

Electronic Supplementary Information for

**“A spiro-centered thermopolymerizable fluorinated macromonomer:
synthesis and conversion to the high performance polymer”**

*Yuanqiang Wang, Yijie Luo, Kaikai Jin, Jing Sun and Qiang Fang**

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China.

1. EXPERIMENTAL SECTION

Materials: 1,2-Dibromo-tetrafluoroethane was purchased from Top Fluorochem Co., China and used without further purification. Spirophenol (**S-1**) and compound **1~2** (see scheme 1) were synthesized according to the previously reported procedures.^{1,2} THF was purified by distillation before use. Other solvents and reagents were purchased from TCI, Adamas and Adrich companies and used as received.

Instrumentation. ¹H NMR, ¹⁹F NMR and ¹³C NMR were measured on a Bruker AV400 instrument. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet spectrometer with KBr pellets. Mass spectrometry was performed on an Agilent Technologies 5973N and a Thermo Fisher Scientific LTQ FT Ultra, respectively. Differential scanning calorimetric (DSC) analysis was determined with a TA Instrument DSC Q200 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The contact angle of water on the film was characterized at the 20 °C on a dynamic contact angle measurement instrument (JC2000C) using a sessile drop method. Water

uptake was determined by weighing the change of the cured sample with a diameter of 1 cm and a thickness of 1.3 mm before and after keeping in boiling water for 72 h. Dielectric constant and dissipation factor were measured on cured cylindrical samples (average diameters were 10 mm and thicknesses were 2-3 mm, respectively) at room temperature using a 4294A Precision Impedance Analyser (Agilent). Thermogravimetric analysis (TGA) was measured on a TG 209F1 apparatus with a heating rate of 10 °C min⁻¹ under N₂. Thermomechanical analysis (TMA) was performed with a heating rate of 3 °C min⁻¹ in air on a Mettler Toledo TMA/SDTS 841e instrument. Surface toughness of cured **PD1** film was measured by atom force microscopy (AFM) on an environment control scanning probe microscope (Nanonavi E-sweep). The mechanical properties of cured films were measured on a nano-indenter system named as UNHT/NST (CSM Company).

Synthesis. *Synthesis of 1-(bromomethyl)-4-(1,1,2,2-tetrafluoroethoxy)benzene (compound 3).* To a solution of 1-(1,1,2,2-tetrafluoroethoxy)-4-methylbenzene (**2**, 27.50 g, 132.11 mmol) in CCl₄ (150 mL) was added NBS (4.70g, 26.40 mmol) and BPO (0.30g, 1.45 mmol) with vigorous stirring under N₂ at room temperature. The obtained mixture was heated to 80 °C and kept at the temperature for 2 h, followed by adding NBS (20.00 g, 112.30 mmol) in small portions. After addition, the mixture was stirred at the temperature until the feedstock disappeared (monitored by TLC). The mixture was cooled to room temperature, and the precipitate was filtered. The filtrate was poured to water (150 mL), and extracted with CHCl₃ (3 × 100 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and

filtrated. The filtrate was evaporated under reduced pressure to yield a yellow oil, which was purified by flash chromatography on SiO₂ gel using petroleum ether (60-90) as an eluent to afford compound **3** as a pale yellow oil in a yield of 82%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.40 (d, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 5.89 (tt, *J* = 53.1, 2.8 Hz, 1H), 4.44 (d, *J* = 23.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 139.01, 129.00, 124.51, 117.30, 113.20 (tt, *J* = 272.0, 28.9 Hz), 106.15 (tt, *J* = 252.0, 41.4 Hz), 45.83. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -88.34 (2F, d, *J* = 5.3 Hz), -136.70 (2F, dt, *J* = 52.9, 5.3 Hz). HR-MS (*m/z*): [M]⁺ Calcd for C₉H₇BrF₄O, 285.9616. Found 285.9619.

Synthesis of 1-(bromomethyl)-4-(trifluoroethenoxy)benzene (compound 4). A solution of *n*-BuLi (26.13 mL, 1.6 M in hexane, 41.8 mmol) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (9.41 mL, 55.74 mmol) in anhydrous THF (20 mL) with vigorous stirring at -78 °C under dry N₂. The resulting mixture was stirred at -78 °C for 5 min, then naturally warmed to room temperature and maintained at the temperature for 20 min, and cooled to -78 °C again. The freshly prepared lithium 2,2,6,6-tetramethylpiperidine (LTMP) was thus obtained, which was added through syringe to a solution of compound **3** (8.00 g, 27.87 mmol) in THF (30 mL) at -78 °C. The mixture was stirred for an additional 10 min, quenched with saturated aq. NaHCO₃ solution (100 mL), and extracted with hexane (3 × 150 mL). The obtained organic phase was combined, washed with brine (3 × 200 mL), dried over anhydrous Na₂SO₄, and filtered. After evaporation of the solvent, the crude product was purified through column chromatography on silicon gel using *n*-hexane

as the eluent. Compound **4** was obtained as light yellow oil in a yield of 79 %. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.39 (d, 2H), 7.12 (d, 2H), 5.04 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm): δ 143.96, 137.58 (td, $J = 223.5, 218.8, 49.1$ Hz), 127.69, 127.72 (dt, $J = 223.5, 218.8, 49.1$ Hz), 124.70, 113.01, 45.98. ^{19}F NMR (376 MHz, CDCl_3 , ppm): δ -115.34 (1F, dd), -121.06 (1F, dd), -126.81 (1F, dd). HR-MS (m/z): $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_6\text{BrF}_3\text{O}$, 265.9554. Found 265.9562.

Synthesis of trifluorovinyl ether macromonomer D₁. A mixture of compound **4** (9.42 g, 35.28 mmol), K_2CO_3 (6 g, 42.3 mmol), spirophenol **S-1** (2.40 g, 7.08 mmol) and DMF (100 mL) was stirred for 24 h at room temperature, and then poured into water (300 mL). The mixture was extracted with ethyl acetate (3×150 mL), and the organic layer was combined, washed with brine (3×200 mL), dried over anhydrous Na_2SO_4 , and filtered. After evaporation of the solvent, the residue was purified by recrystallization from methanol to give a white solid in a yield of 85%. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.45 (d, $J = 8.6$ Hz, 4H), 7.34 (d, $J = 8.6$ Hz, 4H), 7.09 (d, $J = 8.4$ Hz, 4H), 7.02 (d, $J = 8.4$ Hz, 4H), 6.74 (s, $J = 12.7$ Hz, 2H), 6.38 (s, 2H), 5.09 (s, 4H), 4.96 ~ 4.83 (m, 4H), 2.28 (d, $J = 13.0$ Hz, 2H), 2.13 (d, $J = 13.0$ Hz, 2H), 1.30 (s, $J = 4.9$ Hz, 6H), 1.29 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3 , ppm): δ 143.79, 139.00, 136.40, 136.00 (td), 134.60, 127.37, 126.10 (dt), 123.5, 112.72, 108.97, 107.12, 76.86, 67.67, 66.01, 54.64, 45.28, 44.35. ^{19}F NMR (376 MHz, CDCl_3 , ppm): δ -119.35 ~ -119.87 (2F, dd), -126.25 ~ -126.90 (2F, dd), -133.70 ~ -134.15 (2F, dd). HR-MS (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{57}\text{H}_{44}\text{F}_{12}\text{O}_8$, 1084.2845, Found 1084.2845. Anal. Calcd for $\text{C}_{57}\text{H}_{44}\text{F}_{12}\text{O}_8$: C, 63.10; H, 4.09; F, 21.01. Found: C, 63.35; H, 4.24; F, 19.81.

Preparation of cured samples. Monomer **D**₁ (about 1.00 g) was placed in a flat bottom tube with a diameter of 10 mm. The tube was placed into a quartz tube furnace, which was heated to 150 °C, and kept at the temperature for 3 h. Then the furnace was maintained at 200 °C for 3 h and 250 °C for 3 h, respectively. The fully cured sample was thus obtained, which was then used for measurement of dielectric properties and TMA, as well as for the investigation of water uptake.

Preparation of PD1 Films for AFM and Nanoindentation/Scratch Tests

Monomer **D**₁ was treated in 1,3,5-trimethylbenzene at 180 °C for 5 h. The obtained oligomer solution was spin-coated on the silicon wafers, which were then placed into a quartz tube furnace and kept at 150 °C for 3 h, 200 °C for 3 h and 250 °C for 3 h, respectively. Full cured samples were thus obtained.

2. NMR spectra of the intermediates and the monomers

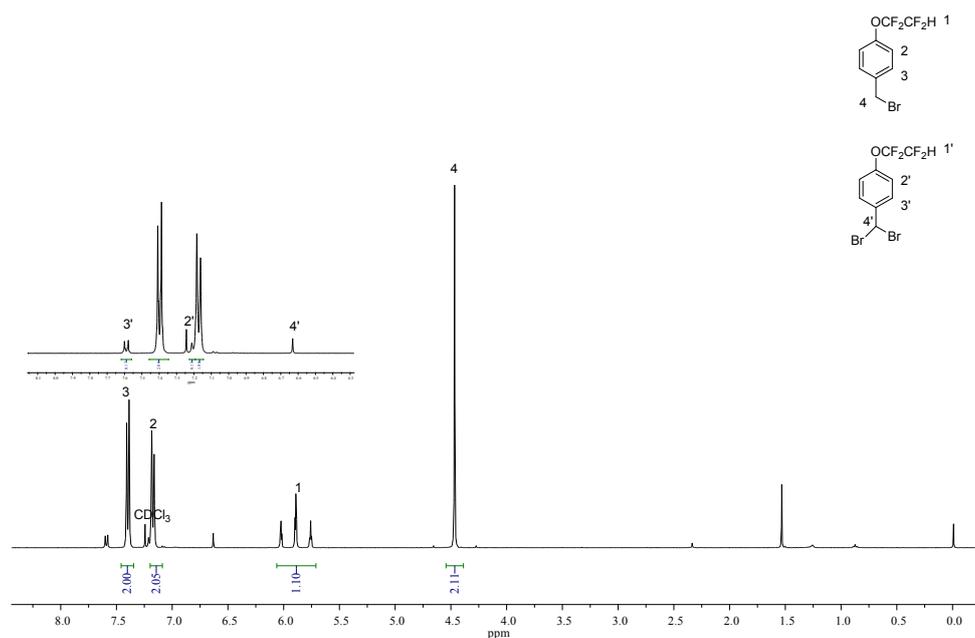


Fig. S1. ¹H NMR spectrum of compound **3** (400 MHz, CDCl₃).

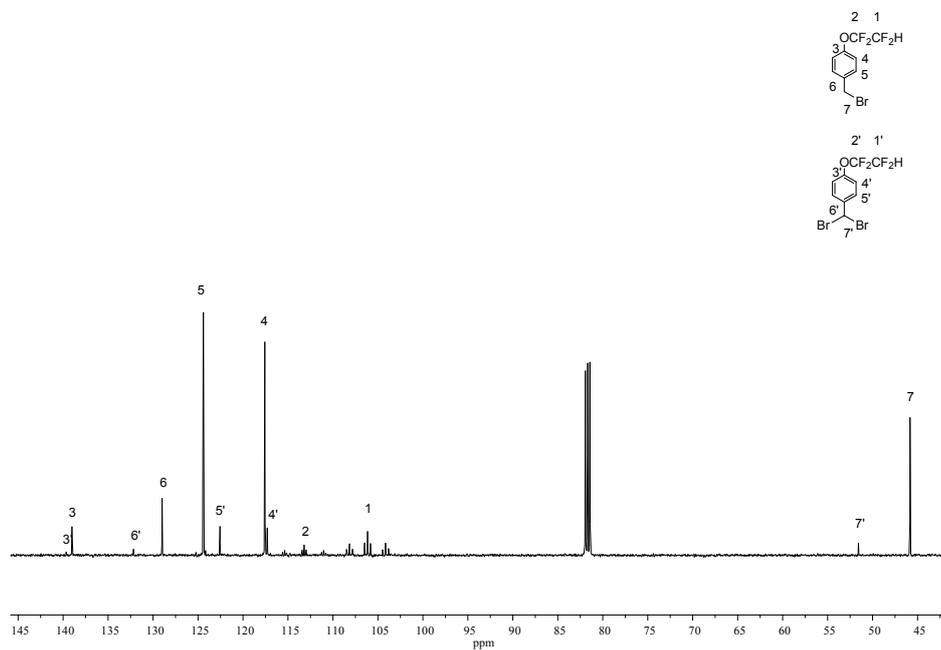


Fig. S₂. ^{13}C NMR spectrum of compound **3** (101 MHz, CDCl_3).

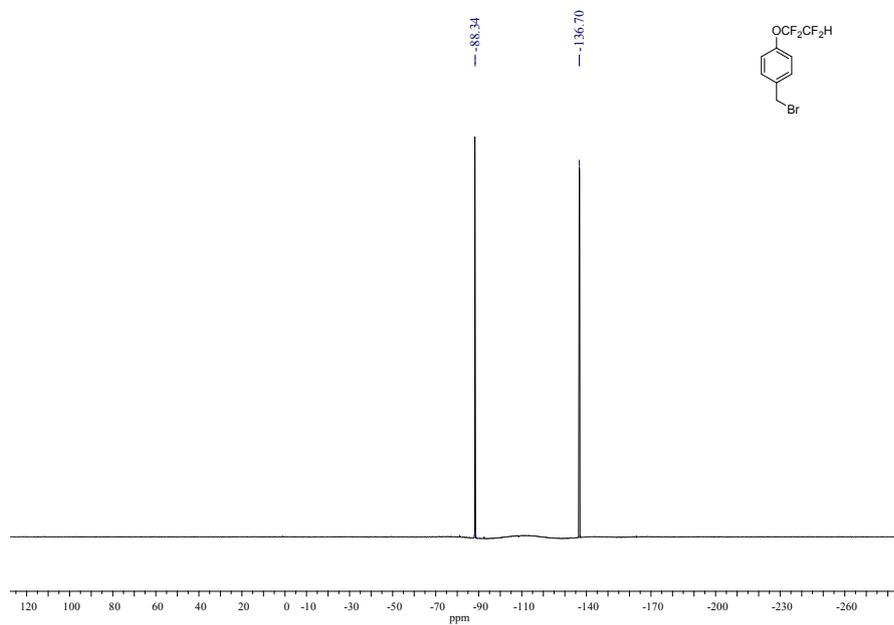


Fig. S₃. ^{19}F NMR spectrum of compound **3** (376 MHz, CDCl_3).

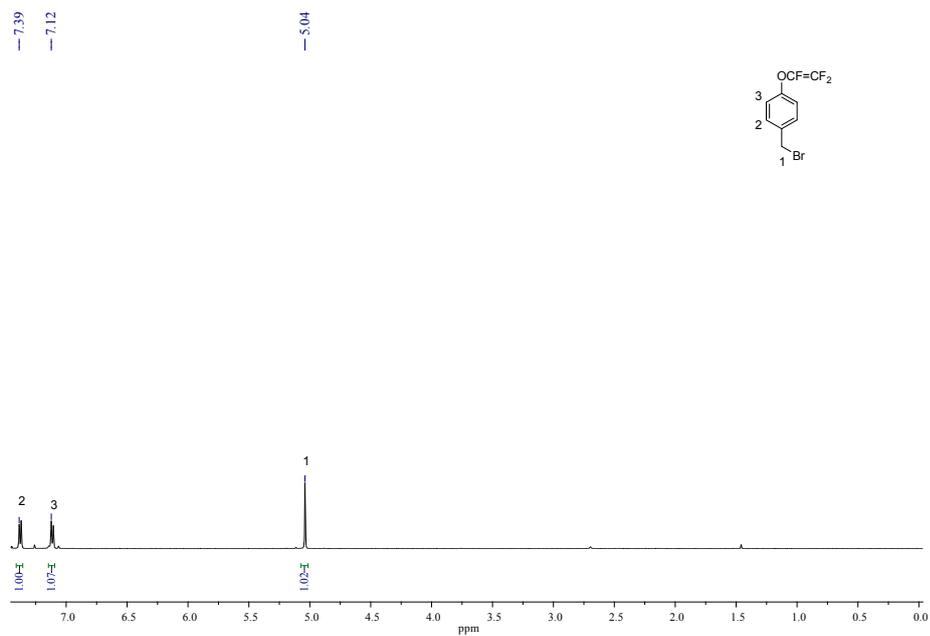


Fig. S4. ¹H NMR spectrum of compound **4** (400 MHz, CDCl₃).

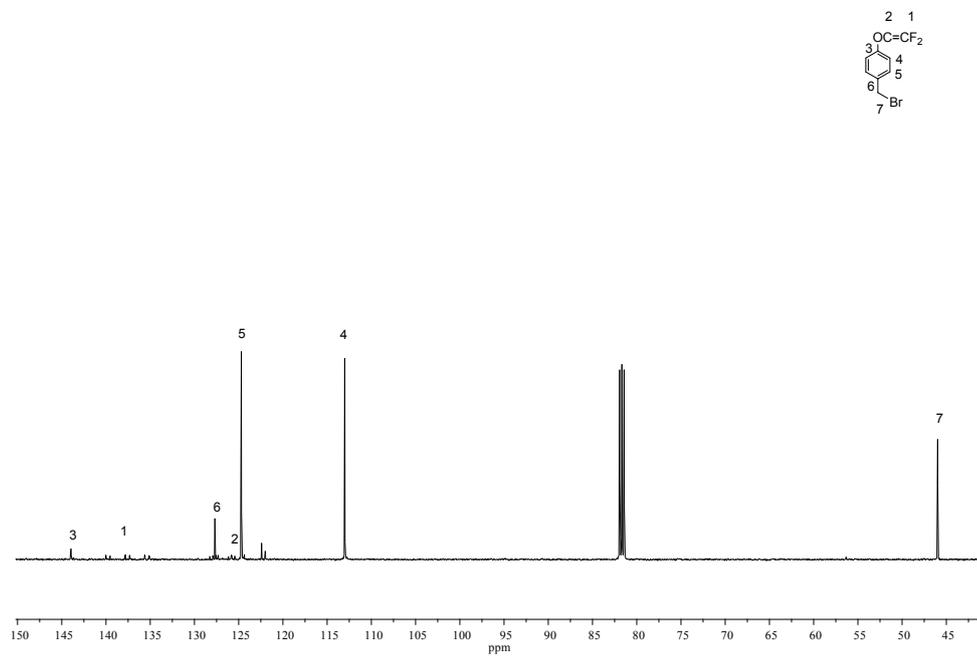


Fig. S5. ¹³C NMR spectrum of compound **4** (101 MHz, CDCl₃).

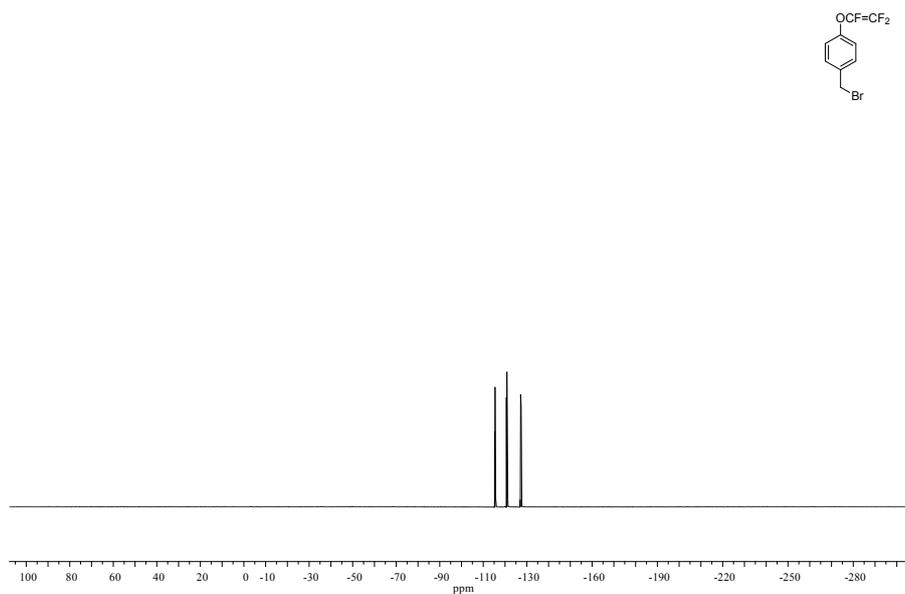


Fig. S6. ^{19}F NMR spectrum of compound **4** (376 MHz, CDCl_3).

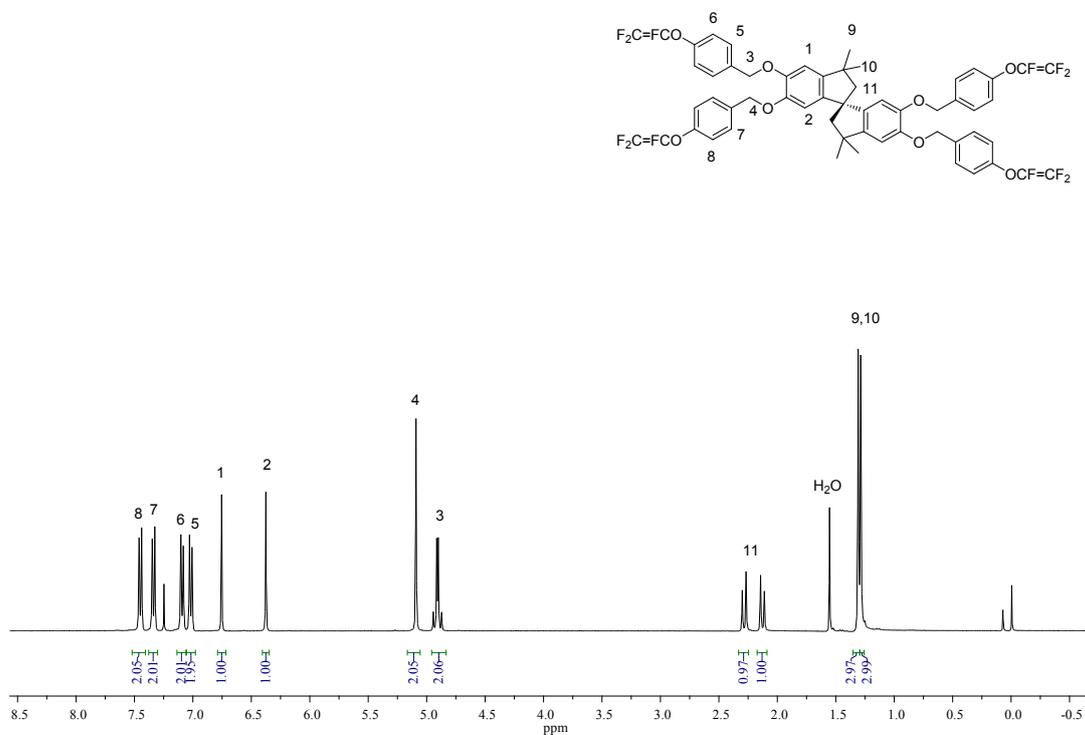


Fig. S7. ^1H NMR spectrum of **D₁** (400 MHz, CDCl_3).

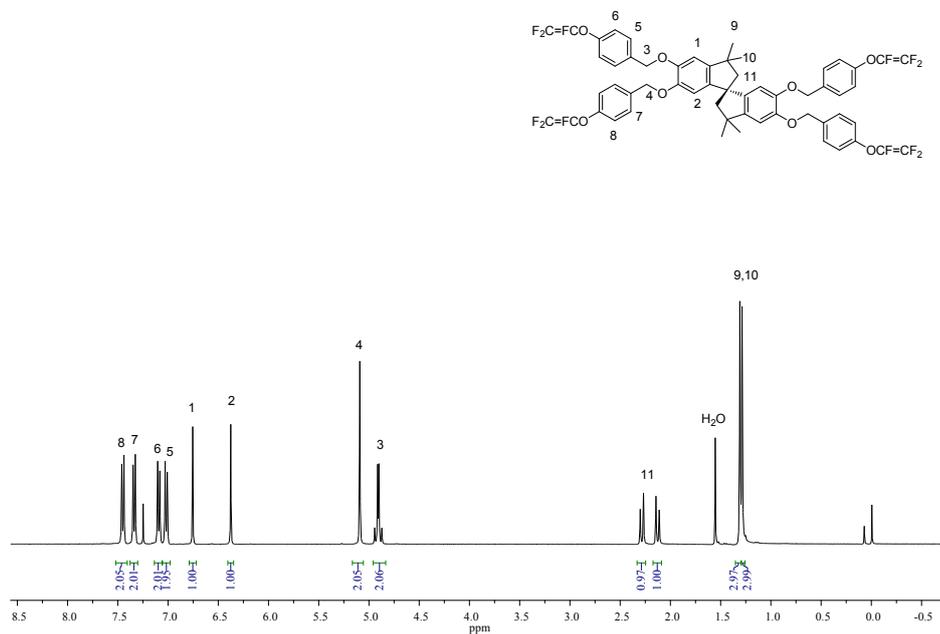


Fig. S8. ^{13}C NMR spectrum of **D1** (101 MHz, CDCl_3).

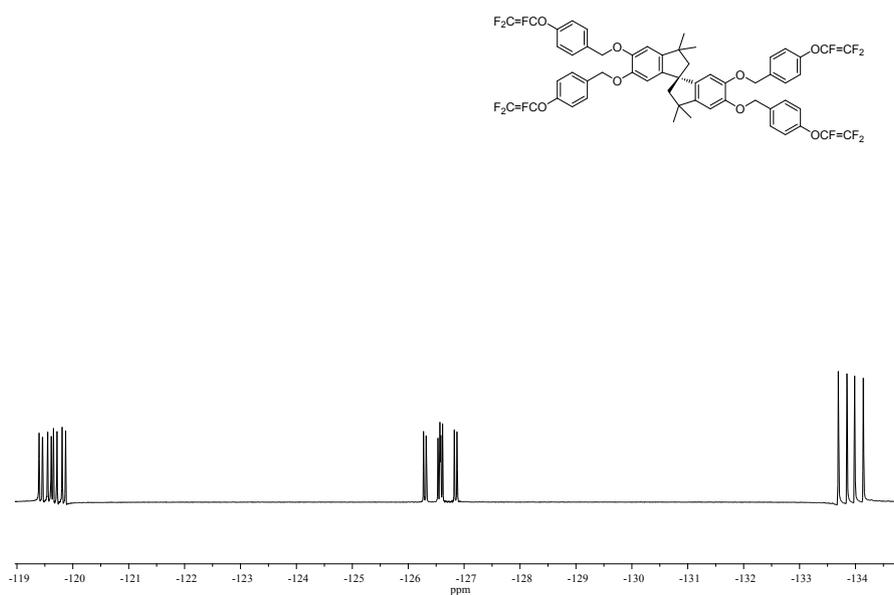


Fig. S9. ^{19}F NMR spectrum of **D1** (376 MHz, CDCl_3).

2. The nanoindentation/scratch tests of PD₁ films.

Table S1. Data of Hardness and Young's modulus of PD1 films

Test	1	2	3	4	5	6	7	8	9	mean
Hardness (GPa)	0.41	0.42	0.41	0.41	0.410	0.42	0.40	0.400	0.41	0.41
Young's Modulus (Gpa)	15.00	14.68	14.63	14.75	14.91	15.06	14.56	14.91	14.81	14.82

Table S2. Data of scratch tests of PD1 films.

Test	Critical Load (μN)	Penetration Depth At Critical Load (nm)	Scratch Width (μm)
1	1099.16	207.12	1.02
2	1177.15	244.82	1.21
3	1148.76	224.11	1.11
4	1158.75	226.00	1.12
5	1158.75	231.35	1.15

References

1. Fritsch, D.; Bengtson, G.; Carta, M.; McKeown, N. B. *Synthesis and Gas Permeation Properties of Spirobischromane-Based Polymers of Intrinsic Microporosity*. *Macromol. Chem. Phys.* **2011**, *212*, 1137-1146.

2. Luo, Y.; Jin, K.; He, C.; Wang, J.; Sun, J.; He, F.; Zhou, J.; Wang, Y.; Fang, Q. *An Intrinsically Microporous Network Polymer with Good Dielectric Properties at High Frequency*. *Macromolecules* **2016**, *49*, 7314-7321.