

Table S1 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1**

MO	Energy	Contribution (%)				Assignment
		Ir	SF ₅ -ppy1	SF ₅ -ppy2	SF ₅ -ppy3	
L+10	-0.33	4	46	1	50	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy3})$
L+9	-0.39	4	34	32	31	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+8	-0.86	1	62	25	12	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+7	-0.87	1	17	27	55	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+6	-0.87	0	24	42	34	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+5	-0.88	2	14	38	45	$\pi^*(\text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+4	-0.88	2	47	32	19	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+3	-1.15	2	33	33	33	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
L+2	-1.54	4	62	8	26	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy3})$
L+1	-1.54	4	2	55	38	$\pi^*(\text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
LUMO	-1.67	1	33	33	33	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
HOMO	-6.03	51	16	16	17	d(Ir)+ $\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-1	-6.17	45	32	10	13	d(Ir)+ $\pi(\text{SF}_5\text{-ppy1})$
H-2	-6.17	45	5	27	23	d(Ir)+ $\pi(\text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-3	-6.97	6	14	19	61	$\pi(\text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-4	-6.98	6	48	44	2	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-5	-7.08	7	31	31	31	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-6	-7.64	10	30	30	30	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-7	-7.8	18	10	27	45	d(Ir)+ $\pi(\text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-8	-7.81	18	45	27	10	d(Ir)+ $\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-9	-7.99	14	29	29	29	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$
H-10	-8.27	10	17	43	30	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{SF}_5\text{-ppy3})$

Table S2 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2**

MO	Energy	Contribution (%)				Assignment
		Ir	SF ₅ -ppy1	SF ₅ -ppy2	thd	
L+10	0.71	0	50	50	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+9	0.61	1	49	49	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+8	-0.34	7	46	46	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+7	-0.49	2	49	49	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+6	-0.88	0	50	50	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+5	-0.88	0	49	49	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+4	-0.91	2	1	1	96	$\pi^*(\text{thd})$
L+3	-0.96	2	49	49	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+2	-1.08	3	48	48	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+1	-1.65	4	48	48	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
LUMO	-1.7	4	48	48	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
HOMO	-5.9	45	24	24	6	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-1	-6.06	30	3	3	64	$d(\text{Ir}) + \pi(\text{thd})$
H-2	-6.69	68	12	12	8	$d(\text{Ir})$
H-3	-6.85	6	44	44	6	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-4	-6.94	12	15	15	58	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{thd})$
H-5	-7.11	8	45	45	2	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-6	-7.22	26	11	11	52	$d(\text{Ir}) + \pi(\text{thd})$
H-7	-7.43	1	47	47	5	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-8	-7.95	6	17	17	59	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{thd})$
H-9	-8.39	18	37	37	9	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-10	-8.69	1	49	49	2	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$

Table S3 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **3**

MO	Energy	Contribution (%)				Assignment
		Ir	SF ₅ -ppy1	SF ₅ -ppy2	ptd	
L+10	0.45	9	1	3	87	$\pi^*(\text{ptd})$
L+9	-0.11	0	0	1	99	$\pi^*(\text{ptd})$
L+8	-0.42	7	47	45	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+7	-0.56	3	47	49	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+6	-0.91	0	98	2	0	$\pi^*(\text{SF}_5\text{-ppy1})$
L+5	-0.91	0	2	98	0	$\pi^*(\text{SF}_5\text{-ppy2})$
L+4	-1.02	2	49	48	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+3	-1.16	3	47	48	3	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+2	-1.16	2	2	1	95	$\pi^*(\text{ptd})$
L+1	-1.72	4	49	46	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
LUMO	-1.78	4	46	49	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
HOMO	-6.04	33	15	16	36	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{ptd})$
H-1	-6.05	29	13	11	46	$d(\text{Ir}) + \pi(\text{ptd})$
H-2	-6.84	65	9	18	8	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy2})$
H-3	-6.91	12	46	36	5	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-4	-7.07	32	18	20	30	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{ptd})$
H-5	-7.19	9	44	45	2	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-6	-7.33	12	9	8	72	$\pi(\text{ptd})$
H-7	-7.5	2	46	44	8	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-8	-7.91	1	3	3	93	$\pi(\text{ptd})$
H-9	-7.95	3	7	6	84	$\pi(\text{ptd})$
H-10	-8.43	10	24	27	39	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{ptd})$

Table S4 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **4**

MO	Energy	Contribution (%)				Assignment
		Ir	SF ₅ -ppy1	SF ₅ -ppy2	ntd	
L+10	0.29	3	3	1	93	$\pi^*(\text{ntd})$
L+9	-0.41	7	47	46	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+8	-0.56	3	47	48	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+7	-0.91	0	16	84	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+6	-0.91	0	84	16	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+5	-1.03	2	45	53	0	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+4	-1.16	3	53	44	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+3	-1.71	4	48	46	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+2	-1.79	4	40	45	11	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+1	-1.87	2	7	4	87	$\pi^*(\text{ntd})$
LUMO	-2.11	1	1	0	99	$\pi^*(\text{ntd})$
HOMO	-6.02	42	24	24	9	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-1	-6.23	27	5	4	64	$d(\text{Ir}) + \pi(\text{ntd})$
H-2	-6.86	58	8	27	7	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy2})$
H-3	-6.95	10	52	32	6	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-4	-7.07	28	16	21	35	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{ntd})$
H-5	-7.21	14	39	43	4	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-6	-7.48	8	41	41	9	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-7	-7.62	5	17	12	66	$\pi(\text{SF}_5\text{-ppy1} + \text{ntd})$
H-8	-7.93	2	1	3	94	$\pi(\text{ntd})$
H-9	-8.23	2	7	6	85	$\pi(\text{ntd})$
H-10	-8.39	9	22	22	46	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{ntd})$

Table S5 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **5**

MO	Energy	Contribution (%)				Assignment
		Ir	SF ₅ -ppy1	SF ₅ -ppy2	tpip	
L+10	-0.29	1	3	1	96	$\pi^*(\text{tpip})$
L+9	-0.37	7	40	49	4	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+8	-0.5	2	51	45	2	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+7	-0.85	0	2	5	92	$\pi^*(\text{tpip})$
L+6	-0.89	0	95	5	0	$\pi^*(\text{SF}_5\text{-ppy1})$
L+5	-0.89	0	4	95	0	$\pi^*(\text{SF}_5\text{-ppy2})$
L+4	-0.9	0	7	1	91	$\pi^*(\text{tpip})$
L+3	-0.92	2	33	52	12	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+2	-1.08	3	55	38	4	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
L+1	-1.63	5	31	63	1	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
LUMO	-1.71	4	62	32	2	$\pi^*(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
HOMO	-5.9	46	24	24	6	$d(\text{Ir}) + \pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2})$
H-1	-6.45	62	10	12	16	$d(\text{Ir}) + \pi(\text{tpip})$
H-2	-6.49	64	11	8	17	$d(\text{Ir}) + \pi(\text{tpip})$
H-3	-6.86	0	26	32	42	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{tpip})$
H-4	-6.91	6	22	15	57	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{tpip})$
H-5	-7.08	4	36	42	18	$\pi(\text{SF}_5\text{-ppy1} + \text{SF}_5\text{-ppy2} + \text{tpip})$
H-6	-7.11	5	5	5	85	$\pi(\text{tpip})$
H-7	-7.22	1	1	0	98	$\pi(\text{tpip})$
H-8	-7.28	0	1	1	98	$\pi(\text{tpip})$
H-9	-7.36	0	2	2	96	$\pi(\text{tpip})$
H-10	-7.37	0	3	1	95	$\pi(\text{tpip})$

Table S6 Selected calculated wavelength (nm) /energies (eV), oscillator strength (f), major contribution and transition characters for **1–5** in MeCN media from TDDFT. H indicates HOMO, L indicates LUMO

	State	λ/E	f	Configuration	Assignment	Nature	Exptl. ^a	
1	S ₁	366/3.39	0.0144	H→L (96%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2 +SF ₅ -ppy3)	MLCT/LLCT/ILCT	363	
	S ₂₄	265/4.69	0.2459	H-3→L+2 (19%)	π (SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy3)	LLCT/ILCT		
				H-4→L+1 (18%)	π (SF ₅ -ppy1 + SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy2 + SF ₅ -ppy3)			
	S ₃₀	262/4.73	0.1953	H-5→L (35%)	π (SF ₅ -ppy1+SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2+ SF ₅ -ppy3)	LLCT/ILCT		
	S ₄₀	254/4.88	0.1899	H-2→L+9 (52%)	d(Ir)+ π (SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2+ SF ₅ -ppy3)	MLCT/LLCT/ILCT		
	S ₄₄	250/4.96	0.1963	H-2→L+10 (35%),	d(Ir)+ π (SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy3)	MLCT/LLCT/ILCT		
				H-1→L+11 (35%)	d(Ir)+ π (SF ₅ -ppy1) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2+SF ₅ -ppy3)			
S ₅₁	239/5.20	0.2068	H-9→L (28%),	π (SF ₅ -ppy1+SF ₅ -ppy2+SF ₅ -ppy3) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2+ SF ₅ -ppy3)	LLCT/ILCT			
2	S ₁	387/3.20	0.0537	H→L (95%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
	S ₁₉	275/4.52	0.1754	H→L+7 (62%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
	S ₃₀	260/4.77	0.2034	H-1→L+8 (30%)	d(Ir)+ π (thd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT		
				H-6→L+1 (21%)	d(Ir)+ π (thd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)			
	S ₃₈	240/5.16	0.1358	H-4→L+3 (52%)	π (SF ₅ -ppy1+SF ₅ -ppy2+thd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT		
	S ₄₁	239/5.19	0.2598	H-3→L+4 (35%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (thd)	LLCT		
				H-3→L+3 (26%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)			
S ₅₃	229/5.42	0.0606	H→L+12 (43%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow d(Ir)	MLCT			
3	S ₁	381/3.26	0.0552	H→L (61%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ptd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
	S ₁₈	277/4.48	0.1535	H-1→L (34%)	d(Ir)+ π (ptd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
				H-4→L+1 (55%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ptd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)			
	S ₂₃	266/4.67	0.1464	H-5→L (22%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT		
				H-2→L+2 (22%)	d(Ir)+ π (SF ₅ -ppy2) \rightarrow π^* (ptd)			
	S ₃₇	245/5.06	0.1331	H-1→L+9 (25%)	d(Ir)+ π (ptd) \rightarrow π^* (ptd)	MLCT/ILCT		
				H→L+9 (21%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ptd) \rightarrow π^* (ptd)			
S ₄₀	241/5.15	0.3135	H-3→L+4 (37%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT			
			H-4→L+4 (15%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ptd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)				
S ₅₀	233/5.32	0.0979	H→L+14 (23%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ptd) \rightarrow d(Ir)+ π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT			
			H-1→L+14 (17%)	d(Ir)+ π (ptd) \rightarrow d(Ir)+ π^* (SF ₅ -ppy1+SF ₅ -ppy2)				
4	S ₁	392/3.16	0.0226	H→L+1 (53%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (ntd)	MLCT/LLCT		
	S ₉	317/3.91	0.1001	H→L (43%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (ntd)	MLCT/LLCT		
				H-2→L (22%)	d(Ir)+ π (SF ₅ -ppy2) \rightarrow π^* (ntd)			
	S ₃₃	265/4.68	0.1317	H-5→L+1 (18%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (ntd)	LLCT		
				H-5→L+2 (18%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)			
	S ₃₆	259/4.79	0.1569	H-2→L+4 (50%)	d(Ir)+ π (SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
	S ₄₆	250/4.96	0.1011	H-2→L+5 (21%)	d(Ir)+ π (SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT		
H-6→L+3 (18%)				π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)				
S ₅₄	238/5.22	0.2003	H-3→L+5 (28%)	π (SF ₅ -ppy1+SF ₅ -ppy2) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT			
			H-4→L+5 (13%)	d(Ir)+ π (SF ₅ -ppy1+SF ₅ -ppy2+ntd) \rightarrow π^* (SF ₅ -ppy1+SF ₅ -ppy2)				

5	S ₁	389/3.19	0.0454	H→L (94%)	d(Ir)+π(SF ₅ -ppy1+SF ₅ -ppy2)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT
	S ₅	327/3.79	0.1102	H-2→L (48%)	d(Ir)+π(tpip)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT
				H-1→L+1 (44%)	d(Ir)+π(tpip)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	
	S ₁₇	275/4.51	0.1205	H→L+8 (43%)	d(Ir)+π(SF ₅ -ppy1+SF ₅ -ppy2)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT/ILCT
	S ₂₃	261/4.74	0.2310	H-5→L (41%)	π(SF ₅ -ppy1+SF ₅ -ppy2+tpip)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT
	S ₃₀	254/4.88	0.0497	H-1→L+9 (35%)	d(Ir)+π(tpip)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	MLCT/LLCT
	S ₅₁	242/5.13	0.0628	H-3→L+2 (35%)	π(SF ₅ -ppy1+SF ₅ -ppy2+tpip)→π*(SF ₅ -ppy1+SF ₅ -ppy2)	LLCT/ILCT

^a Ref. 18

Table S7 Partial frontier molecular orbital composition (%) of complexes **1–5** in the triplet excited states. (H and L indicate HOMO and LUMO, respectively)

	MO	Energy/eV	MO composition (%)			Assignment
			Ir	Main ligand	Ancillary ligand	
1	L	-1.96	3	94	3	π*(SF ₅ -ppy)
	H	-5.92	42	47	10	d(Ir)+π(SF ₅ -ppy)
2	L	-2.00	4	95	1	π*(SF ₅ -ppy)
	H	-5.78	41	48	11	d(Ir)+π(SF ₅ -ppy)
3	L	-2.09	5	95	1	π*(SF ₅ -ppy)
	H	-5.92	36	46	18	d(Ir)+π(SF ₅ -ppy+ptd)
4	L	-2.45	1	0	99	π*(ntd)
	H	-6.04	43	49	7	d(Ir)+π(SF ₅ -ppy)
5	L	-1.99	4	94	1	π*(SF ₅ -ppy)
	H	-5.82	43	52	5	d(Ir)+π(SF ₅ -ppy)

Table S8 The xyz coordinates for the optimized structures for **1** in the S_0 and T_1 states at PBE0/6-31G(d,p) level

	S_0			T_1			
Ir	0.00285000	-	-0.00015700	1.14207800	-0.02957400	-0.00367900	1.11633600
S	3.00619400		-5.01301300	-1.94640900	3.45630200	4.72417200	-1.91530500
F	-4.41969400		-4.23400600	-2.07650000	4.79049300	3.81602200	-2.03416400
F	-3.49008800	-	-5.65463100	-0.53964400	3.98192300	5.31005500	-0.50019800
F	1.66820000		-5.92449600	-1.89118900	2.20757200	5.75394500	-1.86765900
F	-2.59700000		-4.50345700	-3.42780800	3.01519000	4.25964900	-3.40157600
F	-3.72897900		-6.26951700	-2.67012900	4.29988000	5.91001100	-2.62514000
S	5.84491900		-0.08539300	-1.95672100	-5.85368300	0.49963300	-1.98957700
F	5.88158300		-1.69888700	-2.08580800	-5.77739700	2.11252100	-2.10479000
F	6.64458600		-0.18072500	-0.55114100	-6.64356800	0.63883600	-0.58248900
F	5.96005300		1.52951400	-1.90167500	-6.07845000	-1.10343300	-1.94648800
F	5.19651200		0.01134300	-3.43710500	-5.21244800	0.36939200	-3.47015800
F	7.29334500		-0.07877600	-2.68268700	-7.29824700	0.59919800	-2.71460700
S	-2.85574200		5.09897300	-1.94876500	2.54548900	-5.26612900	-1.90702500
F	-1.47692000		5.93566600	-2.09361700	1.11400300	-6.00749400	-2.05027500
F	-3.16063500		5.84600200	-0.54403500	2.80170300	-6.03996600	-0.50920900
F	-4.31228800		4.39369600	-1.87898500	4.04208300	-4.65467600	-1.83379000
F	-2.62960900		4.48255300	-3.42874000	2.35659700	-4.61823300	-3.37783300
F	-3.59079500		6.34737500	-2.67380500	3.19408600	-6.55172600	-2.64518200
C	1.98337100		-0.90205800	-1.03082200	-1.94057600	1.02972900	-1.07003700
C	3.22031400		-0.90104100	-1.66286000	-3.17608200	1.11925600	-1.69973200
C	4.23800900		-0.09540500	-1.15458300	-4.24883700	0.39216400	-1.18737500
C	4.03310200		0.69939500	-0.03732200	-4.10351500	-0.41054400	-0.06682500
C	2.78194200		0.68852100	0.58483900	-2.85430800	-0.48888400	0.55514900
C	1.71349300		-0.11778200	0.10437000	-1.73201900	0.23169800	0.06595200
C	2.49587000		1.50928300	1.76629200	-2.63486000	-1.31030500	1.75245900
C	3.39345400		2.38411300	2.38528200	-3.59676600	-2.10765300	2.37881600
C	2.99678200		3.10405300	3.50212700	-3.25939500	-2.83381600	3.51137100
C	1.70212500		2.94328900	3.99002900	-1.96099000	-2.75717500	4.01074900
N	1.23969100		1.36535700	2.25515200	-1.37663000	-1.25011400	2.25383200
C	-0.95528700		-1.42167900	0.10605800	1.05957100	1.33665300	0.09877000
C	-1.77306100		-1.26232400	-1.02647200	1.87929300	1.09797600	-1.01642600
C	-2.39554300		-2.33336000	-1.65473500	2.60539700	2.10841900	-1.63378100
C	-2.20615000		-3.61784300	-1.14688300	2.52133000	3.40500600	-1.12961600
C	-1.41098000		-3.83873100	-0.03308000	1.72725000	3.69912600	-0.03257100
C	-0.79144800		-2.75021900	0.58660200	0.99906400	2.67336800	0.57584600
C	0.06600900		-2.91304600	1.76566400	0.12993800	2.91817500	1.73216600
C	0.37516900		-4.12699700	2.38573000	-0.09007600	4.15950400	2.33512900
C	1.20196700		-4.14296800	3.49899900	-0.94868400	4.25584200	3.42000900
C	1.71500900		-2.94150100	3.98199900	-1.58229900	3.10841300	3.89111400

C	1.37443400	-1.77053600	3.32379900	-1.32434500	1.90669300	3.25115100
N	0.57284800	-1.75281200	2.25057400	-0.49089300	1.81220700	2.20748300
C	-0.21397500	2.16297600	-1.03074200	0.04305900	-2.18018900	-1.02172700
C	-0.75262600	1.54058100	0.10924600	0.60299900	-1.57294600	0.10393500
C	-2.62000100	3.14230300	-0.02594300	2.42458500	-3.31200800	0.00210200
C	-2.03949200	3.71431600	-1.14709300	1.80459800	-3.82843900	-1.09655800
C	-0.83565800	3.23343200	-1.66094300	0.60579300	-3.29346600	-1.64311000
C	-1.98256200	2.06487500	0.59434900	1.84505100	-2.16670500	0.65460800
C	-2.54643400	1.40622300	1.77712300	2.38526000	-1.58465300	1.80091200
C	-3.74787000	1.74766300	2.40466100	3.56777500	-2.01054500	2.49435200
C	-4.16936700	1.03995600	3.52028800	4.01336900	-1.32615800	3.58972600
C	-3.38468200	-0.00686900	3.99825100	3.29281400	-0.18649300	4.03583200
C	-2.20469200	-0.29957500	3.33258900	2.14049200	0.18532500	3.34600400
N	-1.79475200	0.38561300	2.25721900	1.67666100	-0.46979000	2.28865000
H	1.74747200	-0.80701400	3.65433900	-1.78837200	0.98163000	3.57581100
H	2.36665800	-2.90628700	4.84795000	-2.26248800	3.13773500	4.73493800
H	1.44489500	-5.08352700	3.98385100	-1.12327700	5.21766700	3.89225800
H	-0.02689100	-5.05635700	1.99878700	0.40501800	5.04657800	1.95745200
H	-1.27840200	-4.84597700	0.34373300	1.67760000	4.71491700	0.34099800
H	-3.01832300	-2.16779400	-2.52683700	3.22607500	1.88514200	-2.49425900
H	-1.92867300	-0.26851900	-1.43625700	1.94339700	0.09333700	-1.42390700
H	1.34826800	3.48647600	4.85919400	-1.65558700	-3.30929100	4.89246100
H	3.69050500	3.78478700	3.98598700	-4.00347900	-3.45529200	4.00003000
H	4.39779800	2.50343200	1.99536700	-4.60416600	-2.16303800	1.98273000
H	4.84005200	1.31586100	0.34046000	-4.95352800	-0.96363600	0.31438900
H	3.38683400	-1.52001000	-2.53752300	-3.29818300	1.74513400	-2.57654800
H	1.20088500	-1.53402900	-1.44074300	-1.11297700	1.59878600	-1.48378700
C	0.85727500	2.06329400	3.33217400	-1.05038700	-1.95138000	3.34695600
H	-0.16174500	1.90142500	3.66668300	-0.02409000	-1.85114400	3.68400100
H	-1.55538500	-1.10487900	3.65909100	1.56051100	1.04727800	3.66372800
H	-3.67617500	-0.58842300	4.86574300	3.61505000	0.39039700	4.89484400
H	-5.10198300	1.30153700	4.01077300	4.90768800	-1.64811500	4.11416100
H	-4.35196500	2.56236900	2.02194700	4.10481300	-2.88398500	2.14100700
H	-3.55628500	3.53262800	0.35517500	3.33965900	-3.75294300	0.37655700
H	-0.38794400	3.68372500	-2.53991600	0.14858800	-3.73516100	-2.51880400
H	0.72089600	1.79761600	-1.44619100	-0.86652300	-1.76452200	-1.44525600

Table S9 The xyz coordinates for the optimized structures for **2** in the S_0 and T_1 states at PBE0/6–31G(d,p) level

	S_0			T_1		
Ir	0.00000000	0.88437800	0.00000000	0.02223400	0.87721400	-0.05443300
S	4.89584500	-3.50140200	-0.31668800	-5.14110100	-3.13298500	0.38371300
F	4.48759800	-4.14835700	1.11056900	-4.70503700	-3.94668900	-0.94572700
F	4.01734000	-4.62822100	-1.07777300	-4.35211000	-4.21109900	1.29708600
F	5.43166900	-2.96369900	-1.74649200	-5.70818600	-2.41712500	1.71980500
F	5.90092200	-2.48323700	0.44224900	-6.05742000	-2.15544200	-0.52383900
F	6.12419600	-4.55672400	-0.34775300	-6.42136400	-4.11983600	0.46851500
O	1.42900700	2.44744600	-0.39881800	-1.24655300	2.59430600	0.22249500
N	0.74580300	0.83627900	1.90214500	-0.65601900	0.81729200	-1.95943500
C	1.81922100	0.02512800	2.09587700	-1.78139400	-0.00338700	-2.15027800
C	2.43103700	-0.03554200	3.34848600	-2.32743800	-0.12038800	-3.46129300
H	3.28922100	-0.68005700	3.50182800	-3.19078700	-0.75933300	-3.61729600
C	1.93734600	0.72885600	4.39555600	-1.77243800	0.56090300	-4.50932900
H	2.40970200	0.68532600	5.37200500	-2.18988600	0.47049400	-5.50736100
C	0.82985700	1.54573000	4.17852900	-0.63875600	1.38985100	-4.27864700
H	0.40825200	2.15541900	4.96971400	-0.16996500	1.94623600	-5.08199700
C	0.26319300	1.57073100	2.91483800	-0.12741800	1.47653600	-2.99609600
H	-0.60105000	2.18095700	2.67827900	0.74275200	2.08360000	-2.76721800
C	2.20209300	-0.73469500	0.90576100	-2.23783600	-0.62437400	-0.97918300
C	1.40167500	-0.49840000	-0.24273100	-1.48336700	-0.33750200	0.24483800
C	1.71263200	-1.23142300	-1.39815000	-1.89925600	-0.92382700	1.44201500
H	1.12532700	-1.09379200	-2.30173300	-1.34628200	-0.72576600	2.35629500
C	2.76495600	-2.13844100	-1.43162900	-3.00485000	-1.76726800	1.51025500
H	2.98158400	-2.68738800	-2.34122300	-3.31477900	-2.21003000	2.44749200
C	3.53317400	-2.33101700	-0.28347400	-3.70767200	-2.03138100	0.30738600
C	3.26386000	-1.64025300	0.88897100	-3.36275500	-1.50168200	-0.90716300
H	3.87008900	-1.80783800	1.77166100	-3.93359200	-1.73810100	-1.79674900
C	2.26182600	6.05318500	-0.45618600	-1.68550700	6.25071300	0.57748100
H	3.20904600	6.57076200	-0.64649800	-2.57823000	6.85606600	0.77132700
H	1.91995600	6.34661000	0.54273900	-1.24955600	6.59791200	-0.36589900
H	1.53496600	6.41457800	-1.19244000	-0.97113600	6.44839800	1.38466600
C	2.48419900	4.54419700	-0.56362700	-2.08356700	4.77604100	0.51484900
C	1.22459100	3.69981500	-0.30017500	-0.90724500	3.82203000	0.25047700
C	-0.00000100	4.32041300	0.00000100	0.39277400	4.31814200	0.06355000
H	-0.00000100	5.39880200	0.00000200	0.52050100	5.38530600	0.15170500
C	3.54574000	4.12172500	0.46463200	-3.10020200	4.57806900	-0.62120100
H	3.21854800	4.35213200	1.48573500	-2.66932300	4.86203900	-1.58867200
H	4.48127800	4.66221500	0.27916000	-3.98114200	5.20603100	-0.44522700
H	3.74447200	3.04822700	0.40059700	-3.42225300	3.53458000	-0.67984100
C	2.98562200	4.21231100	-1.97761900	-2.72698300	4.37328800	1.85088800

H	3.17920900	3.14073800	-2.08156800	-3.03418200	3.32360600	1.83686000
H	3.91643700	4.75414100	-2.18197500	-3.61196900	4.99160800	2.03987700
H	2.25043700	4.50846500	-2.73610100	-2.03042500	4.52157900	2.68546600
S	-4.89584400	-3.50140300	0.31668900	4.61105600	-3.82252300	-0.23413600
F	-4.48759700	-4.14835800	-1.11056800	4.14011800	-4.41820700	1.19413600
F	-4.01733900	-4.62822200	1.07777400	3.66633100	-4.89421300	-0.99158400
F	-5.43166800	-2.96370000	1.74649300	5.19278500	-3.33406000	-1.66162400
F	-5.90092100	-2.48323800	-0.44224800	5.66547100	-2.85784600	0.52421600
F	-6.12419500	-4.55672500	0.34775400	5.76645500	-4.95354800	-0.23723000
O	-1.42900800	2.44744600	0.39881700	1.56009800	2.31675600	-0.48682100
N	-0.74580300	0.83627900	-1.90214600	0.76628200	0.85000200	1.87024400
C	-1.81922100	0.02512700	-2.09587700	1.76978000	-0.03867700	2.08781600
C	-2.43103700	-0.03554300	-3.34848600	2.38178100	-0.10928900	3.33841300
H	-3.28922100	-0.68005900	-3.50182800	3.18148600	-0.81949400	3.51392300
C	-1.93734600	0.72885400	-4.39555600	1.96135100	0.73293500	4.35848800
H	-2.40970200	0.68532400	-5.37200600	2.43298400	0.68234700	5.33478700
C	-0.82985800	1.54572900	-4.17853000	0.93006100	1.63583800	4.11514200
H	-0.40825300	2.15541700	-4.96971500	0.56801300	2.30806300	4.88466600
C	-0.26319300	1.57073000	-2.91483900	0.35736500	1.66244300	2.85322700
H	0.60104900	2.18095700	-2.67828000	-0.45568800	2.33417800	2.60333100
C	-2.20209300	-0.73469600	-0.90576100	2.09769200	-0.85872900	0.91896900
C	-1.40167400	-0.49840100	0.24273100	1.32996600	-0.60320200	-0.24467900
C	-1.71263200	-1.23142300	1.39815000	1.59753800	-1.36388300	-1.38937300
H	-1.12532600	-1.09379300	2.30173300	1.02969300	-1.19299600	-2.29865200
C	-2.76495500	-2.13844200	1.43162900	2.58651300	-2.34045700	-1.39511200
H	-2.98158300	-2.68738900	2.34122300	2.77773700	-2.91724800	-2.29259900
C	-3.53317300	-2.33101800	0.28347400	3.32336200	-2.56247200	-0.23291200
C	-3.26385900	-1.64025400	-0.88897100	3.09319100	-1.83647400	0.92704900
H	-3.87008800	-1.80783900	-1.77166000	3.68119900	-2.03053600	1.81615000
C	-2.26182800	6.05318400	0.45618900	2.85029200	5.78046200	-0.32291800
H	-3.20904800	6.57076100	0.64650200	3.85252000	6.18696000	-0.49969200
H	-1.91995700	6.34661100	-0.54273500	2.55918800	6.05089500	0.69827300
H	-1.53496800	6.41457600	1.19244400	2.16591700	6.27356700	-1.02239800
C	-2.48420000	4.54419500	0.56362700	2.88184300	4.26556200	-0.52661700
C	-1.22459300	3.69981400	0.30017500	1.52880900	3.57569800	-0.29546000
C	-3.54574200	4.12172500	-0.46463200	3.88787900	3.64782800	0.45819200
H	-3.21854800	4.35213400	-1.48573500	3.60083200	3.85436800	1.49632000
H	-4.48127900	4.66221500	-0.27916000	4.88307200	4.07532600	0.29045800
H	-3.74447400	3.04822700	-0.40059900	3.94802200	2.56386100	0.32593000
C	-2.98562400	4.21230800	1.97761900	3.32462800	3.96263500	-1.96659200
H	-3.17921000	3.14073400	2.08156600	3.38587200	2.88435900	-2.13922000
H	-3.91643900	4.75413600	2.18197600	4.31228100	4.40034400	-2.15186600
H	-2.25044000	4.50846100	2.73610200	2.62339100	4.39152900	-2.69271200

Table S10 The xyz coordinates for the optimized structures for **3** in the S_0 and T_1 states at PBE0/6–31G(d,p) level

	S_0			T_1		
Ir	-0.34202500	-0.83059100	0.04368300	-0.35629500	-0.82677300	0.00109200
S	-2.35671300	5.41354100	0.39515000	-2.07414000	5.50398300	0.31961200
F	-1.64469000	5.80190000	1.00619400	-1.32798700	5.83211500	1.07772800
F	-1.04661500	5.91898900	-1.19999300	-0.74984000	5.95402600	-1.13115200
F	-3.12257500	5.17984200	-1.80169800	-2.86363900	5.32266200	-1.71913900
F	-3.72055100	5.06484600	0.40513200	-3.44206600	5.20311800	0.49041500
F	-2.88278500	6.94353100	-0.45655800	-2.52775400	7.05534700	-0.35251600
O	-2.38098500	-1.48730900	-0.31567700	-2.41966500	-1.38086400	-0.38837400
N	-0.94752900	-0.37482200	1.94244500	-0.96522300	-0.39146500	1.91995500
C	-1.45852600	0.87250900	2.11451700	-1.40260300	0.87926500	2.11335800
C	-1.94168700	1.26220200	3.36381000	-1.87869100	1.27112700	3.36366600
H	-2.35149400	2.25653800	3.50049500	-2.22713600	2.28556300	3.51978800
C	-1.89316300	0.37489900	4.42923300	-1.90327800	0.35624000	4.40727500
H	-2.26773600	0.67283900	5.40356000	-2.27214200	0.65469200	5.38349800
C	-1.35573400	-0.89550200	4.23408700	-1.44856000	-0.94150500	4.18810700
H	-1.29330100	-1.61762900	5.04028900	-1.44657400	-1.68532600	4.97664600
C	-0.89318200	-1.23163500	2.97256400	-0.98581000	-1.27621600	2.92560900
H	-0.45885300	-2.20018900	2.75225300	-0.60796000	-2.26445200	2.69001100
C	-1.41563000	1.69458200	0.90509200	-1.30950400	1.72231900	0.91940300
C	-0.85795200	1.06183300	-0.23604300	-0.78722300	1.09235200	-0.23795400
C	-0.77020900	1.82047800	-1.41167500	-0.67289500	1.85358300	-1.40691900
H	-0.34506400	1.38292500	-2.31029500	-0.27935800	1.40287200	-2.31260800
C	-1.22167300	3.13384300	-1.47042800	-1.05992400	3.18842500	-1.44127200
H	-1.14356900	3.69467400	-2.39496000	-0.96414600	3.75924900	-2.35764100
C	-1.77191500	3.71524900	-0.32883900	-1.56905100	3.77522900	-0.28424600
C	-1.87396700	3.01185800	0.86216800	-1.69926600	3.06158400	0.89828700
H	-2.30126000	3.48334700	1.73945300	-2.09782700	3.54184200	1.78388300
C	-5.17531000	-3.23175600	0.69627400	-5.33950300	-2.83454000	0.71013700
H	-6.25348400	-3.20385000	0.49851600	-6.41377300	-2.72697100	0.51911100
H	-4.98249800	-2.62265000	1.58749900	-5.08751300	-2.20465000	1.57162700
H	-4.88555600	-4.26321500	0.90604300	-5.13151800	-3.87609100	0.96301200
C	-4.42629400	-2.67209500	-0.52474500	-4.56201500	-2.39196800	-0.54137400
C	-2.91793000	-2.62443000	-0.23845800	-3.05462900	-2.46314800	-0.26577100
C	-2.17701700	-3.80606600	0.08474100	-2.40858300	-3.68715700	0.09187200
C	-4.93772300	-1.25613800	-0.80422200	-4.95335900	-0.95048400	-0.87813400
H	-4.77738900	-0.59237900	0.05111200	-4.72423700	-0.26626000	-0.05507200
H	-6.01359900	-1.30217200	-1.00693100	-6.03181500	-0.91167600	-1.06743500
H	-4.44346300	-0.81088100	-1.67309800	-4.43498400	-0.58854900	-1.77139400
C	-4.69678100	-3.54426100	-1.76275300	-4.91794000	-3.29215700	-1.73682100
H	-4.17680200	-3.14850100	-2.64357200	-4.37183400	-2.98455300	-2.63658500

H	-5.77189100	-3.53513700	-1.97835700	-5.98975600	-3.19817100	-1.94759300
H	-4.38073900	-4.57679800	-1.60198200	-4.69308100	-4.34022900	-1.52956600
S	6.08080400	0.54723500	0.32351600	6.09393900	0.25817900	0.36307600
F	6.04616100	1.30078100	-1.10932100	6.08249400	1.15433200	-0.98381000
F	5.87957200	1.96677100	1.07464100	5.90865300	1.59741800	1.25167600
F	6.27737200	-0.17622700	1.75801100	6.26151600	-0.61449000	1.71508800
F	6.44369200	-0.84159100	-0.42571500	6.43420800	-1.05315100	-0.52082800
F	7.67062400	0.85159900	0.35150000	7.68726800	0.52749400	0.43399000
O	0.08239400	-2.91800000	0.50027000	-0.07494200	-2.96220800	0.37641400
N	0.32205500	-1.19946900	-1.85811900	0.25597700	-1.16246400	-1.89982900
C	1.65478900	-1.02362400	-2.06048100	1.63789700	-0.98029400	-2.10414800
C	2.21300800	-1.29262000	-3.31041200	2.17135600	-1.17779600	-3.41319600
H	3.27634200	-1.15449400	-3.47003700	3.23349000	-1.02835500	-3.57701900
C	1.40399800	-1.73475600	-4.34696200	1.35666600	-1.54770100	-4.44650500
H	1.83337800	-1.94533100	-5.32143500	1.76222000	-1.69752600	-5.44203400
C	0.03925500	-1.89981900	-4.12197400	-0.03273400	-1.73141000	-4.20333600
H	-0.63056900	-2.23818900	-4.90434200	-0.71312100	-2.02329800	-4.99473000
C	-0.46182700	-1.62089400	-2.86135600	-0.52180000	-1.52387200	-2.92377900
H	-1.51448600	-1.72470500	-2.62488200	-1.57674200	-1.63753200	-2.69665800
C	2.36651800	-0.53141000	-0.88131900	2.33855600	-0.61536100	-0.95140600
C	1.55900700	-0.32193900	0.26609800	1.54258600	-0.46747100	0.27635900
C	2.19143000	0.17624300	1.41434700	2.19545200	-0.11108100	1.45815300
H	1.61433000	0.36012100	2.31609300	1.62257400	0.00842700	2.37351700
C	3.55553800	0.44057300	1.44136700	3.56901800	0.10078000	1.50896500
H	4.01797200	0.82108000	2.34508400	4.05947400	0.36928300	2.43507000
C	4.31555100	0.21044000	0.29516500	4.30970400	-0.03785200	0.30326200
C	3.73759200	-0.27134500	-0.86998500	3.74903600	-0.37584900	-0.89552500
H	4.34587000	-0.43885700	-1.75115200	4.35693100	-0.46535500	-1.78723900
C	-0.78847600	-3.82428600	0.40118300	-1.01345100	-3.80458100	0.34858300
S	-0.31973400	-5.50756600	0.72346600	-0.66024100	-5.50673700	0.70461400
C	-1.97009400	-5.99532900	0.41535600	-2.35628000	-5.87276900	0.48568500
H	-2.25091200	-7.04083600	0.48564600	-2.71236200	-6.89045400	0.60545600
N	-2.78619200	-5.05197600	0.11103400	-3.11145400	-4.87881300	0.18462000

Table S11 The xyz coordinates for the optimized structures for **4** in the S_0 and T_1 states at PBE0/6–31G(d,p) level

	S_0			T_1		
Ir	-0.52870100	-0.02455700	-0.18643600	0.54178700	-0.01216300	0.16272900
S	4.28929900	-4.40201100	0.77832500	-4.25730400	-4.42707300	-0.71178200
F	5.03378800	-3.95416100	-0.58811500	-4.98242000	-3.98197100	0.66524200
F	5.21903300	-3.37912300	1.62013100	-5.20759500	-3.41291300	-1.53994200
F	3.66382000	-4.96245300	2.16197200	-3.64755500	-4.98288300	-2.10356200
F	3.47942600	-5.53623200	-0.04602100	-3.42267300	-5.55052200	0.10136800
F	5.46838000	-5.49585200	0.96365000	-5.42855500	-5.53123800	-0.87614000
O	-2.07118400	-1.54200700	0.00545500	2.08603600	-1.51947100	-0.04880800
N	-0.21341700	-0.83148700	-2.03841800	0.25429000	-0.80735000	2.02895000
C	0.73003100	-1.80711600	-2.10484900	-0.67959800	-1.79065000	2.11141600
C	0.98763500	-2.44343400	-3.31941500	-0.91873500	-2.42246900	3.33175700
H	1.73961100	-3.22233300	-3.37592600	-1.66293500	-3.20764200	3.39979300
C	0.27929900	-2.07517000	-4.45439900	-0.20328100	-2.04115900	4.45753300
H	0.47654300	-2.56681900	-5.40191700	-0.38584900	-2.52969800	5.40944900
C	-0.68228200	-1.07119800	-4.36333200	0.74543100	-1.02662100	4.35196500
H	-1.25661000	-0.75310600	-5.22607300	1.32378700	-0.69578200	5.20699200
C	-0.90017900	-0.47350700	-3.13291100	0.94531800	-0.43427300	3.11653200
H	-1.63294600	0.31231900	-2.98544200	1.66610100	0.36173200	2.96829000
C	1.39437600	-2.06808000	-0.82712800	-1.35918800	-2.06289600	0.84490700 -
C	0.94884100	-1.27263800	0.26122000	-0.93926600	-1.26918900	0.25232500
C	1.57406600	-1.47509700	1.50006900	-1.57864200	-1.47717900	-1.48121900
H	1.27375700	-0.88608500	2.36209100	-1.29698000	-0.88866200	-2.34925200
C	2.58039800	-2.41918700	1.66792800	-2.57939600	-2.43067800	-1.63098000
H	3.04508900	-2.55228200	2.63837900	-3.05706900	-2.56948000	-2.59416100
C	2.98231200	-3.18534800	0.57452200	-2.95750400	-3.19746100	-0.53045400
C	2.40104600	-3.02223100	-0.67423700	-2.35929000	-3.02646400	0.70882500
H	2.73084500	-3.62675900	-1.51096400	-2.67077700	-3.63171900	1.55183000
C	-5.06411600	-2.95571900	-1.23370700	5.06308900	-2.96615700	1.17435900
H	-5.42229600	-3.98797300	-1.31379700	5.43556000	-3.99524600	1.22234100
H	-4.63664700	-2.67493800	-2.20300100	4.61916200	-2.72642300	2.14735000
H	-5.93304600	-2.31985600	-1.05457900	5.91977600	-2.30761300	1.02348700
C	-3.99614300	-2.88880300	-0.12888500	4.00651500	-2.87847800	0.05961200
C	-3.31447600	-1.50407600	-0.06600800	3.33228800	-1.49560900	0.01469900
C	-2.92468900	-3.93719600	-0.46380200	2.93214600	-3.93369400	0.35808000
H	-2.44199900	-3.72456100	-1.42334100	2.44034200	-3.74489300	1.31798300
H	-3.40382200	-4.91963100	-0.53107200	3.41063300	-4.91756900	0.40562600
H	-2.14829900	-3.98372200	0.30373800	2.16320100	-3.96128100	-0.41804500
C	-4.57806800	-3.26246900	1.24988700	4.60669100	-3.21530500	-1.32111800
H	-3.80321200	-3.21168800	2.02289400	3.83323700	-3.17881100	-2.09637800
H	-4.94060600	-4.29551200	1.20667600	5.00140800	-4.23689800	-1.28917900

H	-5.41447500	-2.63641600	1.56970500	5.42152900	-2.55526600	-1.62618800
S	3.48965200	5.17223600	-0.30953300	-3.54790200	5.13107200	0.32211400
F	4.04319400	4.85548100	1.17865700	-4.14800400	4.76898400	-1.13668600
F	4.73599400	4.35943800	-0.94635700	-4.75457400	4.31120700	1.02183900
F	3.03222900	5.62137000	-1.79569600	-3.04418100	5.62065700	1.77960900
F	2.34149100	6.11853200	0.32907600	-2.43898800	6.07919200	-0.37887000
F	4.45117600	6.47453400	-0.30020200	-4.53085200	6.41615800	0.31820700
O	-2.19436900	1.17174800	-0.83654400	2.20445600	1.19700600	0.70440100
N	-0.74075400	0.79943300	1.67611000	0.68475700	0.78377300	-1.72096000
C	-0.02626300	1.93405800	1.90069600	-0.06170200	1.89780000	-1.94356100
C	-0.13269500	2.59746300	3.12342400	-0.00948100	2.53550400	-3.18269400
H	0.43600300	3.50348300	3.29909900	-0.60352700	3.42467100	-3.35979500
C	-0.96420100	2.09311400	4.11236800	0.80278900	2.02761000	-4.18620600
H	-1.05072000	2.60523500	5.06551800	0.84689900	2.52021700	-5.15237800
C	-1.67925700	0.92287000	3.86782500	1.55438000	0.88101000	-3.94023200
H	-2.33593800	0.48965400	4.61365500	2.19860900	0.44812500	-4.69684500
C	-1.53927300	0.30741300	2.63534400	1.46699300	0.28844600	-2.69188700
H	-2.06728500	-0.60675900	2.39066300	2.02369600	-0.60781700	-2.44456700
C	0.82173800	2.32345700	0.77533000	-0.87604000	2.29818500	-0.79686500
C	0.76190000	1.46296700	-0.35093600	-0.76011200	1.46965800	0.34700800
C	1.57592400	1.78116400	-1.44756400	-1.53194800	1.80095300	1.46773300
H	1.56930500	1.14982200	-2.33099900	-1.48052800	1.19289600	2.36568400
C	2.40002000	2.90001700	-1.44518900	-2.37388500	2.90722800	1.46988700
H	3.01610200	3.12271900	-2.30900800	-2.95843700	3.14218400	2.35206900
C	2.42361100	3.72527700	-0.32147400	-2.45630500	3.70172000	0.32781700
C	1.64489000	3.45021500	0.79267900	-1.71770300	3.41127500	-0.80939900
H	1.68104600	4.10277900	1.65722300	-1.79829800	4.04074000	-1.68782400
C	-4.04969800	-0.23657200	-0.11080200	4.08153500	-0.23001000	0.05603700
C	-3.42537000	1.00687200	-0.52733400	3.44686200	1.00218900	0.46356600
C	-5.41099200	-0.20900500	0.22565400	5.44727700	-0.18731700	-0.24235200
C	-4.26962500	2.16038300	-0.64736400	4.27502000	2.18165700	0.64651000
C	-6.16159400	0.94684100	0.14982800	6.21241200	1.01691100	-0.11635200
C	-5.59277800	2.14892600	-0.31108200	5.60792200	2.20084900	0.35216400
H	-6.20395600	3.04135900	-0.38293700	6.21401100	3.09110200	0.46690800
H	-5.91281500	-1.09483800	0.58371600	5.99152200	-1.04972800	-0.58685100
H	-3.79118200	3.07068900	-0.99483700	3.76258900	3.06918800	1.00421800
N	-7.54411400	0.91139500	0.53356400	7.56560400	1.01179000	-0.42876400
O	-8.19481000	1.94853900	0.43893400	8.22628000	2.09334400	-0.33559200
O	-8.01723500	-0.14850400	0.93649100	8.07528900	-0.09258300	-0.80234600

Table S12 The xyz coordinates for the optimized structures for **5** in the S_0 and T_1 states at PBE0/6–31G(d,p) level

	S_0			T_1		
Ir	-0.10505800	-0.05345900	-0.00182800	-0.10451700	-0.07549300	0.00077200
S	-4.08497800	5.14710300	0.56097000	-4.13228600	5.08169600	0.54297500
F	-4.82234600	4.81198400	-0.84118200	-4.87080300	4.71840000	0.84980500
F	-5.24259800	4.34599000	1.35990600	-5.26843800	4.26761000	1.35620300
F	-3.44597400	5.61740600	1.97189000	-3.48688800	5.56972200	1.94313300
F	-3.02582900	6.08288800	-0.22986500	-3.08931400	6.01990400	-0.26340800
F	-5.03955200	6.45199400	0.65389000	-5.10318900	6.37165600	0.63031100
O	1.57883600	1.28353600	0.59704900	1.55722100	1.27057600	0.57894000
N	-0.14731700	0.73727000	-1.88638300	-0.13364100	0.71875000	-1.89942100
C	-0.90573200	1.85386600	-2.04023600	-0.91180000	1.81988700	-2.05456600
C	-0.99416000	2.47267900	-3.28709000	-1.00162800	2.44300700	-3.29806900
H	-1.60032100	3.36330100	-3.40906200	-1.62590900	3.32022700	-3.42400100
C	-0.30743800	1.94216600	-4.36989400	-0.28928600	1.93229300	-4.37466900
H	-0.37260100	2.41892900	-5.34304700	-0.35490500	2.41131500	-5.34654000
C	0.45795600	0.79200900	-4.19252700	0.50236900	0.80140800	-4.19376100
H	1.00671900	0.34196800	-5.01225500	1.07112100	0.36891600	-5.00907900
C	0.51304800	0.21940200	-2.93219000	0.55431300	0.22205600	-2.93559100
H	1.08478700	-0.67594600	-2.71487600	1.14195200	-0.66270600	-2.71752300
C	-1.58591800	2.27141600	-0.81430500	-1.60133600	2.22995300	-0.82953400
C	-1.36088800	1.44052200	0.31482500	-1.37065000	1.41552600	0.30731700
C	-2.01827800	1.78609100	1.50482000	-2.01158500	1.75756200	1.50375100
H	-1.88437800	1.17855200	2.39509500	-1.85543500	1.15665300	2.39405100
C	-2.84251600	2.90223600	1.58940600	-2.84826200	2.86507900	1.58481500
H	-3.33348200	3.14536000	2.52504700	-3.33324700	3.11288200	2.52196900
C	-3.02566100	3.69942900	0.46020600	-3.05060600	3.64471500	0.44749900
C	-2.40753800	3.39676400	-0.74440500	-2.43895600	3.34328800	-0.76092500
H	-2.56476300	4.02756300	-1.61160400	-2.61215100	3.96614500	-1.63037100
S	-4.86184900	-4.56811700	-0.43700300	-4.86590700	-4.55114600	-0.43217000
F	-5.49546900	-4.11677700	0.98318600	-5.53110400	-4.07112700	0.96274500
F	-5.89658000	-3.59128300	-1.20856900	-5.85601300	-3.55958900	-1.24160300
F	-4.34696400	-5.13714100	-1.86227400	-4.31644900	-5.14506000	-1.83376900
F	-3.94519300	-5.66131100	0.32947500	-3.99323500	-5.65197900	0.37124400
F	-6.01729200	-5.70165500	-0.49588300	-6.04107300	-5.66109200	-0.51587200
O	1.33637700	-1.64149500	-0.61699400	1.38275000	-1.62483700	-0.57240600
N	-0.20997000	-0.83692800	1.88336300	-0.18303200	-0.81873200	1.87973900
C	-1.12815800	-1.82203200	2.06187300	-1.15978700	-1.81452900	2.06672700
C	-1.27609100	-2.42207800	3.31242200	-1.31993200	-2.38466400	3.36519100
H	-2.01041700	-3.20701400	3.45458800	-2.07676600	-3.14756600	3.51655800
C	-0.48589100	-2.00523600	4.37407600	-0.53733200	-1.96954700	4.40593400
H	-0.59862400	-2.46595400	5.35065000	-0.66214400	-2.40010600	5.39467500

C	0.44617200	-0.99059600	4.17087200	0.44245100	-0.96242700	4.18071200
H	1.08293400	-0.63445500	4.97293500	1.08371000	-0.60774300	4.97931800
C	0.55576100	-0.43304400	2.90734000	0.57463900	-0.42922000	2.90949500
H	1.25943600	0.35736100	2.67039600	1.30053200	0.34376100	2.67986700
C	-1.90081600	-2.12544400	0.85710600	-1.88256300	-2.12459700	0.91040800
C	-1.58083400	-1.33856300	-0.28066800	-1.54399500	-1.35964500	-0.29671400
C	-2.31483800	-1.57829700	-1.45175600	-2.25381400	-1.61389200	-1.47140800
H	-2.11183000	-0.99919200	-2.34779600	-2.02308400	-1.05040200	-2.37095300
C	-3.30550400	-2.55161100	-1.51004200	-3.25397500	-2.58000500	-1.53891700
H	-3.85364000	-2.71485100	-2.43114200	-3.78453700	-2.77185500	-2.46207200
C	-3.58128700	-3.30947600	-0.37271500	-3.55668700	-3.30497800	-0.35621300
C	-2.89063500	-3.10772100	0.81353800	-2.91840600	-3.10920800	0.83675000
H	-3.12197300	-3.70613100	1.68707200	-3.18982300	-3.68647100	1.71195900
P	3.01150800	1.23810600	0.02810300	3.00681600	1.26127800	0.04486500
P	2.85211500	-1.59099500	-0.33080400	2.90478700	-1.56956100	-0.30918800
N	3.60992700	-0.17839100	-0.44136200	3.64324300	-0.14553600	-0.39808700
C	3.65370000	-2.68750000	-1.53148100	3.69114600	-2.63022400	-1.55015000
C	5.00058700	-2.51560000	-1.86835700	5.02610100	-2.42869600	-1.91674600
C	2.92499300	-3.73294700	-2.10880000	2.96480800	-3.67638800	-2.12931200
C	5.61113700	-3.38123900	-2.77179100	5.62749400	-3.26627200	-2.85212100
H	5.56159600	-1.69525700	-1.42931700	5.58439200	-1.60758800	-1.47572400
C	3.53792200	-4.59626700	-3.01388000	3.56883600	-4.51130500	-3.06633100
H	1.87542300	-3.85883800	-1.85808500	1.92405200	-3.82516400	-1.85528700
C	4.88100400	-4.42256200	-3.34381600	4.90012000	-4.30838100	-3.42616800
H	6.65655200	-3.24116600	-3.03299100	6.66345400	-3.10351200	-3.13663900
H	2.96572200	-5.40274300	-3.46426000	2.99875700	-5.31840400	-3.51818100
H	5.35839900	-5.09650400	-4.05003500	5.37035800	-4.96024000	-4.15743000
C	3.14188800	-2.34591300	1.29976900	3.22605300	-2.35677000	1.29780800
C	4.18156100	-1.90097900	2.12183700	4.25920500	-1.90471300	2.12383000
C	2.33613700	-3.41011500	1.72280700	2.45008900	-3.45136100	1.69853000
C	4.41109200	-2.50998600	3.35395600	4.51321100	-2.53889400	3.33833000
H	4.80011200	-1.06861300	1.79734900	4.85248400	-1.04772200	1.81666800
C	2.56801200	-4.01862800	2.95248400	2.70803900	-4.08592800	2.90961600
H	1.51885700	-3.74995400	1.09251300	1.63464200	-3.79387000	1.06739300
C	3.60675600	-3.56985500	3.76845400	3.74054900	-3.63052700	3.72992000
H	5.21714700	-2.15566900	3.99086100	5.31359000	-2.17937300	3.97938700
H	1.93595900	-4.84045900	3.27781600	2.09985600	-4.93189700	3.21806700
H	3.78648700	-4.04506000	4.72911600	3.93981000	-4.12539600	4.67666800
C	3.13656800	2.37543200	-1.38334600	3.13068400	2.39201600	-1.37041200
C	2.43307500	3.58551700	-1.35574200	2.40222300	3.58764500	-1.36275100
C	3.94909600	2.07414400	-2.48034800	3.96458300	2.09750200	-2.45318200
C	2.54034100	4.48131700	-2.41568300	2.50616400	4.47597400	-2.42918000
H	1.79326300	3.81937600	-0.50869800	1.74621500	3.81677600	-0.52684500
C	4.05659500	2.97307100	-3.53923800	4.06886300	2.98960400	-3.51809000

H	4.48261800	1.12797200	-2.50029600	4.51735400	1.16225900	-2.45762900
C	3.35357700	4.17615300	-3.50707700	3.34082700	4.17801100	-3.50632800
H	1.98761200	5.41655000	-2.39235200	1.93432900	5.39985700	-2.42189700
H	4.68670100	2.73284900	-4.39137700	4.71575600	2.75515300	-4.35910800
H	3.43699100	4.87639900	-4.33390700	3.42154000	4.87269200	-4.33805800
C	4.09247400	1.94492000	1.30662300	4.03559400	1.99667400	1.34719300
C	5.47316400	1.71768800	1.27279500	5.42087000	1.79599200	1.34792200
C	3.54911100	2.74113100	2.31995900	3.45118900	2.78667700	2.34244900
C	6.29877200	2.27666200	2.24421600	6.21095600	2.37583300	2.33625500
H	5.89671700	1.09357500	0.49001000	5.87572200	1.17663900	0.57904200
C	4.37735600	3.29829600	3.29209100	4.24448900	3.36421800	3.33163400
H	2.47664500	2.91198500	2.34859600	2.37517900	2.93674400	2.34496800
C	5.75117800	3.06762100	3.25427000	5.62307300	3.16045500	3.32842800
H	7.36934600	2.09321300	2.21561700	7.28524400	2.21337900	2.33490600
H	3.94911800	3.91076400	4.08090600	3.78511400	3.97146800	4.10676400
H	6.39611900	3.50214800	4.01322000	6.24046200	3.61101200	4.10077500