Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supplementary Information

Table S1 The calculated geometry parameters obtained by different computational methods and basis sets together with the experimental results of complex **2a**

	PBE0			B3LYP			
Complex **2a**	6-31G(d)	6-31+G(d)	6-311+G(d)	6-31G(d)	6-31+G(d)	6-311+G(d)	Exp[a]
Ir-N1	2.112	2.111	2.110	2.146	2.146	2.149	2.113
Ir-N2	2.162	2.160	2.160	2.206	2.200	2.212	2.131
Ir-C1	2.031	2. 027	2. 024	2.053	2.054	2.053	2.030
Ir-C2	2.033	2.025	2.027	2.051	2.053	2.054	2.014
Ir-C3	2.060	2.061	2.062	2.069	2.071	2.070	2.065
Ir-C4	2.033	2.034	2.033	2.056	2.055	2.053	2.038
N1-Ir-N2	75.73	75.51	75.01	75.01	74.45	73.58	75.98
C1-Ir-C2	78.90	78.46	78.23	78.85	79.55	78.91	79.79
C3-Ir-C4	78.94	77.75	76.93	78.81	76.56	77.60	79.37
N1-Ir-C1	90.90	90.15	91.44	90.38	91.34	90.11	93.70
C1-Ir-C3	94.52	93.24	89.98	95.16	93.12	92.37	91.02

[a] Data from ref. 18.

Table S2 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **1a**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.72	8	90	2	π*(C^C)
L+9	1.59	50	44	6	d(Ir)+π*(C^C)
L+8	1.42	83	13	4	d(Ir)
L+7	1.07	4	96	0	π*(C^C)
L+6	1.03	5	95	0	π*(C^C)
L+5	0.68	6	92	2	π*(C^C)
L+4	0.44	7	90	3	π*(C^C)
L+3	0.00	6	93	1	π*(C^C)
L+2	-0.15	8	88	4	π*(C^C)
L+1	-0.49	1	4	95	π*(N^N)
L	-0.68	2	2	96	π*(N^N)
Energy gap = 4.03 eV					
H	-4.71	13	14	73	π(N^N)
H-1	-4.80	30	42	28	d(Ir)+π(C^C+N^N)
H-2	-5.02	36	26	38	d(Ir)+π(C^C+N^N)
H-3	-5.36	20	71	9	d(Ir)+π(C^C)
H-4	-5.53	19	69	12	d(Ir)+π(C^C)
H-5	-5.81	23	71	6	d(Ir)+π(C^C)
H-6	-5.99	5	88	7	π(C^C)
H-7	-6.12	14	59	27	d(Ir)+π(C^C+N^N)
H-8	-6.78	14	64	22	d(Ir)+π(C^C+N^N)
H-9	-6.91	18	56	26	d(Ir)+π(C^C+N^N)
H-10	-7.09	24	58	18	d(Ir)+π(C^C+N^N)

H = HOMO; L= LUMO

Table S3 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **1b**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.70	9	89	2	π*(C^C)
L+9	1.49	57	35	8	d(Ir)+π*(C^C)
L+8	1.35	77	19	4	d(Ir)+π*(C^C)
L+7	1.01	4	96	0	π*(C^C)
L+6	0.90	4	96	0	π*(C^C)
L+5	0.61	6	92	2	π*(C^C)
L+4	0.35	7	89	4	π*(C^C)
L+3	-0.05	6	93	1	π*(C^C)
L+2	-0.18	8	88	4	π*(C^C)
L+1	-0.51	1	4	95	π*(N^N)
L	-0.72	3	1	96	π*(N^N)
Energy gap = 4.11 eV					
H	-4.83	37	50	13	d(Ir)+π(C^C)
H-1	-4.87	7	6	87	π(N^N)
H-2	-5.10	32	24	44	d(Ir)+π(C^C+N^N)
H-3	-5.42	16	74	10	d(Ir)+π(C^C)
H-4	-5.59	21	68	11	d(Ir)+π(C^C)
H-5	-5.87	26	68	6	d(Ir)+π(C^C)
H-6	-6.04	6	87	7	π(C^C)
H-7	-6.15	16	60	24	d(Ir)+π(C^C+N^N)
H-8	-6.86	13	63	24	d(Ir)+π(C^C+N^N)
H-9	-6.97	20	55	25	d(Ir)+π(C^C+N^N)
H-10	-7.17	23	59	18	d(Ir)+π(C^C+N^N)

Table S4 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **1c**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.68	9	88	3	π*(C^C)
L+9	1.51	54	40	6	d(Ir)+π*(C^C)
L+8	1.33	79	16	5	d(Ir)+π*(C^C)
L+7	1.00	4	96	0	π*(C^C)
L+6	0.89	4	96	0	π*(C^C)
L+5	0.61	6	93	1	π*(C^C)
L+4	0.35	7	90	3	π*(C^C)
L+3	-0.06	6	93	1	π*(C^C)
L+2	-0.19	8	89	3	π*(C^C)
L+1	-0.61	0	3	97	π*(N^N)
L	-1.26	3	1	96	π*(N^N)
Energy gap = 3.54 eV					
H	-4.80	21	25	54	d(Ir)+π(C^C+N^N)
H-1	-4.89	21	32	47	d(Ir)+π(C^C+N^N)
H-2	-5.14	35	29	36	d(Ir)+π(C^C+N^N)
H-3	-5.45	15	73	12	π(C^C)
H-4	-5.61	20	69	11	d(Ir)+π(C^C)
H-5	-5.90	27	68	5	d(Ir)+π(C^C)
H-6	-6.05	6	88	6	π(C^C)
H-7	-6.20	14	58	28	d(Ir)+π(C^C+N^N)
H-8	-6.91	16	64	20	d(Ir)+π(C^C+N^N)
H-9	-6.99	20	57	23	d(Ir)+π(C^C+N^N)
H-10	-7.20	23	59	18	d(Ir)+π(C^C+N^N)

Table S5 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **2a**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.68	43	53	4	d(Ir)+π*(C^C)
L+9	1.47	80	12	8	d(Ir)
L+8	1.11	4	96	0	π*(C^C)
L+7	1.10	5	95	0	π*(C^C)
L+6	0.74	6	89	5	π*(C^C)
L+5	0.55	4	51	45	π*(C^C+N^N)
L+4	0.47	4	44	52	π*(C^C+N^N)
L+3	0.07	5	94	1	π*(C^C)
L+2	-0.07	8	89	3	π*(C^C)
L+1	-0.50	1	2	97	π*(N^N)
L	-1.31	2	1	97	π*(N^N)
Energy gap = 3.33 eV					
H	-4.64	13	14	73	π(N^N)
H-1	-4.74	31	44	25	d(Ir)+π(C^C+N^N)
H-2	-4.97	37	28	35	d(Ir)+π(C^C+N^N)
H-3	-5.30	20	70	10	d(Ir)+π(C^C)
H-4	-5.49	18	70	12	d(Ir)+π(C^C)
H-5	-5.74	22	70	8	d(Ir)+π(C^C)
H-6	-5.92	3	90	7	π(C^C)
H-7	-6.09	12	52	36	π(C^C+N^N)
H-8	-6.29	1	8	91	π(N^N)
H-9	-6.64	10	55	35	π(C^C+N^N)
H-10	-6.84	17	57	26	d(Ir)+π(C^C+N^N)

Table S6 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **2b**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.51	54	23	23	d(Ir)+π*(C^C+N^N)
L+9	1.11	12	25	63	d(Ir)+π*(C^C+N^N)
L+8	1.07	5	73	22	π*(C^C+N^N)
L+7	1.04	5	94	1	π*(C^C)
L+6	0.69	6	92	2	π*(C^C)
L+5	0.45	7	88	5	π*(C^C)
L+4	0.03	1	10	89	π*(N^N)
L+3	0.03	5	87	8	π*(C^C)
L+2	-0.14	8	89	3	π*(C^C)
L+1	-0.71	1	2	97	π*(N^N)
L	-1.64	2	1	97	π*(N^N)
Energy gap = 2.81 eV					
H	-4.45	13	4	83	π(N^N)
H-1	-4.78	38	50	12	d(Ir)+π(C^C)
H-2	-4.90	8	9	83	π(N^N)
H-3	-5.29	11	83	6	π(C^C)
H-4	-5.45	33	58	9	d(Ir)+π(C^C)
H-5	-5.75	27	61	12	d(Ir)+π(C^C)
H-6	-5.86	25	65	10	d(Ir)+π(C^C)
H-7	-5.99	7	86	7	π(C^C)
H-8	-6.35	1	8	91	π(N^N)
H-9	-6.56	3	38	59	π(C^C+N^N)
H-10	-6.77	13	55	32	π(C^C+N^N)

Table S7 Frontier molecular orbital energies (eV) and compositions (%) in the ground state at the PBE0/6-31G(d) level for complex **2c**

MO	Energy	Contribution(%)			Assign
		Ir	C^C	N^N	
L+10	1.44	59	19	22	d(Ir)+π*(C^C+N^N)
L+9	1.09	13	6	81	π*(N^N)
L+8	0.99	4	91	5	π*(C^C)
L+7	0.94	5	95	0	π*(C^C)
L+6	0.61	6	92	2	π*(C^C)
L+5	0.35	8	88	4	π*(C^C)
L+4	0.11	1	2	97	π*(N^N)
L+3	-0.06	6	93	1	π*(C^C)
L+2	-0.23	8	90	2	π*(C^C)
L+1	-0.68	1	2	97	π*(N^N)
L	-1.69	2	1	97	π*(N^N)
Energy gap = 3.13 eV					
H	-4.82	32	31	37	d(Ir)+π(C^C+N^N)
H-1	-4.93	27	32	41	d(Ir)+π(C^C+N^N)
H-2	-5.08	4	3	93	π(N^N)
H-3	-5.39	9	82	9	π(C^C)
H-4	-5.55	30	62	8	d(Ir)+π(C^C)
H-5	-5.85	26	58	16	d(Ir)+π(C^C+N^N)
H-6	-5.95	24	64	12	d(Ir)+π(C^C)
H-7	-6.07	7	84	9	π(C^C)
H-8	-6.34	2	6	92	π(N^N)
H-9	-6.52	2	12	86	π(N^N)
H-10	-6.80	8	51	41	π(C^C+N^N)

Table S8 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution, transition characters and the experimental wavelength (nm) for **1a-2c** in CH_2Cl_2 medium at TDDFT/PBE0/6-31G(d) level

	State	λ/E	Oscillator	Configuration	Assignment	Nature	Exp[a]
1a	S_1	361/ 3.42	0.011	H→L(95%)	π(N^N)→π*(N^N)	ILCT	
	S_5	322/ 3.84	0.143	H-1→L(47%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_9	303/ 4.08	0.141	H-3→L(59%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_{17}	275/ 4.49	0.091	H-2→L+2(59%)	d(Ir)+π(C^C+N^N)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{33}	243/ 5.08	0.119	H-5→L+2(64%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{49}	223/ 5.54	0.102	H-2→L+7(51%)	d(Ir)+π(C^C+N^N)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{55}	219/ 5.66	0.199	H-4→L+5(37%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	T_1	460/ 2.69	0.000	H→L(59%)	π(N^N)→π*(N^N)	ILCT	
1b	S_1	357/ 3.45	0.002	H→L(97%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_6	316/ 3.91	0.134	H-1→L+1(48%)	π(N^N)→π*(N^N)	ILCT	
	S_9	300/ 4.12	0.218	H-3→L (75%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_{49}	223/ 5.54	0.086	H-4→L+4(45%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{54}	219/ 5.64	0.176	H-5→L+4(46%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	T_1	451/ 2.74	0.000	H-1→L(81%)	π(N^N)→π*(N^N)	ILCT	
1c	S_1	420/ 2.94	0.006	H→L(92%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_8	318/ 3.88	0.133	H-2→L+1(48%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_9	315/ 3.93	0.146	H-2→L+1(51%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{11}	299/ 4.13	0.129	H-5→L(81%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_{36}	242/ 5.11	0.092	H-5→L+2(52%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{58}	219/ 5.65	0.092	H→L+8(34%)	d(Ir)+π(C^C+N^N)→d(Ir)+π*(C^C)	MLCT/LLCT/ILCT	
	T_1	521/ 2.37	0.000	H-1→L(68%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
2a	S_1	430/ 2.87	0.019	H→L(91%)	π(N^N)→π*(N^N)	ILCT	420
	S_2	408/ 3.03	0.196	H-1→L(56%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_5	340/ 3.63	0.084	H→L+1(81%)	π(N^N)→π*(N^N)	ILCT	324
	S_{21}	274/ 4.51	0.070	H-3→L+2(72%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	272
	S_{40}	243/ 5.09	0.138	H-5→L+2(62%)	d(Ir)+π(C^C)→π*(C^C)	MLCT/LLCT/ILCT	
	S_{46}	236/ 5.24	0.120	H-4→L(45%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_{57}	225/ 5.49	0.114	H-7→L+3(40%)	π(C^C+N^N)→π*(C^C)	LLCT/ILCT	
	S_{58}	223/ 5.53	0.282	H-9→L+1(47%)	π(C^C+N^N)→π*(N^N)	LLCT/ILCT	
	T_1	584/ 2.12	0.000	H→L(75%)	π(N^N)→π*(N^N)	ILCT	
2b	S_1	508/ 2.43	0.034	H→L(96%)	π(N^N)→π*(N^N)	ILCT	
	S_3	420/ 2.94	0.332	H-2→L(91%)	π(N^N)→π*(N^N)	ILCT	
	S_5	375/ 3.30	0.084	H-4→L(90%)	d(Ir)+π(C^C)→π*(N^N)	MLCT/LLCT	
	S_{11}	322/ 3.83	0.083	H-2→L+1(80%)	π(N^N)→π*(N^N)	ILCT	
	S_{25}	277/ 4.46	0.088	H-2→L+3(50%)	π(N^N)→π*(C^C)	LLCT	
	S_{51}	239/ 5.17	0.121	H→L+9(39%)	π(N^N)→d(Ir)+π*(C^C+N^N)	MLCT/LLCT/ILCT	
	T_1	653/ 1.89	0.000	H→L(84%)	π(N^N)→π*(N^N)	ILCT	
2c	S_1	487/ 2.54	0.000	H→L(98%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_3	406/ 3.04	0.167	H-2→L(81%)	π(N^N)→π*(N^N)	ILCT	
	S_4	387/ 3.20	0.226	H-3→L (83%)	π(C^C)→π*(N^N)	LLCT	
	S_{28}	265/ 4.67	0.141	H-5→L+1(50%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	S_{57}	231/ 5.34	0.248	H→L+4(54%)	d(Ir)+π(C^C+N^N)→π*(N^N)	MLCT/LLCT/ILCT	
	T_1	553/ 2.23	0.000	H-2→L(45%)	π(N^N)→π*(N^N)	ILCT	

[a] Data from ref. 18.