Highly phosphorescent iridium(III) complexes based on 2-(biphenyl-4-yl)benzo[d]oxazole derivatives: Synthesis, structures, properties and DFT calculations

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Supplementary Information

Table S1 Selected bond distances (Å) and angles (◦) for complexes **3a**–**3d**

3a			
Ir(1)-O(3)	2.127(3)	N(1)-C(13)	1.300(6)
Ir(1)-O(4)	2.123(4)	N(2)-C(32)	1.297(6)
Ir(1)-N(1)	2.025(3)	O(1)-C(13)	1.360(5)
Ir(1)-N(2)	2.042(3)	O(2)-C(32)	1.348(5)
Ir(1)-C(11)	2.002(4)	C(7)-C(6)	1.490(6)
Ir(1)-C(30)	2.006(5)	C(26)-C(25)	1.482(6)
N(1)-Ir(1)-N(2)	174.26(16)	O(4)-Ir(1)-O(3)	88.73(15)
C(11)-Ir(1)-O(4)	176.86(15)	N(1)-Ir(1)-O(3)	87.23(13)
C(30)-Ir(1)-O(3)	176.78(14)	N(1)-Ir(1)-C(11)	80.55(16)
C(11)-Ir(1)-C(30)	89.30(17)	C(11)-Ir(1)-O(3)	90.61(16)
3b			
Ir(1)-O(3)	2.135(3)	N(1)-C(7)	1.318(6)
Ir(1)-O(4)	2.147(4)	N(2)-C(26)	1.320(7)
Ir(1)-N(1)	2.028(4)	O(1)-C(7)	1.363(6)
Ir(1)-N(2)	2.042(4)	O(2)-C(26)	1.343(6)
Ir(1)-C(13)	2.008(5)	F(1)-C(17)	1.361(8)
Ir(1)-C(32)	2.007(5)	F(2)-C(36)	1.328(10)
N(1)-Ir(1)-N(2)	175.48(15)	O(4)-Ir(1)-O(3)	88.98(15)
C(13)-Ir(1)-O(4)	172.99(18)	N(1)-Ir(1)-O(3)	89.24(14)
C(32)-Ir(1)-O(3)	175.57(17)	N(1)-Ir(1)-C(13)	80.58(19)
C(13)-Ir(1)-C(32)	94.7(2)	C(13)-Ir(1)-O(3)	85.88(17)
3c			
Ir(1)-O(3)	2.136(2)	N(1)-C(7)	1.310(4)
Ir(1)-O(4)	2.141(2)	N(2)-C(27)	1.303(4)
Ir(1)-N(1)	2.035(3)	O(1)-C(7)	1.357(4)
Ir(1)-N(2)	2.036(3)	O(2)-C(27)	1.362(4)
Ir(1)-C(13)	2.017(3)	C(17)-C(20)	1.509(6)

Ir(1)-C(29)	2.013(3)	C(45)-C(43)	1.505(6)
N(1)-Ir(1)-N(2)	173.92(11)	O(4)-Ir(1)-O(3)	88.29(9)
C(13)-Ir(1)-O(4)	176.36(11)	N(1)-Ir(1)-O(3)	87.71(10)
C(29)-Ir(1)-O(3)	175.61(10)	N(1)-Ir(1)-C(13)	80.40(12)
C(13)-Ir(1)-C(29)	93.44(12)	C(13)-Ir(1)-O(3)	89.40(11)
3d			
Ir(1)-O(2)	2.123(4)	N(1)-C(7)	1.309(7)
Ir(1)-N(1)	2.028(4)	O(1)-C(7)	1.353(6)
Ir(1)-C(13)	2.005(5)	C(16)-F(1)	1.342(8)
C(14)-C(11)	1.514(7)	C(18)-F(2)	1.365(7)
N(1)-Ir(1)-N(1i)	172.1(3)	O(2)-Ir(1)-O(2i)	89.2(2)
C(13)-Ir(1)-O(2i)	176.37(17)	N(1)-Ir(1)-O(2)	88.95(15)
C(13)-Ir(1)-C(13i)	89.7(3)	N(1)-Ir(1)-C(13)	79.69(19)

Table S2 Main experimental and calculated optical transitions for complexes **3a**–**3e**

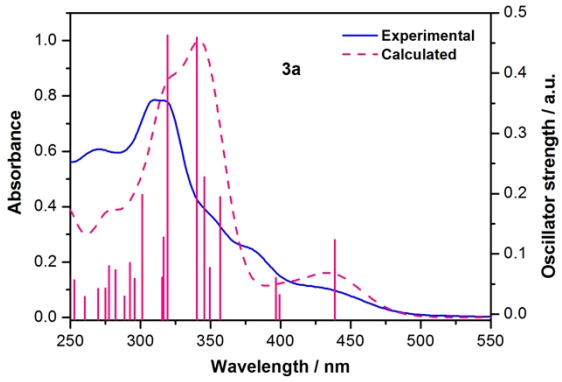
Complex	Orbital Excitations	Character	Oscillation Strength	Calcd (nm)	Exptl (nm)
3a	HOMO → LUMO	MLCT ($\pi\rightarrow\pi^*$)	0.1231	438	430
	HOMO-1 → LUMO+1	MLCT ($\pi\rightarrow\pi^*$)	0.0602	396	378
	HOMO-3 → LUMO	ILCT ($\pi\rightarrow\pi^*$)	0.1941	356	349
	HOMO-2 → LUMO		0.2271	345	
	HOMO-2 → LUMO+1		0.459	340	
	HOMO-4 → LUMO	ILCT ($\pi\rightarrow\pi^*$)	0.4628	319	313
	HOMO-4 → LUMO+1		0.1271	316	
	HOMO → LUMO+4 HOMO → LUMO+5	ILCT ($\pi\rightarrow\pi^*$)	0.0799	277	270
	HOMO-2 → LUMO+10	ILCT ($\pi\rightarrow\pi^*$)	0.0501	225	227
3b	HOMO → LUMO	MLCT ($\pi\rightarrow\pi^*$)	0.1246	438	438

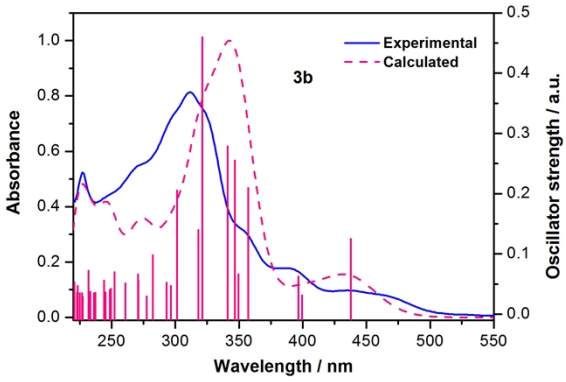
	HOMO-1 → LUMO+1	MLCT ($\pi \rightarrow \pi^*$)	0.0621	396	390
	HOMO-3 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.2094	357	353
	HOMO-2 → LUMO		0.2548	346	
	HOMO → LUMO+2		0.2092	341	
	HOMO → LUMO+2 HOMO-2 → LUMO+1		0.2783	340	
	HOMO-4 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.4596	321	312
	HOMO-4 → LUMO+1		0.1395	318	
	HOMO-5 → LUMO+1		0.2049	301	
	HOMO-8 → LUMO HOMO-9 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.0661	270	270
	HOMO-4 → LUMO+7 HOMO-17 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.0469	223	225
3c	HOMO → LUMO	MLCT ($\pi \rightarrow \pi^*$)	0.1287	438	438
	HOMO-1 → LUMO+1	MLCT ($\pi \rightarrow \pi^*$)	0.0782	396	390
	HOMO-2 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.288	358	357
	HOMO-3 → LUMO		0.2645	349	
	HOMO-3 → LUMO+1		0.4648	343	
	HOMO-4 → LUMO		0.4498	325	
	HOMO-4 → LUMO+1	ILCT ($\pi \rightarrow \pi^*$)	0.1213	321	316
	HOMO-5 → LUMO+1		0.1814	301	
	HOMO-7 → LUMO HOMO-10 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.152	272	271
	HOMO-16 → LUMO+1	ILCT ($\pi \rightarrow \pi^*$)	0.0649	226	227
3d	HOMO → LUMO	MLCT ($\pi \rightarrow \pi^*$)	0.1192	442	440
	HOMO-1 → LUMO+1	MLCT ($\pi \rightarrow \pi^*$)	0.0409	401	389
	HOMO-3 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.1525	359	355

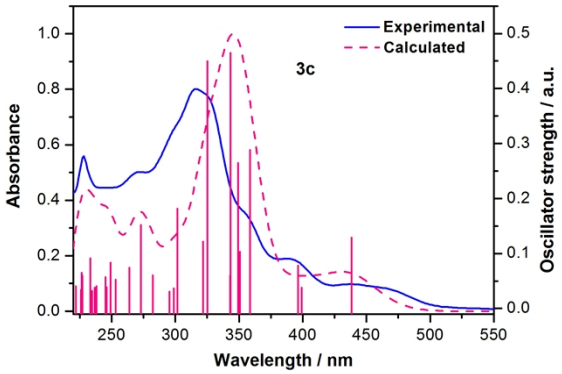
	HOMO-2 → LUMO		0.2386	346	
	HOMO-2 → LUMO+1		0.4438	341	
	HOMO-4 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.4481	314	309
	HOMO-4 → LUMO+1		0.1902	311	
	HOMO-5 → LUMO+1		0.2899	304	
	HOMO → LUMO+5 HOMO → LUMO+9	ILCT ($\pi \rightarrow \pi^*$)	0.2278	279	271
	HOMO-5 → LUMO+3 HOMO-2 → LUMO+10	ILCT ($\pi \rightarrow \pi^*$)	0.0407	226	225
3e	HOMO → LUMO	MLCT ($\pi \rightarrow \pi^*$)	0.1171	440	438
	HOMO-1 → LUMO+1	MLCT ($\pi \rightarrow \pi^*$)	0.0457	396	388
	HOMO-2 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.1975	358	355
	HOMO-3 → LUMO		0.2224	344	
	HOMO-3 → LUMO+1		0.471	338	
	HOMO-4 → LUMO		0.4249	317	
	HOMO-4 → LUMO+1	ILCT ($\pi \rightarrow \pi^*$)	0.148	313	309
	HOMO-5 → LUMO+1		0.212	302	
	HOMO → LUMO+9 HOMO → LUMO+7	ILCT ($\pi \rightarrow \pi^*$)	0.1376	279	271
	HOMO-3 → LUMO+10 HOMO-17 → LUMO	ILCT ($\pi \rightarrow \pi^*$)	0.0576	225	226

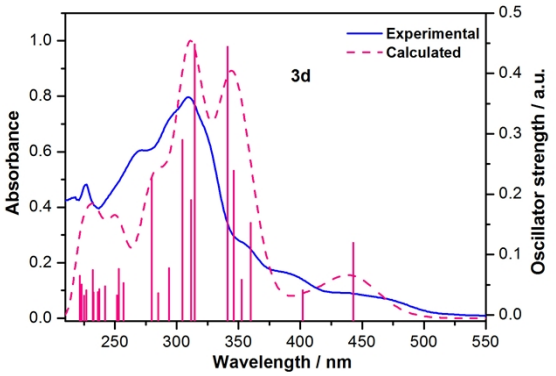
Table S3 Frontier orbital energy and electron density distribution for complexes **3a**–**3e**

Complex	Orbital	Energy (eV)	Composition (%)			
			Ir	benzoxazole	Biphenyl-R	acac
3a	LUMO	-1.800	8.28	42.58	48.07	1.07
	HOMO	-5.330	50.56	10.25	34.11	5.08
3b	LUMO	-1.817	2.30	51.31	45.31	1.08
	HOMO	-5.353	49.58	12.92	32.40	5.09
3c	LUMO	-1.777	2.29	48.85	49.00	1.08
	HOMO	-5.307	49.09	11.20	35.46	4.97
3d	LUMO	-1.928	2.02	44.63	52.49	0.87
	HOMO	-5.421	50.72	10.66	33.25	5.37
3e	LUMO	-1.831	2.11	47.69	49.19	1.01
	HOMO	-5.354	50.90	10.43	33.38	5.29









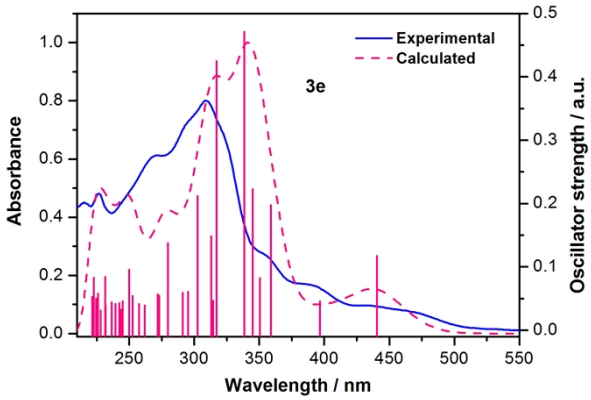


Fig. S1 Experimental (blue lines) and calculated (pink lines) absorption spectra for **3a**–**3e**. The pink vertical bars represent the mean contributions of the absorption spectra.