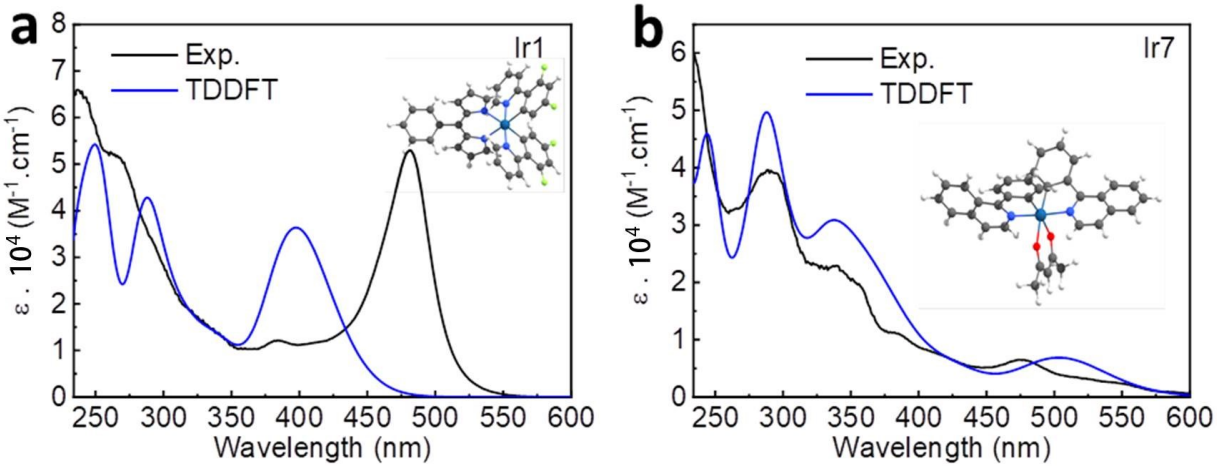


Figure S61. Calculated spectra of **Ir1** (left) and **Ir7** (right) *vs* experimental absorption in DCM.

Table S26. Experimental and calculated positions for absorption and emission maxima.

Complex	λ_{abs} (nm)		λ_{em} (nm)	
	experimental	calculated[a]	experimental	calculated
Ir1	481	449	679	656
Ir2	481	489	682	656
Ir3	480	491	683	653
Ir4	483	519	687	656
Ir5	388	399	493	415
Ir6	492	500	525	449
Ir7	475	505	628	532
Ir8	518	563	645	577

[a]position of the 0-0 peaks

Table S27. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as calculated by CV and DFT for the eight Ir(III) complexes, **Ir1-Ir8**.

Complex	E_{ox} (V)[a]	E_{re} (V)	E_g (eV)			E_{HOMO} (eV)[e]	E_{LUMO} (eV)	E_{HOMO}^{comput} (eV)[e]	E_{LUMO}^{comput} (eV)
			E_g^{opt}[c]	E_g^{cv}[d]	E_g^{comput}				
Ir1	1.06	-1.45[b]	2.42	2.51	3.25	-5.38	-2.87[f]	-5.40	-2.15
Ir2	0.96	-1.48[b]	2.42	2.44	3.22	-5.28	-2.84[f]	-5.28	-2.06
Ir3	0.92	-1.49[b]	2.42	2.41	3.19	-5.24	-2.83[f]	-5.26	-2.07
Ir4	0.73	-1.50[b]	2.42	2.23	2.88	-5.05	-2.82[f]	-4.93	-2.05
Ir5	1.14		2.56		4.35	-5.46	-2.90[g]	-5.49	-1.59
Ir6	0.76		2.43		3.67	-5.08	-2.65[g]	-5.17	-1.50
Ir7	0.81		2.18		3.17	-5.13	-2.95[g]	-5.17	-2.00
Ir8	0.70		2.18		2.77	-5.02	-2.84[g]	-4.94	-1.93

[a]The values are obtained from the onset potential of the first oxidation wave of the CV curves. [b]Reversible, the values are obtained from the onset potential of the first reduction wave of the CV curves. [c]Optical energy gap E_g^{opt} calculated from the absorption onset of the UV−vis absorption spectra. [d]CV energy gap E_g^{cv} calculated from the potential between the oxidation and reduction waves. [e]HOMO levels are calculated according to the equation HOMO = − (4.8 + ΔE_{ox}) eV. [f]LUMO levels are calculated according to the equation LUMO = HOMO + E_g^{cv}. [g]LUMO levels are calculated according to the equation LUMO = HOMO + E_g^{opt}.

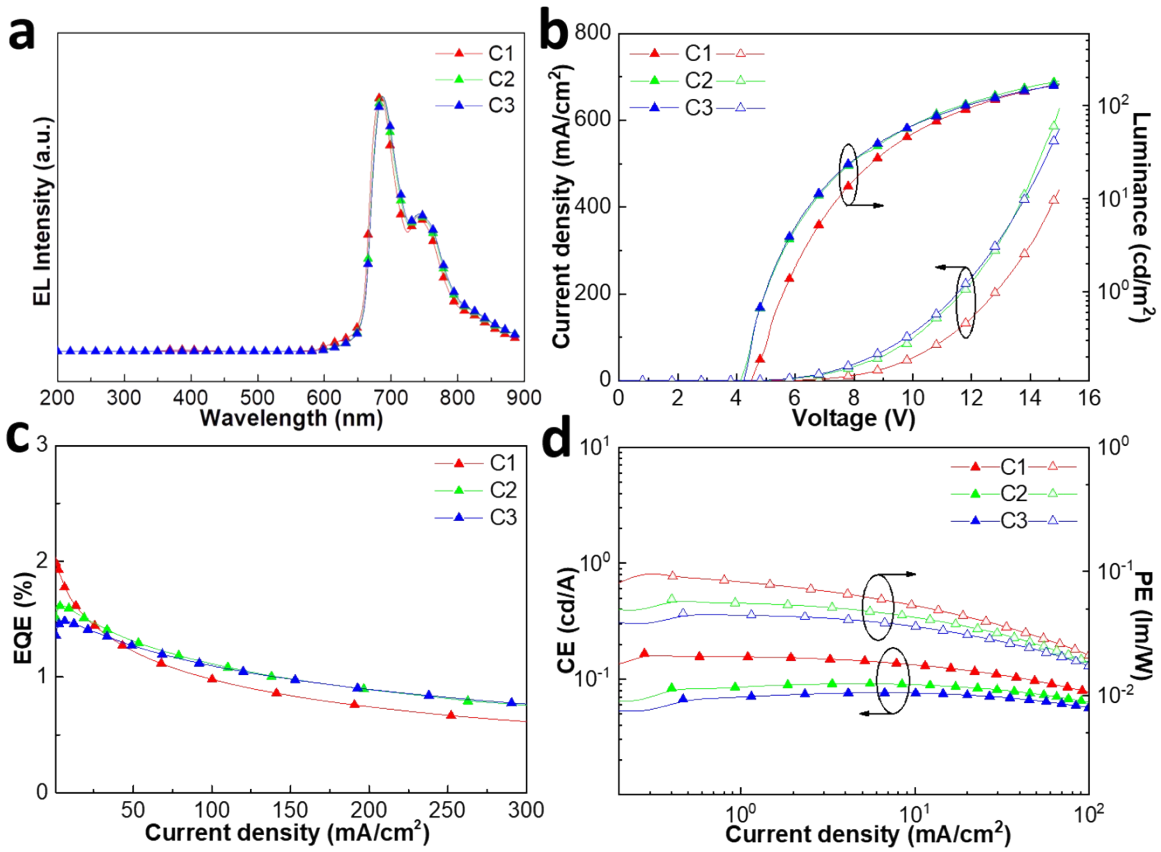


Figure S62. (a) Electroluminescence spectra, (b) current density-voltage-luminance (*J-V-L*) curves, (c) EQE-current density curves and (d) the curves of CE and PE versus current density for devices **C1-C3**.

Table S28. The EL performances of OLEDs **C1-C3**.

Device	EQE [%]	CE [cd A^{-1}]	PE [lm W^{-1}]	L_{max} [cd m^{-2}]	λ_{max}[nm]	V_{on} [V][c]	CIE [x, y]
C1	2.2[a], 1.0[b]	0.17[a]	0.12[a]	175	684, 742	5.6	0.69, 0.29
C2	1.6[a], 1.1[b]	0.09[a]	0.06[a]	170	686, 742	5.0	0.71, 0.28
C3	1.5[a], 1.1[b]	0.08[a]	0.05[a]	180	687, 742	5.0	0.71, 0.28

[a]Maximum efficiency. [b]Efficiency recorded at the current density of 100 mA cm^{-2}. [c]Turn-on voltage recorded at the luminance of 1 cd m^{-2}.