

Supporting Information

Highly Efficient and Stable Blue Polymer Light Emitting Diodes based on Polysilafluorenes with Pendent Hole Transporting Groups

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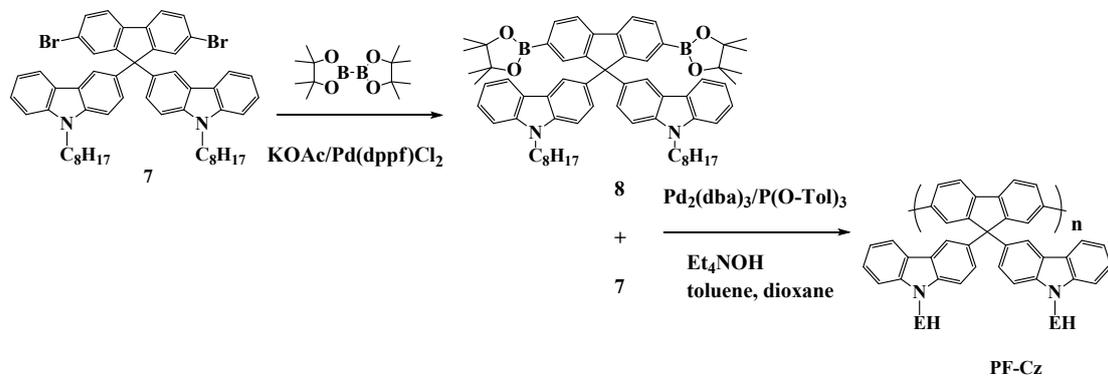
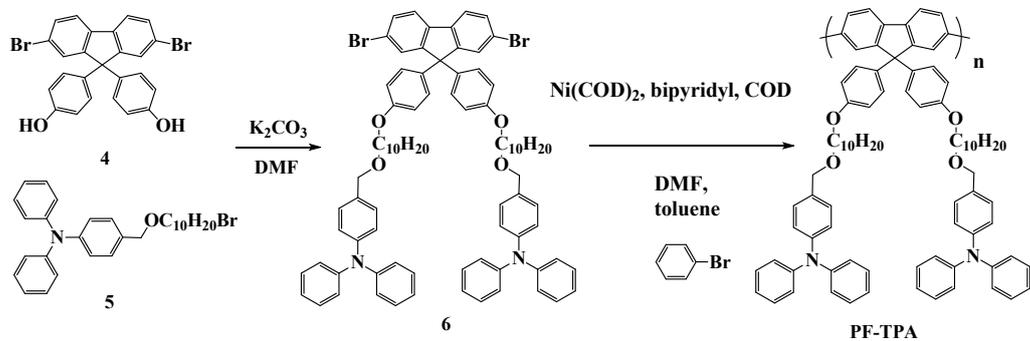
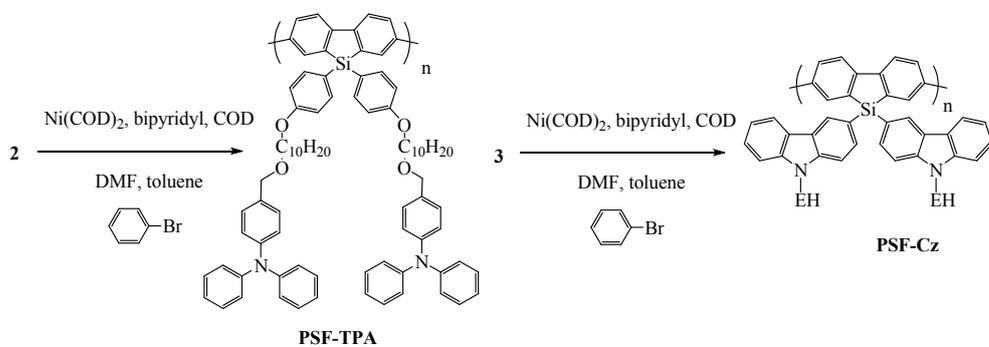
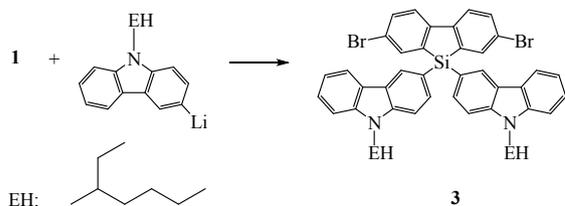
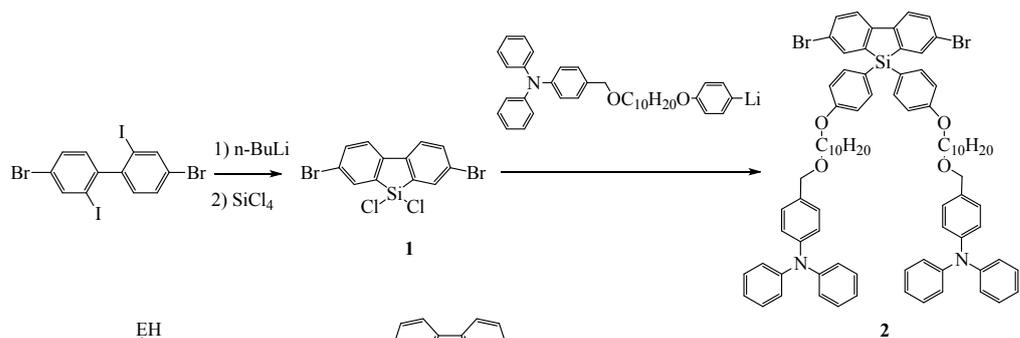
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Experimental section

Characterization

NMR (400 MHz) spectra were obtained using a Bruker 400M Hz spectrometer with tetramethylsilane as an internal standard. C, H, N elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) and Br elemental content was analyzed by chemical titration. Si elemental analyses were performed on a DX2500 (Dionex Co.) Ion chromatography. GPC analysis was conducted with a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV-visible absorption spectra were recorded on a HP 8453 UV-vis spectrophotometer. The PL spectra were obtained with a Fluorolog JY luminescence spectrometer. Cyclic voltammetry was carried out on a Potentiostat / Galvanostat Model 283 (Princeton Applied Research Co.) in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile at a scanning rate of 100 mV/s at a room temperature under the protection of argon.

Materials

All chemicals and reagents were used as received from Aldrich unless specified otherwise. All solvents were carefully dried and purified before use. All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere. 4,4'-Dibromo-2,2'-diiodobiphenyl was prepared according to the literatures.¹

4-[(10-(4'-bromophenoxy)-decyloxy)methyl]-N,N-diphenylbenzenamine

A mixture of 4.94 gram (10mmol) of 4-((10-bromodecyloxy)methyl)-N,N-diphenylbenzenamine, 2 gram (11.56mmol) of 4-bromophenol, 2.76 gram (20mmol) of K_2CO_3 , 0.23 gram of KI and 100mL of DMSO was stirred at 132°C under argon over night. After cooled down, the reaction was quenched with water and the aqueous layer was extracted with toluene, washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography and

recrystallization from ethanol to afford 4.92 gram of 4-[(10-(4'-bromophenoxy)-decyloxy)methyl]-N,N-diphenylbenzenamine as a pale brown solid (mp: 58~60°C, yield: 84%). Anal. Calcd for C₃₅H₄₀BrNO₂ (%):C, 71.66; H, 6.87; Br, 13.62; N, 2.39; O, 5.45. Found: C, 71.60; H, 6.85; Br, 13.60; N, 2.38. ¹H NMR (400 MHz, CDCl₃, ppm): 7.256 (d, 2H, J=8.8), 7.257~7.212 (6H), 7.10~7.05 (6H), 7.000(t,2H), 6.770 (d, 2H, J=8.8), 4.442 (s, 2H), 3.910 (t, 2H), 3.496 (t, 2H), 1.765 (m, 2H), 1.632 (m, 2H), 1.40~1.20 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): 158.222, 147.795, 147.218, 132.882, 132.17, 129.183, 128.855, 124.117, 124.019, 122.661, 116.279, 112.53, 72.629, 70.607, 68.229, 29.781, 29.524, 29.505, 29.48, 29.36, 29.169, 26.215, 25.994.

9,9-bis(4-(10-(diphenylamine-4'-phenylmethoxy)-decyloxy)-phenyl)-2,7-dibromosilafluorene (2)

30 mL of n-Butyllithium (1.6 M in pentane) was added over 2 h to a solution 6.78 gram of 4,4'-dibromo-2,2'-diiodobiphenyl (12.0 mmol) in 60 mL of dry THF at -90 °C under nitrogen atmosphere. The mixture was stirred for a further 2 h at -90 °C. 27.6 mL of SiCl₄ (240 mmol) was added in one portion and the mixture was stirred for a further 1.5 h at -90 °C, eventually allowed to raise to room temperature. The solvent and excess SiCl₄ was stripped by the vacuum distillation to afford crude 9,9-dichloro-2,7-dibromosilafluorene (**1**) without further purification.

45 mL of n-Butyllithium (1.6 M in pentane) was added dropwise to a solution of 42.2 gram of 4-[(10-(4'-bromophenoxy)-decyloxy)methyl]-N,N-diphenylbenzenamine (72.0 mmol) in 40 mL of THF. The mixture was stirred for a further 2 h at -60 °C. The solution of 9,9-dichloro-2,7-dibromosilafluorene (**1**) prepared above in 70 mL of THF was added dropwise over 1 h. The mixture was allowed to raise to room temperature and stirred overnight. The reaction was quenched with aqueous NH₄Cl and the aqueous layer was extracted with ethyl acetate for three times, and the combined organic layer dried over Na₂SO₄ and concentrated.

The crude product was purified by silica gel chromatography and further purified by recrystallization from ethanol to afford 2.4 gram of a colorless oil **2** (yield: 15%). Anal. Calcd for C₈₂H₈₆Br₂ N₂O₄Si (%):C, 72.87; H, 6.41; Br, 11.82; N, 2.07; O, 4.74; Si, 2.08. Found: C, 72.80; H, 6.40; Br, 11.81; N, 2.06; Si, 2.06. ¹H NMR (400 MHz, CDCl₃, ppm):7.789 (d, 2H, *J*=2.4), 7.683 (d, 2H, *J*=10.8), 7.568 (dd, 2H, *J*₁=10.8, *J*₂=2.4), 7.499 (d, 4H, *J*=7.6), 7.26~7.20 (12H), 7.10~7.00(12H), 6.99 (m, 4H), 6.901(d, 4H, *J*=7.6), 4.433 (s, 4H), 3.943 (t, 2H), 3.485 (t, 2H), 1.764 (m, 4H), 1.621 (m, 4H), 1.40~1.20 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): 161.26, 147.79, 147.208, 146.239, 139.492, 137.06, 136.443, 133.572, 132.872, 129.179, 128.865, 124.110, 124.018, (122.758), 122.651, (121.338), 114.699, 72.621, 70.603, 67.79, 29.768, 29.537, 29.515, 29.475, 29.366, 29.165, 26.203, 26.025.

Poly(9,9-bis(4-(10-(diphenylamine-4'-phenylmethoxy)-decyloxy)-phenyl)-2,7-silafluorene) (PSF-TPA)

In a Schlenk tube, bis(1,5-cyclooctadiene) nickel(0) 0.21 g, 1.1 mmol), 1,5-cyclooctadiene (0.12 g, 1.1 mmol), and 2,2'- bipyridine (0.17 g, 1.1 mmol) were dissolved in DMF (1.5 mL) and heated at 85 °C for 30 min under nitrogen atmosphere. A toluene solution (4.5 mL) of monomer **2** (0.837 g, 0.62 mmol) was added, and the reaction mixture was heated at 85°C for two days and then bromobenzene (0.1 mL) was added to the mixture and stirred for 4 h. The mixture was poured into an equivolume mixture of methanol and acetone. The organic layer was extracted with toluene, washed with brine, and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude polymer was dissolved in a small amount of chloroform and reprecipitated twice from methanol before Soxhlet extraction with methanol, acetone, hexane and chloroform from which 0.26 g of **PSF-TPA** was obtained as greenish fibers (yield 35 %). Anal. Calcd for C₈₂H₈₈N₂O₄Si (%):C, 82.51; H, 7.43; N, 2.35; O, 5.36; Si, 2.35. Found: C, 82.45; H,

7.41; N, 2.34; Si, 2.33. ¹H NMR (600 MHz, CDCl₃, ppm): 7.9~6.8 (aromatic H), 4.4(PhCH₂O H), 3.85(OCH₂), 3.45 (OCH₂), 1.8~1.2 (aliphatic H).

9,9-bis(N- (2'-ethylhexyl) -carbazole-3-yl)-2,7-dibromosilafluorene (3)

Firstly, 9,9-dichloro-2,7-dibromosilafluorene (**1**) was prepared according to the procedure mentioned above with 6.78 gram of 4,4'-dibromo-2,2'-diiodobiphenyl (12.0 mmol) and 27.6 mL of SiCl₄ (240 mmol).

Then, 45 mL of n-Butyllithium (1.6 M in pentane) was added dropwise to a solution of 25.8 gram of 3-bromo- N-(2'-ethylhexyl)-carbazole (72.0 mmol) in 40 mL of THF. The mixture was stirred for a further 2 h at -60 °C. The solution of freshly prepared **1** in 70 mL of THF was added dropwise over 1 h. The mixture was allowed to raise to room temperature and stirred overnight. The reaction was quenched with aqueous NH₄Cl and the aqueous layer was extracted with ethyl acetate for three times, and the combined organic layer dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel chromatography and further purified by recrystallization in ethanol to afford 1.93 gram of a white solid **3** (yield: 18%), mp. 106-108 °C. Anal. Calcd for C₅₂H₅₄SiBr₂ (%):C, 69.79; H, 6.08; Br, 17.86; N, 3.13; Si, 3.14. Found: C, 69.71; H, 6.05; Br, 17.81; N, 3.12; Si, 3.13. ¹H NMR (400 MHz, CDCl₃, ppm): 8.413 (2H), 8.050 (2H), 7.970 (2H), 7.750 (2H), 7.705 (2H), 7.615 (2H), 7.50~7.35 (6H), 7.30~7.20 (4H), 7.20~7.10(4H), 4.162 (m, 4H), 2.055 (m, 2H), 1.40~1.20 (m, 16H), 0.9~0.8(m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): 146.362, 142.467, 140.977, 140.403, 136.719, 133.533, 132.534, 128.192, 125.925, 123.164, 122.842, 122.757, 122.454, 120.561, 119.368, 119.208, 109.343, 109.065, 47.436, 39.476, 31.028, 28.902, 24.432, 23.102, 14.114, 10.94.

Poly(9,9-bis(N- (2'-ethylhexyl) -carbazole-3-yl)-2,7-silafluorene) (PSF-Cz)

PSF-Cz from monomer **3** was synthesized according to the similar procedure used for preparation of **PSF-TPA** as greenish fibers (yield 68%). Anal. Calcd for

C₅₂H₅₆N₂Si (%): C, 84.73; H, 7.66; N, 3.80; Si, 3.81. Found: C, 84.70; H, 7.65; N, 3.78; Si, 3.79. ¹H NMR (600 MHz, CDCl₃, ppm): 8.5~7.0 (aromatic H), 4.1 (NCH₂), 2.0~0.8 (aliphatic H).

Poly(9,9-bis(4-(10-(diphenylamine-4'-phenylmethoxy)-decyloxy)-phenyl)-2,7-fluorene) (PF-TPA)

9,9-bis(4-(10-(diphenylamine-4'-phenylmethoxy)-decyloxy)-phenyl)-2,7-dibromosilafluorene (**6**) was prepared according to the literature. **PF-TPA** from monomer **6** was synthesized according to the similar procedure used for preparation of **PSF-TPA** as greenish fibers (yield 65%). Anal. Calcd for C₈₃H₈₈Br₂N₂O₄ (%): C, 84.65; H, 7.53; N, 2.38; O, 5.43 Found: C, 84.60; H, 7.51; N, 2.37. ¹H NMR (600 MHz, CDCl₃, ppm): 7.9~6.8 (aromatic H), 4.39(PhCH₂O H), 3.87(OCH₂), 3.46 (OCH₂), 1.8~1.2 (aliphatic H).

2,7-bis(4,4,5,5-tetramethyl-1-3-2-dioxaborolan-2-yl)-9,9-Bis(3,3'-N-(2'-ethylhexyl)-9H-carbazole)fluorene (8)

A mixture of potassium acetate (2.355g, 24 mmol), dry dioxane (70 mL), PdCl₂(dppf) (0.716 g, 0.24 mmol), bis(pinacolato)diboron (3.084 g, 12 mmol) and 9,9-Bis(3,3'-N-(2'-ethylhexyl)-9H-carbazole)-2,7-dibromofluorene (**7**) (2.816 g, 4 mmol) was stirred at 80 °C for 24 h under argon. The reaction mixture was diluted with ethyl acetate, washed with water for 3 times, dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography and recrystallization from methanol for several times to yield diboronate **8** (2.67 g, 69 %) as white powder. Anal. Calcd for C₆₅H₇₈B₂N₂O₄ (%): C, 80.24; H, 8.08; B, 2.22; N, 2.88; O, 6.58. Found: C, 80.20, H, 8.06, N, 2.88. ¹H NMR (600 MHz, CDCl₃) δ 8.01 (d, J = 1.5 Hz, 2H), 7.95 (s, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.85 (s, 4H), 7.44 – 7.36 (m, 4H), 7.25 (d, J = 8.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 2H), 4.23 (t, J = 7.2 Hz, 4H), 1.93 – 1.76 (m, 4H), 1.40 – 1.19 (m, 44H), 0.85 (t, J = 6.9 Hz, 6H). ¹³C NMR

(151 MHz, CDCl₃) δ 152.94, 142.81, 140.78, 139.33, 136.74, 134.08, 132.66, 126.88, 125.31, 123.00, 122.49, 120.61, 120.12, 119.86, 118.43, 108.53, 108.41, 83.68, 65.68, 43.19, 31.86, 29.43, 29.21, 29.10, 27.39, 24.91, 22.64, 14.12.

Poly(9,9-bis(N- (2'-ethylhexyl) -carbazole-3-yl)-2,7-fluorene) (PF-Cz)

A mixture of **7** (0.132 g, 0.15 mmol), **8** (0.146 g, 0.15mmol), tris(dibenzylideneacetone)dipalladium(0) (1.35 mg, 0.0015 mmol), tris(2-methylphenyl)phosphine (2.7 mg, 0.009mmol) and tetraethyl ammonium hydroxide aqueous solution (1 mL, 25%) in 2.5 mL of toluene and 1.5 mL of dioxane was stirred at 93 °C for 72 h under argon. Then, 40 mg of phenylboronic acid was added and stirred for 12 h followed by the addition of 0.1 mL of bromobenzene and stirred for another 12 h. The mixture was cooled down, added 5 mL of toluene and 5 mL of 10% and stirred for another 2 hours. The aqueous layer was separated and the organic layer was washed with H₂O for 3 times. The solvent was removed under reduced pressure, and the crude polymer was refluxed with 50 mg trithiocyanuric acid (TMT) and 5 g carbon black in 100 mL of THF for 24 hr, filtered, concentrated and Soxhlet extracted with methanol, acetone, hexane and THF. The solvent was stripped off and the residue was purified by column chromatography (silica gel, toluene as eluent). After concentration followed by reprecipitation twice from methanol, 40 mg of **PF-Cz** can be obtained as a white fiber (199 mg, yield 92 %). Anal. Calcd for C₅₃H₅₆N₂ (%):C, 88.29; H, 7.83; N, 3.89 Found: C, C, 88.22; H, 7.82; N, 3.88. ¹H NMR (600 MHz, CDCl₃, ppm): 8.0~6.9 (aromatic H), 4.15 (NCH₂), 2.0~0.8 (aliphatic H).

Device Fabrication and Characterization

Polymers and PVK (Alfa) were dissolved in o-xylene with the concentration of 10 g L and chlorobenzene with concentration of 15 g L⁻¹, respectively. ITO substrates were cleaned by a series of ultrasonication treatments in acetone, deionized water and isopropyl alcohol. A 40-nm-thick PEDOT:PSS (Bayer Baytron P 4083) used as HIL was spin-coated on the pre-cleaned and O₂-plasma-treated ITO and baked at 120 °C for 20 min to remove residual water. A 35-nm-thick PVK was spin-coated on 40-nm-thick PEDOT:PSS layer. A 75-nm-thick blue polymer was spin-coated on top of these HILs. Except the PEDOT:PSS layer, all the fabrication processes were carried out in a

nitrogen-circulated glove box. Finally, 1 nm cesium-fluoride (CsF) and 100 nm Al were evaporated in sequence at a pressure of 3×10^{-4} Pa. The thickness of the evaporated CsF and Al were monitored by a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). The thickness of relatively thick films was determined by a surface profiler (XP-2, Ambios). The active emission area of the devices is 0.14 cm².

The current density-luminance-voltage (J - L - V) characteristics were measured by a Keithley 2400 source measurement unit and a calibrated silicon photodiode. The luminance (L) and the luminance efficiency (LE) were calibrated by a spectrophotometer (SpectraScan PR-705, Photo Research). The quantum efficiency (QE) was amended by measuring the total light output in all direction in an integrating sphere (ISO-080, Labsphere). The electroluminescence (EL) spectra were collected via an optics photometer (USB4000, Ocean Optics).

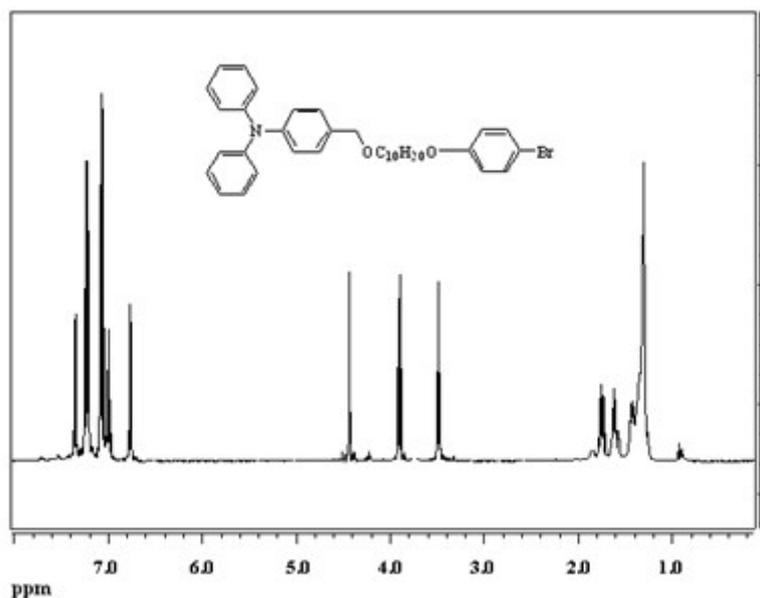


Fig S1. ¹H NMR of {4-[10-(4-Bromo-phenoxy)-decyloxymethyl]-phenyl}-diphenyl-amine

¹H NMR (400 MHz, CDCl₃, ppm): 7.256 (d, 2H, J=8.8), 7.257~7.212 (6H), 7.10~7.05 (6H), 7.000(t,2H), 6.770 (d, 2H, J=8.8), 4.442 (s, 2H), 3.910 (t, 2H), 3.496 (t, 2H), 1.765 (m, 2H), 1.632 (m, 2H), 1.40~1.20 (m, 12H).

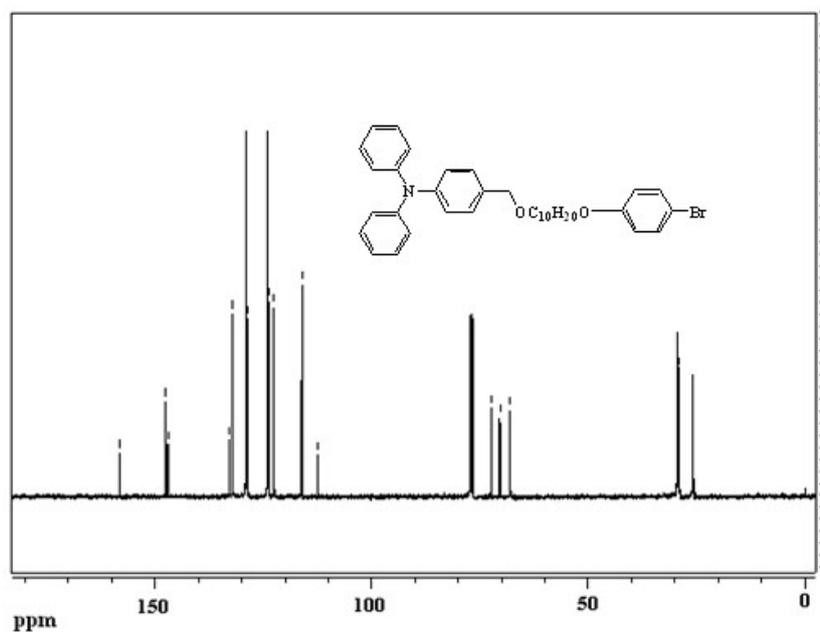


Fig S2. ¹³C NMR of {4-[10-(4-Bromo-phenoxy)-decyloxymethyl]-phenyl}-diphenyl-amine

^{13}C NMR (100 MHz, CDCl_3 , ppm): 158.222, 147.795, 147.218, 132.882, 132.17, 129.183, 128.855, 124.117, 124.019, 122.661, 116.279, 112.53, 72.629, 70.607, 68.229, 29.781, 29.524, 29.505, 29.48, 29.36, 29.169, 26.215, 25.994.

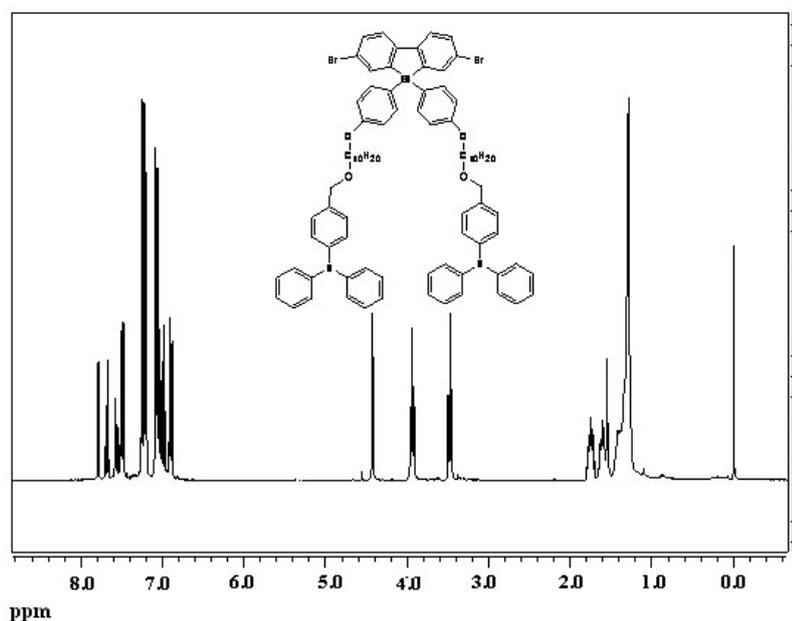


Fig S3. ^1H NMR of **2**.

^1H NMR (400 MHz, CDCl_3 , ppm): 7.789 (d, 2H, $J=2.4$), 7.683 (d, 2H, $J=10.8$), 7.568 (dd, 2H, $J_1=10.8$, $J_2=2.4$), 7.499 (d, 4H, $J=7.6$), 7.26~7.20 (12H), 7.10~7.00(12H), 6.99 (m, 4H), 6.901(d, 4H, $J=7.6$), 4.433 (s, 4H), 3.943 (t, 2H), 3.485 (t, 2H), 1.764 (m, 4H), 1.621 (m, 4H), 1.40~1.20 (m, 24H)

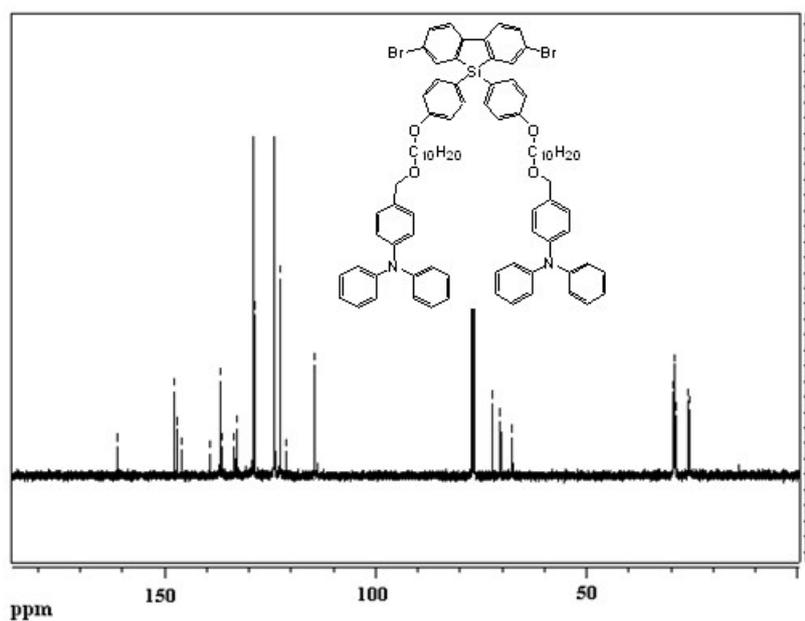


Fig S4. ^{13}C NMR of **2**.

^{13}C NMR (100 MHz, CDCl_3 , ppm): 161.26, 147.79, 147.208, 146.239, 139.492, 137.06, 136.443, 133.572, 132.872, 129.179, 128.865, 124.110, 124.018, (122.758), 122.651, (121.338), 114.699, 72.621, 70.603, 67.79, 29.768, 29.537, 29.515, 29.475, 29.366, 29.165, 26.203, 26.025.

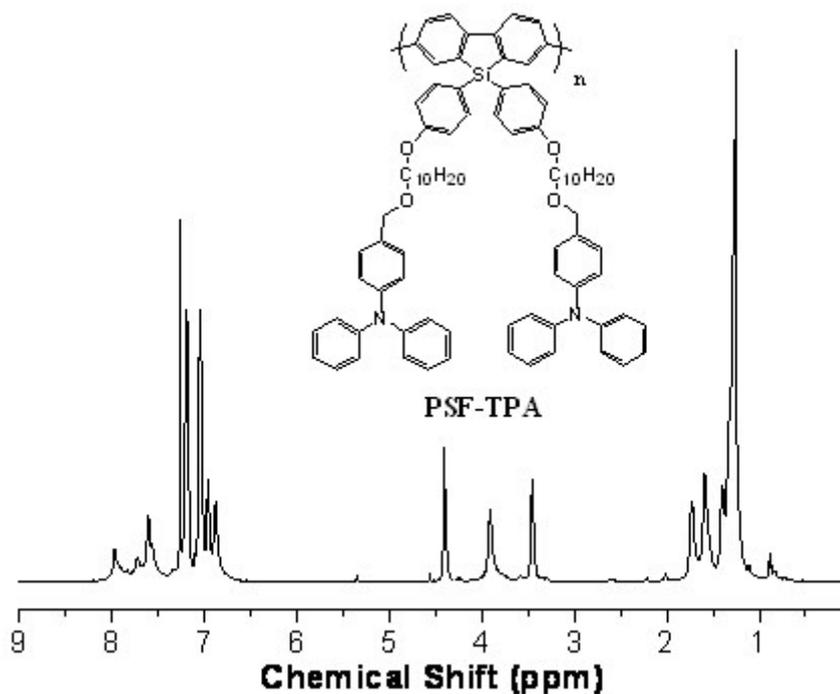


Fig S5. ^1H NMR of **PSF-TPA**.

^1H NMR (600 MHz, CDCl_3 , ppm): 7.9~6.8 (aromatic H), 4.4(PhCH₂O H), 3.85(OCH₂), 3.45 (OCH₂), 1.8~1.2 (aliphatic H).

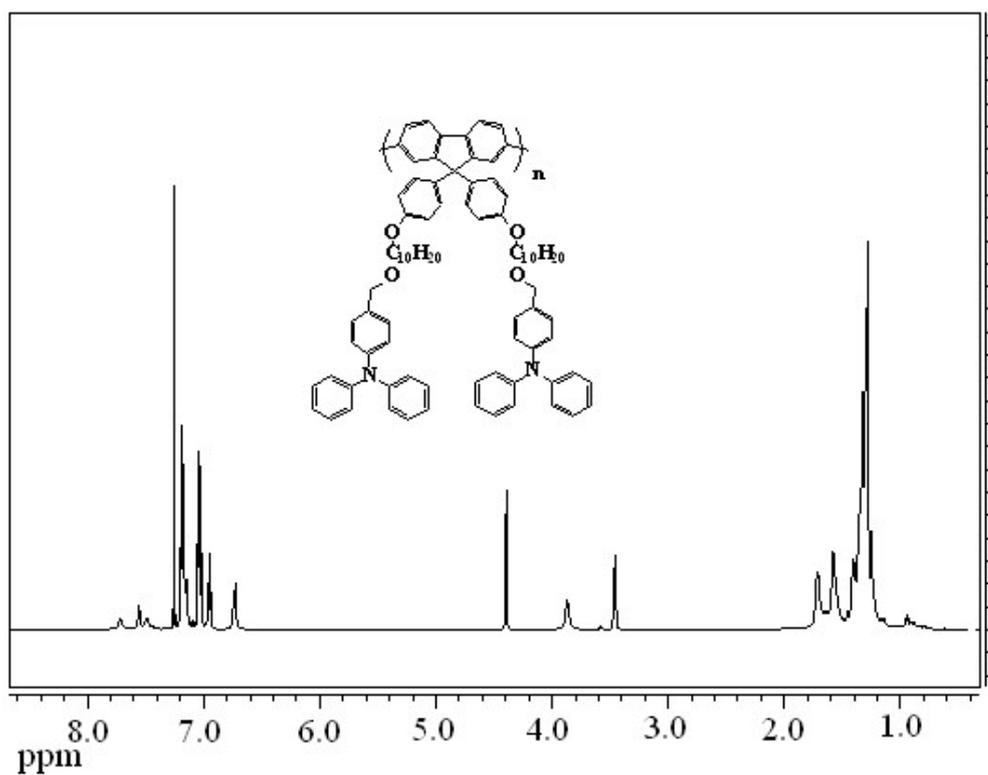


Fig S6. ^1H NMR of **PF-TPA**

^1H NMR (600 MHz, CDCl_3 , ppm): 7.9~6.8 (aromatic H), 4.39(PhCH₂O H), 3.87(OCH₂), 3.46 (OCH₂), 1.8~1.2 (aliphatic H).

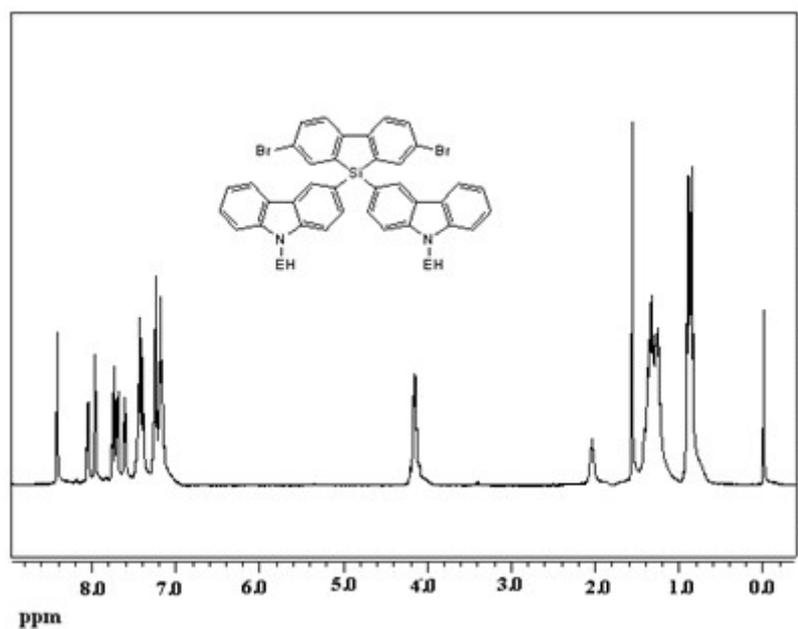


Fig S7. ^1H NMR of **3**

^1H NMR (400 MHz, CDCl_3 , ppm): 8.413 (2H), 8.050 (2H), 7.970 (2H), 7.750 (2H), 7.705 (2H), 7.615 (2H), 7.50~7.35 (6H), 7.30~7.20 (4H), 7.20~7.10(4H), 4.162 (m, 4H), 2.055 (m, 2H), 1.40~1.20 (m, 16H), 0.9~0.8(m, 12H).

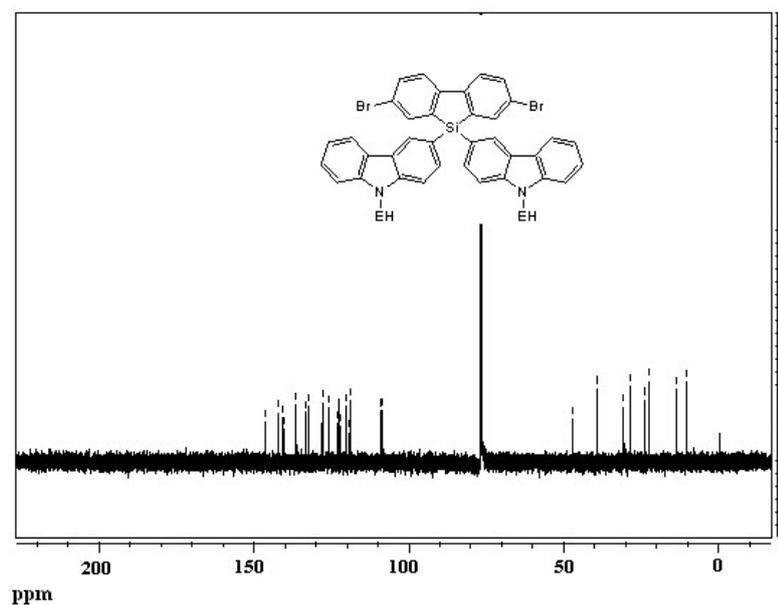


Fig S8. ^{13}C NMR of **3**

^{13}C NMR (100 MHz, CDCl_3 , ppm): 146.362, 142.467, 140.977, 140.403, 136.719, 133.533, 132.534, 128.192, 125.925, 123.164, 122.842, 122.757, 122.454, 120.561, 119.368, 119.208, 109.343, 109.065, 47.436, 39.476, 31.028, 28.902, 24.432, 23.102, 14.114, 10.94

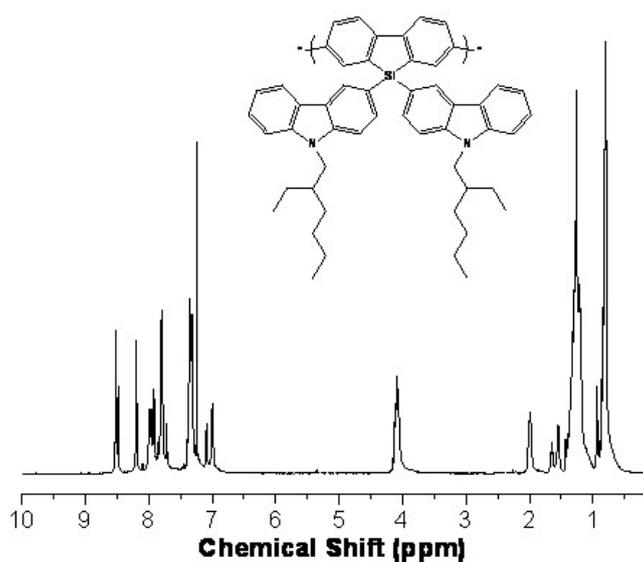


Fig S9. ^1H NMR of **PSF-Cz**.

^1H NMR (600 MHz, CDCl_3 , ppm): 8.5~7.0 (aromatic H), 4.1 (NCH_2), 2.0~0.8 (aliphatic H).

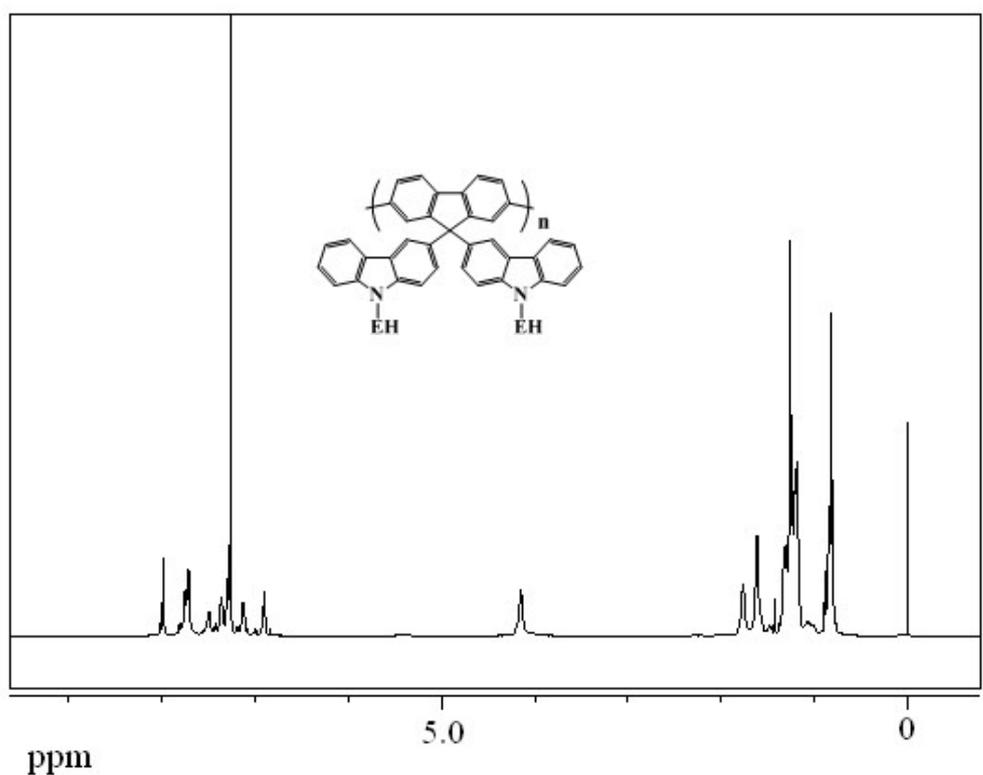


Fig S10. ^1H NMR of **PF-Cz**.

^1H NMR (600 MHz, CDCl_3 , ppm): 8.0~6.9 (aromatic H), 4.15 (NCH_2), 2.0~0.8 (aliphatic H).

1. Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662–7663.