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Supporting Information

Shedding light on the photophysical properties of iridium(III) complexes with a dicyclometalated phosphate ligand via N-substitution from a theoretical viewpoint†

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

MO	Energy	Contribution(%)				Assign
		Ir	P^C_2	$P(OPh)_3$	N^N	
L+8	-0.40	0	5	95	0	π*($P(OPh)_3$)
L+7	-0.42	2	64	33	1	π*(P^C_2 + $P(OPh)_3$)
L+6	-0.43	1	20	78	1	π*(P^C_2+ $P(OPh)_3$)
L+5	-0.53	2	69	28	1	π*(P^C_2 + $P(OPh)_3$)
L+4	-0.56	3	33	62	1	π*(P^C_2 + $P(OPh)_3$)
L+3	-0.61	15	39	41	5	d(Ir)+π*(P^C_2+ $P(OPh)_3$)
L+2	-0.69	7	18	72	3	π*(P^C_2+ $P(OPh)_3$)
L+1	-1.24	1	1	1	98	π*(N^N)
L	-1.87	2	1	1	95	π*(N^N)
H	-6.47	22	73	2	3	d(Ir)+π(P^C_2)
H-1	-6.59	2	96	1	1	π(P^C_2)
H-2	-6.98	13	60	5	22	d(Ir)+π(P^C_2+ N^N)
H-3	-7.07	1	89	1	8	π(P^C_2)
H-4	-7.11	6	36	2	55	π(P^C_2+ N^N)
H-5	-7.21	0	1	99	0	π($P(OPh)_3$)
H-6	-7.24	0	1	97	1	π($P(OPh)_3$)
H-7	-7.49	0	99	0	1	π(P^C_2)
H-8	-7.57	0	1	98	1	π($P(OPh)_3$)

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

MO	Energy	Contribution(%)				Assign
		Ir	P^C_2	P(OPh)$_3$	N^N	
L+8	-0.36	4	78	17	1	π*(P^C_2+ P(OPh)$_3$)
L+7	-0.39	0	5	94	0	π*(P(OPh)$_3$)
L+6	-0.41	0	2	98	0	π*(P(OPh)$_3$)
L+5	-0.49	2	76	21	1	π*(P^C_2+ P(OPh)$_3$)
L+4	-0.52	9	49	39	3	π*(P^C_2 + P(OPh)$_3$)
L+3	-0.59	7	20	71	2	π*(P^C_2 + P(OPh)$_3$)
L+2	-0.68	6	14	78	2	π*(P^C_2+ P(OPh)$_3$)
L+1	-1.84	0	0	0	99	π*(N^N)
L	-2.27	3	1	1	95	π*(N^N)
H	-6.47	19	77	2	3	d(Ir)+π(P^C_2)
H-1	-6.58	5	93	1	1	π(P^C_2)
H-2	-6.98	2	89	6	4	π(P^C_2)
H-3	-7.07	2	95	1	2	π(P^C_2)
H-4	-7.21	0	1	99	0	π(P(OPh)$_3$)
H-5	-7.23	1	4	92	3	π(P(OPh)$_3$)
H-6	-7.33	12	13	10	66	π(N^N)
H-7	-7.44	0	98	0	2	π(P^C_2)
H-8	-7.57	0	1	98	0	π(P(OPh)$_3$)

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

MO	Energy	Contribution(%)				Assign
		Ir	P^C_2	P(OPh)$_3$	N^N	
L+8	-0.41	0	11	88	0	π*(P^C_2+ P(OPh)$_3$)
L+7	-0.42	2	72	25	1	π*(P^C_2+ P(OPh)$_3$)
L+6	-0.44	0	8	92	0	π*(P(OPh)$_3$)
L+5	-0.53	1	85	13	0	π*(P^C_2 + P(OPh)$_3$)
L+4	-0.57	3	13	83	1	π*(P(OPh)$_3$)
L+3	-0.65	13	31	52	4	d(Ir)+π*(P^C_2+ P(OPh)$_3$)
L+2	-0.72	13	27	55	5	d(Ir)+π*(P^C_2+ P(OPh)$_3$)
L+1	-1.53	1	1	1	98	π*(N^N)
L	-2.30	2	1	1	96	π*(N^N)
H	-6.53	21	76	2	2	d(Ir)+π(P^C_2)
H-1	-6.63	2	95	1	1	π(P^C_2)
H-2	-7.04	1	90	7	3	π(P^C_2)
H-3	-7.11	2	96	1	2	π(P^C_2)
H-4	-7.23	0	1	99	0	π(P(OPh)$_3$)
H-5	-7.25	1	3	95	1	π(P(OPh)$_3$)
H-6	-7.37	13	13	8	66	π(N^N)
H-7	-7.51	0	99	0	1	π(P^C_2)
H-8	-7.59	0	2	98	0	π(P(OPh)$_3$)

Table S4 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1c**

MO	Energy	Contribution(%)				Assign
		Ir	P^C_2	P(OPh)$_3$	N^N	
L+8	-0.42	0	4	96	0	π*(P(OPh)$_3$)
L+7	-0.44	1	41	58	0	π*(P^C_2+ P(OPh)$_3$)
L+6	-0.45	1	47	51	1	π*(P^C_2 + P(OPh)$_3$)
L+5	-0.55	1	81	18	0	π*(P^C_2)
L+4	-0.59	3	17	80	1	π*(P(OPh)$_3$)
L+3	-0.67	12	27	58	4	d(Ir)+π*(P^C_2 + P(OPh)$_3$)
L+2	-0.74	16	32	46	6	d(Ir)+π*(P^C_2 + P(OPh)$_3$)
L+1	-1.57	0	1	1	98	π*(N^N)
L	-2.41	2	1	1	95	π*(N^N)
H	-6.55	20	76	2	2	d(Ir)+π(P^C_2)
H-1	-6.64	3	95	1	1	π(P^C_2)
H-2	-7.04	2	84	7	8	π(P^C_2)
H-3	-7.12	2	94	1	3	π(P^C_2)
H-4	-7.23	2	4	80	15	π(P(OPh)$_3$)
H-5	-7.24	5	13	43	39	π(P(OPh)$_3$+ N^N)
H-6	-7.28	2	2	76	21	π(P(OPh)$_3$+ N^N)
H-7	-7.52	0	99	0	1	π(P^C_2)
H-8	-7.59	0	1	98	0	π(P(OPh)$_3$)

Table S5 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1d**

MO	Energy	Contribution(%)				Assign
		Ir	P^C$_2$	P(OPh)$_3$	N^N	
L+8	-0.42	0	3	96	0	π*(P(OPh)$_3$)
L+7	-0.44	1	37	61	0	π*(P^C$_2$ + P(OPh)$_3$)
L+6	-0.45	2	50	47	1	π*(P^C$_2$+ P(OPh)$_3$)
L+5	-0.55	1	77	21	1	π*(P^C$_2$+ P(OPh)$_3$)
L+4	-0.58	2	21	76	1	π*(P^C$_2$+ P(OPh)$_3$)
L+3	-0.66	14	31	51	4	d(Ir)+π*(P^C$_2$ + P(OPh)$_3$)
L+2	-0.72	13	28	53	5	π*(P^C$_2$+ P(OPh)$_3$)
L+1	-1.81	0	1	1	99	π*(N^N)
L	-2.08	2	1	1	96	π*(N^N)
H	-6.52	21	75	2	2	d(Ir)+π(P^C$_2$)
H-1	-6.63	3	96	1	1	π(P^C$_2$)
H-2	-7.03	1	88	6	4	π(P^C$_2$)
H-3	-7.11	2	95	1	2	π(P^C$_2$)
H-4	-7.23	0	1	99	1	π(P(OPh)$_3$)
H-5	-7.26	1	5	91	4	π(P(OPh)$_3$)
H-6	-7.34	11	11	11	67	π(N^N)
H-7	-7.52	0	99	0	1	π(P^C$_2$)
H-8	-7.59	0	1	98	1	π(P(OPh)$_3$)

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

MO	Energy	Contribution(%)				Assign
		Ir	P^C$_2$	P(OPh)$_3$	N^N	
L+8	-0.37	4	51	44	2	π*(P^C$_2$ + P(OPh)$_3$)
L+7	-0.39	2	27	71	0	π*(P^C$_2$+ P(OPh)$_3$)
L+6	-0.40	0	6	93	1	π*(P(OPh)$_3$)
L+5	-0.50	7	53	37	3	π*(P^C$_2$ + P(OPh)$_3$)
L+4	-0.52	6	76	16	2	π*(P^C$_2$ + P(OPh)$_3$)
L+3	-0.56	7	24	66	3	π*(P^C$_2$ + P(OPh)$_3$)
L+2	-0.66	3	10	85	2	π*(P(OPh)$_3$)
L+1	-1.08	0	1	1	97	π*(N^N)
L	-1.69	2	2	1	95	π*(N^N)
H	-6.36	20	69	4	7	d(Ir)+π(P^C$_2$)
H-1	-6.52	6	79	1	14	π(P^C$_2$)
H-2	-6.56	5	40	0	55	π(P^C$_2$+ N^N)
H-3	-6.96	1	93	4	2	π(P^C$_2$)
H-4	-7.01	2	95	1	2	π(P^C$_2$)
H-5	-7.18	0	1	99	0	π(P(OPh)$_3$)
H-6	-7.20	0	1	98	1	π(P(OPh)$_3$)
H-7	-7.40	11	24	13	53	π(P^C$_2$+ N^N)
H-8	-7.47	1	93	2	4	π(P^C$_2$)

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

MO	Energy	Contribution(%)				Assign
		Ir	P^C$_2$	P(OPh)$_3$	N^N	
L+8	-0.32	5	69	25	1	π*(P^C$_2$ + P(OPh)$_3$)
L+7	-0.38	0	5	94	0	π*(P(OPh)$_3$)
L+6	-0.39	0	3	97	0	π*(P(OPh)$_3$)
L+5	-0.46	9	57	31	3	π*(P^C$_2$ + P(OPh)$_3$)
L+4	-0.48	4	87	7	1	π*(P^C$_2$)
L+3	-0.55	3	12	84	1	π*(P(OPh)$_3$)
L+2	-0.65	3	8	87	1	π*(P(OPh)$_3$)
L+1	-1.65	0	0	0	99	π*(N^N)
L	-2.11	2	1	1	95	π*(N^N)
H	-6.38	20	68	2	10	d(Ir)+π(P^C$_2$)
H-1	-6.52	5	94	1	1	π(P^C$_2$)
H-2	-6.71	7	19	2	72	π(P^C$_2$+ N^N)
H-3	-6.96	1	90	3	6	π(P^C$_2$)
H-4	-7.02	3	93	1	3	π(P^C$_2$)
H-5	-7.18	0	1	99	0	π(P(OPh)$_3$)
H-6	-7.20	0	1	99	0	π(P(OPh)$_3$)
H-7	-7.41	0	98	0	1	π(P^C$_2$)
H-8	-7.50	9	22	29	40	π(P^C$_2$ + P(OPh)$_3$+ N^N)

Table S8 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2b**

MO	Energy		Contribution(%)			Assign
		Ir	P^C_2	P(OPh)$_3$	N^N	
L+8	-0.39	2	20	77	1	π*(P^C_2 + P(OPh)$_3$)
L+7	-0.48	1	91	8	0	π*(P^C_2)
L+6	-0.56	3	1	96	0	π*(P(OPh)$_3$)
L+5	-0.57	2	2	96	0	π*(P(OPh)$_3$)
L+4	-0.66	5	47	48	0	π*(P^C_2+ P(OPh)$_3$)
L+3	-1.02	17	29	49	6	d(Ir)+π*(P^C_2 + P(OPh)$_3$)
L+2	-1.34	21	39	29	11	d(Ir)+π*(P^C_2+ P(OPh)$_3$+ N^N)
L+1	-1.62	1	1	1	97	π*(N^N)
L	-2.43	2	2	3	93	π*(N^N)
H	-6.57	22	74	1	3	d(Ir)+π(P^C_2)
H-1	-6.73	2	97	1	1	π(P^C_2)
H-2	-7.03	4	61	6	29	π(P^C_2+ N^N)
H-3	-7.15	6	49	4	42	π(P^C_2+ N^N)
H-4	-7.21	2	57	38	3	π(P^C_2+ P(OPh)$_3$)
H-5	-7.23	1	16	82	1	π(P(OPh)$_3$)
H-6	-7.25	1	15	75	9	π(P(OPh)$_3$)
H-7	-7.41	0	97	1	2	π(P^C_2)
H-8	-7.64	0	1	99	0	π(P(OPh)$_3$)

Table S9 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2c**

MO	Energy	Contribution(%)				Assign
		Ir	P^C$_2$	P(OPh)$_3$	N^N	
L+8	-0.40	1	23	76	1	π*(P^C$_2$+ P(OPh)$_3$)
L+7	-0.41	2	53	44	1	π*(P^C$_2$ + P(OPh)$_3$)
L+6	-0.43	1	13	85	1	π*(P(OPh)$_3$)
L+5	-0.53	2	76	21	1	π*(P^C$_2$+ P(OPh)$_3$)
L+4	-0.56	5	30	63	2	π*(P^C$_2$+ P(OPh)$_3$)
L+3	-0.61	15	38	42	5	d(Ir)+π*(P^C$_2$+ P(OPh)$_3$)
L+2	-0.69	5	14	78	2	π*(P(OPh)$_3$)
L+1	-1.39	0	1	1	98	π*(N^N)
L	-2.23	2	1	1	95	π*(N^N)
H	-6.45	19	63	2	16	d(Ir)+π(P^C$_2$+ N^N)
H-1	-6.58	4	94	1	2	π(P^C$_2$)
H-2	-6.68	6	21	1	72	π(P^C$_2$+ N^N)
H-3	-7.01	1	92	5	3	π(P^C$_2$)
H-4	-7.07	2	95	1	2	π(P^C$_2$)
H-5	-7.21	0	1	99	0	π(P(OPh)$_3$)
H-6	-7.24	0	2	98	0	π(P(OPh)$_3$)
H-7	-7.48	1	93	1	5	π(P^C$_2$)
H-8	-7.54	9	22	28	42	π(P^C$_2$+ P(OPh)$_3$+ N^N)

Table S10 Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2d**

MO	Energy	Contribution(%)				Assign
		Ir	P^C_2	$P(OPh)_3$	N^N	
L+8	-0.39	1	12	86	1	π*($P(OPh)_3$)
L+7	-0.41	3	63	34	1	π*(P^C_2 + $P(OPh)_3$)
L+6	-0.42	1	12	87	1	π*($P(OPh)_3$)
L+5	-0.52	3	70	27	1	π*(P^C_2+ $P(OPh)_3$)
L+4	-0.55	5	39	53	2	π*(P^C_2+ $P(OPh)_3$)
L+3	-0.59	14	38	43	5	d(Ir)+π*(P^C_2 + $P(OPh)_3$)
L+2	-0.68	4	13	81	2	π*($P(OPh)_3$)
L+1	-1.64	0	1	1	99	π*(N^N)
L	-1.89	2	1	1	95	π*(N^N)
H	-6.43	21	66	2	11	d(Ir)+π(P^C_2)
H-1	-6.56	3	95	1	2	π(P^C_2)
H-2	-6.72	7	18	1	74	π(N^N)
H-3	-7.00	1	91	4	4	π(P^C_2)
H-4	-7.05	3	94	1	3	π(P^C_2)
H-5	-7.20	0	1	99	0	π($P(OPh)_3$)
H-6	-7.23	0	1	98	0	π($P(OPh)_3$)
H-7	-7.48	1	91	2	6	π(P^C_2)
H-8	-7.53	8	25	28	39	π(P^C_2+ $P(OPh)_3$+ N^N)

Table S11 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution and transition characters for **1-1d** in CH_2Cl_2 media, along with the experimental data for **1**

	state	λ/E	*f*	Configuration	Assignment	Exptl.[a]
1	S_1	326/3.79	0.022	H→L(85%)	[d(Ir)+π(P^C$_2$)→π*(N^N)] MLCT/LLCT	310
	S_3	288/4.30	0.125	H-2→L(55%)	[d(Ir)+π(P^C$_2$+ N^N)→π*(N^N)] MLCT/LLCT/ILCT	
	S_6	271/4.57	0.057	H-4→L (46%)	[π(P^C$_2$+ N^N)→π*(N^N)] LLCT/ILCT	
	S_{11}	251/4.94	0.081	H-7→L (59%)	[π(P^C$_2$)→π*(N^N)] LLCT/ILCT	
	S_{13}	247/5.01	0.073	H-2→L+1(53%)	[π(P^C$_2$+ N^N)→π*(N^N)] MLCT/LLCT/ILCT	
1a	S_1	363/3.41	0.038	H→L(70%)	[d(Ir)+π(P^C$_2$)→π*(N^N)] MLCT/LLCT/ILCT	
	S_7	293/4.21	0.059	H-6→L(58%)	[π(N^N)→π*(N^N)] ILCT	
	S_{15}	263/4.70	0.085	H-6→L+1(61%)	[π(N^N)→π*(N^N)] ILCT	
	S_{31}	239/5.17	0.110	H-8→L+2(54%)	[π(P(OPh)$_3$)→π*(P^C$_2$ + P(OPh)$_3$)] LLCT/ILCT	
1b	S_1	359/3.44	0.017	H→L(80%)	[d(Ir)+π(P^C$_2$)→π*(N^N)] MLCT/LLCT	
	S_4	302/4.10	0.047	H-2→L (64%)	[π(P^C$_2$)→π*(N^N)] LLCT	
	S_6	286/4.30	0.122	H-6→L (46%)	[π(N^N)→π*(N^N)] ILCT	
	S_{15}	260/4.76	0.054	H-3→L+4 (57%)	[π(P^C$_2$)→π*(P(OPh)$_3$)] LLCT	
1c	S_1	369/3.35	0.025	H→L(74%)	[d(Ir)+π(P^C$_2$)→π*(N^N)] MLCT/LLCT	
	S_3	315/3.93	0.081	H-2→L (48%)	[π(P^C$_2$)→π*(N^N)] LLCT	
	S_{11}	272/4.54	0.090	H-8→L+2 (51%)	[π(P(OPh)$_3$)→d(Ir)+π*(P^C$_2$ + P(OPh)$_3$)] MLCT/LLCT/ILCT	
	S_{26}	246/5.03	0.057	H-5→L+5 (63%)	[π(P(OPh)$_3$+ N^N)→π*(P^C$_2$)] MLCT/LLCT	
1d	S_1	340/3.64	0.021	H→L(81%)	[d(Ir)+π(P^C$_2$)→π*(N^N)] MLCT/LLCT	
	S_6	289/4.28	0.061	H-2→L (53%)	[π(P^C$_2$)→π*(N^N)] LLCT	
	S_{10}	269/4.59	0.062	H-2→L+1 (58%)	[π(P^C$_2$)→π*(N^N)] LLCT	
	S_{38}	230/5.37	0.107	H-2→L+3 (43%)	[π(P^C$_2$)→d(Ir)+π*(P^C$_2$ + P(OPh)$_3$)] MLCT/LLCT/ILCT	

[a] Ref. 11.

Table S12 Selected calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution and transition characters for **2-2d** in CH_2Cl_2 media, along with the experimental data for **2**

	state	λ/E	*f*	Configuration	Assignment	Exptl.[a]
2	S_1	322/3.84	0.034	H→L(91%)	[d(Ir)+π(P^C_2)→π*(N^N)]MLCT/LLCT	322
	S_2	307/4.02	0.099	H-1→L (74%)	[π(P^C_2)→π*(N^N)] LLCT	
	S_4	273/4.52	0.109	H→L+1(83%)	[d(Ir)+π(P^C_2+ N^N)→π*(N^N)] MLCT/LLCT/ILCT	
	S_{10}	255/4.85	0.051	H-7→L (45%)	[π(P^C_2+ N^N)→π*(N^N)] LLCT/ILCT	
2a	S_1	358/3.45	0.029	H→L(82%)	[d(Ir)+π(P^C_2)→π*(N^N)] MLCT/LLCT	
	S_8	287/4.30	0.103	H-2→L+1(73%)	[π(P^C_2+ N^N)→π*(N^N)] LLCT/ILCT	
	S_{12}	271/4.56	0.065	H-8→L (48%)	[π(P^C_2 + P(OPh)$_3$+ N^N)→π*(N^N)] LLCT/ILCT	
	S_{29}	242/5.10	0.147	H-1→L+4(60%)	[π(P^C_2)→π*(P^C_2)] ILCT	
2b	S_1	371/3.33	0.018	H→L(89%)	[d(Ir)+π(P^C_2)→π*(N^N)] MLCT/LLCT	
	S_3	321/3.85	0.113	H-2→L (64%)	[π(P^C_2+ N^N)→π*(N^N)] LLCT/ILCT	
	S_{19}	264/4.69	0.055	H-2→L+2(45%)	[π(P^C_2+ N^N)→d(Ir)+π*(P^C_2 + P(OPh)$_3$+ N^N)] MLCT/LLCT/ILCT	
	S_{39}	237/5.22	0.061	H-7→L+2 (43%)	[π(P^C_2)→d(Ir)+π*(P^C_2 + P(OPh)$_3$+ N^N)] MLCT/LLCT/ILCT	
2c	S_1	365/3.39	0.026	H→L(86%)	[d(Ir)+π(P^C_2+ N^N)→π*(N^N)] MLCT/LLCT/ILCT	
	S_3	333/3.71	0.080	H-2→L (70%)	[π(P^C_2+ N^N)→π*(N^N)] LLCT/ILCT	
	S_7	286/4.32	0.059	H→L+1 (77%)	[d(Ir)+π(P^C_2+ N^N)→π*(N^N)] MLCT/LLCT/ILCT	
	S_9	279/4.43	0.049	H-5→L (33%)	[π(P(OPh)$_3$)→π*(N^N)] LLCT	
2d	S_1	334/3.71	0.020	H→L(88%)	[d(Ir)+π(P^C_2)→π*(N^N)] MLCT/LLCT	
	S_4	302/4.09	0.087	H-2→L (44%)	[π(N^N)→π*(N^N)] ILCT	
	S_5	294/4.20	0.092	H-1→L+1 (58%)	[π(P^C_2)→π*(N^N)] LLCT	
	S_{16}	257/4.81	0.117	H-8→L (51%)	[π(P^C_2 + P(OPh)$_3$+ N^N)→π*(N^N)] LLCT/ILCT	

[a] Ref. 11.

Table S13 The plots of the hole and virtual natural transition orbitals (NTOs) correspond to electronic transitions from the ground state to the singlet excited states S_1 for all the studied complexes

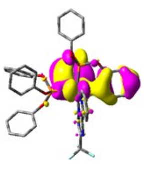
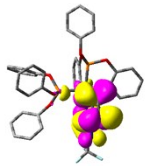
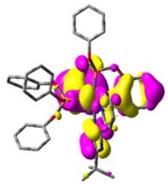
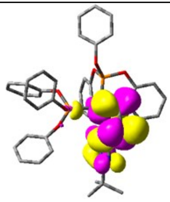
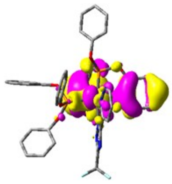
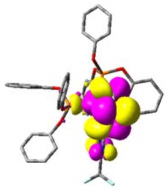
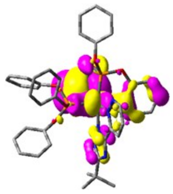
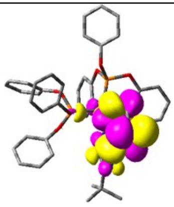
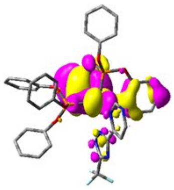
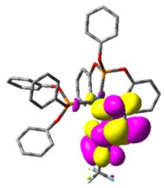
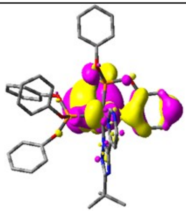
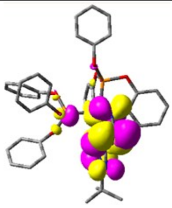
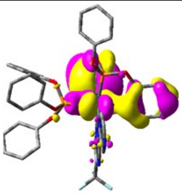
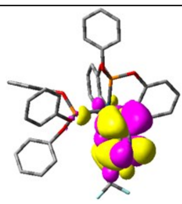
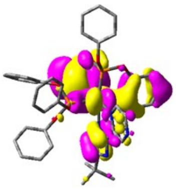
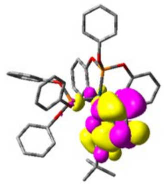
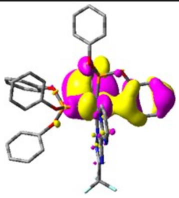
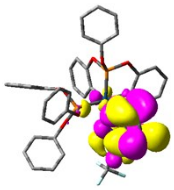
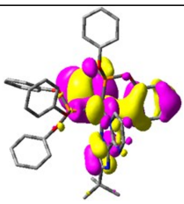
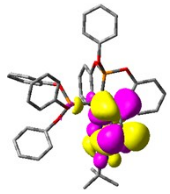
Complexes	Hole	Virtual	Complexes	Hole	Virtual
1			**2**		
1a			**2a**		
1b			**2b**		
1c			**2c**		
1d			**2d**		

Table S14 Calculated phosphorescent emission wavelength (λ, in nm) for **1** and **2** in CH_2Cl_2 media with the TDDFT method at M062X, M052X, BP86 and PBE0 level, respectively, together with the experimental values

	M062X	M052X	BP86	PBE0	Exptl.[a]
1	464	489	533	531	458
2	493	509	537	551	492

[a] Ref. 11.

Table S15 Frontier molecular orbital energies (eV) and composition (%) of **1-6d** and **2-2d** in the lowest lying triplet excited state (L and H represent the LUMO and HOMO, respectively)

	MO	*E*	MO composition(%)				Assign
1			Ir	P^C$_2$	P(OPh)$_3$	N^N	
	L	-2.26	2	1	1	96	π*(N^N)
	H	-6.41	22	62	2	15	d(Ir)+π(P^C$_2$+ N^N)
	H-2	-6.73	4	18	0	77	π(N^N)
1a			Ir	P^C$_2$	P(OPh)$_3$	N^N	
	L	-2.74	4	2	2	92	π*(N^N)
	H	-6.03	26	48	1	25	d(Ir)+π(P^C$_2$+ N^N)
1b			Ir	P^C$_2$	P(OPh)$_3$	N^N	
	L	-2.70	2	1	1	95	π* (N^N)
	H	-6.05	26	69	2	4	d(Ir)+π(P^C$_2$)
	H-1	-6.54	19	9	17	54	d(Ir)+π(P(OPh)$_3$+ N^N)
1c			Ir	P^C$_2$	P(OPh)$_3$	N^N	
	L	-2.72	3	1	1	95	π* (N^N)
	H	-6.49	21	69	2	9	d(Ir)+π(P^C$_2$)
	H-2	-6.92	4	24	1	71	π(P^C$_2$+ N^N)
1d			Ir	P^C$_2$	P(OPh)$_3$	N^N	

	L	-2.52	2	1	1	95	π*(N^N)
	H	-6.40	24	49	1	26	d(Ir)+π(P^C_2+ N^N)
2			Ir	P^C_2	P(OPh)$_3$	N^N	
	L	-1.97	2	1	1	95	π*(N^N)
	H	-6.11	8	10	1	81	π(N^N)
2a			Ir	P^C_2	P(OPh)$_3$	N^N	
	L	-2.30	3	2	1	94	π*(N^N)
	H	-6.23	18	37	2	43	d(Ir)+π(P^C_2+ N^N)
2b			Ir	P^C_2	P(OPh)$_3$	N^N	
	L	-2.68	3	2	3	93	π*(N^N)
	H	-6.50	23	63	2	12	d(Ir)+π(P^C_2)
	H-1	-6.72	4	96	0	0	π(P^C_2)
2c			Ir	P^C_2	P(OPh)$_3$	N^N	
	L	-2.47	3	1	1	95	π*(N^N)
	H	-6.26	11	18	1	70	d(Ir)+π(P^C_2+ N^N)
2d			Ir	P^C_2	P(OPh)$_3$	N^N	
	L	-2.15	2	1	1	95	π*(N^N)
	H	-6.28	15	28	2	55	d(Ir)+π(P^C_2+ N^N)

Table S16 The xyz coordinates for the optimized structures for **1** in the S_0 and T_1 states at PBE0/6-31G* level

	S_0			**T_1**		
Ir	-0.19286700	-1.13309500	-0.03083700	0.22391100	-1.14477900	0.02720800
P	1.95853000	-1.55987500	-0.18215900	-1.92172500	-1.60963700	0.17733300
P	-0.03981300	1.17030400	0.08384300	0.01408000	1.16946500	-0.08881700
O	2.45154000	-1.24948600	-1.68877700	-2.41635900	-1.31644200	1.68648400
O	2.18358700	-3.15201400	0.02163300	-2.11904600	-3.20333700	-0.03648100
O	3.09654000	-0.92172500	0.73561800	-3.07171700	-0.98377900	-0.73340300
O	0.08453200	1.77226300	1.58523000	-0.15817100	1.77133000	-1.58378100
O	-1.28351300	1.96553700	-0.57495600	1.25484300	1.99092800	0.54376600
O	1.26986700	1.74927900	-0.67285200	-1.29300900	1.71107700	0.69877400
N	-0.61572800	-1.34469000	2.08723700	0.62764000	-1.30381500	-2.07130800
N	-2.27529300	-1.07293600	0.06165200	2.29185200	-1.03388700	-0.04455400
N	-3.26551000	-0.92873200	-0.81300100	3.26830300	-0.88754700	0.81844400
N	-4.14600100	-1.18187400	1.25224500	4.21087900	-1.06360900	-1.24739200
C	0.29221400	-1.44910900	3.06268400	-0.22908500	-1.39514300	-3.06216100
H	1.33091300	-1.39291400	2.76126300	-1.28069100	-1.38237000	-2.79485500
C	-0.06176000	-1.60933600	4.39110400	0.14346100	-1.50074300	-4.41212800
H	0.71286500	-1.68935500	5.14396700	-0.63109700	-1.57675500	-5.16441900
C	-1.40992400	-1.66214000	4.72625100	1.53269200	-1.51227600	-4.76592400
H	-1.71792300	-1.78875600	5.75825600	1.83216000	-1.60003400	-5.80353700
C	-2.35653800	-1.54489500	3.72251800	2.44958200	-1.40886500	-3.77603800
H	-3.42000000	-1.57134700	3.92690300	3.51621900	-1.40519000	-3.97035100
C	-1.92578900	-1.38438500	2.41183000	2.01840900	-1.29193100	-2.40533200
C	-2.81654600	-1.22483600	1.28176700	2.85277700	-1.14442600	-1.32358600
C	-4.35891000	-1.00026200	-0.05942800	4.38511400	-0.91231200	0.05178300
C	-5.73027300	-0.87019200	-0.62914600	5.74619800	-0.76174800	0.65809800
C	1.38546800	-1.05285500	-2.57874500	-1.35542800	-1.10329300	2.57770800
C	0.08177100	-0.97715600	-2.07260300	-0.05156500	-1.00363800	2.07284700
C	-0.92579200	-0.77702800	-3.01830800	0.94867900	-0.78875100	3.02502300
H	-1.95460200	-0.71316600	-2.67915900	1.97775100	-0.70532700	2.69239800
C	-0.63897000	-0.65630100	-4.37763500	0.65619100	-0.67672300	4.38365600
H	-1.44949200	-0.50031300	-5.08354000	1.46185500	-0.50886200	5.09236400
C	0.67269800	-0.73624400	-4.83147300	-0.65519400	-0.78015000	4.83334000
H	0.89884000	-0.64334100	-5.88899000	-0.88620300	-0.69399100	5.89035600
C	1.70348200	-0.93963200	-3.92081200	-1.67947100	-0.99883000	3.91869200
H	2.73861700	-1.01082200	-4.23772500	-2.71414500	-1.08860900	4.23228400
C	0.99992200	-3.89268500	-0.11869500	-0.92145000	-3.92379400	0.08705200
C	-0.22122600	-3.21323200	-0.19156700	0.28824000	-3.22390700	0.16054800
C	-1.35116600	-4.01749800	-0.35080600	1.43263200	-4.01115100	0.29974700
H	-2.32723600	-3.55251400	-0.44247200	2.40171500	-3.53168600	0.38973800
C	-1.26309200	-5.40746300	-0.40645900	1.36951000	-5.40291800	0.33718600
H	-2.16549700	-5.99919100	-0.52838300	2.28322500	-5.98009600	0.44329100
C	-0.02689400	-6.03506800	-0.31221800	0.14371200	-6.05061800	0.24486600
H	0.04764000	-7.11706800	-0.35577800	0.08801600	-7.13416500	0.27508200
C	1.12584800	-5.26982300	-0.17230600	-1.02285400	-5.30338300	0.12389800
H	2.10780200	-5.72712800	-0.11006700	-1.99732700	-5.77655400	0.06290800
C	4.47653400	-1.08368200	0.54972200	-4.44876500	-1.16947500	-0.54698400
C	5.10703800	-2.20734300	1.05939200	-5.06189000	-2.29783000	-1.06727300
H	4.52605200	-2.97688000	1.55435600	-4.46942200	-3.05288300	-1.57085600
C	6.48590700	-2.31794000	0.91608800	-6.43868300	-2.43156900	-0.92381200
H	6.99382500	-3.19259500	1.30887900	-6.93317200	-3.31009700	-1.32499200
C	7.20953300	-1.31633300	0.27775100	-7.17736200	-1.44782300	-0.27501700
H	8.28521600	-1.40848900	0.17029600	-8.25137700	-1.55787500	-0.16773500
C	6.55367600	-0.19580800	-0.22173400	-6.53878900	-0.32204200	0.23491900

H	7.11411400	0.58851300	-0.71977100	-7.11104200	0.44849900	0.74096600
C	5.17541600	-0.07170100	-0.08826900	-5.16277800	-0.17489600	0.10154500
H	4.64354600	0.79271800	-0.46981100	-4.64424600	0.69406600	0.49103500
C	0.94321800	2.76051100	2.05253600	-1.05264900	2.73773600	-2.03036100
C	2.27861200	2.44835600	2.27125900	-2.37994100	2.38544900	-2.23633200
H	2.64637500	1.45508400	2.03620900	-2.71170900	1.37768900	-2.01002500
C	3.12342500	3.42594300	2.78428800	-3.26244500	3.34149800	-2.72582300
H	4.16951600	3.19127800	2.95281300	-4.30241700	3.07496700	-2.88446900
C	2.63296500	4.69373000	3.08156400	-2.81719700	4.62831800	-3.01227500
H	3.29591600	5.45330100	3.48259500	-3.50942200	5.37113800	-3.39477500
C	1.28889200	4.98217200	2.86896700	-1.48041000	4.95713800	-2.81304200
H	0.89819100	5.96679100	3.10464100	-1.12443200	5.95666500	-3.04084300
C	0.43315300	4.01520700	2.35174600	-0.58707900	4.01188800	-2.31978000
H	-0.61658100	4.22574900	2.17876200	0.45759400	4.25438100	-2.15885200
C	-1.93888500	3.10241400	-0.11527500	1.86305300	3.15419200	0.08368500
C	-2.88463900	2.97275800	0.89270000	2.75646300	3.07535900	-0.97602000
H	-3.08014700	1.99916300	1.32920900	2.94415700	2.12159500	-1.45691000
C	-3.57192600	4.10218200	1.32210700	3.39950100	4.23131100	-1.40353700
H	-4.31105400	4.00836300	2.11102200	4.09712500	4.17707100	-2.23290800
C	-3.31960100	5.34121800	0.74163700	3.15540300	5.44613900	-0.77091900
H	-3.85936600	6.21999300	1.07880800	3.66069800	6.34564000	-1.10679400
C	-2.38106700	5.44749400	-0.27937800	2.26860900	5.50171500	0.29925000
H	-2.18639000	6.40873700	-0.74393200	2.08013100	6.44402800	0.80342800
C	-1.68338600	4.32646100	-0.71599100	1.61544700	4.35382700	0.73493100
H	-0.95069900	4.39555200	-1.51203700	0.92318100	4.38309200	1.56878500
C	1.36333600	2.81935800	-1.55574300	-1.39603800	2.77737500	1.58543500
C	0.87664600	2.67859100	-2.84781300	-0.88946400	2.64196800	2.87035900
H	0.39789700	1.75155400	-3.14622600	-0.39030000	1.72277600	3.15950100
C	1.01501900	3.74029500	-3.73461900	-1.03569400	3.69830100	3.76237600
H	0.63364800	3.64155800	-4.74580300	-0.63919400	3.60382300	4.76813600
C	1.63838200	4.91782500	-3.33262900	-1.68641700	4.86500800	3.37233500
H	1.74352700	5.74281100	-4.02959100	-1.79763600	5.68593700	4.07313200
C	2.13159200	5.03222900	-2.03692300	-2.19973200	4.97354200	2.08394800
H	2.62362700	5.94565800	-1.71866600	-2.71362400	5.87821000	1.77538000
C	1.99607000	3.98054800	-1.13678900	-2.05704100	3.92711600	1.17887300
H	2.36869500	4.05455000	-0.12103000	-2.44595500	3.99662400	0.16894100
F	-6.38151900	0.18499500	-0.11038700	6.37099600	0.32164700	0.17509300
F	-6.48247700	-1.95091600	-0.36221500	6.52100800	-1.81864600	0.37734600
F	-5.70457200	-0.71462400	-1.95442000	5.68694600	-0.64024600	1.98401800

Table S17 The xyz coordinates for the optimized structures for **2** in the S_0 and T_1 states at PBE0/6-31G* level

	S0			T1		
Ir	0.18083800	-1.12472000	0.02024900	0.22362100	-1.13608700	0.02489300
P	-1.96883000	-1.56313500	0.17180100	-1.92006300	-1.61230700	0.17287200
P	0.02684700	1.17587400	-0.07135800	0.00447600	1.17252200	-0.08777800
O	-2.46173500	-1.26871800	1.68357200	-2.41796500	-1.32898300	1.68431300
O	-2.18689900	-3.15686800	-0.04011600	-2.11023200	-3.20799600	-0.04347600
O	-3.12000400	-0.92834600	-0.73466100	-3.08144300	-0.99377700	-0.73133400
O	-0.08651300	1.79136000	-1.56925600	-0.16625200	1.78359700	-1.58016700
O	1.25899200	1.97641500	0.60548600	1.23865800	2.00345600	0.55095500
O	-1.28711400	1.75244200	0.68325800	-1.30557800	1.71208200	0.69984700
N	0.60234600	-1.30445400	-2.09812700	0.63161700	-1.28832000	-2.07601300
N	2.26045400	-1.06178400	-0.06992700	2.28439700	-1.02094000	-0.04109200
N	3.25753100	-0.94899800	0.80992400	3.26212700	-0.88761800	0.81775400
N	4.13388900	-1.16562000	-1.25130900	4.20192000	-1.05329700	-1.25290600
C	-0.30453400	-1.39356500	-3.07652700	-0.24064900	-1.38284500	-3.06592200
H	-1.34343500	-1.34580900	-2.77373700	-1.28838000	-1.37282500	-2.78400400
C	0.04958100	-1.52829100	-4.40701700	0.11774400	-1.48403000	-4.40863600
H	-0.72398600	-1.59687100	-5.16213500	-0.66075300	-1.56126300	-5.15732000
C	1.39970100	-1.57074400	-4.74059900	1.49965400	-1.48633200	-4.76739800
H	1.70927200	-1.67785900	-5.77457000	1.79804700	-1.56878900	-5.80623300
C	2.34425600	-1.46872500	-3.73475200	2.42548600	-1.37944900	-3.77732800
H	3.40817800	-1.48832500	-3.93764900	3.49044000	-1.36897300	-3.98228300
C	1.91488500	-1.33255900	-2.41863700	2.00760700	-1.27096700	-2.41483000
C	2.80336700	-1.19410100	-1.28756500	2.85527300	-1.12825500	-1.33681100
C	4.36938500	-1.01371200	0.06938800	4.40603300	-0.91033000	0.05327200
C	5.76042400	-0.91850600	0.64203900	5.77218500	-0.77494700	0.65741400
C	-1.39444600	-1.07367600	2.57224300	-1.35863700	-1.11113900	2.57674600
C	-0.09199800	-0.98985000	2.06382900	-0.05518600	-1.00312700	2.07327600
C	0.91750300	-0.79307400	3.00800400	0.94192300	-0.78412900	3.02747100
H	1.94394100	-0.72627900	2.66051800	1.97030500	-0.69540400	2.69295800
C	0.63377900	-0.68158700	4.36883000	0.64751800	-0.67515200	4.38631000
H	1.44525200	-0.52769400	5.07435600	1.45139900	-0.50360100	5.09646200
C	-0.67673400	-0.76832200	4.82542300	-0.66370800	-0.78632900	4.83452800
H	-0.90074500	-0.68248800	5.88409400	-0.89685500	-0.70248500	5.89135900
C	-1.70927700	-0.96977900	3.91607800	-1.68511000	-1.01001200	3.91780300
H	-2.74331900	-1.04633900	4.23557500	-2.71981000	-1.10579000	4.22991000
C	-0.99821000	-3.89126800	0.08887500	-0.90887800	-3.92176200	0.07739600
C	0.21947000	-3.20532800	0.16076900	0.29709900	-3.21544900	0.15218300
C	1.35524100	-4.00359600	0.30866200	1.44537100	-3.99766900	0.28825900
H	2.32743400	-3.52988000	0.39822300	2.41168000	-3.51226900	0.37788900
C	1.27554500	-5.39450600	0.35497000	1.38970800	-5.38999300	0.32225700
H	2.18191300	-5.98212800	0.46821900	2.30666100	-5.96283500	0.42521200
C	0.04258700	-6.02902700	0.26215300	0.16734500	-6.04410100	0.22925900
H	-0.02532800	-7.11181700	0.29836800	0.11721000	-7.12806700	0.25634600
C	-1.11545400	-5.26974200	0.13314400	-1.00289300	-5.30223800	0.11085100
H	-2.09486400	-5.73282800	0.07221600	-1.97500700	-5.78028500	0.04887400
C	-4.49653800	-1.10429200	-0.54418900	-4.45456500	-1.19603000	-0.54169200
C	-5.11870300	-2.23446900	-1.05028100	-5.05743100	-2.32765000	-1.06739400
H	-4.53213900	-2.99932100	-1.54588700	-4.45809700	-3.07270100	-1.57769800
C	-6.49600600	-2.35801400	-0.90255500	-6.43216400	-2.47788700	-0.92068900
H	-6.99674000	-3.23803400	-1.29267200	-6.91796400	-3.35928100	-1.32627000
C	-7.22738800	-1.36248300	-0.26354400	-7.18001000	-1.50684200	-0.26329100
H	-8.30185000	-1.46465800	-0.15276700	-8.25242400	-1.62961700	-0.15352200
C	-6.58052800	-0.23507100	0.23219100	-6.55237500	-0.37729100	0.25188700

H	-7.14683600	0.54479500	0.73065500	-7.13165900	0.38362100	0.76454000
C	-5.20392200	-0.09829700	0.09429500	-5.17852800	-0.21395400	0.11523700
H	-4.67910500	0.77183700	0.47267600	-4.66864400	0.65837900	0.50861200
C	-0.93937700	2.78283200	-2.03714500	-1.06653400	2.74358400	-2.02541000
C	-2.27579600	2.47746600	-2.26022100	-2.39244400	2.38469200	-2.22992100
H	-2.64910900	1.48583600	-2.02684900	-2.71853000	1.37505100	-2.00370400
C	-3.11434200	3.45930900	-2.77541000	-3.28059000	3.33616500	-2.71805600
H	-4.16100900	3.22966400	-2.94735800	-4.31929000	3.06397900	-2.87561100
C	-2.61698900	4.72484300	-3.07089000	-2.84277400	4.62548900	-3.00489100
H	-3.27504900	5.48763900	-3.47389600	-3.53946400	5.36462100	-3.38650000
C	-1.27217700	5.00675300	-2.85401000	-1.50743700	4.96124000	-2.80739800
H	-0.87605400	5.98957200	-3.08827200	-1.15699800	5.96266400	-3.03564800
C	-0.42281700	4.03551100	-2.33442600	-0.60861700	4.02055600	-2.31548400
H	0.62736700	4.24073400	-2.15772700	0.43503200	4.26835500	-2.15587600
C	1.93684700	3.09496600	0.13897400	1.85002200	3.16133600	0.08618100
C	2.88638600	2.94109900	-0.86231400	2.74045200	3.07773800	-0.97618400
H	3.06652700	1.96036700	-1.28974200	2.92120800	2.12284400	-1.45758300
C	3.59544400	4.05552900	-1.29607400	3.38717900	4.23058800	-1.40703700
H	4.33703100	3.94314300	-2.08033200	4.08110600	4.17250300	-2.23931400
C	3.36091700	5.30336600	-0.72675800	3.15037300	5.44738600	-0.77522900
H	3.91754900	6.17017300	-1.06757100	3.65822000	6.34437900	-1.11402200
C	2.41748700	5.43391000	0.28701500	2.26626100	5.50814300	0.29691600
H	2.23581500	6.40228600	0.74201800	2.08249800	6.45213500	0.79977600
C	1.69798100	4.32832700	0.72760200	1.60920400	4.36359100	0.73557900
H	0.95980500	4.41526600	1.51701300	0.91789800	4.39681700	1.57018300
C	-1.37703100	2.82193600	1.56662200	-1.40824000	2.77745900	1.58639700
C	-0.89930400	2.67505800	2.86156100	-0.90445200	2.64058400	2.87248200
H	-0.43039400	1.74315500	3.16071200	-0.40831900	1.71972000	3.16173700
C	-1.03426900	3.73593100	3.74974800	-1.05052000	3.69636600	3.76513600
H	-0.66012100	3.63190700	4.76313600	-0.65650200	3.60016200	4.77176000
C	-1.64526800	4.91961000	3.34655200	-1.69830000	4.86474600	3.37499200
H	-1.74793800	5.74397000	4.04466700	-1.80951800	5.68524700	4.07633800
C	-2.12931000	5.04076200	2.04807500	-2.20902000	4.97511000	2.08574500
H	-2.61173200	5.95892600	1.72862100	-2.72090900	5.88087200	1.77694200
C	-1.99699700	3.98971800	1.14660900	-2.06647900	3.92909800	1.18013300
H	-2.36295600	4.06915100	0.12884500	-2.45365100	4.00018700	0.16964000
C	6.45873100	0.30673900	0.03899300	6.43142700	0.48194600	0.06901000
H	5.93241600	1.22942200	0.30237100	5.86895300	1.38296200	0.33072400
H	7.48472900	0.38294100	0.41345700	7.44525200	0.58714100	0.46677800
H	6.49564900	0.23691000	-1.05098700	6.49049700	0.41908500	-1.01953600
C	6.54082400	-2.18177200	0.26019000	6.59773600	-2.00890500	0.26520800
H	7.56950200	-2.12079000	0.63001600	7.61444700	-1.91341600	0.65789000
H	6.07873100	-3.07529200	0.69113200	6.16031700	-2.92358100	0.67590400
H	6.57271800	-2.30716600	-0.82474300	6.65326100	-2.11387600	-0.82010200
C	5.71333600	-0.78395800	2.16213500	5.70043600	-0.65895300	2.17808200
H	5.16656000	0.11158700	2.46776100	5.12301400	0.21544100	2.48719200
H	5.22576800	-1.64580200	2.62493300	5.23822600	-1.54150300	2.62683200
H	6.73090500	-0.71391100	2.55897300	6.71117800	-0.56021400	2.58442900