Electronic Supplementary Material (ESI) for RSC Advances.

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

MO	Energy	Contribution (%)			Assignment
		Ir	L1	L2	
L+10	1.23	5	5	90	π*(L2)
L+9	0.81	4	96	1	π*(L1)
L+8	0.67	4	94	2	π*(L1)
L+7	0.58	2	95	2	π*(L1)
L+6	0.48	4	63	33	π*(L1+L2)
L+5	0.41	3	37	60	π*(L1+L2)
L+4	0.01	1	95	4	π*(L1)
L+3	-0.11	1	99	0	π*(L1)
L+2	-0.24	3	8	89	π*(L2)
L+1	-0.49	4	94	2	π*(L1)
L	-0.58	4	94	2	π*(L1)
H	-5.25	36	57	7	d(Ir)+π(L1)
H-1	-5.65	29	31	40	d(Ir)+π(L1+L2)
H-2	-5.91	8	73	19	π(L1+L2)
H-3	-6.05	6	72	22	π(L1+L2)
H-4	-6.23	18	64	18	d(Ir)+π(L1+L2)
H-5	-6.38	10	37	53	π(L1+L2)
H-6	-6.46	17	75	8	d(Ir)+π(L1)
H-7	-6.67	2	71	27	π(L1+L2)
H-8	-6.90	4	62	35	π(L1+L2)
H-9	-6.99	18	58	24	d(Ir)+π(L1+L2)
H-10	-7.22	4	95	1	π(L1)

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

MO	Energy	Contribution (%)			Assignment
		Ir	L1	L2	
L+10	0.53	2	96	2	π*(L1)
L+9	0.43	4	7	89	π*(L2)
L+8	0.29	0	97	2	π*(L1)
L+7	0.21	0	99	1	π*(L1)
L+6	0.17	0	99	0	π*(L1)
L+5	0.08	1	99	1	π*(L1)
L+4	-0.24	3	8	89	π*(L2)
L+3	-0.40	1	98	1	π*(L1)
L+2	-0.48	1	96	3	π*(L1)
L+1	-0.63	3	94	2	π*(L1)
L	-0.74	3	96	1	π*(L1)
H	-5.29	32	62	6	d(Ir)+π(L1)
H-1	-5.62	20	60	20	d(Ir)+π(L1+L2)
H-2	-5.82	12	49	39	d(Ir)+π(L1+L2)
H-3	-5.93	10	82	8	d(Ir)+π(L1)
H-4	-6.26	11	60	29	d(Ir)+π(L1+L2)
H-5	-6.32	21	54	24	d(Ir)+π(L1+L2)
H-6	-6.40	18	47	35	d(Ir)+π(L1+L2)
H-7	-6.68	1	64	34	π(L1+L2)
H-8	-6.90	2	88	10	π(L1+L2)
H-9	-6.96	7	67	26	π(L1+L2)
H-10	-7.00	1	94	5	π(L1)

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

MO	Energy	Contribution (%)			Assignment
		Ir	L1	L2	
L+10	0.65	2	96	2	π*(L1)
L+9	0.44	4	18	78	π*(L1+L2)
L+8	0.38	1	88	11	π*(L1+L2)
L+7	0.32	0	96	4	π*(L1)
L+6	0.11	1	99	0	π*(L1)
L+5	0.00	1	99	1	π*(L1)
L+4	-0.23	3	7	90	π*(L2)
L+3	-0.41	2	97	1	π*(L1)
L+2	-0.49	1	95	4	π*(L1)
L+1	-0.66	3	95	2	π*(L1)
L	-0.76	3	97	1	π*(L1)
H	-5.15	28	68	5	d(Ir)+π(L1)
H-1	-5.48	10	85	6	π(L1)
H-2	-5.74	23	25	53	d(Ir)+π(L1+L2)
H-3	-5.79	11	81	8	d(Ir)+π(L1)
H-4	-6.22	16	62	23	d(Ir)+π(L1+L2)
H-5	-6.29	19	59	23	d(Ir)+π(L1+L2)
H-6	-6.35	16	48	36	d(Ir)+π(L1+L2)
H-7	-6.61	3	62	35	π(L1+L2)
H-8	-6.85	1	78	21	π(L1+L2)
H-9	-6.90	2	92	6	π(L2)
H-10	-6.91	1	96	3	π(L2)

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

MO	Energy	Contribution (%)			Assignment
		Ir	L1	L2	
L+10	0.67	4	94	2	π*(L1)
L+9	0.33	2	54	44	π*(L1+L2)
L+8	0.30	2	79	19	π*(L1+L2)
L+7	0.24	1	76	23	π*(L1+L2)
L+6	0.22	1	94	6	π*(L1)
L+5	0.11	2	97	0	π*(L1)
L+4	-0.16	3	93	3	π*(L1)
L+3	-0.34	2	84	14	π*(L1+L2)
L+2	-0.36	3	22	76	π*(L1+L2)
L+1	-0.59	4	95	1	π*(L1)
L	-0.66	4	92	5	π*(L1)
H	-5.06	18	80	2	d(Ir)+π(L1)
H-1	-5.44	4	93	3	π(L1)
H-2	-5.90	22	15	63	d(Ir)+π(L1+L2)
H-3	-6.09	11	84	5	d(Ir)+π(L1)
H-4	-6.37	16	60	24	d(Ir)+π(L1+L2)
H-5	-6.43	5	79	16	π(L1+L2))
H-6	-6.48	17	73	10	d(Ir)+π(L1+L2)
H-7	-6.73	4	36	61	π(L1+L2)
H-8	-6.93	1	98	1	π(L1)
H-9	-6.99	1	99	1	π(L1)
H-10	-7.16	6	50	44	π(L1+L2)

Table S5 Selected calculated wavelength (nm) / energies (eV), oscillator strength (*f*), major contribution and transition characters for complexes **1–4** in CH_2Cl_2 media at TDDFT/M052X level. (H and L indicate HOMO and LUMO, respectively.)

	State	λ/E	*f*	Configuration	Assignment	Nature	Exptl.[a]
1	S_1	328/3.78	0.0104	H→L (93%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	302
	S_5	288/4.31	0.1610	H-1→L+1 (81%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_7	278/4.46	0.1450	H-2→L (10%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
				H→L+4 (69%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
	S_{15}	257/4.82	0.1490	H-2→L+2 (25%)	π(L1+L2)→π*(L2)	LLCT/ILCT	
				H→L+5 (16%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT	
				H→L+6 (23%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT	
	S_{26}	242/5.12	0.1122	H-4→L+2 (11%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT	
				H→L+8 (41%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
	S_{31}	237/5.23	0.1849	H-6→L+1 (20%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
				H-2→L+4 (26%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
				H→L+9 (13%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
	S_{36}	231/5.37	0.2078	H-5→L+2 (21%)	π(L1+L2)→π*(L2)	LLCT/ILCT	
				H-3→L+4 (37%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
	S_{39}	228/5.44	0.1923	H-7→L+1 (14%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
				H-1→L+7 (12%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{43}	225/5.51	0.1020	H-9→L (11%), H-	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				4→L+4 (10%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-3→L+5 (10%)	π(L1+L2)→π*(L1+L2)	LLCT/ILCT	
	S_{48}	223/5.57	0.1014	H-2→L+6 (16%)	π(L1+L2)→π*(L1+L2)	LLCT/ILCT	
				H-1→L+9 (11%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{43}	237/5.23	0.1119	H-1→L+6 (14%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{54}	231/5.38	0.1024	H-4→L+4 (10%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT	
				H-1→L+7 (13%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{56}	229/5.42	0.1485	H-6→L+4 (21%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT	
				H-1→L+8 (13%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-1→L+10 (12%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
2	S_1	335/3.70	0.0258	H→L (91%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
	S_7	294/4.22	0.1426	H-1→L+1 (54%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H→L+3 (24%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
	S_8	287/4.31	0.1741	H-3→L (24%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
				H-2→L (62%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_9	279/4.44	0.1158	H-2→L+1 (72%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{11}	276/4.49	0.1687	H-3→L (27%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT	
				H-2→L (15%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-2→L+1 (15%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-1→L+2 (28%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	

	S_{13}	273/4.55	0.1511	H-3→L+1 (51%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H-1→L+3 (15%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{17}	263/4.72	0.1722	H-2→L+2 (12%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H→L+5 (37%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H→L+7 (13%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_{25}	255/4.86	0.1263	H-3→L+3 (15%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H-2→L+4 (13%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT
				H→L+9 (21%)	d(Ir)+π(L1)→π*(L2)	MLCT/LLCT
	S_{34}	247/5.02	0.1930	H-6→L+1 (17%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H-4→L+2 (10%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H→L+10 (28%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_{43}	237/5.24	0.1130	H-1→L+8 (24%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
3	S_1	345/3.59	0.0332	H→L (87%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_2	338/3.67	0.1349	H→L+1 (87%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_3	313/3.95	0.1247	H-1→L (11%)	π(L1)→π*(L1)	ILCT
				H→L+2 (71%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H→L+4 (10%)	d(Ir)+π(L1)→π*(L2)	MLCT/LLCT
	S_4	311/3.99	0.1678	H-1→L (75%)	π(L1)→π*(L1)	ILCT
	S_5	310/4.00	0.1202	H→L+3 (65%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H→L+4 (22%)	d(Ir)+π(L1)→π*(L2)	MLCT/LLCT
	S_7	302/4.11	0.1534	H-1→L+1 (72%)	π(L1)→π*(L1)	ILCT
	S_8	295/4.21	0.1856	H-3→L (18%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H-2→L (68%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_9	287/4.32	0.1055	H-3→L (30%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H-2→L+1 (44%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{12}	282/4.402	0.1332	H-3→L+1 (61%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_{18}	269/4.61	0.1718	H-5→L (18%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H-4→L (29%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H-3→L+2 (10%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H-2→L+2 (11%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H→L+5 (10%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_{24}	262/4.73	0.1002	H-3→L+3 (22%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H→L+9 (22%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
	S_{43}	237/5.24	0.1130	H-1→L+8 (24%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
4	S_1	347/3.58	0.0391	H→L (59%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
				H→L+1 (35%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_4	311/3.99	0.1013	H-1→L (72%)	π(L1)→π*(L1)	ILCT
				H→L+3 (21%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
	S_5	310/4.00	0.1997	H-1→L (20%)	π(L1)→π*(L1)	ILCT
				H→L+2 (10%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
				H→L+3 (58%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
	S_7	298/4.17	0.1244	H-1→L+1 (21%)	π(L1)→π*(L1)	ILCT
				H→L+4 (66%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
	S_{18}	267/4.64	0.1021	H-1→L+4 (29%)	π(L1)→π*(L1)	ILCT

			H→L+9 (38%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
S_{19}	267/4.65	0.1287	H-3→L (62%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
			H-3→L+1 (13%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
S_{20}	262/4.74	0.1107	H-3→L (19%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
			H-3→L+1 (53%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
S_{22}	256/4.85	0.1935	H-6→L (18%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
			H-4→L (32%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
			H→L+7 (10%)	d(Ir)+π(L1)→π*(L1+L2)	MLCT/LLCT/ILCT
S_{27}	249/4.97	0.1177	H-4→L+1 (30%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
			H→L+10 (12%)	d(Ir)+π(L1)→π*(L1)	MLCT/ILCT
S_{29}	248/5.00	0.1152	H-5→L (10%)	π(L1+L2)→π*(L1)	LLCT/ILCT
			H-4→L+1 (16%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
			H-2→L+4 (11%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
			H-1→L+7 (14%)	π(L1)→π*(L1+L2)	LLCT/ILCT

[a] Ref. 18

Table S6 Partial frontier molecular orbital composition (%) of complexes **1**–**4** in the triplet excited states. (H and L indicate HOMO and LUMO, respectively)

	MO	Energy (eV)	Composition (%)			Assignment
			Ir	L1	L2	
1	L	-1.00	7	92	1	π*(L1)
	H	-4.90	33	59	9	d(Ir)+π(L1)
2	L	-1.27	2	98	1	π*(L1)
	H	-5.15	20	78	3	d(Ir)+π(L1)
3	L	-1.07	2	98	1	π*(L1)
	H	-5.03	19	78	2	d(Ir)+π(L1)
4	L	-0.80	6	89	5	π*(L1)
	H	-4.79	14	83	2	d(Ir)+π(L1)

Table S7 The metal-based charge transfer character (^{3}MLCT) (%) and the energy differences of S_1–T_1 (in eV), along with the transition dipole moment in the $S_0 \rightarrow S_1$ transition μ_{S_1}, together with the measured quantum yields Φ [%] for complexes **1**–**4** in CH_2Cl_2 medium.

	^{3}MLCT	$\Delta E_{S_1\text{-}T_1}$	μ_{S_1}	Φ[a]
1	21.76	0.371	0.119	0.31
2	23.78	1.193	0.285	
3	19.75	1.117	0.377	
4	11.62	1.836	0.446	

[a]Ref. 18