Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

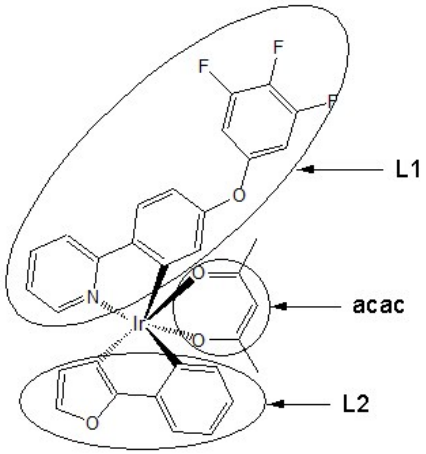

Fig. S1 The names for different ligands in complexes **1**–**6** (taking complex 1 as an example).

Table S1 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	1.03	59	25	9	8	d*(Ir)+π*(L1)
L+9	0.89	37	39	21	4	d*(Ir)+π*(L1+L2)
L+8	0.82	11	85	4	1	d*(Ir)+π*(L1)
L+7	0.12	6	92	1	1	π*(L1)
L+6	-0.24	0	99	1	0	π*(L1)
L+5	-0.50	0	98	1	0	π*(L1)
L+4	-0.83	2	8	89	1	π*(L2)
L+3	-0.97	2	2	3	93	π*(acac)
L+2	-1.05	2	91	5	2	π*(L1)
L+1	-1.46	5	1	92	1	π*(L2)
L	-1.61	4	94	2	1	π*(L1)
HOMO–LUMO energy gap (3.90 eV)						
H	-5.51	33	14	50	3	d(Ir)+π(L1+L2)
H-1	-6.07	36	12	7	45	d(Ir)+π(L1+acac)
H-2	-6.26	6	50	33	10	π(L1+L2+acac)
H-3	-6.52	19	60	16	5	d(Ir)+π(L1+L2)
H-4	-6.62	66	20	10	5	d(Ir)+π(L1+L2)
H-5	-7.02	30	11	9	49	d(Ir)+π(L1+acac)
H-6	-7.16	7	72	10	11	π(L1+L2+acac)
H-7	-7.36	6	45	12	37	π(L1+L2+acac)
H-8	-7.48	2	40	28	30	π(L1+L2+acac)
H-9	-7.64	0	97	3	0	π(L1)
H-10	-8.10	6	13	40	41	π(L1+L2+acac)

Table S2 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	0.62	4	5	91	0	d*(Ir)+π*(L1+L2)
L+9	0.60	16	9	73	2	d*(Ir)+π*(L2)
L+8	0.21	2	96	2	0	π*(L1)
L+7	0.01	3	95	1	1	π*(L1)
L+6	-0.42	1	99	0	0	π*(L1)
L+5	-0.51	0	99	0	0	π*(L1)
L+4	-0.95	2	6	80	11	π*(L2+acac)
L+3	-1.00	1	1	12	85	π*(L2+acac)
L+2	-1.16	2	91	6	1	π*(L1)
L+1	-1.58	5	1	92	1	π*(L2)
L	-1.86	3	95	1	1	π*(L1)
HOMO–LUMO energy gap (3.76 eV)						
H	-5.62	37	15	44	4	d(Ir)+π(L1+L2)
H-1	-6.12	36	5	5	53	d(Ir)+π(acac)
H-2	-6.40	3	69	28	1	π(L1+L2)
H-3	-6.47	10	49	36	5	d(Ir)+π(L1+L2)
H-4	-6.66	63	22	10	5	d(Ir)+π(L1+L2)
H-5	-6.94	7	44	45	3	π(L1+L2)
H-6	-7.02	24	29	9	39	d(Ir)+π(L1+acac)
H-7	-7.22	13	55	21	10	d(Ir)+π(L1+L2+acac)
H-8	-7.39	3	14	13	70	π(L1+L2+acac)
H-9	-7.58	0	98	1	0	π(L1)
H-10	-8.00	10	30	19	41	d(Ir)+π(L1+L2+acac)

Table S3 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **3**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	0.52	3	9	88	0	d*(Ir)+π*(L1+L2)
L+9	0.20	5	12	82	1	π*(L1+L2)
L+8	0.04	7	84	8	1	π*(L1)
L+7	-0.01	1	97	1	0	π*(L1)
L+6	-0.50	0	98	1	0	π*(L1)
L+5	-0.55	0	99	1	0	π*(L1)
L+4	-0.94	3	7	71	19	π*(L2+acac)
L+3	-1.00	1	2	19	77	π*(L1+acac)
L+2	-1.15	3	90	7	0	π*(L1)
L+1	-1.62	5	2	91	1	π*(L2)
L	-1.82	3	94	2	1	π*(L1)
HOMO–LUMO energy gap (3.75 eV)						
H	-5.57	36	15	45	4	d(Ir)+π(L1+L2)
H-1	-6.07	29	30	7	35	d(Ir)+π(L1+acac)
H-2	-6.19	8	71	2	19	π(L1+acac)
H-3	-6.42	8	18	70	4	π(L1+L2)
H-4	-6.62	61	19	15	5	d(Ir)+π(L1+L2)
H-5	-6.80	12	30	51	6	d(Ir)+π(L1+L2)
H-6	-7.03	28	22	9	40	d(Ir)+π(L1+acac)
H-7	-7.20	8	79	7	7	π(L1)
H-8	-7.36	5	12	14	70	π(L1+L2+acac)
H-9	-7.60	1	98	1	1	π(L1)
H-10	-7.89	12	36	17	36	d(Ir)+π(L1+L2+acac)

Table S4 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **4**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	0.52	2	7	91	0	π*(L2)
L+9	0.25	3	62	36	0	π*(L1+L2)
L+8	0.16	8	34	56	2	π*(L1+L2)
L+7	-0.23	2	98	0	0	π*(L1)
L+6	-0.58	0	100	0	0	π*(L1)
L+5	-0.92	3	17	67	13	π*(L1+L2+acac)
L+4	-0.97	1	4	11	83	π*(L2+acac)
L+3	-1.05	2	83	15	0	π*(L1+L2)
L+2	-1.11	1	94	4	1	π*(L1)
L+1	-1.60	5	9	85	1	π*(L2)
L	-1.69	4	87	9	1	π*(L1)
HOMO–LUMO energy gap (3.86 eV)						
H	-5.55	36	19	42	3	d(Ir)+π(L1+L2)
H-1	-6.07	29	25	9	37	d(Ir)+π(L1+acac)
H-2	-6.15	9	65	9	17	π(L1+acac)
H-3	-6.42	14	16	65	4	d(Ir)+π(L1+L2)
H-4	-6.64	66	15	14	5	d(Ir)+π(L1+L2)
H-5	-6.81	5	34	52	9	π(L1+L2)
H-6	-7.03	30	13	15	42	d(Ir)+π(L1+L2+acac)
H-7	-7.33	4	20	11	64	π(L1+L2+acac)
H-8	-7.37	3	90	1	7	π(L1+acac)
H-9	-7.61	0	100	0	0	π(L1)
H-10	-7.88	10	47	13	30	d(Ir)+π(L1+L2+acac)

Table S5 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **5**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	0.44	10	86	4	1	d*(Ir)+π*(L1)
L+9	0.18	6	12	82	1	π*(L1+L2)
L+8	0.03	6	86	8	1	π*(L1)
L+7	-0.06	1	98	1	0	π*(L1)
L+6	-0.40	1	99	0	0	π*(L1)
L+5	-0.64	0	98	1	0	π*(L1)
L+4	-0.95	3	6	74	17	π*(L2+acac)
L+3	-1.01	1	2	17	80	π*(L2+acac)
L+2	-1.18	3	91	6	0	π*(L1)
L+1	-1.63	5	2	92	1	π*(L2)
L	-1.87	3	95	2	1	π*(L1)
HOMO–LUMO energy gap (3.73 eV)						
H	-5.60	36	14	47	4	d(Ir)+π(L1+L2)
H-1	-6.12	36	8	6	50	d(Ir)+π(acac)
H-2	-6.35	1	91	2	5	π(L1)
H-3	-6.43	8	21	68	4	π(L1+L2)
H-4	-6.65	58	22	16	5	d(Ir)+π(L1+L2)
H-5	-6.81	15	30	50	5	d(Ir)+π(L1+L2)
H-6	-7.04	26	28	8	38	d(Ir)+π(L1+acac)
H-7	-7.20	12	69	9	10	d(Ir)+π(L1+acac)
H-8	-7.38	5	11	14	70	π(L1+L2+acac)
H-9	-7.52	0	98	1	1	π(L1)
H-10	-7.93	11	35	17	37	d(Ir)+π(L1+L2+acac)

Table S6 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **6**. (Ir, L1, L2 and acac denote the iridium atom and corresponding ligands presented in Figure S1.)

MO	Energy	Compositions				Assignment
		Ir	L1	L2	acac	
L+10	0.48	2	48	49	0	π*(L1+L2)
L+9	0.20	5	16	78	1	π*(L1+L2)
L+8	0.08	7	80	12	1	π*(L1+L2)
L+7	-0.42	1	99	0	0	π*(L1)
L+6	-0.56	1	99	0	0	π*(L1)
L+5	-0.93	3	12	71	14	π*(L1+L2+acac)
L+4	-0.98	1	3	14	82	π*(L2+acac)
L+3	-1.08	2	86	12	0	π*(L1+L2)
L+2	-1.14	1	96	2	1	π*(L1)
L+1	-1.61	5	4	90	1	π*(L2)
L	-1.74	4	92	4	1	π*(L1)
HOMO–LUMO energy gap (3.82 eV)						
H	-5.56	36	17	43	3	d(Ir)+π(L1+L2)
H-1	-6.09	36	8	7	49	d(Ir)+π(acac)
H-2	-6.24	2	75	18	5	π(L1+L2)
H-3	-6.44	16	19	61	4	d(Ir)+π(L1+L2)
H-4	-6.66	64	16	15	4	d(Ir)+π(L1+L2)
H-5	-6.83	5	37	48	10	π(L1+L2+acac)
H-6	-7.03	29	15	15	41	d(Ir)+π(L1+L2+acac)
H-7	-7.35	4	20	12	64	π(L1+L2+acac)
H-8	-7.37	4	89	1	7	π(L1)
H-9	-7.52	0	100	0	0	π(L1)
H-10	-7.90	11	39	15	35	d(Ir)+π(L1+L2+acac)

Table S7 Selected calculated wavelength λ(nm), oscillator strength *f*, major contribution, transition characters, and the available experimental wavelengths (nm) for complexes **1**–**6**. (H and L indicate HOMO and LUMO, respectively.)

	State	λ(nm)/E(eV)	*f*	Configuration	Assignment	Nature	Exptl[a]
1	S_1	414/2.99	0.0621	H→L (90%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{10}	305/4.05	0.1264	H-2→L+1 (78%)	π(L1+L2+acac)→π*(L2)	LLCT/ILCT	
	S_{14}	295/4.19	0.2577	H-3→L (34%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-1→L+2 (32%)	d(Ir)+π(L1+acac)→π*(L1)	MLCT/LLCT/ILCT	
	S_{22}	267/4.62	0.1402	H-4→L+3 (20%)	d(Ir)+π(L1+L2)→π*(acac)	MLCT/LLCT/ILCT	
				H-4→L+2 (18%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{26}	263/4.70	0.1397	H-2→L+4 (51%)	π(L1+L2+acac)→π*(L2)	LLCT/ILCT	
				H→L+7 (16%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{34}	251/4.93	0.1001	H-6→L+1 (37%)	π(L1+L2+acac)→π*(L2)	LLCT/ILCT	
				H-7→L+1 (17%)	π(L1+L2+acac)→π*(L2)	LLCT/ILCT	
	S_{47}	234/5.28	0.1149	H-5→L+3 (32%)	d(Ir)+π(L1+acac)→π*(acac)	MLCT/LLCT/ILCT	
				H-8→L+1 (18%)	π(L1+L2+acac)→π*(L2)	LLCT/ILCT	
2	S_1	434/2.85	0.0473	H→L (96%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{13}	303/4.09	0.1132	H-2→L+1 (41%)	π(L1+L2)→π*(L2)	LLCT/ILCT	
				H-1→L+2 (19%)	d(Ir)+π(acac)→π*(L1)	MLCT/LLCT	
	S_{17}	287/4.31	0.2114	H-5→L (61%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
				H-1→L+4 (10%)	d(Ir)+π(acac)→π*(L2+acac)	MLCT/LLCT/ILCT	
	S_{26}	267/4.63	0.3298	H-7→L (30%)	d(Ir)+π(L1+L2+acac)→π*(L1)	MLCT/LLCT/ILCT	
				H-2→L+2 (21%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
	S_{30}	262/4.72	0.1015	H-2→L+4 (20%)	π(L1+L2)→π*(L2+acac)	LLCT/ILCT	
				H-2→L+3 (11%)	π(L1+L2)→π*(L2+acac)	LLCT/ILCT	
	S_{41}	247/5.01	0.1572	H-5→L+2 (30%)	π(L1+L2)→π*(L1)	LLCT/ILCT	
				H-6→L+2 (26%)	d(Ir)+π(L1+acac)→π*(L1)	MLCT/LLCT/ILCT	
3	S_1	434/2.85	0.0552	H→L (95%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	418
	S_7	343/3.61	0.1841	H-2→L (84%)	π(L1+acac)→π*(L1)	LLCT/ILCT	
	S_{13}	307/4.03	0.1604	H-3→L+1 (64%)	π(L1+L2)→π*(L2)	LLCT/ILCT	
				H-1→L+2 (11%)	d(Ir)+π(L1+acac)→π*(L1)	MLCT/LLCT/ILCT	
	S_{33}	264/4.68	0.1305	H-2→L+6 (20%)	π(L1+acac)→π*(L1)	LLCT/ILCT	
				H-8→L (19%)	π(L1+L2+acac)→π*(L1)	LLCT/ILCT	
				H-3→L+4 (17%)	π(L1+L2)→π*(L2+acac)	LLCT/ILCT	
4	S_1	421/2.94	0.0824	H→L (88%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_7	332/3.72	0.2531	H-2→L (58%)	π(L1+acac)→π*(L1)	LLCT/ILCT	
				H→L+5 (14%)	d(Ir)+π(L1+L2)→π*(L1+L2+acac)	MLCT/LLCT/ILCT	
	S_8	332/3.72	0.1037	H→L+5 (57%)	d(Ir)+π(L1+L2)→π*(L1+L2+acac)	MLCT/LLCT/ILCT	
				H-2→L (14%)	π(L1+acac)→π*(L1)	LLCT/ILCT	
	S_9	321/3.85	0.1572	H-3→L (33%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-4→L (28%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
	S_{13}	306/4.04	0.1114	H-3→L (48%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	
				H-4→L (39%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT	

	S_{14}	303/4.08	0.0965	H-3→L+1 (44%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT
5	S_1	436/2.83	0.0475	H→L (96%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{11}	315/3.92	0.0995	H-4→L+1 (52%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT
				H-3→L+1 (24%)	π(L1+L2)→π*(L2)	LLCT/ILCT
	S_{12}	306/4.03	0.1553	H-3→L+1 (54%)	π(L1+L2)→π*(L2)	LLCT/ILCT
				H-1→L+2 (16%)	d(Ir)+π(acac)→π*(L1)	MLCT/LLCT
	S_{16}	295/4.19	0.0915	H-5→L (78%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{29}	266/4.64	0.2364	H-7→L (25%)	d(Ir)+π(L1+acac)→π*(L1)	MLCT/LLCT/ILCT
				H-4→L+2 (14%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{30}	265/4.67	0.1428	H-8→L (41%)	π(L1+L2+acac)→π*(L1)	LLCT/ILCT
				H-8→L+3 (14%)	π(L1+L2+acac)→π*(L2+acac)	LLCT/ILCT
	S_{46}	246/5.03	0.1265	H-6→L+2 (42%)	d(Ir)+π(L1+acac)→π*(L1)	MLCT/LLCT/ILCT
				H-9→L (27%)	π(L1)→π*(L1)	ILCT
6	S_1	425/2.91	0.0703	H→L (91%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_8	331/3.73	0.1870	H-2→L (58%)	π(L1+L2)→π*(L1)	LLCT/ILCT
				H→L+5 (14%)	d(Ir)+π(L1+L2)→π*(L1+L2+acac)	MLCT/LLCT/ILCT
	S_9	322/3.84	0.1321	H-3→L (36%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H-4→L (27%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
	S_{12}	313/3.95	0.1294	H-2→L+1 (81%)	π(L1+L2)→π*(L2)	LLCT/ILCT
				H-3→L+1 (11%)	d(Ir)+π(L1+L2)→π*(L2)	MLCT/LLCT/ILCT
	S_{22}	281/4.41	0.1001	H→L+6 (40%)	d(Ir)+π(L1+L2)→π*(L1)	MLCT/LLCT/ILCT
				H-5→L (12%)	π(L1+L2+acac)→π*(L1)	LLCT/ILCT
	S_{45}	251/4.93	0.1481	H-8→L (27%)	π(L1)→π*(L1)	ILCT
				H→L+8 (14%)	d(Ir)+π(L1+L2)→π*(L1+L2)	MLCT/LLCT/ILCT

[a] Ref. 24

Table S8 Partial frontier molecular orbital composition (%) of complexes **1–6** in the triplet excited states. (H and L indicate HOMO and LUMO, respectively)

	MO	Energy/eV	Composition (%)				Assignment
			Ir	L1	L2	acac	
1	L+1	-1.59	4	72	22	1	π*(L1+L2)
	L	-1.70	5	23	71	1	π*(L1+L2)
	H	-5.33	25	8	65	2	d(Ir)+π(L1)
2	L	-2.16	4	94	2	1	π*(L1)
	H	-5.51	36	19	41	4	d(Ir)+π(L1+L2)
	H-2	-6.39	3	54	40	3	π(L1+L2)
3	L+1	-1.80	5	63	31	1	π*(L1+L2)
	L	-1.91	4	33	62	1	π*(L1+L2)
	H	-5.42	27	9	62	2	d(Ir)+π(L2)
4	L	-1.89	6	8	86	1	π*(L2)
	H	-5.40	28	10	60	2	d(Ir)+π(L1+L2)
5	L+1	-1.61	6	2	91	1	π*(L2)
	L	-2.19	3	94	2	1	π*(L1)
	H	-5.47	34	16	45	5	d(Ir)+π(L1+L2)
	H-2	-6.40	2	73	18	6	π(L1+L2)
6	L	-2.14	4	94	2	1	π*(L1)
	H	-5.46	35	18	43	4	d(Ir)+π(L1+L2)
	H-2	-6.39	4	31	59	6	π(L1+L2)