Electronic Supplementary Information

# Air Stable Organometallic Polymer Containing Titanafluorene Moieties by Sonogashira-Hagihara Cross-coupling Polycondensation

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Keywords: π-Conjugated polymers; Polycondensation; Sonogashira-Hagihara cross-coupling reactions; Organometallic polymers; Titanafluorenes

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## 1. NMR Spectra

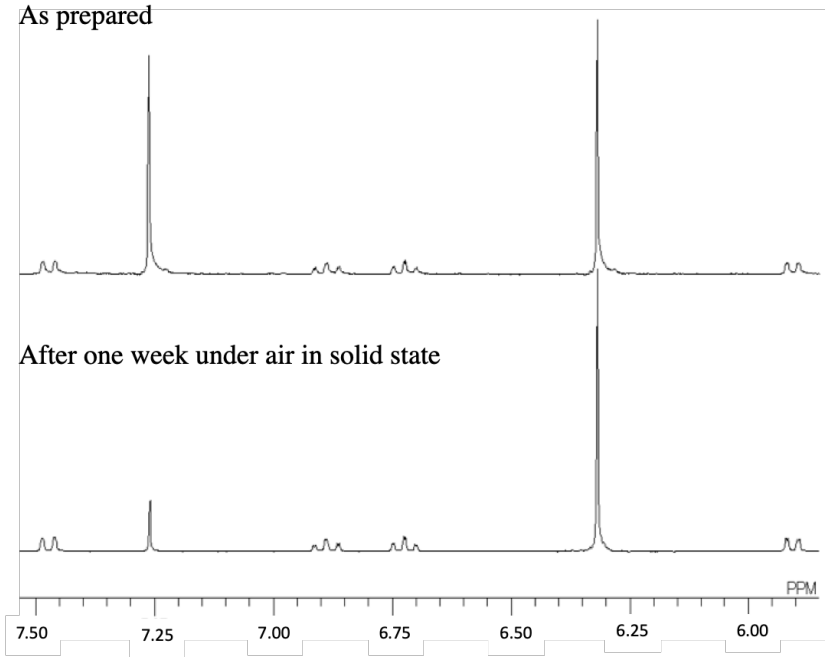



**Figure S1.** $^{1}$H NMR spectra of a titanafluorene derivative (**2**) before and after kept under air at ambient temperature for 1 week.

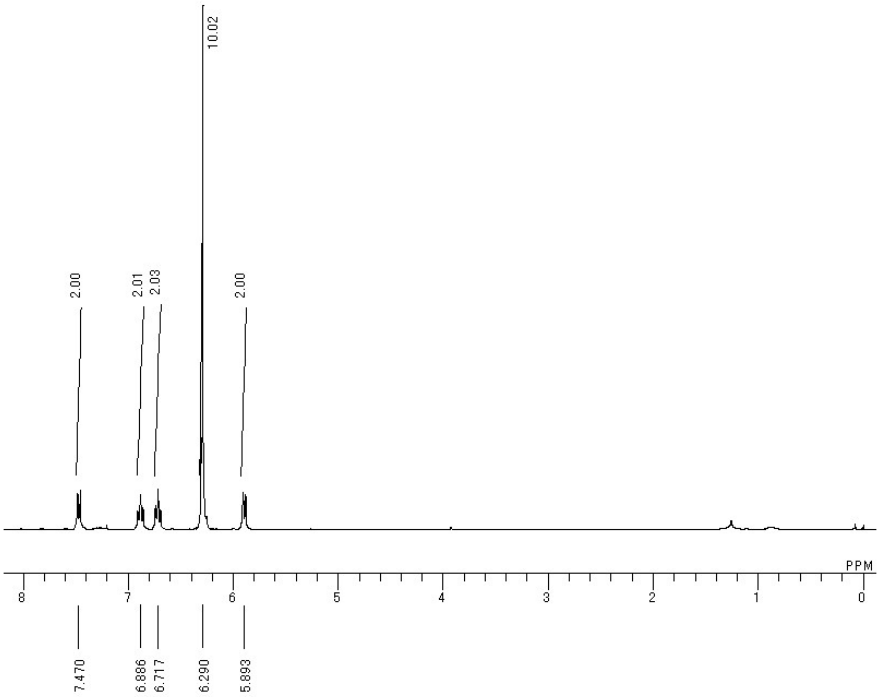



**Figure S2.** $^{1}$H NMR spectrum of **2**.

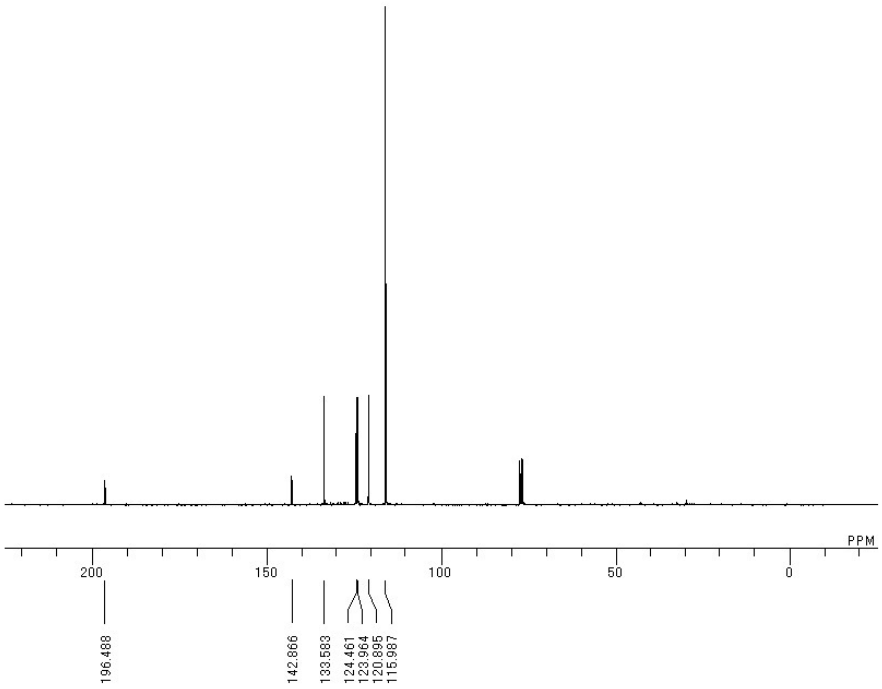



**Figure S3.** $^{13}C\{^{1}H\}$NMR spectrum of **2**.

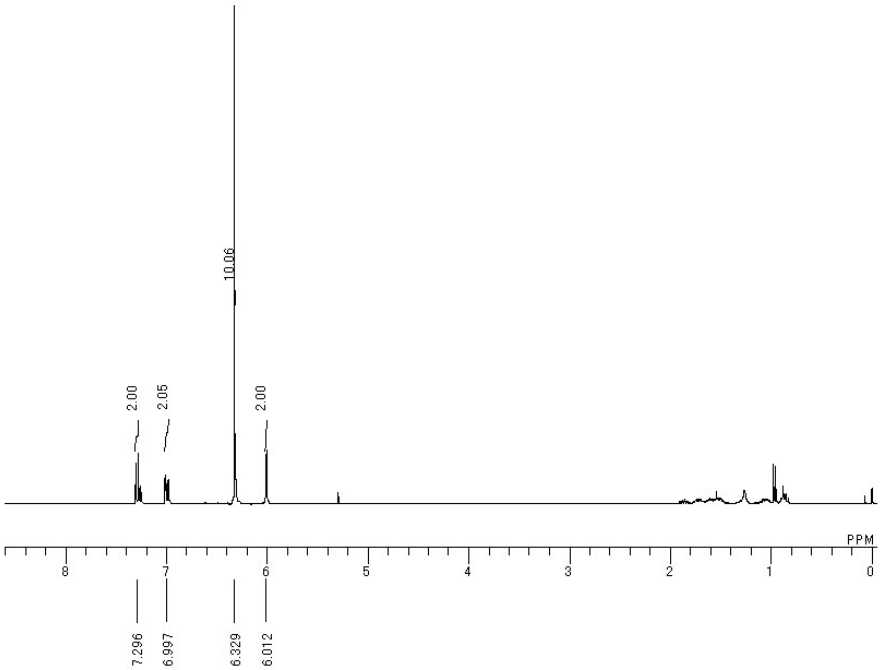



**Figure S4.** $^{1}H$ NMR spectrum of **4**.

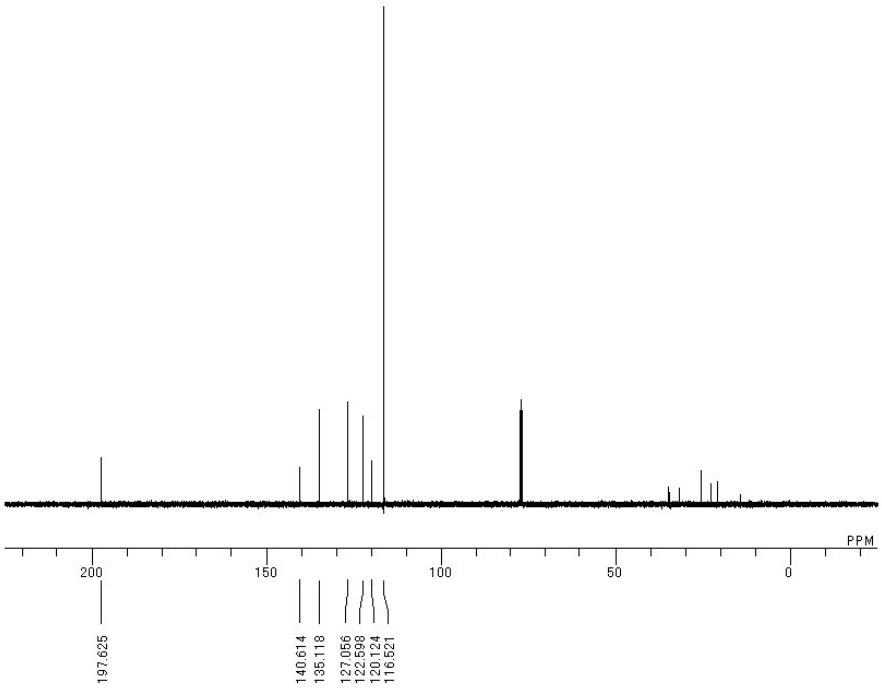



**Figure S5.** $^{13}C\{^{1}H\}$ NMR of spectrum of **4**.

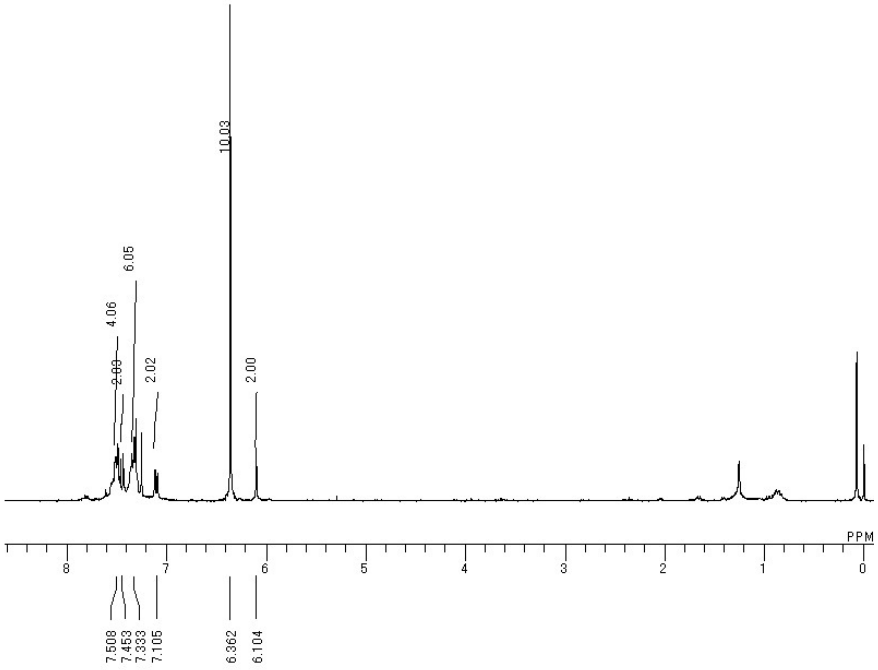



**Figure S6.** $^{1}H$ NMR of spectrum of **6**.

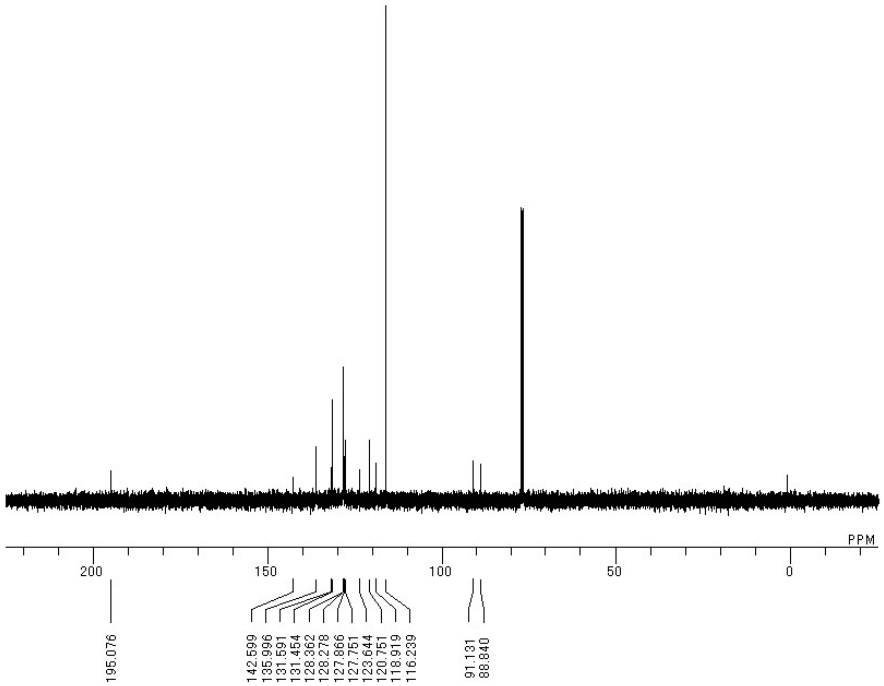



**Figure S7.** $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

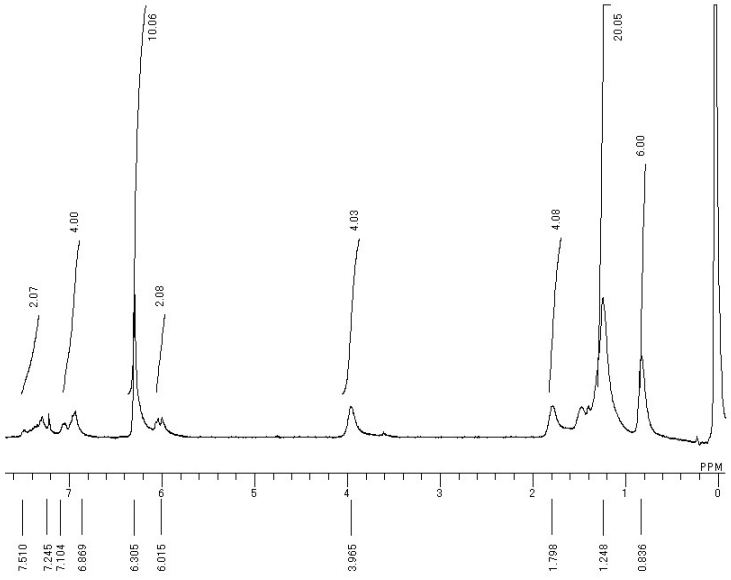



**Figure S8.** $^{1}H$ NMR spectrum of **8**.

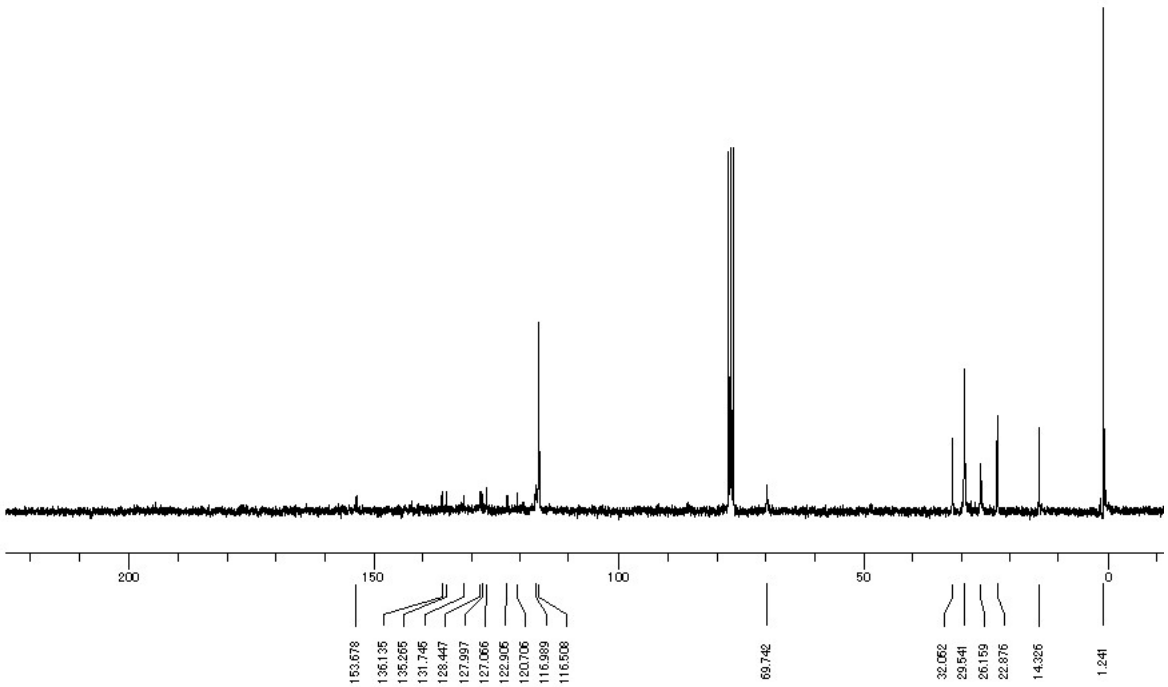



**Figure S9.** $^{13}C\{^{1}H\}$ NMR spectrum of **8**.

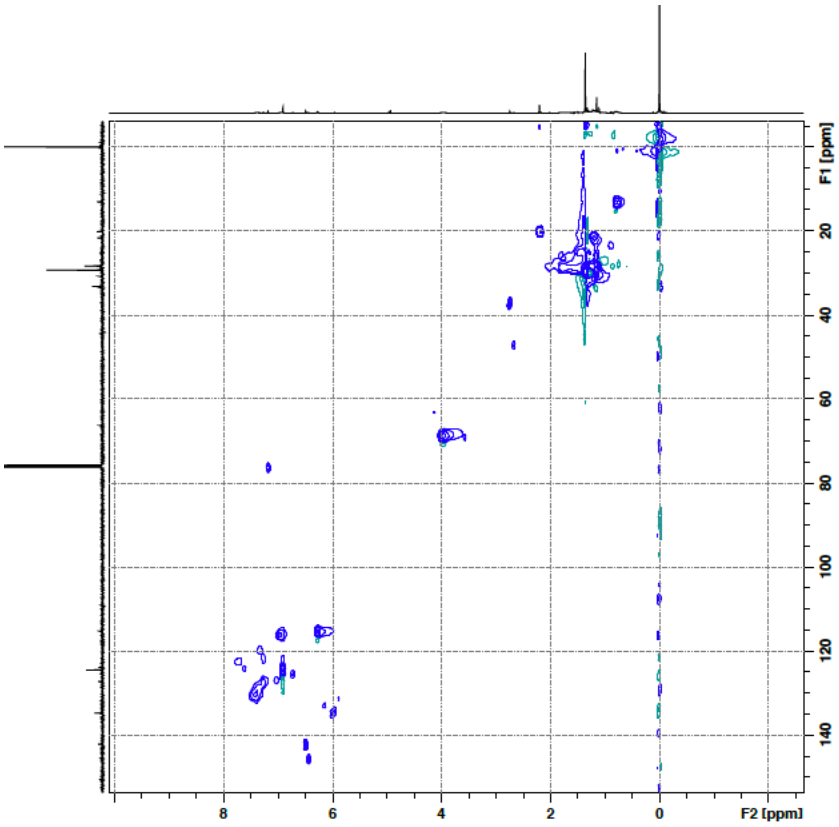



**Figure S10.** 2D $^{1}H$-$^{13}C$ correlation NMR spectrum of **8**.

## 2. IR Spectra

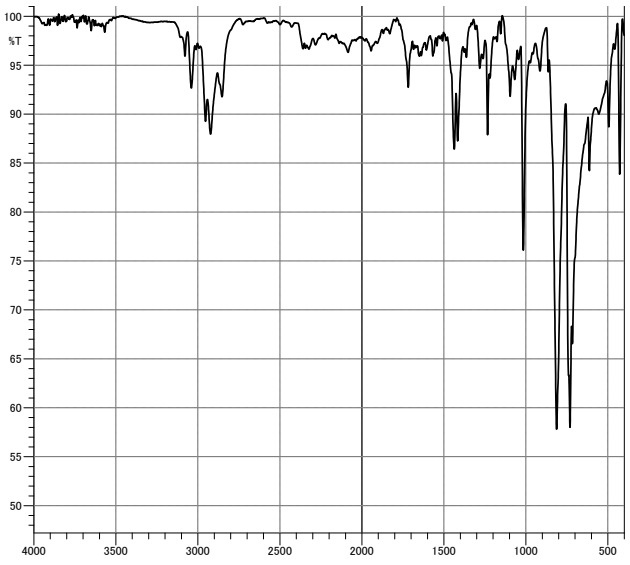



**Figure S11.** IR spectrum of **2**.

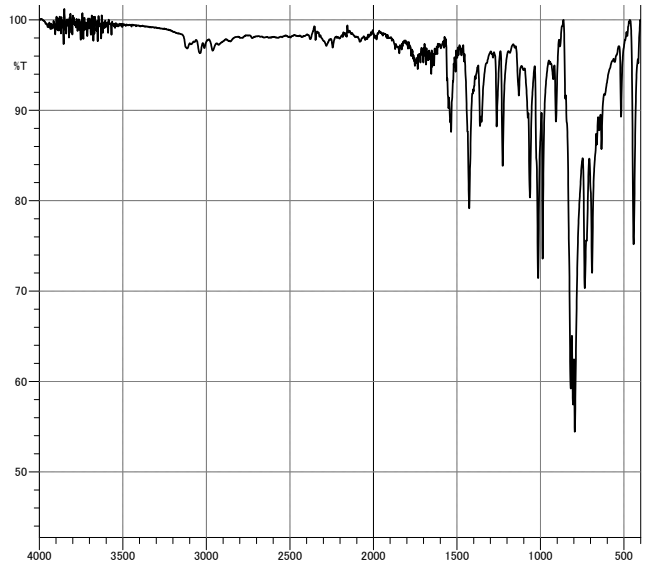



**Figure S12.** IR spectrum of **4**.

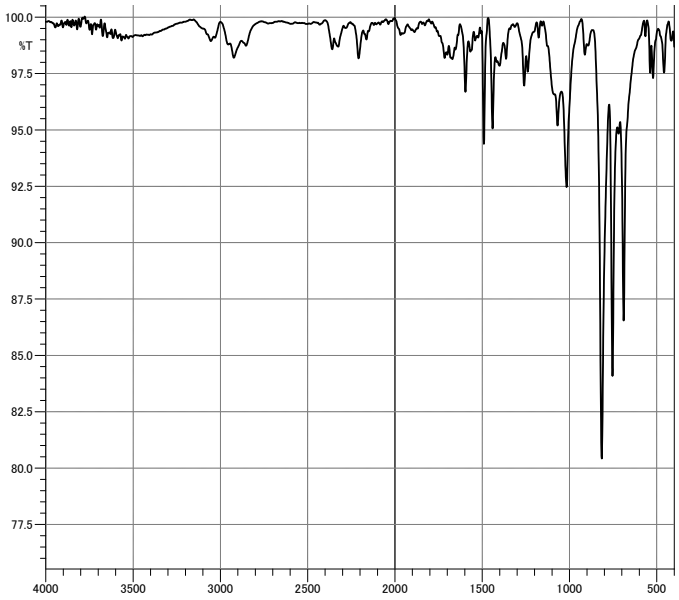



**Figure S13.** IR spectrum of **6**.

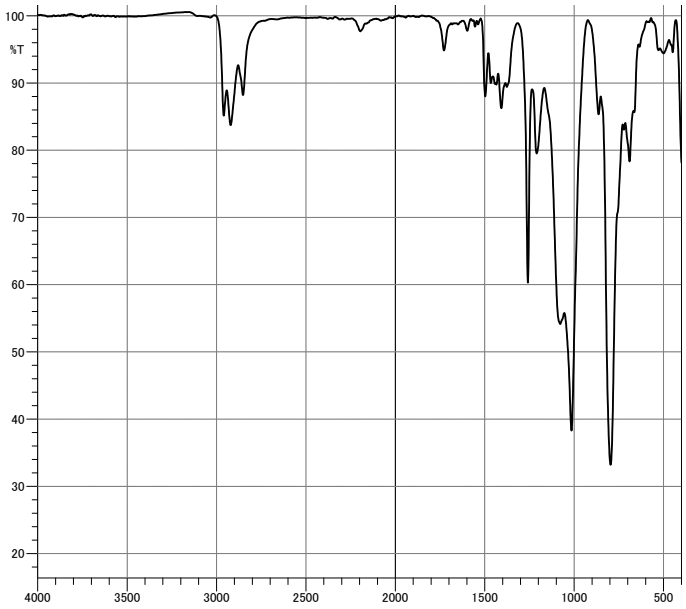



**Figure S14.** IR spectrum of **8**.

## 3. Mass Spectra

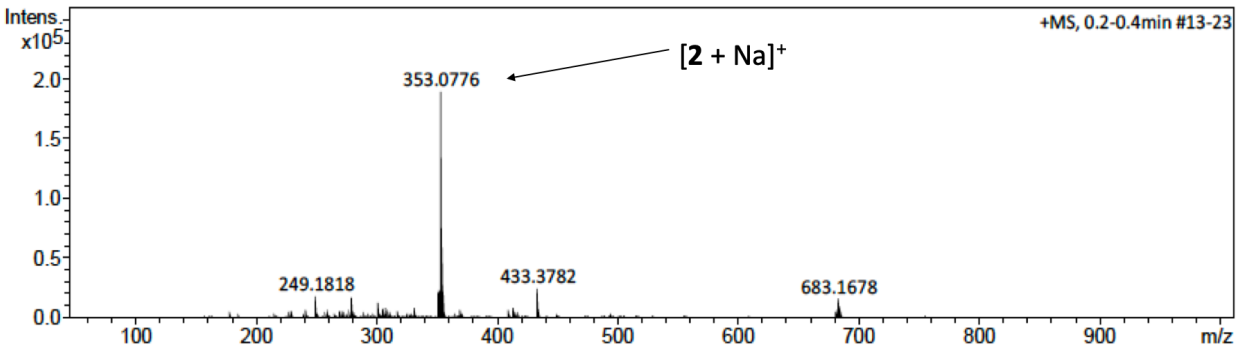



**Figure S15**. ESI-TOF mass spectrum of **2**

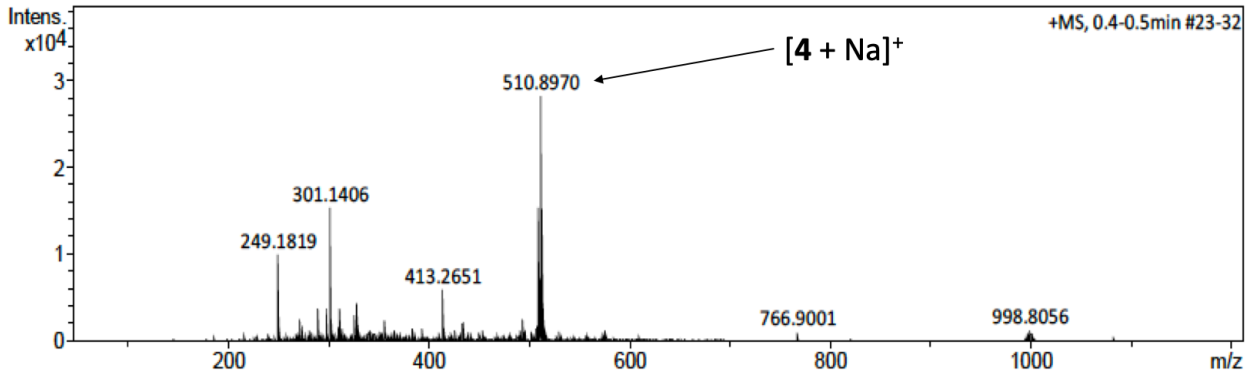



**Figure S16**. ESI-TOF mass spectrum of **4**

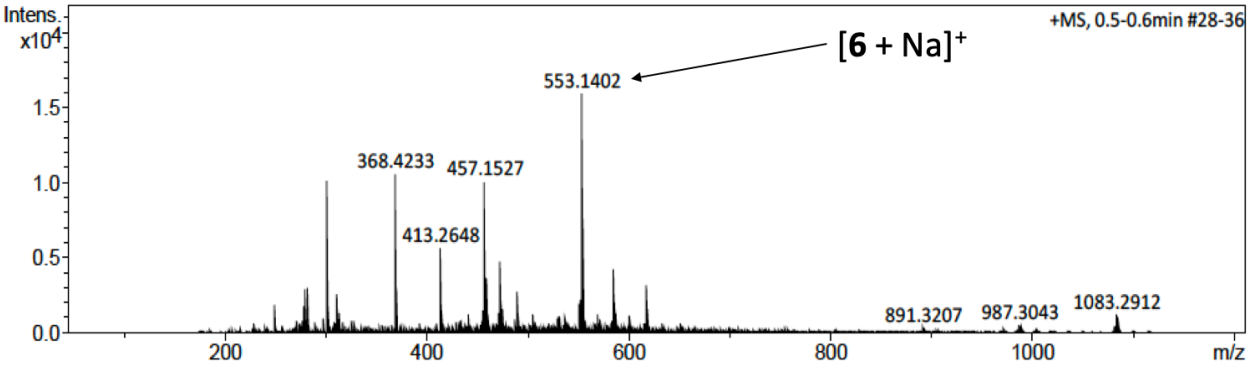
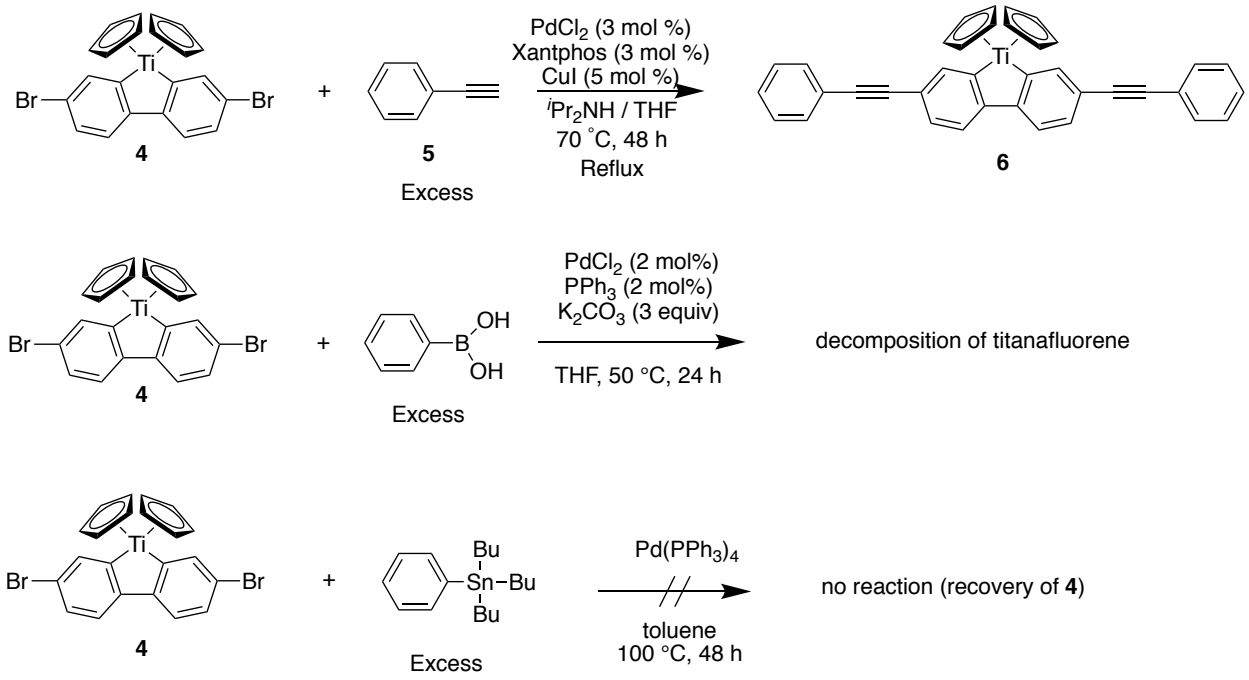



**Figure S17**. ESI-TOF mass spectrum of **6**

## 3. Synthetic Attempts of π-Extended Titanafluorene Derivatives




**Scheme S1.** Coupling reactions of arylene dihalide containing titanafluorene unit (**4**).

## 4. Crystallographic Data

**Table S1.** Crystallographic data of $[C_{22}H_{16}TiBr_2]_2 \bullet CH_2Cl_2$

| Crystal data | $[C_{22}H_{16}TiBr_2]_2 \cdot CH_2Cl_2$ |
|---|---|
| CCDC | 2027344 |
| Empirical formula | $C_{45}H_{34}Br_4Cl_2Ti_2$ |
| Formula weight | 1061.06 |
| Crystal size/mm$^3$ | 0.308 x 0.106 x 0.07 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a, Å | 9.2921 (2) |
| b, Å | 14.6419 (4) |
| c, Å | 14.6728 (3) |
| α, deg | 90 |
| β, deg | 99.445 (2) |
| γ, deg | 90 |
| Volume, Å | 1969.23 (8) |
| Density$_{calcd}$, g cm$^{-3}$ | 1.789 |
| Z | 2 |
| F(000) | 1044.0 |
| Temperature, deg | -183.15 |
| 2θmax, deg | 149.374 |
| $T_{min}/T_{max}$ | 0.251/1.000 |
| Absorption correction | Multi-scan |
| No. of Reflection | 7706 |
| No. of Parameters | 478 |
| Goodness-of-fit on F2 | 1.059 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0283, wR2 = 0.0734 |
| Final R indexes [all data] | R1 = 0.0287, wR2 = 0.0737 |
| Largest diff. peak/hole / | 1.18 and -0.64 e Å$^{-3}$ |

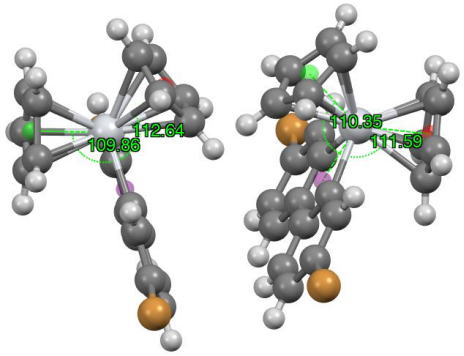



**Fig S18.** Angle of Cp(centroid) to fluorene(centroid)

## 5. Size Exclusion Chromatographic Analysis

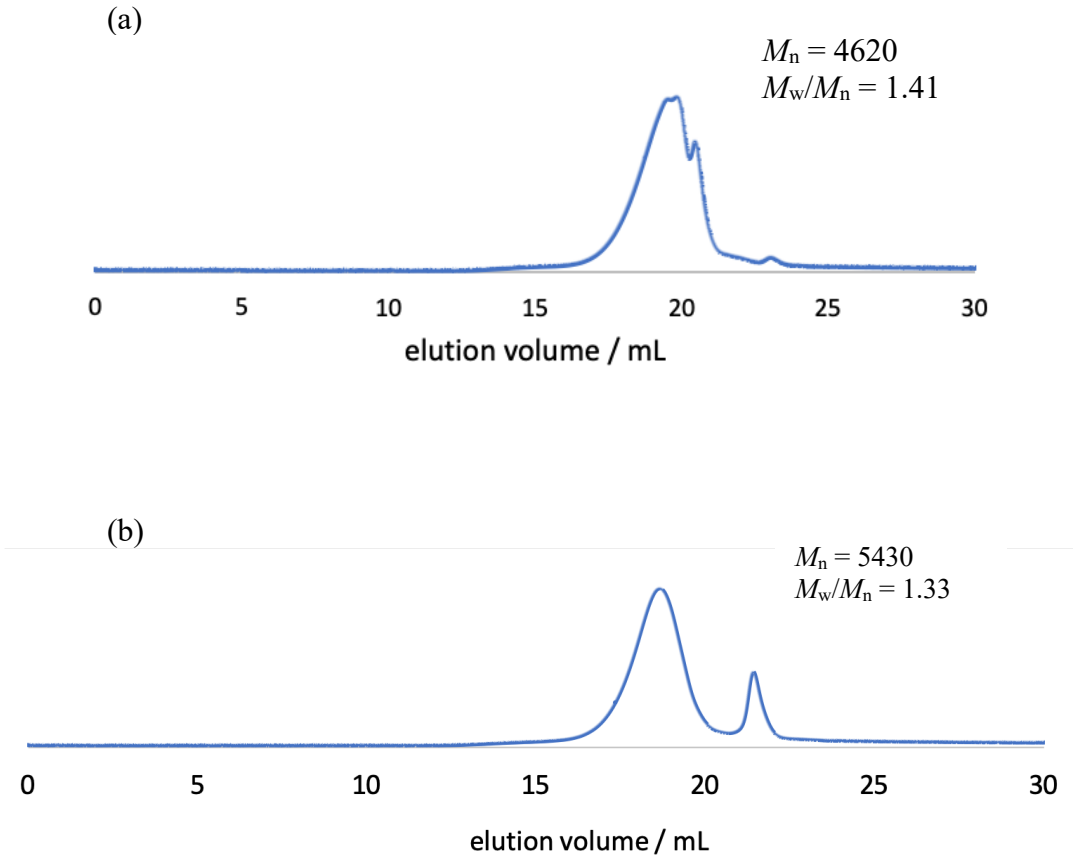



**Figure S19.** SEC profiles of **8** after isolation by precipitation into ethanol (a) and by precipitation into ethanol/ethyl acetate (v/v = 9/1).

**6. DFT and TD-DFT** Optimized Molecular Diagrams

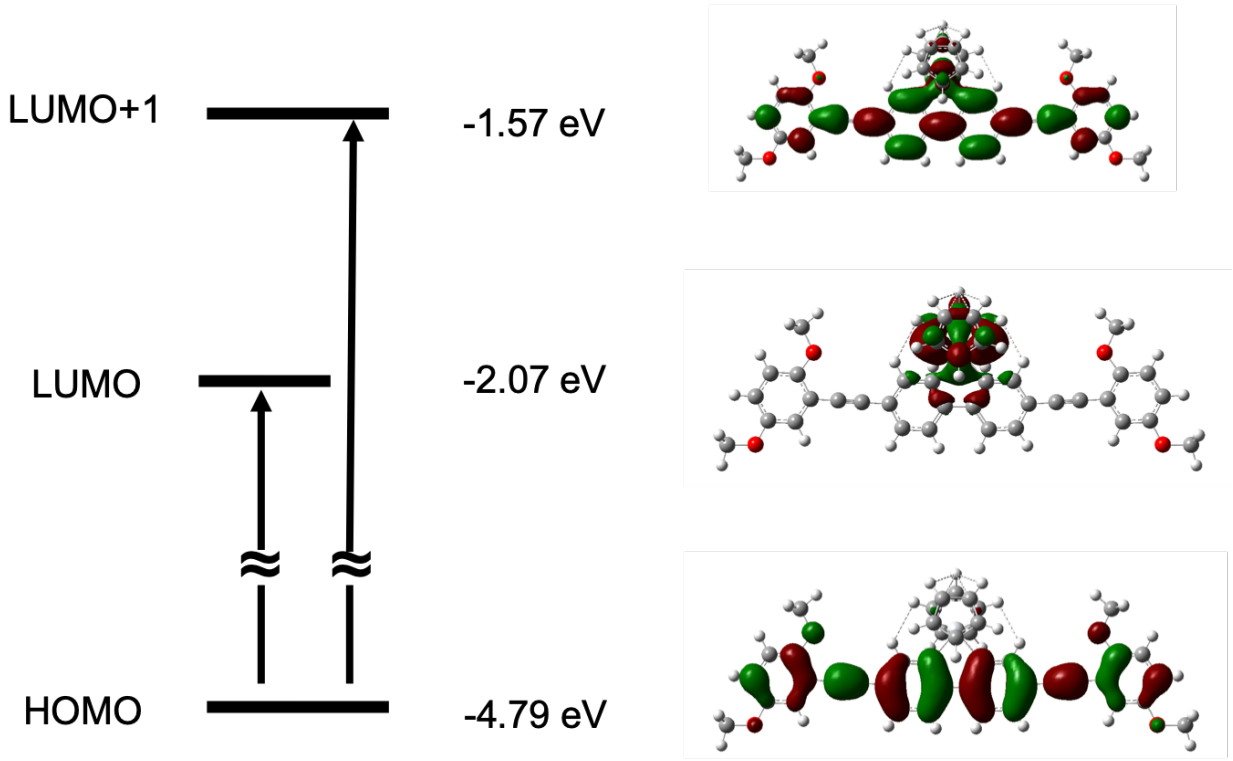



**Fig S20.** Energy profiles and molecular orbital diagrams of HOMO, LUMO, and LUMO+1 of **9**.

**Table S2.** HOMO to LUMO and HOMO to LUMO+1 transitions by TD-DFT calculations.

| Assignment | HOMO to LUMO | HOMO to LUMO+1 |
|---|---|---|
| $\lambda_{max}$ (nm) [a)] | 596.86 | 416.03 |
| f [b)] | 0.002 | 0.688 |
| Excitation energy (eV) | 2.08 | 2.98 |

a) Calculated absorption maximum in the UV-vis spectrum. b) Oscillator strength.