

Supporting Information

for

A 3-Dimensional Spiro-functionalized Platinum(II) Complex to Suppress Intermolecular π - π or Pt \cdots Pt Supramolecular Interactions for High-performance Electrophosphorescent Device

Xiang-Hua Zhao^a, Guo-Hua Xie^b, Zheng-Dong Liu^a, Wei-Jie Li^a, Ming-dong Yi^a,
Ling-Hai Xie^{*a}, Chao-Peng Hu^a, Rui Zhu^a, Qiang Zhao^a, Yi Zhao^b, Jian-Feng Zhao^a,
Yan Qian^a and Wei Huang^{*a}.

Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210046, China.

State Key Laboratory on Integrated Optoelectronics, College of Electronics Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China.

Table of Contents

Materials and Methods

Computational Details

Device Fabrication

Experimental Section

¹H NMR and ¹³C NMR Spectra

Absorption, Normalized EL and Photoluminescence Spectra

TG and DSC Spectra

Computational Spectra

Cyclic Voltammograms of the Complex

Device Structure and Performance

Materials and Methods: All the solvents and chemicals were obtained from Nanjing Fountain Global Displays. Fluorenone, 2-bromopyridine, and phenol,

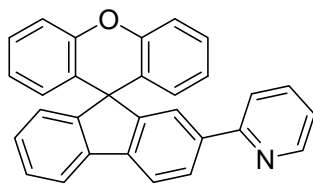
methanesulfonic acid, *n*-butyl-lithium tetrakis(triphenylphosphine) palladium(0), tetrabutyl ammonium bromide, tributyl borate, were used without further purification. 2-Bromospiro[fluorene-9,9'-xanthene] and 2-(spiro[fluorene-9,9'-xanthene]-2-yl)-1,3,2-dioxaborinane were synthesized according to the literature reports.¹ Ligand 9-(pyridin-2-yl)fluoren-9-ol was prepared according to the already published procedures.² All reactions involving organometallic reagents were carried out under nitrogen. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra measurements were recorded on a Bruker 400 MHz spectrometer in CDCl₃. Mass spectra were carried out on a Shimadzu GCMS 2010 PLUS. Absorption and emission spectra were performed on a Shimadzu UV-3600 and Shimadzu RF-5301(PC)S luminescence spectrometer at 25 °C, respectively. Cyclic voltammetric (CV) was conducted on a CHI660C Electrochemical Workstation in a typical three-electrode cell with a platinum sheet working electrode, a reference electrode (Ag/Ag⁺, referenced against ferrocene/ferrocenium (FOC)), and a platinum wire counter electrode. CV measurements were performed by coating film under nitrogen atmosphere in a solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in acetonitrile at room temperature at a sweeping rate of 100 mV/s. The HOMO/LUMO energy levels of the complex are estimated according to the empirical formula HOMO/LUMO = $-[E_{onset} - E_{(Fc/Fc^+) + 4.8}]$ eV, where $E_{(Fc/Fc^+)}$ is about 0.0095 V. Differential scanning calorimeter measurement (DSC) was researched by a Shimadzu DSC-60A from 25 °C to 180 °C at a scan rate of 10 °C/min under N₂ atmosphere. The thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 from 25 °C to 750 °C at a heating rate of 10 °C/min under N₂ atmosphere.

Computational Details: Calculations of the compounds were performed on the electronic ground state by Becke's three-parameter density functional in combination with LeeYang Parr's correlation functional (B3LYP) employed 6-31G(d) basis sets.³ The ground-state geometries were fully optimized at the B3LYP level. All computations were performed on the Gaussian 03 package.

Device Fabrication: The pre-patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10 Ω /square was used as the starting substrate. Before device fabrication, the substrates were cleaned by ultrasonic sequentially with detergent, acetone, ethanol, and deionized water. After this, all of them were dried in an oven and treated in an ultraviolet-ozone chamber. Then, 100-nm-thick Al serving as cathode was directly on the organic layers after the organic compounds were deposited on the ITO substrate. The active device area was 2 x 2 mm² defined through a shadow mask. The external quantum efficiency was evaluated by the method mentioned in the literature.⁴ Current-voltage-luminance (J-V-L) characteristics were recorded simultaneously by a PR650 spectrascan spectrometer and a Keithley 2400 programmable voltage-current source. All the measurements were carried out in the ambient environment without encapsulation.

Experimental Section

(1a) Synthesis of 2-(spiro [fluorene-9, 9'-xanthene]-2-yl)pyridine (SFXPy)

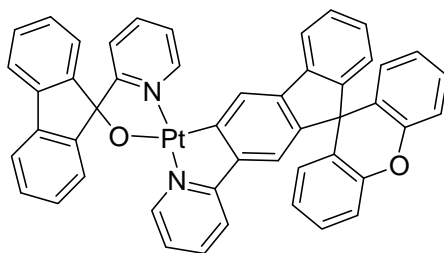


To a three-neck flask was added compounds 2-bromospiro[fluorene-9,9'-xanthene] (1.25 g, 3.0 mmol), 2-bromopyridine (0.29 mL, 3.0 mmol), Pd(PPh₃)₄ (0.02 g, 0.02 mmol), degassed toluene and THF (1:1, 60 mL) and K₂CO₃ (2M, 10 mL) was added. The mixture was heated to reflux and avoided light exposure under N₂ atmosphere for 48 h. The product was extracted with dichloromethane and dried over anhydrous Na₂SO₄. The organic solvent was removed by rotary evaporation under vacuum, and the crude product was purified by column chromatography using on silica gel with ethyl acetate/petroleum ether (8:1) as eluent to afford white solid; yield: 78%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.61 (d, J = 4.19 Hz, 1H), 8.11(dd, 1H), 7.91 (d, J = 7.99 Hz, 1H), 7.83 (d, J = 7.61 Hz, 1H), 7.77(s, 1H), 7.64 (m, 2H), 7.38 (t, J = 6.33 Hz, 1H), 7.22 (t, J = 6.87 Hz, 4H), 7.12 (m, 3H), 6.77 (t, J = 7.41 Hz, 2H), 6.46(d, J = 7.83 Hz, 2H).

(1b) Synthesis of [Pt(SFXPy)(μ -Cl)]₂

The chloride bridged platinum complex [Pt(SFXPy)(μ -Cl)]₂ was prepared by heating 2-2.5 equiv of cyclometalating ligand with 1 equiv K₂PtCl₄ salt in a mixture of 2-ethoxyethanol (Aldrich)/water (3:1) at 80 °C for 16 h.⁴ The dimer was isolated by filtration under vacuum and prepared for next reaction without purification.

(1c) Pt(SFXPy)(PyFO)



A mixture of [Pt(SFXPy)(μ -Cl)]₂ (0.26 g, 0.20 mmol), PyFOH (0.08 g, 0.30 mmol) and Na₂CO₃ (0.21 g, 2.0 mmol) in 10 mL of 2-methoxyethanol was heated at 100 °C for 16 h. After cooling to room temperature, 20 mL of water was added into the reaction mixture to induce precipitation. The precipitate was collected by filtration. The yellowish green [Pt(SFXPy)(PyFO)] (0.11 g, 0.13 mmol) was recrystallized from a mixture of CH₂Cl₂ and hexane at room temperature; yield: 33%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.47 (d, J = 5.65 Hz, 1H), 9.08 (d, J = 4.78 Hz, 1H), 8.12 (t, J = 8.09 Hz 3H), 7.88 (d, J = 7.58 Hz, 1H), 7.71 (d, J = 7.47 Hz, 2H), 7.63 (m, 2H), 7.47 (d, J = 8.31 Hz, 1H), 7.37 (m, 5H), 7.27 (s, 1H), 7.25 (m, 4H), 7.20 (m, 3H), 6.87 (t, J = 6.02 Hz, 1H), 6.82 (t, J = 6.58 Hz, 2H), 6.60 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 177.78, 166.90, 156.32, 153.13, 151.42, 150.11, 149.75, 146.44, 145.09, 141.37, 139.93, 139.54, 138.16, 137.00, 128.55, 128.47, 128.33, 128.03, 127.65, 125.73, 125.23, 125.12, 123.35, 122.98, 122.76, 121.25, 121.00, 120.77, 119.97, 118.25, 116.69, 94.02, 54.01.

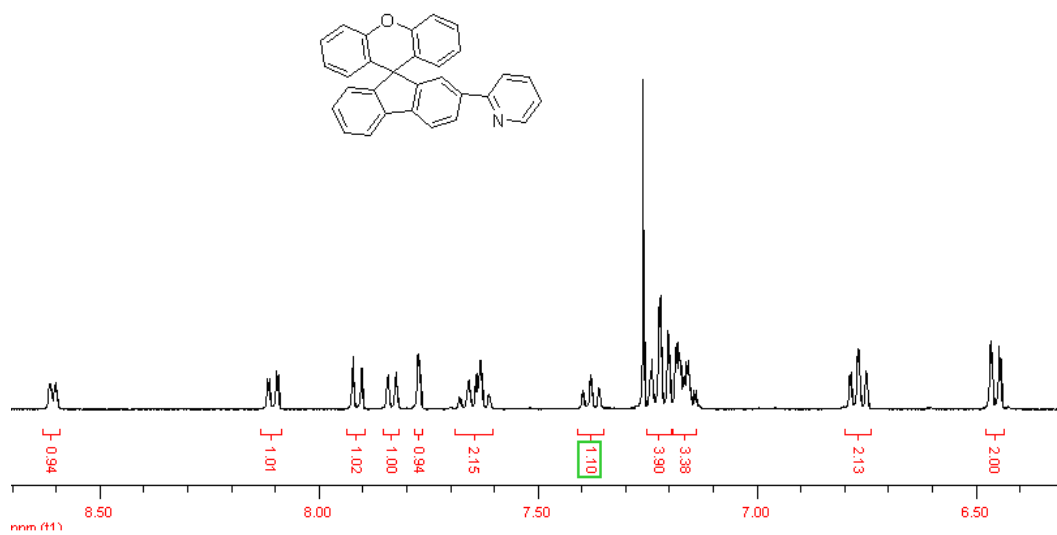


Fig. S1a ^1H NMR of PySFX in CDCl_3 .

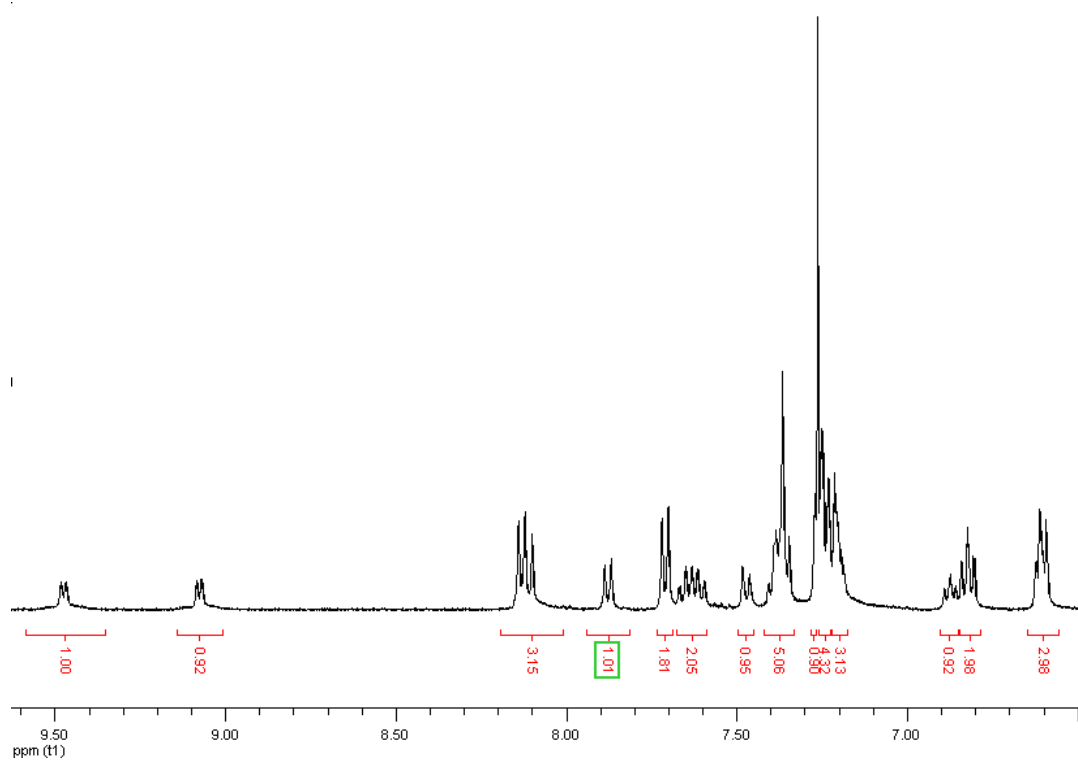


Fig. S2a ^1H NMR of $\text{Pt}(\text{PySFX})(\text{PyFO})$ in CDCl_3 .

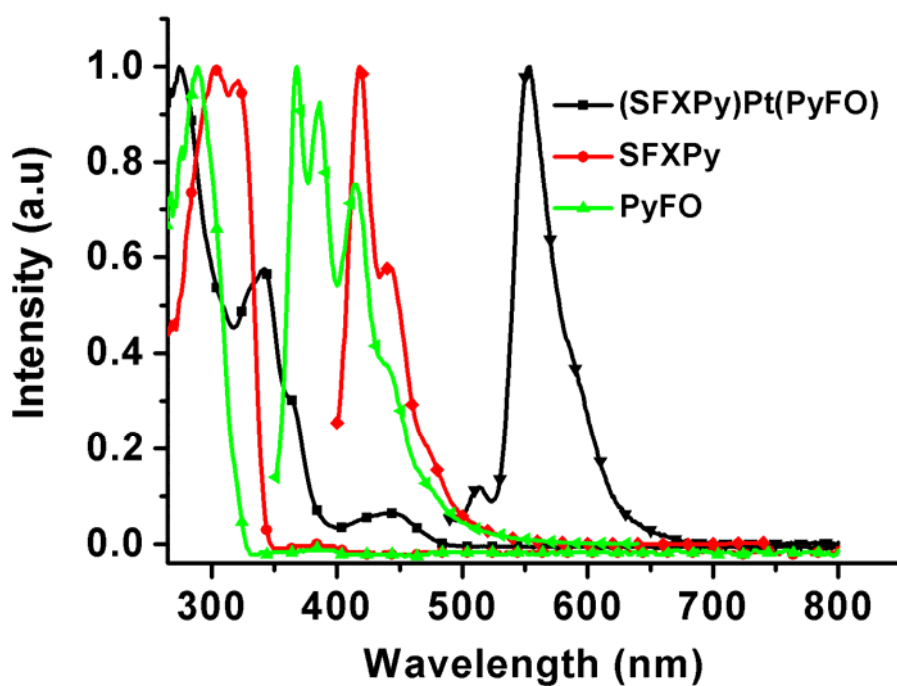


Fig. S3 The normalized absorption and photoluminescence spectra of Pt(SFXPy)-(PyFO), SFXPy and PyFO in CH_2Cl_2 .

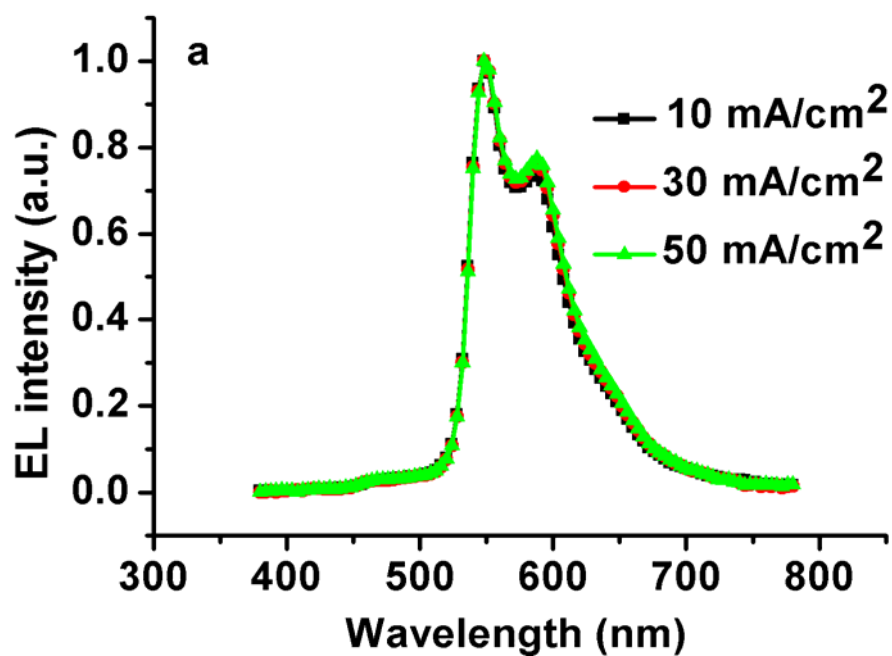


Fig. S4 Normalized EL spectra of Devices A at different current density

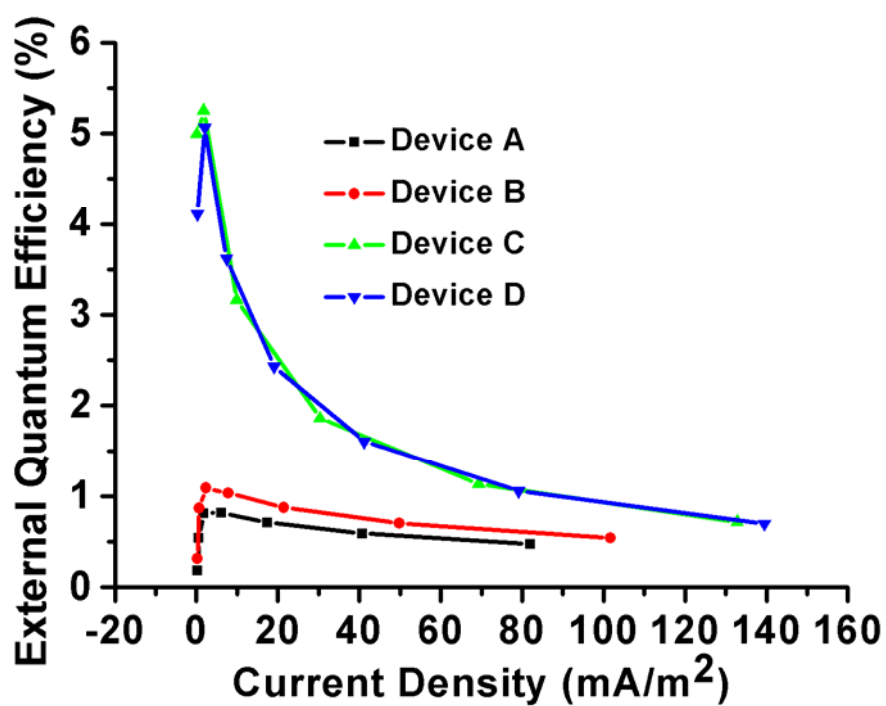
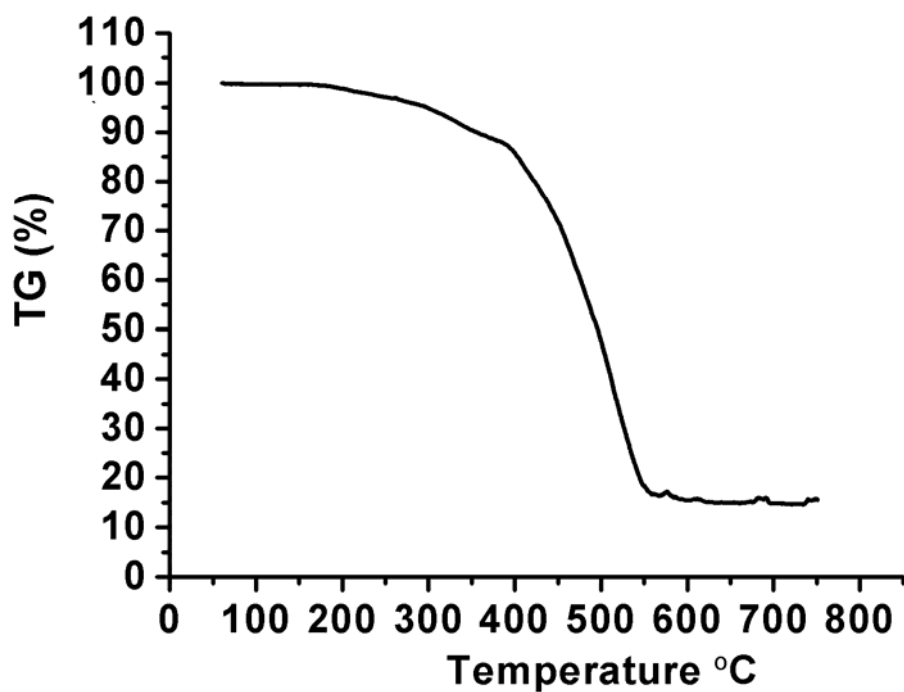


Fig. S5 Current density-external quantum efficiency characteristics of Devices A-D



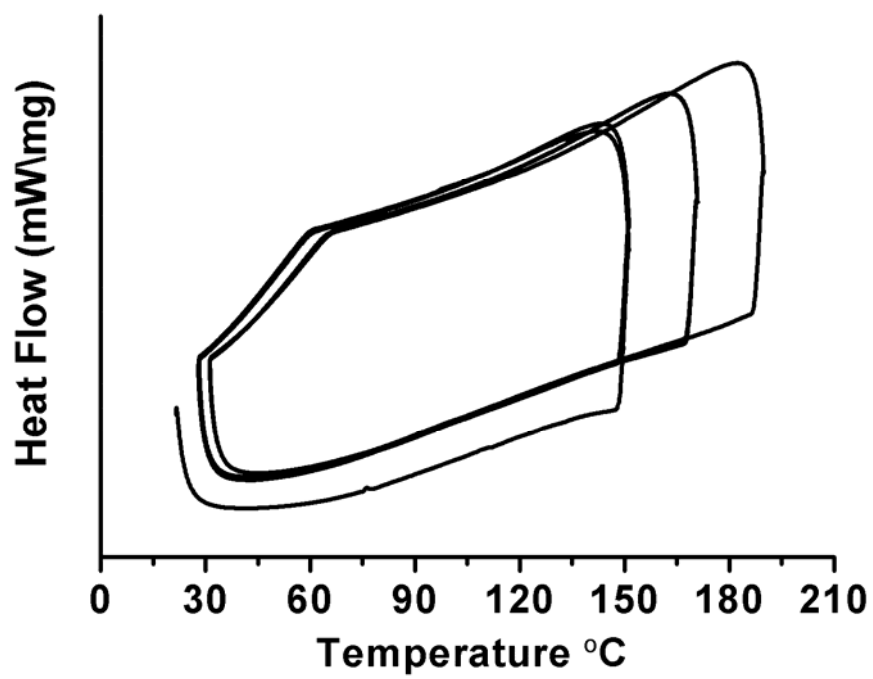


Fig. S6 The TGA and DSC curve of the complex.

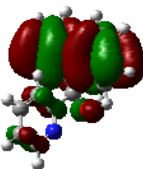
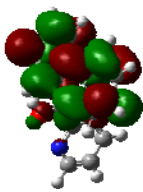
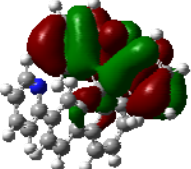
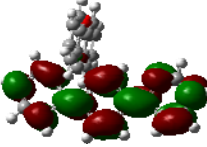
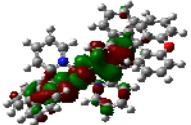
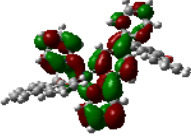
Molecule	HOMO	LUMO
PyFOH	 -5.89eV	 -0.99eV
SFXPy	 -5.59eV	 -1.36eV
(SFXPy)Pt(PyFO)	 -4.92eV	 -1.71eV

Fig. S7 Molecular orbital diagram for the LUMO/HOMO and their energy levels of Pt(II) complex and its ligands.

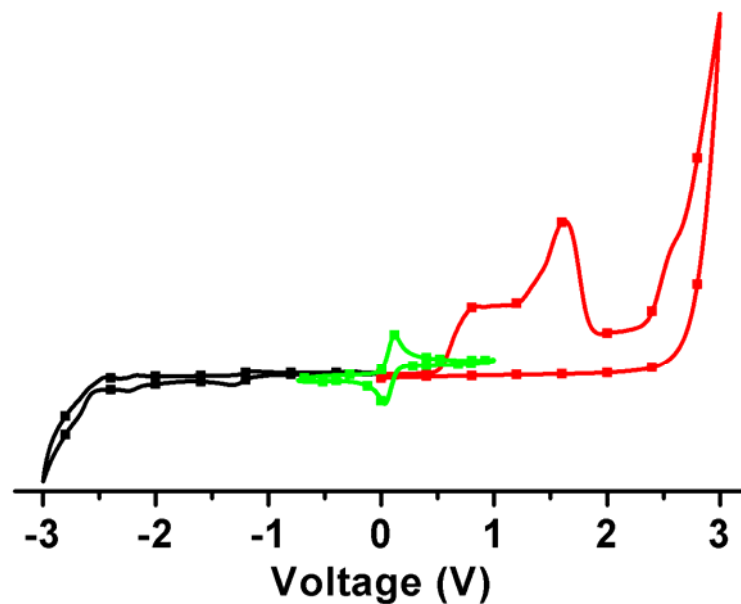


Fig. S8 Cyclic voltammogram of the four complexes and ferrocene measured with a scan rate of 100 mV s^{-1} in acetonitrile solution.

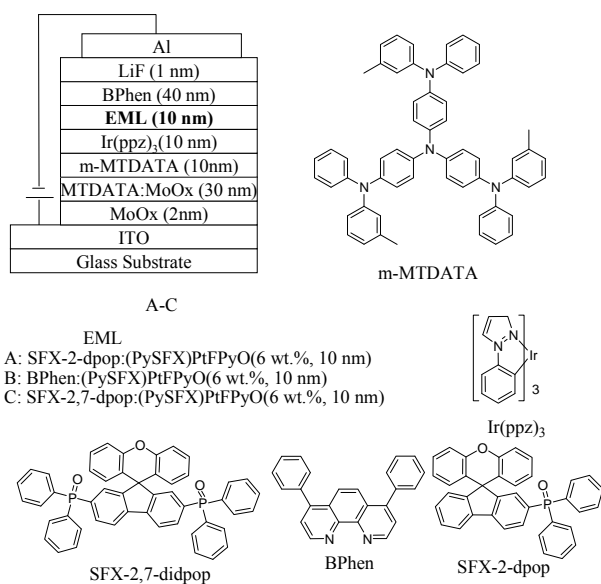


Fig. S9 The structure for OLEDs and the molecular structures of the used compounds used in these devices. Bphen: 4, 7-Diphenyl-1, 10-diazaphenanthrene ; SFX-2-dop: 2-phenylphosphoryl-spiro[fluorine-9, 9'-xanthene]; SFX-2, 7-diddop: 2, 7-bis(diphenylphosphoryl)spiro[fluorine-9, 9'-xanthene]; m-MTDATA: 4, 4', 4''-Tris(N-3-methylphenyl-N-phenylamino) triphenylamine; ITO: indium tin oxide.

Table S1. The comparison of EL performance of the devices

Device	L/V^a ($\text{cd m}^{-2}/\text{V}$)	$\eta_{\text{ext,max}} [\%]^b$	η^c cd A^{-1}	η^d lm W^{-1}	$\lambda_{\text{max}}/\text{nm}$ (CIE) ^e
A	2439/8.0	0.8	2.6 (5.7)	1.8 (1.9)	547 (0.47, 0.51)
B	3005/8.0	1.1	3.4 (2.3)	2.4 (2.3)	547 (0.48, 0.52)
C	3325/6.0	5.2	16.0 (1.6)	16.8 (1.1)	550 (0.45, 0.50)
D	3244/6.0	5.1	15.5 (1.9)	16.2 (1.5)	550 (0.46, 0.50)

^aLuminance/Voltage, and ^bmaximum external quantum efficiency, ^ccurrent efficiency (CE) and ^dpower efficiency (PE) (The current densities (mA/cm^2) of the measured CE and PE are shown in brackets). ^eCIE chromaticity coordinates.

References

1. (a) L. H. Xie, F. Liu, C. Tang, X. Y. Hou, Y. R. Hua, Q. L. Fan and W. Huang, *Organic Letters.*, 2006, **8**, 2787-2790; (b) J. F. Gu, G. H. Xie, L. Zhang, S. F. Chen, Z. Q. Lin, Z. S. Zhang, J. F. Zhao, L. H. Xie, C. Tang and Y. Zhao, *The Journal of Physical Chemistry Letters.*, 2010, **1**, 2849-2853.
2. A. Soldatenkov, N. Kolyadina, L. Kuleshova and V. Khrustalev, *Chemistry of Heterocyclic Compounds.*, 1996, **32**, 817-821.
3. (a) A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Physical Review B.*, 1988, **37**, 785.
4. R. Meerheim, R. Nitsche and K. Leo, *Applied physics letters.*, 2008, **93**, 043310.