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Supporting Information

High-*k* Polymers of Intrinsic Microporosity: A New Class of High Temperature and Low Loss Dielectric for Printed Electronics

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Materials Characterization, Film Preparation, FET Fabrication, and Instrumentation Synthesis of SO₂-PIM

- 2. Broadband Dielectric Spectra of SO₂-PIM
- 3. *I–V* Curves for InSe-Based Field Effect Transistors

1. Experimental Section *Materials*

Pentafluorobenzene (PFB), 3-chloroperbenzoic acid (*m*-CPBA), diethyl disulfide, dimethylacetamide (DMAc), anhydrous potassium carbonate (K_2CO_3), and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) were purchased from Sigma-Aldrich. Organic solvents such as diethylether, toluene, and chloroform were purchased from Fisher Scientific. TTSBI was purified by recrystallization using chloroform and methanol.

Characterization, Film Preparation, FET Fabrication, and Instrumentation

¹H NMR spectroscopy was performed on a Varian Mercury 600 MHz spectrometer. The samples were dissolved in CDCl₃ or DMSO- d_6 using a 5 mm pulsed field gradient indirect detection probe. Molecular weights were determined by size-exclusion chromatography (SEC) using a Waters 515 HPLC and a Waters 2414 differential refractive index (RI) detector. Two Jordi Gel DVB columns (mixed bed, 5 µm pore size, 25 cm × 10 mm) were used with HPLC grade DMF as the mobile phase. Polystyrene standards were used for conventional calibration.

Polymer films were obtained by solution-casting from DMAc on gold-coated glass slides. The thickness of the film was controlled from ~200 nm to 8 μ m, depending on the concentration of the solution. The cast solution on the glass slide was placed on a flat surface in a vacuum oven, which was gradually pumped down over 1 h and remained in high vacuum for about 4 h. Then, temperature was raised to 110 °C for overnight, and the sample was finally annealed at 140 °C under vacuum for additional 12 h. Gold electrodes (2.4 mm in diameter) were deposited on the top surface of the film using a Q300TD sputter coater (Quantum Technologies, Ltd., U.K.) for subsequent dielectric characterization.

Two-dimensional (2D) wide-angle X-ray diffraction (WAXD) patterns were collected at the 11-BM Complex Materials Scattering (CMS) beamline of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. The monochromatized X-ray wavelength was $\lambda = 0.0918$ nm. An in-vacuum CCD (Photonic Science) detector was used for WAXD experiments. The distance between the sample and detector was calibrated using silver behenate with the first-order reflection at a scattering vector of q = 1.076 nm⁻¹. The data acquisition time for each WAXD pattern was 10 s. The 2D WAXD pattern was integrated to obtain the one-dimensional (1D) curve.

Transmission electron microscopy (TEM) was performed on an FEI Tecnai TF20 electron microscope at an accelerating voltage of 200 kV. The SO₂-PIM was drop-cast from chloroform solution (0.01 wt.%) onto an ultrathin lacey carbon-coated TEM grid (≤ 3 nm, purchased from Ted Pella), which was then stained by RuO₄ vapor for a pre-set amount of time (5, 10, 30, and 60 min) at room temperature. The optimal staining time was found to be 10 min.

Broadband dielectric spectroscopy (BDS) measurements were performed on a Novocontrol Concept 80 broadband dielectric spectrometer (Montabaur, Germany) with temperature control. The applied voltage was 1 V_{rms} (root-mean square AC voltage). The frequency ranged from 10^2 to 10^6 Hz, and the temperature ranged from -125 to 200 °C. High-voltage BDS (HV-BDS) measurements were performed on the Novocontrol Concept 80 broadband dielectric spectrometer with a high-voltage interface, HVB4000. The interface could provide up to ± 2000 peak-to-peak V_{AC} with frequency up to 10^4 Hz. Samples were heated at 0.3 °C min⁻¹. Simultaneously, the electric field was increased from 23.8 to 71.4 MV m⁻¹ and the test frequency was maintained at 100 Hz.

Electric displacement - electric field (D-E) loop tests were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM) in combination with a Trek

10/10B-HS high voltage amplifier (0-10 KV AC, Lockport, NY). Voltages with a bipolar or unipolar triangular waveform were applied at a frequency of 1 kHz. The metallized film samples were immersed in silicone oil (Fisher 460-M3001) to avoid corona discharge in air. The temperature was controlled by using an IKA RCT temperature controller (Wilmington, NC).

Leakage current was measured using the Novocontrol Concept 80 broadband dielectric spectrometer equipped with a Keithley 6517B electrometer. Immediately after the application of a DC voltage, the leakage current was recorded for 30 min at each temperature. To avoid the interference of discharge currents and to minimize ionic conduction, the leakage current experiments were conducted with the DC voltage from low to high and the temperature from high to low. Gold electrode (1 mm diameter) was deposited on the top surface of the film.

The InSe-based field effect transistor (FET) devices were fabricated based on a InSe nanoflake/SO₂-PIM/SiO₂/*n*-doped Si configuration, as reported before.^{S1} The SO₂-PIM film was fabricated by solution-casting onto the SiO₂/*n*-Si substrate from DMAc, and then was annealed in a vacuum oven for 24 h. Afterwards, the InSe nano-flake samples were mechanically exfoliated on the top of the SO₂-PIM dielectric layer. About 40 nm thick Ti/Ni was deposited using a shadow mask to finish the transistor devices. The electrical characteristics of the FET devices were measured at room temperature in the air by using a Keithley 2650A analyser and a Lakeshore probe station. The electron mobility was extracted from the linear region of the transfer curve by using the equation of $I_{ds} = \frac{W}{L} \cdot C_i \left(V_G - V_T - \frac{V_{DS}}{2}\right) V_{DS}$.



Scheme S1. Modified synthetic route for SO₂-PIM.



Scheme S2. Proposed crosslinking mechanism when the disulfonyl monomer is directly used for the condensation polymerization to prepare SO₂-PIM.

Synthesis of SO₂-PIM

The synthesis route is presented in **Scheme S1**. Although the exact SO₂-PIM had been synthesized in the past, ^{S2} we discovered that the reported method easily led to a crosslinked product for the homopolymer (not so severe crosslinking for the random copolymer though). We propose that the electron-withdrawing ability of sulfonyl group is so strong that the adjacent CH₂ is quite acidic. The sulfonyl monomer can readily react with K_2CO_3 to cause potential crosslinking by further reacting with the Ar-F group in another polymer chain before the ring closes (see **Scheme S2**). Therefore, we modified the condensation polymerization route by using the disulfinyl monomer **2**, because the sulfinyl group has a weaker electron-withdrawing ability than the sulfonyl group. In this way, crosslinking reaction can be largely suppressed by carefully controlling the reaction temperature and time.



Figure S1. ¹H NMR spectra of (A) dithioether precursor 1 and (B) disulfinyl monomer 2.

Synthesis of Disulfinyl Monomer 2. 1,4-bis(ethylthio)-2,3,5,6-tetrafluorobenzene (1) was synthesized using the known procedure published before.^{S3} PFB (5 mmol), ethanethiol (8 mmol), KOH (8 mmol), and DMAc (20 ml) were added into a 100 mL round-bottom flask with a magnetic stirrer. The reaction proceeded smoothly at room temperature for 10 h before quenched with water. The product was extracted with ethyl acetate, washed with brine, and dried over anhydrous Na₂SO₄. After the solvent was evaporated, the product was dissolved in acetone and recrystallized in a freezer. Proton nuclear magnetic resonance (¹H NMR, 600 MHz, DMSO-*d*₆, δ in ppm): 2.98 (q, *J*=8.0 Hz, 4H; CH₃C<u>H₂</u>S), 1.18 (t, *J*=8.0 Hz, 6H; C<u>H₃CH₂S) (see Figure S1A).</u>

The dithioether **1** (1 g, 3.7 mmol) was then oxidized with *m*-CPBA (7.5 mmol) for 1 h, resulting in white powder of the disulfinyl monomer **2**, which was collected and purified by recrystallization from acetone. ¹H-NMR (DMSO-*d*₆, δ in ppm): 3.38 (q, *J*=8.0 Hz, 4H; CH₃C<u>*H*₂SO), 1.23 (t, *J*=8.0</u>

Hz, 6H; C<u>*H*</u>₃CH₂SO) (see **Figure S1B**). ¹³C-NMR (CDCl₃, δ in ppm): 145.7, 143.7, 126.0, 48.4, and 7.5.

Syntheses of SO-PIM and SO₂-PIM. Into a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, an argon inlet, and a Dean-Stark trap, TTSBI (2.5 mmol), the disulfinyl monomer 2 (2.5 mmol), anhydrous K₂CO₃ (7.5 mmol), DMAc (10 mL), and toluene (5 mL) were added. Toluene was added in DMAc to avoid potential crosslinking side reactions. The mixture was refluxed at 160 °C for 80 min, and then the resulting viscous polymer solution was precipitated into methanol. A yellow polymer was obtained. The polymer product was dissolved in chloroform and precipitated in methanol; this procedure was repeated for three times to remove impurities. The resulting polymer was refluxed for several hours with deionized water to remove impurities, and then dried in a vacuum oven at 50 °C for 3 d. ¹H NMR (600 MHz, DMSO-*d*₆, δ in ppm): 6.74 (s, 2H, Ar-<u>H</u>), 6.37 (s, 2H, Ar-<u>H</u>), 3.60-3.30 (q, 4H, -SOC<u>H</u>₂CH₃), 2.29/2.14 [s, 4H, 2 CC<u>H</u>₂C(CH₃)₂], 1.34/1.26 (12H, C(C<u>H</u>₃)₂ and 6H, SOCH₂C<u>H</u>₃) (see Figure S2A).

The SO-PIM was then oxidized with *m*-CPBA in chloroform to afford the SO₂-PIM. The product was washed by ethyl ether and slowly precipitated from acetone to remove low molecular weight fractions. ¹H NMR (600 MHz, DMSO- d_6 , δ in ppm): 6.77 (s, 2H, Ar- \underline{H}), 6.39 (s, 2H, Ar- \underline{H}), 3.60-3.30 (q, 4H, -SO₂C $\underline{H_2}$ CH₃), 2.30/2.13 [s, 4H, 2 CC $\underline{H_2}$ C(CH₃)₂], 1.50-1.20 (12H, C(C $\underline{H_3}$)₂ and 6H, SO₂CH₂C $\underline{H_3}$) (see **Figure S2B**). The number-average molecular weight (M_n) of the SO₂-PIM polymer was determined by size-exclusion chromatography (SEC) using DMF as the solvent and polystyrene (PS) as standards: $M_n = 360,000$ Da and molecular weight distribution was 3.3 (see **Figure S3**).



Figure S2. ¹H NMR spectra of (A) SO-PIM and (B) SO₂-PIM.



Figure S3. SEC curve for SO₂-PIM. Differential refractive index (RI) detector was used to record signals.

2. Broadband Dielectric Spectra of SO₂-PIM



Figure S4. Temperature-scan BDS result of imaginary part (ε_r'') of relative permittivity at different frequencies for SO₂-PIM.



Figure S5. Frequency-scan BDS results of (A) real (ε_r') and (B) imaginary (ε_r'') parts of relative permittivity and (C) tan δ at different temperatures for SO₂-PIM.

The ε_r' of SO₂-PIM did not change much at different temperatures, as shown from the frequency-scan BDS results in **Figure S5**. In the ε_r'' plot, the β transition was observed. Between 10³ and 10⁶ Hz, the loss from the conduction of impurity ions was not noticeable until 175 °C. For polar polymers, a trace amount of impurity ions is difficult to avoid, and even a sub-ppm level of impurity ions could cause significant loss and low frequencies.^{S4-S5} Remarkbly, SO₂-PIM was capable of preserving a relatively low ion conduction loss (tan $\delta < 0.02$) even at 200 °C and 10³ Hz.



Figure S6. HV-BDS temperature-scan results of tan δ for the SO₂-PIM film under different electric fields at 100 Hz. The heating rate was 0.3 °C min⁻¹.

3. I-V Curves for InSe-Based Field Effect Transistors



Figure S7. (A) The I_{ds} - V_g transfer curve in logarithmic scale. Dashed lines show the hypothetical OFF state because of the limit of instrument sensitivity. (B) Typical I-V curves obtained from an InSe device on SO₂-PIM-coated Si/SO₂ substrate upon the application of different gate voltages at room temperature.

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