

## Electronic Supplementary Information

### **Poly(silylene arylacetylene)s containing hexafluoroisopropylidene with attractive mechanical properties and dielectric performance for wave-transparent composites**

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#### **S1. Experimental section**

##### *S1.1. Materials*

*N,N*-Dimethylformamide (DMF), dichloromethane (DCM), tetrahydrofuran (THF), triethylamine (Et<sub>3</sub>N), pyridine, methanol, ethyl acetate, toluene, hexane, petroleum ether, concentrated hydrochloric acid, acetic acid, sodium hydroxide, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>), sodium nitrite (NaNO<sub>2</sub>), potassium iodide (KI), and urea were purchased from Shanghai Titan Scientific Co., Ltd. Bisphenol AF were purchased from Shanghai Meryer Chemical Technology Co., Ltd. Trifluoromethanesulfonic anhydride, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, dichlorobis(triphenylphosphine) palladium(II), cuprous iodide, ethyl bromide, and 2-methyl-3-butyn-2-ol were purchased from Shanghai Adamas Reagent Co., Ltd. 1-Fluoro-4-iodo-2-(trifluoromethyl)benzene and trimethylsilylacetylene were purchased from Shanghai Bide Pharmatech Co., Ltd. Dichloromethylphenylsilane was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used as received.

## *SI.2. Characterizations*

All NMR spectra were recorded on an AVANCE 400 spectrometer (Bruker, Switzerland). High-resolution mass spectra (HRMS) were determined with the GCT Premier EI-TOF mass spectrometer (Waters, USA). Fourier transform infrared (FT-IR) spectra for monomers and resins were both measured on a Nicolet iS10 infrared spectrometer (Thermo Scientific, USA) with KBr pellets. High-resolution mass spectra (HRMS) were determined with the GCT Premier EI-TOF mass spectrometer (Waters, USA). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was measured by 4800 Plus MALDI TOF/TOF (ABS, Singapore) with dithranol and NaI as the matrix. Differential scanning calorimetric (DSC) analysis was carried out on the TA Instruments Q2000 analyzer (TA, USA) at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  in a nitrogen atmosphere with a flowing rate of  $50\text{ mL}\cdot\text{min}^{-1}$ . Thermogravimetric analysis (TGA) was performed with a TGA/DSC 1LF analyzer (Mettler Toledo, Switzerland) at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  in a nitrogen atmosphere with a protective flowing rate of  $10\text{ mL}\cdot\text{min}^{-1}$  and a purge flowing rate of  $60\text{ mL}\cdot\text{min}^{-1}$ . Dielectric properties were investigated on a 4294A precision impedance analyzer (Agilent, USA) in a range of frequencies from 40 Hz to 30 MHz at room temperature. Dielectric properties of composite samples (cured cylindrical laminates with an average diameter of 50.5 mm and thicknesses of 3.3 mm) were measured on a waveguide cavity resonator in the range of frequency from 7 GHz to 17 GHz. Dynamic mechanical analysis (DMA) was performed on a DMA 1 mechanical analyzer (Mettler Toledo, Switzerland) in nitrogen with a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ . Rheological behaviors were measured by Mars III rotational rheometer (Thermo Haake, USA)

with a heating rate of  $2^{\circ}\text{C}\cdot\text{min}^{-1}$  and a shear rate of  $0.01\text{ S}^{-1}$ . The density of the cured resins was carried out on a MH-124S densitometer (Matsuhaku, China) with deionized water. Gel permeation chromatography analysis was conducted on a Waters 1515 chromatography instrument (Waters, USA) with polystyrene as the standard sample and tetrahydrofuran as a solvent at a flow rate of  $1\text{ mL}\cdot\text{min}^{-1}$ , with styragel HR 1 ( $100\text{ \AA}$ ,  $5\text{ }\mu\text{m}$ ,  $7.8\text{ mm} \times 300\text{ mm}$  column, Part No: WAT044234). X-ray diffraction patterns were recorded at room temperature by monitoring the diffraction angle  $2\theta$  from  $5^{\circ}$  to  $75^{\circ}$  on a D/Max 2550 VB/PC rotating anode X-ray power diffractometer (Rigaku, Japan). The flexural properties were measured in a 3-point bend test at a crosshead speed of  $2\text{ mm}\cdot\text{min}^{-1}$  at room temperature on a CMT 4204 universal testing machine (SANS, Shenzhen, China). The SEM images were obtained on a field emission scanning electron microscope (S4800, Hitachi, Japan) at the magnification of 10000-600000, and the surface of the sample was treated by spraying gold. Water uptake was determined by weighing the changes of the cured disk samples with a diameter of 10.0 mm and a thickness of 4.00 mm before and after immersion in deionized water at  $25^{\circ}\text{C}$  for 7 days.

### *S1.3. Synthesis of 6FBE*

The synthetic route of 2,2-bis(4-ethynylphenyl)hexafluoropropane (6FBE) shown in Scheme S1.

#### *S1.3.1. Synthesis of 2,2-Bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane (1)*

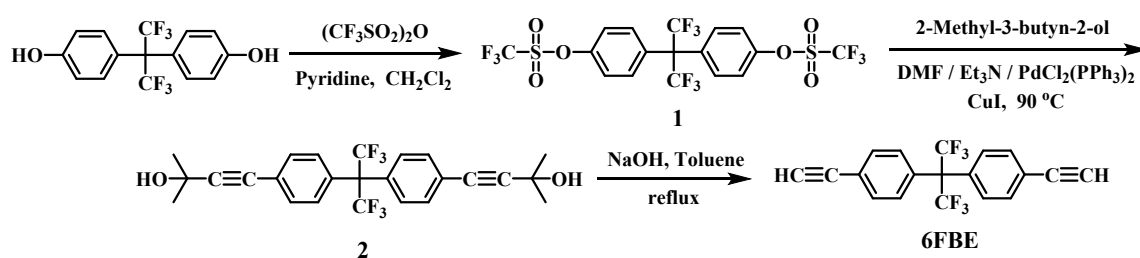
Bisphenol AF (30 g, 0.090 mol), pyridine (16 g, 0.20 mol) and  $\text{CH}_2\text{Cl}_2$  (300 mL) were added to a flame-dried 500 mL three-necked round-bottom flask under the nitrogen atmosphere and cooled to  $-5^{\circ}\text{C}$ . A mixture of trifluoromethanesulfonic anhydride (55 g, 0.20 mol) and

CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added dropwise to the flask at -5°C. After stirring at the temperature for 0.5 h, the reaction mixture was allowed to warm to room temperature and maintained at 12 h. The mixture was poured into 400 mL of 10% aqueous hydrochloric acid. The organic phase was separated and then washed by brine three times, dried over anhydrous MgSO<sub>4</sub>, and concentrated by rotary evaporation. The crude product was recrystallized with hexane to obtain 51 g (95% yield) of **1** as a white crystalline solid (m.p. 97-98°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.34 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.48 (d, *J* = 8.8 Hz, 4H, Ar-H). IR (KBr, cm<sup>-1</sup>): 1510 (s, Ar), 1211-1142 (s, CF<sub>3</sub>), 896 (s, triflates). HRMS (EI, *m/z*): 599.9581 [M + H]<sup>+</sup>, calcd for C<sub>17</sub>H<sub>8</sub>O<sub>6</sub>F<sub>12</sub>S<sub>2</sub>, 599.9571.

### *SI.3.2. Synthesis of 2,2-bis(4-ethynylphenyl)hexafluoropropane (6FBE)*

**1** (36 g, 0.060 mol) was dissolved into 200 mL Et<sub>3</sub>N/DMF (1:1, vol) solution under the nitrogen atmosphere in a flask. The solution was stirred and degassed for 30 min at 90°C, then cooled to room temperature. PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.1 g, 1.6 mmol) and CuI (0.60 g, 3.1 mmol) were added to the flask. Then 2-methyl-3-butyn-2-ol (17 g, 0.20 mol) was added dropwise into the flask under a nitrogen atmosphere. The reaction mixture was heated to 90°C and maintained for 16 h. After the completion of the reaction, the mixture was poured into water and extracted with dichloromethane, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated by rotary evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/petrol ether (1:2, vol) as an eluent and then recrystallized with ethyl acetate/petrol ether to obtain 23 g (80% yield) of intermediate **2** as a white crystalline solid (m.p. 164-165°C). The intermediate **2**, sodium hydroxide (6.0 g, 0.15 mol) and toluene (200 mL) were added into the flask under a nitrogen atmosphere, the mixture was heated to reflux and maintained for 14 h.

After the completion of the reaction, the mixture was filtered and the solvent was removed, the crude product was purified by column chromatography through silica gel using petrol ether as an eluent to afford 16 g (95% yield) of 6FBE as a pale-yellow solid (m.p. 37-38°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.16 (s, 2H, ≡C-H), 7.35 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.51 (d, *J* = 8.8 Hz, 4H, Ar-H). IR (KBr, cm<sup>-1</sup>): 3304 (s, ≡C-H), 2111 (w, C≡C), 1509 (s, Ar), 1253-1170 (s, CF<sub>3</sub>). HRMS (EI, *m/z*): 352.0692 [M + H]<sup>+</sup>, calcd for C<sub>19</sub>H<sub>10</sub>F<sub>6</sub>, 352.0687.



**Scheme S1.** Synthesis of 2,2-bis(4-ethynylphenyl)hexafluoropropane (6FBE).

#### *SI.4. Synthesis of 6FOBE*

The synthetic route of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane (6FOBE) shown in Scheme S2.

##### *SI.4.1. Synthesis of 2,2-bis[4-(4-iodophenoxy)phenyl]hexafluoropropane (3)*

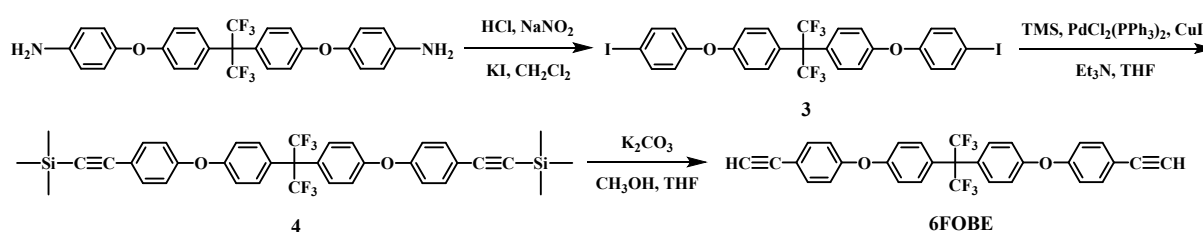
2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (52 g, 0.10 mol), concentrated hydrochloric acid (200 mL, 2.4 mol), and ice water (200 mL) were added to 1000 mL flask, and were stirred and cooled to -15°C. Then, a 50 mL aqueous solution of sodium nitrite (21 g, 0.30 mol) was added dropwise to the flask and kept the temperature under -5°C. In the end, the slurry changed to an orange clear solution. The solution was stirred for an additional 1 h below 0°C, and then 40 mL aqueous solution of urea (9.0 g, 0.15 mol) was added dropwise to

neutralize excess nitrous acid. The resulting solution was added dropwise to a mixture of potassium iodide (66 g, 0.40 mol), dichloromethane (200 mL) and water (100 mL). The reaction mixture was stirred at room temperature for 16 h. After the completion of the reaction, saturated sodium sulfite solution was added. The organic phase was separated and washed with water, dried over anhydrous  $\text{MgSO}_4$ , and concentrated by rotary evaporation. The crude product was purified through silica gel column chromatography using dichloromethane/petrol ether (1:10, vol) as eluent, and then recrystallized with petrol ether to obtain 63 g (85% yield) of **3** as a white crystalline solid (m.p. 128-130°C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.83 (d,  $J = 8.8$  Hz, 4H, Ar-H), 6.96 (d,  $J = 8.8$  Hz, 4H, Ar-H), 7.35 (d,  $J = 8.8$  Hz, 4H, Ar-H), 7.66 (d,  $J = 8.8$  Hz, 4H, Ar-H). IR (KBr,  $\text{cm}^{-1}$ ): 1510, 1481 (s, Ar), 1248-1174 (s,  $\text{CF}_3$ ), 1002 (m, C-O-C), 493 (s, C-I). HRMS (EI,  $m/z$ ): 739.9149  $[\text{M} + \text{H}]^+$ , calcd for  $\text{C}_{27}\text{H}_{16}\text{F}_6\text{I}_2\text{O}_2$ , 739.9144.

#### *SI.4.2. Synthesis of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane (6FOBE).*

**3** (60 g, 0.080 mol) was dissolved into 600 mL  $\text{Et}_3\text{N}/\text{THF}$  (1:1, vol) solution in a flask under the nitrogen atmosphere. The produced solution was stirred and degassed for 30 min at 70°C, and then cooled to room temperature. After  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.85 g, 1.2 mmol) and  $\text{CuI}$  (0.46 g, 2.4 mmol) were added to the flask, trimethylsilylacetylene (24 g, 0.24 mol) was added dropwise at room temperature. The reaction mixture was maintained at 25°C for 16 h. After the completion of the reaction, the resulting mixture was filtered and the filtrate was concentrated. The residue was purified through column chromatography on silica gel using ethyl acetate /petrol ether (1:40, vol) as eluent to obtain 52 g (95% yield) of **4** as a light-yellow solid. The intermediate **4**, anhydrous potassium carbonate (32 g, 0.23 mol), methanol (150 mL), and THF (200 mL) were added into the flask under nitrogen atmosphere, the mixture was stirred at room

temperature for 8 h. After the completion of the reaction, the mixture was filtered and the solvent was removed, the crude product was purified through column chromatography on silica gel using ethyl acetate /petrol ether (1:40, vol) as an eluent to afford 39 g (95% yield) of 6FOBE as a white solid (m.p. 57-59°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.06 (s, 2H, ≡C-H), 6.98-7.02 (m, 8H, Ar-H), 7.37 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.50 (d, *J* = 8.4 Hz, 4H, Ar-H). IR (KBr, cm<sup>-1</sup>): 3295 (s, ≡C-H), 2108 (m, C≡C), 1596, 1501 (s, Ar), 1258-1174 (s, -CF<sub>3</sub>), 1017 (m, C-O-C). HRMS (EI, *m/z*): 536.1216 [M + H]<sup>+</sup>, calcd for C<sub>31</sub>H<sub>18</sub>F<sub>6</sub>O<sub>2</sub>, 536.1211.



**Scheme S2.** Synthesis of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane (6FOBE).

### S1.5. Synthesis of 12FOBE

The synthetic route of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane (12FOBE) shown in Scheme S3.

#### S1.5.1. Synthesis of 2,2-bis[4-(2-trifluoromethyl-4-iodophenoxy)phenyl]hexafluoropropane (5).

Bisphenol AF (50 g, 0.15 mol), 1-fluoro-4-iodo-2-(trifluoromethyl)benzene (87 g, 0.30 mol), cesium carbonate (147 g, 0.45 mol) and DMF (600 mL) were added to a flame-dried 1000 mL flask under the nitrogen atmosphere, and the mixture was heated at 110°C for 12 h under stirring. Then the mixture was cooled to room temperature and poured into ice water to get crude product. After filtering and drying in a vacuum oven, the crude product was purified

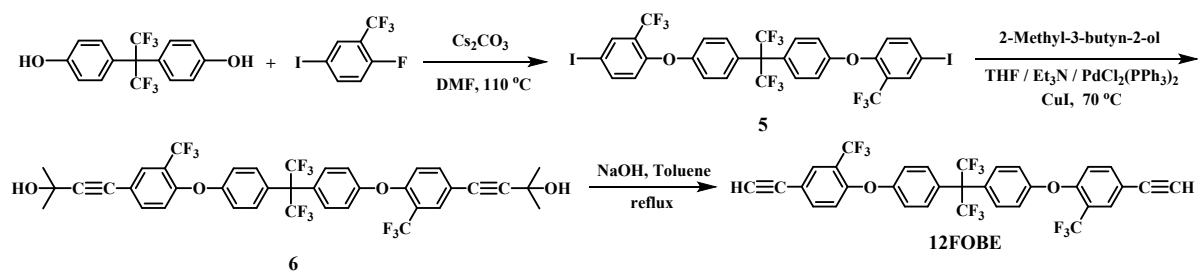
through column chromatography on silica gel using petrol ether as the eluent to afford 125 g (95% yield) of **5** as a white solid (m.p. 92-93°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.80 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.2 Hz, 4H, Ar-H), 7.40 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.80 (dd, *J* = 1.6, 2.0 Hz, 2H, Ar-H), 7.99 (d, *J* = 2.0 Hz, 2H, Ar-H). IR (KBr, cm<sup>-1</sup>): 1510, 1479 (s, Ar), 1311 (s, Ar-CF<sub>3</sub>), 1052 (s, C-O-C), 523 (s, C-I). HRMS (EI, *m/z*): 875.8902 [M + H]<sup>+</sup>, calcd for C<sub>29</sub>H<sub>14</sub>F<sub>12</sub>I<sub>2</sub>O<sub>2</sub>, 875.8892.

*SI.5.2. Synthesis of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane (12FOBE).*

**5** (88 g, 0.10 mol) was dissolved into 600 mL Et<sub>3</sub>N/THF (1:2, vol) solution under the nitrogen atmosphere. The solution was stirred and degassed for 30 min at 70°C, then PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.5 g, 2.2 mmol) and CuI (0.84 g, 4.4 mmol) were added to the flask. 2-Methyl-3-butyn-2-ol (25 g, 0.30 mol) was added dropwise into the mixture in the flask under a nitrogen atmosphere. The reaction mixture was heated to 70°C and maintained for 16 h. After the completion of the reaction, the resulting mixture was filtered and the filtrate was concentrated. The product was purified through column chromatography on silica gel using ethyl acetate/petrol ether (1:3, vol) as eluent, and then recrystallized with ethyl acetate/petrol ether to obtain 73 g (92% yield) of **6** as a white solid. The intermediate **6**, sodium hydroxide (12 g, 0.29 mol) and toluene (400 mL) were added into the flask under a nitrogen atmosphere, and heated to reflux and maintained for 14 h. After the completion of the reaction, the mixture was filtered and the solvent was removed. The crude product was purified through column chromatography on silica gel using petrol ether as eluent to afford 59 g (96% yield) of 12FOBE as a white solid (m.p. 73-75°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.12 (s, 2H, ≡C-H), 6.97 (d, *J* = 8.8 Hz, 2H,



Ar-H), 7.04 (d,  $J = 9.2$  Hz, 4H, Ar-H), 7.41 (d,  $J = 8.8$  Hz, 4H, Ar-H), 7.60 (dd,  $J = 1.6, 2.0$  Hz, 2H, Ar-H), 7.82 (d,  $J = 1.6$  Hz, 2H, Ar-H). IR (KBr,  $\text{cm}^{-1}$ ): 3307 (s,  $\equiv\text{C-H}$ ), 2113 (w,  $\text{C}\equiv\text{C}$ ), 1607, 1490 (s, Ar), 1323 (s, Ar- $\text{CF}_3$ ), 1054 (s, C-O-C). HRMS (EI,  $m/z$ ): 672.0961 [ $\text{M} + \text{H}$ ] $^+$ , calcd for  $\text{C}_{33}\text{H}_{16}\text{F}_{12}\text{O}_2$ , 672.0959.



**Scheme S3.** Synthesis of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane (12FOBE).

## S2. The solubility of the PFSA, PFOSA and PTFOSA

**Table S1.** The solubility of the PFSA, PFOSA and PTFOSA.

Solvent	<i>n</i> -Hexane	EtOH	Toluene	$\text{CH}_2\text{Cl}_2$	$\text{CCl}_3$	DMF	DMSO	THF	EtOAc
PFSA	-	-	++	++	++	++	++	++	++
PFOSA	-	-	++	++	++	++	++	++	++
PTFOSA	-	-	++	++	++	++	++	++	++

Note: “+ +”: soluble; “+”: partially soluble; “-”: insoluble.

## S3. The MALDI-TOF-MS spectra of the PFSA, PFOSA and PTFOSA

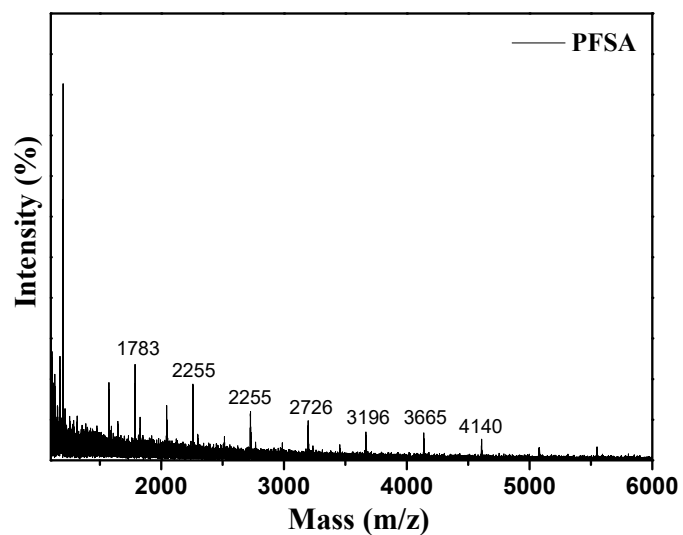


Figure S1. MALDI-TOF-MS of PFSA resin.

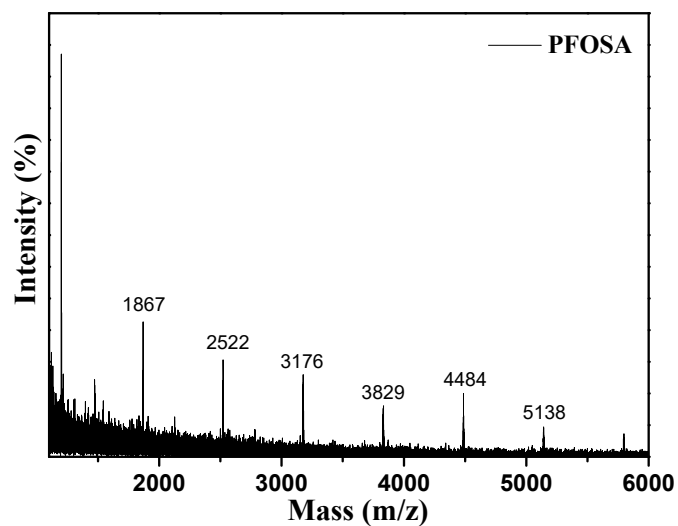


Figure S2. MALDI-TOF-MS of PFOSA resin.

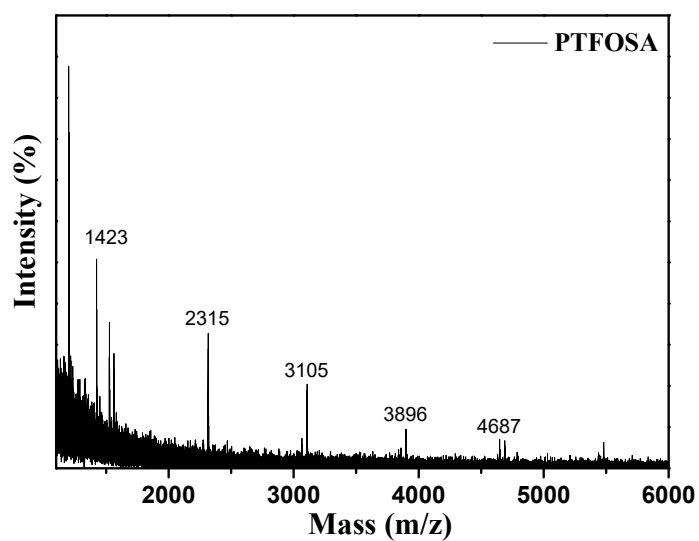


Figure S3. MALDI-TOF-MS of PTFOSA resin.

#### S4. The apparent curing reaction activation energy of PFOSA and PTFOSA resins

The DSC curves of PFOSA and PTFOSA resins at different heating rates are shown in Fig. S4(a) and Fig. S5(a), respectively. The apparent activation energy was calculated by Kissinger (1) and Ozawa (2) methods:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (\text{S1})$$

$$\ln \beta = -1.052 \frac{E_a}{RT_p} + C \quad (\text{S2})$$

where  $\beta$  is the heating rate,  $E_a$  is the apparent activation energy,  $R$  is the universe gas constant,  $A$  is the pre-exponential factor, and  $T_p$  is the exothermic peak temperature of the curing reaction. Hence, the activation energy ( $E_a$ ) and pre-exponential factors ( $A$ ) can be acquired from the slope and the intercept of the linear plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  and the linear plot of  $\ln(\beta)$  versus  $1/T_p$  (see Fig. S4(b) and Fig. S5(b)).

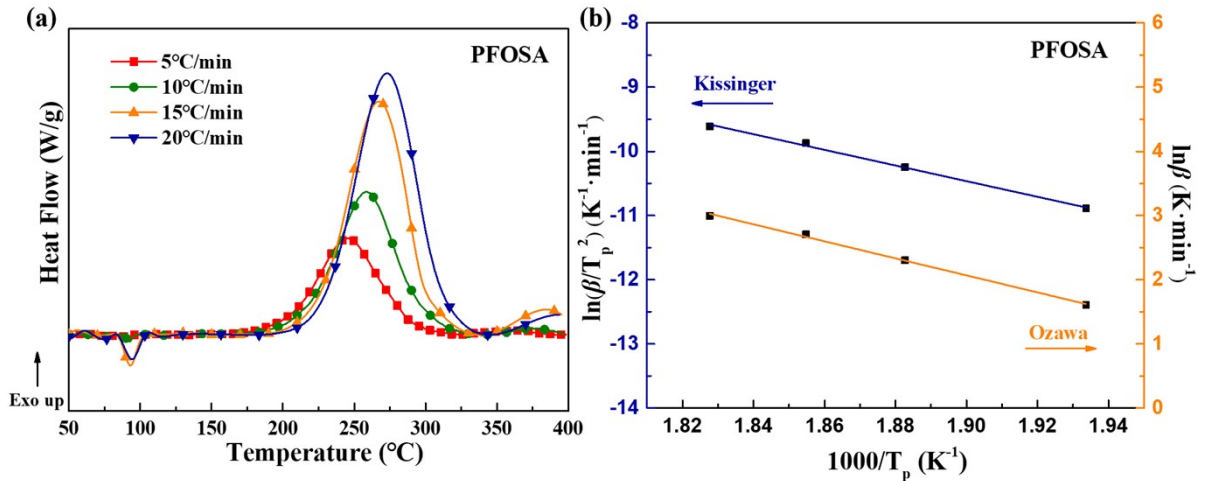
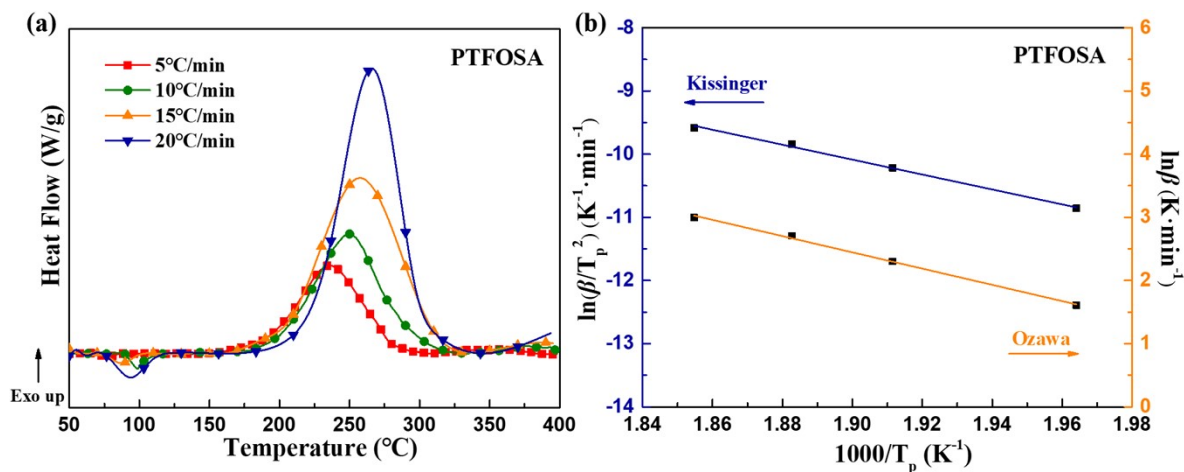


Figure. S4. (a) DSC curves of PFOSA at different heating rates. (b)  $\ln(\beta/T_p^2)$  and  $\ln(\beta)$  versus  $1000/T_p$

plots for the curing of PFOSA.

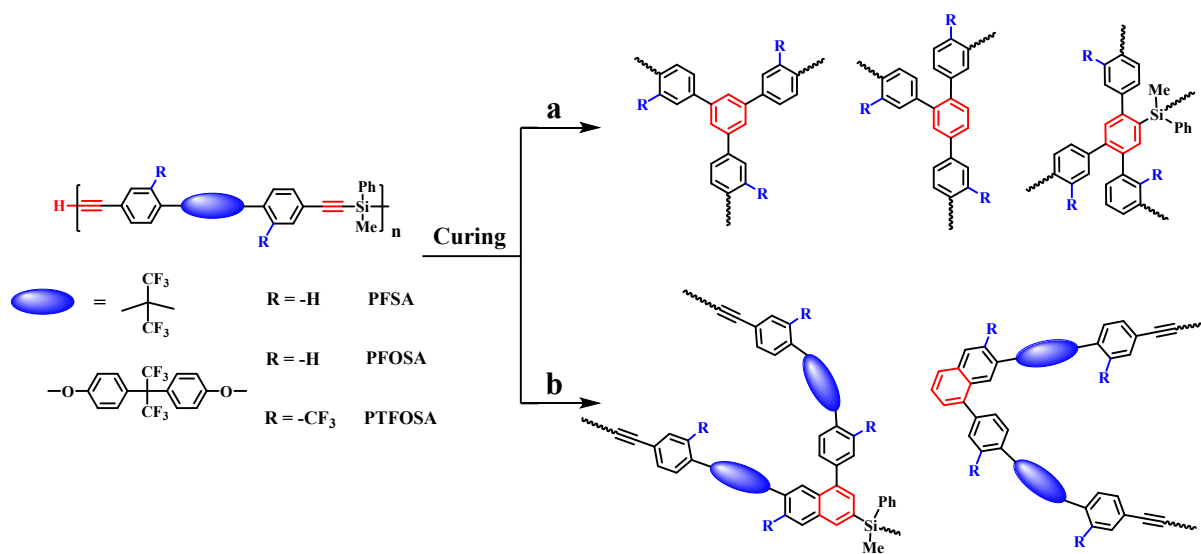


**Figure. S5.** (a) DSC curves of PTFOSA at different heating rates. (b)  $\ln(\beta/T_p^2)$  and  $\ln(\beta)$  versus  $1000/T_p$  plots for the curing of PTFOSA.

**Table S2.** The apparent activation energies for the curing reactions of the PFSA, PFOSA and PTFOSA.

Resins	$E_a/(\text{kJ}\cdot\text{mol}^{-1})$	
	Kissinger method	Ozawa method
PFSA	95.7	99.2
PFOSA	101	105
PTFOSA	98.2	102

### S5. The curing reactions of PFSA, PFOSA and PTFOSA at high temperature



**Figure S6.** The curing reactions of PFSA, PFOSA and PTFOSA: (a) the cyclotrimerization of C≡C group,  
(b) the Diels-Alder reaction between Ph-C≡C and C≡C.

### S6. The conversion rate of the acetylene groups ( $\alpha$ ) of the resins at different temperatures

To analyze the absorption intensity changes of -C≡C- groups before and after thermal crosslinking, some absorptions are normalized and the conversion rate of the acetylene groups ( $\alpha$ ) of the resins at different temperatures is determined as follows:

$$\alpha(\%) = \left[ 1 - \frac{(Ai / Ar)_T}{(Ai / Ar)_{T=25^\circ\text{C}}} \right] \times 100 \quad (\text{S3})$$

where T is the curing temperature,  $Ai$  is the integrated intensity of the specified peak, and  $Ar$  is the integrated intensity of the internal standard peak. The intensity of the absorption peaks for C-F at 1252-1173  $\text{cm}^{-1}$  and 1323  $\text{cm}^{-1}$  in the cured resins have no changes during the thermal crosslinking, they can be used as an internal standard to calculate the conversion rate ( $\alpha$ ) of the terminal acetylene ( $\equiv\text{C-H}$ , 3303  $\text{cm}^{-1}$ ) and internal acetylene (-C≡C-, 2165  $\text{cm}^{-1}$ ).

### S7. Wave-transparent model of single-layer thin-walled plate

During the propagation of electromagnetic waves, reflection, energy loss, and transmission occur at interfaces between the dielectrics and air. the relationship between reflection coefficient ( $R$ ), energy loss ( $A$ ), and wave transmission coefficient ( $T$ ) during transmittance of the electromagnetic wave are shown in Eqns. S4-6:

$$A = \frac{2\pi d \varepsilon \tan \delta}{\lambda (\varepsilon - \sin^2 \theta)^{1/2}} \quad (\text{S4})$$

$$\Gamma = \frac{(\varepsilon - \sin^2 \theta)^{1/2} - \varepsilon \cos \theta}{(\varepsilon - \sin^2 \theta)^{1/2} + \varepsilon \cos \theta} \quad (\text{S5})$$

$$|T|^2 = 1 - |\Gamma|^2 - A \quad (\text{S6})$$

where  $d$  is the thickness of the medium,  $\lambda$  is the wavelength of the electromagnetic wave,  $\theta$  is the angle of incidence on the surface of the medium,  $\varepsilon$  and  $\tan \delta$  represent respectively the values for the dielectric constant and dielectric loss tangent of materials.

### S8. The chemical structures of reported poly(silylene arylacetylene)s

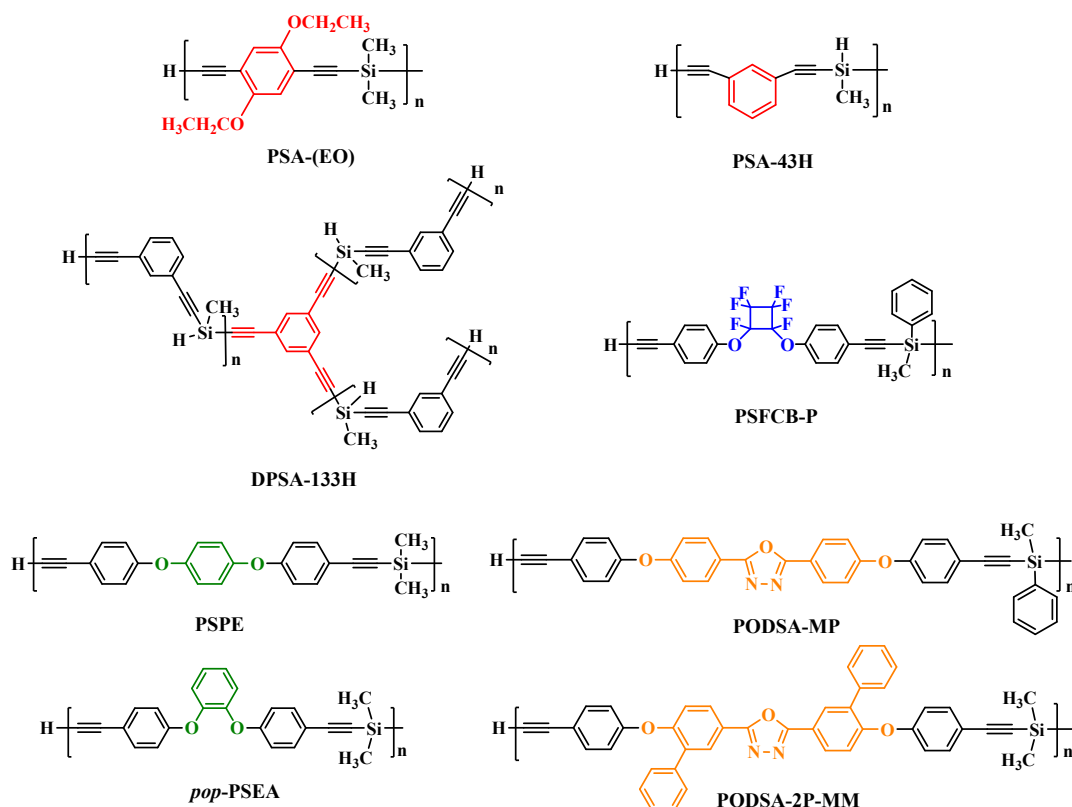


Figure S7. The chemical structures of reported poly(silylene arylacetylene)s.

### S9. A variety of figures collection for the structural characterization of diynes (6FBE, 6FOBE and 12FOBE) and their previous intermediates

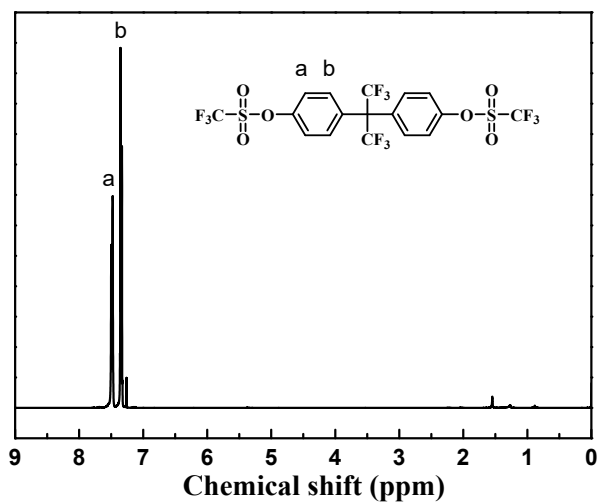


Figure S8.  $^1\text{H}$ -NMR spectra of 2,2-bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane.

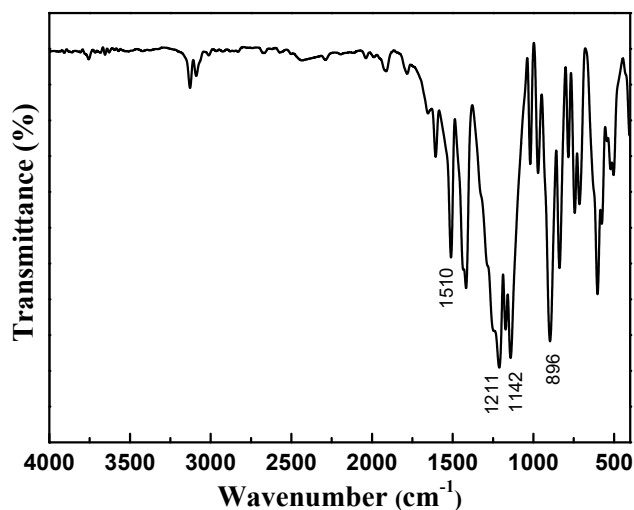


Figure S9. FT-IR spectra of 2,2-bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane.

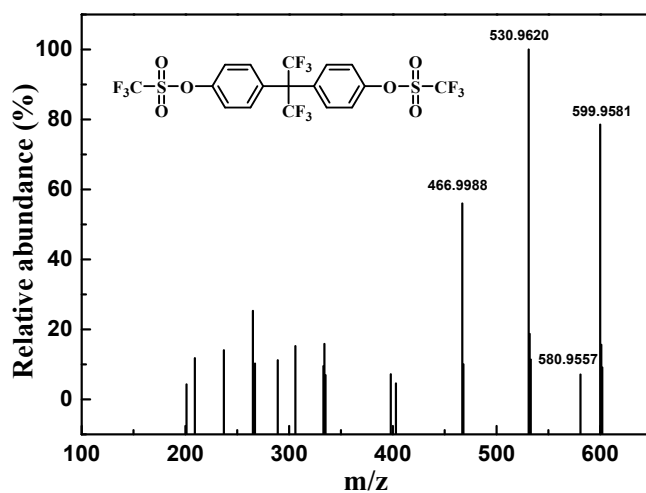


Figure S10. HRMS of 2,2-bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane.

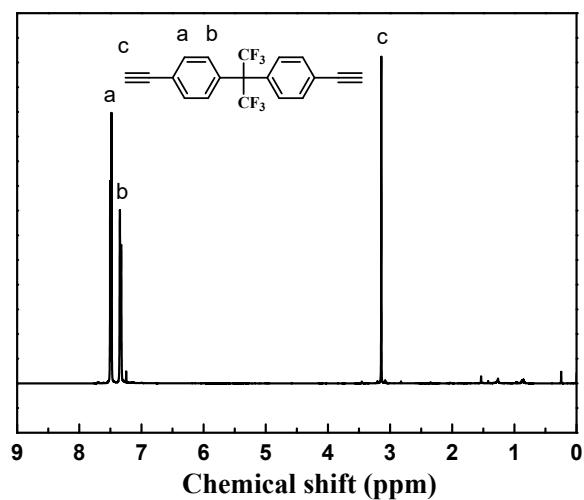


Figure S11.  $^1\text{H-NMR}$  spectra of 2,2-bis(4-ethynylphenyl)hexafluoropropane.

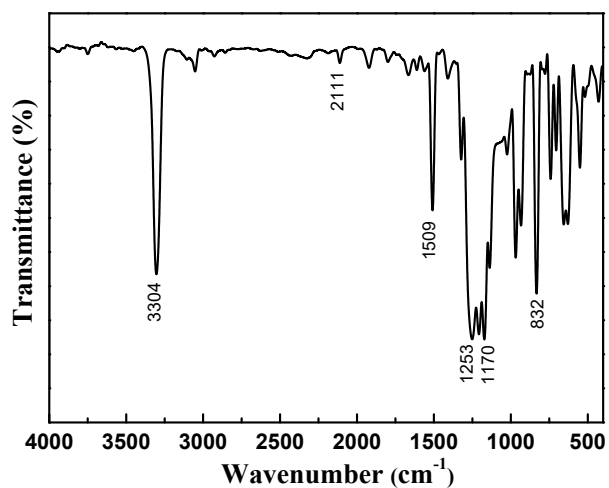


Figure S12. FT-IR spectra of 2,2-bis(4-ethynylphenyl)hexafluoropropane.

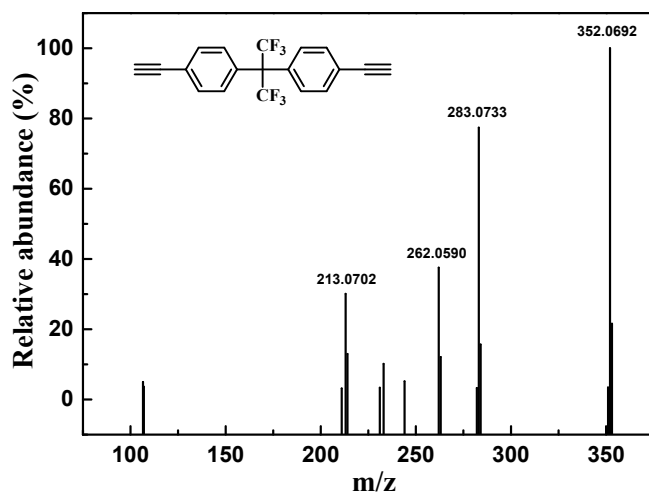


Figure S13. HRMS of 2,2-bis(4-ethynylphenyl)hexafluoropropane.



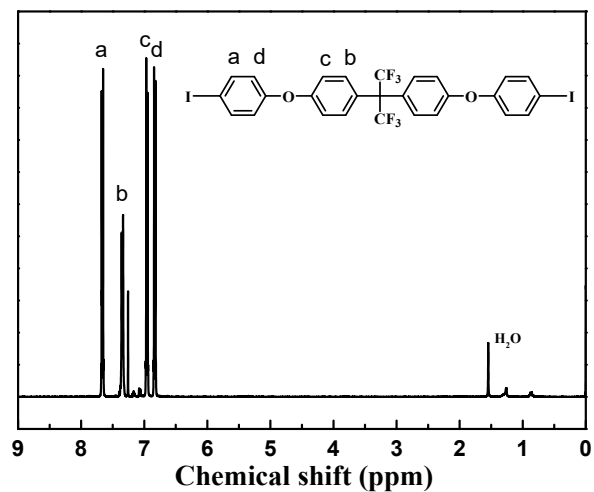


Figure S14. <sup>1</sup>H-NMR spectra of 2,2-bis[4-(4-iodophenoxy)phenyl]hexafluoropropane.

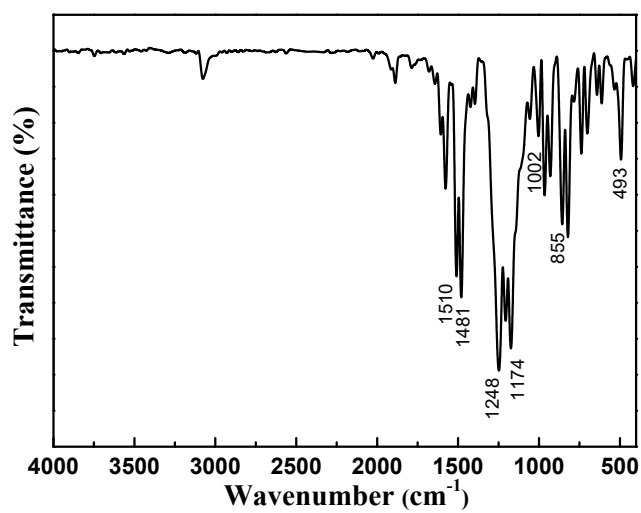


Figure S15. FT-IR spectra of 2,2-bis[4-(4-iodophenoxy)phenyl]hexafluoropropane.

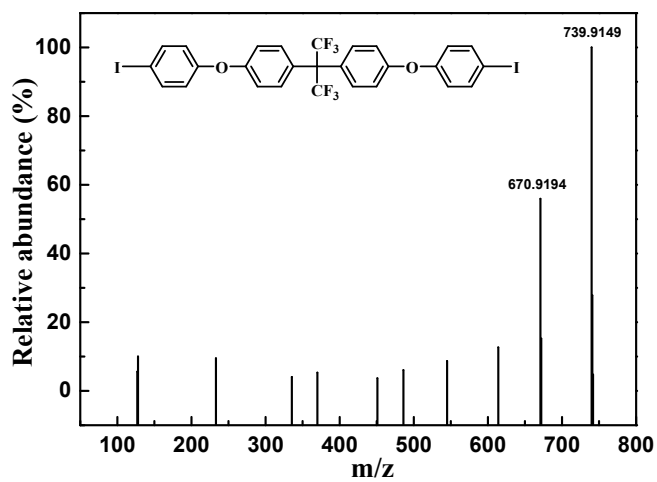


Figure S16. HRMS of 2,2-bis[4-(4-iodophenoxy)phenyl]hexafluoropropane.

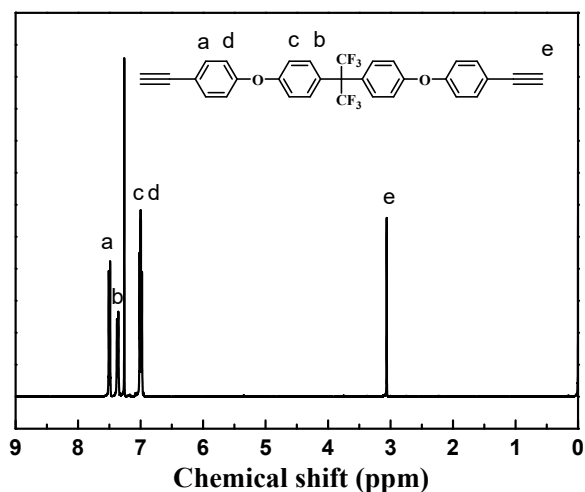


Figure S17.  $^1\text{H-NMR}$  spectra of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane.

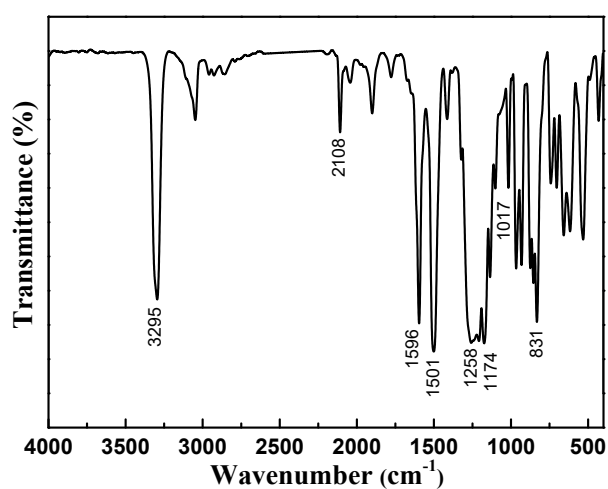


Figure S18. FT-IR spectra of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane.

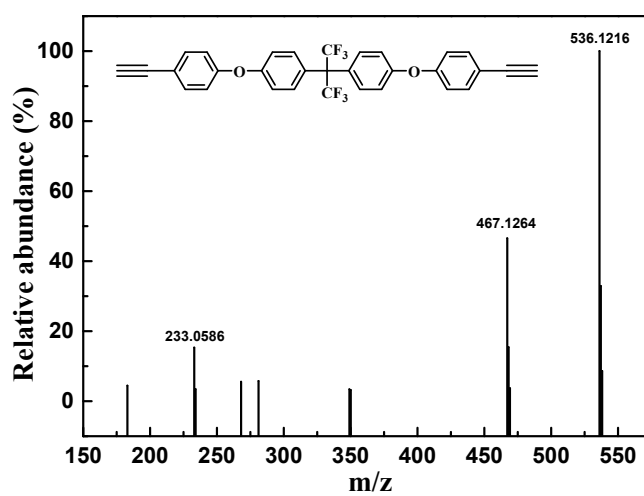


Figure S19. HRMS of 2,2-bis[4-(4-ethynylphenoxy)phenyl]hexafluoropropane.

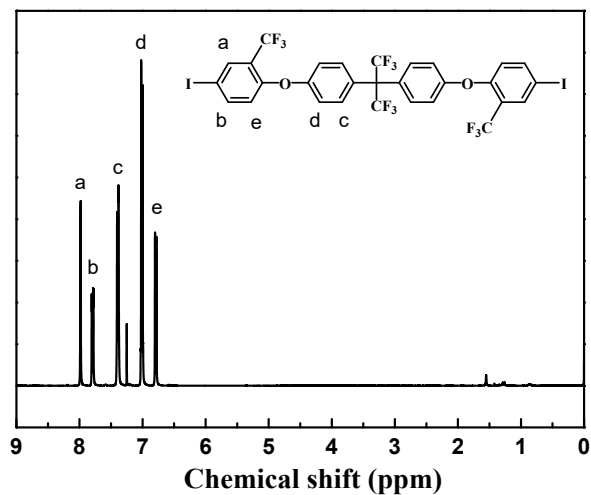


Figure S20.  $^1\text{H-NMR}$  spectra of 2,2-bis[4-(2-trifluoromethyl-4-iodophenoxy)phenyl]hexafluoropropane.

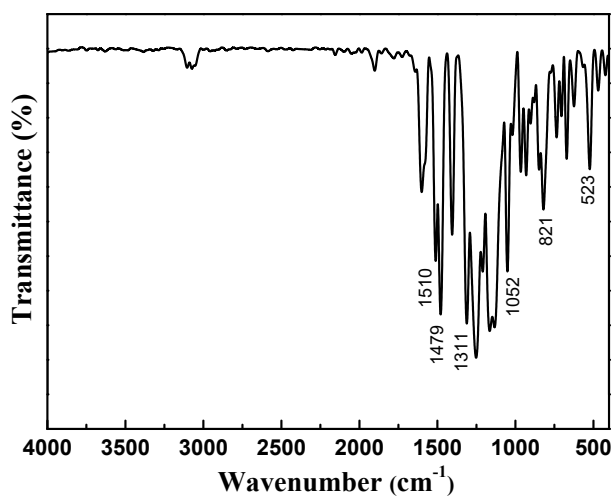


Figure S21. FT-IR spectra of 2,2-bis[4-(2-trifluoromethyl-4-iodophenoxy)phenyl]hexafluoropropane.

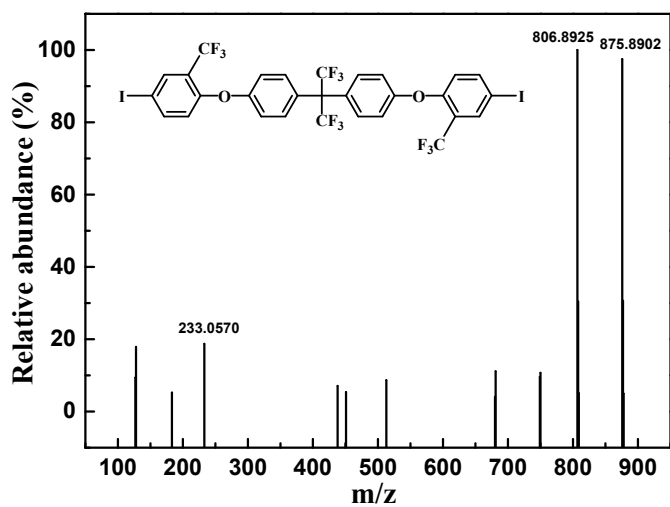
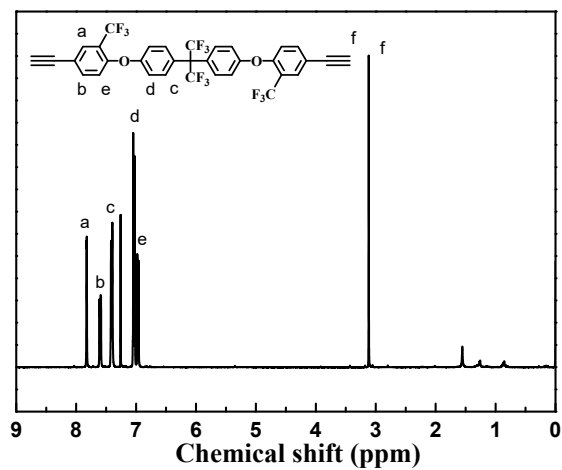
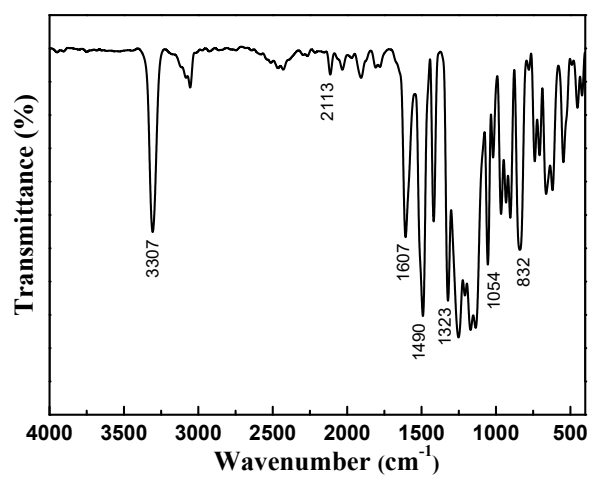


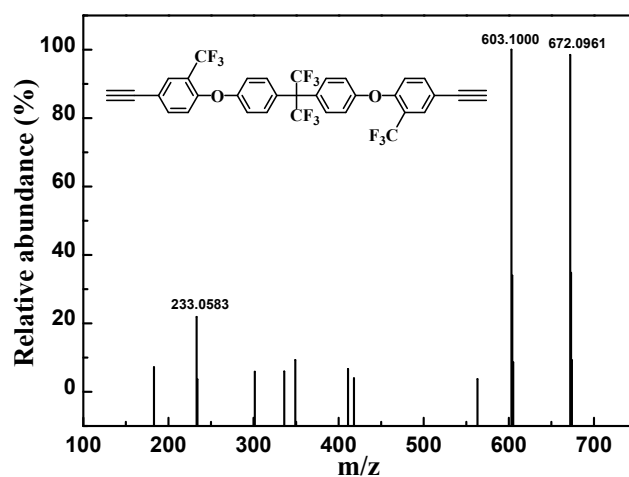
Figure S22. HRMS of 2,2-bis[4-(2-trifluoromethyl-4-iodophenoxy)phenyl]hexafluoropropane.



**Figure S23.**  $^1\text{H-NMR}$  spectra of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane.



**Figure S24.** FT-IR spectra of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane.



**Figure S25.** HRMS of 2,2-bis[4-(2-trifluoromethyl-4-ethynylphenoxy)phenyl]hexafluoropropane.