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Enhancing the electronic properties and quantum efficiency of sulfonyl/phosphoryl-substituted blue iridium complexes via different ancillary ligands

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Table S1 Main optimized geometry structural parameters of the complex **1a** in the ground at the DFT/PBE0, DFT/ B3LYP and DFT/ M062X level, respectively, together with the experimental values

item	PBE0	B3LYP	M062X	Exp.[21]
Bond Length				
Ir-N1	2.037	2.062	2.052	2.020
Ir-C1	1.986	2.005	1.978	1.989
Ir-C2	1.992	2.008	1.984	1.998
Ir-N2	2.048	2.074	2.070	2.039
Ir-N3	2.163	2.205	2.213	2.140
Ir-O1	2.149	2.172	2.183	2.149
Bond Angle				
N1-Ir-C1	80.7	80.4	80.7	81.3
N1-Ir-C2	95.18	95.5	95.1	95.0
N1-Ir-N2	175.5	175.6	175. 6	175.7
N1-Ir-O1	93.4	93.4	93.2	92.3
N1-Ir-N3	88.5	88.4	88.2	88.3
C1-Ir-C2	90.7	91.4	87.0	88.0
C1-Ir-N2	98.2	98.4	97.8	96.8
C1-Ir-O1	171.9	171.5	172.0	171.0
C1-Ir-N3	97.0	97.3	98.2	95.9
C2-Ir-N2	80.5	80.2	80.7	81. 1
C2-Ir-O1	95.3	95.1	99.1	98.8
C2-Ir-N3	171.8	170.9	174.3	175.2
N2-Ir-O1	88.1	88.2	88.5	90.0
N2-Ir-N3	95.9	95.9	96.2	95.7
O1-Ir-N3	77.1	76.5	76.0	77.6
Dihedral Angle/deg				
C-C-S1-C	96. 8	95.8	83.7	103.9
C-C-S2-C	-84.73	-86.3	-70.6	-79.2

Table S2 Calculated phosphorescent emission wavelength (nm)/energies (eV), of the complexes **1a** and **2a** in CH_2Cl_2 media with the TDDFT method at the B3LYP, M062X and PBE0 level, respectively, together with the experimental values

	λ_{cal}/E(eV) (B3LYP)	λ_{cal}/E(eV) (M062X)	λ_{cal}/E(eV) (PBE0)	Exp.[21]
1a	525/2.36	460/ 2.69	537/2.31	459
2a	525/2.36	461/2.69	537/2.31	460

Table S3 Calculated wavelength (nm), oscillator strength (*f*) and dominant orbital excitations of the lowest singlet and triplet absorptions for **2a**-**2d**

	state	λ_{cal}	*f*	Configuration	Character	Exp.[21]
2a	S_1	379	0.0537	HOMO->LUMO (76%),	MLCT/ILCT/LLCT	374
				HOMO->L+1 (16%)	MLCT/ILCT/LLCT	
	S_{21}	283	0.4047	HOMO->L+6 (38%),	MLCT/ILCT	
				HOMO->L+7 (16%)	MLCT/ILCT	
	T_1	427	0.0000	H-1->L+2 (12%),	MLCT/ILCT/LLCT	
				HOMO->LUMO (32%),	MLCT/ILCT/LLCT	
				HOMO->L+1 (11%)	MLCT/ILCT/LLCT	
2b	S_1	365	0.0407	HOMO->LUMO (84%)	MLCT/ILCT/LLCT	
	S_{37}	257	0.2810	H-4->L+4 (14%),	ILCT	
				H-3->L+4 (14%),	MLCT/ILCT	
				H-2->L+4 (24%)	ILCT/LLCT	
	T_1	420	0.0000	HOMO->LUMO (25%),	MLCT/ILCT/LLCT	
				HOMO->L+2 (20%)	MLCT/ILCT	
2c	S_1	365	0.0392	HOMO->LUMO (93%)	MLCT/ILCT	
	S_{29}	258	0.2976	H-4->L+4 (13%),	ILCT	
				H-3->L+4 (17%),	MLCT/ILCT	
				H-2->L+4 (31%)	ILCT/LLCT	
	T_1	420	0.0000	H-2->L+1 (17%),	ILCT/LLCT	
				HOMO->LUMO (28%),	MLCT/ILCT	
				HOMO->L+1 (16%)	MLCT/ILCT	
2d	S_1	364	0.0446	HOMO->LUMO (72%),	MLCT/ILCT/LLCT	
				HOMO->L+1 (21%)	MLCT/ILCT/LLCT	
	S_{21}	276	0.2948	HOMO->L+7 (55%)	MLCT/ILCT	
	T_1	419	0.0000	H-1->L+2 (19%),	MLCT/ILCT/LLCT	
				HOMO->LUMO (22%),	MLCT/ILCT/LLCT	
				HOMO->L+2 (15%)	MLCT/ILCT	

Table S4 Molecular orbital composition (%) of **1a** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	SOF1	SOF2	pic	
L+5	-1.13	1	71	11	17	π*(SOF+pic)
L+4	-1.18	2	61	28	9	π*(SOF)
L+3	-1.43	1	33	17	49	π*(SOF+pic)
L+2	-1.79	4	1	73	22	π*(SOF+pic)
L+1	-1.83	3	16	15	66	π*(SOF+pic)
LUMO	-1.93	3	78	7	11	π*(SOF+pic)
HOMO	-6.2	39	24	30	7	d(Ir)+π(SOF)
H-1	-6.58	47	5	18	29	d(Ir)+π(SOF+pic)
H-2	-6.85	3	14	62	21	π(SOF+pic)
H-3	-6.95	23	50	21	7	d(Ir)+π(SOF)
H-4	-6.97	10	10	19	61	d(Ir)+π(SOF+pic)
H-5	-7.1	27	32	25	16	d(Ir)+π(SOF+pic)

Table S5 Molecular orbital composition (%) of **1b** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	SOF1	SOF2	taz	
L+5	-1.2	1	39	28	31	π*(SOF+taz)
L+4	-1.27	2	51	26	21	π*(SOF+taz)
L+3	-1.47	1	47	16	35	π*(SOF+taz)
L+2	-1.85	4	1	85	10	π*(SOF+taz)
L+1	-1.91	3	7	9	81	π*(SOF+taz)
LUMO	-2.04	3	87	2	7	π*(SOF)
HOMO	-6.41	35	20	41	4	d(Ir)+π(SOF)
H-1	-6.62	28	5	8	59	d(Ir)+π(SOF+taz)
H-2	-6.9	4	11	76	9	π(SOF)
H-3	-7.04	11	59	27	2	d(Ir)+π(SOF)
H-4	-7.15	29	33	23	15	d(Ir)+π(SOF+taz)
H-5	-7.28	21	25	27	28	d(Ir)+π(SOF+taz)

Table S6 Molecular orbital composition (%) of **1c** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	SOF1	SOF2	bptz	
L+5	-1.17	1	89	3	7	π*(SOF)
L+4	-1.21	2	45	42	12	π*(SOF+bptz)
L+3	-1.4	1	54	18	26	π*(SOF+bptz)
L+2	-1.71	3	1	4	92	π*(bptz)
L+1	-1.81	3	3	90	4	π*(SOF)
LUMO	-1.98	4	92	2	3	π*(SOF)
HOMO	-6.34	36	20	40	4	d(Ir)+π(SOF)
H-1	-6.53	27	5	8	61	d(Ir)+π(SOF+bptz)
H-2	-6.84	5	11	75	9	π(SOF+bptz)
H-3	-6.98	16	56	25	3	d(Ir)+π(SOF)
H-4	-7.08	30	29	22	19	d(Ir)+π(SOF+bptz)
H-5	-7.22	24	17	27	32	d(Ir)+π(SOF+bptz)

Table S7 Molecular orbital composition (%) of **1d** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	SOF1	SOF2	N4	
L+5	-1.23	1	76	12	11	π*(SOF+N4)
L+4	-1.28	2	56	17	26	π*(SOF+N4)
L+3	-1.48	1	43	16	40	π*(SOF+N4)
L+2	-1.87	4	1	88	7	π*(SOF)
L+1	-1.93	3	7	6	84	π*(SOF+N4)
LUMO	-2.05	3	86	3	8	π*(SOF)
HOMO	-6.4	34	21	40	5	d(Ir)+π(SOF)
H-1	-6.8	32	7	35	26	d(Ir)+π(SOF+N4)
H-2	-6.95	11	12	51	26	d(Ir)+π(SOF+N4)
H-3	-7.05	9	59	26	5	π(SOF)
H-4	-7.16	27	29	22	22	d(Ir)+π(SOF+N4)
H-5	-7.27	14	18	31	37	d(Ir)+π(SOF+N4)

Table S8 Molecular orbital composition (%) of **2a** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	POF1	POF2	pic	
L+5	-0.93	2	61	7	30	π*(POF+pic)
L+4	-0.97	1	20	72	6	π*(POF)
L+3	-1.26	1	17	19	63	π*(POF+pic)
L+2	-1.61	4	13	77	6	π*(POF)
L+1	-1.64	5	67	5	22	π*(POF+pic)
LUMO	-1.72	2	14	13	71	π*(POF+pic)
HOMO	-5.95	39	25	30	6	d(Ir)+π(POF)
H-1	-6.38	45	6	24	25	d(Ir)+π(POF+pic)
H-2	-6.62	8	14	64	14	π(POF+pic)
H-3	-6.69	21	62	13	3	d(Ir)+π(POF)
H-4	-6.8	8	9	22	62	π(POF+pic)
H-5	-6.9	13	14	69	4	d(Ir)+π(POF)

Table S9 Molecular orbital composition (%) of **2b** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	POF1	POF2	taz	
L+5	-1.07	1	9	44	46	π*(POF+taz)
L+4	-1.11	2	60	33	5	π*(POF)
L+3	-1.32	1	30	21	48	π*(POF+taz)
L+2	-1.71	4	1	88	7	π*(POF)
L+1	-1.78	4	29	4	63	π*(POF+taz)
LUMO	-1.85	2	65	4	28	π*(POF+taz)
HOMO	-6.2	35	22	40	3	d(Ir)+π(POF)
H-1	-6.5	31	6	11	52	d(Ir)+π(POF+taz)
H-2	-6.7	4	10	73	13	π(POF+taz)
H-3	-6.84	12	68	18	1	d(Ir)+π(POF)
H-4	-6.9	2	2	96	0	π(POF)
H-5	-7	24	34	31	11	d(Ir)+π(POF+taz)

Table S10 Molecular orbital composition (%) of **2c** in the ground state

MO	Energy(eV)	Composition (100%)				Assign
		Ir	POF1	POF2	pbtz	
L+5	-1	1	10	30	59	π*(POF+bptz)
L+4	-1.06	2	51	44	3	π*(POF)
L+3	-1.25	1	37	24	37	π*(POF+bptz)
L+2	-1.6	4	1	7	88	π*(bptz)
L+1	-1.67	3	5	85	7	π*(POF)
LUMO	-1.79	4	89	3	4	π*(POF)
HOMO	-6.15	36	21	40	3	d(Ir)+π(POF)
H-1	-6.42	30	5	9	56	d(Ir)+π(POF+bptz)
H-2	-6.65	4	10	75	11	π(POF+bptz)
H-3	-6.79	16	64	18	2	d(Ir)+π(POF)
H-4	-6.87	2	3	94	1	π(POF)
H-5	-6.94	27	29	29	15	d(Ir)+π(POF+bptz)

Table S11 Molecular orbital composition (%) of **2d** in the ground state

MO	Energy(eV)	Composition (100%)				Assign
		Ir	POF1	POF2	N4	
L+5	-1.09	1	4	59	36	π*(POF+N4)
L+4	-1.12	2	68	20	10	π*(POF+N4)
L+3	-1.34	1	28	19	52	π*(POF+N4)
L+2	-1.72	4	2	90	5	π*(POF)
L+1	-1.8	4	31	2	63	π*(POF+N4)
LUMO	-1.86	2	63	4	31	π*(POF+N4)
HOMO	-6.2	35	21	39	5	d(Ir)+π(POF)
H-1	-6.63	25	9	51	14	d(Ir)+π(POF+N4)
H-2	-6.79	22	11	34	32	d(Ir)+π(POF+N4)
H-3	-6.85	11	65	20	4	d(Ir)+π(POF)
H-4	-6.9	1	2	97	0	π(POF)
H-5	-7.01	24	32	28	16	d(Ir)+π(POF+N4)

Table S12 Optimized S_0 structure for the complex **1a**

Ir	2.12858400	-0.70346200	0.11878700	C	2.92958100	0.71896500	4.08470200
O	3.38976300	-2.26381900	0.88861200	H	3.39556400	0.30842400	4.97365000
N	1.83519500	-1.85673900	-1.54816100	C	1.12362500	1.97229600	0.47677200
N	4.11216700	-0.02913000	-0.42072500	C	0.54105200	1.13855200	-1.71909900
C	0.41519000	-1.58409300	0.62408100	H	0.50872400	0.36482500	-2.48000500
O	5.53263500	-2.94087500	1.00304300	C	-0.05689300	3.42518100	-1.11049800
C	1.14904200	0.91655800	-0.48152100	C	0.52676400	3.18360700	0.13489800
C	0.76218400	-2.69742500	-1.51232900	C	-0.04998900	2.35548800	-2.01816700
C	-0.04800200	-2.55039000	-0.30884600	S	-0.72581600	5.04626400	-1.48456000
C	4.43825100	1.11400700	-1.04030800	F	0.48966800	4.17359400	1.03630300
H	3.61159100	1.76534900	-1.30698900	F	-0.61987200	2.48469600	-3.20996600
C	2.47390100	-2.70378300	-3.69138000	O	-3.12308800	-5.42797500	1.01985900
H	3.16840400	-2.67068800	-4.52351400	O	-3.88065600	-3.78159800	2.79580800
C	4.65805100	-2.15558600	0.67110700	C	-4.82118400	-3.99163500	-0.92472200
C	-0.33897300	-1.36310500	1.77573200	H	-4.24689200	-4.87290800	-1.19065400
H	-0.04839400	-0.62567100	2.51643500	C	-4.62125100	-3.38769300	0.31229600
C	0.53544800	-3.57411800	-2.58012800	C	-5.35984400	-2.27066900	0.69776100
H	-0.30852800	-4.24695400	-2.54364000	H	-5.20161800	-1.83134100	1.67820900
C	-1.96167200	-3.06870100	1.13672000	C	-6.30182800	-1.75089300	-0.17984900
C	2.83954200	-0.05129400	2.93756000	H	-6.88334000	-0.88008400	0.11415200
H	3.21323600	-1.06848000	2.87423500	O	0.22878700	6.03369000	-0.99015700
C	1.81136100	2.48544500	2.89823700	O	-1.14562300	5.04497400	-2.88045100
H	1.39541400	3.48201500	2.86440600	C	-2.19001400	5.13747200	-0.47721400
C	2.65741200	-1.86456900	-2.60732900	C	-2.14045400	5.77588700	0.75817100
H	3.48439400	-1.16619100	-2.56415600	H	-1.20910800	6.21683300	1.09733200
C	5.08096600	-0.88588600	-0.05506100	C	-4.51967900	4.66172700	-0.17354900
C	2.40866000	2.00957800	4.05648800	H	-5.44881700	4.23164500	-0.53995400
H	2.46092500	2.64510100	4.93578400	C	-3.37531400	4.58369700	-0.95647600
C	6.42134000	-0.62362900	-0.31295200	H	-3.39538700	4.11276500	-1.93474000
H	7.14694900	-1.36271200	0.00945900	C	-3.29734400	5.84670700	1.52588200
C	-1.21537400	-3.25859400	-0.02763100	H	-3.26821200	6.34603900	2.49149900
C	5.75575000	1.44211900	-1.32788100	C	-4.49960000	5.29202400	1.07615800
H	5.97756400	2.37759600	-1.83100100	C	-5.75132500	5.39895800	1.90046100
C	1.73929100	1.66599800	1.76644800	H	-5.52369400	5.46701700	2.96872800
C	-1.49625400	-2.08339300	2.01909400	H	-6.40823200	4.53727500	1.74522400
S	-3.42185000	-4.06382400	1.44147200	H	-6.32107000	6.29690200	1.62898300
F	-1.67441600	-4.14905400	-0.91652200	C	-5.77132700	-3.45817700	-1.78894300
F	-2.17276000	-1.80163800	3.12639500	H	-5.93665800	-3.92671900	-2.75628900
C	1.39169100	-3.57866800	-3.66882700	C	-6.52299400	-2.33457600	-1.43321900
H	1.21428500	-4.26199200	-4.49408100	C	-7.56975800	-1.78216300	-2.35908100
C	6.76644000	0.55608200	-0.95941800	H	-7.60203000	-0.68831600	-2.32034000
H	7.80630200	0.78683100	-1.17321700	H	-8.56710600	-2.14671200	-2.08190900
N	2.26946900	0.41267000	1.81636600	H	-7.38731900	-2.08140500	-3.39562000

Table S13 Optimized S_0 structure for the complex **2a**

Ir	-0.01647600	-2.16005600	0.01228800	F	-3.77364400	0.25718800	-2.68860400
O	1.33942600	-3.83214300	-0.03445000	F	-3.25738200	1.77633400	1.71836000
N	0.59808900	-1.80799900	1.93369700	O	4.59903500	3.27825700	-1.90462700
N	-1.29814500	-3.83900000	0.48947900	C	5.90097200	3.15472600	1.78340700
C	1.38459700	-0.78768600	-0.33531200	H	6.67626600	2.40491900	1.65321200
O	1.46625300	-6.04526700	0.35369100	C	4.90303000	3.30560700	0.81834500
C	-1.43803700	-0.77611800	-0.08098700	C	3.92726700	4.29458000	0.98422100
C	1.65666300	-0.95950900	2.07631900	H	3.17742500	4.44066100	0.21114000
C	2.10860900	-0.38162900	0.81799700	C	3.93475200	5.10268000	2.11632000
C	-2.62247800	-3.81325900	0.69454000	H	3.17319800	5.86808500	2.23970900
H	-3.09798800	-2.83999600	0.61988600	O	-6.01848900	1.55649500	-1.82437700
C	0.51971700	-2.17207500	4.29623200	C	-4.47887600	3.73968800	-1.10308100
H	0.04350700	-2.66746000	5.13514400	C	-5.13481100	4.44760300	-2.11430000
C	0.85877500	-4.98723600	0.28027100	H	-5.96397700	3.97359600	-2.63253900
C	1.75083000	-0.24410500	-1.56617800	C	-2.96841300	5.59875700	-0.78891400
H	1.24715100	-0.51906700	-2.48678700	H	-2.11838100	6.04398100	-0.27908500
C	2.16941100	-0.70719800	3.35576100	C	-3.38723600	4.31702100	-0.44521700
H	3.00555700	-0.03266700	3.46707000	H	-2.86072100	3.76902200	0.33123700
C	3.52950400	1.10241100	-0.54151800	C	-4.70987600	5.72834900	-2.45605500
C	0.05649600	-3.22660400	-2.76926900	H	-5.21876200	6.27433900	-3.24580300
H	0.87134800	-3.79013500	-2.32573700	C	-3.62963800	6.30458000	-1.79268600
C	-2.01364000	-1.69837600	-3.70258900	C	5.91027700	3.96982800	2.91193300
H	-2.82971100	-1.08310400	-4.05239400	H	6.69260100	3.85069100	3.65693100
C	0.05403000	-2.38962700	3.01233400	C	4.92543900	4.93963200	3.08246100
H	-0.78458700	-3.04720600	2.81747300	H	-3.29540500	7.30282200	-2.06263700
C	-0.63892400	-5.00830900	0.55622600	H	4.93579800	5.57574700	3.96375700
C	-1.37925000	-2.58434700	-4.56038300	P	-5.11904500	2.07736700	-0.74818100
H	-1.70732900	-2.66132100	-5.59301400	P	4.84026300	2.36830600	-0.74293300
C	-1.29422100	-6.19891100	0.84846400	C	-6.00625300	2.15380800	0.84169900
H	-0.69569600	-7.10272600	0.88807600	C	-6.96695400	1.15779400	1.04709300
C	3.16191800	0.52260500	0.66902600	C	-5.85047400	3.16678800	1.79055300
C	-3.34194500	-4.96344000	0.98739800	C	-7.74041200	1.15887800	2.20365400
H	-4.41357800	-4.89994100	1.14584100	H	-7.12033900	0.40324200	0.28033400
C	-1.58873800	-1.59210600	-2.37292400	C	-6.63077000	3.16974000	2.94256400
C	2.79117300	0.66549400	-1.65236800	H	-5.12654000	3.95993900	1.62806000
F	3.89851800	0.84349900	1.75315300	C	-7.57106700	2.16358800	3.15337200
F	3.10883300	1.12547400	-2.85899500	H	-8.48539100	0.38266400	2.35724600
C	1.60248800	-1.31326300	4.46426100	H	-6.50828600	3.96321400	3.67492600
H	2.00331600	-1.11427800	5.45394700	H	-8.18037600	2.16993200	4.05342600
C	-2.66521500	-6.17898300	1.06872100	C	6.39310900	1.43622800	-0.88349900
H	-3.20293200	-7.09492400	1.29737300	C	7.29321600	1.87403300	-1.85863800
N	-0.56078200	-2.37374200	-1.93882400	C	6.70781000	0.32450100	-0.09432300
C	-0.32311800	-3.36242900	-4.09353800	C	8.50480700	1.21131300	-2.03521500

H	0.20245000	-4.06035000	-4.73594400	H	7.02057800	2.72384200	-2.47862100
C	-2.10700400	-0.70251300	-1.33619600	C	7.92128200	-0.33260700	-0.27241300
C	-1.86404800	0.08268000	0.93627600	H	6.00705200	-0.03142000	0.65636000
H	-1.37572700	0.10352400	1.90532000	C	8.81978000	0.11129600	-1.24160800
C	-3.64082700	1.02376800	-0.48007200	H	9.20106600	1.55083100	-2.79730400
C	-3.17228200	0.18843400	-1.49774500	H	8.16230400	-1.19772900	0.33936800
C	-2.92122300	0.94596700	0.71708500	H	9.76428200	-0.40777800	-1.38205600