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Effective Bipolar Host *via* Dipole Moment Engineering for Phosphorescent Emitter and White OLEDs

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Contents

Experimental part

Except for carbazole, which was synthesized by ourselves, other materials were purchased from Energy Chemical Company Ltd. and used directly for the reaction. All reactions were carried out under N_2 atmosphere. To determine the structure of the compound, ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker Dex-300/400 NMR instrument using $CDCl_3$ or DMSO as solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix.

To investigate the possibility of using the material as a fully evaporated OLED emitter, thermogravimetric analysis (TGA) was performed using a NETZSCH STA449 at a heating rate of 20°C/min under N_2 atmosphere from 30°C to 600°C. Differential Scanning Calorimetry (DSC) measures heating and cooling at a rate of 10 $^{o}C\ min^{-1}$ at the phase transition temperature.

UV-Vis absorption spectra and steady-state photoluminescence (PL) spectra of the two host materials were obtained at room temperature using a Shimadzu UV-1650PC and a PTI QuantaMaster 40 steady-state fluorescence spectrometer. Low temperature (77 K) fluorescence and phosphorescence spectra were measured in toluene solution (10^{-5} M) using an Edinburgh FLS920 transient fluorescence spectrophotometer.

Electrochemical performance was evaluated by cyclic voltammetry using a 273A (Princeton Applied Research) in degassed CH_3CN solution at a rate of 100 mV/s. The CV system uses Bu4NPF6 as the electrolyte. The platinum disk is the working electrode, the platinum wire is the counter electrode, and the silver wire is the

reference electrode. Ferrocene/Ferrocene (Fc/Fc^{+}) was used as the external standard compound. Each oxidation potential was calibrated using ferrocene as a reference.

Synthesis

Synthesis of compounds 1: A mixture of 3-Bromo-2-fluoropyridine (5 g, 28.4 mmol), Bis(pinacolato)diboron (8.7 g, 34.1 mmol), Pd(dppf)Cl_2 (208 mg, 0.28 mmol), KOAc (8.4 g, 85 mmol) and 60 mL Toluene was heated to 80 ^oC under a nitrogen atmosphere and refluxed for 24 hours. After the reaction stopped, Tol was removed by vacuum distillation; The remaining mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed with water and dried over anhydrous $MgSO_4$. The product was purified by column chromatography on silica (PE/EA, 6:1, v/v) to give a yellow liquid. (5.8 g, yield 91 %). ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.27 (m, 1H), 8.21 - 8.14 (m, 1H), 7.19 (ddd, *J* = 7.3, 4.9, 2.6 Hz, 1H), 1.37 (s, 12H). (**Figure S1**).

Synthesis of compounds 2 and 3: A mixture of SM1 (4 g, 17.9 mmol), 3-Bromo-2-fluoropyridine (3.14 g, 17.9 mmol) or 2-Bromofluorobenzene (3.2 g, 17.9 mmol), $Pd(pph_3)_4$ (206 mg, 0.18 mmol), K_2CO_3 (10 g, 72.5 mmol) and 60 mL Tetrahydrofuran and 15 mL water was heated to 80 ^oC under a nitrogen atmosphere and refluxed for 24 hours. After the reaction stopped, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed with water and dried over anhydrous $MgSO_4$. The product was purified by column chromatography on silica (PE/EA, 8:1, v/v) to give a white solid. 2: (1.7 g, yield 48 %), 3: (1.83 g, yield 53 %).

2: ^1H NMR (400 MHz, DMSO) δ 8.37 (d, *J* = 4.4 Hz, 2H), 8.17 (dd, *J* = 11.0, 5.5 Hz, 2H), 7.58 - 7.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 159.12, 148.21 147.78, 141.91, 121.79, 121.50, 116.72, 116.47. (**Figure S2, S3**).

3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.7 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 12.5, 5.5 Hz, 2H), 7.32 - 7.28 (m, 1H), 7.26 – 7.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.70, 161.04, 159.31, 158.56, 147.19, 142.04, 131.38, 130.59, 124.34, 121.44, 118.60, 118.29, 116.17, 115.95. (**Figure S4, S5**).

Synthesis of compound o-CBPy and o-CPPy: A mixture of compound Carbazole (4.17 g, 10.4 mmol), sodium hydride (0.42 g, 10.4 mmol) in 15 mL dry N,N-Dimethylformamide was stirred for 0.5 h at 50 ^{o}C. After adding 2 (0.8 g, 4.2 mmol) or 3 (0.8 g, 4.2 mmol), the mixture was stirred for 24 h at 140 ^{o}C and poured into water (120 mL), which was extracted with ethyl acetate (3 × 30 mL). The organic phase was washed with water (200 mL) and concentrated under vacuum. The crude product was purified by flash chromatography (EA/PE, 1/6) to get white solid. *o*-CBPy: (0.9 g, yield 44 %), *o*-CPPy: (0.8 g, yield 39 %).

o-CBPy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.5 Hz, 2H), 8.29 (d, *J* = 7.7 Hz, 2H), 7.66 - 7.48 (m, 6H), 6.93 (dt, *J* = 15.0, 7.1 Hz, 8H), 6.33 (d, *J* = 5.4 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.29, 148.18, 142.23, 130.14, 124.96, 124.49, 122.73, 120.15, 119.56, 110.49. MALDI-MS (m/z) of $C_{34}H_{22}N_4$ for [M]+: calcd. 486.58; found, 486.11. (**Figure S6, S7, S8**).

o-CPPy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 - 8.39 (m, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.73 - 7.56 (m, 5H), 7.46 (dd, *J* = 7.5, 5.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.03 - 6.78 (m, 8H), 6.33 (d, *J* = 73.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.68, 142.72, 139.68, 139.14, 136.06, 135.82, 133.25, 132.09, 129.62, 129.07, 128.38, 125.02, 124.44, 123.87, 122.65, 120.00,

119.67, 110.77, 109.66. MALDI-MS (m/z) of $C_{35}H_{23}N_3$ for [M]+: calcd. 485.59; found, 485.09. (**Figure S9, S10, S11**).

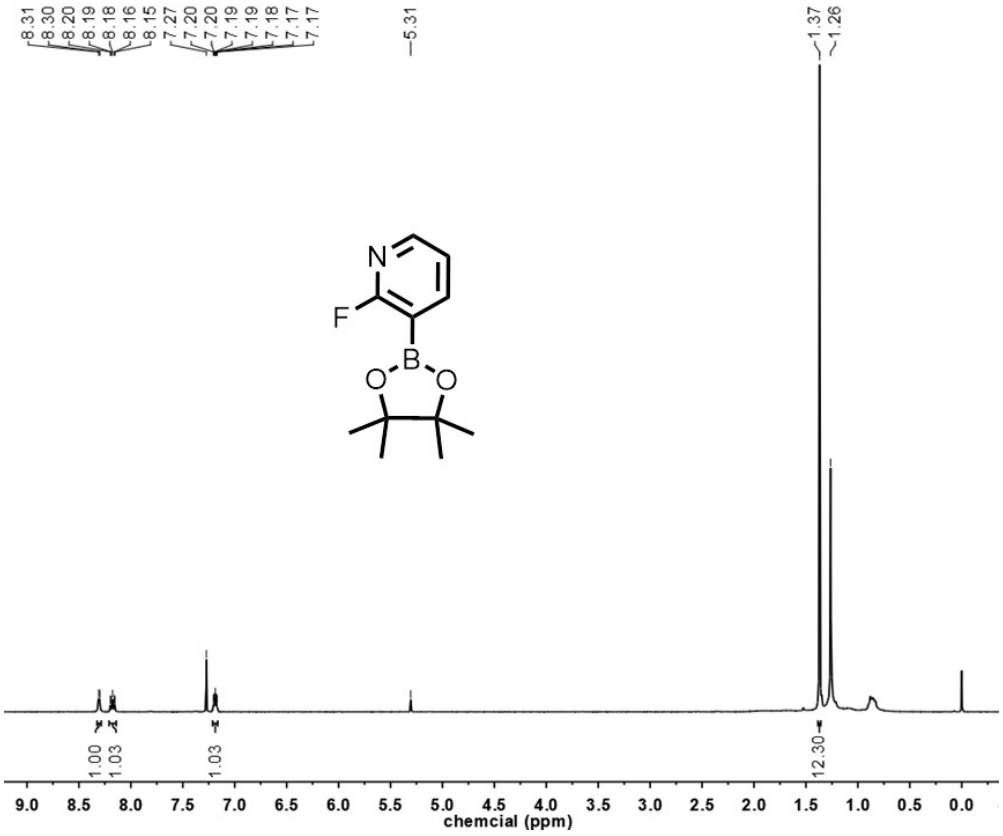

Figure S1. ^{1}H NMR spectrum of 1 in $CDCl_3$.

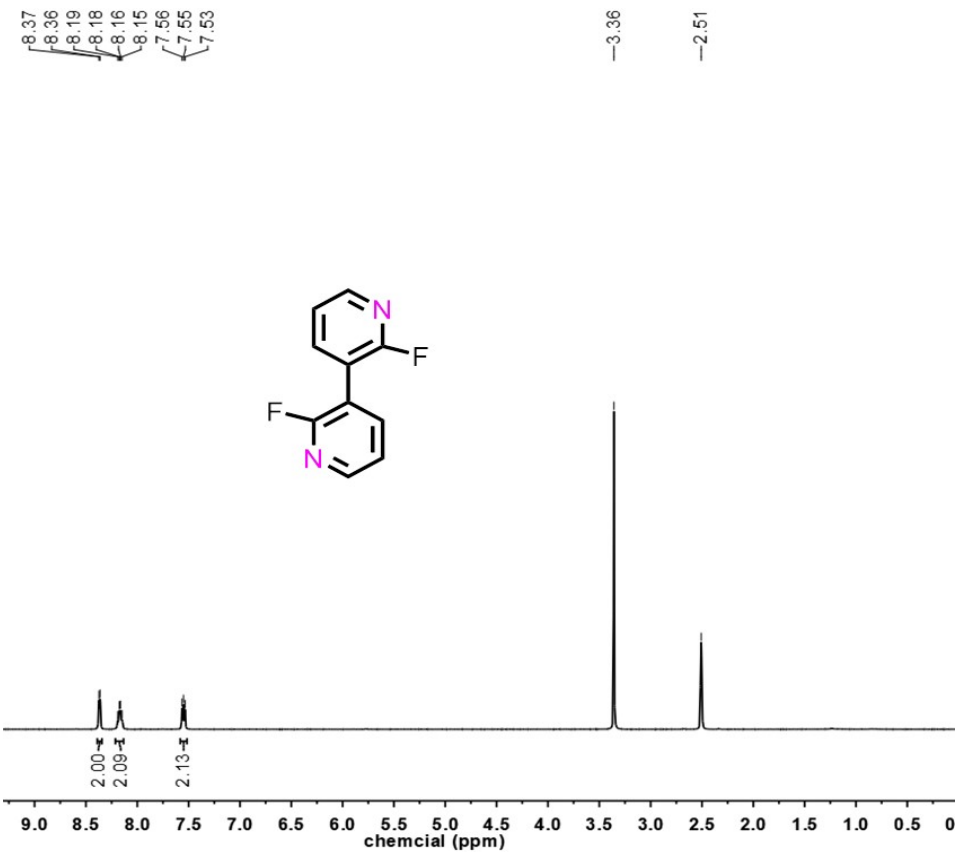

Figure S2. ^{1}H NMR spectrum of 2 in DMSO.

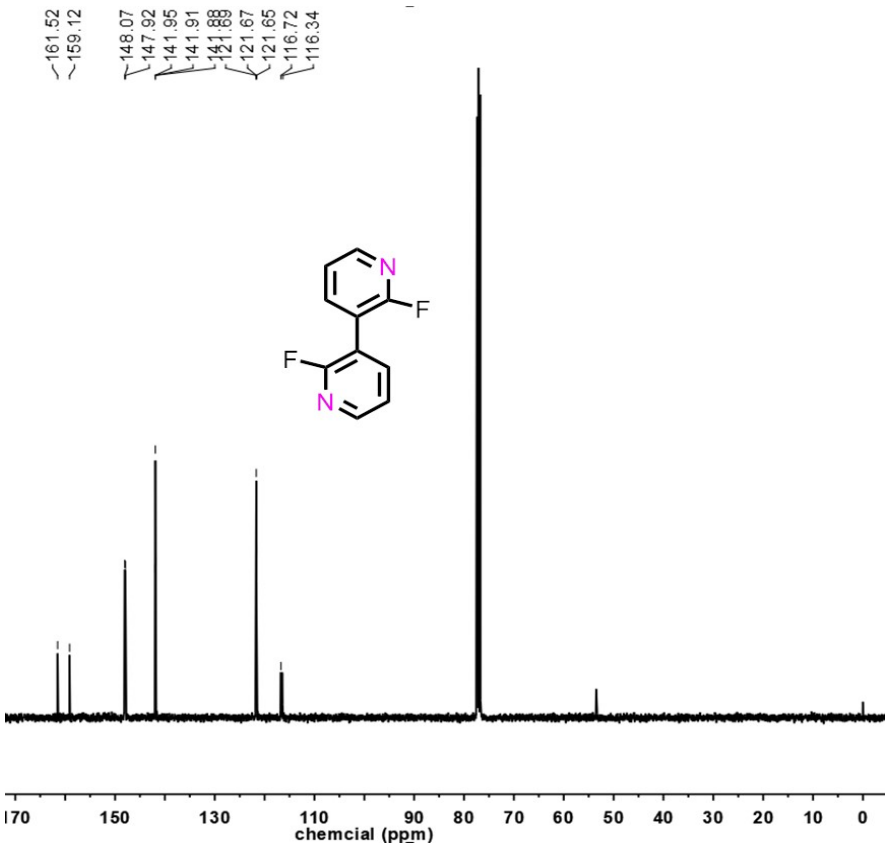

Figure S3. ^{13}C NMR spectrum of 2 in $CDCl_3$.

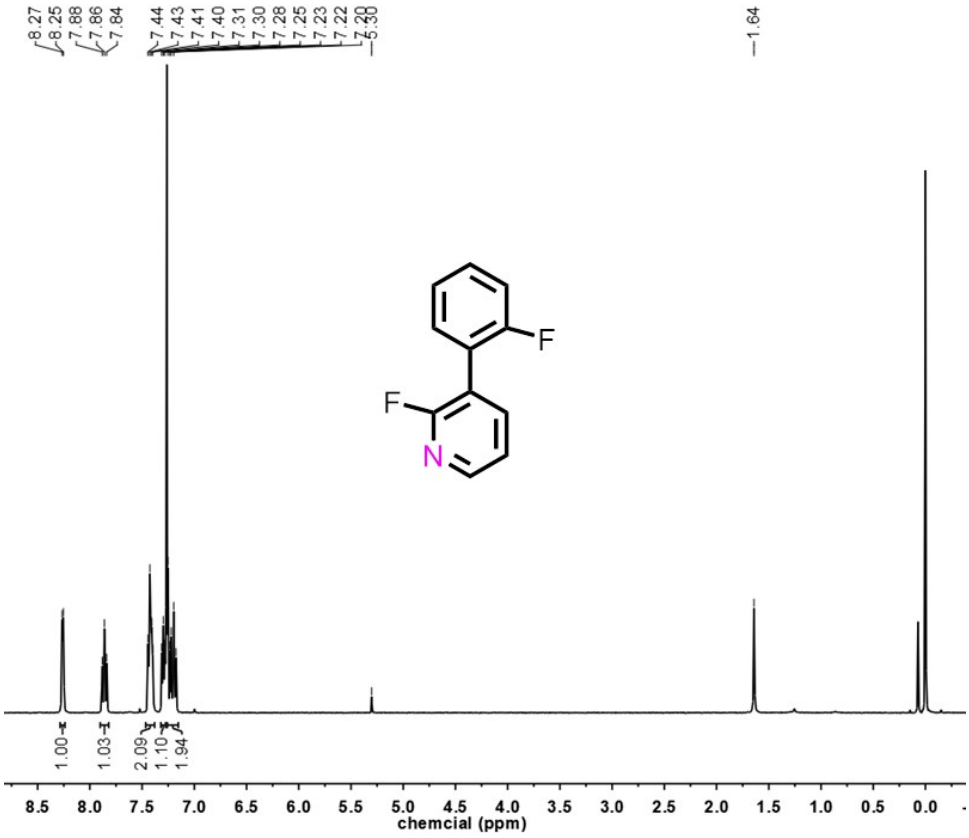

Figure S4. ^{1}H NMR spectrum of 3 in $CDCl_3$.

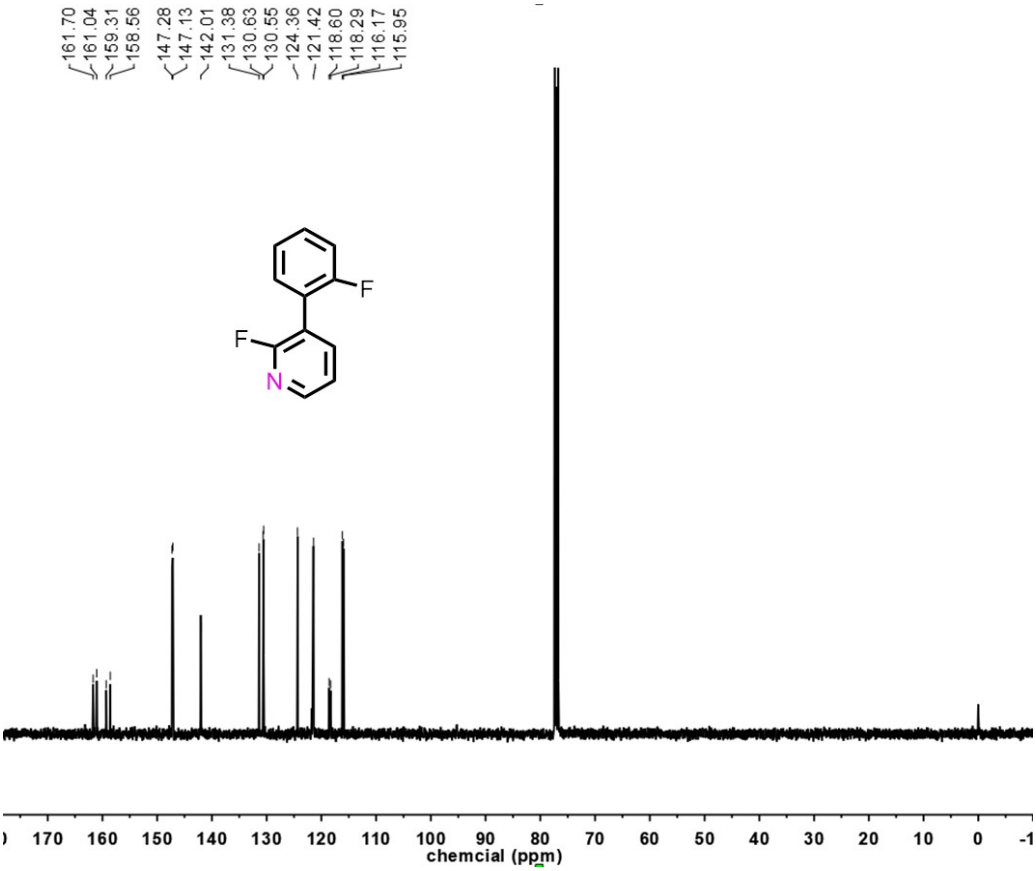

Figure S5. ^{13}C NMR spectrum of 3 in $CDCl_3$.

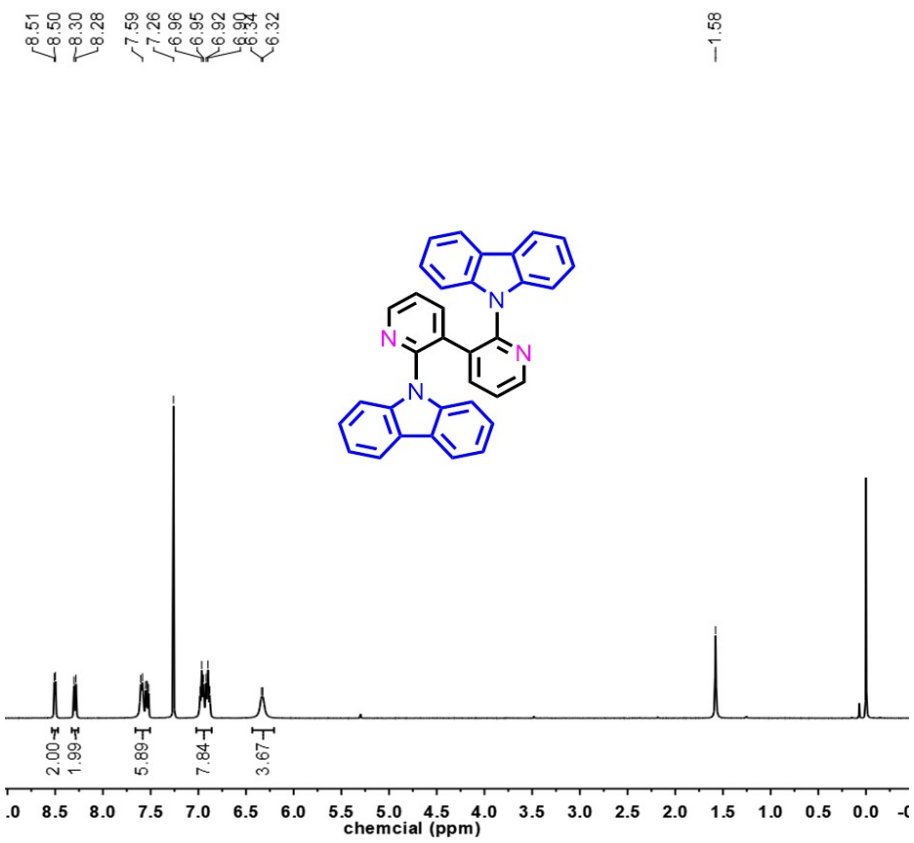

Figure S6. ^{1}H NMR spectrum of *o*-CBPy in $CDCl_3$.

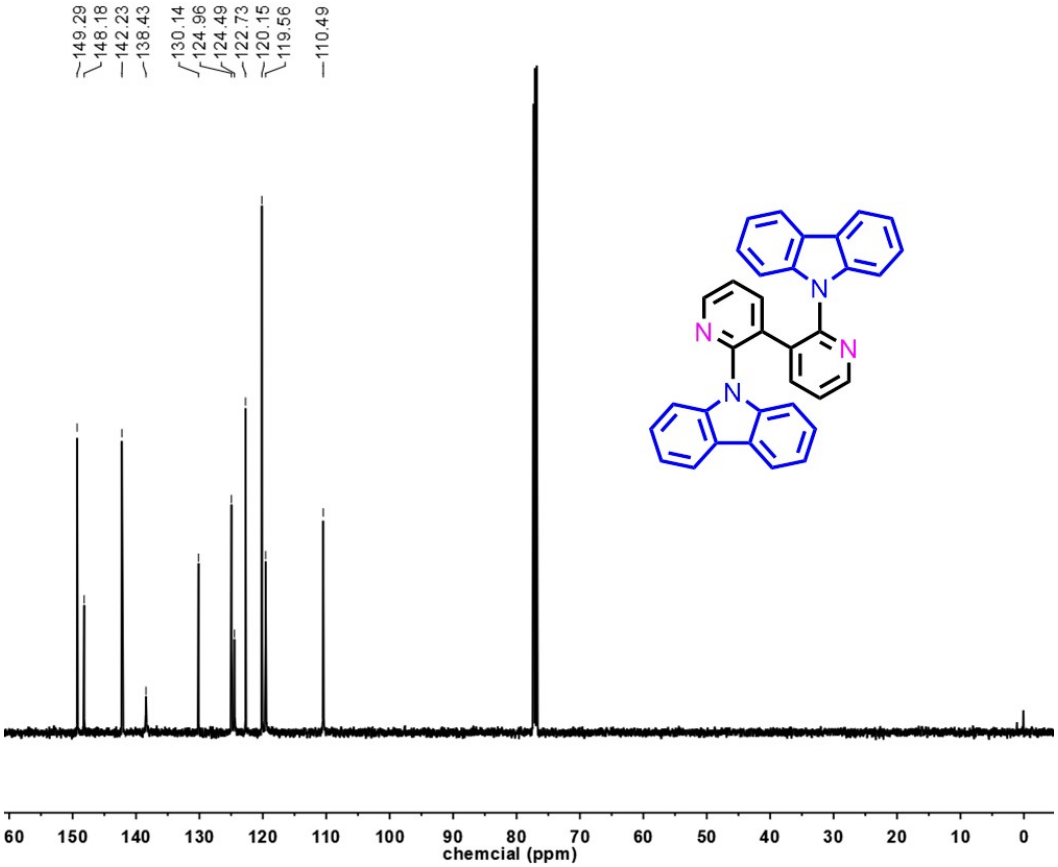

Figure S7. ^{13}C NMR spectrum of *o*-CBPy in $CDCl_3$.

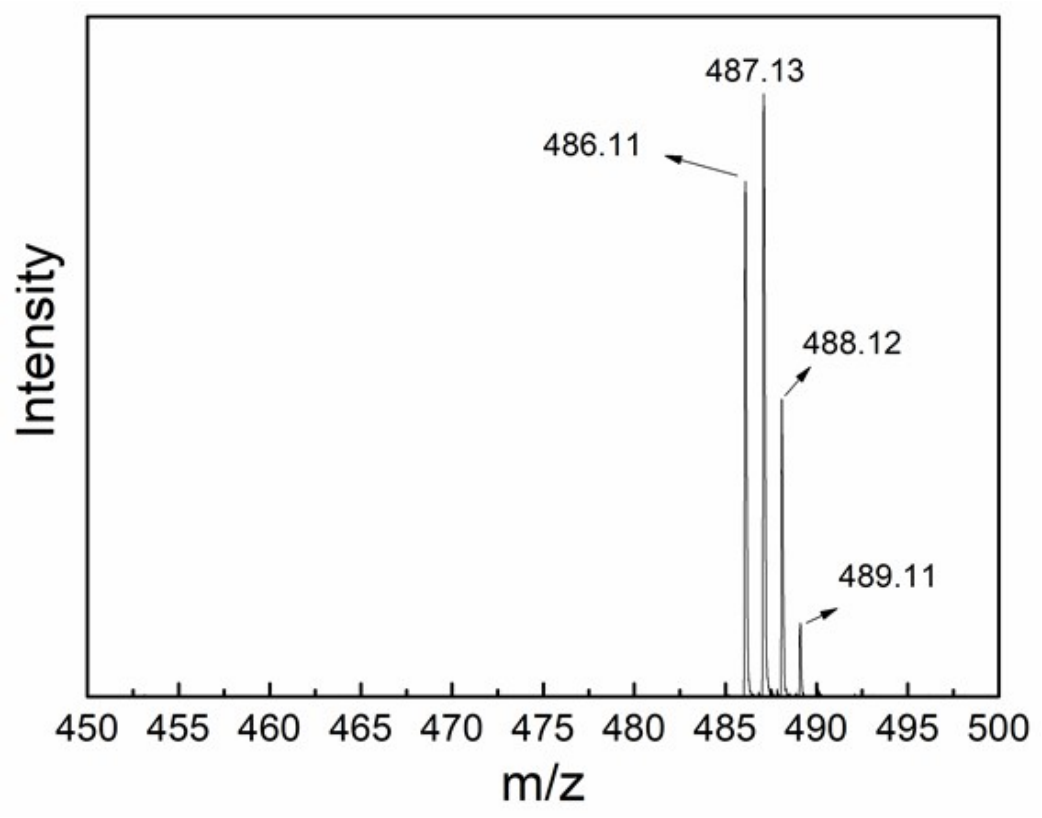

Figure S8. Mass spectrum of *o*-CBPy.

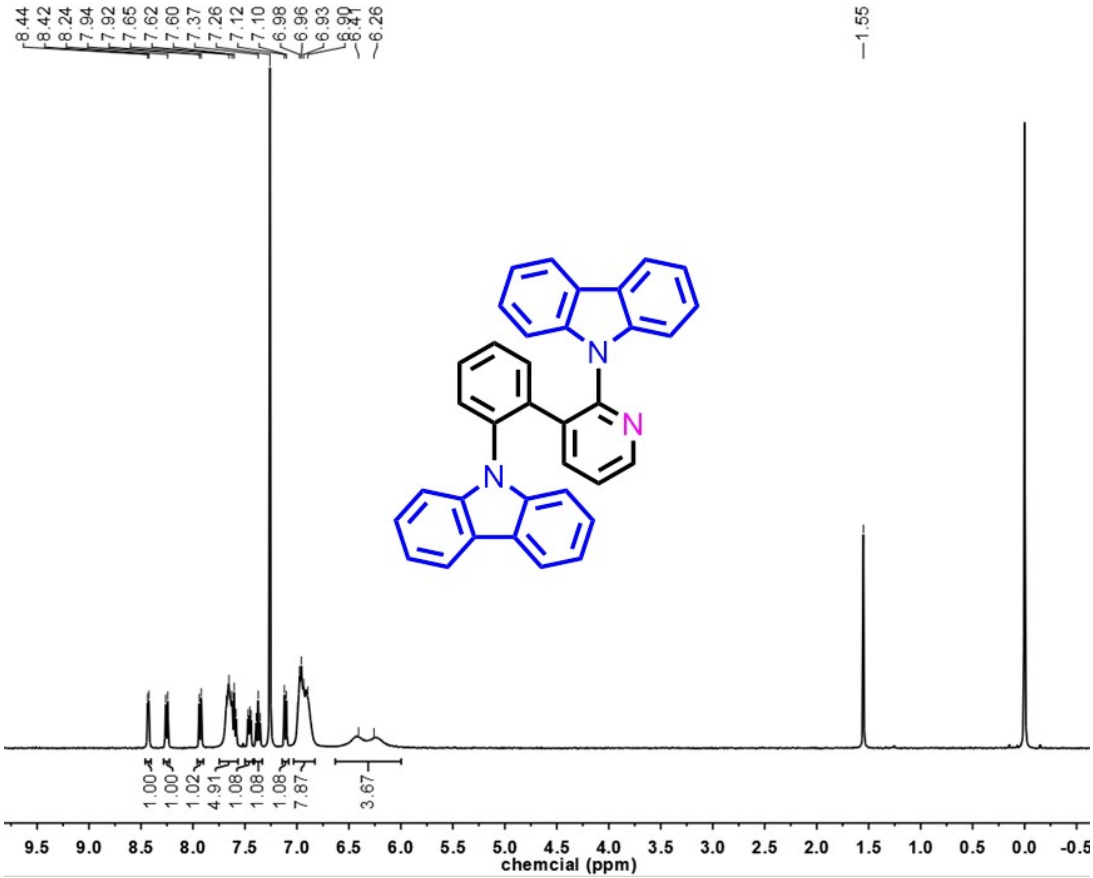

Figure S9. ^{1}H NMR spectrum of *o*-CPPy in $CDCl_3$.

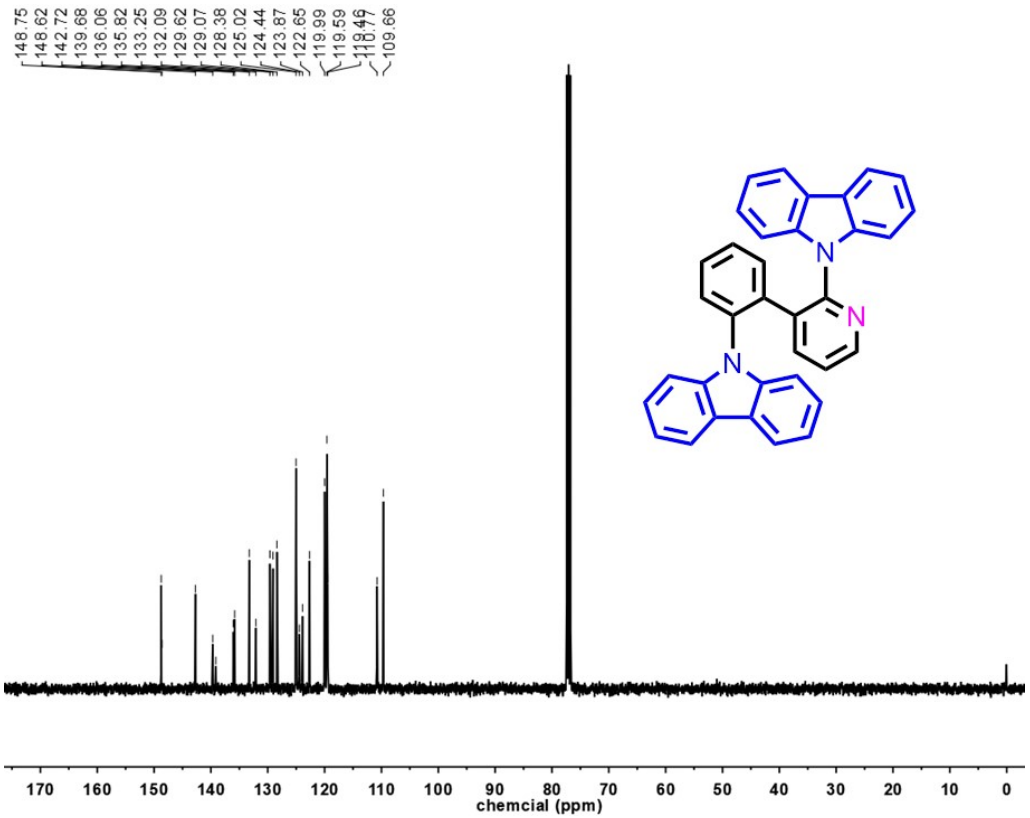

Figure S10. ^{13}C NMR spectrum of o-CPPy in $CDCl_3$.

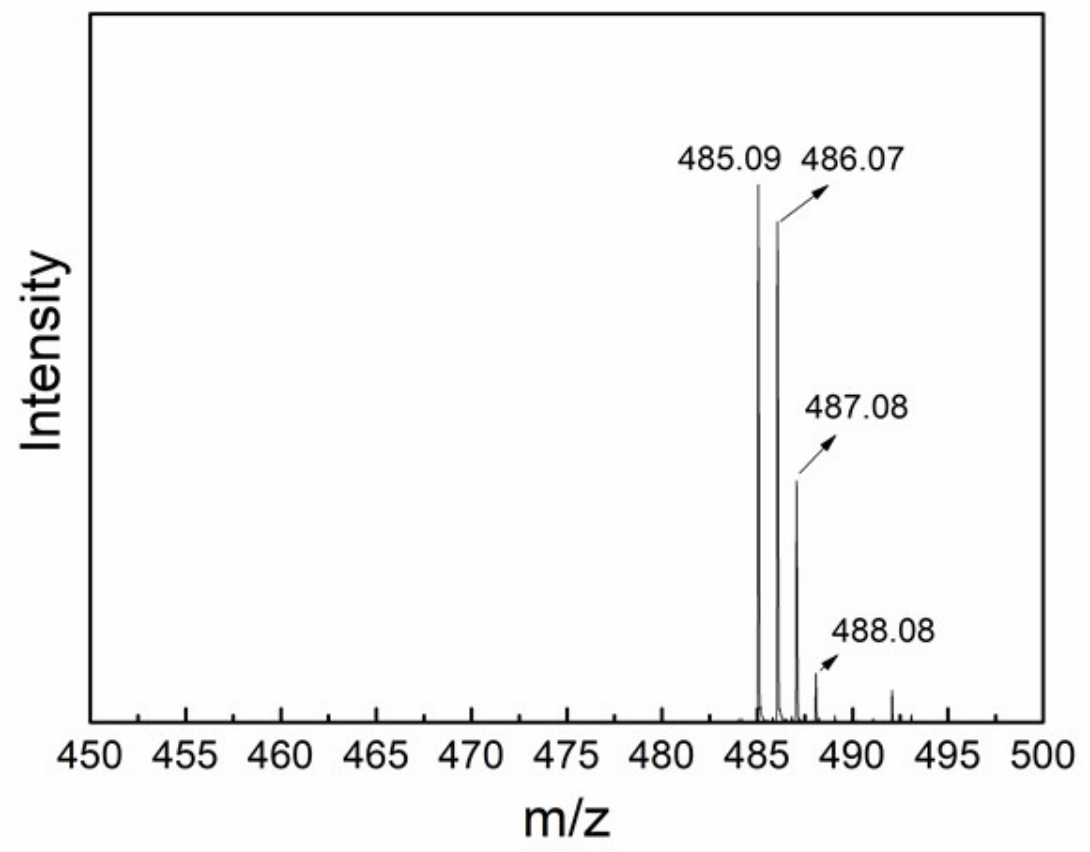

Figure S11. Mass spectrum of *o*-CPPy.

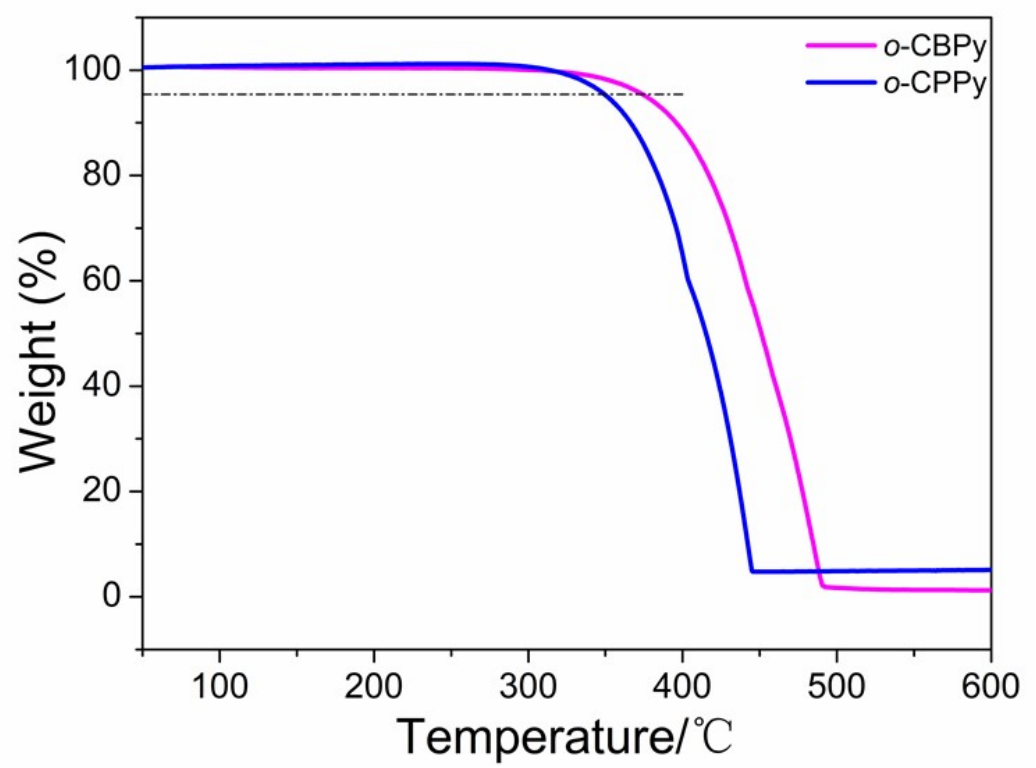

Figure S12. TGA curves of the compounds at N_2 atmosphere with a heating rate of 20 $^{o}C\ min^{-1}$.

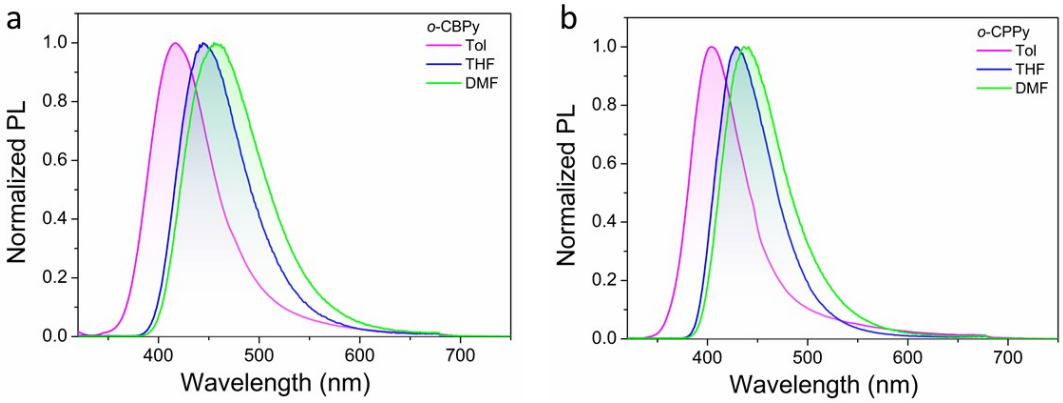

Figure S13. Fluorescence spectra of *o*-CBPy and *o*-CPPy measured in the solvents with different polarities.

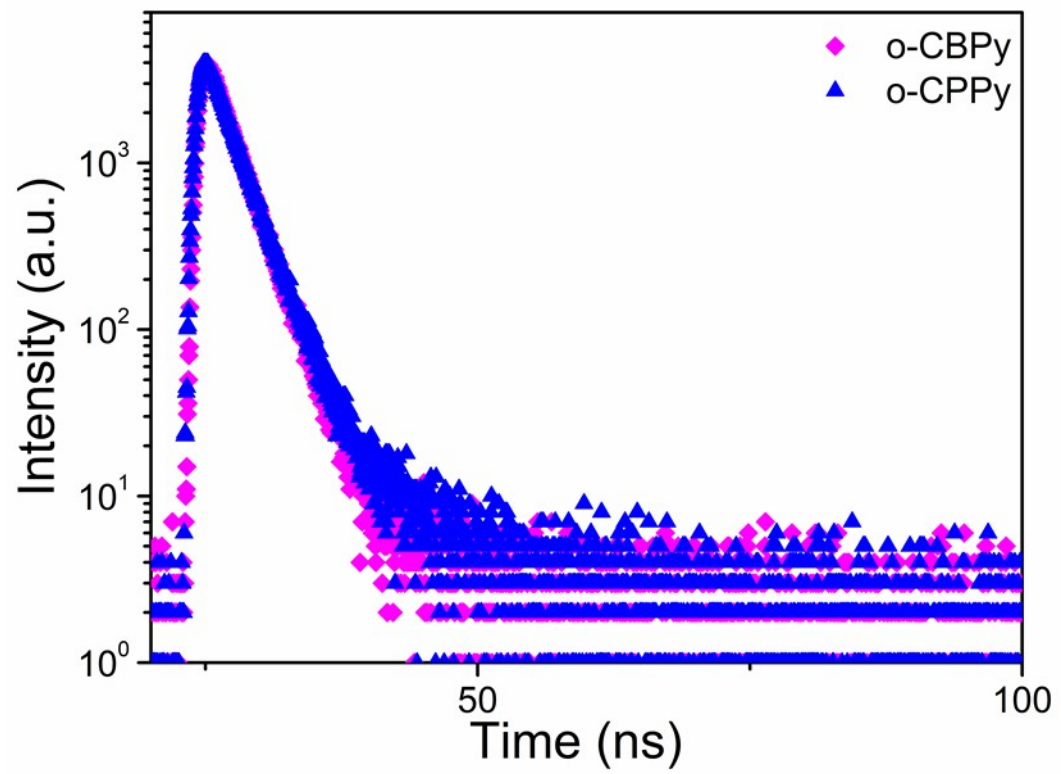

Figure S14. Transient PL prompt of *o*-CBPy and *o*-CPPy in 10 wt% doped PMMA film at room temperature.

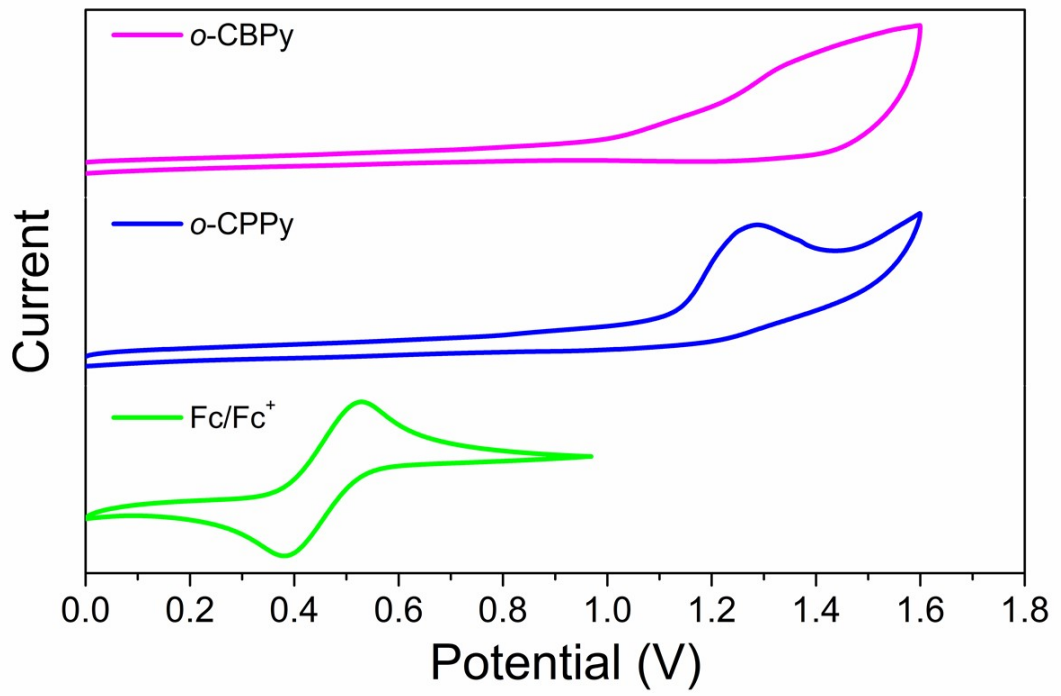

Figure S15. CV curves of compounds in CH_3CN solution.

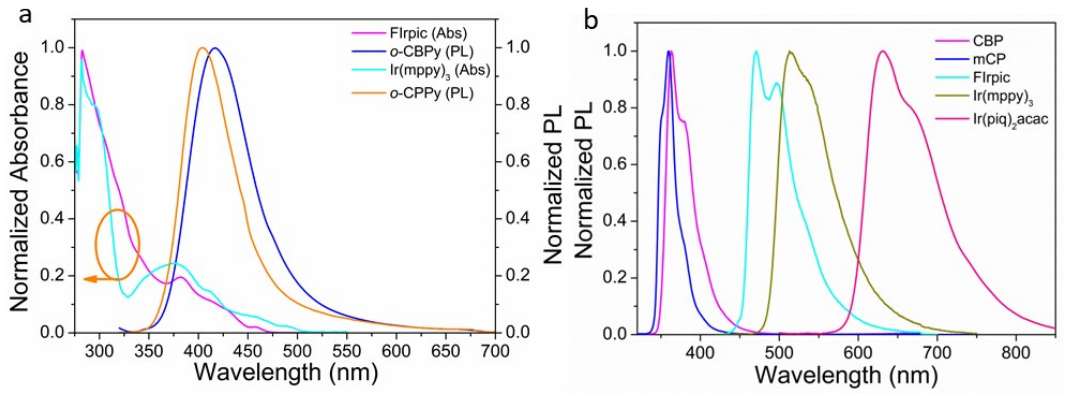

Figure S16. (a) The absorption spectrum of the FIrpic and $Ir(mppy)_3$ in toluene solvent and photoluminescence (PL) spectra of *o*-CBPy or *o*-CPPy in 10 wt% PMMA films; (b) the PL spectrums of hosts and emmiters in toluene solvent..

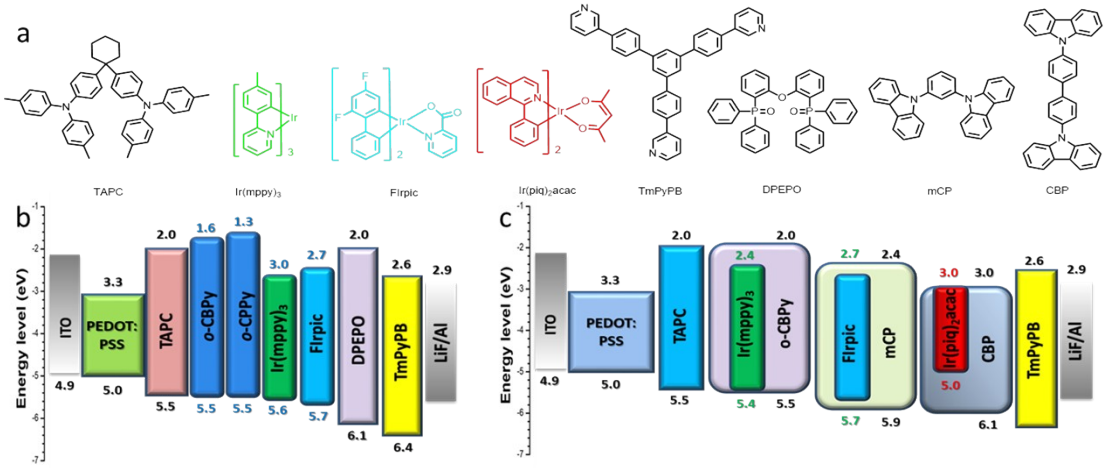

Figure S17. (a) The chemical structures of the corresponding materials; device configurations of (b) FIrpic and $Ir(mppy)_3$, (c) W1.

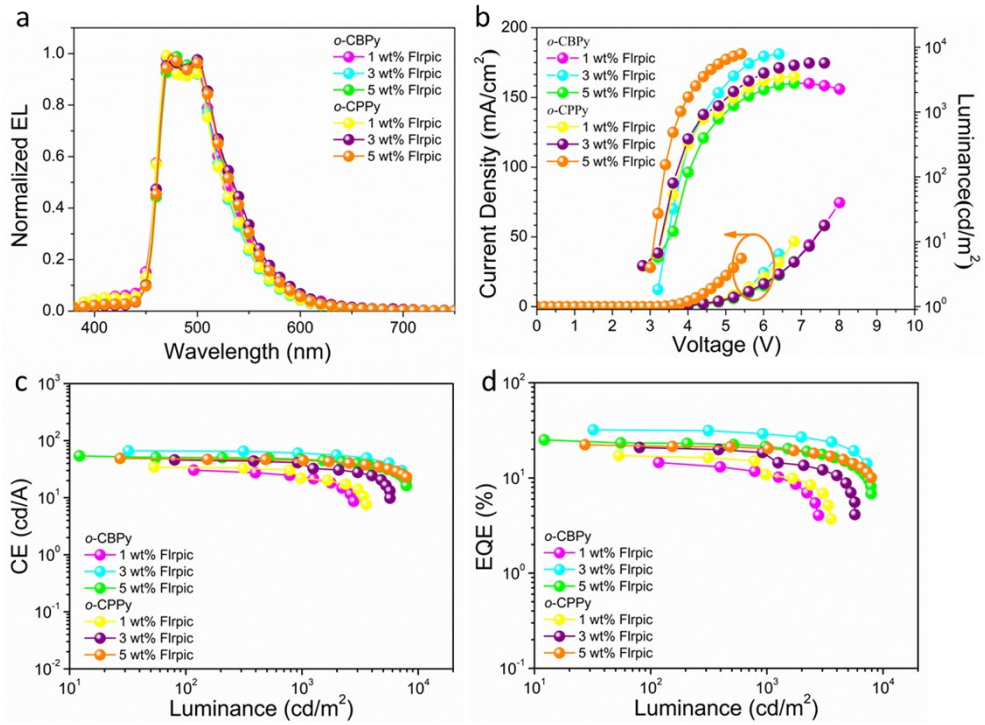

Figure S18. The EL performance of FIrpic based on *o*-CBPy and *o*-CPPy.

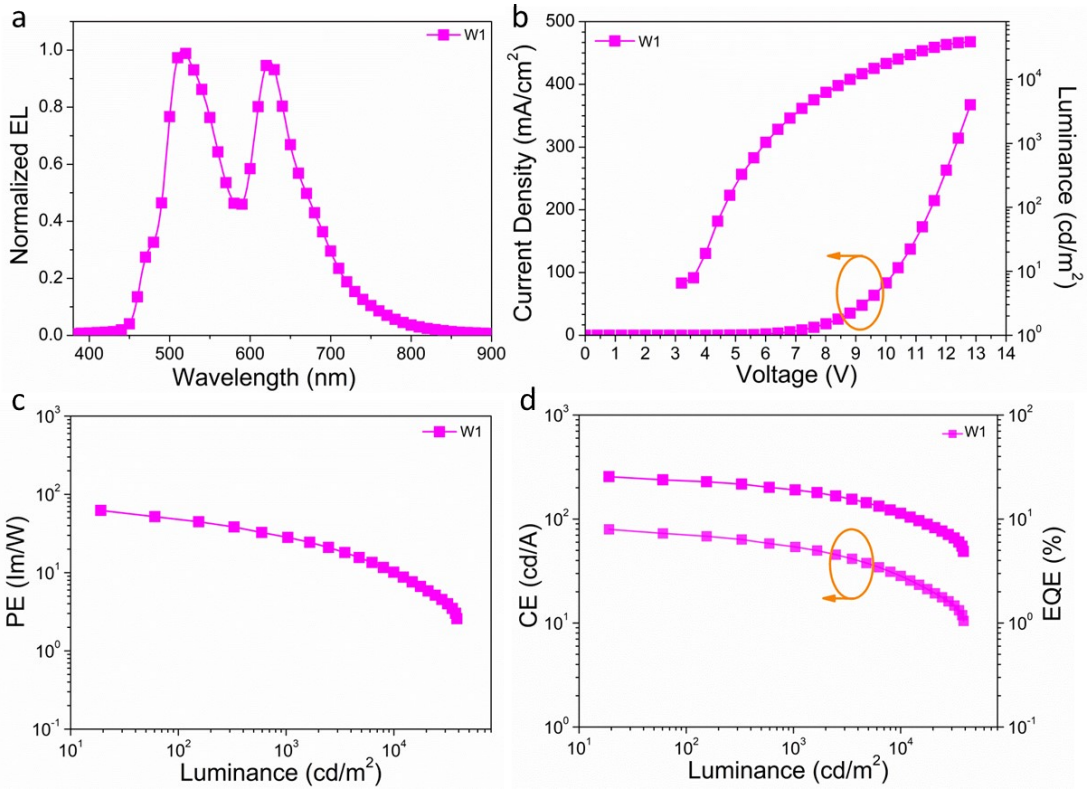

Figure S19. The EL performance of white device.

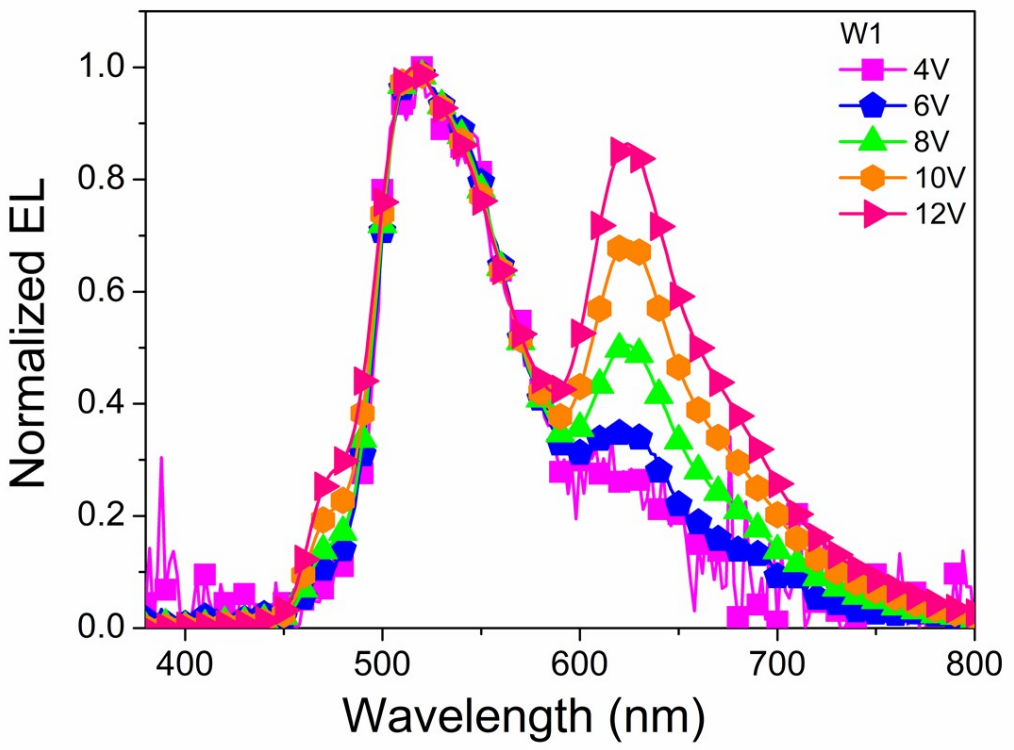

Figure S20. The EL spectra of white device at different voltages.

Table S1. Crystal data of compounds (All crystals were obtained via slow evaporation of a $CHCl_3$/methanol (v:v/1:1) mixture solvent).

Identification code	*o*-CBPy	*o*-CPPy
Empirical formula	$C_{34}H_{22}N_4$	$C_{35}H_{23}N_3$
Formula weight	486.55	485.56
Temperature/K	150.0	170.0
Crystal system	monoclinic	monoclinic
Space group	Cc	Cc
a/Å	10.4058 (6)	10.5020(7)
b/Å	17.8601(9)	17.3495(12)
c/Å	13.3858(6)	13.9993(13)
α/°	90	90
β/°	98.342(10)	97.443(2)
γ/°	90	90
Volume/Å^3	2461.4(2)	2529.3(3)
Z	4	4
ρ_{calc}g/cm^3	1.313	1.275
μ/mm^{-1}	0.079	0.075
F(000)	1016.0	1016.0
Crystal size/mm^3	0.15 × 0.08 × 0.06	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.562 to 52.802	4.562 to 52.814
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 22$, $-14 \le l \le 16$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-17 \le l \le 16$
Reflections collected	12188	9490
Independent reflections	4312 [R_{int} = 0.0660, R_{sigma} = 0.0740]	4154 [R_{int} = 0.0599, R_{sigma} = 0.0753]
Data/restraints/parameters	4312/2/343	4154/2/343
Goodness-of-fit on F^2	1.098	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.0960	R_1 = 0.0607, wR_2 = 0.1218
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1139	$1R_1$ = 0.1122, wR_2 = 0.1512
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22	0.17/-0.21

Table S2. EL Performance Comparison of FIrpic-Based PhOLEDs Containing Various Host Materials Reported in this Work and in the Literature.

Host type	***Host***	***CE(cd/A)***	***PE(lm/W)***	***EQE/%***	***CIE(x,y)***	***Reference***
Conventional hosts	***o*-CBPy**	**66.4**	**57.9**	**32.0**	**(0.16,0.36)**	**This work**
	***o*-CPPy**	**48.9**	**47.9**	**22.3**	**(0.17,0.38)**	
	o-PyCNBCz	61.7	56.2	34.6	(0.14,0.29)	19
	m-POPyCz	51.9	46.5	27.0	(0.14, 0.31)	20
	o-CzTP	52.3	40.5	27.1	(0.15,0.34)	21
	4-CbzBiz	64.1	66.3	30.9	-	22
	CzBPCb	53.6	50.6	30.1	-	23
	CbOTCb	47.4	44.0	28.8	(0.14,0.30)	24
	o-DiCbzBz	57.5	48.9	27.0	-	25
	mCPCN	67.8	73.4	30.6	(0.16,0.36)	26
	PCPO25	-	53.1	31.4	-	27
	DCzCO	63.7	53.3	31.2	(0.16,0.34)	28
TADF hosts	BT-01	73.5	64.4	31.8	(0.16,0.36)	29
	BT-02	78.8	64.0	30.7	(0.17,0.40)	
Exciplex hosts	mCBP:PO-T2T	-	79.6	34.1	-	30
	mCP:B3PYMPM	62.2	55.4	29.5	-	31
	mCP:PO-T2T	-	66.0	30.3	-	32