Supporting Information

Impact of Peripheral Groups on Pyrimidine Acceptors-based HLCT Materials for Efficient Deep Blue OLED Devices

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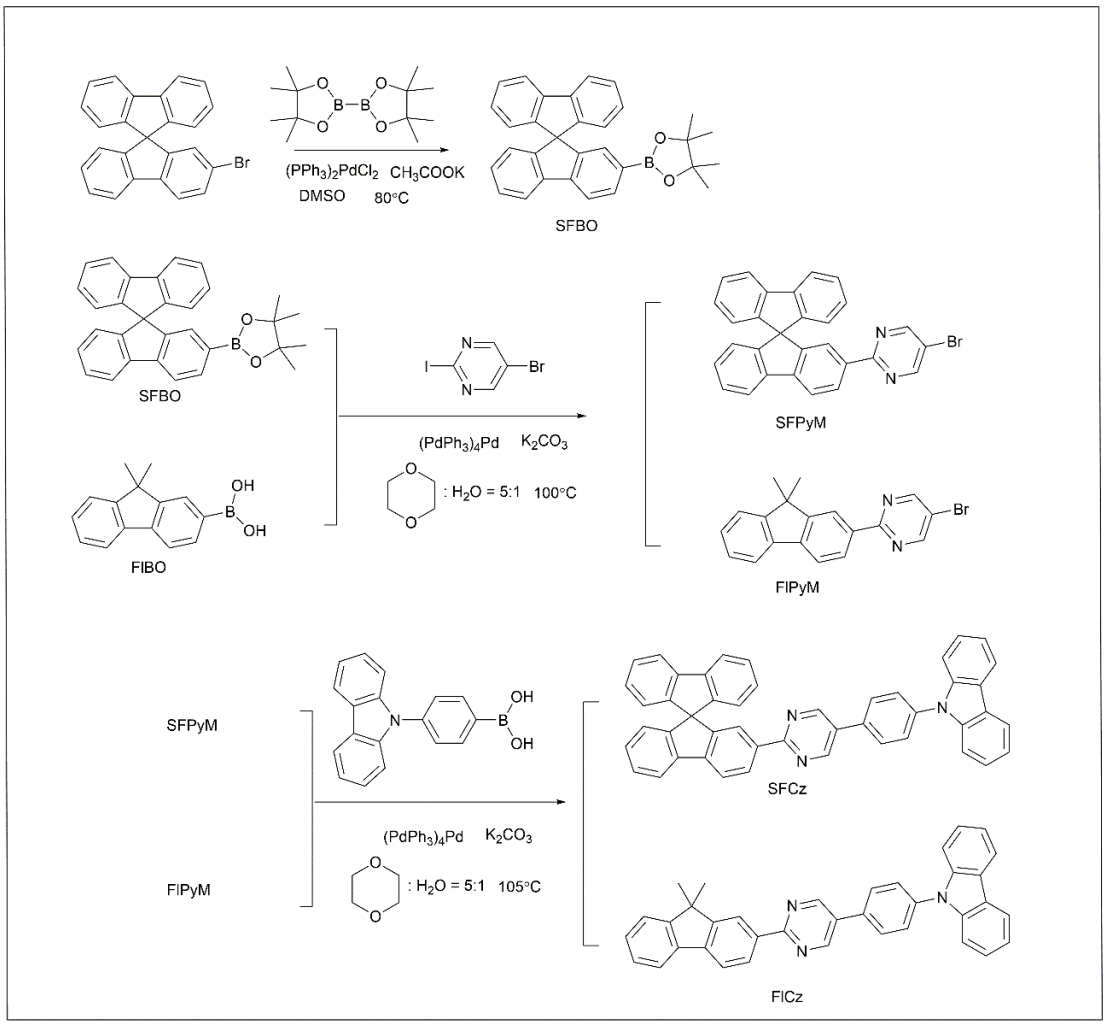

Figure S1. Synthetic routes of FlCz and SfCz.

(1)*Synthesis of 2-(9,9'-spirobi[fluoren]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxolane (SF-Bo)*

2-Bromo-9,9-spirobifluorene (3.95 g, 10 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,3,2-dioxolan (3.07 g, 12 mmol), Potassium acetate (0.98 g, 10 mmol), bis(triphenylphosphine) palladium dichloride (0.35 g, 0.5 mmol) and anhydrous dimethyl sulfoxide (50 ml) were added to a 100 ml double-necked flask. The reaction was carried out by thin layer chromatography. Reaction solution was washed with water and extracted with dichloromethane in small amounts. The solvent was removed by distillation under reduced pressure and purified by silica gel column chromatography, eluting with a solvent mixture of petroleum ether/dichloromethane (v) = 6:1. A white solid of 4.03 g was obtained in 91.2 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 - 7.70 (m, 6H), 7.41 - 7.23 (m, 3H), 7.18 (d, J = 3.0 Hz, 1H), 7.11 (s, 1H), 7.02 (td, J = 7.4, 3.2 Hz, 2H), 6.72 - 6.58 (m, 2H), 1.17 (s, 12H).

(2)*Synthesis of 2-(9,9'-spirobi[fluoren]-2-yl)-5-bromopyrimidine (SF-PyM)*

2-(9,9'-Spiro-bis[fluoren]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxolane (2.21 g, 5 mmol), 5-bromo-2-iodopyrimidine (1.73 g, 6 mmol), potassium carbonate (1.38 g, 10 mmol), tetrakis(triphenylphosphine)palladium (0.2889 g, 0.25 mmol) were added to a 50 ml double-necked flask, followed by the addition of 20 ml of a 5:1 volume mixture of 1-4 dioxane and water, and refluxed at 100 °C. The reaction was stopped by thin layer chromatography. The organic phase was dried over anhydrous magnesium sulphate, filtered and spun dry, and the crude product was purified by column chromatography to give 1.38 g of a white solid in 58.5 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 8.49 (d, J = 9.7 Hz, 1H), 8.10 - 7.74 (m, 5H), 7.38 (d, J = 4.8 Hz, 3H), 7.25 (s, 1H), 7.20 - 7.05 (m, 2H), 6.75 (d, J = 7.6 Hz, 2H).

(3)Synthesis of 9-(4-(2-(9,9'-spirobi[fluoren]-2-yl)pyrimidin-5-yl)phenyl)-9H-carbazole (SFCz)

2-(9,9'-Spiro-bis[fluoren]-2-yl)-5-bromopyrimidine (2.37 g, 5 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (1.73 g, 6 mmol), potassium carbonate (1.38 g 10 mmol), tetrakis(triphenylphosphine)palladium (0.2889 g, 0.25 mmol) were added to a 50 ml double-necked flask and 20 ml of a mixture of 1,4-dioxane and water in a volume ratio of 5:1, refluxed at 105 °C for 12 h. The reaction was stopped after thin layer chromatography detection to the end point. The organic phase was dried over anhydrous magnesium sulphate, filtered and spun dry, and the crude product was purified by

column chromatography to give 1.68 g of a white solid in 53.2 % yield. MALDI-TOF-MS: m/z calcd: 635.77; found:635.84. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.62 (dd, J = 8.1, 1.6 Hz, 1H), 8.16 (d, J = 7.7 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.95 - 7.88 (m, 4H), 7.80 - 7.77 (m, 2H), 7.73 - 7.70 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.45 - 7.37 (m, 5H), 7.33 - 7.28 (m, 2H), 7.14 (dtd, J = 12.1, 7.5, 1.0 Hz, 3H), 6.80 (d, J = 7.6 Hz, 2H), 6.75 (d, J = 7.5 Hz, 1H), ^{13}C NMR (101 MHz, CDCl3) δ 162.32, 153.90, 148.92, 148.20, 147.37, 143.61, 140.92, 139.96, 139.45, 137.06, 135.81, 132.30, 129.27, 127.05, 126.76, 125.05, 123.05, 122.46, 119.48, 119.37, 119.22, 119.10, 119.01, 108.66, 65.07.

(4)Synthesis of 5-bromo-2-(9,9-dimethyl-9H-fluoren-2-yl)pyrimidine (FlPyM)

(9,9-Dimethyl-9H-fluoren-2-yl)boronic acid (1.20 g, 5 mmol), 5-bromo-2-iodopyrimidine (1.73 g, 6 mmol), potassium carbonate (1.38 g, 10 mmol), tetrakis(triphenylphosphine)palladium (0.2889 g, 0.25 mmol) were added to a 50 ml double-necked flask followed by a 5:1 volume ratio of 1,4-dioxane to water mixture of 20 ml of solvent was added and then refluxed at 100 °C. The reaction was stopped after thin layer chromatography. The organic phase was dried over anhydrous magnesium sulphate, filtered and spun dry, and the crude product was purified by column chromatography to give 0.77 g of white fluffy solid in 43.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 2H), 8.59 - 8.41 (m, 2H), 7.94 - 7.74 (m, 2H), 7.60 - 7.32 (m, 3H), 1.57 (s, 6H).

(5)Synthesis of 9-(4-(2-(9,9-dimethyl-9H-fluoren-2-yl) pyrimidin-5-yl)phenyl)-9H-carbazole (FlCz)

5-Bromo-2-(9,9-dimethyl-9H-fluoren-2-yl)pyrimidine (1.38 g, 5 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (1.73 g, 6 mmol), potassium carbonate (1.38 g, 10 mmol), tetrakis(triphenylphosphine)palladium (0.2889 g, 0.25 mmol) were added to a 50 ml double-necked flask and The reaction was refluxed at 105 ° C for 12 hours, which stopped by thin-layer chromatography. The organic conpounds was dried with anhydrous magnesium sulfate, filtered and spun dry. The crude product was purified by column chromatography to obtain 1.50 g of white fluffy solid in 58.6 % yield. MALDI-TOF-MS: m/z calcd: 513.64; found: 514.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.62 (dd, J = 8.1, 1.6 Hz, 1H), 8.16 (d, J = 7.7 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.95 - 7.88 (m, 4H), 7.80 - 7.77 (m, 2H), 7.73 - 7.70 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.45 - 7.37 (m , 5H), 7.33 - 7.28 (m, 2H), 7.14 (dtd, J = 12.1, 7.5, 1.0 Hz, 3H), 6.80 (d,

J = 7.6 Hz, 2H), 6.75 (d, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 162.93, 154.13, 153.68, 153.11, 141.13, 139.63, 137.43, 137.24, 135.03, 132.40, 129.50, 127.13, 126.83, 126.57, 126.09, 125.08, 122.55, 121.72, 121.34, 119.58, 119.41, 119.25, 119.21, 108.77, 45.84, 25.85.

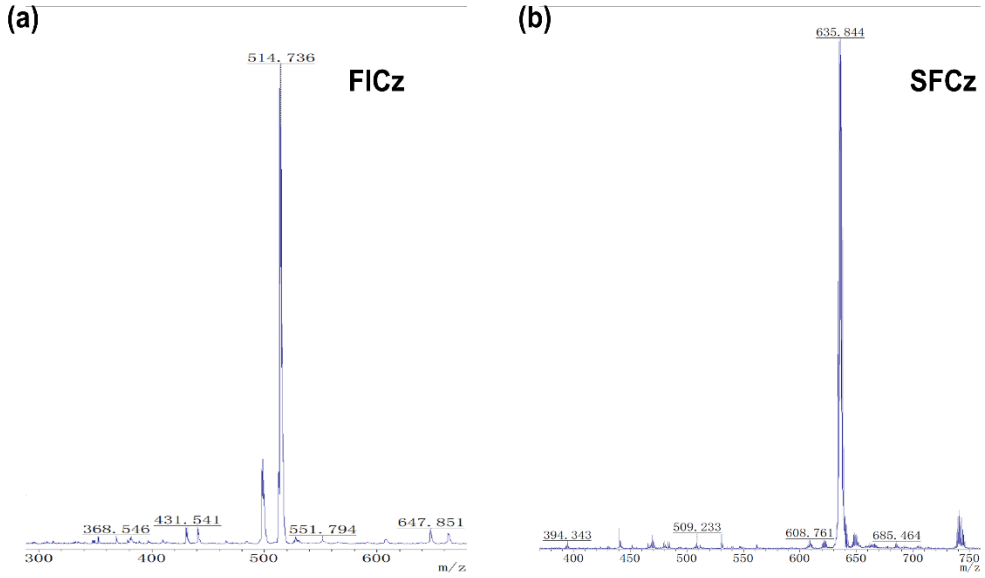

Figure S2. MALDI-TOF mass spectrums of FlCz and SFCz.

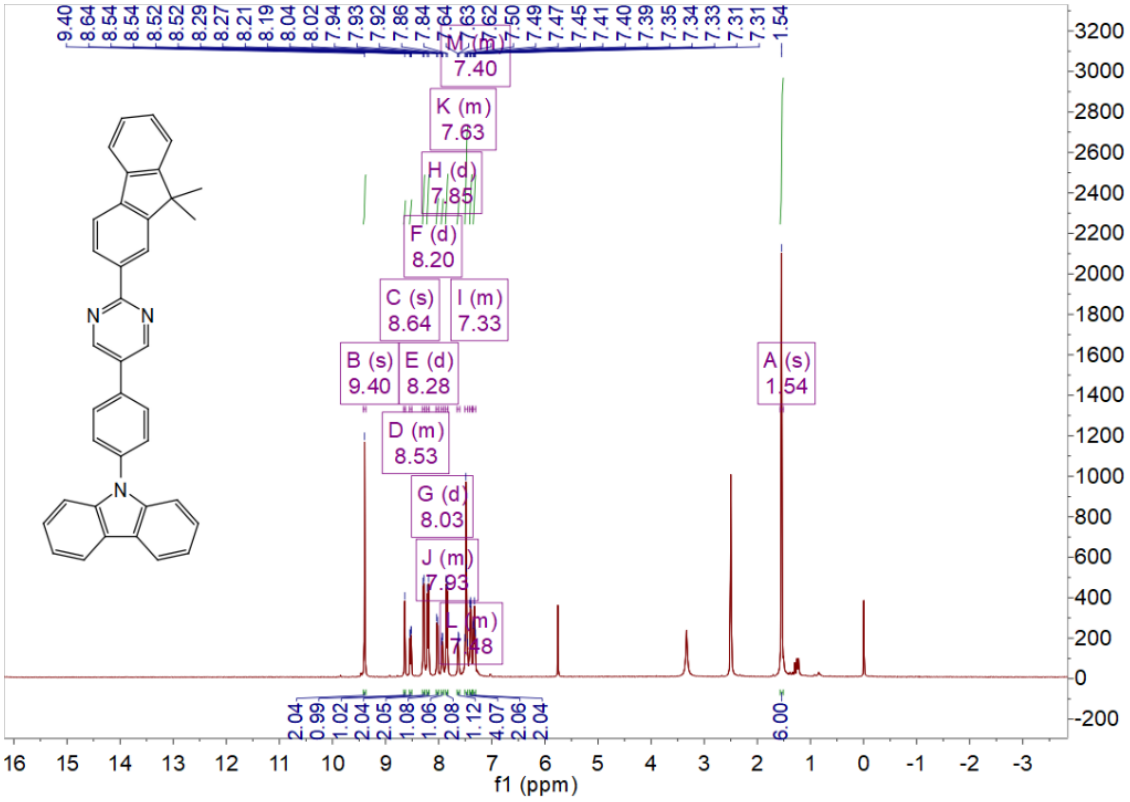

Figure S3. ^{1}H NMR spectrum of FlCz in $CDCl_3$.

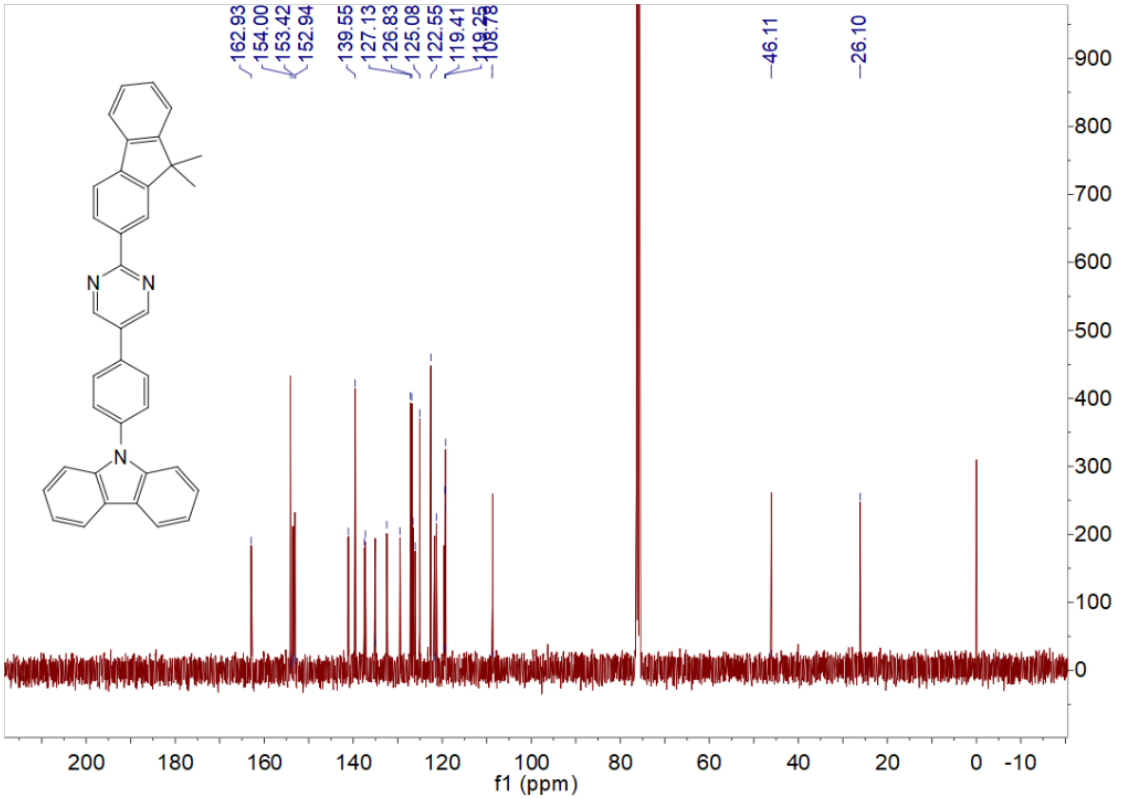

Figure S4. ^{13}C NMR spectrum of FlCz in $CDCl_3$.

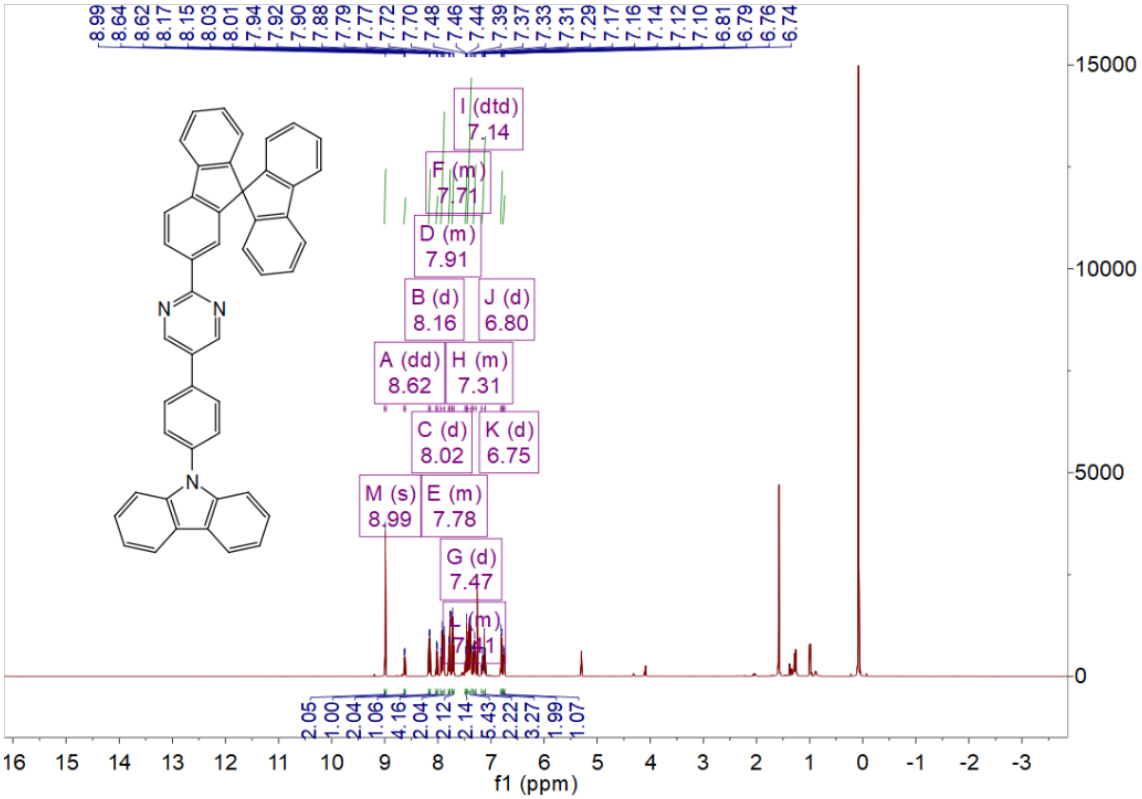

Figure S5. ^{1}H NMR spectrum of SFCz in $CDCl_3$.

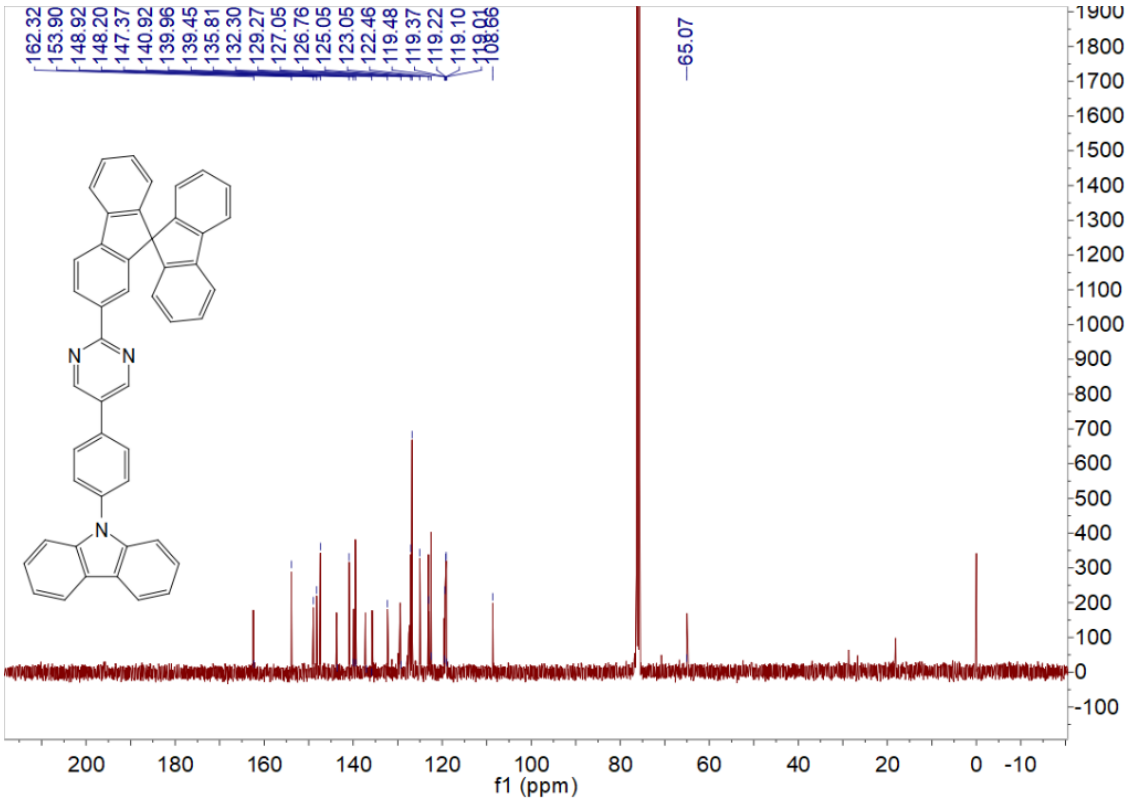

Figure S6. ^{13}C NMR spectrum of FlCz in $CDCl_3$.

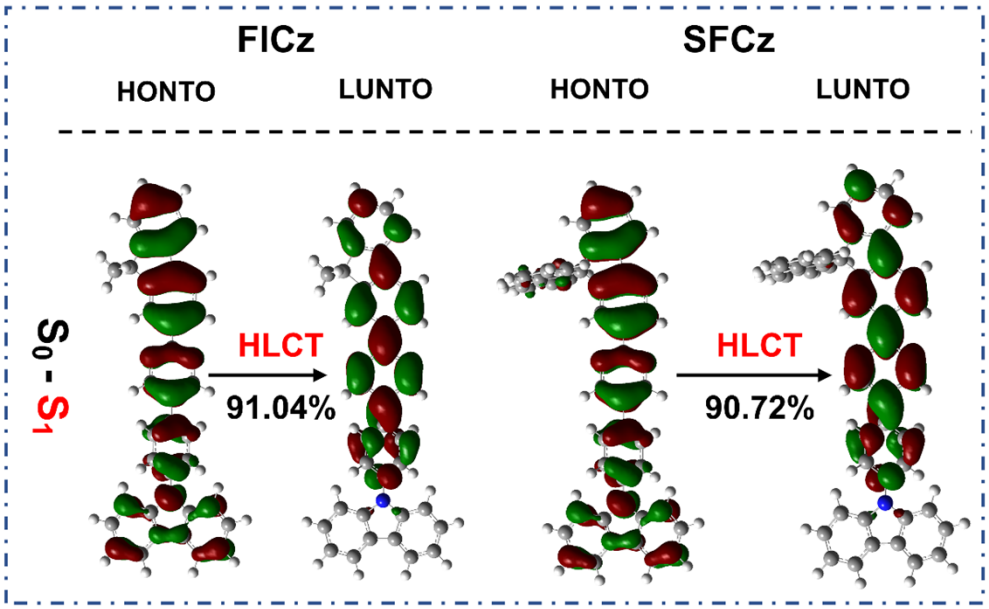

Figure S7. The natural transition orbital distribution of the two molecules.

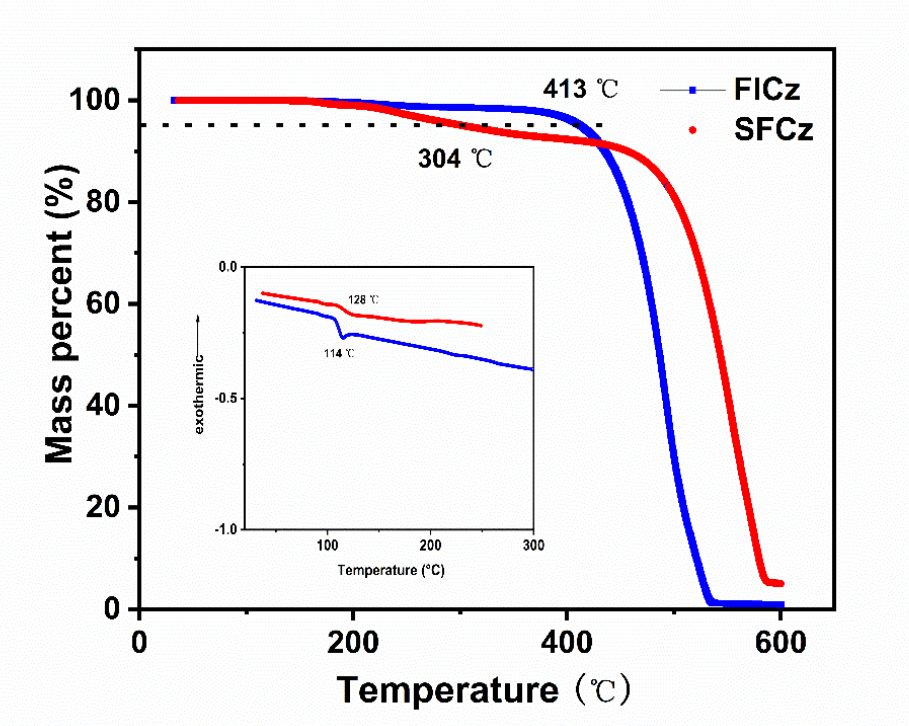

Figure S8. Thermogravimetric analysis and Differential scanning calorimetry curves of FlCz and SFCz.

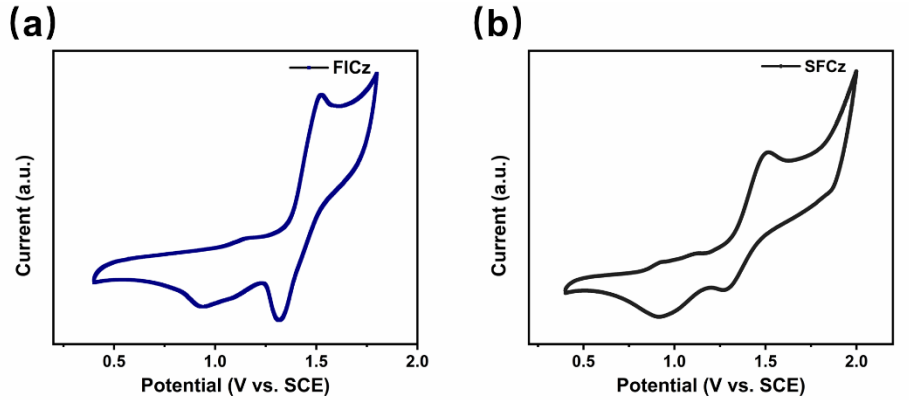

Figure S9. Cyclic voltammetric curves of FlCZ (a) and SFCz (b).

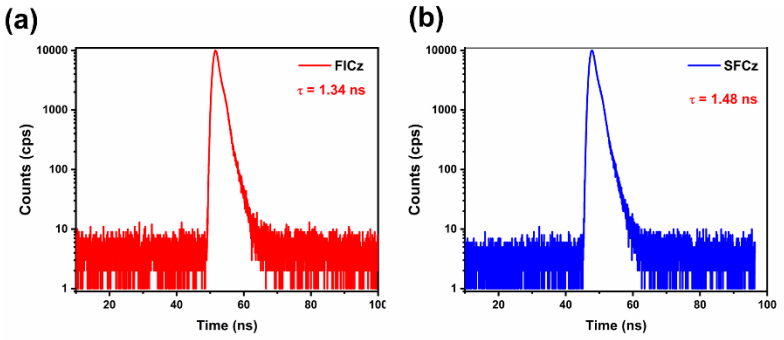

Figure S10. The lifetime measurement of FlCz (a) and SFCz (b) in film by using time-correlated single photon counting method under the excitation of a laser (365 nm).

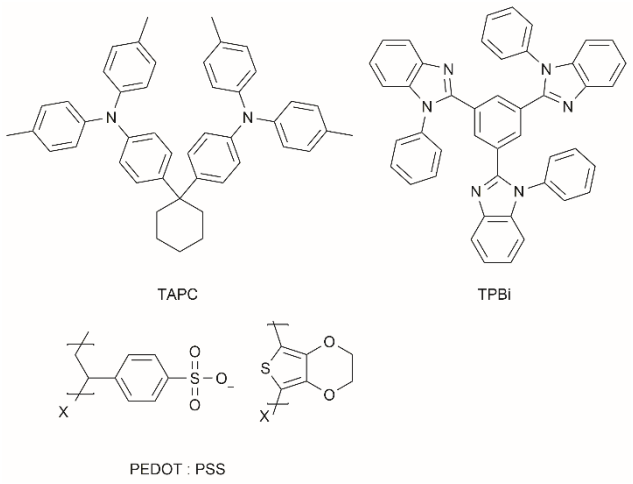

Figure S11. The chemical structures of the used materials.

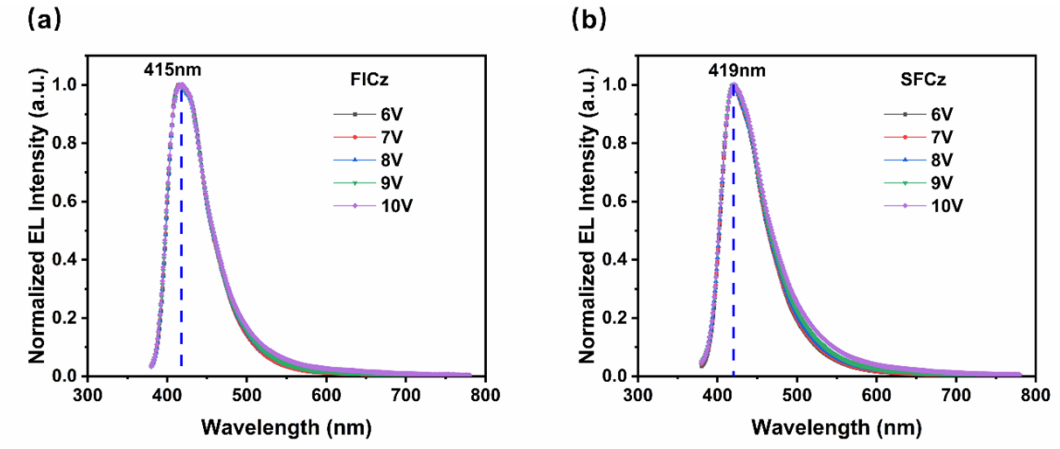

Figure S12. Normalized EL spectra of the non-doped devices of FlCz (a) and SFCz (b)from 6 V to 10 V.

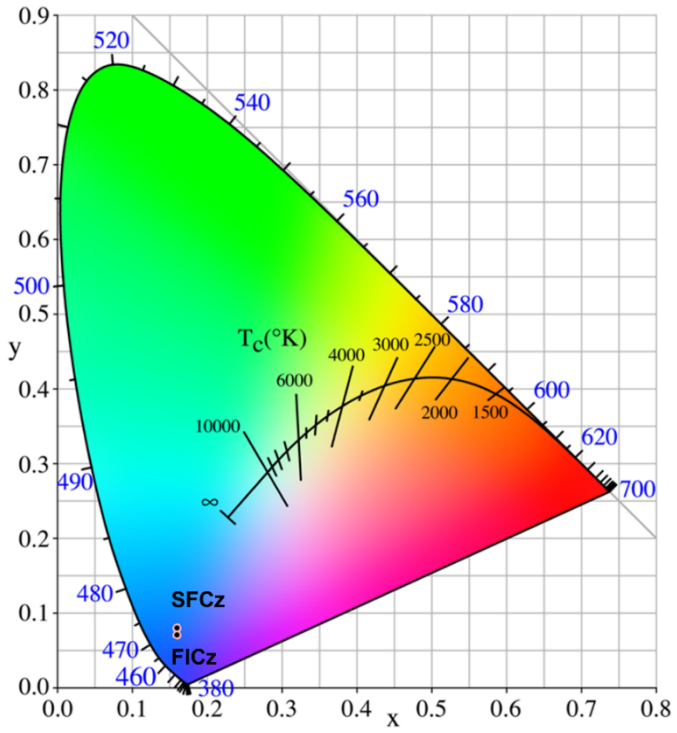

Figure S13. The color coordinates of the two devices at an operating voltage of 7 V.

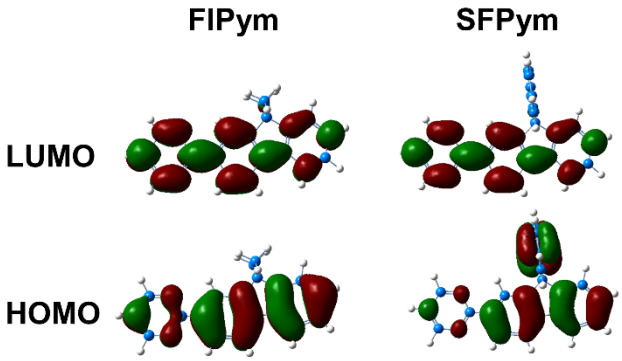

Figure S14. The frontier molecular orbital distributions of FlPym and SFPym.

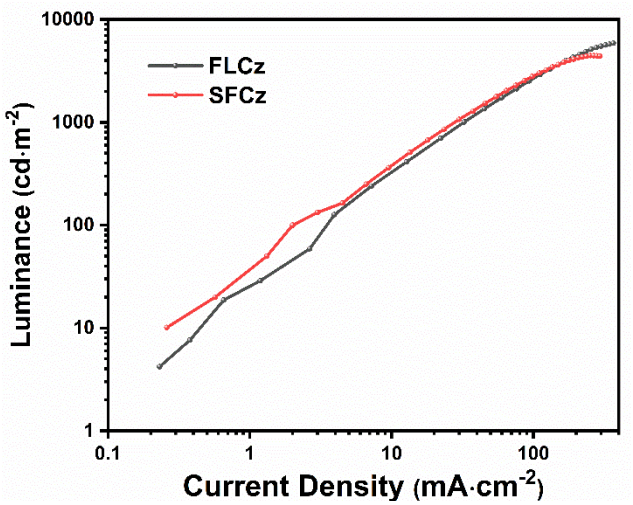

Figure S15. The luminance-current density (L-J) characteristics.

Tabel S1 The detail Stokes shift date of FlCz and SFCz in different solvents.

compound	Solvents	Δf	V_a (nm)	V_f (nm)	V_f-V_a (nm)	V_a-V_f (cm^{-1})
FlCz	Toluene	0.014	342	411	69	4908.866
	Chlorobenzene	0.143	344	426	82	5595.589
	Tertrahydrofuran	0.208	342	422	80	5543.084
	Dichloromethane	0.218	342	438	96	6408.716
	Dimethyl formamide	0.275	340	461	121	7719.790
	Acetone	0.285	324	452	128	8740.304
	Acetonitrile	0.305	340	466	126	7952.537
SFCz	Toluene	0.014	342	411	69	4908.866
	Chlorobenzene	0.143	344	421	77	5595.589
	Tertrahydrofuran	0.208	342	434	92	5543.084
	Dichloromethane	0.218	340	441	101	6408.716
	Dimethyl formamide	0.275	344	471	127	7719.790
	Acetone	0.285	326	457	131	8740.304
	Acetonitrile	0.305	340	478	138	7952.537

Table S2. The PLQY value and CIE coordinates of FlCz and SFCz in different solvents.

Compound	Solvent	PLQY (%)	CIE (x,y)
FlCz	Toluene	93.76	(0.16, 0.03)
	Chlorobenzene	85.26	(0.15, 0.05)
	Tetrahydrofuran	60.03	(0.15, 0.03)
	Dichloromethane	70.34	(0.15,0.09)
	Dimethylformamide	96.09	(0.14, 0.27)
	Acetone	92.02	(0.16, 0.26)
	Acetonitrile	93.94	(0.16, 0.27)
SFCz	Toluene	75.41	(0.16, 0.03)
	Chlorobenzene	86.87	(0.15, 0.06)
	Tetrahydrofuran	97.43	(0.15, 0.06)
	Dichloromethane	99.62	(0.15, 0.10)
	Dimethylformamide	99.29	(0.18, 0.26)
	Acetone	94.24	(0.17, 0.28)
	Acetonitrile	98.79	(0.20, 0.30)