

## Supporting Information

### Ultraviolet Emitting conjugated polymer based on poly(9,9'-alkyl-3,6-silafluorene) with wide band-gap 4.0eV

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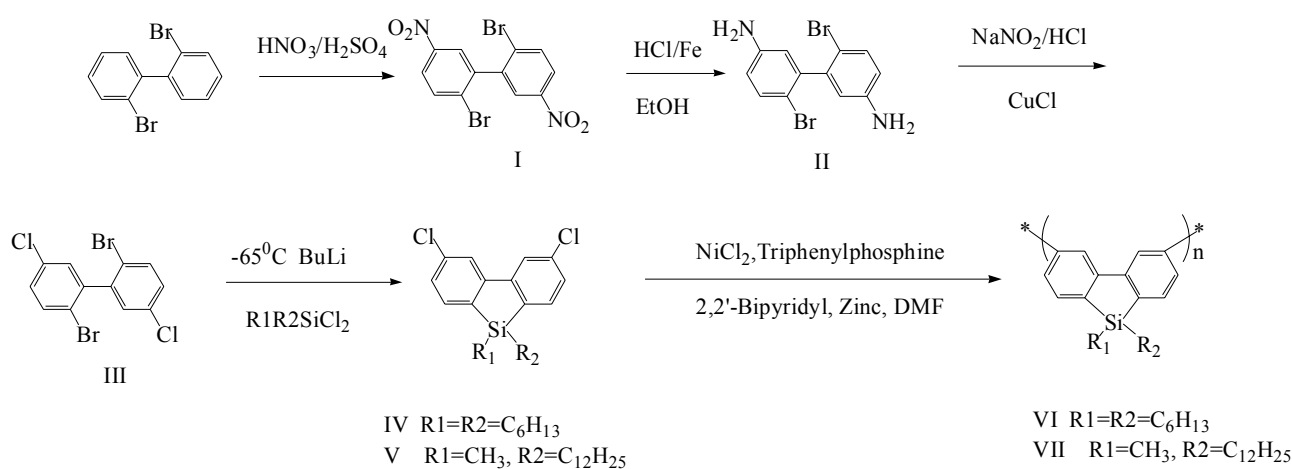
#### Characterization Methods.

NMR (400 MHz) spectra were obtained using a Bruker DRX 400 spectrometer with tetramethylsilane as an internal standard. C,H,N elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) and Cl 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. TGA were performed on a TA Instrument TGA0250 thermal analyzer system and DSC on a TA Instrument MDSC2910 thermal analyzer system. For DSC scans, poly(9,9'-diakylfluorene) was scanned between -30<sup>0</sup>C until 250<sup>0</sup>C for two cycles at a heating and cooling rate of 15<sup>0</sup>C/min. UV-visible absorption spectra were recorded on a HP 8453 UV-vis spectrophotometer. Cyclic voltammetry was carried out on a Potentiostat / Galvanostat Model 283 (Princeton Applied Reserch Co.) in a solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) (0.1 M) in acetonitrile at a scan rate of 50mV/s at room temperature under the protection of argon. The PL spectra were obtained with a Fluorolog JY

luminescence spectrometer. PL decay rate of polysilafluorene and polyfluorene (ADS) were compared on a films of 120 nm-thick spin-coated on top of quartz substrate before and after exposure in air under room light illumination or dark.

## Synthesis of monomers and polymers

**Scheme S1. synthesis route of poly(3,6-silafluorene)**



## Reagents and Solvents.

All starting materials were purchased from Aldrich Co. and TCI Co. without further purification. 2,2'-dibromobiphenyl was prepared in our lab. All the solvent was purified before use.

## **Preparation of 2, 2'-dibromo-5, 5' -dinitrobiphenyl I**

24mL of H<sub>2</sub>SO<sub>4</sub>(98%, d=1.84, 441mmol) was mixed with 20ml HNO<sub>3</sub> (60%, d=1.4, 267mmol) in a 250mL flask in a water bath and stirred for 0.5 h. This mixed acid was added dropwise in 30min into a slurry of 20g 2,2'-dibromobiphenyl(64.1mmol) in 2mL of dichloromethane at room temperature. The mixture was stirred at 100<sup>0</sup>C for another 1 h, cooled down to room temperature and then poured into ice.

The solid crude product was washed and dried, after crystallization from acetone, yield: 10.3g white powder **I** (yield 40%, m.p. above 200 °C, sublimation was observed above 170°C)

<sup>1</sup>H NMR(400M, CDCl<sub>3</sub>, δ): 8.181(dd, 2H, *J*<sub>1</sub>=8.2Hz, *J*<sub>2</sub>=3.0Hz), 8.133(d, 2H, *J*=3.0 Hz), 7.906(d, 2H, *J*=8.2 Hz)

<sup>13</sup>C NMR(400M, CDCl<sub>3</sub>, δ):147.1, 141.3, 134.2, 130.8, 125.6, 124.9

Element Analysis(C<sub>12</sub>H<sub>6</sub>BrN<sub>2</sub>O<sub>4</sub>, M=402.00)-Calculated: C 35.58%; H 1.49%; N 6.97%;

Found: C 35.58%; H 1.50%; N 6.96;

### **Preparation of 2,2'-dibromo-5,5'- dichlorobiphenyl **III****

The mixture of 10g **I** (24.87mmol) and 10g Fe powder(17.8mmol) in 400mL of ethanol was refluxed in a 1000mL flask. 4mL of concentrated HCl(d=1.18□36%□47.2mmol) was added in 30min under mechanism stirring. The solution was refluxed for another 1 h under stirring. The resulting \ clear green solution was cooled down and the excess of Fe powder was filtered off. The ethanol was removed under vacuum and yielded yellow-brownish solid. The crude product **2,2'-dibromo-5,5'- diaminobiphenyl **II**** was added in portion to the solution of 68g Na, K-tartrat in 400mL water under strong stirring. Aqueous NaHCO<sub>3</sub> and NH<sub>3</sub>.H<sub>2</sub>O was added dropwise and the solution turned black till the pH of the solution reached 10. The precipitate was filtered and white-yellowish solid **II** was washed by water for several times without further purification. **II** was mixed with 28.5mL of HCl (d=1.18, 77mmol) and 7mL of H<sub>2</sub>O to form a clear ammonium solution of **II** for storage.

To the clear ammonium solution of **II** was added very slowly 6.3g NaNO<sub>2</sub>(90mmol) in 50mL of concentrated HCl(d=1.18, 35%) at 0~5°C. KI test paper and urea was conducted to prevent from the excess of HNO<sub>2</sub>. The solution was stirred at 0~5°C for another 10min and added to the solution of 12g

CuCl(120mmol) in 30mL of HCl. Stirred overnight and filtered to yield a brownish powder. The cruder material was purified by column chromatography(silica gel, hexane as eluent,  $R_f=0.85$ ) and yielded white powder of **III** (total yield 60%, m.p.114~116 °C)

$^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ): 7.576(d, 2H,  $J=8.8\text{Hz}$ ), 7.245(dd, 2H,  $J_1=8.8\text{ Hz}$ ,  $J_2=3.2\text{ Hz}$ ), 7.216(d, 2H,  $J=3.2\text{ Hz}$ )

$^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ):142.6, 134.2, 133.7, 131.1, 130.3, 121.7

Element Analysis( $\text{C}_{12}\text{H}_6\text{Br}_2\text{Cl}_2$ ,  $M=380.89$ )-Calculated: C 37.84%; H 1.59%;

Found: C 37.77%; H 1.58%

#### **Preparation of 9,9'-dihexyl-3,6-dichlorosilafluorene IV /9-methy-9'-dodecyl-3,6-dichlorosilafluorene V**

To a rapidly stirred solution of 4.56g of **III**(11mmol) in 60ml dry THF was slowly added in 30min 16mL of 1.5M n-BuLi(24mmol) solution in hexane at  $-80^\circ\text{C}$ .The yellowish solution was stirred at  $-60^\circ\text{C}$  for another 4 h and 4.5g of  $(\text{C}_6\text{H}_{13})_2\text{SiCl}_2$  (17.7mmol) / 5g of  $\text{CH}_3\text{C}_{12}\text{H}_{25}\text{SiCl}_2$ (16.7mmol) in 10mL THF was added. The solution was gradual warmed up to room temperature and stirred overnight. The mixture was quenched with 50mL of saturated  $\text{NH}_4\text{Cl}$  and stirred for 30min. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over added  $\text{MgSO}_4$ , filtered and solvent removed to give an oil. The cruder material was purified by column chromatography(silica gel, hexane as eluent,  $R_f=0.8$ ) and yielded colorless oil of **VI** / **V** (total yield 60%)

$^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ) spectra of **VI** : 7.735(d, 2H,  $J=1.5\text{Hz}$ ), 7.514(d, 2H,  $J=7.2\text{ Hz}$ ), 7.259(dd, 2H,  $J_1=7.2\text{ Hz}$ ,  $J_2=1.5\text{ Hz}$ ), 1.3058~1.1795(m, 16H), 0.9391~0.8998(m, 4H), 0.825(t, 6H,  $J=7.1\text{ Hz}$ )

$^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ )spectra of **VI** :149.1, 136.8, 136.4, 134.3, 127.7, 121.5, 32.9, 31.3, 23.8, 22.6, 14.0, 12.1

Element Analysis( $\text{C}_{24}\text{H}_{32}\text{Cl}_2\text{Si}$ ,  $M=419.51$ )-Calculated: C 68.73%; H 7.637%; Cl 16.94%;

Found: C 68.95%; H 7.65% Cl 17.2%

$^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ) spectra of **V** : 7.768 (d, 2H,  $J=2.1\text{Hz}$ ), 7.555(d, 2H,  $J=8.0\text{ Hz}$ ), 7.300(dd, 2H,  $J_1=8.0\text{ Hz}$ ,  $J_2=2.1\text{ Hz}$ ), 1.40~1.20(m, 20H), 0.96~0.85(m, 5H), 0.425(t, 3H,  $J=7.1\text{ Hz}$ )

$^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ) spectra of **V**: 149.3, 137.0, 136.9, 134.2, 127.9, 121.6, 33.4(4C), 32.1, 29.8, 29.6, 29.5, 29.3, 23.8, 22.8, 14.3, 13.6

Element Analysis ( $\text{C}_{25}\text{H}_{34}\text{Cl}_2\text{Si}$ ,  $M=433.54$ )- Calculated: C 69.28%; H 7.85%; Cl 16.4%

Found: C 68.96%; H 7.85% Cl 16.7%

### **Preparation of Poly(9,9'-hexyl-3,6-silafluorene)(PSFC6C6) VI**

1.3g 9,9'- dialkyl-3,6-dichloro-silafluorene, (about 2.6mmol), 0.43g triphenylphosphine(1.64mmol), 0.7g zinc dust(10.7mmol), 0.015g 2,2'-dipyridyl(0.096mmol), 0.013g  $\text{NiCl}_2$ (0.103mmol) and 10ml dimethylacetamide(DMAc) was charged in a 100ml flask under argon. The solution was stirred and heated in an  $80^\circ\text{C}$  oil bath for 48 h. The mixture was cooled down to room temperature and poured into 20 ml methanol. 30 ml of saturated  $\text{NH}_4\text{Cl}$  aqueous solution was added, and the mixture was stirred

overnight to produce a sticky mass, which was collected by filtration and dissolved in THF to form a clear solution. A white solid was precipitated by pouring the solution into water. The white solid was collected by filtration and purified by dissolution in THF and subsequent precipitation in methanol. Washed with acetone for several times, dried in vacuum at 50°C to produce white solid **VI**.

Similar procedure has been taken to synthesize **VII (PSFC1C12)**.

<sup>1</sup>H-NMR(400M, CDCl<sub>3</sub>, δ) spectra of **VI (PSFC6C6)**: 8.16(s, 2H), 7.72(d, 2H, *J*=6.6), 7.59(d, 2H, *J*=6.6), 1.42(m, 4H), 1.27(m, 4H), 1.20(m, 8H), 1.00(m, 4H), 0.80(t, 6H)

<sup>13</sup>C-NMR(400M, CDCl<sub>3</sub>, δ) spectra of **VI (PSFC6C6)**: 149.9, 143.7, 137.3, 133.6, 126.6, 120.0, 33.1, 31.4, 24.0, 22.5, 14.0, 12.4

Element Analysis of **VI (PSFC6C6)**: Calculated: C 82.75%; H 9.19%; Cl 0.0%, Si 8.00%.

Found: C 82.50%; H 9.16%; Cl <0.1%; Si 7.94%

<sup>1</sup>H-NMR(400M, CDCl<sub>3</sub>, δ) spectra of **VII (PSFC1C12)**: 8.14(s, 2H), 7.70(d, 2H, *J*=6.4), 7.58(d, 2H, *J*=6.4), 1.4 (m, 2H), 1.21(m, 18H), 0.95(m, 2H), 0.84(t, 3H), 0.43(t, 3H).

<sup>13</sup>C-NMR(400M, CDCl<sub>3</sub>, δ) spectra of **VII (PSFC1C12)**: 148.6, 143.7, 137.9, 133.4, 126.8, 120.0, 33.4, 31.9, 29.6(4), 29.5, 29.3, 29.2, 24.0, 22.6, 14.1, 13.9

Element Analysis of **VII (PSFC1C12)**: Calculated: C 82.87%; H 9.39%; Cl 0.0%, Si 7.73%.

Found: C 82.71%; H 9.35%; Cl <0.1%; Si 7.64%

**Table S1.** UV-Vis Absorption, Electrochemical, and Photoluminescent Properties of the polysilafluorene

Compound	$\lambda$ Abs-max [nm]	optical band-gap[eV]	Eox [V]	HOMO [eV]	LUMO [eV] (calculated)	$\lambda$ PL-max [nm]	PL quantum efficiency yield*
PSFC6C6	270	4.0	+1.7	-6.1	-2.1	355~370	30%
PSFC1C12	270	4.0	+1.7	-6.1	-2.1	360~375	25%

\*:solvent: 1,2-dichloroethane, concentration:  $1.4 \times 10^{-6}$  g/ml, absorbance 0.236, reference is p-terphenyl whose yield is 91% in 1,2-dichloroethane.

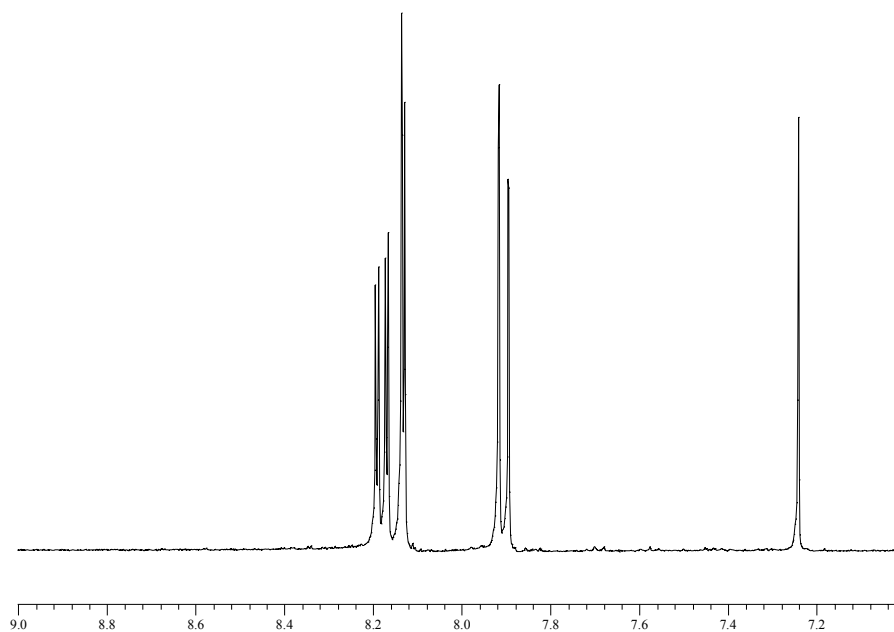


Fig. S1. <sup>1</sup>H NMR(400M, CDCl<sub>3</sub>) spectra of 2,2'-dibromo-5,5'- dinitrophenyl I

<sup>1</sup>H NMR(400M, CDCl<sub>3</sub>, δ): 8.181(dd, 2H,  $J_1=8.2\text{Hz}$ ,  $J_2=3.0\text{Hz}$ ), 8.133(d, 2H,  $J=3.0\text{ Hz}$ ), 7.906(d, 2H,  $J=8.2\text{ Hz}$ )

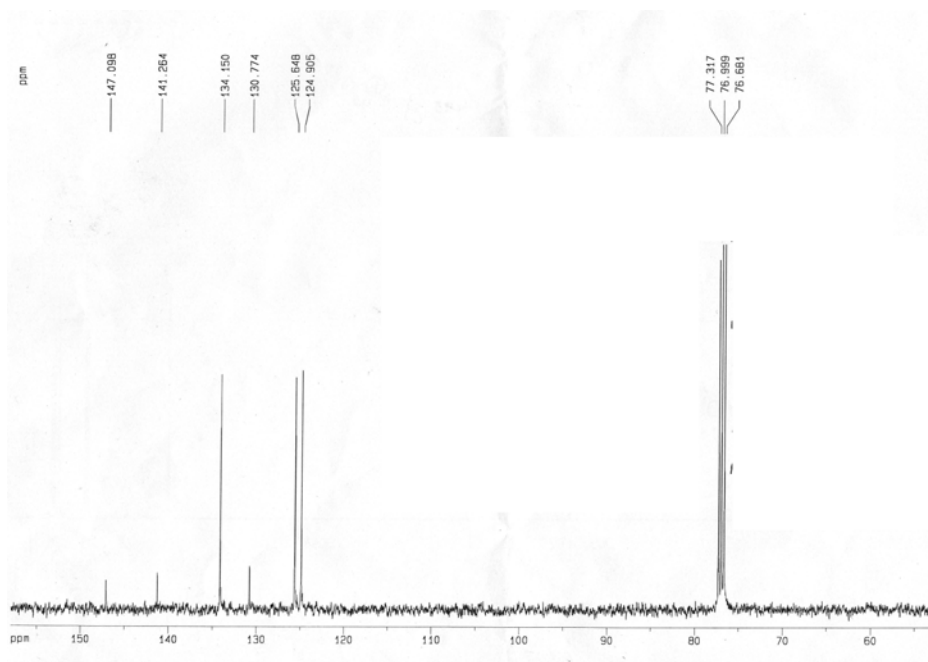


Fig. S2. <sup>13</sup>C NMR(400M, CDCl<sub>3</sub>) spectra of 2,2'-dibromo-5,5'- dinitrophenyl I

<sup>13</sup>C NMR(400M, CDCl<sub>3</sub>, δ):147.1, 141.3, 134.2, 130.8, 125.6, 124.9



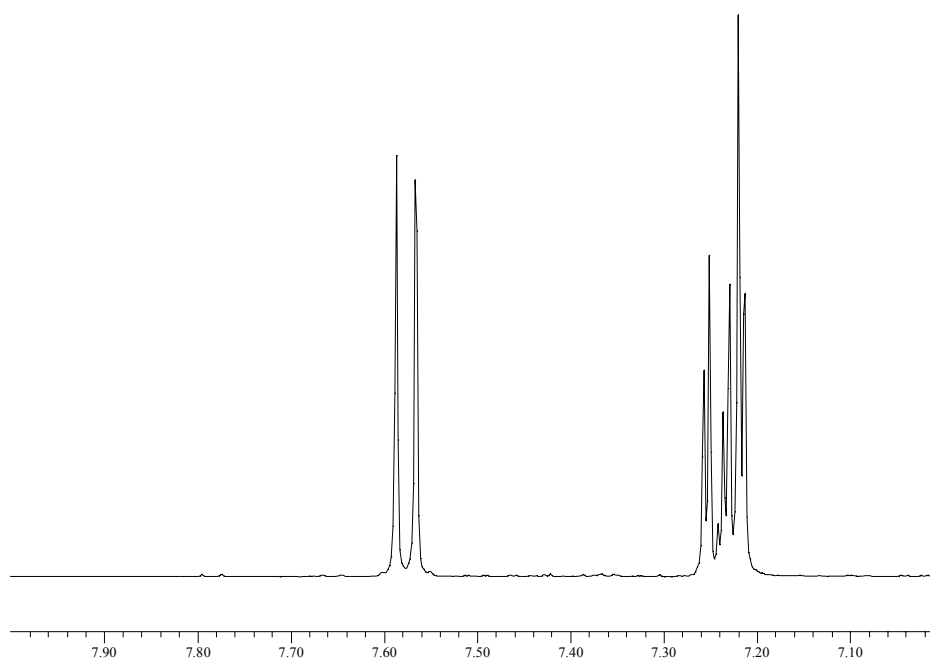


Fig. S3. <sup>1</sup>H NMR(400M, CDCl<sub>3</sub>) spectra of 2,2'-dibromo-5,5'- dichlorobiphenyl **III**

<sup>1</sup>H NMR(400M, CDCl<sub>3</sub>, δ): 7.576(d, 2H, *J*=8.8Hz), 7.245(dd, 2H, *J*<sub>1</sub>=8.8 Hz, *J*<sub>2</sub>=3.2 Hz), 7.216(d, 2H, *J*=3.2 Hz)

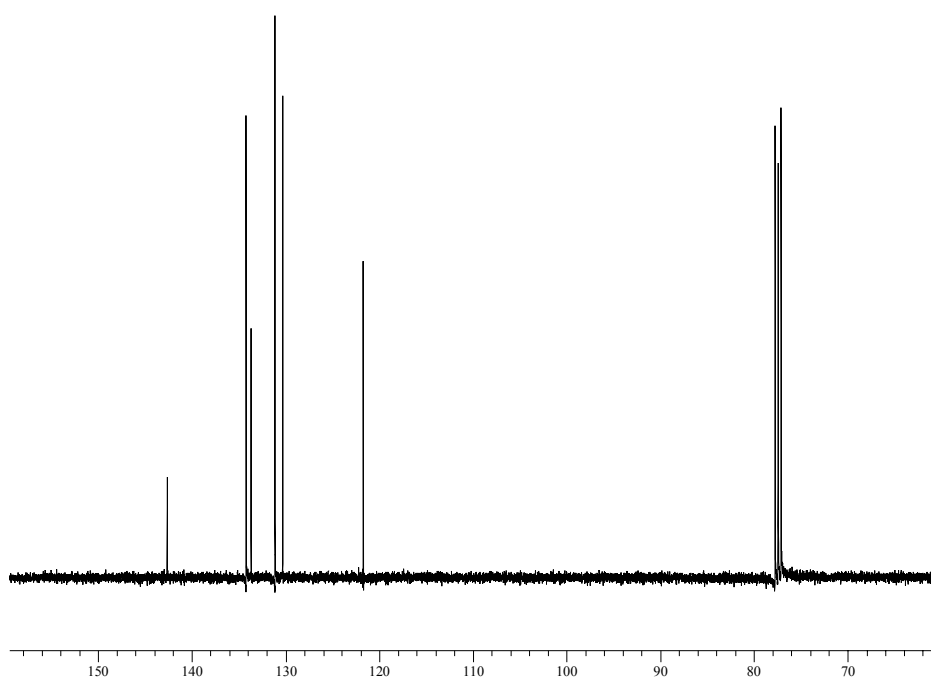


Fig. S4. <sup>13</sup>C NMR(400M, CDCl<sub>3</sub>) spectra of 2,2'-dibromo-5,5'- dichlorobiphenyl **III**

<sup>13</sup>C NMR(400M, CDCl<sub>3</sub>, δ):142.6, 134.2, 133.7, 131.1, 130.3, 121.7

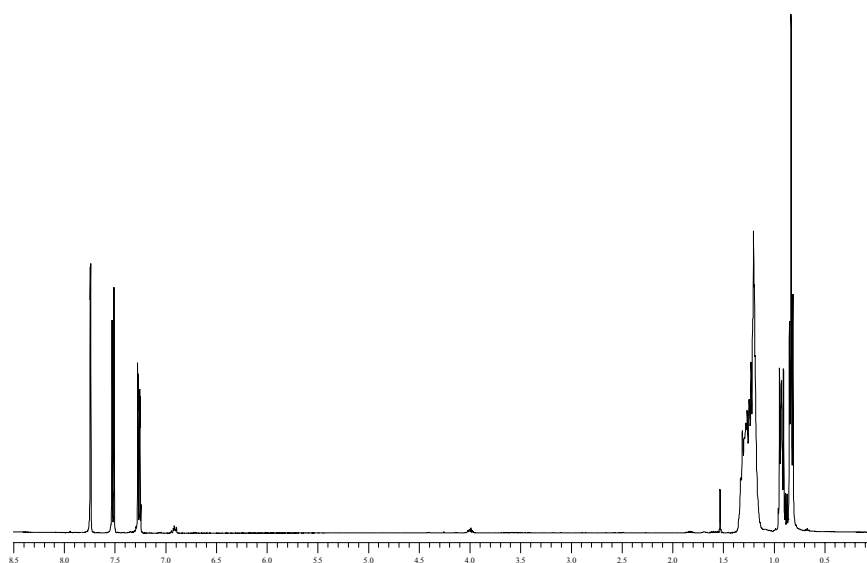


Fig. S5.  $^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ) spectra of 9,9'-dihexyl-3,6- dichlorosilafluorene **IV**

$^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ): 7.735(d, 2H,  $J=1.5\text{Hz}$ ), 7.514(d, 2H,  $J=7.2$  Hz), 7.259(dd, 2H,  $J_1=7.2$  Hz,  $J_2=1.5$  Hz), 1.3058~1.1795(m, 16H), 0.9391~0.8998(m, 4H), 0.825(t, 6H,  $J=7.1$  Hz)

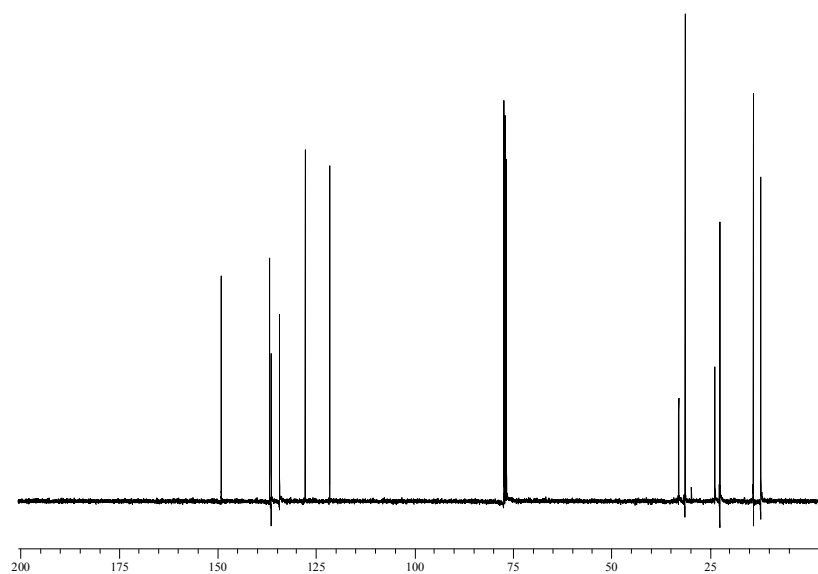


Fig. S6.  $^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ) spectra of 9,9'-dihexyl-3,6- dichlorosilafluorene **IV**

$^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ):149.1, 136.8, 136.4, 134.3, 127.7, 121.5, 32.9, 31.3, 23.8, 22.6, 14.0, 12.1

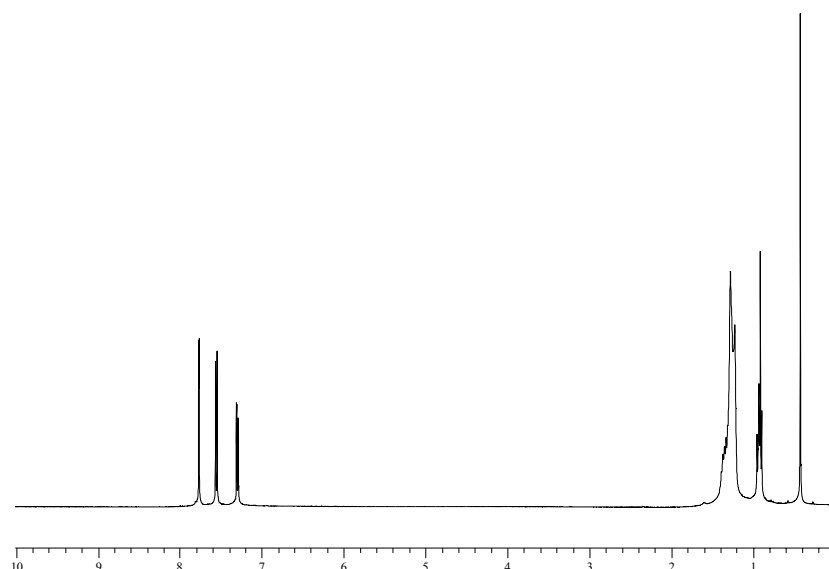


Fig. S7.  $^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ) spectra of 9-methyl-9'-dodecyl-3,6- dichlorosilafluorene **V**

$^1\text{H}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ): 7.768 (d, 2H,  $J=2.1\text{Hz}$ ), 7.555(d, 2H,  $J=8.0$  Hz), 7.300(dd, 2H,  $J_1=8.0$  Hz,  $J_2=2.1$  Hz), 1.40~1.20(m, 20H), 0.96~0.85(m, 5H), 0.425(t, 3H,  $J=7.1$  Hz)

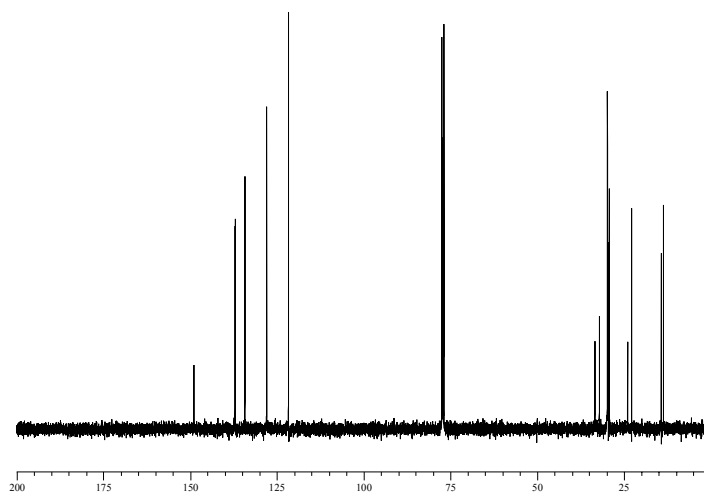


Fig. S8.  $^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ) spectra of 9-methyl-dodecyl-3,6- dichlorosilafluorene **V**

$^{13}\text{C}$  NMR(400M,  $\text{CDCl}_3$ ,  $\delta$ ): 149.3, 137.0, 136.9, 134.2, 127.9, 121.6, 33.4(4C), 32.1, 29.8, 29.6, 29.5, 29.3, 23.8, 22.8, 14.3, 13.6

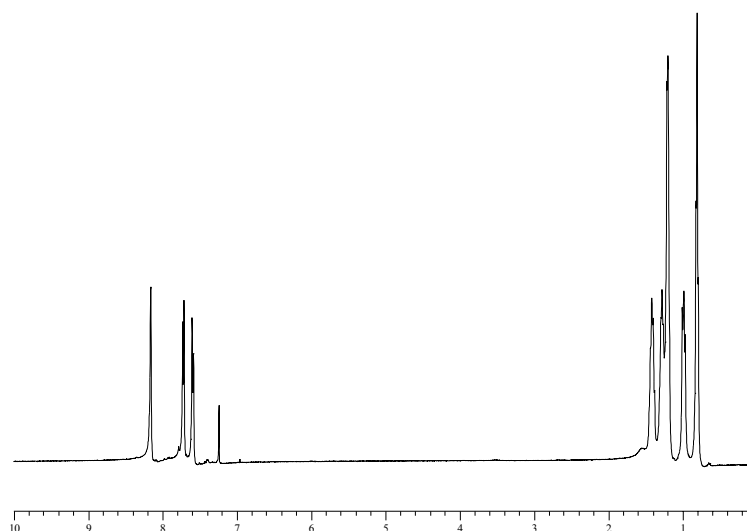


Fig. S9.  $^1\text{H-NMR}$ (400M,  $\text{CDCl}_3$ ) spectra of poly(9,9'-dihexyl-3,6-silafluorene) VI

$^1\text{H-NMR}$ (400M,  $\text{CDCl}_3$ ,  $\delta$ ): 8.16(s, 2H), 7.72(d, 2H,  $J=6.6$ ), 7.59(d, 2H,  $J=6.6$ ), 1.42(m, 4H), 1.27(m, 4H), 1.20(m, 8H), 1.00(m, 4H), 0.80(t, 6H)

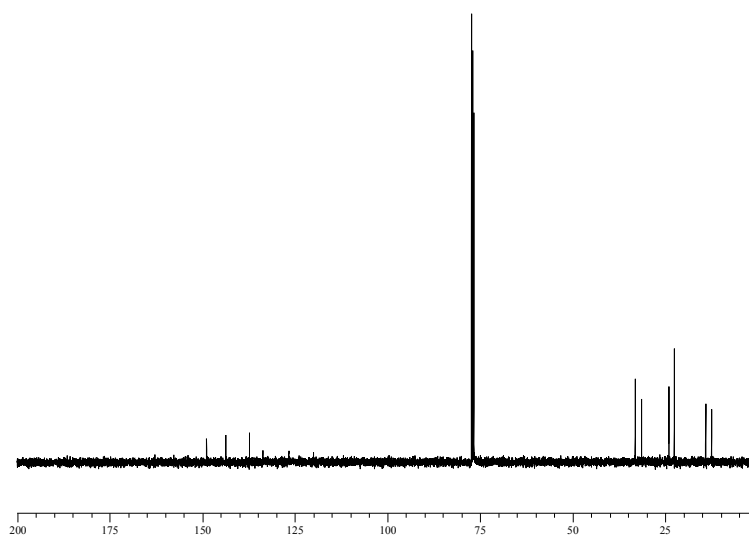


Fig. S10.  $^{13}\text{C-NMR}$ (400M,  $\text{CDCl}_3$ ) spectra of poly(9,9'-dihexyl-3,6-silafluorene) VI

$^{13}\text{C-NMR}$ (400M,  $\text{CDCl}_3$ ,  $\delta$ ): 149.9, 143.7, 137.3, 133.6, 126.6, 120.0, 33.1, 31.4, 24.0, 22.5, 14.0, 12.4

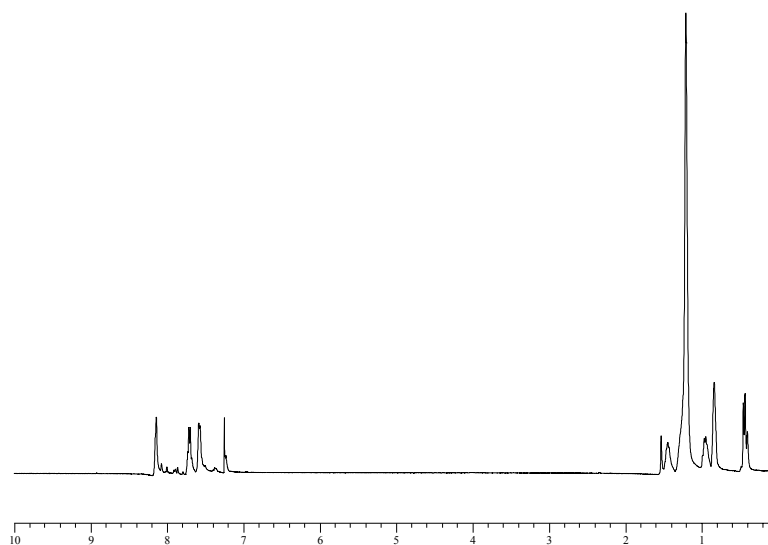


Fig. S11.  $^1\text{H-NMR}$ (400M,  $\text{CDCl}_3$ ) spectra of poly(9-methyl-9'-dodecyl-3,6-silafluorene) **VII**

$^1\text{H-NMR}$ (400M,  $\text{CDCl}_3$ ,  $\delta$ ): 8.14(s, 2H), 7.70(d, 2H,  $J=6.4$ ), 7.58(d, 2H,  $J=6.4$ ), 1.4 (m, 2H), 1.21(m, 18H), 0.95(m, 2H), 0.84(t, 3H), 0.43(t, 3H).

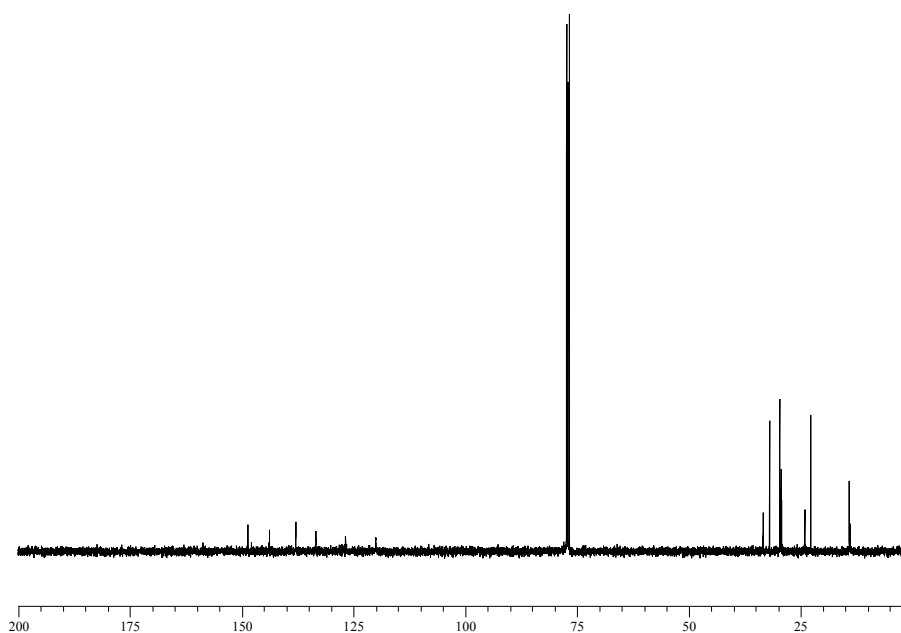


Fig. S12.  $^{13}\text{C-NMR}$ (400M,  $\text{CDCl}_3$ ) spectra of poly(9-methyl-9'-dodecyl-3,6-silafluorene) **VII**

$^{13}\text{C-NMR}$ (400M,  $\text{CDCl}_3$ ,  $\delta$ ): 148.6, 143.7, 137.9, 133.4, 126.8, 120.0, 33.4, 31.9, 29.6(4), 29.5, 29.3, 29.2, 24.0, 22.6, 14.1, 13.9

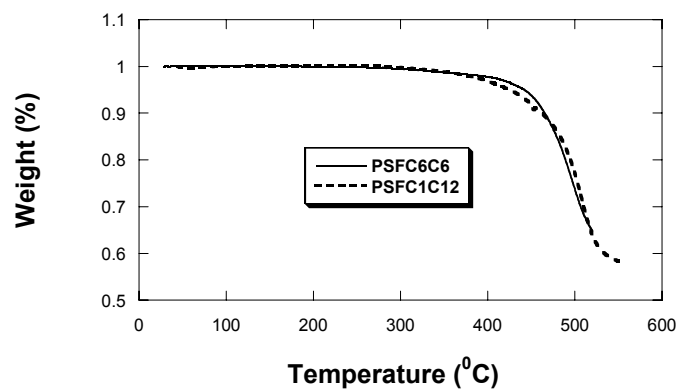


Fig. S13. Thermogravimetric analysis (TGA) for poly(9,9'- dialkyl-3,6-silafluorene)

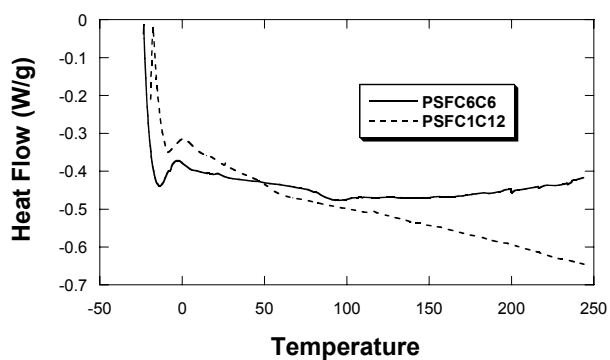


Fig. S14. Heating and cooling curves of differential scanning calorimetry (DSC) for poly(9,9'- dialkyl-3,6-silafluorene)

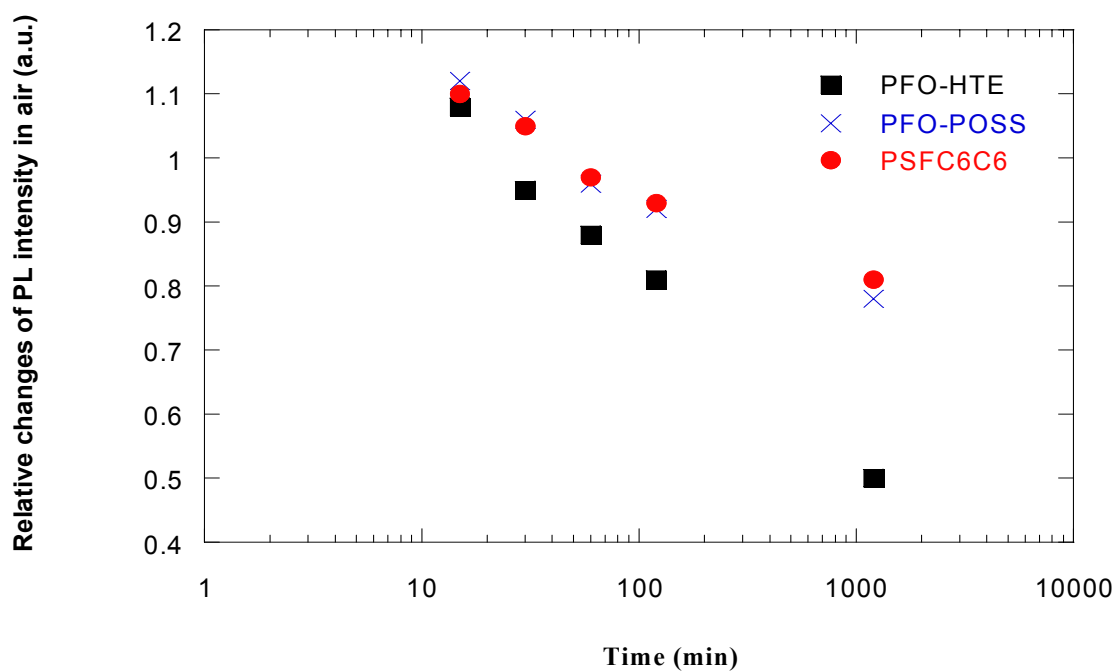


Fig. S15. Comparison of oxidative stability of polysilafluorene and polyfluorene under room light illumination. PFO-THE and PFO-POSS are blue-emitting polyfluorene purchased from ADS corporation.

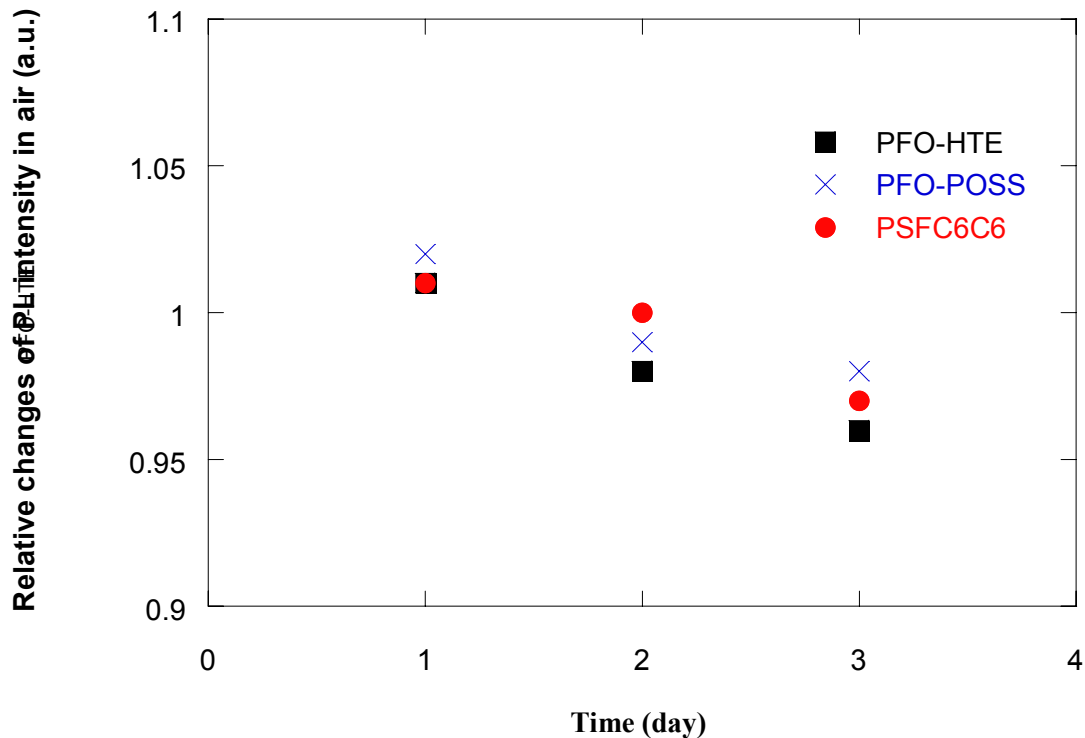


Fig. S16. Comparison of oxidative stability of polysilafluorene and polyfluorene in air under dark. PFO-THE and PFO-POSS are blue-emitting polyfluorene purchased from ADS corporation.