Supplementary Information

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

MO	Energy	Contribution (%)			Assignment
		Ir	L	dipdtc	
L+10	0.80	38	47	15	d*(Ir)+π*(L)
L+9	0.60	38	44	18	d*(Ir)+π*(L)
L+8	0.42	1	99	0	π*(L)
L+7	0.31	1	98	1	π*(L)
L+6	0.08	9	84	7	π*(L)
L+5	-0.10	10	84	6	π*(L)
L+4	-0.69	4	2	94	π*(dipdtc)
L+3	-1.13	3	97	0	π*(L)
L+2	-1.23	3	94	3	π*(L)
L+1	-1.96	3	95	2	π*(L)
L	-2.10	3	96	1	π*(L)
HOMO–LUMO energy gap (3.84 eV)					
H	-5.94	40	49	11	d(Ir)+π(L)
H-1	-6.14	30	12	58	d(Ir)+π(dipdtc)
H-2	-6.24	40	11	49	d(Ir)+π(dipdtc)
H-3	-6.48	1	36	63	π(L+dipdtc)
H-4	-7.09	2	89	9	π(L)
H-5	-7.16	22	52	26	d(Ir)+π(L+dipdtc)
H-6	-7.35	17	71	12	π(L)
H-7	-7.36	1	95	4	π(L)
H-8	-7.56	34	21	45	d(Ir)+π(L+dipdtc)
H-9	-7.72	21	37	42	d(Ir)+π(L+dipdtc)
H-10	-8.14	3	96	1	π(L)

Table S2 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1b**

MO	Energy	Contribution (%)			Assignment
		Ir	L	dipdtc	
L+10	0.39	19	71	10	d*(Ir)+π*(L)
L+9	0.32	17	74	9	d*(Ir)+π*(tfmdq)
L+8	0.21	2	98	0	π*(L)
L+7	0.16	2	97	1	π*(L)
L+6	-0.69	4	1	95	π*(dipdtc)
L+5	-0.94	3	96	1	π*(L)
L+4	-1.04	2	97	1	π*(L)
L+3	-1.57	1	99	0	π*(L)
L+2	-1.60	1	99	0	π*(L)
L+1	-2.02	3	96	1	π*(L)
L	-2.10	2	97	1	π*(L)
HOMO–LUMO energy gap (3.81 eV)					
H	-5.91	35	57	8	d(Ir)+π(L)
H-1	-6.11	30	10	60	d(Ir)+π(dipdtc)
H-2	-6.24	38	14	48	d(Ir)+π(dipdtc)
H-3	-6.40	1	54	45	π(L+dipdtc)
H-4	-6.78	2	76	22	π(L+dipdtc)
H-5	-6.79	2	94	4	π(L)
H-6	-6.86	1	93	6	π(L)
H-7	-7.08	13	78	9	π(L)
H-8	-7.31	29	40	31	d(Ir)+π(L+dipdtc)
H-9	-7.39	13	65	22	π(L+dipdtc)
H-10	-7.73	26	37	37	d(Ir)+π(L+dipdtc)

Table S3 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1c**

MO	Energy	Contribution (%)			Assignment
		Ir	L	dipdtc	
L+10	0.70	28	60	12	d*(Ir)+π*(L)
L+9	0.58	11	84	5	π*(4tfmpq)
L+8	0.01	10	83	7	π*(L)
L+7	-0.14	6	89	5	π*(L)
L+6	-0.51	1	99	0	π*(L)
L+5	-0.55	1	99	0	π*(L)
L+4	-0.68	4	3	93	π*(dipdtc)
L+3	-1.04	2	98	0	π*(L)
L+2	-1.11	3	93	4	π*(L)
L+1	-2.34	4	95	1	π*(L)
L	-2.53	3	96	1	π*(L)
HOMO–LUMO energy gap (3.39 eV)					
H	-5.92	41	46	13	d(Ir)+π(L)
H-1	-6.12	31	21	48	d(Ir)+π(L+dipdtc)
H-2	-6.19	40	15	45	d(Ir)+π(dipdtc)
H-3	-6.42	1	37	62	π(L+dipdtc)
H-4	-6.84	0	90	10	π(L)
H-5	-6.87	9	68	23	π(L+dipdtc)
H-6	-7.22	23	60	17	d(Ir)+π(L)
H-7	-7.32	3	88	9	π(L)
H-8	-7.49	23	40	37	d(Ir)+π(L+dipdtc)
H-9	-7.61	2	96	2	π(L)
H-10	-7.67	4	91	5	π(L)

Table S4 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2a**

MO	Energy	Contribution (%)			Assignment
		Ir	L	czdtc	
L+10	0.33	2	96	2	π*(L)
L+9	0.23	1	98	1	π*(L)
L+8	-0.04	11	72	17	π*(L)
L+7	-0.06	1	7	92	π*(czdtc)
L+6	-0.21	12	80	8	π*(L)
L+5	-0.97	0	1	99	π*(czdtc)
L+4	-1.23	3	97	0	π*(L)
L+3	-1.32	2	96	2	π*(L)
L+2	-1.96	4	1	95	π*(czdtc)
L+1	-2.07	3	96	1	π*(L)
L	-2.19	3	95	2	π*(L)
HOMO–LUMO energy gap (3.91 eV)					
H	-6.10	39	53	8	d(Ir)+π(L)
H-1	-6.28	15	4	81	π(czdtc)
H-2	-6.43	31	10	59	d(Ir)+π(czdtc)
H-3	-6.49	4	1	95	π(czdtc)
H-4	-6.77	3	45	52	π(L+czdtc)
H-5	-7.05	36	45	19	d(Ir)+π(L)
H-6	-7.31	6	81	13	π(L)
H-7	-7.32	17	61	22	π(L+czdtc)
H-8	-7.47	1	92	7	π(L)
H-9	-7.51	9	25	66	π(L+czdtc)
H-10	-7.51	21	21	58	d(Ir)+π(L+czdtc)

Table S5 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2b**

MO	Energy	Contribution (%)			Assignment
		Ir	L	czdtc	
L+10	0.14	4	95	1	π*(L)
L+9	0.10	4	93	3	π*(L)
L+8	-0.05	0	0	100	π*(czdtc)
L+7	-0.96	0	2	98	π*(czdtc)
L+6	-1.01	3	96	1	π*(L)
L+5	-1.11	3	94	3	π*(L)
L+4	-1.64	1	99	0	π*(L)
L+3	-1.66	1	98	1	π*(L)
L+2	-1.95	3	2	95	π*(czdtc)
L+1	-2.11	3	96	1	π*(L)
L	-2.19	3	96	1	π*(L)
HOMO–LUMO energy gap (3.86 eV)					
H	-6.05	32	62	6	d(Ir)+π(L)
H-1	-6.28	15	4	81	π(czdtc)
H-2	-6.39	34	11	55	d(Ir)+π(czdtc)
H-3	-6.48	2	1	97	π(czdtc)
H-4	-6.58	1	78	21	π(L+czdtc)
H-5	-6.86	1	96	3	π(L)
H-6	-6.89	1	97	2	π(L)
H-7	-7.01	13	48	39	π(L+czdtc)
H-8	-7.15	36	32	32	d(Ir)+π(L+czdtc)
H-9	-7.17	10	81	9	π(L)
H-10	-7.49	11	18	71	π(czdtc)

Table S6 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2c**

MO	Energy	Contribution(%)			Assignment
		Ir	L	czdtc	
L+10	-0.02	9	81	10	π*(L)
L+9	-0.04	0	3	97	π*(czdtc)
L+8	-0.32	12	81	7	π*(L)
L+7	-0.58	1	99	0	π*(L)
L+6	-0.60	2	97	1	π*(L)
L+5	-0.96	1	1	98	π*(czdtc)
L+4	-1.12	2	98	0	π*(L)
L+3	-1.16	2	97	1	π*(L)
L+2	-1.94	3	1	96	π*(czdtc)
L+1	-2.52	3	96	1	π*(L)
L	-2.52	3	96	1	π*(L)
HOMO–LUMO energy gap (3.55 eV)					
H	-6.07	37	55	8	d(Ir)+π(L)
H-1	-6.24	18	8	74	π(czdtc)
H-2	-6.40	33	12	55	d(Ir)+π(czdtc)
H-3	-6.47	3	1	96	π(czdtc)
H-4	-6.73	18	43	39	π(L+czdtc)
H-5	-6.81	1	70	29	π(L+czdtc)
H-6	-6.95	4	84	12	π(L)
H-7	-7.19	26	44	30	d(Ir)+π(L+czdtc)
H-8	-7.39	3	90	7	π(L)
H-9	-7.43	21	49	30	d(Ir)+π(L+czdtc)
H-10	-7.50	2	2	96	π(czdtc)

Table S7 Selected calculated wavelength (nm) /energies (eV), oscillator strength (*f*), major contribution and transition characters for all studied complexes in CH_2Cl_2 media from TDDFT. H indicates HOMO, L indicates LUMO

	State	λ/E	*f*	Configuration	Assignment	Nature	Exptl.[a]
1a	S_1	426/2.90	0.054	H→L (96%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_3	392/3.15	0.049	H-1→L (95%)	d(Ir)+π(dipdtc)→π*(L)	MLCT/LLCT	
	S_{19}	284/4.36	0.079	H-4→L+1 (72%)	π(L)→π*(L)	ILCT	
	S_{14}	296/4.17	0.044	H-5→L (82%)	d(Ir)+π(L+dipdtc)→π*(L)	MLCT/LLCT/ILCT	
	S_{22}	275/4.50	0.150	H-6→L (42%)	π(L)→π*(L)	ILCT	
				H-3→L+3 (35%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
	S_{23}	275/4.51	0.060	H-7→L (64%)	π(L)→π*(L)	ILCT	
	S_{24}	274/4.51	0.118	H-3→L+3 (28%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
				H-3→L+4 (23%)	π(L+dipdtc)→π*(dipdtc)	LLCT/ILCT	
	S_{29}	265/4.67	0.217	H-2→L+4 (82%)	d(Ir)+π(dipdtc)→π*(dipdtc)	MLCT/ILCT	
	S_{32}	261/4.74	0.075	H→L+5 (39%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{40}	245/5.05	0.235	H-5→L+2 (62%)	d(Ir)+π(L+dipdtc)→π*(L)	MLCT/LLCT/ILCT	
	S_{44}	239/5.17	0.063	H-4→L+3 (75%)	π(L)→π*(L)	ILCT	
	S_{58}	224/5.52	0.466	H-3→L+5 (76%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
1b	S_1	424/2.92	0.072	H→L (92%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_3	394/3.14	0.076	H-1→L (91%)	d(Ir)+π(dipdtc)→π*(L)	MLCT/LLCT	
	S_6	372/3.33	0.081	H-2→L+1 (92%)	d(Ir)+π(dipdtc)→π*(L)	MLCT/LLCT	
	S_7	352/3.51	0.053	H→L+2 (96%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{10}	346/3.58	0.053	H-3→L+1 (92%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
	S_{43}	267/4.63	0.053	H-9→L+1 (64%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
	S_{50}	258/4.79	0.103	H-3→L+5 (80%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
1c	S_1	500/2.47	0.066	H→L(97%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	592
	S_3	450/2.75	0.103	H-1→L (96%)	d(Ir)+π(L+dipdtc)→π*(L)	MLCT/LLCT/ILCT	453
	S_9	344/3.59	0.062	H-5→L (88%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	
	S_{11}	326/3.80	0.287	H-4→L+1 (65%)	π(L)→π*(L)	ILCT	
	S_{14}	313/3.95	0.101	H→L+2 (61%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{36}	267/4.63	0.090	H-3→L+3 (53%)	π(L+dipdtc)→π*(L)	LLCT/ILCT	285
	S_{46}	253/4.88	0.156	H-1→L+5 (55%)	d(Ir)+π(L+dipdtc)→π*(L)	MLCT/LLCT/ILCT	263
2a	S_1	416/2.97	0.069	H→L (95%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_5	367/3.38	0.089	H-1→L (80%)	π(czdtc)→π*(L)	LLCT	
	S_6	363/3.41	0.317	H-1→L+2 (56%)	π(czdtc)→π*(czdtc)	ILCT	
	S_7	356/3.47	0.058	H-2→L+1 (50%)	d(Ir)+π(czdtc)→π*(L)	MLCT/LLCT	
	S_{10}	342/3.62	0.101	H-4→L+2 (73%)	π(L+czdtc)→π*(czdtc)	LLCT/ILCT	
	S_{49}	255/4.86	0.223	H-3→L+5 (43%)	π(czdtc)→π*(czdtc)	ILCT	
	S_{56}	248/5.00	0.052	H-5→L+4 (44%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{60}	241/5.14	0.128	H-6→L+3 (46%)	π(L)→π*(L)	ILCT	
2b	S_1	415/2.98	0.096	H→L (93%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_4	374/3.31	0.071	H-2→L (90%)	d(Ir)+π(czdtc)→π*(L)	MLCT/LLCT	
	S_8	357/3.47	0.064	H-1→L+1 (82%)	π(czdtc)→π*(L)	LLCT	

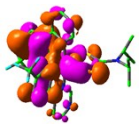
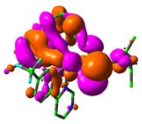
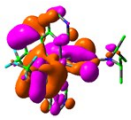
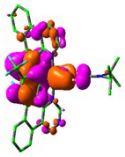
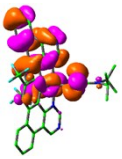
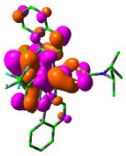
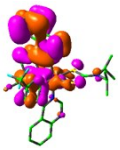
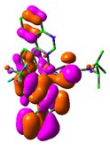
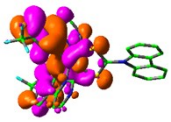
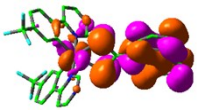
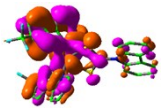
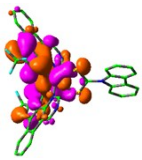
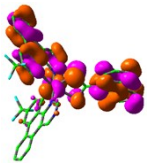
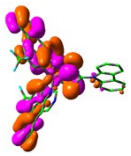
	S_{11}	344/3.59	0.057	H→L+3 (94%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{15}	335/3.69	0.089	H-4→L+1 (83%)	π(L+czdtc)→π*(L)	LLCT/ILCT	
	S_{32}	291/4.26	0.096	H-4→L+4 (70%)	π(L+czdtc)→π*(L)	LLCT/ILCT	
	S_{46}	275/4.50	0.051	H-2→L+5 (62%)	d(Ir)+π(czdtc)→π*(L)	MLCT/LLCT	
2c	S_1	466/2.66	0.110	H→L+1 (84%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	532
				H→L (13%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_8	364/3.40	0.469	H-1→L+2 (80%)	π(czdtc)→π*(czdtc)	ILCT	357
	S_{18}	331/3.74	0.052	H-6→L (80%)	π(L)→π*(L)	ILCT	
	S_{19}	330/3.75	0.068	H-6→L+1 (83%)	π(L)→π*(L)	ILCT	
	S_{20}	318/3.89	0.159	H-7→L (77%)	d(Ir)+π(L+czdtc)→π*(L)	MLCT/LLCT/ILCT	
	S_{25}	303/4.08	0.047	H→L+3 (77%)	d(Ir)+π(L)→π*(L)	MLCT/ILCT	
	S_{37}	279/4.44	0.352	H-1→L+4 (70%)	π(czdtc)→π*(L)	LLCT	282
	S_{57}	255/4.85	0.088	H-3→L+3 (64%)	π(czdtc)→π*(L)	LLCT	

[a]Ref. 19

Table S8 Partial frontier molecular orbital composition (%) of all studied complexes in the triplet excited states. (H and L indicate HOMO and LUMO, respectively)

	MO	Energy/eV	Composition (%)			Assignment
			Ir	L	dipdtc/czdtc	
1a	L	-2.33	3	95	2	π*(L)
	H	-5.61	34	54	12	d(Ir)+π(L)
	H-4	-7.07	2	86	12	π(L)
1b	L	-2.29	3	95	1	π*(L)
	H	-5.60	32	58	10	d(Ir)+π(L)
1c	L	-2.71	3	96	1	π*(L)
	H	-5.76	36	53	10	d(Ir)+π(L)
	H-4	-6.75	3	79	18	π(L)
2a	L	-2.41	3	95	2	π*(L)
	H	-5.82	34	57	9	d(Ir)+π(L)
	H-5	-7.00	37	42	21	d(Ir)+π(L+czdtc)
2b	L	-2.38	3	95	2	π*(L)
	H	-5.78	31	61	9	d(Ir)+π(L)
	H-5	-6.87	2	94	4	π(L)
2c	L	-2.72	4	95	2	π*(L)
	H	-5.77	32	58	10	d(Ir)+π(L)
	H-4	-6.70	14	63	23	π(L+czdtc)

Table S9 Transitions responsible for the phosphorescent emissions for all studied complexes simulated in CH_2Cl_2 medium

	L	H	H-4	H-5
1a				
1b				
1c				
2a				
2b				
2c