Electronic Supplementary Information

Boosting efficiency of deep-red Ir(III) complexes by modulating nitrogen atom for high-performance OLEDs

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General Information

Physical Methods.

NMR experiments were recorded using a Bruker Avance 500 NMR spectrometer in $CDCl_3$ and DMSO-d_6 with the TMS as standard. Mass spectra (MS) was obtained with matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF). TGA measurements were carried out on a TGA Q50 analyzer and DSC curves with DSC Q2000 differential scanning calorimeter. UV-vis absorption spectra were recorded in CH_2Cl_2 solutions using a Cary 50 spectrophotometer. Steady-state emission properties were recorded using a FL-4600 spectrophotometer at room temperature. The cyclic voltammetry analysis was performed by a standard three-electrode method on a 620E electrochemical workstation at the scan rates from 100 mV/s. Platinum wire was used as a counter electrode; the reference electrode was a saturated calomel electrode, and the working electrode was a glassy carbon electrode. The experiments were carried out in degassed CH_2Cl_2 and DMF solutions containing tetrabutylammonium perchlorate salt (0.1 M) as the electrolyte and the concentration of the complexes is ca. 1×10^{-3} mol L^{-1}. The potentials are calculated vs the Fc^+/Fc couple. The single crystal structure was mounted on a Bruker Apex II CCD diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å).

Computations

To analyze the emission properties of **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO**, TD-DFT calculations were carried out using the Gaussian 16 C01 code. Theoretical calculation were performed utilizing the BL3YP functional, the SDD basis set and effective core potentials for Ir atom, and 6-31G* basis set for all nonmetal atoms.

Fabrication and Measurement of OLEDs

OLED devices were prepared on ITO-coated glass substrates (25 Ω sq^{-1}) by vacuum evaporation method. Prior to evaporation, the ITO substrates were deal with a regular procedure. All the organic layers and cathodes were successively deposited on the substrate by thermal evaporation at a base pressure of ~5×10^{-4} Pa. EL performance measurement of OLED were recorded by Ocean Optics Maya 2000-PRO spectrometer and a Keithley 2400 source meter.

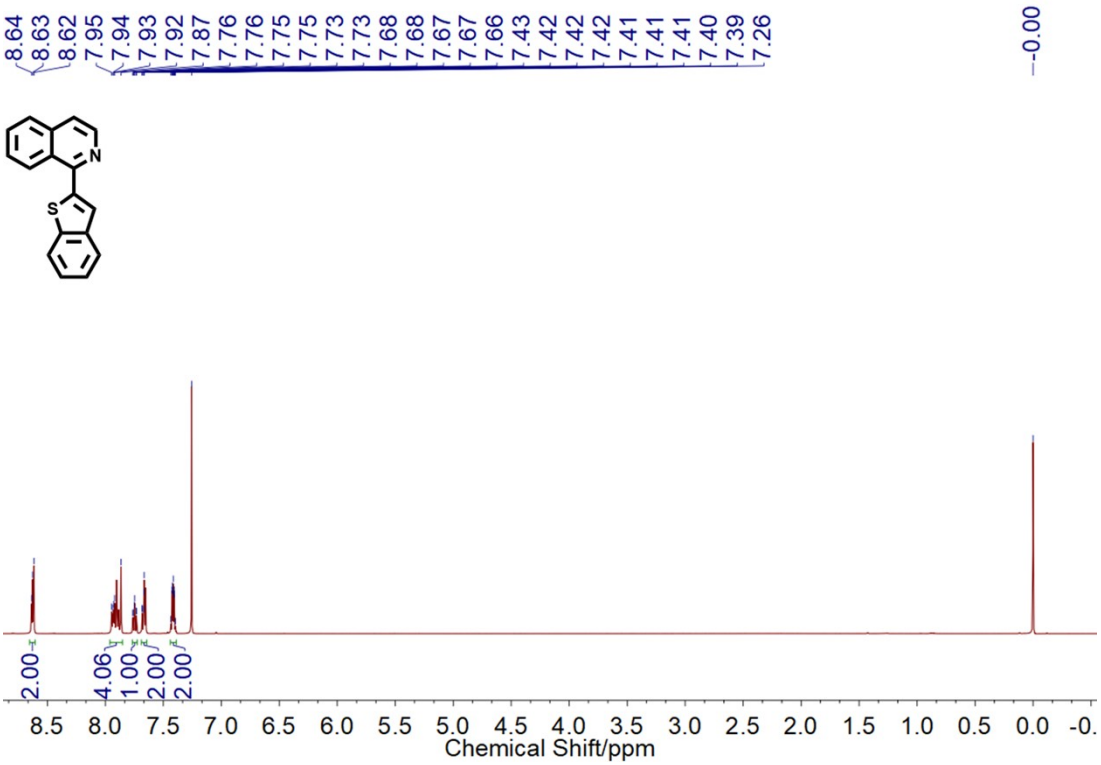

Figure S1. The ^{1}H NMR spectrum of ligand iqbt.

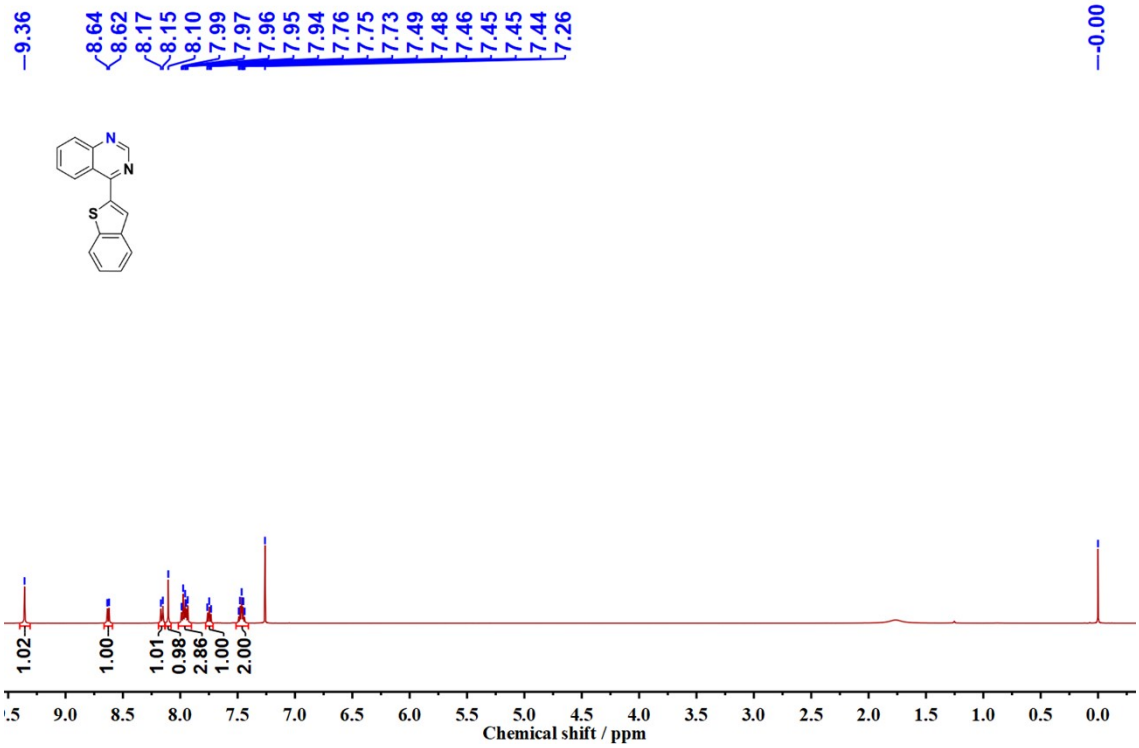

Figure S2. The ^{1}H NMR spectrum of ligand qabt.

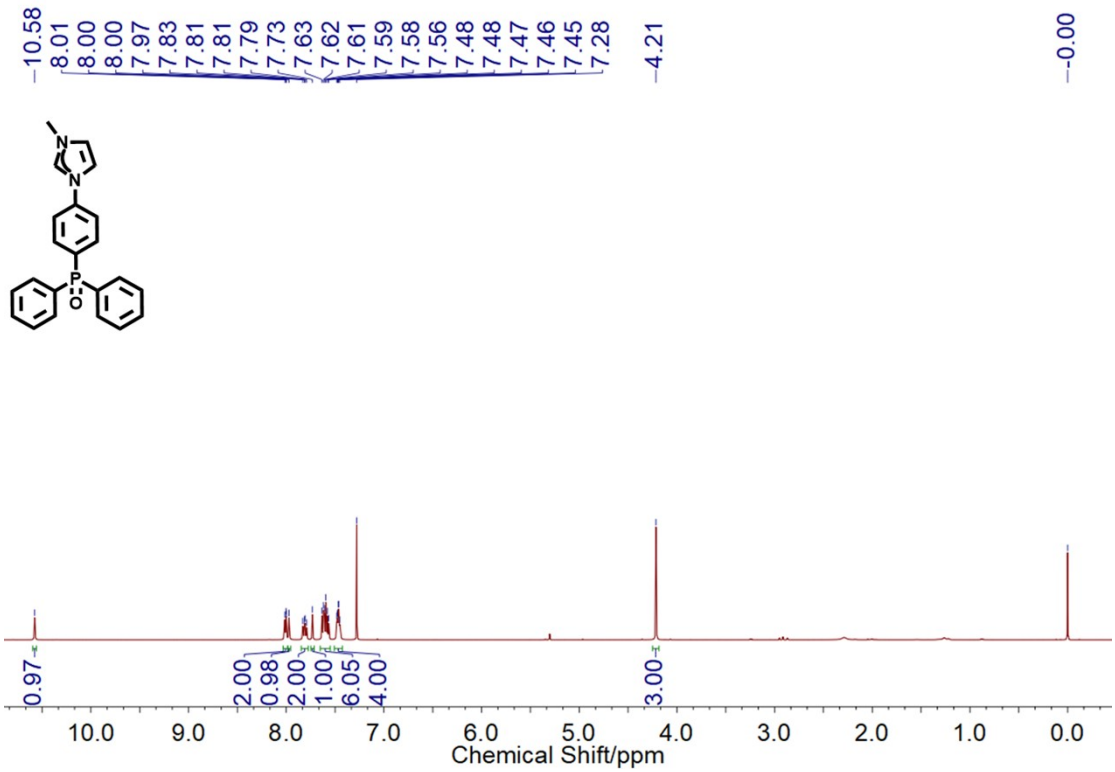

Figure S3. The ^{1}H NMR spectrum of ligand IPO.

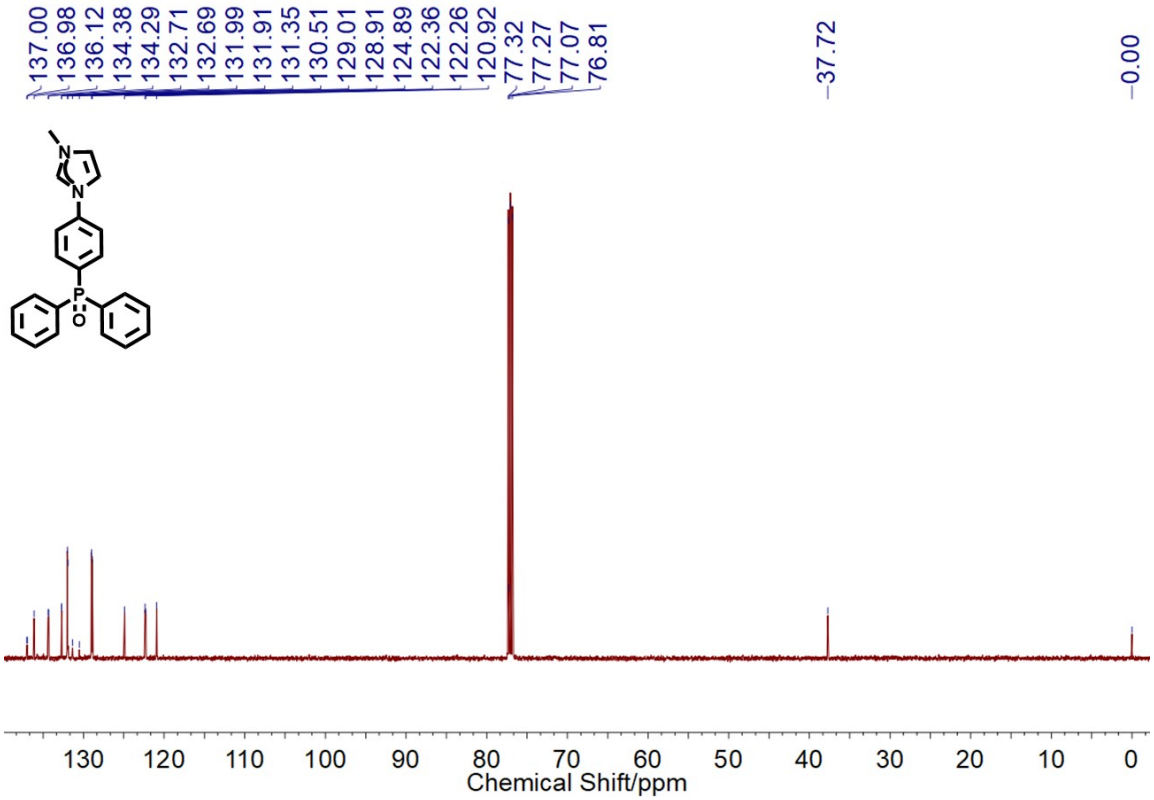

Figure S4. The ^{13}C NMR spectrum of ligand IPO.

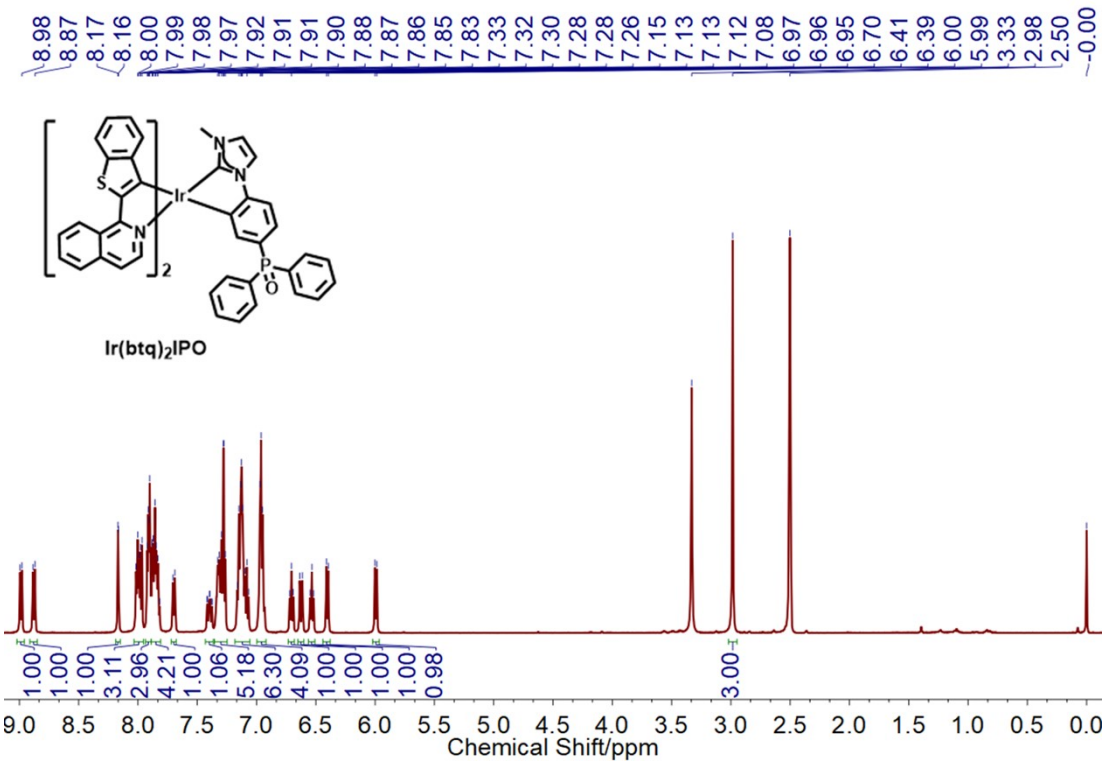

Figure S5. The ^{1}H NMR spectrum of complex **Ir(iqbt)$_2$IPO**.

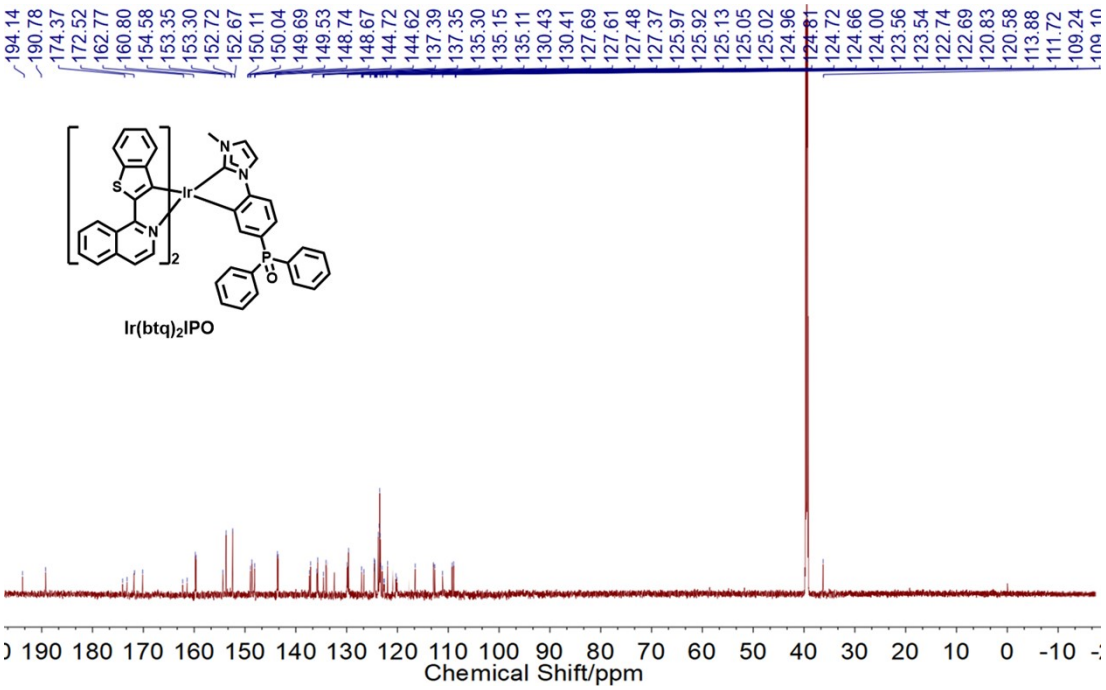

Figure S6. The ^{13}C NMR spectrum of complex **Ir(iqbt)$_2$IPO**.

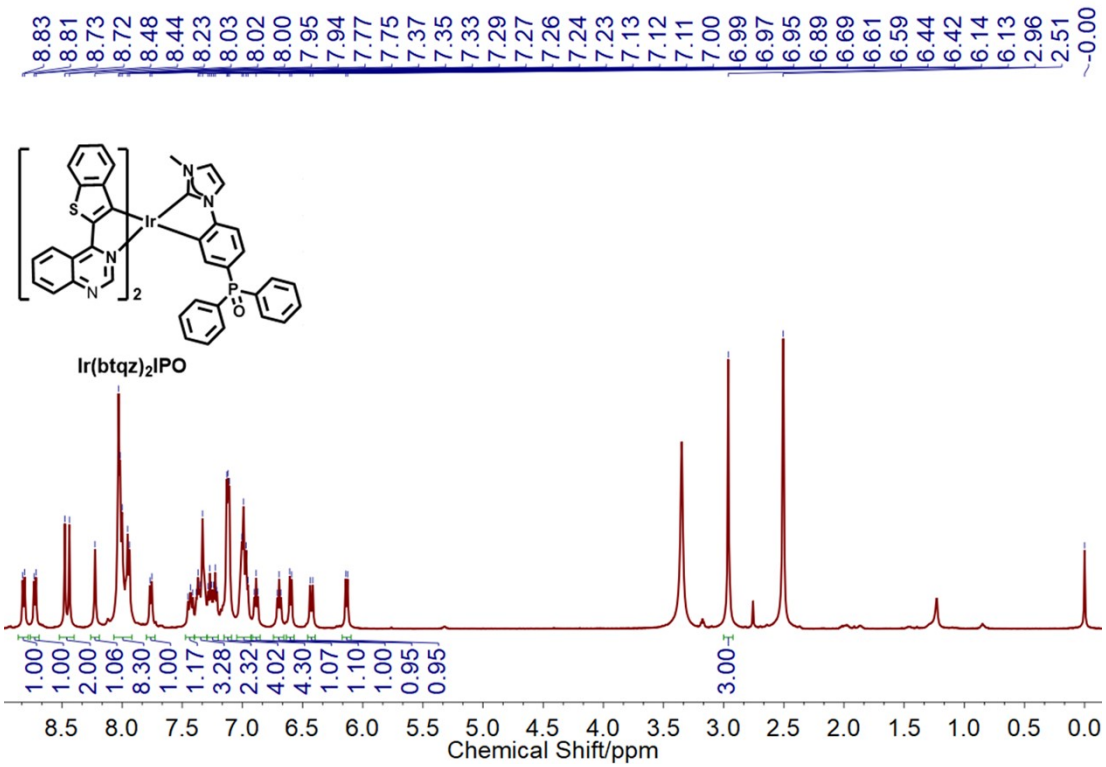

Figure S7. The ^{1}H NMR spectrum of complex **Ir(qabt)$_2$IPO**.

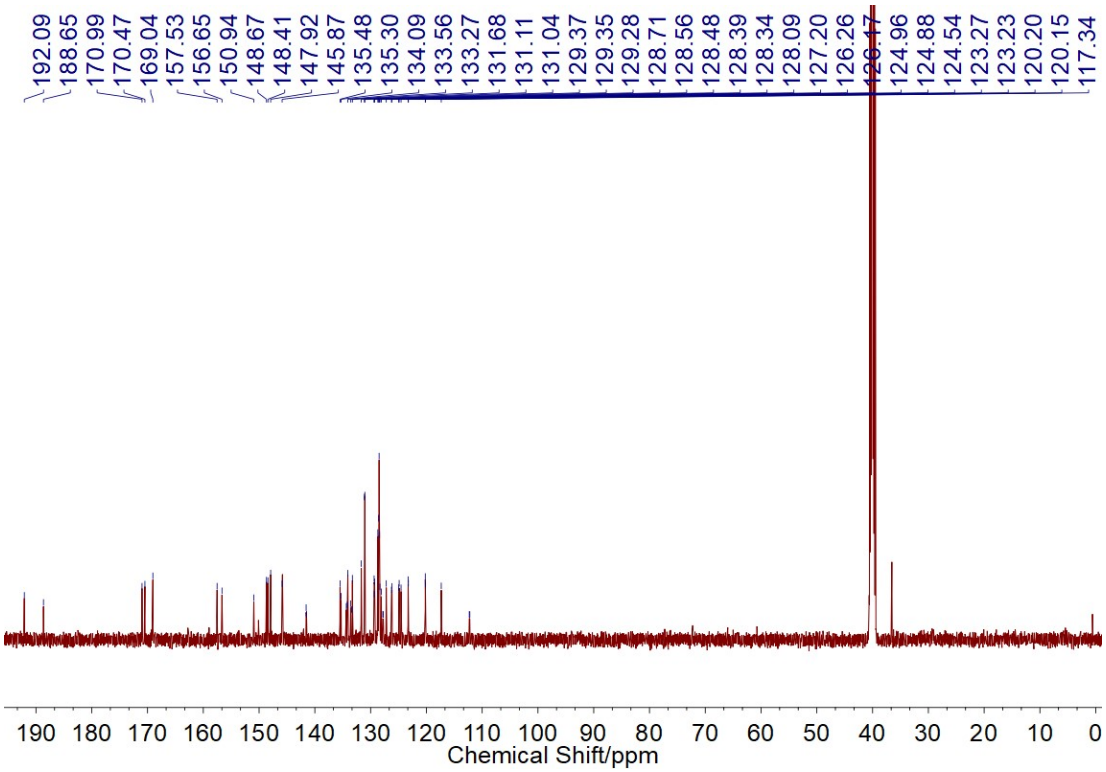

Figure S8. The ^{13}C NMR spectrum of complex **Ir(qabt)$_2$IPO**.

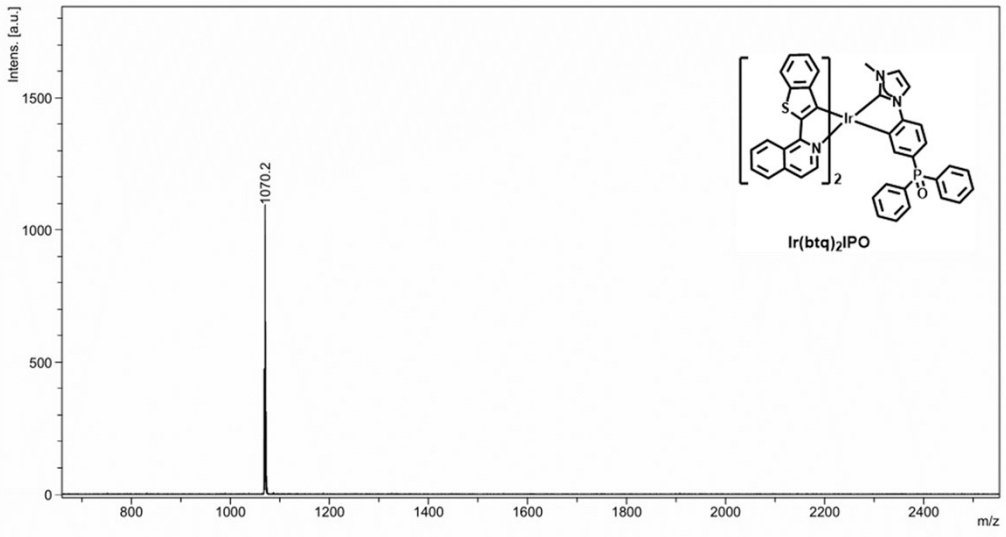

Figure S9. The MS of iridium(III) **Ir(iqbt)$_2$IPO**.

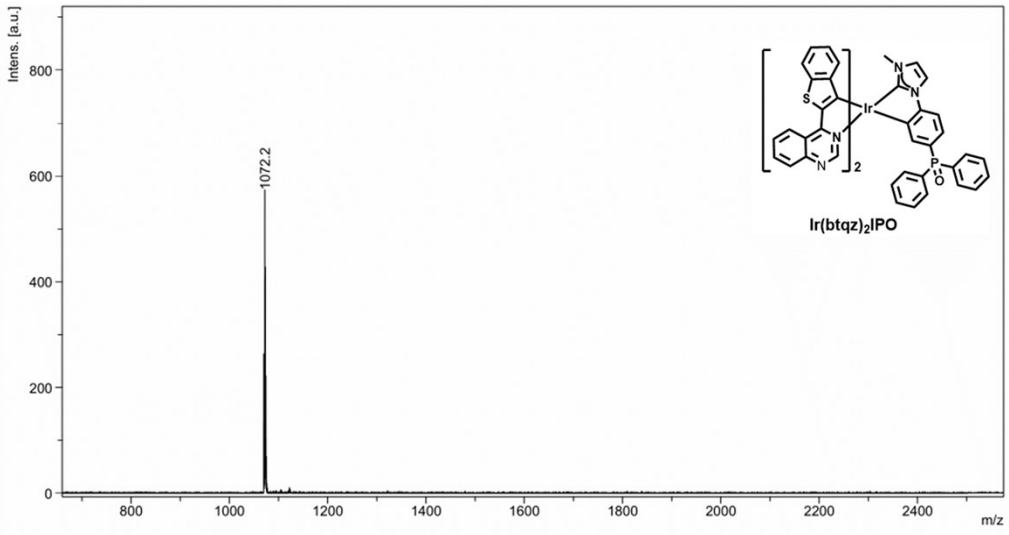

Figure S10. The MS of iridium(III) **Ir(qabt)$_2$IPO**

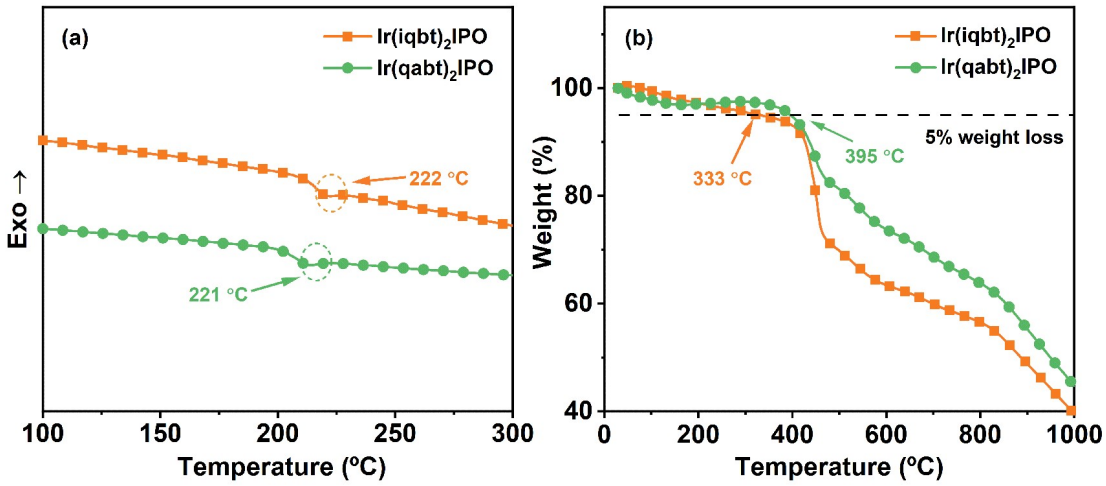

Figure S11. The DSC (a) and TGA (b) of designed Ir(III) complexes **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO**.

Table S1. The detailed crystallographic data of **Ir(iqbt)$_2$IPO**.

complex	**Ir(iqbt)$_2$IPO**
Empirical formula	$C_{56}H_{38}IrN_4OPS_2$
Formula weight	1070.19
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.1339(3)
b/Å	17.3611(4)
c/Å	21.2247(5)
α/°	90
β/°	98.0580(10)
γ/°	90
Volume/Å^3	4791.85(19)
Z	4
ρcalcg/cm^3	1.483
μ/mm^{-1}	6.868
F(000)	2136.0
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.604 to 127.508
Index ranges	-15 ≤ h ≤ 14, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	45873
Independent reflections	7889 [R_{int} = 0.0559, R_{sigma} = 0.0366]
Goodness-of-fit on F^2	1.199
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1174
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1099

Table S2. The selected bond lengths and angles of **Ir(iqbt)$_2$IPO**.

Ir(iqbt)$_2$IPO	
Selected bonds	Bond length (Å)
Ir-C(1)	2.054(6)
Ir-C(18)	2.076(6)
Ir-C(35)	2.058(7)
Ir-C(40)	2.086(6)
Ir-N(1)	2.059(5)
Ir-N(2)	2.072(5)
Selected angles	(°)
C(1)-Ir-N(1)	78.9(2)
C(18)-Ir-N(2)	77.9(2)
C(35)-Ir-C(40)	77.8(3)
C(1)-Ir-C(35)	165.7(2)
C(18)-Ir-C(40)	171.8(2)
N(1)-Ir-N(2)	177.4(2)

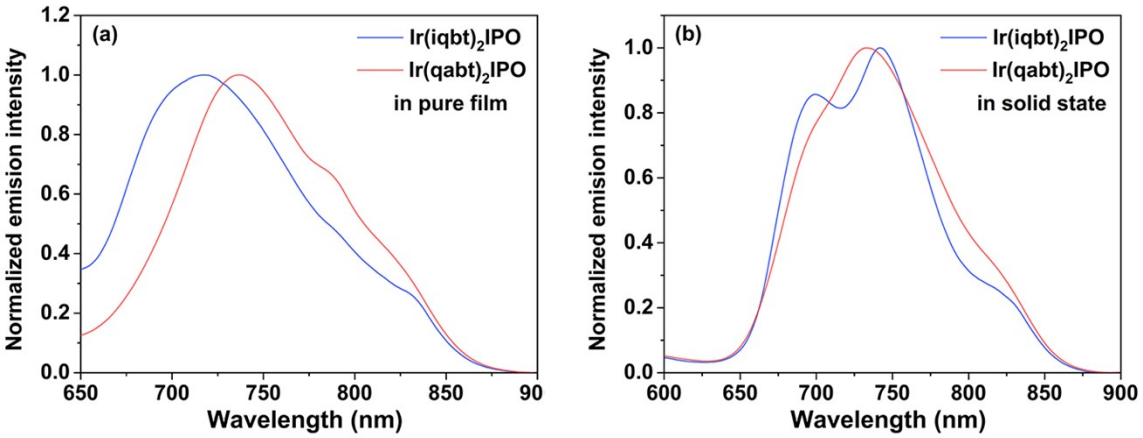

Figure S12. The PL spectra of **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO**: (a) measured at room temperature in their pure films (λ_{ex} = 460 nm), (b) measured at room temperature in their solid state (λ_{ex} = 460 nm).

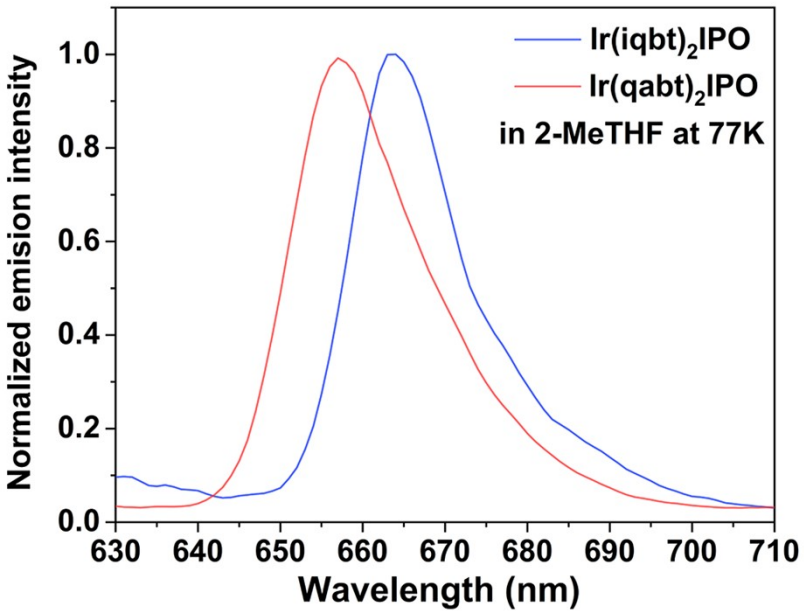

Figure S13. The PL spectra of complexes **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO** in degassed 2-methyltetrahydrofuran at 77 K (5×10^{-5} M and λ_{ex} = 520 nm).

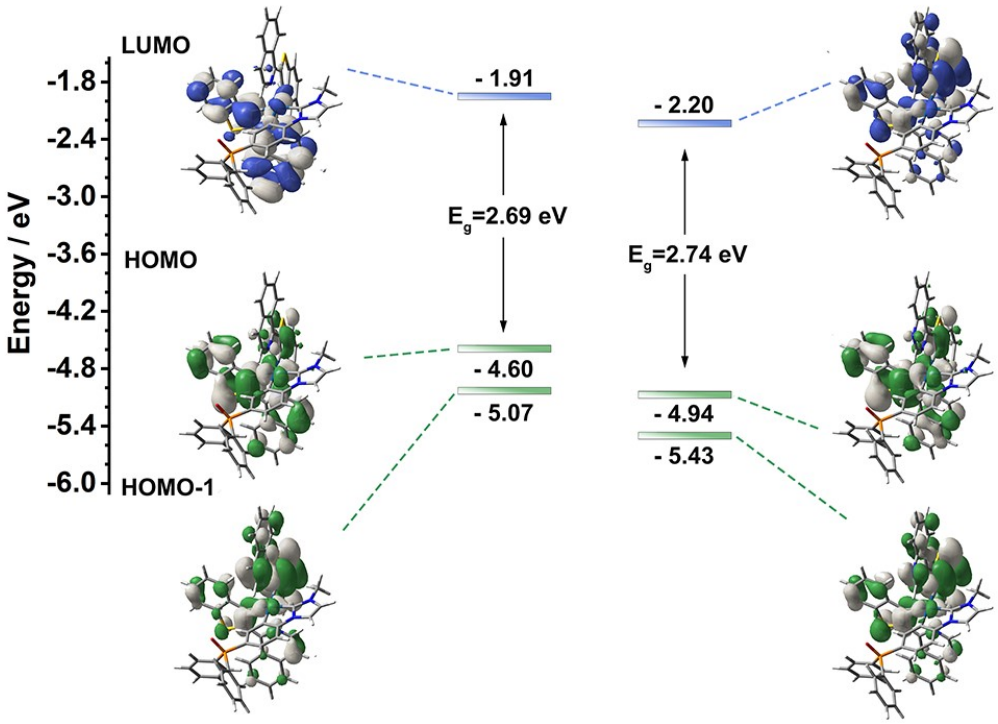

Figure S14. Theoretical contours and energy levels of the HOMO, HOMO-1, and LUMO for **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO** based on its optimized T_1 geometry from different angles.

Table S3 The Cartesian coordinates of the optimized triplet-state geometry of designed complexes studied in this work.

Ir(iqbt)$_2$IPO

Ir	7.6739577018	6.4267161328	15.2293143945
S	10.7460824038	3.1169953980	16.1786011104
S	4.6180435084	5.5860294358	18.5052638106
P	2.2318036824	7.9474570331	13.1793456030
N	7.9694038801	4.8879305745	13.8205336171
N	7.3982024595	7.8784634528	16.7075773542
N	8.2160423141	8.4818029544	13.1528831347
O	1.8003204995	6.7281057384	12.4071837648
C	6.2393673237	7.5130387443	14.0696746582
C	6.2432051967	5.5117585785	16.3812073395
C	6.7880186192	8.4407812363	13.1571589773
C	6.3620096762	7.6455484422	17.6432167585
C	5.5840807996	4.2444090164	16.4349303351
C	6.8280825639	9.8513237663	18.6829543177
C	9.1479470038	5.2552655226	16.1574401977
C	8.8942995308	7.6566263392	14.0118724215
C	9.5695864190	4.1886552454	15.3699326123
N	10.2064839049	7.9228999112	13.7650378084
C	6.0244319347	8.6635998694	18.6263690884
C	5.7184859994	3.1244352018	15.5770641366
H	6.4054083129	3.1728121361	14.7429332983
C	4.6419128439	9.1408228992	12.3477784270
H	4.0409992647	9.7580594325	11.6880814218
C	9.8084811823	5.2238516351	17.4467594511
C	8.1083890473	9.0098939657	16.7821705203
H	8.8981032816	9.1222403341	16.0502234074

C	9.6659365021	6.1159777709	18.5313050572
H	8.9799691932	6.9496542576	18.4468532188
C	5.8002829015	6.3660954292	17.4761405260
C	11.4371225785	3.9299960832	18.7778525897
H	12.1150236395	3.0865587692	18.8744845038
C	9.0863773118	9.2409734891	12.3870834671
H	8.7547739833	9.9503234296	11.6466228256
C	9.3123668808	3.0089869194	13.0687353590
C	1.6766993364	7.8922657014	14.9231866336
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H	6.4981480631	9.9506968547	11.6237526966
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C	4.6629697343	4.1132476929	17.5153859074
C	4.0337093882	8.2369617227	13.2294111525
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H	0.6351911471	8.3224370334	10.8671702998
C	4.0750005076	1.8821507956	16.8680956519

H	3.4973991587	0.9764754244	17.0285027473
C	7.2270665690	4.8003886417	12.6783183297
H	6.4353786612	5.5316793086	12.5877738095
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H	1.0949634733	12.8278375564	12.9050856854
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C	4.6995619324	9.5788594778	20.4739077304
H	3.8632692980	9.4633665169	21.1582607201

Ir(iqbt)$_2$IPO

Ir	7.6137410540	6.3758949540	15.2568852293
S	10.8949697592	3.3808883282	16.3040094106
S	4.5048494187	5.3077686330	18.3690457462
P	2.2130624588	7.9917421751	13.1572843264
N	8.0295615777	4.8540845115	13.8730758051
N	7.1985077219	7.7999706295	16.7309716780
N	8.2101897374	8.4188000855	13.1395683284
O	1.7200028507	6.8148312814	12.3585846722
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C	6.1355703610	5.4313819327	16.2666214935
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C	8.8662027606	7.6374722612	14.0488622073

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C	5.4305341440	3.2184050650	15.1263130862
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H	4.0628457126	9.7324022171	11.6333059093
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H	10.7660456058	7.4586931966	20.1497364785
C	4.8166825320	7.4052207358	14.0180301658
H	4.3194232751	6.7124777947	14.6903507611
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H	0.5545051054	8.4978013592	10.9169652964
C	3.7411374431	1.9038958057	16.2777011510
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C	7.4852427226	4.7729829358	12.6354012162
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C	1.1366372392	11.9587765992	12.5707641289
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H	4.6690359902	1.3464049834	14.4115665000
C	8.8449761010	1.8263216457	11.1512735749
H	8.3360080445	1.8935806878	10.1950488060
C	1.7202534815	10.8142079082	13.1134256383
H	2.3339244020	10.9002399606	14.0060044714
C	0.3406478367	11.8630140605	11.4253775751
H	-0.1147052571	12.7559939263	11.0049546571
C	9.6905057352	0.7738696048	11.4588342813
H	9.8681751573	-0.0147079305	10.7328962989
C	2.2957719854	8.6340401645	15.9456856010

H	3.1470312136	9.2767745182	15.7385674923
C	5.5057794112	10.3508070273	20.7130160722
H	5.3147217873	11.1048763715	21.4713746434
C	11.3085634480	7.2884786308	14.5395235529
H	12.2177565506	7.8233031126	14.2575348428
H	11.4081696042	6.2348889241	14.2703727496
H	11.1602374186	7.3679187242	15.6160614958
C	10.3090937339	0.7216594035	12.7202070951
H	10.9578632399	-0.1125222404	12.9723575427
C	0.1291337413	10.6207926467	10.8252626578
H	-0.4912849980	10.5432848231	9.9362661300
C	1.8184630723	8.5291819374	17.2530826066
H	2.2940523196	9.0959969305	18.0489314900
C	0.7430705801	7.6837726709	17.5383404375
H	0.3732541979	7.6013511371	18.5571407578
C	5.1272046602	8.1144900478	19.8478255215
H	4.6540469112	7.1486569177	19.9673103127
C	4.8954320900	9.0867438753	20.8079379670
H	4.2388216972	8.8634903330	21.6441459411
N	7.7329039048	3.8576419015	11.7323894224
N	7.4673922226	9.9824340318	17.6437390253

Table S4. Calculated transition wavelength and molecular orbital analysis in the triplet state for **Ir(iqbt)$_2$IPO** and **Ir(qabt)$_2$IPO** calculated by TDDFT approach.

	λ_{Expt}			Configuration [d]			^{3}MLCT(%
	λ[a]	[b]	E [c]			Nature	)
	71	682	1.7		(83%	^{3}MLCT/^{3}LC/^{3}LLC	13.72
Ir(iqbt)$_2$IPO	2		4	H→L	)	T	
				H-1→L	(8%)	^{3}MLCT/^{3}LLCT/^{3}LC	
Ir(qabt)$_2$IPO	67 4	680	1.8 4	H→L	(81%)	^{3}MLCT/^{3}LC/^{3}LLCT	16.45

	H-1→L	(11%)	^{3}MLCT/^{3}LLCT/^{3}LC

[a] Calculated emission wavelengths. [b] Measured emission wavelengths. [c] Excitation energy. [d] H, H-1 and L denote HOMO, HOMO-1 and LUMO, respectively; data in parentheses are the contributions of corresponding excitations.

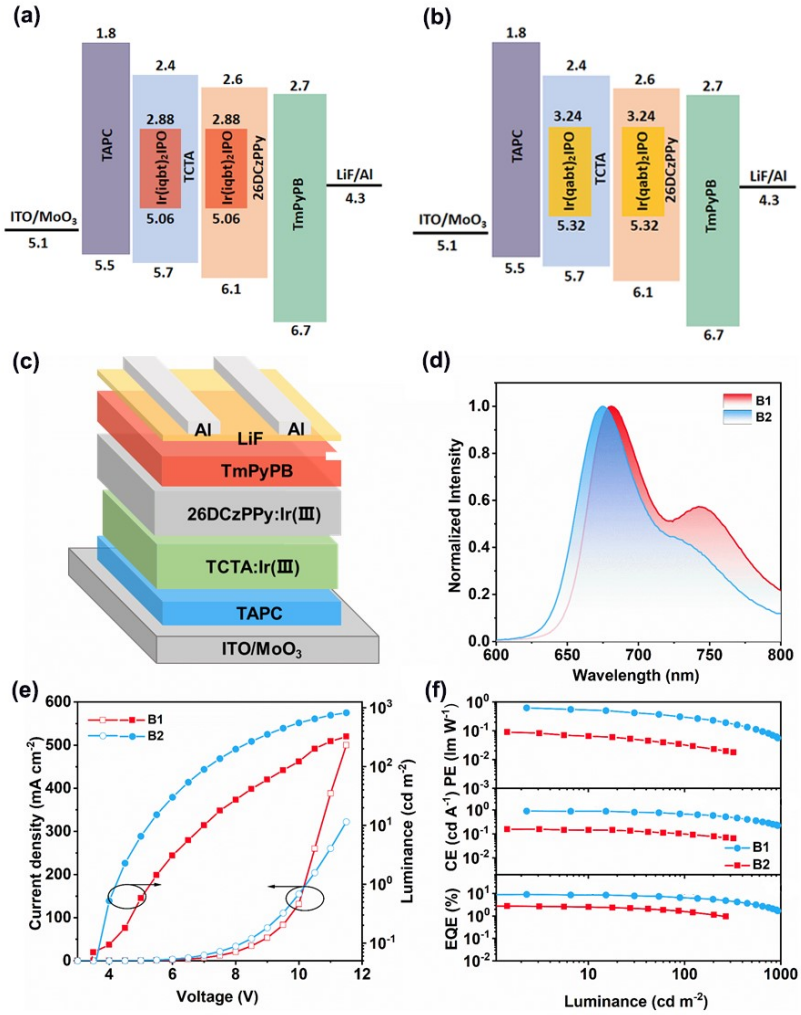

Figure S15. (a) The energy levels diagram of devices B1. (b) The energy levels diagram of devices B2. (c) Device structure of B1 and B2. (d) EL spectra of both devices B1 and B2. (e) J−V−L characteristics. (f) CE, PE, EQE vs luminance.