

Supporting information

Efficient sky-blue organic light-emitting diodes with extremely low efficiency roll-off based on stable iridium complexes with bis(diphenylphorothioyl)amide ligand

Lin Zhang¹, Zhiping Yan¹, You-Xuan Zheng*^{1,2}

¹State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China, E-mail: yxzheng@nju.edu.cn

²Shenzhen Research Institute of Nanjing University, Shenzhen 518057, P. R. China

General information

¹H NMR spectra were measured on Bruker AM 500 spectrometer. The high resolution electrospray ionization mass spectra (HR ESI-MS) were recorded on an Bruker MTQ III q-TOF. Thermal analysis were measured on PerkinElmer Pyris 1 DSC. UV-vis absorption and photoluminescence spectra were measured on Shimadzu UV-3100 and Hitachi F-4600 spectrophotometer at room temperature, respectively. Cyclic voltammetry measurements were carried out using chi600 electrochemical workstation with Fc⁺/Fc as the standard at the rate of 0.1 V s⁻¹. The decay lifetimes were measured with a HORIBA Scientific 3-D fluorescence spectrometer. The ionization potentials were measured with Ionization Energy Measurement System (Model IPS-4) in vacuum with solid compounds.

X-ray crystallography

X-ray crystallographic measurements of the single crystals were carried out on Bruker APEX-II CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Cell parameters were retrieved using SMART software and refined using *SAINTE*¹ 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*² supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on F² using the program *SHELXS-2014*³. The positions of metal atoms and their first coordination spheres were located from direct-Emaps,

other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and during 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 $15 \Omega \text{ sq}^{-1}$. The deposition rate for organic compounds is $1\text{-}2 \text{ \AA s}^{-1}$. The phosphor and host were co-evaporated from different sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 \AA s^{-1} and then by evaporation of Al metal with a rate of 3 \AA s^{-1} . The effective area of the emitting diode is 0.1 cm^2 . The characteristics of the devices were measured with a computer 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 CIE coordinates were calculated using a test program of the spectra scan PR650 spectrophotometer.

Synthesis of ancillary ligand

Hexamethyldisilazane (9.0 mmol) was added dropwise to a solution of chlorodiphenylphosphine (18.2 mmol) in 40 mL toluene under N_2 atmosphere at $115 \text{ }^\circ\text{C}$. The mixture was stirred for 8 h, and purified by rapid column chromatography. Then, the white intermediate product and S_8 (2.5 mmol) was dissolved in 20 mL toluene and refluxed for 8 h. The solvent was removed under vacuum, and the crude product was dissolved in 40 mL CH_2Cl_2 . Aqueous solution of KOH (1 M) was added dropwise until the pH turned to 7-8. The solution was stirred and concentrated to give the desired bis(diphenylphosphorothioyl)amide potassium salt (3.6 mmol, 40% yield).

Table S1 Crystallographic data of complexes $(\text{dfppy})_2\text{Ir}(\text{Stpip})$ and $(\text{dfppm})_2\text{Ir}(\text{Stpip})$.

	$(\text{dfppy})_2\text{Ir}(\text{Stpip})$	$(\text{dfppm})_2\text{Ir}(\text{Stpip})$
formula	$\text{C}_{46}\text{H}_{32}\text{N}_3\text{F}_4\text{P}_2\text{S}_2\text{Ir}$	$\text{C}_{44}\text{H}_{30}\text{N}_5\text{O}_4\text{P}_2\text{S}_2\text{Ir}$
Formula weight	1021	1022.99
Temperature/K	296.15	296.15
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a (Å)	10.5036(5)	44.788(3)
b (Å)	12.3151(7)	15.7609(12)
c (Å)	16.8096(9)	26.088(2)
α /°	102.2130(10)	90
β /°	98.1790(10)	103.012(2)
γ /°	96.3050(10)	90

$V/\text{\AA}^3$	2081.43(19)	17943(2)
Z	2	16
$\rho_{\text{calc}}/\text{g/cm}^3$	1.629	1.515
μ (Mo K α)/mm ⁻¹	3.44	3.193
$F(000)$	1008	8064
Reflns collected	11654	61023
Unique	7265	20638
Data/restraints/parameters	7265/0/523	20638/1861/1045
GOF on F^2	1.072	1.045
$R_I^a, wR_2^b[I > 2\sigma(I)]$	0.0307, 0.0891	0.0401, 0.0878
R_I^a, wR_2^b (all data)	0.0342, 0.0921	0.0718, 0.0973

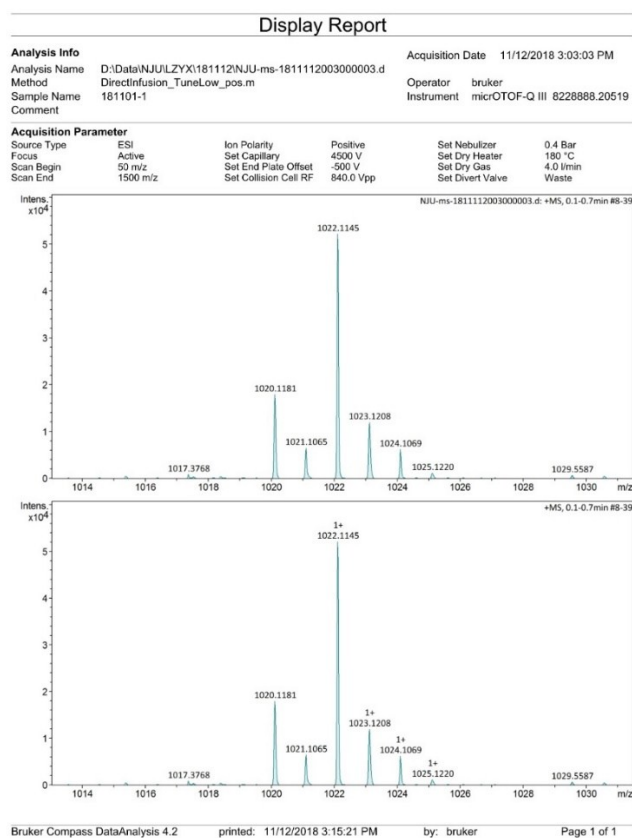
$$R_I^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, wR_2^b = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table S2 Selected bond lengths and angles of (dfppy)₂Ir(Stpip) and (dfppm)₂Ir(Stpip).

Selected bonds	Bond Lengths (Å)	Selected bonds	Bond Lengths (Å)
Ir ₁ C ₁₂	2.015(5)	Ir ₁ C ₂₉	2.019(5)
Ir ₁ N ₂	2.066(4)	Ir ₁ N ₃	2.054(3)
Ir ₁ C ₁	2.012(5)	Ir ₁ C ₈₂	2.012(6)
Ir ₁ N ₁	2.061(4)	Ir ₁ N ₁	2.057(3)
Ir ₁ S ₁	2.486(1)	Ir ₁ S ₁	2.474(1)
Ir ₁ S ₂	2.486(1)	Ir ₁ S ₂	2.465(2)
Selected Angles	(°)	Selected Angles	(°)
C ₁₂ Ir ₁ C ₁	90.51(17)	C ₂₉ Ir ₁ C ₈₂	90.80(2)
C ₁₂ Ir ₁ N ₁	94.80(17)	C ₂₉ Ir ₁ N ₁	92.47(18)
C ₁₂ Ir ₁ N ₂	80.51(17)	C ₂₉ Ir ₁ N ₃	80.45(18)
C ₁₂ Ir ₁ S ₂	83.47(12)	C ₂₉ Ir ₁ S ₂	86.40(15)
S ₁ Ir ₁ S ₂	102.55(4)	S ₁ Ir ₁ S ₂	101.25(5)
S ₁ Ir ₁ N ₁	89.19(11)	S ₁ Ir ₁ N ₁	93.52(11)
S ₁ Ir ₁ C ₁	83.88(13)	S ₁ Ir ₁ C ₈₂	82.29(13)
S ₁ Ir ₁ N ₂	94.91(12)	S ₁ Ir ₁ N ₃	92.87(11)
N ₂ Ir ₁ S ₂	89.17(11)	N ₃ Ir ₁ S ₂	89.45(12)
N ₂ Ir ₁ C ₁	94.85(17)	N ₃ Ir ₁ C ₈₂	95.85(18)
C ₁ Ir ₁ N ₁	79.95(17)	C ₈₂ Ir ₁ N ₁	79.65(18)
N ₁ Ir ₁ S ₂	95.47(12)	N ₁ Ir ₁ S ₂	94.61(13)
N ₁ Ir ₁ N ₂	173.02(15)	N ₁ Ir ₁ N ₃	171.63(15)
C ₁₂ Ir ₁ S ₁	172.46(12)	C ₂₉ Ir ₁ S ₁	169.87(14)
C ₁ Ir ₁ S ₂	172.13(13)	C ₈₂ Ir ₁ S ₂	173.51(14)

Table S3 Theoretical calculation data of orbital distribution.

Complex	Orbital	Composition (%)		
		Ir	Main Ligands	Ancillary ligand
(dfppy) ₂ Ir(Stpip)	LUMO+2	2.18	7.59	90.24
	LUMO+1	5.98	89.25	4.77
	LUMO	5.25	77.64	17.11
	HOMO	47.46	40.49	12.05
	HOMO-1	40.00	14.47	45.52
	HOMO-2	35.03	12.90	52.07
(dfppm) ₂ Ir(Stpip)	HOMO-2	37.42	13.88	48.87
	HOMO-1	34.16	16.72	49.25
	HOMO	46.69	33.33	20.02
	LUMO	5.09	80.45	14.5
	LUMO+1	6.03	89.63	4.39
	LUMO+2	2.68	79.55	17.89

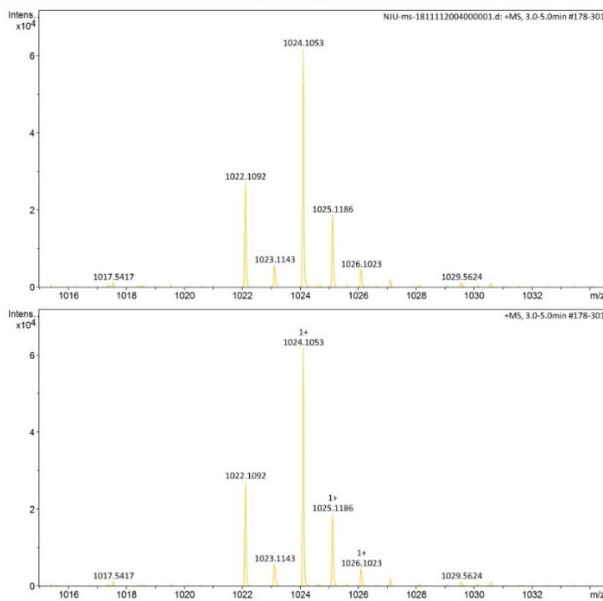
Fig.S1 The mass spectra of (dfppy)₂Ir(Stpip).

Display Report

Analysis Info
 Analysis Name: D:\Data\NJULZY\X181112\NJU-ms-1811112004000001.d
 Method: DirectInfusion_TuneLow_pos.ms
 Sample Name: 181101-2
 Comment:
 Acquisition Date: 11/12/2018 3:10:52 PM
 Operator: bruker
 Instrument: micrOTOF-Q III 8228888.20519

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	840.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.2 printed: 11/12/2018 3:21:29 PM by: bruker Page 1 of 1

Fig.S2 The mass spectra of (dfppy)₂Ir(Stpip)

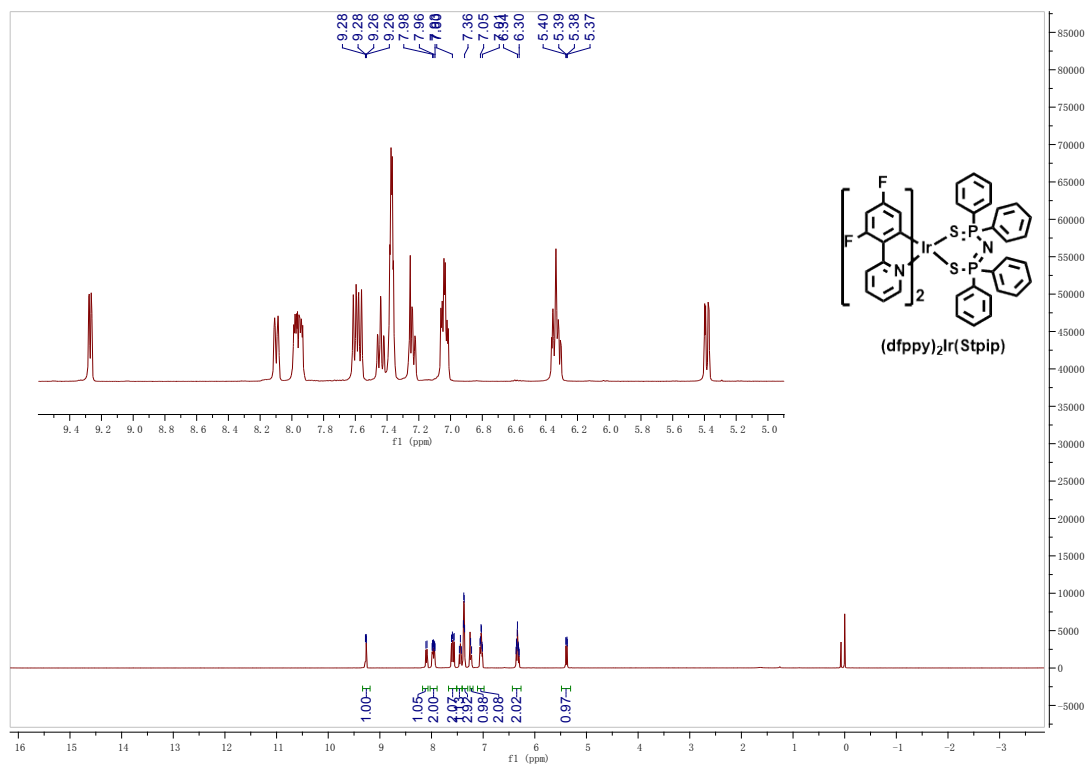


Fig.S3 The ¹H NMR spectra of (dfppy)₂Ir(Stpip).

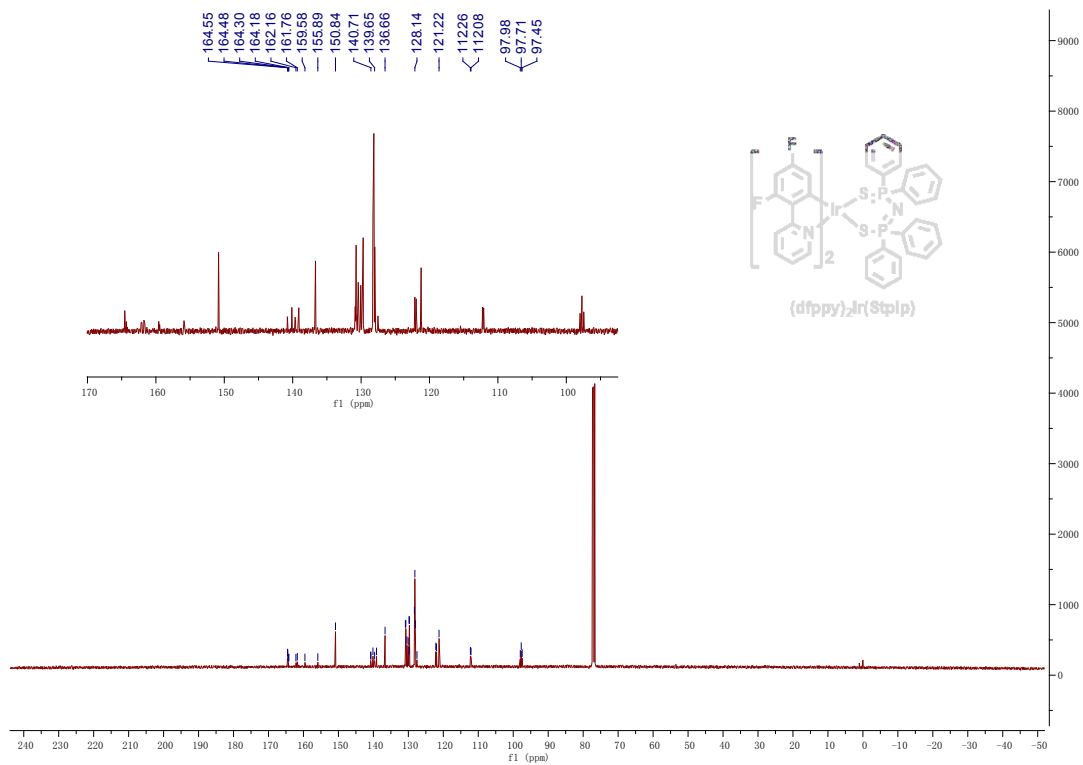


Fig.S4 The ^{13}C NMR spectra of $(\text{dfppy})_2\text{Ir}(\text{Stpip})$.

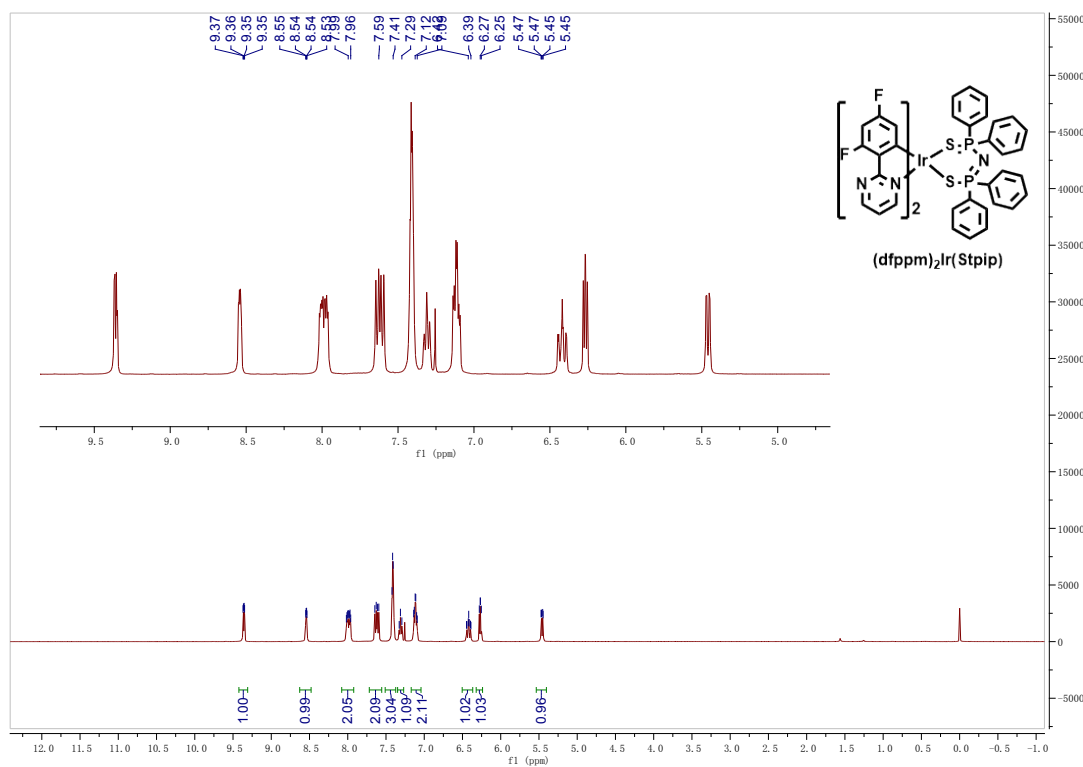


Fig.S5 The ^1H NMR spectra of $(\text{dfppm})_2\text{Ir}(\text{Stpip})$.

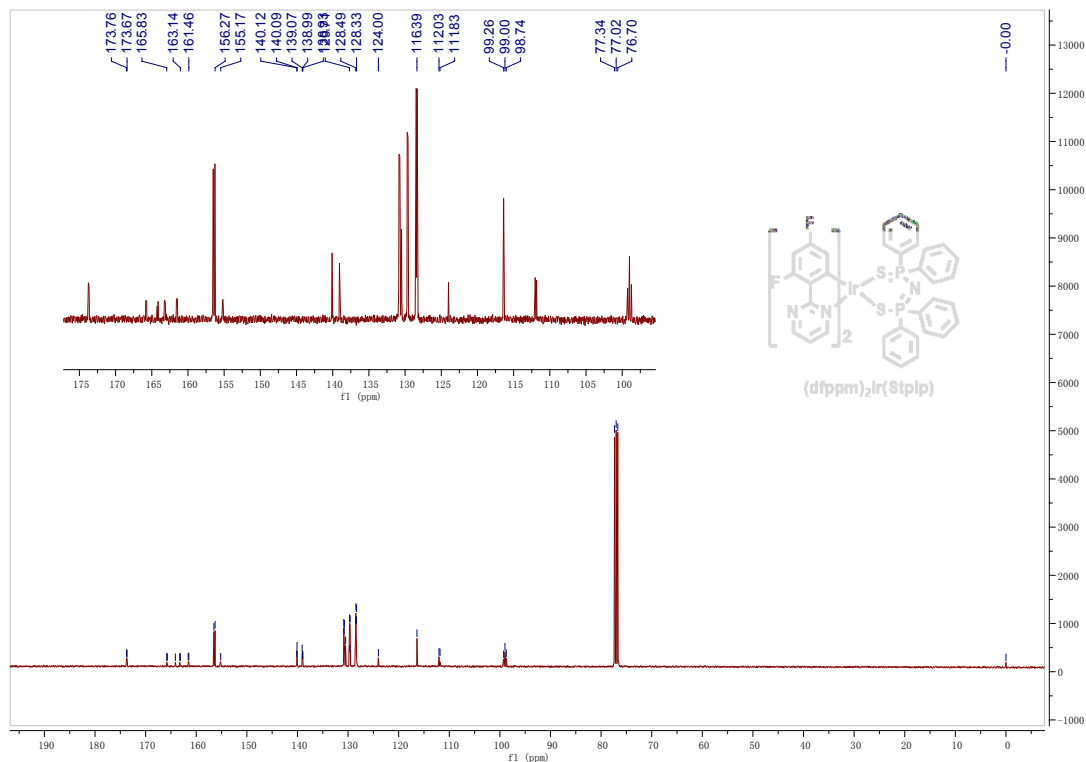


Fig.S6 The ^{13}C NMR spectra of $(\text{dfppm})_2\text{Ir}(\text{Stpip})$.

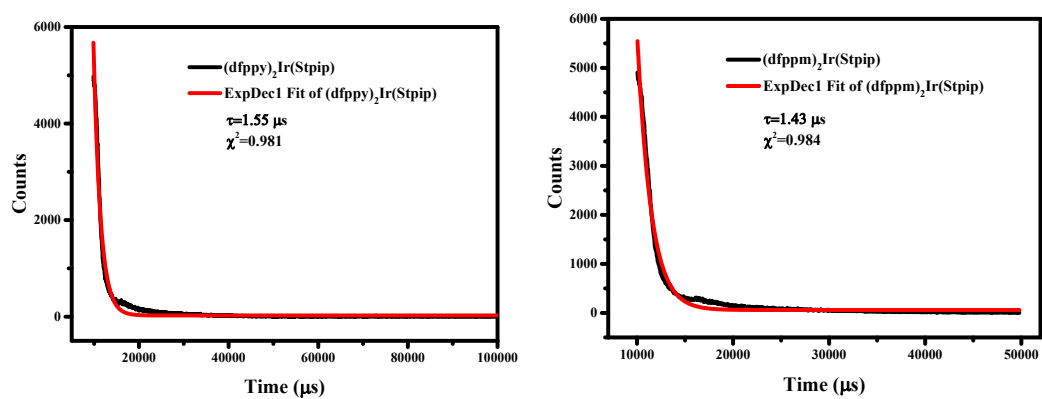


Fig. S7 The lifetime curves of $(\text{dfppy})_2\text{Ir}(\text{Stpip})$ and $(\text{dfppm})_2\text{Ir}(\text{Stpip})$ in degassed CH_2Cl_2 solution at room temperature.

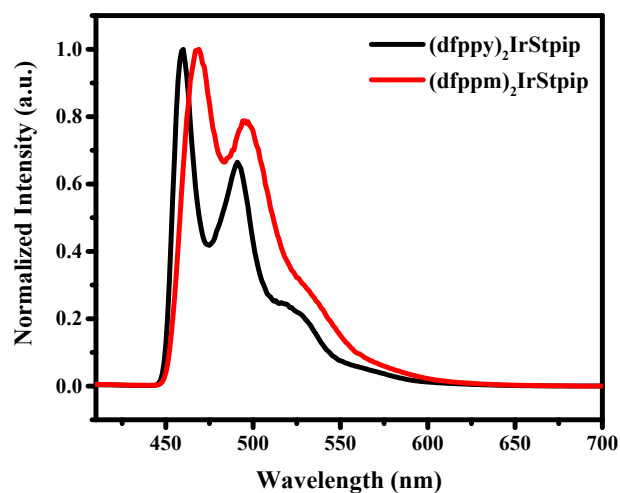


Fig. S8 Emission spectra of $(dfppy)_2Ir(Stpip)$ and $(dfppm)_2Ir(Stpip)$ in CH_2Cl_2 ($5 \times 10^{-5} \text{ mol L}^{-1}$) at 77 K.

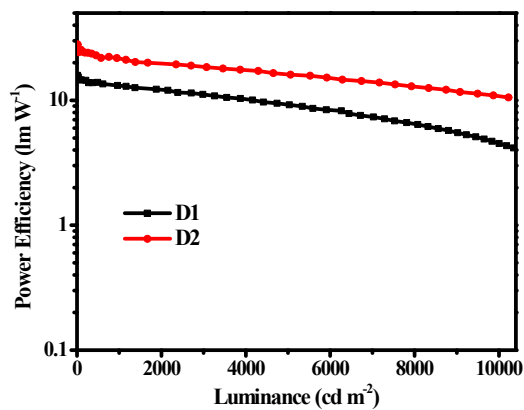


Fig. S9 Power efficiency-Luminance (η_p-L) curves of D1 and D2.

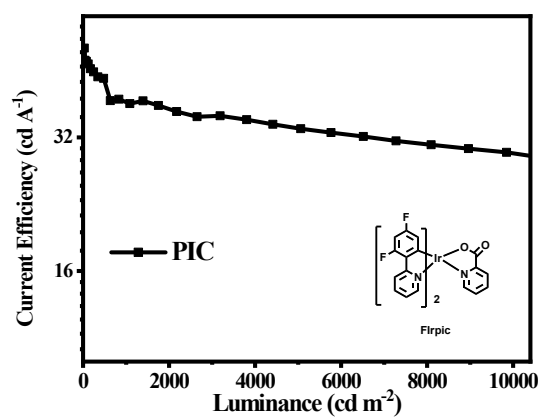


Fig. S10 Current Efficiency-luminance (η_c-L) curves of PIC.

[Device structure of PIC: ITO/ MoO_3 (3 nm)/ TAPC (50 nm)/ Firpic (16 wt%): TCTA, 5 nm/ Firpic (16 wt%):2,6-DCzPPy, 15 nm/ TmPyPB (50 nm)/ LiF (1 nm)/ Al (100 nm)]

Table S4 Device performances of several reported sky-blue devices.

complex	Device performance					
	$V_{\text{turn-on}}^{\text{a}}$ (V)	CIE ^b (x, y)	EQE _{max} (%)	EQE (%)	Roll-off(%)	Ref.
(dfppm) ₂ IrStpip	3.4	(0.13, 0.27)	19.4	19.2 ^c	1.0	this work
B-CzG2	–	(0.16, 0.32)	9.1	7.1 ^c	21.9	4
B-CzPO	–	(0.16, 0.32)	10.8	9.9 ^c	8.3	4
(mpmi) ₂ Ir(dmpypz)	3.2	(0.13, 0.18)	15.4	13.6 ^c	11.7	5
Ir(pypy) ₂ (Pr)	3	(0.16, 0.24)	14.3	10.8 ^c	24.5	6
B-TCz2TPO1	3.4	(0.18, 0.37)	11.5	10.9 ^c	5.2	7
FK306	2.9	(0.16, 0.25)	15.3	12.7 ^c	17	8
<i>fac</i> -6, device III	4	(0.15, 0.28)	5.9	–	–	9
(fpmpzt) ₂ Ir(pypz)	2.7	(0.19, 0.27)	2.0	–	–	10
Ir(bptz) ₂ (bdp)	3	(0.207, 0.440)	17.8	14.0 ^d	21.3	11
2c	4.1	(0.179, 0.286)	11	8.4 ^d	23.6	12
Ir(mpmi) ₂ (pypz)	4.2	(0.14, 0.27)	15.2	10.5 ^e	30.9	13
(F ₂ CH ₃ ppy) ₂ Ir(pic-N-oxide)	–	(0.161, 0.278)	19.6	10.8 ^f	44.9	14
Ir(tpim) ₃	–	(0.170, 0.298)	19.2	17.7 ^c	7.8	15
Ir(mtpim) ₃	–	(0.166, 0.281)	21.1	19.1 ^c	9.5	15
Ir(tpim) ₃	–	(0.167, 0.288)	21.3	20.1 ^c	5.6	15
Ir(Me-pep) ₃	3.3	(0.158, 0.272)	11.6	9.6 ^g	17.2	16
Ir(^t Bu-pep) ₃	3.6	(0.152, 0.277)	9.6	9.3 ^e	3.1	16

^a The voltage at luminance of 1 cd m⁻². ^b Commission Internationale de l'Eclairage 1931 coordinates. ^c efficiency recorded at the luminance of 1000 cd m⁻². ^d efficiency recorded at the luminance of 100 cd m⁻². ^e efficiency recorded at the luminance of 500 cd m⁻². ^f values collected at a current density of 20 mA cm⁻². ^g efficiency recorded at the luminance of 2000 cd m⁻².

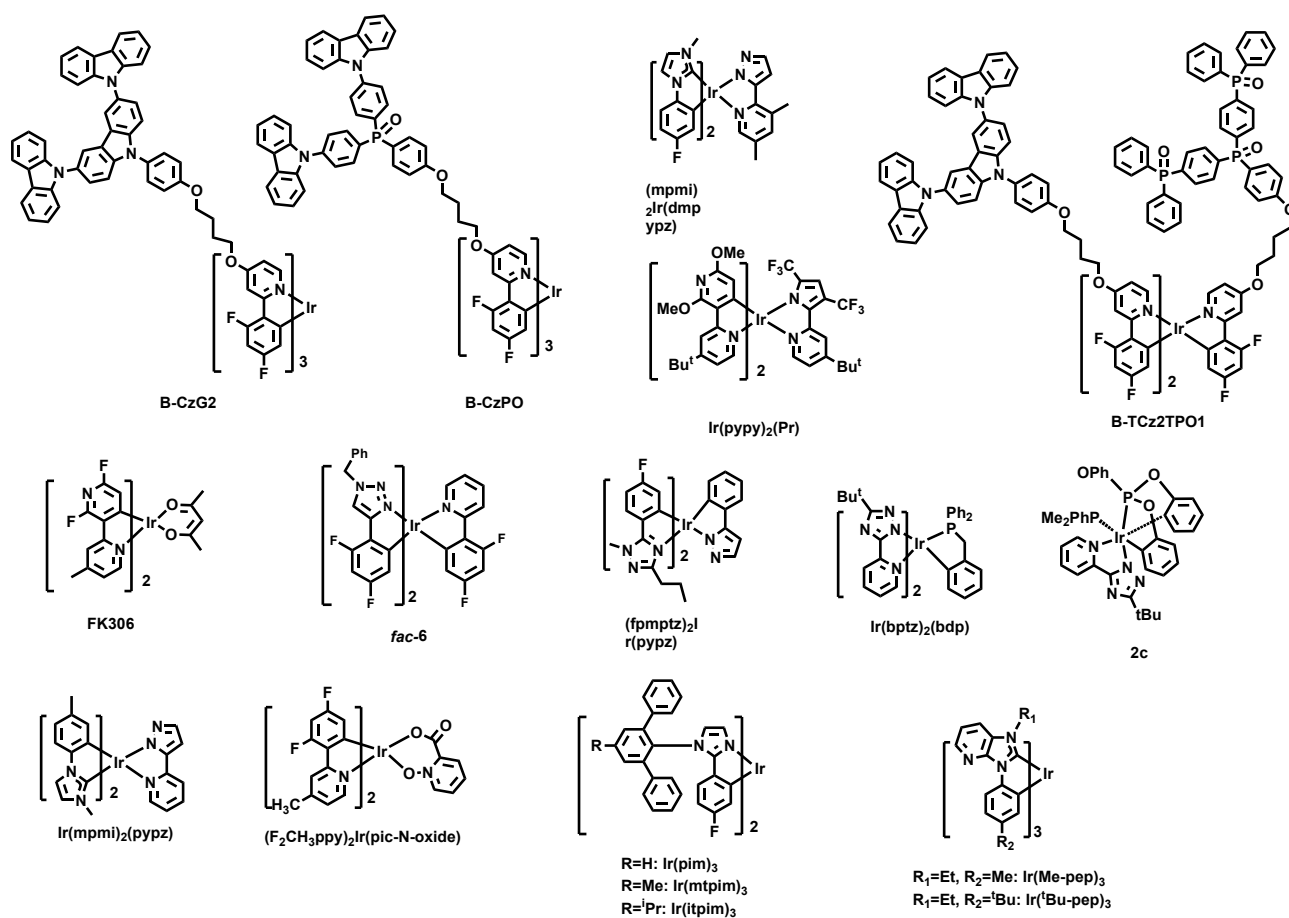


Fig. S11 Chemical structure of the complexes listed in Table S5.

References

1. *SAINTE-Plus, version 6.02*, Bruker Analytical X-ray System, Madison, WI, 1999.
2. G. M. Sheldrick, *SADABS An empirical absorption correction program*, Bruker Analytical X-ray Systems, Madison, WI, 1996.
3. G. M. Sheldrick, *SHELXTL-2014*, Universität of Göttingen, Göttingen, Germany, 2014.
4. Y. Wang, Y. Lu, B. Gao, S. Wang, J. Ding, L. Wang, X. Jing and F. Wang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 29600.
5. K. Lu, H. Chou, C. Hsieh, Y. Yang, H. Tsai, H. Tsai, L. Hsu, C. Chen, I. Chen and C. Cheng, *Adv. Mater.*, 2011, **23**, 4933.
6. T. Duan, T.-K. Chang, Y. Chi, J.-Y. Wang, Z.-N. Chen, W.-Y. Hung, C.-H. Chen and G.-H. Lee, *Dalton Trans.*, 2015, **44**, 14613.
7. Y. Wang, Y. Lu, B. Gao, S. Wang, J. Ding, L. Wang, X. Jing and F. Wang, *Chem. Commun.*, 2016, **52**, 11508.
8. F. Kessler, Y. Watanabe, H. Sasabe, H. Katagiri, M. Nazeeruddin, M. Grätzel and J. Kido, *J. Mater. Chem. C*, 2012, **1**, 1070.
9. J. Fernández-Hernández, J. Beltrán, V. Lemaure, M.-D. Gálvez-López, C.-H. Chien, F. Polo, E. Orselli, R. Fröhlich, J. Cornil and L. Cola, *Inorg. Chem.*, 2013, **52**, 1812.
10. H.-T. Cao, G.-G. Shan, Y.-M. Yin, H.-Z. Sun, Y. Wu, W.-F. Xie and Z.-M. Su, *Dyes and Pigments*, 2015, **113**, 655.
11. C.-H. Chang, C.-L. Ho, Y.-S. Chang, I.-C. Lien, C.-H. Lin, Y.-W. Yang, J.-L. Liao and Y. Chi, *J. Mater. Chem. C*, 2013, **1**, 2639.
12. C. Lin, Y. Chang, J. Hung, C. Lin, Y. Chi, M. Chung, C. Lin, P. Chou, G. Lee, C. Chang and W. Lin, *Angew. Chem. Int. Ed.*, 2011, **50**, 3182.
13. C. Hsieh, F. Wu, C. Fan, M. Huang, K. Lu, P. Chou, Y. Yang, S. Wu, I. Chen, S. Chou, K. Wong and C. Cheng, *Chem. Eur. J.*, 2011, **17**, 9180.
14. H.-J. Seo, K.-M. Yoo, M. Song, J. Park, S.-H. Jin, Y. Kim and J.-J. Kim, *Org. Electron*, 2010, **11**, 564.
15. H. Cho, J. Lee, J.-I. Lee, N. Cho, J. Park, J. Lee and Y. Kang, *Org. Electron*, 2016, **34**, 91.
16. Z. Chen, L. Wang, S. Su, X. Zheng, N. Zhu, C.-L. Ho, S. Chen and W.-Y. Wong, *ACS Appl. Mater. Interfaces*, 2017, **9**, 40497.