Supporting Information

New Journal of Chemistry

For

Theoretical investigation on the effects of N-substitution on the photophysical properties of two series of iridium(III) complexes

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Fig. S1 Calculated bond length variations of complexes 1 and 2 compared with experimental results.

Fig. S2 Calculated bond length variations between the lowest singlet state and the lowest triplet state for complexes 1-1d and 2-2d (The negative values represent the bond distances that are contracted in the lowest triplet state, while the positive ones indicate an elongation for the bonds in the T_1 state).

Table S1 The calculated geometry parameters obtained by different computational methods together with the experimental results of complexes 1 and 2

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

Table S3 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1a

Table S4 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1b

Table S5 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1c

Table S6 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1d

Table S7 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2

Table S8 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2a

Table S9 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2b

Table S10 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2c

Table S11 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2d

Table S12 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution, transition characters, and the available experimental wavelength (nm) for these studied complexes in CH_2Cl_2 media at TDDFT/PBE0/LANL2DZ+6-31G(d) level

Table S13 Calculated phosphorescent emission wavelength (nm)/energies (eV), of the complexes 1 and 2 in CH_2Cl_2 media with the TDDFT method at the M062X, M052X, B3LYP and PBE0 level, respectively, together with the experimental values

Table S14 Partial molecular orbital composition (%) of 1-1d and 2-2d in the excited states

Table S15 Cartesian coordinates from the optimized structures of S_0 at PBE0 (B3LYP) /6-31G(d) level for 1

Table S16 Cartesian coordinates from the optimized structures of S_0 at PBE0 (B3LYP) /6-31G(d) level for 2

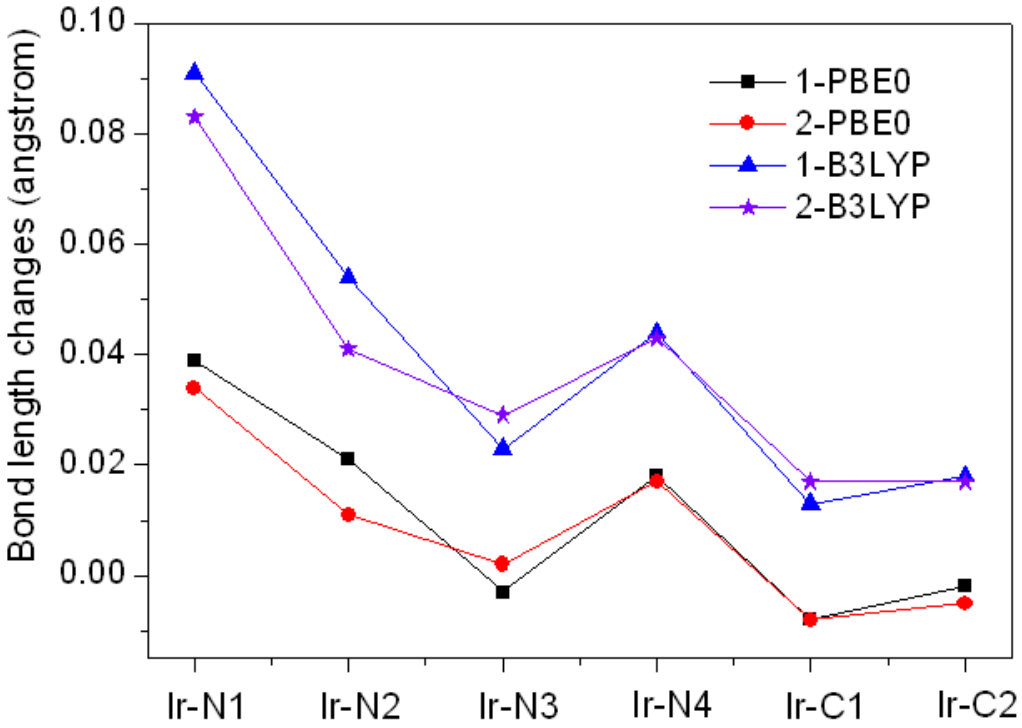

Fig. S1 Calculated bond length variations of complexes 1 and 2 compared with experimental results.

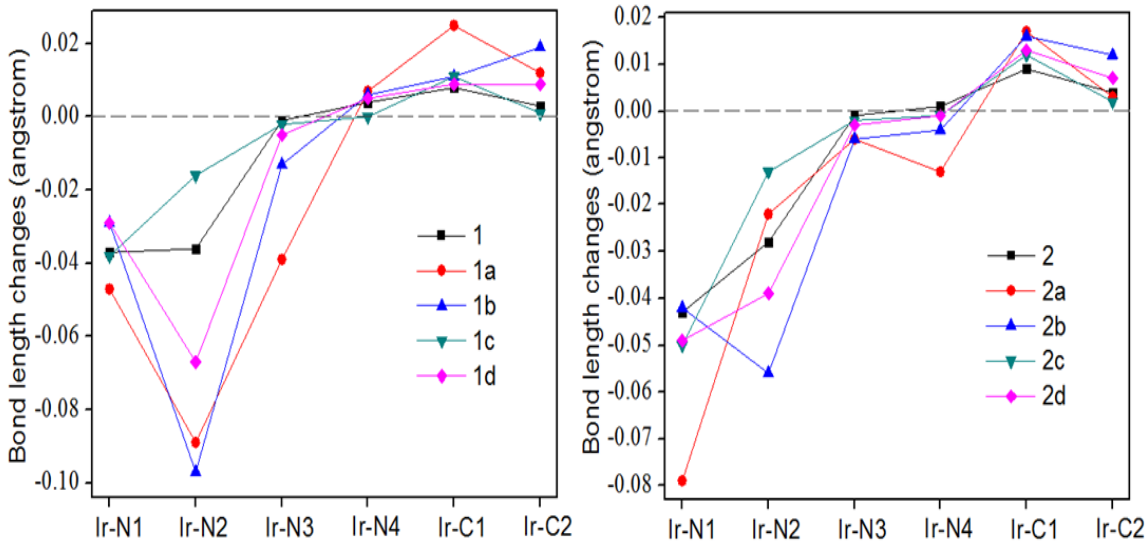

Fig. S2 Calculated bond length variations between the lowest singlet state and the lowest triplet state for complexes 1-1d and 2-2d (The negative values represent the bond distances that are contracted in the lowest triplet state, while the positive ones indicate an elongation for the bonds in the T_1 state).

Table S1 The calculated geometry parameters obtained by different computational methods together with the experimental results of complexes 1 and 2

	B3LYP		PBE0		Exptl.[a]	
	1	2	1	2	1	2
bond length (Å)						
Ir-N1	2.271	2.256	2.219	2.207	2.180	2.173
Ir-N2	2.169	2.130	2.136	2.100	2.115	2.089
Ir-N3	2.072	2.070	2.046	2.044	2.028	2.027
Ir-N4	2.062	2.071	2.036	2.044	2.039	2.042
Ir-C1	2.042	2.061	2.022	2.039	2.024	2.044
Ir-C2	2.052	2.081	2.031	2.056	2.039	2.064
bond angle (°)						
N1-Ir-N2	75.0	75.7	75.8	76.4	76.1	76.5
C1-Ir-N3	88.7	86.0	88.7	86.0	90.2	86.7
C2-Ir-N3	92.5	94.8	92.1	94.6	89.3	95.9

[a] Reference 19

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

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.90	30	32	38	d(Ir)+π*(C^N+ N^N)
L+7	0.63	8	91	1	π*(C^N)
L+6	0.47	10	88	2	π*(C^N)
L+5	0.23	4	95	1	π*(C^N)
L+4	0.04	8	90	2	π*(C^N)
L+3	-0.06	6	92	2	π*(C^N)
L+2	-0.44	5	92	3	π*(C^N)
L+1	-1.22	0	3	97	π*(N^N)
L	-1.76	2	2	96	π*(N^N)
Energy gap = 4.24 eV					
H	-6.00	36	62	2	d(Ir)+π(C^N)
H-1	-6.18	44	41	15	d(Ir)+π(C^N)
H-2	-6.38	2	97	1	π(C^N)
H-3	-6.59	27	21	52	d(Ir)+π(C^N + N^N)
H-4	-6.70	6	90	4	π(C^N)
H-5	-6.87	12	86	2	π(C^N)
H-6	-7.16	39	14	47	d(Ir)+π(N^N)
H-7	-7.61	3	46	51	π(C^N + N^N)
H-8	-7.74	6	81	13	π(C^N)

H = HOMO; L= LUMO

Table S3 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1a

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.84	9	9	82	π*(N^N)
L+7	0.67	8	92	1	π*(C^N)
L+6	0.56	11	88	1	π*(C^N)
L+5	0.38	4	96	0	π*(C^N)
L+4	0.23	11	84	4	π*(C^N)
L+3	0.00	5	94	2	π*(C^N)
L+2	-0.39	5	94	1	π*(C^N)
L+1	-1.82	0	0	99	π*(N^N)
L	-2.28	3	2	95	π*(N^N)
Energy gap = 3.73 eV					
H	-6.01	35	63	2	d(Ir)+ π(C^N)
H-1	-6.14	39	53	9	d(Ir)+π(C^N)
H-2	-6.34	3	97	1	π(C^N)
H-3	-6.51	2	97	1	π(C^N)
H-4	-6.67	32	31	36	d(Ir)+π(C^N + N^N)
H-5	-6.78	25	65	10	d(Ir)+π(C^N)
H-6	-7.35	26	18	56	d(Ir)+π(C^N + N^N)
H-7	-7.60	4	62	34	π(C^N + N^N)
H-8	-7.70	6	80	14	π(C^N)

Table S4 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1b

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.73	15	14	71	π*(N^N)
L+7	0.53	8	91	1	π*(C^N)
L+6	0.37	11	89	1	π*(C^N)
L+5	0.15	4	95	1	π*(C^N)
L+4	-0.04	9	88	3	π*(C^N)
L+3	-0.17	6	92	2	π*(C^N)
L+2	-0.55	5	92	2	π*(C^N)
L+1	-1.52	1	3	96	π*(N^N)
L	-2.16	2	1	97	π*(N^N)
Energy gap = 3.96 eV					
H	-6.12	36	62	2	d(Ir)+π(C^N)
H-1	-6.31	42	48	10	d(Ir)+π(C^N)
H-2	-6.49	2	97	1	π(C^N)
H-3	-6.75	5	91	4	π(C^N)
H-4	-6.85	32	32	36	d(Ir)+π(C^N + N^N)
H-5	-6.98	20	74	6	d(Ir)+π(C^N)
H-6	-7.42	26	16	58	d(Ir)+π(C^N + N^N)
H-7	-7.76	3	56	42	π(C^N + N^N)
H-8	-7.86	5	89	6	π(C^N)

Table S5 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1c

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.73	32	34	34	d(Ir)+π*(C^N + N^N)
L+7	0.49	9	91	1	π*(C^N)
L+6	0.33	11	88	1	π*(C^N)
L+5	0.09	4	95	1	π*(C^N)
L+4	-0.10	8	89	3	π*(C^N)
L+3	-0.21	6	92	2	π*(C^N)
L+2	-0.59	6	93	2	π*(C^N)
L+1	-1.51	0	3	97	π*(N^N)
L	-2.33	3	2	95	π*(N^N)
Energy gap = 3.84 eV					
H	-6.17	35	63	2	d(Ir)+π(C^N)
H-1	-6.37	42	44	14	d(Ir)+π(C^N)
H-2	-6.52	3	96	1	π(C^N)
H-3	-6.78	21	36	43	d(Ir)+π(C^N + N^N)
H-4	-6.84	10	77	14	π(C^N)
H-5	-7.02	14	84	3	π(C^N)
H-6	-7.38	39	17	45	d(Ir)+π(C^N + N^N)
H-7	-7.74	3	44	53	π(C^N + N^N)
H-8	-7.89	4	81	15	π(C^N)

Table S6 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 1d

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.81	39	41	20	d(Ir)+π*(C^N + N^N)
L+7	0.55	9	90	1	π*(C^N)
L+6	0.38	11	87	1	π*(C^N)
L+5	0.12	4	95	1	π*(C^N)
L+4	-0.07	8	90	3	π*(C^N)
L+3	-0.16	6	91	2	π*(C^N)
L+2	-0.54	5	92	2	π*(C^N)
L+1	-1.76	0	2	98	π*(N^N)
L	-2.01	3	2	96	π*(N^N)
Energy gap =4.09 eV					
H	-6.10	35	62	3	d(Ir)+π(C^N)
H-1	-6.31	43	43	13	d(Ir)+π(C^N)
H-2	-6.46	2	97	1	π(C^N)
H-3	-6.73	28	28	44	d(Ir)+π(C^N + N^N)
H-4	-6.81	9	84	7	π(C^N)
H-5	-6.98	13	85	2	π(C^N)
H-6	-7.35	33	17	50	d(Ir)+π(C^N + N^N)
H-7	-7.66	3	21	76	π(C^N + N^N)
H-8	-7.82	8	60	32	π(C^N + N^N)

Table S7 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.77	44	50	6	d(Ir)+π*(C^N)
L+7	0.14	6	92	1	π*(C^N)
L+6	0.05	5	95	0	π*(C^N)
L+5	-0.12	1	99	0	π*(C^N)
L+4	-0.25	4	95	1	π*(C^N)
L+3	-0.45	6	92	3	π*(C^N)
L+2	-0.68	3	96	1	π*(C^N)
L+1	-1.10	1	1	98	π*(N^N)
L	-1.73	3	1	96	π*(N^N)
Energy gap = 4.25 eV					
H	-5.98	39	56	5	d(Ir)+π(C^N)
H-1	-6.35	40	27	33	d(Ir)+π(C^N + N^N)
H-2	-6.68	38	38	24	d(Ir)+π(C^N + N^N)
H-3	-6.82	8	52	40	π(C^N + N^N)
H-	-7.00	10	79	12	π(C^N)
H-5	-7.33	7	86	8	π(C^N)
H-6	-7.43	9	71	20	π(C^N + N^N)
H-7	-7.55	5	21	73	π(C^N + N^N)
H-8	-7.70	1	90	9	π(C^N)

Table S8 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2a

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.81	45	50	5	d(Ir)+π*(C^N)
L+7	0.15	6	93	1	π*(C^N)
L+6	0.08	4	95	0	π*(C^N)
L+5	0.01	5	95	1	π*(C^N)
L+4	-0.07	3	97	1	π*(C^N)
L+3	-0.41	4	94	2	π*(C^N)
L+2	-0.47	4	95	1	π*(C^N)
L+1	-1.74	0	1	99	π*(N^N)
L	-2.21	3	1	96	π*(N^N)
Energy gap =3.72 eV					
H	-5.93	37	59	4	d(Ir)+π(C^N)
H-1	-6.41	49	33	18	d(Ir)+ π(C^N + N^N)
H-2	-6.65	26	68	6	d(Ir)+ π(C^N)
H-3	-6.93	9	66	26	π(C^N + N^N)
H-4	-7.05	2	57	40	π(C^N + N^N)
H-5	-7.10	4	84	13	π(C^N)
H-6	-7.39	15	59	27	d(Ir)+ π(C^N + N^N)
H-7	-7.61	12	41	47	d(Ir)+ π(C^N + N^N)
H-8	-7.71	2	92	6	π(C^N)

Table S9 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2b

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.64	44	51	5	d(Ir)+π*(C^N)
L+7	0.02	7	92	1	π*(C^N)
L+6	-0.06	5	95	0	π*(C^N)
L+5	-0.21	2	98	1	π*(C^N)
L+4	-0.32	4	95	1	π*(C^N)
L+3	-0.56	6	92	2	π*(C^N)
L+2	-0.74	3	96	1	π*(C^N)
L+1	-1.39	1	1	98	π*(N^N)
L	-2.13	2	1	97	π*(N^N)
Energy gap = 3.97 eV					
H	-6.10	38	58	4	d(Ir)+π(C^N)
H-1	-6.54	48	33	19	d(Ir)+π(C^N + N^N)
H-2	-6.83	34	55	12	d(Ir)+π(C^N)
H-3	-7.03	5	68	28	π(C^N + N^N)
H-4	-7.18	4	54	42	π(C^N + N^N)
H-5	-7.40	4	91	5	π(C^N)
H-6	-7.56	13	60	27	π(C^N + N^N)
H-7	-7.75	8	40	51	π(C^N + N^N)
H-8	-7.83	3	83	14	π(C^N)

Table S10 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2c

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.59	44	51	5	d(Ir)+π*(C^N)
L+7	0.00	7	93	1	π*(C^N)
L+6	-0.09	5	95	0	π*(C^N)
L+5	-0.25	1	98	0	π*(C^N)
L+4	-0.38	4	95	1	π*(C^N)
L+3	-0.59	6	92	3	π*(C^N)
L+2	-0.81	3	96	1	π*(C^N)
L+1	-1.42	1	1	98	π*(N^N)
L	-2.28	3	1	96	π*(N^N)
Energy gap =3.87 eV					
H	-6.15	38	58	5	d(Ir)+π(C^N)
H-1	-6.53	40	29	31	d(Ir)+π(C^N + N^N)
H-2	-6.88	35	46	19	d(Ir)+π(C^N + N^N)
H-3	-6.99	5	54	41	π(C^N + N^N)
H-4	-7.15	10	75	15	π(C^N)
H-5	-7.47	5	90	5	π(C^N)
H-6	-7.56	8	58	34	π(C^N + N^N)
H-7	-7.71	8	30	62	π(C^N + N^N)
H-8	-7.84	1	88	11	π(C^N)

Table S11 Frontier molecular orbital energies (eV), compositions (%), and assignment in the ground state for complex 2d

MO	Energy	Contribution(%)			Assignment
		Ir	C^N	N^N	
L+8	0.66	44	51	5	d(Ir)+π*(C^N)
L+7	0.06	6	93	1	π*(C^N)
L+6	-0.03	5	95	0	π*(C^N)
L+5	-0.21	1	98	0	π*(C^N)
L+4	-0.35	4	95	1	π*(C^N)
L+3	-0.54	6	92	2	π*(C^N)
L+2	-0.78	3	96	1	π*(C^N)
L+1	-1.66	0	1	98	π*(N^N)
L	-1.95	3	1	96	π*(N^N)
Energy gap =4.14 eV					
H	-6.09	38	57	4	d(Ir)+π(C^N)
H-1	-6.47	43	29	27	d(Ir)+π(C^N + N^N)
H-2	-6.82	37	49	14	d(Ir)+π(C^N)
H-3	-6.97	4	56	41	π(C^N + N^N)
H-4	-7.10	9	66	25	π(C^N + N^N)
H-5	-7.44	8	84	9	π(C^N)
H-6	-7.54	10	68	23	π(C^N + N^N)
H-7	-7.57	1	11	88	π(N^N)
H-8	-7.75	2	66	32	π(C^N + N^N)

Table S12 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution, transition characters, and the available experimental wavelength (nm) for these studied complexes in CH_2Cl_2 media at TDDFT/PBE0/LANL2DZ+6-31G(d) level

	State	λ/E	Oscillator	Configuration	Assignment	Nature	Exptl.[a]
1	S_1	357/3.46	0.007	H→L(93%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	368
	S_2	339/ 3.65	0.079	H-1→L(93%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{12}	256/ 4.82	0.252	H-3→L+1(51%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	261
	S_{13}	248/4.98	0.069	H→L+3(77%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{60}	204/ 6.07	0.102	H-1→L+8(57%)	d(Ir)+π(C^N)→d(Ir)+π*(C^N + N^N)	MLCT/LLCT/ILCT	
	T_1	395/ 3.13	0.000	H-3→L(54%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
1a	S_1	395/3.13	0.003	H→L(95%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_2	381/3.24	0.071	H-1→L(94%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{19}	258/4.80	0.101	H-1→L+2(52%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{21}	248/4.98	0.118	H-6→L+1(50%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{22}	246/ 5.03	0.106	H-7→L(46%)	π(C^N + N^N)→π*(N^N)	LLCT/ILCT	
	T_1	415/ 2.98	0.000	H-1→L(88%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
1b	S_1	383/ 3.23	0.003	H→L(95%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_2	372/ 3.33	0.077	H-1→L (95%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{11}	266/ 4.64	0.191	H-6→L (46%)	d(Ir)+π(C^N + N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{50}	212/ 5.84	0.096	H-2→L+3 (45%)	π(C^N)→π*(C^N)	LLCT/ILCT	
	T_1	404/ 3.06	0.000	H-1→L(66%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
1c	S_1	399/ 3.10	0.000	H→L(56%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
				H→L+1(38%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_2	385/ 3.21	0.068	H-1→L (90%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{10}	290/ 4.26	0.091	H-6→L (81%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{11}	270/ 4.58	0.134	H-3→L+1 (46%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	T_1	430/ 2.88	0.000	H-1→L(40%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
1d	S_1	363/ 3.40	0.007	H→L(94%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_2	354/ 3.50	0.067	H-1→L (94%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{14}	263/ 4.70	0.124	H-6→L (57%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{17}	257/ 4.81	0.078	H-1→L+2 (65%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{19}	248/ 4.98	0.106	H→L+3 (70%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	T_1	398/ 3.11	0.000	H-3→L(43%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
2	S_1	360/3.44	0.003	H→L(97%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	370

	S_4	292/ 4.24	0.108	H→L+1(72%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	284
	S_{17}	246/ 5.03	0.091	H→L+4(51%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	261
	S_{20}	239/5.16	0.084	H-3→L+1(63%)	π(C^N + N^N)→π*(N^N)	LLCT/ILCT	
	S_{48}	209/5.91	0.085	H-3→L+4(39%)	π(C^N + N^N)→π*(C^N)	LLCT/ILCT	
	T_1	402/ 3.08	0.000	H→L(49%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
2a	S_1	413/ 2.99	0.003	H→L(98%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_4	322/ 3.83	0.092	H-2→L (89%)	d(Ir)+ π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{15}	261/ 4.74	0.072	H-3→L+1(73%)	π(C^N + N^N)→π*(N^N)	LLCT/ILCT	
	S_{28}	241/ 5.13	0.125	H-6→L+1(54%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{59}	206/ 6.00	0.112	H-4→L+3(52%)	π(C^N + N^N)→π*(C^N)	LLCT/ILCT	
	T_1	431/ 2.87	0.000	H→L(73%)	d(Ir)+ π(C^N)→π*(N^N)	MLCT/LLCT	
2b	S_1	402/ 3.07	0.006	H→L(98%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_3	320/ 3.86	0.078	H-2→L (81%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_7	280/ 4.42	0.192	H→L+2 (48%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{58}	205/ 6.04	0.121	H-5→L+3(50%)	π(C^N)→π*(C^N)	LLCT/ILCT	
	T_1	419/ 2.95	0.000	H→L(68%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
2c	S_1	418/ 2.96	0.001	H→L(53%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
				H→L+1(38%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_3	329/ 3.77	0.087	H-2→L (89%)	d(Ir)+π(C^N+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{25}	242/ 5.10	0.139	H-2→L+2(52%)	d(Ir)+π(C^N+N^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{40}	224/ 5.52	0.110	H-1→L+4(56%)	d(Ir)+π(C^N+N^N)→π*(C^N)	MLCT/LLCT/ILCT	
	T_1	444/ 2.78	0.000	H→L(51%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
2d	S_1	380/ 3.26	0.002	H→L(97%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_5	303/ 4.08	0.113	H-2→L (60%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	
	S_{23}	245/ 5.05	0.122	H→L+4 (55%)	d(Ir)+π(C^N)→π*(C^N)	MLCT/LLCT/ILCT	
	S_{52}	211/ 5.85	0.099	H-7→L+2(58%)	π(N^N)→π*(C^N)	LLCT	
	S_{60}	205/ 6.04	0.119	H-5→L+3(55%)	π(C^N)→π*(C^N)	LLCT/ILCT	
	T_1	409/ 3.03	0.000	H→L(56%)	d(Ir)+π(C^N)→π*(N^N)	MLCT/LLCT	

[a] Reference 19

Table S13 Calculated phosphorescent emission wavelength (nm)/energies (eV), of the complexes 1 and 2 in CH_2Cl_2 media with the TDDFT method at the M062X, M052X, B3LYP and PBE0 level, respectively, together with the experimental values

	λ_{cal}/E(eV) M062X	λ_{cal}/E(eV) M052X	λ_{cal}/E(eV) B3LYP	λ_{cal}/E(eV) PBE0	Exptl.[a]

1	456	474	577	498	460
2	457	453	556	471	457

[a] Reference 19

Table S14 Partial molecular orbital composition (%) of 1-1d and 2-2d in the excited states

	MO	Energy/eV	MO composition (%)			Assignment
			Ir	C^N	N^N	
1	L	-2.03	3	2	96	π*(N^N)
	H	-6.02	35	63	3	d(Ir)+π(C^N)
1a	L	-2.63	4	2	94	π*(N^N)
	H	-5.96	37	49	14	d(Ir)+π(C^N)
1b	L	-2.45	3	2	96	π*(N^N)
	H	-6.13	35	58	6	d(Ir)+π(C^N)
1c	L	-2.56	4	2	95	π*(N^N)
	H	-6.19	34	64	3	d(Ir)+π(C^N)
	H-2	-6.52	3	96	1	π(C^N)
1d	L	-2.25	3	2	95	π*(N^N)
	H	-6.12	35	62	3	d(Ir)+π(C^N)
2	L	-2.01	3	2	96	π*(N^N)
	H	-5.97	36	47	17	d(Ir)+π(C^N + N^N)
2a	L	-2.53	5	1	94	π*(N^N)
	H	-5.89	36	57	7	d(Ir)+π(C^N)
2b	L	-2.44	3	1	96	π*(N^N)
	H	-6.08	38	53	8	d(Ir)+π(C^N)
2c	L	-2.55	4	1	95	π*(N^N)
	H	-6.13	36	51	13	d(Ir)+π(C^N)
2d	L	-2.24	3	2	96	π*(N^N)
	H	-6.08	38	52	11	d(Ir)+π(C^N)

Table S15 Cartesian coordinates from the optimized structures of S_0 at PBE0 (B3LYP) /6-31G(d) level for 1

	PBE0			B3LYP		
Ir	-0.22227300	-0.19407300	0.09392100	-0.23533100	-0.18735800	0.09233000
N	-0.22667500	-0.53686500	-1.91375900	-0.25067900	-0.56431400	-1.93495300
N	-1.16180800	-1.24369500	-2.56402100	-1.20557800	-1.27776600	-2.57567000
N	-0.14928600	0.23272700	2.09364600	-0.13728500	0.25962400	2.11396900
N	0.39693600	1.36309000	2.56527600	0.40735000	1.41068200	2.57274500
N	0.28694200	-2.29968500	0.57905600	0.31434200	-2.33383400	0.59423600
N	1.91094400	-0.25421800	-0.00925900	1.93085000	-0.24988800	-0.01817300
N	2.89303200	0.58956900	-0.33514500	2.92112500	0.60064900	-0.34816200
N	3.78665800	-1.46153900	0.01646300	3.81910000	-1.45465300	0.01712400
C	0.58144100	-0.01246500	-2.83764000	0.56315700	-0.06936700	-2.87792700
H	1.40116700	0.62012800	-2.52713600	1.39297900	0.55777300	-2.58728500
C	0.16114700	-0.40329300	-4.11264000	0.13323400	-0.48192900	-4.14733100
H	0.60299300	-0.13899100	-5.06121000	0.57708100	-0.24196300	-5.10140500
C	-0.95276800	-1.19012000	-3.89454500	-0.99304200	-1.25199900	-3.91314500
H	-1.60539900	-1.71713200	-4.57539400	-1.65150700	-1.78367900	-4.58439700
C	-2.12639200	-2.04921300	-1.83675800	-2.17954300	-2.07469200	-1.83050800
H	-1.58169100	-2.89662100	-1.40157400	-1.64073300	-2.92701500	-1.39903400
H	-2.81462100	-2.45286700	-2.58084200	-2.87773400	-2.47134300	-2.56797000
C	-2.88456600	-1.27355400	-0.79304000	-2.92571200	-1.28901100	-0.77465600
C	-4.27153000	-1.41366100	-0.75780300	-4.31537400	-1.43470800	-0.72128600
C	-5.08016700	-0.76151600	0.15439300	-5.12038500	-0.78610400	0.20143500
H	-6.15545500	-0.89160000	0.15797500	-6.19458500	-0.92219400	0.21689500
C	-4.43418900	0.07832400	1.04956800	-4.46571900	0.05647800	1.09218400
C	-3.06067300	0.25635400	1.05068400	-3.08993300	0.24130500	1.07788800
H	-2.63887300	0.95765000	1.76251800	-2.66614500	0.94104400	1.78838200
C	-2.23950700	-0.42613600	0.13731000	-2.27200700	-0.43642400	0.15187000
C	-0.59531400	-0.44967200	3.15198900	-0.55139600	-0.42310800	3.19198400
H	-1.09832100	-1.39362000	3.00862900	-1.04195200	-1.37573600	3.06840500
C	-0.32538800	0.25375300	4.32734800	-0.26574600	0.29342500	4.36049000
H	-0.56497000	-0.03283000	5.33996600	-0.48039800	0.00836100	5.37910300
C	0.30791700	1.40841900	3.90616300	0.34439000	1.45795500	3.92142600
H	0.70075800	2.25239900	4.45404900	0.73674900	2.30824900	4.45948600

C	1.00121000	2.34178100	1.66820100	0.99786500	2.39558600	1.65545400
H	1.92205000	1.91270400	1.25906700	1.92305600	1.97424200	1.25143600
H	1.26135400	3.20244000	2.28561200	1.24651900	3.26475600	2.26444200
C	0.07279800	2.73890700	0.55827400	0.05896900	2.77397800	0.53759800
C	-0.16743800	4.09015800	0.32668300	-0.18445000	4.12621300	0.29168000
C	-0.97057400	4.55318600	-0.70030300	-0.99011200	4.58329000	-0.74038800
H	-1.13530000	5.61154900	-0.86116700	-1.15476000	5.64013000	-0.90955100
C	-1.55322000	3.58593500	-1.50424900	-1.57333200	3.60616100	-1.53680400
C	-1.35546100	2.22885100	-1.30663900	-1.37448400	2.24757200	-1.32744300
H	-1.87246900	1.53701100	-1.96346600	-1.89138000	1.55304200	-1.97942500
C	-0.52741800	1.77142800	-0.27102000	-0.54380900	1.79625000	-0.28603800
C	-0.56406700	-3.26428300	0.95293000	-0.51885600	-3.31908200	0.97280200
H	-1.61382000	-2.98108700	0.97177700	-1.57296800	-3.05837200	0.99863100
C	-0.14689500	-4.54351000	1.28871600	-0.07558500	-4.59386400	1.30725200
H	-0.87726300	-5.29000600	1.58250500	-0.79047300	-5.35396400	1.60428200
C	1.21631000	-4.83765300	1.23509400	1.29620500	-4.86299800	1.24737800
H	1.57706300	-5.83086300	1.48669700	1.67678600	-5.84915200	1.49738100
C	2.10614900	-3.84311800	0.86405700	2.16789600	-3.84995200	0.87073300
H	3.17759400	-4.00509000	0.81412800	3.24101700	-3.99514900	0.81602800
C	1.61055900	-2.57605200	0.54956100	1.64886800	-2.58699200	0.55660300
C	2.46380100	-1.46394400	0.18781300	2.48999100	-1.46235400	0.18744700
C	3.98989100	-0.17558600	-0.30255000	4.02400500	-0.16519400	-0.30906400
C	5.34841500	0.36212900	-0.61844300	5.38567800	0.37216000	-0.62879200
F	-4.86479100	-2.23285400	-1.65184700	-4.92126500	-2.26322500	-1.61437200
F	-5.17901900	0.74326200	1.94442600	-5.20749100	0.72159900	2.00406500
F	0.41399100	5.00198400	1.13253300	0.40108100	5.05372900	1.09405400
F	-2.34752800	3.98761900	-2.50866200	-2.37427800	4.00024700	-2.55189900
F	5.84421500	-0.18752000	-1.73967500	5.87691500	-0.16923000	-1.76711400
F	6.21878100	0.09396100	0.36684500	6.26882900	0.08793500	0.35266200
F	5.31975100	1.68710800	-0.79348200	5.36395800	1.70766100	-0.79047200

Table S16 Cartesian coordinates from the optimized structures of S_0 at PBE0 (B3LYP) /6-31G(d) level for 2

	PBE0			B3LYP		
Ir	0.18635100	-0.43602700	0.16884500	0.18027300	-0.43241100	0.16894800
N	-0.18775300	-1.44118400	-1.57178300	-0.20076100	-1.45296900	-1.59277900
N	-1.36116100	-1.37524400	-2.21391400	-1.39045600	-1.39508300	-2.23189200
N	0.60856700	0.55620800	1.90587900	0.61116900	0.57172900	1.92817300
N	-0.05134400	1.65434400	2.29573400	-0.04717900	1.68712900	2.31393100
N	0.92264000	-2.36063000	0.96082100	0.94659800	-2.39280200	0.98134500
N	2.24942200	-0.37190500	-0.22320600	2.27333600	-0.38242200	-0.22766100
N	3.09457000	0.50347200	-0.75704300	3.12944100	0.48936800	-0.77697000
N	4.26860600	-1.29505300	-0.02544600	4.29522200	-1.32682100	-0.05298500
C	0.58727100	-2.27192900	-2.26982400	0.57648900	-2.27745700	-2.30603900
H	1.60016400	-2.46253900	-1.94901200	1.59284200	-2.46364000	-1.99669200
C	-0.10625700	-2.75411100	-3.38276500	-0.12384000	-2.76237100	-3.41867000
H	0.25098400	-3.43895900	-4.13655500	0.23458800	-3.44140900	-4.17712700
C	-1.34901000	-2.15605700	-3.31055100	-1.37494400	-2.17547100	-3.33678800
H	-2.22044200	-2.22530600	-3.94501600	-2.24817700	-2.25141600	-3.96764800
C	-2.43072200	-0.52001600	-1.73281200	-2.47152600	-0.54034400	-1.74376800
H	-3.24996100	-0.63833600	-2.43723900	-3.29274700	-0.67374900	-2.44149700
H	-2.08338800	0.51603900	-1.78586900	-2.13497300	0.49694800	-1.81093100
C	-2.80921300	-0.85296500	-0.30940300	-2.84216500	-0.86698400	-0.30848400
C	-4.13086300	-1.19772300	0.02457300	-4.16662800	-1.21662300	0.03201300
C	-4.47252700	-1.48044900	1.34379900	-4.50420100	-1.49854600	1.35695600
H	-5.49332900	-1.73833600	1.60011400	-5.52263300	-1.75932400	1.61719300
C	-3.49099200	-1.43653600	2.32238600	-3.51772000	-1.44990600	2.33475100
H	-3.71295500	-1.65416200	3.36248200	-3.73563300	-1.66799500	3.37541200
C	-2.19561300	-1.10661700	1.95595700	-2.22255000	-1.11391300	1.96185300
C	-1.78013200	-0.79409800	0.65441600	-1.80906500	-0.79966200	0.65741700
C	-5.20416000	-1.27177600	-1.02259100	-5.24927500	-1.29568600	-1.01213300
C	1.55782900	0.33510300	2.81569200	1.55676500	0.34925700	2.84955900
H	2.22856700	-0.50296000	2.70632300	2.22199400	-0.49348400	2.75078200
C	1.50663000	1.31296600	3.81177900	1.50786400	1.33541400	3.84342600
H	2.14547300	1.40804300	4.67637500	2.14343400	1.42802100	4.71070600

C	0.46677000	2.14136300	3.43829200	0.47440900	2.17400500	3.46252800
H	0.06405000	3.03879700	3.88439700	0.07845800	3.07549700	3.90596900
C	-1.13206000	2.20131300	1.49504400	-1.13067700	2.24226900	1.50394100
H	-1.47794000	3.08647600	2.02246400	-1.46542400	3.13291400	2.02686500
H	-1.94906100	1.47514100	1.48239100	-1.95362300	1.52450300	1.50104100
C	-0.66981400	2.48519400	0.08671000	-0.66896200	2.51655500	0.08503500
C	-0.75504500	3.78139800	-0.45317400	-0.74936000	3.81694800	-0.45962100
C	-0.31433200	4.03116600	-1.74822900	-0.31283700	4.06219300	-1.76153500
H	-0.38251100	5.02929100	-2.16464100	-0.37696400	5.05924100	-2.17961000
C	0.22087100	2.99343500	-2.49544300	0.21252900	3.01761400	-2.51204300
H	0.58754600	3.14852300	-3.50495000	0.57360800	3.16879100	-3.52399400
C	0.30203600	1.72936700	-1.93511400	0.28774500	1.75136000	-1.94825900
C	-0.13450800	1.40709700	-0.64269800	-0.14244600	1.43154600	-0.64992400
C	-1.31698600	4.91923100	0.34542000	-1.30268800	4.96560000	0.33883400
C	0.19639400	-3.35238800	1.48853000	0.23348900	-3.38713500	1.53504100
H	-0.87292400	-3.18467800	1.53505900	-0.83437200	-3.22410900	1.60508400
C	0.76229400	-4.53566700	1.93984500	0.81451600	-4.56734800	1.98606300
H	0.12753800	-5.30773200	2.36123300	0.19189500	-5.33875700	2.42643600
C	2.14285500	-4.70184500	1.83875800	2.19745100	-4.72846500	1.85915300
H	2.61679800	-5.61490800	2.18765700	2.68217100	-5.63686400	2.20527400
C	2.90348000	-3.68937800	1.27635200	2.94521200	-3.71335800	1.27646000
H	3.97918000	-3.76161500	1.15583700	4.01882100	-3.78320600	1.14123200
C	2.26291200	-2.52964600	0.83792000	2.29213900	-2.55443300	0.83917100
C	2.96347400	-1.43003200	0.20964100	2.98611600	-1.45181800	0.19953600
C	4.28476500	-0.09023500	-0.61822700	4.31977600	-0.11957800	-0.65260700
C	5.55404600	0.54158900	-1.09095300	5.59596900	0.52183800	-1.10501500
F	-4.91538900	-2.18445600	-1.97816500	-4.96568600	-2.21834300	-1.97343900
F	-5.37116800	-0.09712200	-1.66524200	-5.42162700	-0.11660200	-1.66533800
F	-6.39488500	-1.61026600	-0.51242400	-6.44636000	-1.63336900	-0.49419700
F	-1.28555400	-1.10273300	2.95449700	-1.30455000	-1.10863100	2.96825200
F	-2.58876200	4.68586400	0.73980900	-2.58319200	4.74200400	0.74349000
F	-0.61299100	5.14444800	1.47906000	-0.58939400	5.19386400	1.47765000
F	-1.32741200	6.07064500	-0.33698000	-1.31012900	6.12309500	-0.34974100
F	0.81673800	0.76933700	-2.71896200	0.79752100	0.78252100	-2.74214700
F	5.32977500	1.73216800	-1.65223800	5.36483800	1.55250100	-1.93708300
F	6.41693800	0.71974300	-0.07668900	6.31129200	0.99825400	-0.05823000
F	6.17404700	-0.23154500	-1.99815100	6.38669200	-0.36376500	-1.74774700