

## Carbazole/oligofluorene End-capped Hexanes: Solution-processable Host Materials for Phosphorescent Organic Light-emitting Diodes

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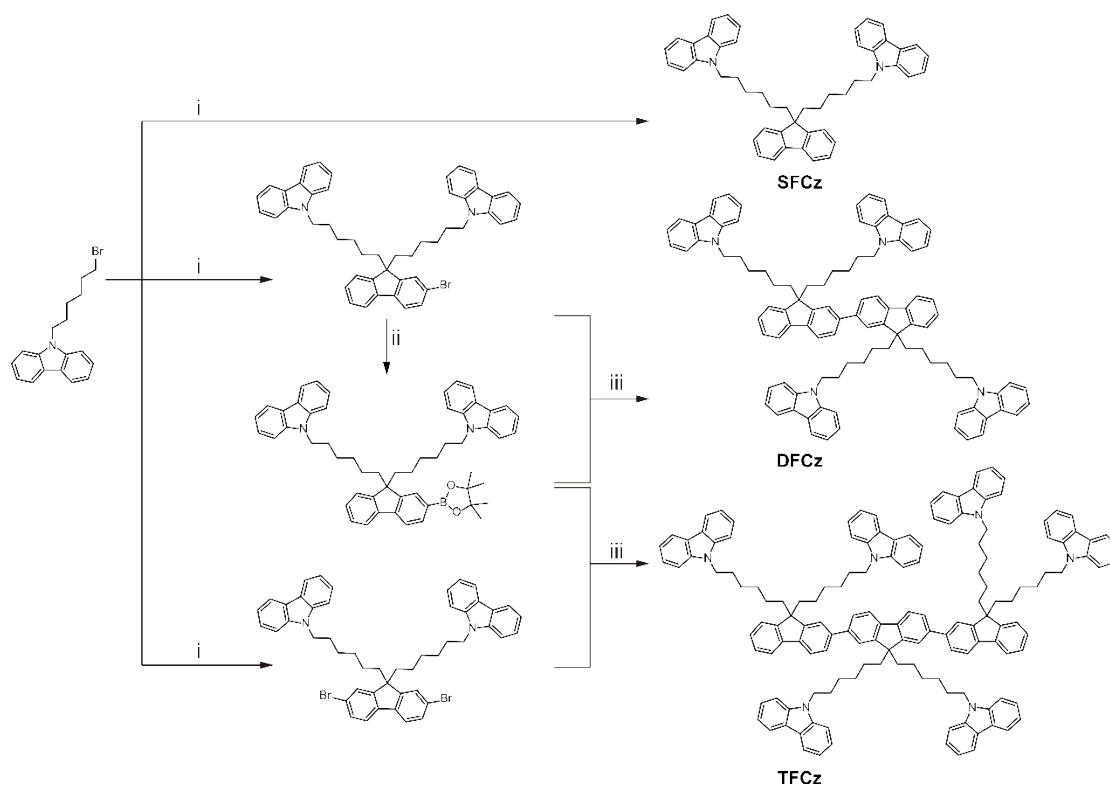
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## 1. Synthesis and characterization

**Materials:** Chemicals and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich or Acros, and used without further purification. Tetrahydrofuran (THF) was dried and purified in a standard procedure. The manipulations involving air-sensitive reagents were performed in an atmosphere of dry N<sub>2</sub>.

**Characteristic Methods:** <sup>1</sup>H and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz instrument using CDCl<sub>3</sub> or *d*-DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. The quoted chemical shifts are in *ppm* and the *J* values are expressed in Hz. The splitting patterns have been designed as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets) and m (multiplet). The MALDI-TOF-MS was performed on a Buker Daltonics flex Analysis. High resolution mass spectroscopy (HRMS) were recorded on a LCT Premier XE (Waters) mass spectrometer.



**Scheme S1.** Synthetic procedure of SFCz, DFCz, and TFCz: (i) Br-(CH<sub>2</sub>)<sub>6</sub>-Br, NaH, THF, at r.t. for 24 h (ii) PdCl<sub>2</sub>(dppf), KOAc, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane), 1,4-dioxane, at 80°C for 24 h (iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, toluene, at 90°C for 48 h.

### Synthesis of 9-(6-bromohexyl)-9H-carbazole

To a solution of carbazole (8.35 g, 50 mmol) in dry THF (40 mL) was added NaH (2.52 g, 63 mmol) in several portions. The resulting solution was stirred for 10 min at room temperature, followed by being added dropwise to a refluxing solution of 1,6-dibromohexane (45 mL, 292 mmol) in THF (100 mL). After refluxed for 24 h, the reaction mixture was cooled to room temperature and quenched by adding several drops of water to destroy the excessive NaH. The solvent of THF and excessive 1,6-dibromohexane were removed by rotatory evaporation and vacuum distillation, respectively. The residual was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with water for three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated for flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=1:10 as eluent), affording the title compound as a white solid. Yield: 13.81 g (82.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.10 (d, *J*=8.0 Hz, 2H), 7.48 (t, *J*=8.0 Hz, 2H), 7.40 (d, *J*=8.0 Hz, 2H), 7.22 (t, *J*=7.2 Hz, 2H), 4.32 (d, *J*=8.0 Hz, 2H), 3.36 (t, *J*=7.2 Hz, 2H), 1.90 (d, *J*=7.2 Hz, 2H), 1.81 (m, 2H), 1.47 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 140.41, 125.63, 122.86, 120.39, 118.79, 108.60, 42.87, 33.72, 32.58, 28.84, 27.94, 26.49.

### Synthesis of 9,9'-((9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (SFCz)

To a solution of 9-(6-bromohexyl)-9H-carbazole (0.66 g, 2 mmol) in dry THF (10 mL) was added NaH (0.072 g, 3 mmol) in several portions. The resulting solution was stirred for 10 min at room temperature, followed by being added dropwise to a refluxing solution of 9H-fluorene (0.14 g, 0.8 mmol) in THF (10 mL). Following the same procedure in synthesizing 9-(6-bromohexyl)-9H-carbazole, **SFCz** was obtained in a white solid after flash column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/PE=1:5 as eluent. Yield: 0.39 g (73.6%). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, ppm): δ 8.10 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=7.2 Hz, 2H), 7.46 (d, *J*=7.2 Hz, 4H), 7.30-7.21 (m, 14H), 4.53 (t, *J*=7.2 Hz, 4H), 1.89 (m, 4H), 1.67 (m, 4H), 1.08 (m, 8H), 0.58 (s, 4H); <sup>13</sup>C NMR (100 MHz, *d*-DMSO, ppm): δ 151.36, 150.63, 140.57, 140.27, 139.87, 127.60, 127.30, 126.29, 125.98, 123.21, 122.38, 121.19, 120.61, 120.38, 118.97, 109, 45, 55.04, 42.31, 31.75, 29.12, 28.50, 26.26, 23.64, 22.55. MALDI-TOF: *m/z* calcd for C<sub>49</sub>H<sub>48</sub>N<sub>2</sub>: 664.9188 [M]; found: 665.8943. HRMS (EI): *m/z* calcd: 665.3896 [M+H]<sup>+</sup>; found: 665.3897.

### Synthesis of 9,9'-((2-bromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole)

With the similar procedure in preparing SFCz, the title compound (a white solid) was synthesized using 2-bromo-9H-fluorene (0.20 g, 0.8 mmol) and purified by flash column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE=1:3 as eluent. Yield: 0.46 g (76.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.10 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=7.2 Hz, 2H), 7.46 (d, *J*=7.2 Hz, 4H), 7.30-7.21 (m, 13H), 4.53 (t, *J*=7.2 Hz, 4H), 1.89 (m, 4H), 1.67 (m, 4H), 1.08 (m, 8H), 0.58 (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 150.30, 141.08, 140.37, 127.09, 126.83, 125.54, 122.78, 122.71, 120.31, 118.67, 108.63, 54.82, 42.91, 40.21, 29.63, 28.73, 26.79, 23.49.

### Synthesis of 9,9'-((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole)

A mixture of 9,9'-((2-bromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (1.0 g, 0.71 mmol), 4,4,4',4',5,5,5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (0.216 g, 0.85 mmol), PdCl<sub>2</sub>(dppf) (0.014 g, 0.02 mmol) and KOAc (0.221 g, 2.13 mmol) dissolved in degassed 1,4-dioxane (6 mL) was stirred at 80°C for 24 h. The reaction was quenched by adding water and the title compound was extracted by CH<sub>2</sub>Cl<sub>2</sub> for three times. The organic layers were collected, combined, dried with anhydrous magnesium sulphate, and concentrated for silica gel chromatography by petroleum ether/ dichloromethane (3:2) to afford the desired compound as a white solid in 63% yield (0.65 g). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, ppm): δ 8.10 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=7.2 Hz, 2H), 7.46 (d, *J*=7.2 Hz, 4H), 7.30-7.21 (m, 13H), 4.53 (t, *J*=7.2 Hz, 4H), 1.89 (m, 4H), 1.67 (m, 4H), 1.37 (s, 12H), 1.08 (m, 8H), 0.58 (s, 4H); <sup>13</sup>C NMR (100 MHz, *d*-DMSO, ppm): δ 151.36, 150.63, 140.57, 140.27, 139.87, 127.60, 127.30, 126.29, 125.98, 123.21, 122.38, 121.19, 120.61, 120.38, 118.97, 109, 45, 55.04, 42.31, 40.26, 40.21, 31.75, 29.12, 28.50, 26.26, 23.64, 22.55.

### Synthesis of 9,9,9',9'-tetrakis(6-(9H-carbazol-9-yl)hexyl)-9H,9'H-2,2'-bifluorene (DFCz)

To a degassed toluene solution (10 mL) of 9,9'-((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (0.098 g, 0.17 mmol), 9,9'-((2-bromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (0.257 g, 0.34 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.023 g, 0.02 mmol) were a solution of Na<sub>2</sub>CO<sub>3</sub> (2.0 M, 2 mL). The reaction mixture

was stirred at 90°C for 2 days under a nitrogen atmosphere. At the end of Suzuki reaction, water was added to the reaction mixture and the mixture was extracted for several times using chloroform. The organic phase was collected and dried over anhydrous magnesium sulfate. After filtration and evaporation to remove the drying agent and solvent respectively. **DFCz** in a white solid was finally obtained by column chromatography using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> as the eluent (yield: 55 %). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, *ppm*): δ 8.10 (d, *J*=8.0 Hz, 8H), 7.70 (d, *J*=7.2 Hz, 4H), 7.46 (d, *J*=7.2 Hz, 8H), 7.30-7.21 (m, 26H), 4.53 (t, *J*=7.2 Hz, 8H), 1.89 (m, 8H), 1.67 (m, 8H), 1.08 (m, 16H), 0.58 (s, 8H); <sup>13</sup>C NMR (100 MHz, *d*-DMSO, *ppm*): δ 151.36, 150.63, 140.57, 140.27, 139.87, 127.60, 127.30, 126.29, 125.98, 123.21, 122.38, 121.19, 120.61, 120.38, 118.97, 109, 45, 55.04, 42.31, 31.75, 29.12, 28.50, 26.26, 23.64, 22.55. MALDI-TOF: *m/z* calcd for C<sub>98</sub>H<sub>94</sub>N<sub>4</sub>: 1327.8218 [M]; found: 1327.1385. HRMS (EI): *m/z* calcd: 1327.7557 [M+H]<sup>+</sup>; found: 1327.7568.

#### **Synthesis of 9,9'-((2,7-dibromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole)**

Following a similar procedure in preparing **SFCz**, the title compound was synthesized using 2,7-dibromo-9H-fluorene (0.20 g, 0.8 mmol) and purified by flash column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE=1:3 as eluent to give a white solid. Yield: 0.46 g (76.7%). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, *ppm*): δ 8.10 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=7.2 Hz, 2H), 7.46 (d, *J*=7.2 Hz, 4H), 7.30-7.21 (m, 12H), 4.53 (t, *J*=7.2 Hz, 4H), 1.89 (m, 4H), 1.67 (m, 4H), 1.08 (m, 8H), 0.58 (s, 4H); <sup>13</sup>C NMR (100 MHz, *d*-DMSO, *ppm*): δ 151.36, 150.63, 140.57, 140.27, 139.87, 127.60, 127.30, 126.29, 125.98, 123.21, 122.38, 121.19, 120.61, 120.38, 118.97, 109, 45, 55.04, 42.31, 31.75, 29.12, 28.50, 26.26, 23.64, 22.55.

#### **Synthesis of 9,9',9'',9''',9''''',9''''''-(9H,9'H,9''H-[2,2':7',2''-terfluorene]-9,9,9',9'',9''',9''''-hexaylhexakis(hexane-6,1-diyl))hexakis(9H-carbazole) (TFCz)**

With the similar synthetic conditions and purification procedures in the preparation of **DFCz**, **TFCz** was prepared using 9,9'-((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (0.098 g, 0.17 mmol) and 9,9'-((2-bromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole) (0.257 g, 0.34 mmol). After column chromatography using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> as the eluent, a white solid of **TFCz** was obtained (yield: 55 %). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, *ppm*): δ 8.10 (d, *J*=8.0 Hz, 12H), 7.70 (d, *J*=7.2 Hz,

6H), 7.46 (d,  $J=7.2$  Hz, 12H), 7.30-7.21 (m, 38H), 4.53 (t,  $J=7.2$  Hz, 12H), 1.89 (m, 12H), 1.67 (m, 12H), 1.08 (m, 24H), 0.58 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz, *d*-DMSO, *ppm*):  $\delta$  151.36, 150.63, 140.57, 140.27, 139.87, 127.60, 127.30, 126.29, 125.98, 123.21, 122.38, 121.19, 120.61, 120.38, 118.97, 109, 45, 55.04, 42.31, 31.75, 29.12, 28.50, 26.26, 23.64, 22.55. MALDI-TOF: *m/z* calcd for  $\text{C}_{147}\text{H}_{140}\text{N}_6$ : 1990.7247 [M]; found: 1992.1324. HRMS (EI): *m/z* calcd: 1990.7247 [M+H]<sup>+</sup>; found: 1992.1345.

## 2. Solubility test

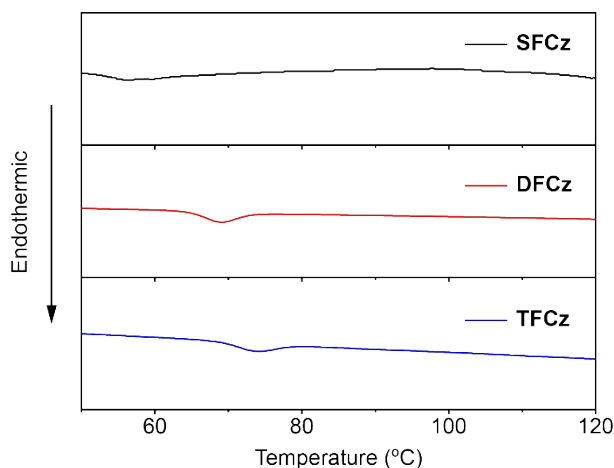
The solubilities of **SFCz**, **DFCz** and **TFCz** in different organic solvents of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , tetrahydrofuran (THF), toluene and chlorobenzene were measured at room temperature. The conventional small molecules such as *N,N*-dicarbazolyl-3,5-benzene (*mCP*) and *N,N'*-dicarbazolyl-4,4'-biphenyl (CBP) was also tested for comparison.

**Table S1.** The solubility test of **SFCz**, **DFCz** and **TFCz** (in mg mL<sup>-1</sup>).

Compound	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	THF	Toluen e	Chlorobenzen e
<b>SFCz</b>	55.6	48.2	53.1	50.3	52.9
<b>DFCz</b>	56.2	49.6	54.2	55.7	57.1
<b>TFCz</b>	55.2	50.4	53.4	54.6	58.7
<i>mCP</i>	33.4	25	25	20	16.8
<b>CBP</b>	33.3	20	20	15.7	12.9

## 3. Thermal properties

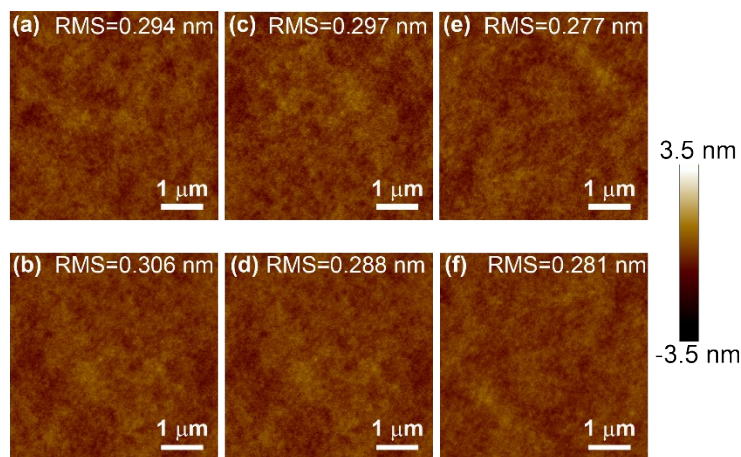
Thermogravimetric analysis (TGA) were performed to investigate the thermal properties of the compounds. TGA measurements were conducted on a Shimadzu DTG-60H thermogravimetric analyses at a heating rate of 10°C min<sup>-1</sup> and a nitrogen flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. Differential scanning calorimetry (DSC) analyses were performed on a PERKIN ELMER Co instrument under a heating rate of 10°C min<sup>-1</sup> and a nitrogen flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>.



**Figure S1.** DSC curves of **SFCz**, **DFCz** and **TFCz**.

#### 4. Atomic force microscopy

The film-forming abilities and morphologies of **SFCz**, **DFCz** and **TFCz** thin films were investigated by atomic force microscopy (AFM) at room temperature using a Bruker Dimension Icon AFM equipped with Scanasyt-Air peak force tapping mode AFM tips from Bruker.



**Figure S2.** The AFM height images ( $5 \times 5 \mu\text{m}^2$ ) of spin-coated **SFCz** (a, b), **DFCz** (c, d) and **TFCz** (e, f) films on glass substrates before (a, c, and e) and after (b, d, and f) thermal annealing at  $50^\circ\text{C}$  for 20 min.

#### 5. Electrochemical properties

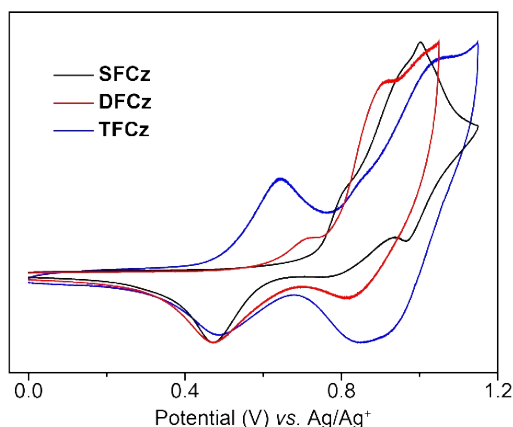
Cyclic voltammogram (CV) measurements were performed at room temperature to investigate the electrochemical properties of the compounds on a CHI660E system in a typical three-electrode

cell with a working electrode (glass carbon), a reference electrode (Ag/Ag<sup>+</sup>, referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in an acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) (0.1 M) at a sweeping rate of 100 mV s<sup>-1</sup>. The organic molecules were deposited on the glass carbon electrode surface in thin solid films for the CV tests. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels ( $E_{HOMO}$  and  $E_{LUMO}$ ) of the materials are measured based on the reference energy level of ferrocene (4.8 eV below the vacuum) according to the Equations 2 and 3:

$$E_{HOMO} = -[E_{onset}^{Ox} - (0.04)] - 4.8 eV \dots\dots\dots 2$$

$$E_{LUMO} = -[E_{onset}^{Red} - (0.04)] - 4.8 eV \dots\dots\dots 3$$

where the value of 0.04 V is the onset oxidative voltage of FOC vs Ag/Ag<sup>+</sup> and  $E_{onset}^{Ox}$  and  $E_{onset}^{Red}$  are the onset potentials of the oxidation and reduction, respectively.



**Figure S3.** Circle voltammograms of **SFCz**, **DFCz** and **TFCz** thin films deposited on the glass carbon electrode surface.

## 6. Optical properties

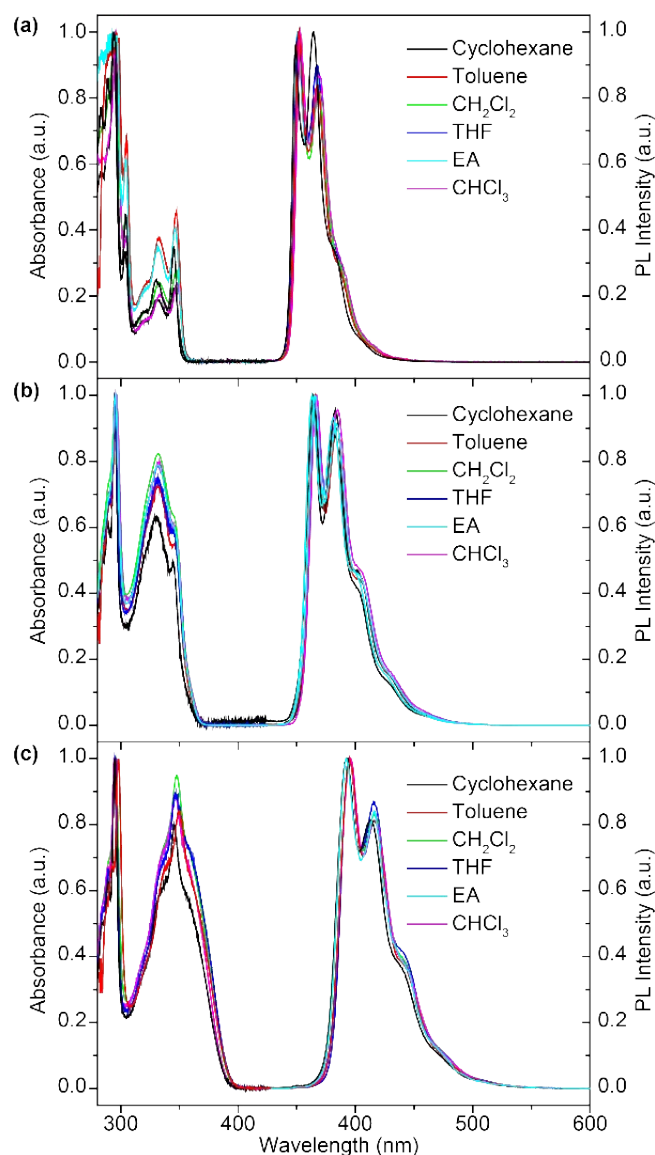
Ultraviolet-visible (UV-Vis) spectra were recorded on an UV-3600 SHIMADZU UV-VIS-NIR spectrophotometer. Fluorescence spectra were obtained using an RF-5301PC spectrofluorophotometer with a Xenon lamp as light source. Phosphorescence spectra were measured in 2-Methyltetrahydrofuran using a time-resolved Edinburgh LFS920 fluorescence



spectrophotometer at 77 K with a 10 ms delay time after the excitation ( $\lambda=330$  nm) using a microsecond flash lamp. For the optical property measurements, the concentrations of the compound solutions (in  $\text{CH}_2\text{Cl}_2$ ) were adjusted to be at about  $1.0 \times 10^{-5}$  mol  $\text{L}^{-1}$ ; thin solid films were prepared by spin casting solutions of the compounds on quartz substrates. The solvent effects on the absorption and emission of these derivatives were investigated by orientational polarizability ( $\Delta f$ ), which was chosen as a measure of the solvent polarity and calculated using Equation 1:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \dots\dots\dots 1$$

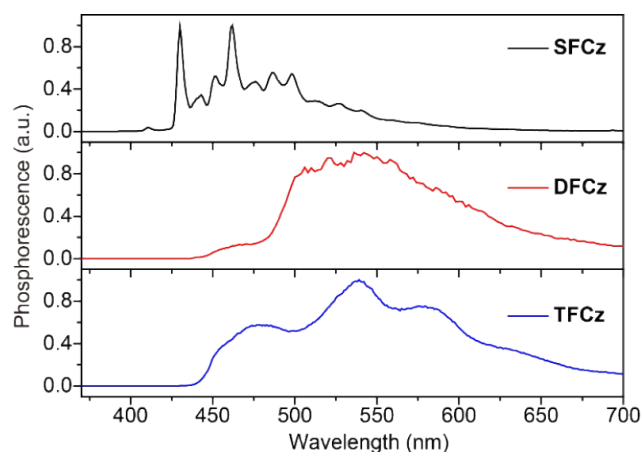
where  $\varepsilon$  is the static dielectric constant and  $n$  is the optical refractive index of the solvent.



**Figure S4.** Normalized optical absorption and photoluminescent spectra of (a) **SFCz** (b) **DFCz** and (c) **TFCz** in different organic solvents.

**Table S2.** Steady-state absorption ( $\lambda_a$ ) and emission ( $\lambda_f$ ) peaks in different solvents with varied polarity, dielectric constant ( $\epsilon$ ), and refractive index ( $n$ ).

solvent	polarity	$\epsilon$	$n$	$\Delta f$	SFCz		DFCz		TFCz	
					$\lambda_a$	$\lambda_f$	$\lambda_a$	$\lambda_f$	$\lambda_a$	$\lambda_f$
Cyclohexane	0.1	2.00	1.427	0.003	294	348	295	364	295	391
Toluene	2.4	2.38	1.496	0.014	294	352	295	364	295	391
CH <sub>2</sub> Cl <sub>2</sub>	3.4	9.1	1.424	0.218	294	352	295	364	295	392
THF	4.2	7.58	1.405	0.210	294	352	295	365	295	392
Ethyl Acetate	4.3	6.02	1.370	0.201	294	352	295	366	295	394
CHCl <sub>3</sub>	4.4	4.81	1.446	0.148	294	352	295	366	295	394



**Figure S5.** Phosphorescence spectra (excited at 330 nm) of SFCz, DFCz and TFCz recorded at 77 K in 2-methyltetrahydrofuran with a delay time of 5 ms.

## 7. DFT calculations

Theoretical calculations were performed on Gaussian 09 program with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G (d) basis sets. The geometries at the ground state ( $S_0$ ) and the lowest triplet excited state ( $T_1$ ) were fully optimized by spin-restricted and spin-unrestricted DFT calculations respectively at the B3LYP/6-31G (d) level. Vibrational frequencies analysis was performed for the

optimized geometries to confirm all stationary points are minima (zero imaginary frequencies) on the respective potential energy hypersurfaces. The theoretical HOMO and LUMO were calculated on the optimized structures at the ground state. The band-gap ( $E_g$ ) was achieved from the energy difference between HOMO and LUMO of the compound. The photophysical properties including absorption and emission spectra were calculated using TD-B3LYP/6-31G(d) at the optimized ground ( $S_0$ ) and excited ( $S_1$ ) states, respectively.

**Table S3.** TD-B3LYP/6-31G(d) predicted absorption peak wavelength ( $\lambda_{\text{abs}}$ ), main transition configuration, excitation energy ( $E_\lambda$ ) and oscillator strength (f) in vacuum.

Molecule	Electron transition	$E_\lambda$ (eV)	$\lambda_{\text{abs}}$ (nm)	Main transition configurations	f
SFCz	$S_0 \rightarrow S_1$	3.9739	312.00	HOMO <sub>-3</sub> →LUMO <sub>+4</sub> (2.2%) HOMO <sub>-2</sub> →LUMO <sub>+5</sub> (2.2%) HOMO <sub>-1</sub> →LUMO <sub>+1</sub> (23.0%) HOMO <sub>-1</sub> →LUMO <sub>+2</sub> (23.9%) HOMO→LUMO <sub>+1</sub> (23.9%) HOMO→LUMO <sub>+2</sub> (23.0%)	0.0692
	$S_0 \rightarrow S_{11}$	4.6237	268.15	HOMO <sub>-8</sub> →LUMO (10.3%) HOMO <sub>-8</sub> →LUMO <sub>+3</sub> (2.6%) HOMO <sub>-4</sub> →LUMO (74.0%) HOMO <sub>-4</sub> →LUMO <sub>+3</sub> (11.2%)	0.2550
DFCz	$S_0 \rightarrow S_1$	3.7265	332.71	HOMO <sub>-4</sub> →LUMO (6.5%) HOMO <sub>-2</sub> →LUMO (79.9%) HOMO→LUMO (13.5%)	0.0874
	$S_0 \rightarrow S_5$	3.7442	331.14	HOMO <sub>-4</sub> →LUMO (92.5%), HOMO <sub>-2</sub> →LUMO (6.1%)	1.0752
TFCz	$S_0 \rightarrow S_1$	3.4230	362.21	HOMO <sub>-6</sub> →LUMO (97.3%)	1.9412

## 8. Device fabrications and measurements

In a general procedure, ITO-coated glass substrates were etched, patterned, and washed with detergent, alcohol and acetone, deionized water and then dried at 120°C in a vacuum oven for more than an hour followed by ultraviolet (UV)-ozone treatment for 15 min. A 30 nm PEDOT: PSS thin film was spin-coated on the ITO substrate and dried at 120°C in a vacuum oven for 15 min. Then, the hole-transporting layer of PVK (30 nm) was spin-coated on the surface of PEDOT: PSS film. The emissive layers (EMLs, 20 nm) were casted on the top of PVK layer through spin-processing from chlorobenzene and annealed on a hot plate at 80°C for 20 min to remove residual solvents. After that, the samples were transferred to a thermal evaporator chamber to deposit TPBi (55 nm), Ca (25 nm), and Al (100 nm) subsequently *via* thermal evaporation under a low pressure of  $5 \times 10^{-4}$

Pa. The layer thickness was measured using Bruker Dektak XT stylus profiler and the deposition rate were monitored *in situ* by an oscillating quartz thickness monitor. The devices without encapsulation were measured immediately after fabrication under ambient conditions at room temperature. Electroluminescent (EL) spectra of the devices were measured by a PR655 spectrascan spectrometer. The luminance-voltage and current-voltage characteristics were recorded using an optical power meter and a Keithley 2400 voltage current source. And the external quantum efficiency (EQE) was achieved by equation 4.

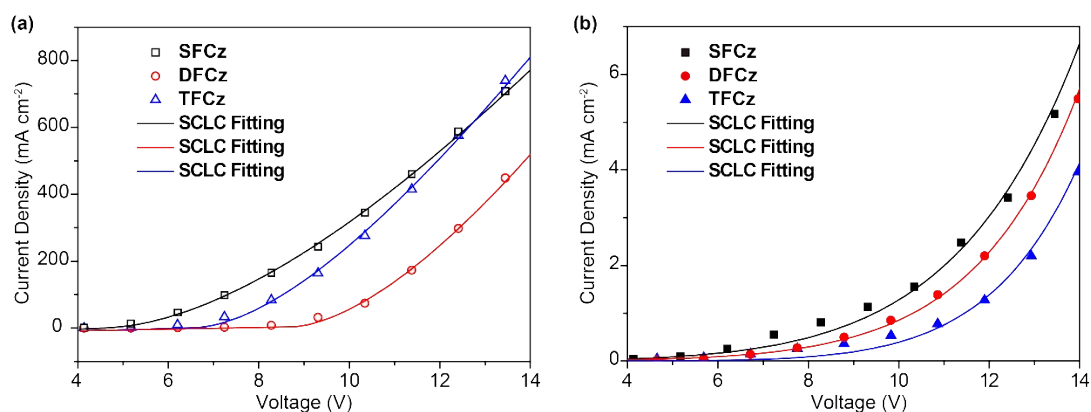
$$EQE = \frac{\pi e \eta_{cd/A} \int \lambda p_{\lambda} d_{\lambda}}{hc K_m \int p_{\lambda} d_{\lambda}} \quad 4$$

where  $\eta_{cd/A}$  is the current efficiency (cd A<sup>-1</sup>);  $h$  is the Planck constant;  $c$  is the speed of light in vacuum;  $\lambda$  is the wavelength (nm);  $e$  is the electron charge;  $p(\lambda)$  is the electroluminescent intensity;  $\Phi(\lambda)$  is the luminous efficiency;  $K_m$  is a constant of 683 lm/W.

The charge transport properties of **SFCz**, **DFCz** and **TFCz** were experimentally investigated by single-carrier charge transport devices, under the device structures of ITO/PEDOT:PSS (30 nm)/ host molecules (20 nm)/Al (100 nm) for hole only device and ITO/ host molecules (20 nm)/TPBi (55 nm)/Ca (25 nm)/Al (100 nm) for electron only device, respectively. The current density ( $J$ ) in these devices follows the field-dependent space charge limited current (SCLC) model of Mott-Gurney law:

$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \exp\left(0.89 \beta \sqrt{\frac{V}{d}}\right) \frac{V^2}{d^3} \dots\dots\dots 5$$

where  $V$  is the electrical voltage,  $d$  is the film thickness,  $\mu_0$  is the average mobility,  $\varepsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12}$  F m<sup>-1</sup>), and  $\varepsilon$  is the dielectric constant of the film.



**Figure S6.** Current density-voltage characteristics of the (a) hole-only and (b) electron-only devices in configurations of ITO/PEDOT:PSS (30 nm)/PVK(30 nm)/ host molecules (20 nm)/Al (100 nm) and ITO/host molecules (20 nm)/TPBi (55 nm)/Ca (25 nm)/Al (100 nm), respectively. Symbols show the experimental data, while lines are the fitting curves according to field-dependent SLCL model to deduce the charge mobilities.

**Table S4.** A brief summary of recent reported solution-processed PhOLEDs based on Ir(mppy)<sub>3</sub>.

Device structure	Turn-on Voltage [V]	Maximum Efficiency <sup>a</sup>			Ref.
		CE	PE	EQE	
ITO/PEDOT:PSS/X-F6-TAPC/EML/SPPO13/CsF/Al	5.2	24.4	8.1	-	1
ITO/PEDOT:PSS/EML/TPBi/Liq/Al	7.1	15.3	5.6	4.6%	2
ITO/PEDOT:PSS/EML/TPBi/CsF/Al	4.6	24.5	14.1	8.0%	3
ITO/PEDOT:PSS/EML/TmPyPb/LiF/Al	5.1	26.0	-	7.8%	4
ITO/PEDOT:PSS/EML/TPBi/Cs <sub>2</sub> CO <sub>3</sub> /Al	4.6	34.8	-	9.8%	5
ITO/PEDOT:PSS/EML/CsF/Al	10	4.4	-	1.26%	6
ITO/PEDOT:PSS/EML/CsF/Al	6.5	27.6	-	10.2%	7
ITO/PEDOT:PSS/HTL/EML/TPBi/CsF/Al	3.1	31.4	21.8	-	8
ITO/PEDOT:PSS/EML/CsF/Al	6.5	20.9	6.4	-	9
ITO/PEDOT:PSS/EML/TrOH/Al	5.4	23.4	-	6.7%	10
ITO/PEDOT:PSS/EML/LiF/Al	-	22.6	-	-	11
ITO/PEDOT:PSS/PVK/EML/TPBi/Ca/Al	5.5	28.0	11.6	7.8%	This work

<sup>a</sup> CE is in (cd A<sup>-1</sup>), while PE is in lm W<sup>-1</sup>

**Table S5.** Device performance of the solution-processed green PhOLEDs hosted by **SFCz**, **DFCz** and **TFCz**.

Comp.	Operating Voltage(V) <sup>a</sup>	Maximum Efficiency <sup>b</sup>	Efficiency <sup>c</sup>			Roll-off <sup>c</sup>		
			CE	PE	EQE	CE	PE	EQE
<b>SFCz</b>	9.4, <14.8, <-	3.5, 0.7, 1.0	3.3, -	0.7, -	0.96, -	5.7, -	0, -	4, -
<b>DFCz</b>	5.5, <8.4, <11.2	28.0, 11.6, 7.8	23.9, 16.9	9.0, 4.7	6.6, 4.7	14.6, 39.6	22.4, 59.5	15.4, 39.7
<b>TFCz</b>	6.6, <10.6, <15	12.8, 6.7, 3.7	7.4, 2.9	2.2, 0.6	2.1, 0.9	42.2, 77.3	67.2, 91.0	43.2, 75.7

<sup>a</sup>In the order of 1, 100 and 1000 cd m<sup>-2</sup>; <sup>b</sup>In the order of CE (cd A<sup>-1</sup>), PE (lm W<sup>-1</sup>) and EQE (%); <sup>c</sup>In the order of 100 and 1000 cd m<sup>-2</sup>.

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