Supporting Information

Highly efficient green and red electroluminescence with extremely low efficiency roll-off based on iridium(III) complexes containing bis(diphenylphorothioyl)amide ancillary ligand

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General information

^{1}H NMR spectra were measured on a Bruker AM 400 spectrometer. The high resolution electrospray ionization mass spectra (HR ESI-MS) were recorded on an Bruker MTQ III q-TOF. TG measurements were carried out on a TG/DSC_STA449F3 analyzer (METTLER). UV-vis absorption and photoluminescence spectra were measured on a Shimadzu UV-2550 and a Hitachi F-4600 spectrophotometer at room temperature, respectively. Cyclic voltammetry measurements were conducted on a chi600e electrochemical workstation using Fc+/Fc as the internal standard and scan rate of 0.1 V s^{-1}. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)$_3$) and the unknown sample.[1] The decay lifetimes were measured with a HORIBA Scientific 3-D fluorescence spectrometer.

Synthesis of cyclometalated ligands.

2-Bromopyrimidine (24 mmol) or 4-chloroquinazoline (24 mmol), 4-(trifluoromethyl)phenyl boronic acid (20 mmol), Na_2CO_3 (60 mmol), and $Pd(PPh_3)_4$ (0.40 mmol) were dissolved in tetrahydrofuran/water (3:1, v/v; 40 mL). The solution was refluxed for 24 h and extracted twice with CH_2Cl_2 at room temperature. The combined organic solution was concentrated and purified by column chromatography to give 2-(4-(trifluoromethyl)phenyl)pyrimidine (tfpmd; yield: 75 %) and 4-(4-(trifluoromethyl)phenyl)quinazoline (tfpqz; yield: 70 %), respectively.

Synthesis of ancillary ligand.

A solution of chlorodiphenylphosphine (18.4 mmol) and hexamethyldisilazane (9.23 mmol) in toluene (30 mL) was refluxed overnight, after which the intermediate product was purified by rapid column chromatography. The intermediate product was then dissolved in toluene (30 mL) with S_8 (2.3 mmol) and refluxed overnight giving the bis(diphenylphorothioyl)amide (stpip) crude. The mixture was purified by recrystallized from CH_2Cl_2 (50 mL) and dissolved in methanol. After the addition of potassium hydroxide in methanol (0.74 M, 5 mL), the solution was stirred and concentrated to give the desired bis(diphenylphorothioyl)amide potassium salt (3.70 mmol, 40% yield). ^{1}H NMR (400 MHz, CD_3OD) δ 7.95-8.01 (m, 8H), 7.22-7.29 (m, 12H). ^{31}P NMR (162 MHz, CD_3OD) δ 37.56(2P). MS(ESI): m/z calcd for $C_{24}H_{20}P_2S_2N^-[M]^-$: 448.02, found 448.17.

X-ray crystallography

X-ray crystallographic measurements of the single crystals were carried out on a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using *SAINT* [2] program in order to reduce the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s per frame. Absorption corrections were applied using *SADABS* [3] supplied by Bruker. The structures were solved by Patterson methods and refined by full-matrix leastsquares on F^2 using the program *SHELXS-2014*.[4] The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps, other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and uring the final cycles refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso}.

OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω / sq. The deposition rate for organic compounds (TAPC (di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane), TCTA (4,4',4''-tri(9-carbazoyl)triphenylamine), 2,6DCzPPy (2,6-bis(3-(carbazol-9-yl)phenyl)pyridine), TmPyPB (1,3,5-*tri*(m-pyrid-3-yl-phenyl) benzene)) is 1 Å/s. The phosphor and the host were co-evaporated to form emitting layer from two separate sources. The cathode of LiF and Al were deposited with deposition rates of 0.1 and 3 Å/s, respectively. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

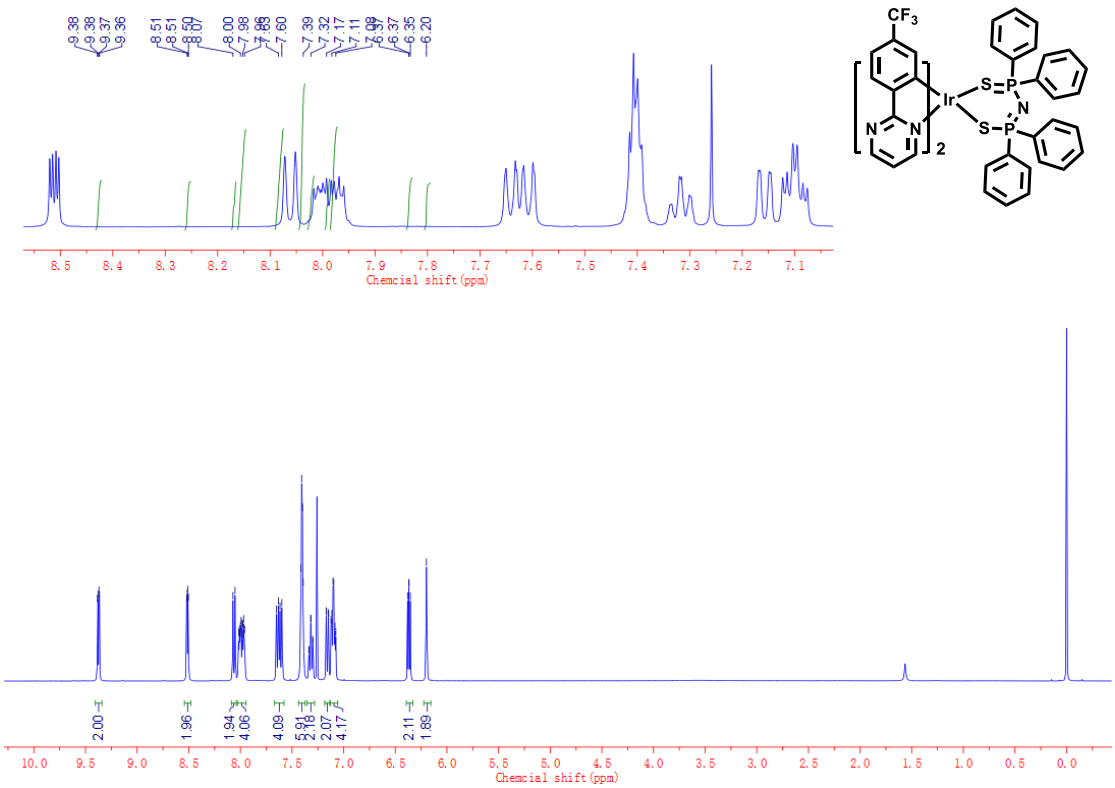

Fig. S1. The ^{1}H NMR spectrum of **Ir(tfpmd)$_2$(stpip)**.

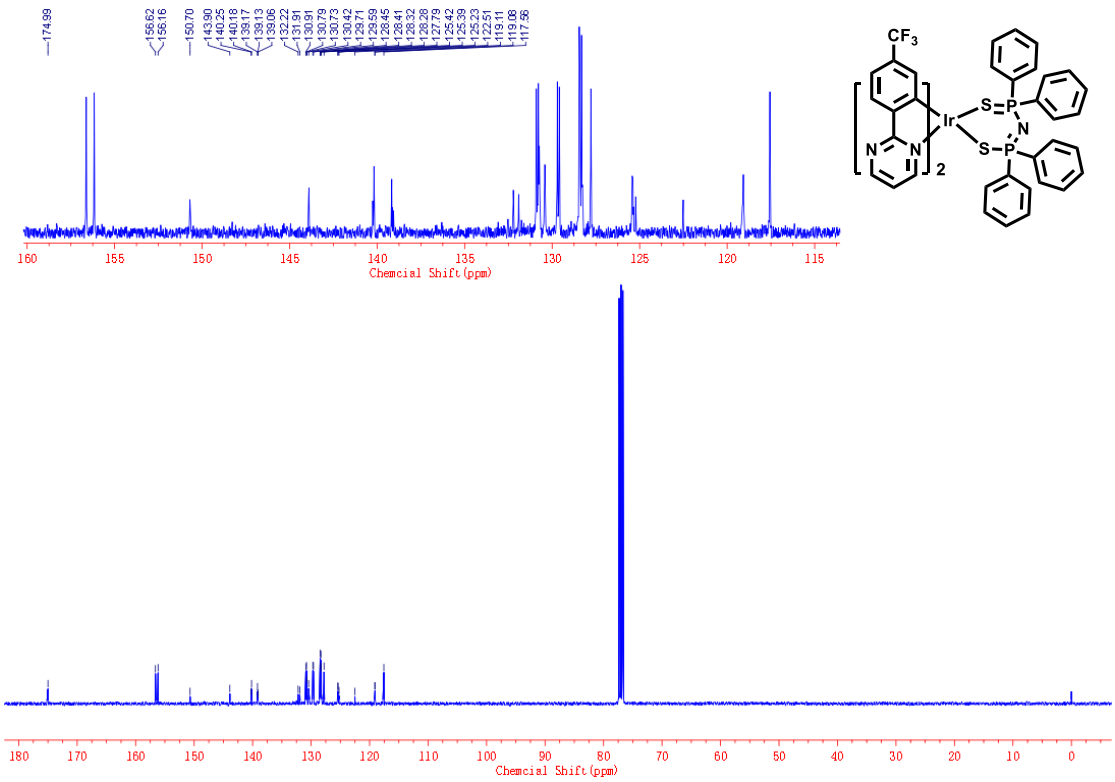

Fig. S2. The ^{13}C NMR spectrum of **Ir(tfpmd)$_2$(stpip)**.

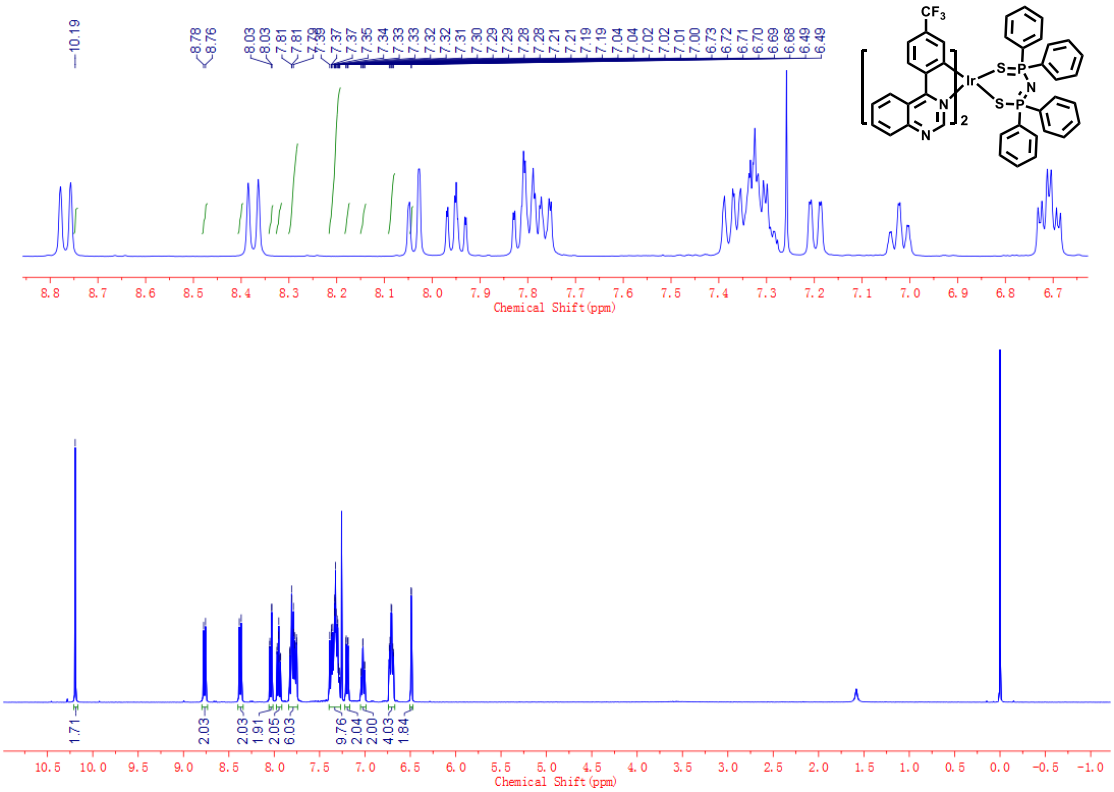

Fig. S3. The ^{1}H NMR spectrum of **Ir(tfpqz)$_2$(stpip)**.

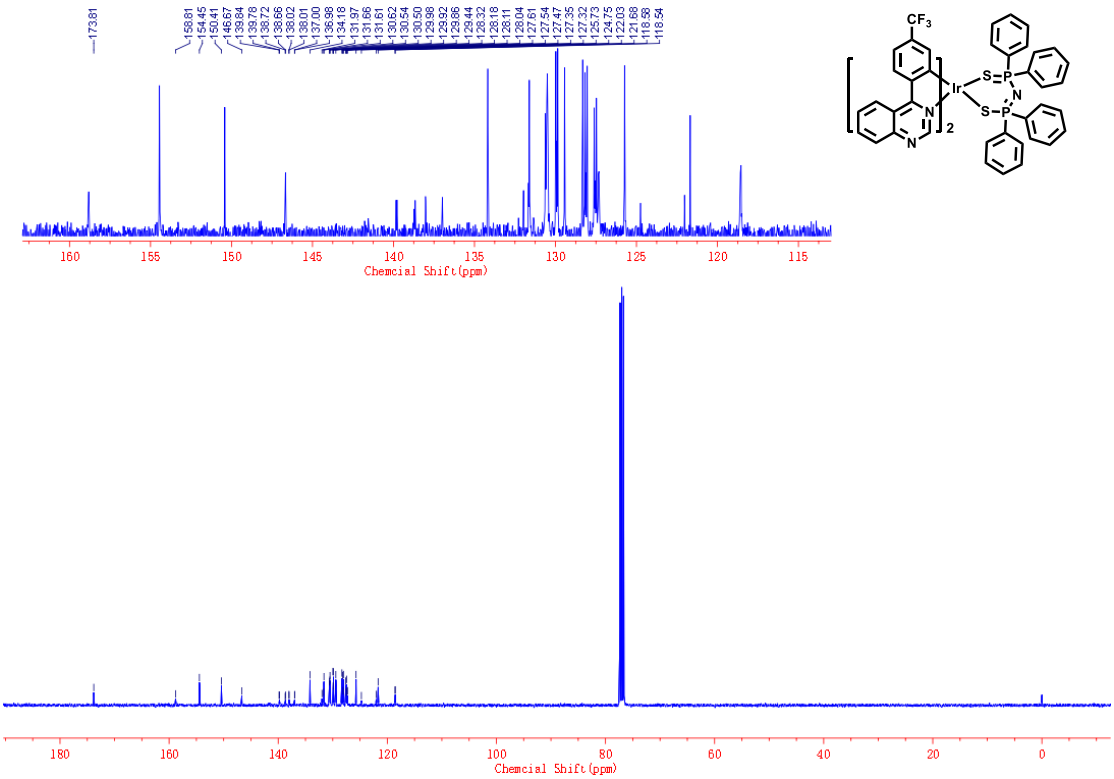

Fig. S4. The ^{13}C NMR spectrum of **Ir(tfpqz)$_2$(stpip)**.

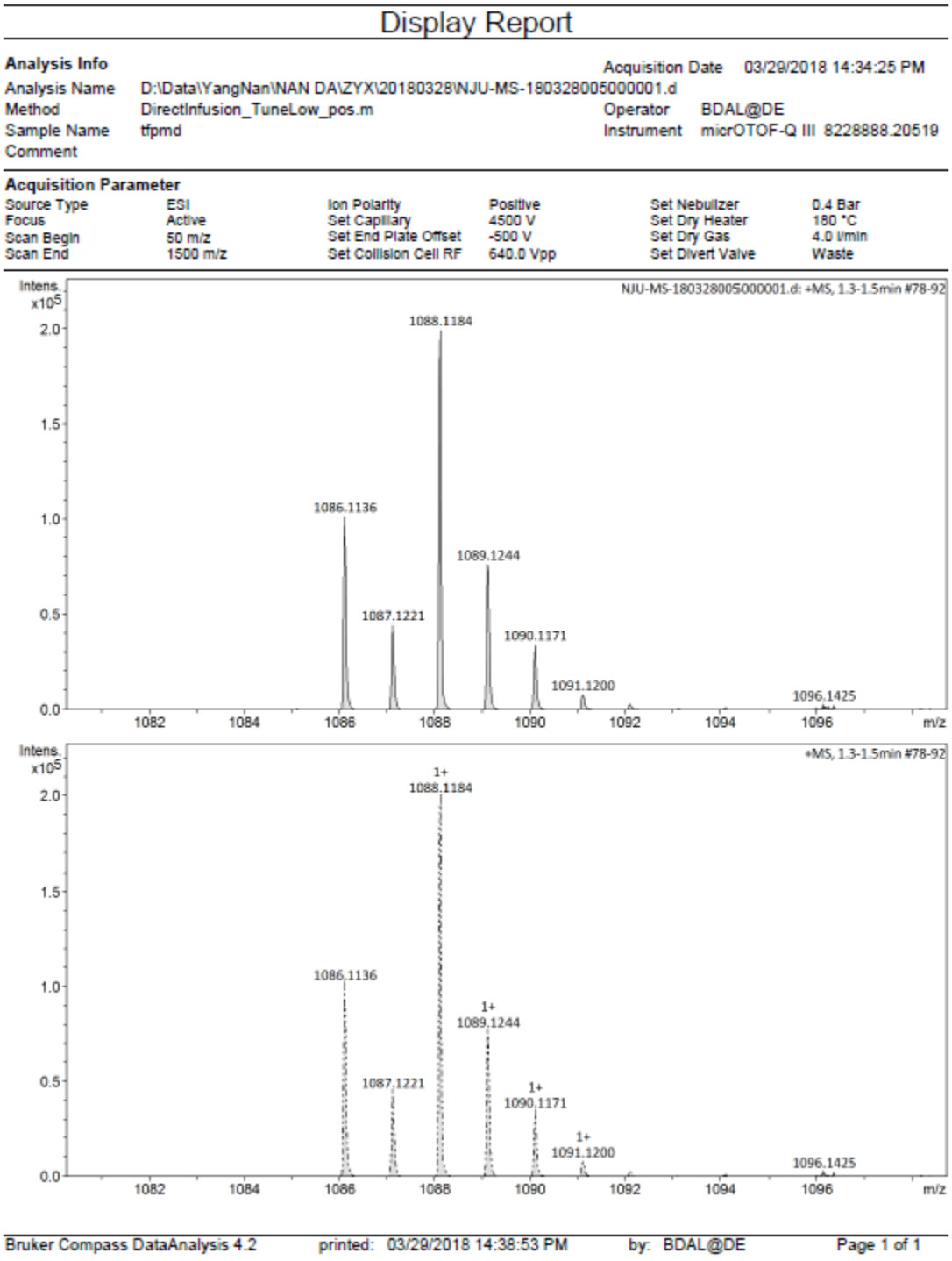

Fig. S5. The mass spectrum of **Ir(tfpmd)$_2$(stpip)**.

Display Report

Analysis Info

Analysis Name	D:\Data\YangNan\NAN DA\ZYX\20180328\NJU-MS-180328009000001.d	Acquisition Date	03/29/2018 14:55:43 PM
Method	DirectInfusion_TuneLow_pos.m	Operator	BDAL@DE
Sample Name	Tfqzl	Instrument	micrOTOF-Q III 8228888.20519
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	640.0 Vpp	Set Divert Valve	Waste

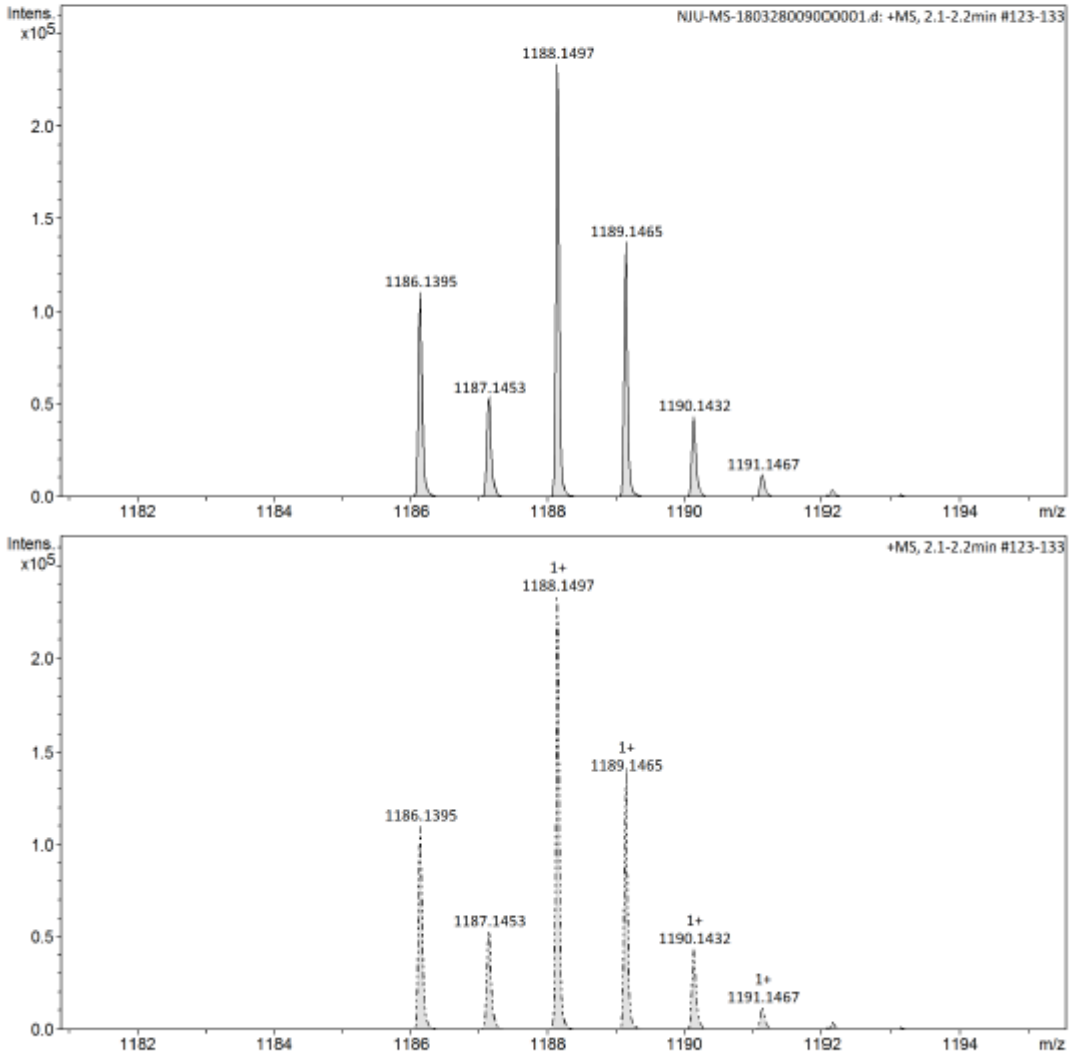

Fig. S6. The mass spectrum of **Ir(tfpqz)$_2$(stpip)**.

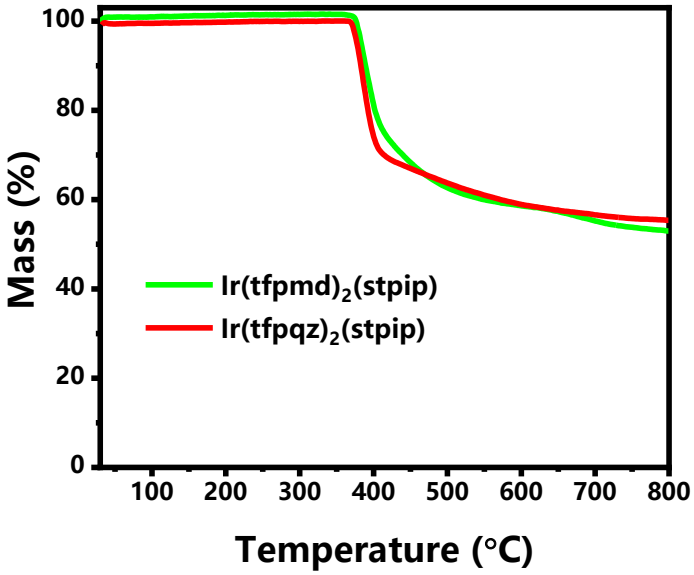

Fig. S7. The TGA curves of **Ir(tfpmd)$_2$(stpip)** and **Ir(tfpqz)$_2$(stpip)**.

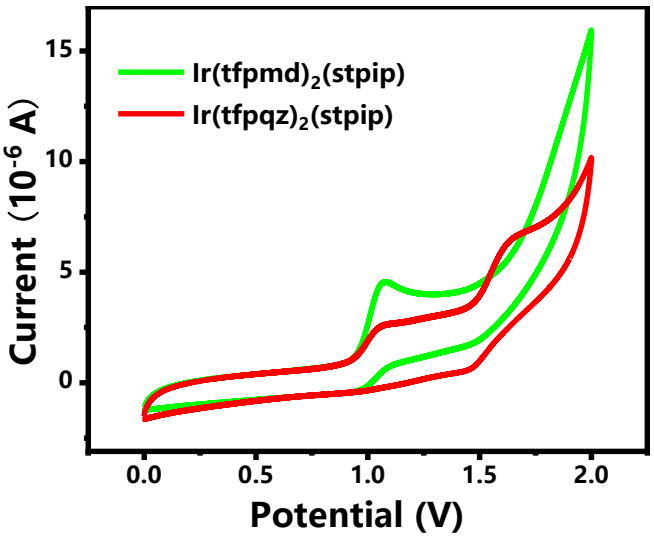

Fig. S8. The cyclic voltammogram curves of **Ir(tfpmd)$_2$(stpip)** and **Ir(tfpqz)$_2$(stpip)** in the range of 0-2V.

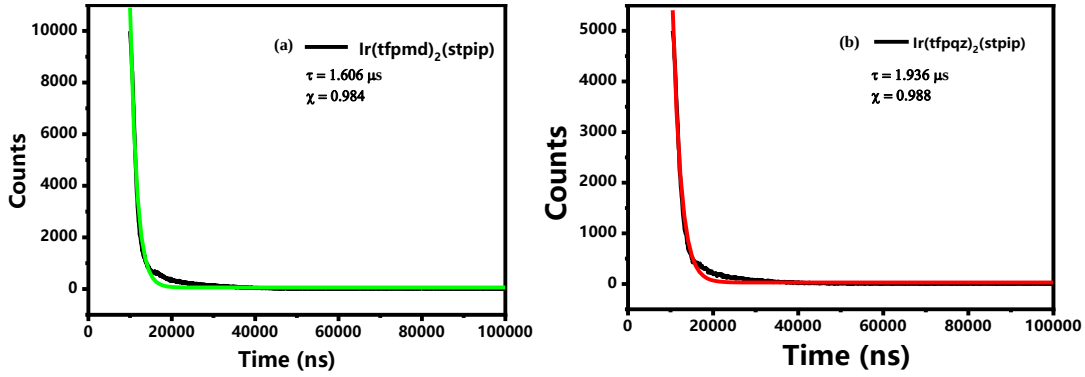

Fig. S9. The lifetime curves of **Ir(tfpmd)$_2$(stpip)** and **Ir(tfpqz)$_2$(stpip)** complexes.

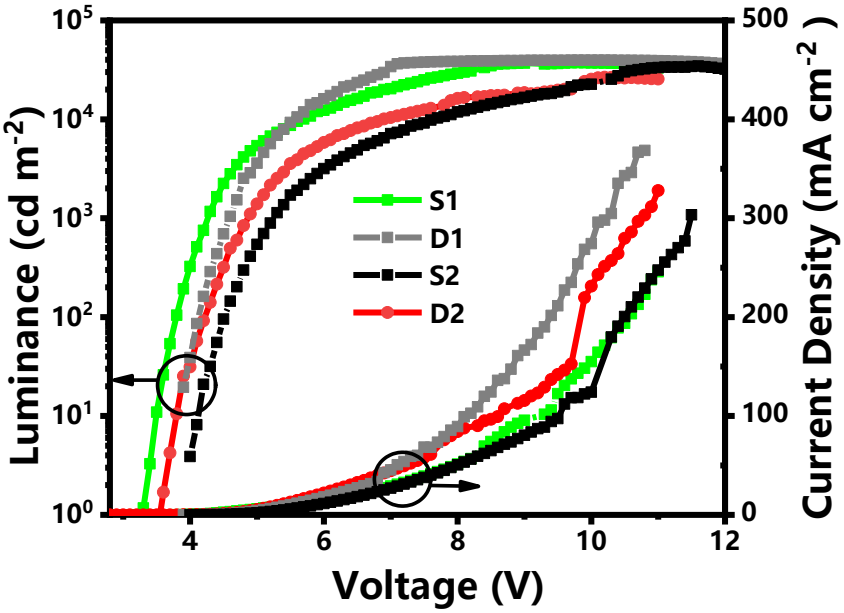

Fig. S10. Luminance-voltage-current density (L–V–J) curves of devices S1, D1, S2 and D2.

Table S1. Crystallographic data of **Ir(tfpmd)$_2$(stpip)** and **Ir(tfpqz)$_2$(stpip).**

	Ir(tfpmd)$_2$(stpip)	Ir(tfpqz)$_2$(stpip)
Formula	C46 H32 F6 Ir N5 P2 S2	C54 H36 F6 Ir N5 P2 S2
FW	1087.02	1187.14
T(K)	296(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P-1
a (Å)	11.5684(6)	20.775(3)
b (Å)	16.2297(9)	22.658(4)
c (Å)	23.9520(14)	10.1503(16)
α (deg)	90	90
β (deg)	101.5870(10)	90
γ (deg)	90	90
V (Å^3)	4405.4(4)	4777.9(13)
Z	4	4
ρ_{calcd} (mg/cm^3)	1.639	1.650
μ (Mo Kα) (mm^{-1})	3.263	3.017
F (000)	2144	2352
Reflns collected	24504	33901
Unique	7767	4215
Data/restraints/params	7767/ 180 / 615	4215 / 102 / 345
GOF on F^2	1.032	1.162
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0278, 0.0622	0.0461, 0.1035
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0379, 0.0666	0.0495, 0.1051
CCDC NO	1878027	1878028

$R_1{}^a = \sum||Fo|-|Fc||/\sum|Fo|$. $wR_2{}^b = [\sum w(F_o{}^2-F_c{}^2)^2/\sum w(F_o{}^2)]^{1/2}$

Table S2a The selected bond lengths and angels of **Ir(tfpmd)$_2$(stpip).**

Selected bonds Å					
C1-C6	1.374(5)	C26-C27	1.384(7)	C40-C43	1.455(5)
C1-C2	1.385(7)	C27-C28	1.370(6)	C41-C42	1.407(5)
C1-H1	0.93	C27-H27	0.93	C41-Ir1	2.030(4)
C2-C3	1.354(8)	C28-C29	1.390(6)	C42-H42	0.93
C2-H2	0.93	C28-H28	0.93	C43-N2	1.337(5)
C3-C4	1.329(7)	C29-C30	1.405(6)	C43-N1	1.369(4)
C3-H3	0.93	C29-C32	1.463(6)	C44-N2	1.334(6)
C4-C5	1.379(7)	C30-C31	1.408(5)	C44-C45	1.374(6)
C4-H4	0.93	C30-Ir1	2.012(4)	C44-H44	0.93
C5-C6	1.378(6)	C31-H31	0.93	C22-C23	1.344(9)
C5-H5	0.93	C32-N4	1.337(5)	C22-H22	0.93
C6-P2	1.812(4)	C32-N3	1.361(5)	C23-C24	1.368(7)
C7-C12	1.381(5)	C33-N4	1.324(6)	C23-H23	0.93
C7-C8	1.392(7)	C33-C34	1.370(7)	C24-H24	0.93
C7-H7	0.93	C33-H33	0.93	C25-F1'	1.255(13)
C8-C9	1.358(8)	C34-C35	1.378(6)	C25-F2	1.283(11)
C8-H8	0.93	C34-H34	0.93	C25-F1	1.353(11)
C9-C10	1.344(8)	C35-N3	1.339(5)	C25-F3	1.352(10)
C9-H9	0.93	C35-H35	0.93	C25-F2'	1.371(13)
C10-C11	1.395(7)	C36-F5'	1.247(11)	C25-F3'	1.431(14)
C10-H10	0.93	C36-F4	1.275(10)	C25-C26	1.471(7)
C11-C12	1.381(6)	C36-F5	1.332(8)	C45-C46	1.369(6)
C11-H11	0.93	C36-F6'	1.360(13)	C45-H45	0.93
C12-P2	1.808(4)	C36-F4'	1.369(11)	C46-N1	1.342(5)
C13-C18	1.372(6)	C36-F6	1.410(9)	C46-H46	0.93
C13-C14	1.401(6)	C36-C37	1.480(7)	Ir1-N1	2.053(3)
C13-H13	0.93	C37-C38	1.386(6)	Ir1-N3	2.052(3)
C14-C15	1.361(7)	C37-C42	1.389(6)	Ir1-S1	2.4700(9)
C14-H14	0.93	C38-C39	1.376(6)	Ir1-S2	2.4762(10)
C15-C16	1.363(7)	C38-H38	0.93	N5-P1	1.582(3)
C15-H15	0.93	C39-C40	1.396(5)	N5-P2	1.588(3)
C16-C17	1.376(5)	C39-H39	0.93	P1-S1	2.0058(13)
C26-C31	1.374(6)	C40-C41	1.389(5)	P2-S2	2.0173(14)
C1-C6	1.374(5)	C26-C27	1.384(7)	C40-C43	1.455(5)
C1-C2	1.385(7)	C27-C28	1.370(6)	C41-C42	1.407(5)
C1-H1	0.93	C27-H27	0.93	C41-Ir1	2.030(4)
Selected angles°					
C6-C1-C2	120.6(5)	C29-C30-Ir1	114.8(3)	C14-C13-H13	119.8
C6-C1-H1	119.7	C31-C30-Ir1	128.2(3)	C15-C14-C13	119.2(5)

C2-C1-H1	119.7	C26-C31-C30	120.7(4)	C15-C14-H14	120.4
C3-C2-C1	121.1(5)	C26-C31-H31	119.6	C13-C14-H14	120.4
C3-C2-H2	119.4	C30-C31-H31	119.6	C14-C15-C16	120.9(4)
C1-C2-H2	119.4	N4-C32-N3	124.6(4)	C14-C15-H15	119.6
C4-C3-C2	118.7(5)	N4-C32-C29	120.9(4)	C16-C15-H15	119.6
C4-C3-H3	120.6	N3-C32-C29	114.5(3)	C15-C16-C17	119.7(4)
C2-C3-H3	120.6	N4-C33-C34	124.0(4)	C15-C16-H16	120.1
C3-C4-C5	121.7(6)	N4-C33-H33	118	C17-C16-H16	120.1
C3-C4-H4	119.2	C34-C33-H33	118	C18-C17-C16	121.0(4)
C5-C4-H4	119.2	C33-C34-C35	117.0(4)	C18-C17-H17	119.5
C6-C5-C4	120.9(5)	C33-C34-H34	121.5	C16-C17-H17	119.5
C6-C5-H5	119.6	C35-C34-H34	121.5	C13-C18-C17	118.8(4)
C4-C5-H5	119.6	N3-C35-C34	120.9(4)	C13-C18-P1	120.4(3)
C1-C6-C5	117.0(4)	N3-C35-H35	119.5	C17-C18-P1	120.8(3)
C1-C6-P2	122.5(3)	C34-C35-H35	119.5	C20-C19-C24	118.9(4)
C5-C6-P2	120.4(3)	F4-C36-F5	109.8(7)	C20-C19-P1	120.6(3)
C12-C7-C8	119.9(5)	F5'-C36-F6'	109.0(9)	C24-C19-P1	120.4(4)
C12-C7-H7	120.1	F5'-C36-F4'	106.0(8)	C19-C20-C21	120.2(4)
C8-C7-H7	120.1	F6'-C36-F4'	100.2(8)	C19-C20-H20	119.9
C9-C8-C7	119.8(5)	F4-C36-F6	103.3(7)	C21-C20-H20	119.9
C9-C8-H8	120.1	F5-C36-F6	99.4(6)	C22-C21-C20	118.6(6)
C7-C8-H8	120.1	F5'-C36-C37	116.0(6)	C22-C21-H21	120.7
C10-C9-C8	121.5(5)	F4-C36-C37	116.3(6)	C20-C21-H21	120.7
C10-C9-H9	119.2	F5-C36-C37	115.4(6)	C23-C22-C21	121.4(5)
C8-C9-H9	119.2	F6'-C36-C37	114.5(6)	C23-C22-H22	119.3
C9-C10-C11	119.5(6)	F4'-C36-C37	109.7(6)	C21-C22-H22	119.3
C9-C10-H10	120.2	F6-C36-C37	110.6(5)	C22-C23-C24	120.5(5)
C11-C10-H10	120.2	C38-C37-C42	121.5(4)	C22-C23-H23	119.8
C12-C11-C10	120.4(5)	C38-C37-C36	119.1(4)	C24-C23-H23	119.8
C12-C11-H11	119.8	C42-C37-C36	119.4(4)	C23-C24-C19	120.4(5)
C10-C11-H11	119.8	C39-C38-C37	119.0(4)	C23-C24-H24	119.8
C11-C12-C7	118.9(4)	C39-C38-H38	120.5	C19-C24-H24	119.8
C11-C12-P2	119.0(3)	C37-C38-H38	120.5	C41-C40-C39	122.5(4)
C7-C12-P2	122.1(3)	C38-C39-C40	119.7(4)	C41-C40-C43	115.5(3)
C18-C13-C14	120.5(4)	C38-C39-H39	120.2	C39-C40-C43	122.0(4)
C18-C13-H13	119.8	C40-C39-H39	120.2	C40-C41-C42	117.0(3)
C40-C41-Ir1	114.6(3)	C30-Ir1-S2	172.41(11)	C29-C30-C31	116.6(4)
C42-C41-Ir1	128.3(3)	C41-Ir1-S2	85.87(11)	N3-Ir1-S2	92.77(9)

C37-C42-C41	120.3(4)	N1-Ir1-S2	90.29(9)	S1-Ir1-S2	102.51(3)
C37-C42-H42	119.8	F2-C25-F1	104.0(8)	C46-N1-C43	117.2(3)
C41-C42-H42	119.8	F2-C25-F3	105.1(9)	C46-N1-Ir1	127.7(2)
N2-C43-N1	123.5(4)	F1-C25-F3	104.1(7)	C43-N1-Ir1	115.1(2)
N2-C43-C40	121.7(3)	F1'-C25-F2'	110.4(10)	C44-N2-C43	117.3(4)
N1-C43-C40	114.7(3)	F1'-C25-F3'	107.4(10)	C35-N3-C32	117.5(3)
N2-C44-C45	122.8(4)	F2'-C25-F3'	98.2(9)	C35-N3-Ir1	127.0(3)
N2-C44-H44	118.6	F1'-C25-C26	117.3(8)	C32-N3-Ir1	115.4(2)
C45-C44-H44	118.6	F2-C25-C26	115.5(6)	C33-N4-C32	115.9(4)
C46-C45-C44	117.1(4)	F1-C25-C26	113.5(7)	P1-N5-P2	133.8(2)
C46-C45-H45	121.4	F3-C25-C26	113.5(6)	N5-P1-C18	106.79(19)
C44-C45-H45	121.4	F2'-C25-C26	110.8(7)	N5-P1-C19	110.29(19)
N1-C46-C45	121.9(4)	F3'-C25-C26	111.1(6)	C18-P1-C19	104.81(16)
N1-C46-H46	119	C31-C26-C27	121.5(4)	N5-P1-S1	119.41(13)
C45-C46-H46	119	C31-C26-C25	120.0(5)	C18-P1-S1	106.00(13)
C30-Ir1-C41	91.68(15)	C27-C26-C25	118.5(5)	C19-P1-S1	108.49(14)
C30-Ir1-N1	96.36(14)	C28-C27-C26	119.3(4)	N5-P2-C12	106.51(18)
C41-Ir1-N1	80.01(13)	C28-C27-H27	120.4	N5-P2-C6	108.60(18)
C30-Ir1-N3	80.24(14)	C26-C27-H27	120.4	C12-P2-C6	104.15(19)
C41-Ir1-N3	94.27(13)	C27-C28-C29	120.0(4)	N5-P2-S2	120.00(14)
N1-Ir1-N3	173.31(12)	C27-C28-H28	120	C12-P2-S2	107.80(15)
C30-Ir1-S1	80.89(10)	C29-C28-H28	120	C6-P2-S2	108.64(14)
C41-Ir1-S1	168.95(11)	C28-C29-C30	121.9(4)	P1-S1-Ir1	108.37(5)
N1-Ir1-S1	92.63(8)	C28-C29-C32	123.3(4)	P2-S2-Ir1	111.20(5)
N3-Ir1-S1	92.51(8)	C30-C29-C32	114.8(4)		

Table S2b The selected bond lengths and angels of **Ir(tfpqz)$_2$(stpip).**

Selected bonds Å					
Ir(1)-C(6)	2.002(6)	C(2)-C(3)	1.383(10)	C(31)-C(32)	1.376(12)
Ir(1)-C(6)#1	2.002(6)	C(2)-C(7)	1.395(9)	C(31)-C(36)	1.395(11)
Ir(1)-N(1)#1	2.043(5)	C(3)-C(4)	1.392(9)	C(32)-C(33)	1.399(11)
Ir(1)-N(1)	2.043(5)	C(3)-H(3)	0.95	C(32)-H(32)	0.95
Ir(1)-S(1)#1	2.4875(16)	C(4)-C(5)	1.400(9)	C(33)-C(34)	1.378(18)
Ir(1)-S(1)	2.4875(16)	C(4)-H(4)	0.95	C(33)-H(33)	0.95
S(1)-P(1)	2.017(2)	C(5)-C(6)	1.432(9)	C(34)-C(35)	1.352(19)
P(1)-N(5)	1.587(4)	C(5)-C(8)	1.460(7)	C(34)-H(34)	0.95
P(1)-C(42)	1.816(7)	C(6)-C(7)	1.397(8)	C(35)-C(36)	1.382(15)

P(1)-C(31)	1.830(8)	C(7)-H(7)	0.95	C(35)-H(35)	0.95
N(1)-C(8)	1.343(7)	C(8)-C(9)	1.430(8)	C(36)-H(36)	0.95
N(1)-C(15)	1.378(8)	C(9)-C(10)	1.401(9)	C(37)-C(38)	1.379(10)
N(2)-C(15)	1.299(8)	C(9)-C(14)	1.424(9)	C(37)-C(42)	1.380(10)
N(2)-C(14)	1.359(9)	C(10)-C(11)	1.358(10)	C(37)-H(37)	0.95
N(5)-P(1)#1	1.587(4)	C(10)-H(10)	0.95	C(38)-C(39)	1.374(13)
C(1)-F(2)	1.266(9)	C(11)-C(12)	1.397(12)	C(38)-H(38)	0.95
C(1)-F(1')	1.268(15)	C(11)-H(11)	0.95	C(39)-C(40)	1.371(13)
C(1)-F(1)	1.327(9)	C(12)-C(13)	1.358(12)	C(39)-H(39)	0.95
C(1)-F(3)	1.373(9)	C(12)-H(12)	0.95	C(40)-C(41)	1.383(11)
C(1)-F(3')	1.378(14)	C(13)-C(14)	1.409(9)	C(40)-H(40)	0.95
C(1)-F(2')	1.419(14)	C(13)-H(13)	0.95	C(41)-C(42)	1.390(10)
C(1)-C(2)	1.499(9)	C(15)-H(15)	0.95	C(41)-H(41)	0.95
Selected angles°					
C(6)-Ir(1)-C(6)#1	91.2(3)	F(2)-C(1)-C(2)	113.4(6)	N(2)-C(14)-C(13)	118.5(6)
C(6)-Ir(1)-N(1)#1	96.8(2)	F(1')-C(1)-C(2)	121.5(9)	N(2)-C(14)-C(9)	122.0(6)
C(6)#1-Ir(1)-N(1)#1	79.5(2)	F(1)-C(1)-C(2)	111.5(6)	C(13)-C(14)-C(9)	119.4(6)
C(6)-Ir(1)-N(1)	79.5(2)	F(3)-C(1)-C(2)	112.1(6)	N(2)-C(15)-N(1)	125.5(6)
C(6)#1-Ir(1)-N(1)	96.8(2)	F(3')-C(1)-C(2)	110.7(8)	N(2)-C(15)-H(15)	117.3
N(1)#1-Ir(1)-N(1)	174.8(3)	F(2')-C(1)-C(2)	113.0(7)	N(1)-C(15)-H(15)	117.3
C(6)-Ir(1)-S(1)#1	83.76(17)	C(3)-C(2)-C(7)	121.2(6)	C(32)-C(31)-C(36)	120.9(8)
C(6)#1-Ir(1)-S(1)#1	171.10(17)	C(3)-C(2)-C(1)	119.6(6)	C(32)-C(31)-P(1)	119.5(6)
N(1)#1-Ir(1)-S(1)#1	93.75(14)	C(7)-C(2)-C(1)	119.1(6)	C(36)-C(31)-P(1)	119.4(8)
N(1)-Ir(1)-S(1)#1	89.53(15)	C(2)-C(3)-C(4)	119.6(6)	C(31)-C(32)-C(33)	118.8(9)
C(6)-Ir(1)-S(1)	171.10(17)	C(2)-C(3)-H(3)	120.2	C(31)-C(32)-H(32)	120.6
C(6)#1-Ir(1)-S(1)	83.76(17)	C(4)-C(3)-H(3)	120.2	C(33)-C(32)-H(32)	120.6
N(1)#1-Ir(1)-S(1)	89.53(15)	C(3)-C(4)-C(5)	119.8(6)	C(32)-C(33)-C(34)	120.3(12)
N(1)-Ir(1)-S(1)	93.75(14)	C(3)-C(4)-H(4)	120.1	C(32)-C(33)-H(33)	119.9
S(1)#1-Ir(1)-S(1)	102.12(8)	C(5)-C(4)-H(4)	120.1	C(34)-C(33)-H(33)	119.9
P(1)-S(1)-Ir(1)	109.61(8)	C(4)-C(5)-C(6)	121.1(5)	C(35)-C(34)-C(33)	119.9(10)
N(5)-P(1)-C(42)	107.8(3)	C(4)-C(5)-C(8)	124.5(6)	C(35)-C(34)-H(34)	120
N(5)-P(1)-C(31)	110.6(3)	C(6)-C(5)-C(8)	113.9(5)	C(33)-C(34)-H(34)	120
C(42)-P(1)-C(31)	104.2(3)	C(7)-C(6)-C(5)	117.1(6)	C(34)-C(35)-C(36)	121.7(12)
N(5)-P(1)-S(1)	119.4(3)	C(7)-C(6)-Ir(1)	128.3(5)	C(34)-C(35)-H(35)	119.1
C(42)-P(1)-S(1)	105.8(2)	C(5)-C(6)-Ir(1)	114.6(4)	C(36)-C(35)-H(35)	119.1
C(31)-P(1)-S(1)	107.9(3)	C(6)-C(7)-C(2)	121.0(6)	C(31)-C(36)-C(35)	118.4(12)
C(8)-N(1)-C(15)	118.8(5)	C(6)-C(7)-H(7)	119.5	C(31)-C(36)-H(36)	120.8
C(8)-N(1)-Ir(1)	116.1(4)	C(2)-C(7)-H(7)	119.5	C(35)-C(36)-H(36)	120.8
C(15)-N(1)-Ir(1)	125.1(4)	N(1)-C(8)-C(9)	118.6(5)	C(38)-C(37)-C(42)	120.8(8)
C(15)-N(2)-C(14)	117.0(5)	N(1)-C(8)-C(5)	113.6(5)	C(38)-C(37)-H(37)	119.6
P(1)#1-N(5)-P(1)	134.1(6)	C(9)-C(8)-C(5)	127.8(5)	C(42)-C(37)-H(37)	119.6
F(2)-C(1)-F(1')	125.0(10)	C(10)-C(9)-C(14)	118.1(6)	C(37)-C(38)-C(39)	120.2(8)
F(2)-C(1)-F(1)	112.3(7)	C(10)-C(9)-C(8)	125.5(6)	C(37)-C(38)-H(38)	119.9

F(1')-C(1)-F(1)	50.1(9)	C(14)-C(9)-C(8)	116.3(6)	C(39)-C(38)-H(38)	119.9
F(2)-C(1)-F(3)	106.8(7)	C(11)-C(10)-C(9)	120.5(7)	C(40)-C(39)-C(38)	119.9(8)
F(1')-C(1)-F(3)	50.0(9)	C(11)-C(10)-H(10)	119.7	C(40)-C(39)-H(39)	120.1
F(1)-C(1)-F(3)	99.9(6)	C(9)-C(10)-H(10)	119.7	C(38)-C(39)-H(39)	120.1
F(2)-C(1)-F(3')	43.5(7)	C(12)-C(11)-C(10)	121.5(8)	C(39)-C(40)-C(41)	120.0(8)
F(1')-C(1)-F(3')	108.9(10)	C(12)-C(11)-H(11)	119.3	C(39)-C(40)-H(40)	120
F(1)-C(1)-F(3')	137.5(9)	C(10)-C(11)-H(11)	119.3	C(41)-C(40)-H(40)	120
F(3)-C(1)-F(3')	68.1(8)	C(11)-C(12)-C(13)	119.7(7)	C(40)-C(41)-C(42)	120.7(8)
F(2)-C(1)-F(2')	53.1(7)	C(11)-C(12)-H(12)	120.2	C(40)-C(41)-H(41)	119.7
F(1')-C(1)-F(2')	104.3(10)	C(13)-C(12)-H(12)	120.2	C(42)-C(41)-H(41)	119.7
F(1)-C(1)-F(2')	63.9(8)	C(12)-C(13)-C(14)	120.4(7)	C(37)-C(42)-C(41)	118.3(7)
F(3)-C(1)-F(2')	134.9(8)	C(12)-C(13)-H(13)	119.8	C(37)-C(42)-P(1)	122.6(5)
F(3')-C(1)-F(2')	95.0(9)	C(14)-C(13)-H(13)	119.8	C(41)-C(42)-P(1)	119.1(6)

Table S3 Data of theoretical calculation of orbital energy level and electron cloud distribution

Complex	Orbital	Energy/ eV	E_{gap}/ eV	Composition (%)		
				Ir	Main ligands	Ancillary ligands
Ir(tfpmd)$_2$(stpip)	HOMO	-5.74	3.74	49.24	33.26	24.24
	LUMO	-2.00		3.33	82.93	17.32
Ir(tfpqz)$_2$(stpip)	HOMO	-5.79	3.24	46.56	35.96	17.48
	LUMO	-2.55		4.19	86.16	9.65

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