

## Supporting information

# Beads-On-String-Shaped Poly(azomethine) Applicable for Solution Processing of Bilayer Devices using a Same Solvent

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## Experimental

### Materials

All the solvents and chemicals used here were obtained as reagent-grade quality and were used without further purification. *para*-Bis(3-aminopropyl)hexaisobutyl-substituted T<sub>8</sub> cage (1) was prepared according to the previous report.<sup>1</sup> 3-Aminopropylheptaisobutyl-substituted T<sub>8</sub> cage (2) was obtained from Hybrid Plastics Co. Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Sigma-Aldrich.

### Reference

1) T. Maegawa, Y. Irie, H. Fueno, K. Tanaka, K. Naka, *Chem. Lett.* **2014**, 43, 1532–1534.

### Instrumentation and Characterization Details.

<sup>1</sup>H- (400 MHz), <sup>13</sup>C- (100 MHz), and <sup>29</sup>Si- (80 MHz) NMR spectra were obtained using a BRUKER DPX-400 instrument (Bruker Biospin, Rheinstetten, Germany). Fourier transform infrared (FTIR) spectra were obtained using a JASCO FT/IR-4600 (JASCO, Tokyo, Japan) spectrometer. UV-vis spectra were obtained using a JASCO spectrophotometer V-670 KKN (JASCO, Tokyo, Japan). Differential scanning calorimetry (DSC) data were obtained using a DSC-60 Plus (Shimadzu, Kyoto, Japan) at a heating rate of 10 °C/min in N<sub>2</sub> flow for the whole temperature range. Thermogravimetric analysis (TGA) was performed using a DTA-60 (Shimadzu, Kyoto, Japan) at a heating rate of 10 °C/min in N<sub>2</sub> and air flows. Powder X-ray diffractometry (XRD) studies were performed on a Rigaku Smartlab X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) in the 2 $\theta$ / $\theta$  mode at room temperature. The 2 $\theta$  scan data were collected at 0.01° intervals and the scan speed was 5° (2 $\theta$ )/min. The rheological measurements were made at 25 °C using an AR-G2 (TA Instruments, Delaware, USA) rheometer with the parallel plate geometry.

### **Preparation of the bottom-gate top-contact organic field-effect transistors (OFETs)**

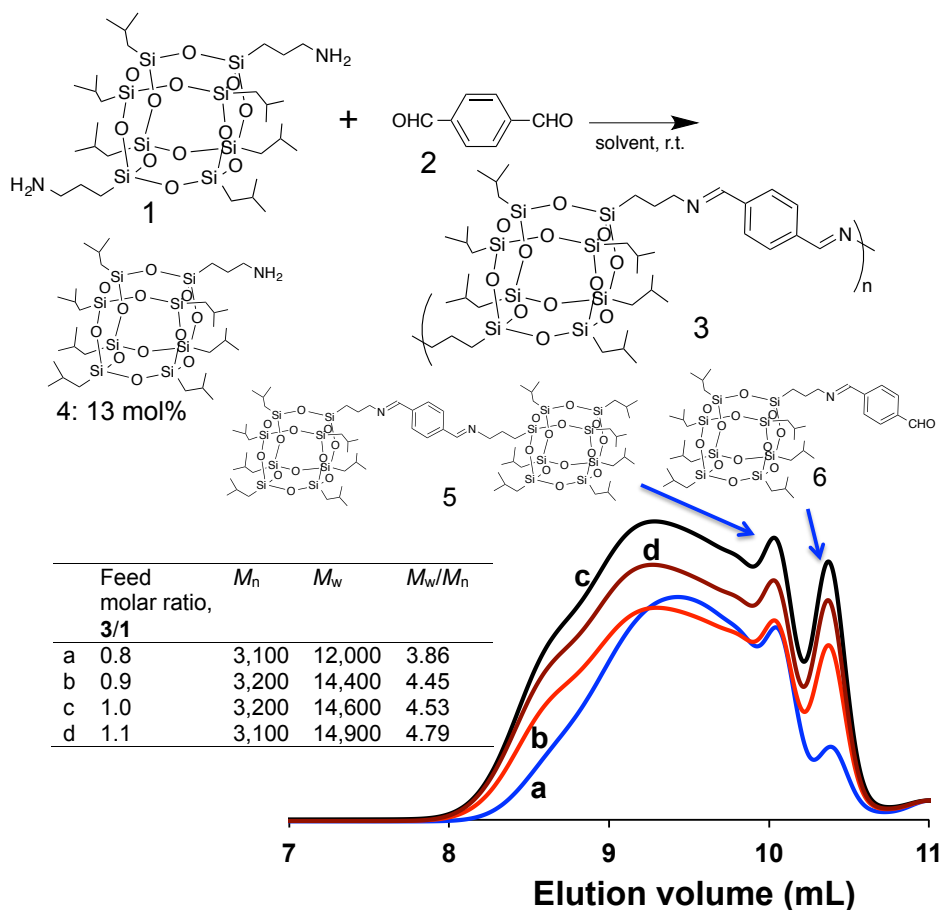
The bottom-gate top-contact organic field-effect transistors (OFETs) with the present poly(azomethine) as gate insulator were fabricated on glass substrates. The Al gate electrode (40 nm) was fabricated by vacuum evaporation through a metal shadow mask on pre-cleaned glass substrates. A solution of the polymer dissolved in toluene in 50~75 mg/mL was spin-coated on the glass substrate at 4000 rpm for 20 sec and dried at 100 °C for 30 min in ambient air. A 1.0 wt% (8.6 mg/mL) solution of regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) dissolved in toluene was spin-coated onto the polymer gate insulator at 2000 rpm for 60 sec in a glove box filled with N<sub>2</sub> (dew point: -80 °C). Finally, Au source-drain electrodes (40 nm in thickness) with channel length ( $L$ ) of 100  $\mu$ m and channel width ( $W$ ) of 2 mm were deposited on the P3HT semiconductor layer by shadow mask evaporation.

### **Synthesis of a polymer**

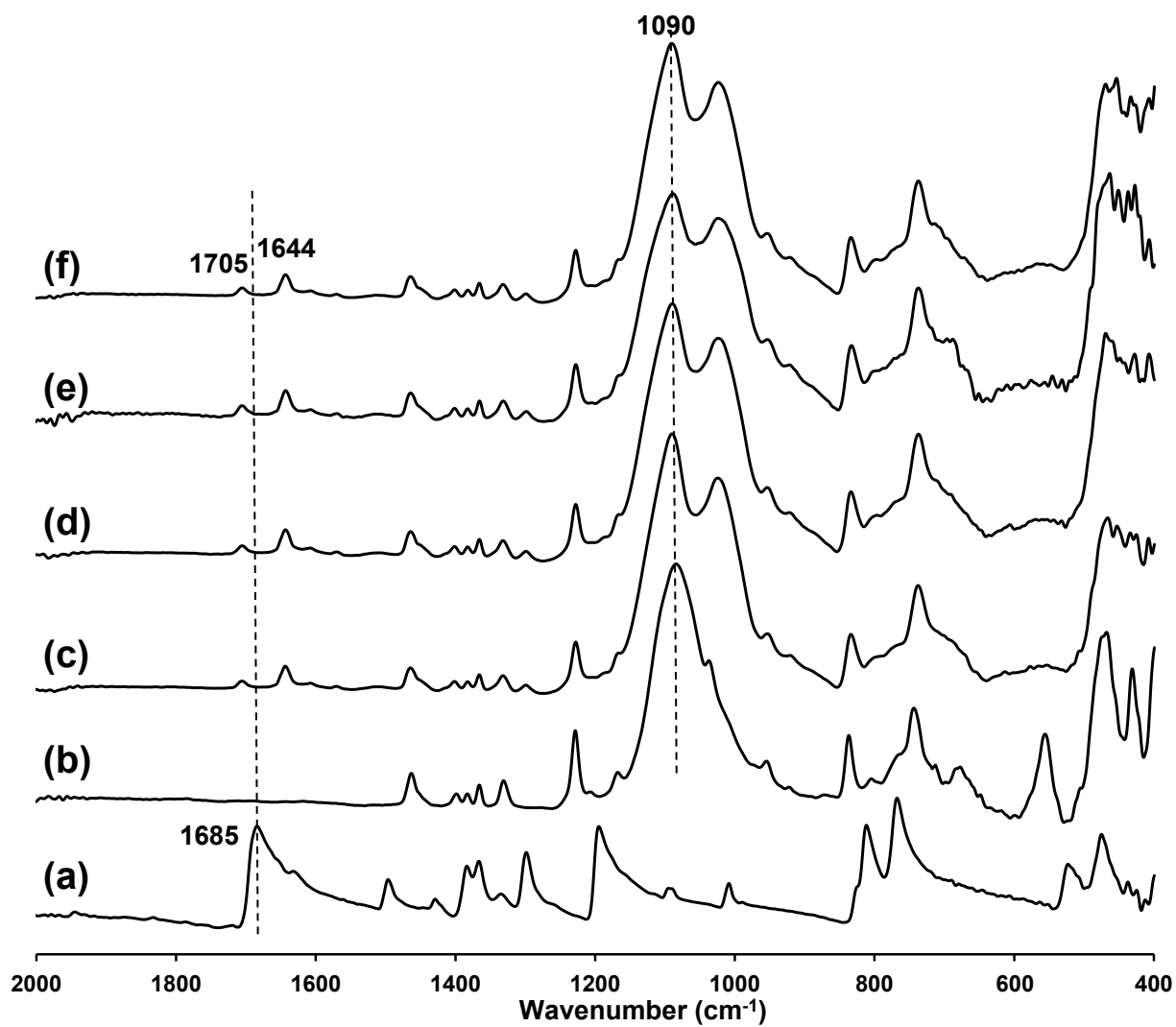
A mixture of *para*-bis(3-aminopropyl)hexaisobutyl-substituted T<sub>8</sub> cage (**1**) (0.144 g, 0.164 mmol) and terephthalaldehyde (0.0220 g, 0.164 mmol) in THF (2.0 mL) was stirred at room temperature for 2 h. The solvent was removed under the reduced pressure to obtain colorless solid. FT-IR (ATR):  $\nu$  = 738, 833, 1024, 1090, 1227, 1465, 1644, 1705, 2871, 2951 cm<sup>-1</sup>.

The polymerization of **1** with terephthalaldehyde was conducted in various monomer feed ratios. The polymerization proceeded in a homogeneous solution. The polymerization solutions were directly injected for GPC analysis (Figure 2). Beside the main polymeric fraction, two oligomeric fractions appeared. Decrease of the feed ratios of terephthalaldehyde decreased the peak at 10.4 mL, corresponding to 1:1 adducts of terephthalaldehyde with **1** or 3-aminopropyl-heptaisobutyl-substituted T<sub>8</sub> cage (**4**). The fraction at 10.0 mL corresponds to

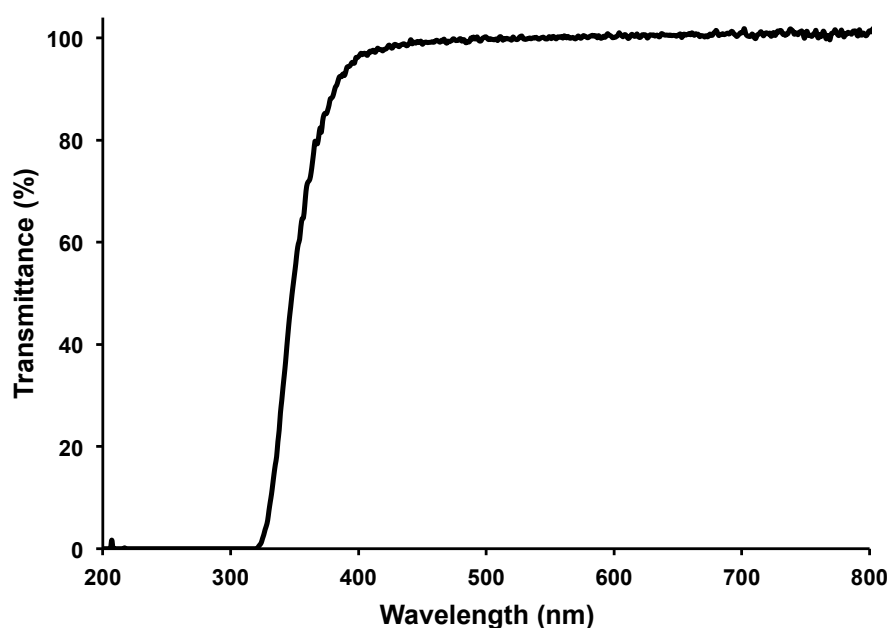
the dumbbell-shaped compound (**5**). The peaks intensity is independent of the feed ratios. According to the  $^1\text{H}$ -NMR analysis, *para*-bis(3-aminopropyl)hexaisobutyl-substituted  $\text{T}_8$  cage (**1**) contains 13 mol% of the mono-functionalized compound, 3-aminopropyl-heptaisobutyl-substituted  $\text{T}_8$  cage (**4**), resulting in the dumbbell-shaped architecture (**5**).



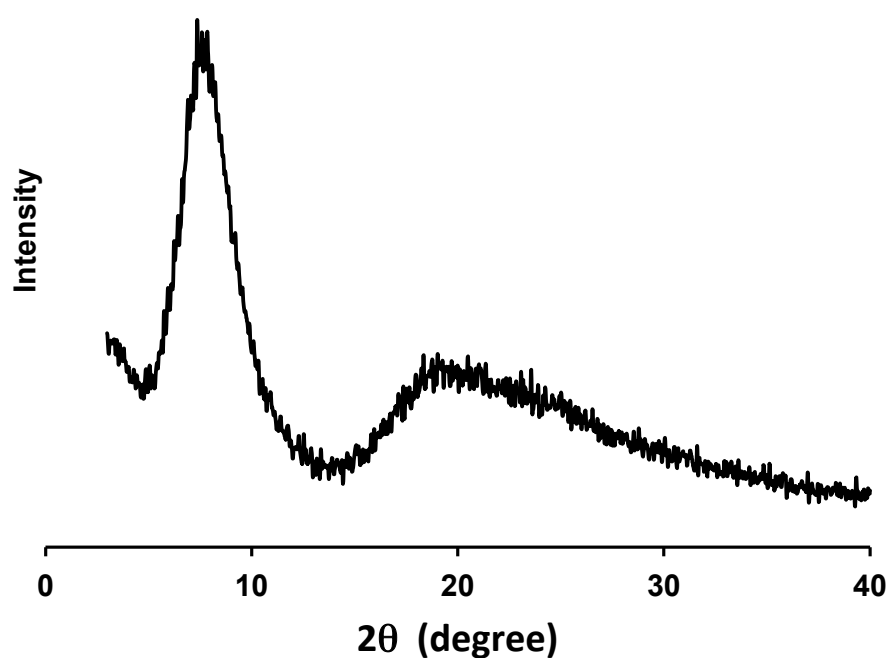
**Figure S1** Polymerization of *para*-bis(3-aminopropyl)hexaisobutyl-substituted  $\text{T}_8$  cage (**1**) with terephthalaldehyde (**2**). GPC traces of the polymerization solutions conducted in various monomer feed molar ratios (**2/1**), measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm. Insert table is a summary of the number and weight average molecular weights and molecular weight distribution of the polymers.



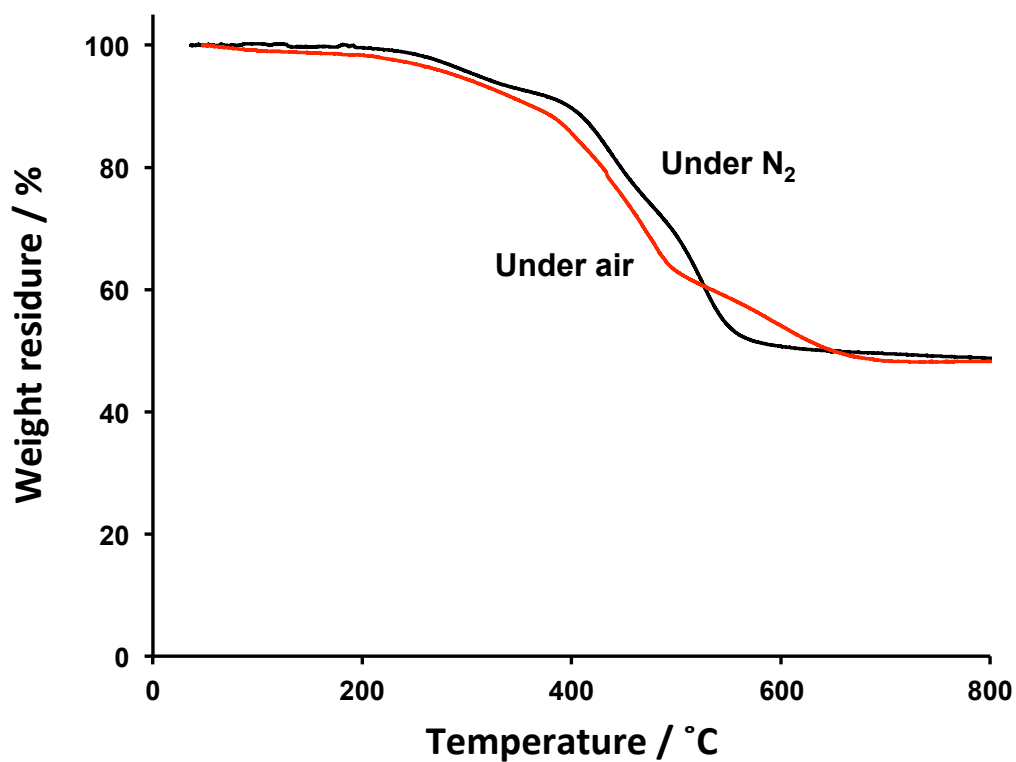
**Figure S2** FT-IR spectra of (a) terephthalaldehyde (**2**), (b) **1**, and the polymers obtained from various monomer feed ratios, (c) 0.8, (d) 0.9, (e) 1.0, and (f) 1.1.



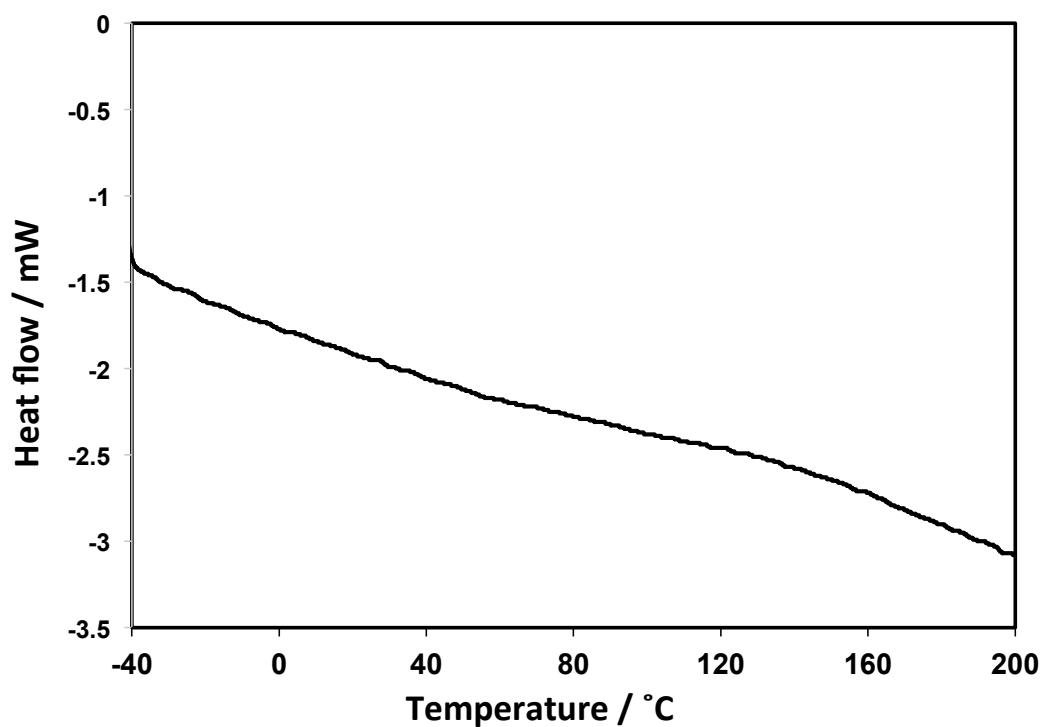
**Figure S3** UV-vis transmittance spectrum of the free-standing film. The thickness was about 0.1 mm.



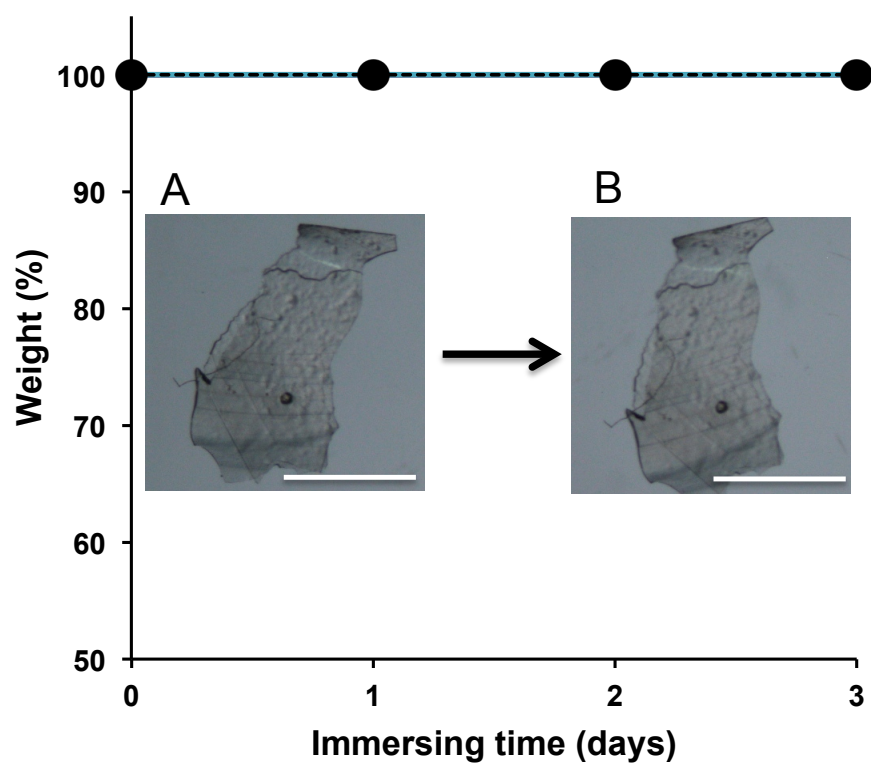
**Figure S4** XRD trace of the poly(azomethine) at room temperature.



**Figure S5** TGA thermogram of the poly(azomethine) at a heating rate of 10 °C/min in N<sub>2</sub> and air flows.

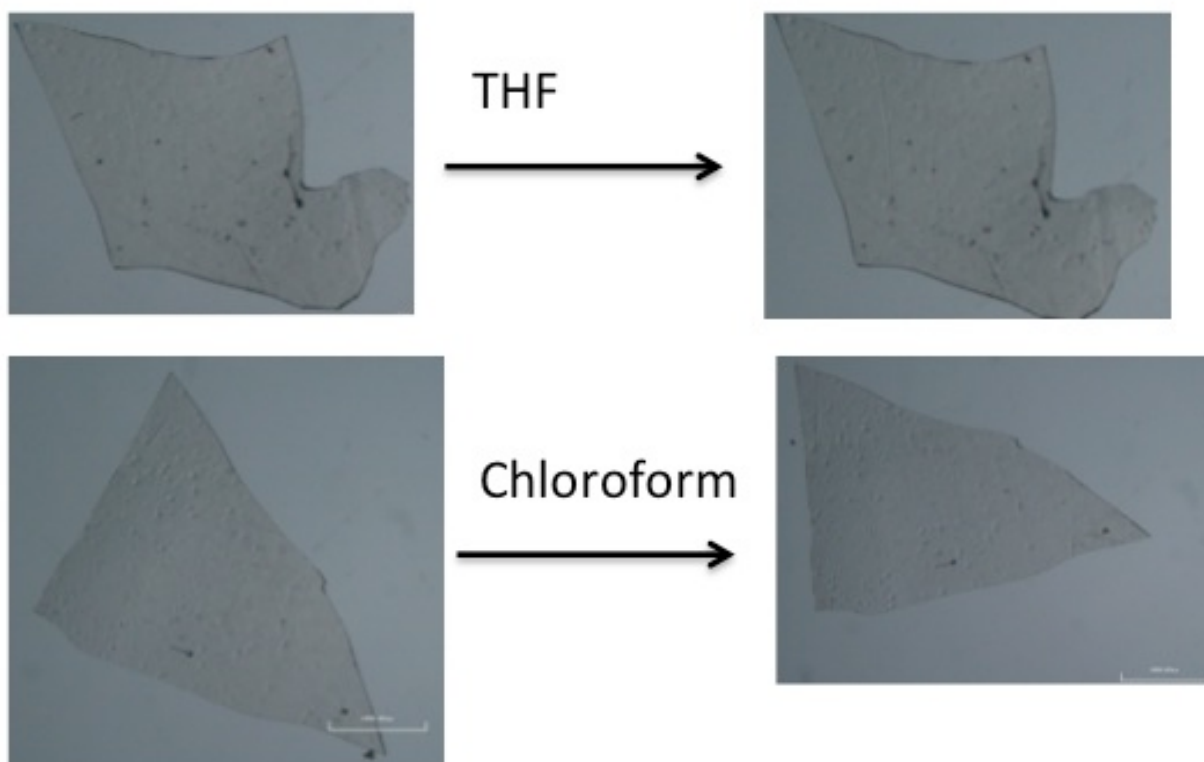


**Figure S6** DSC trace of the poly(azomethine) at a heating rate of 10 °C/min in N<sub>2</sub> flow.

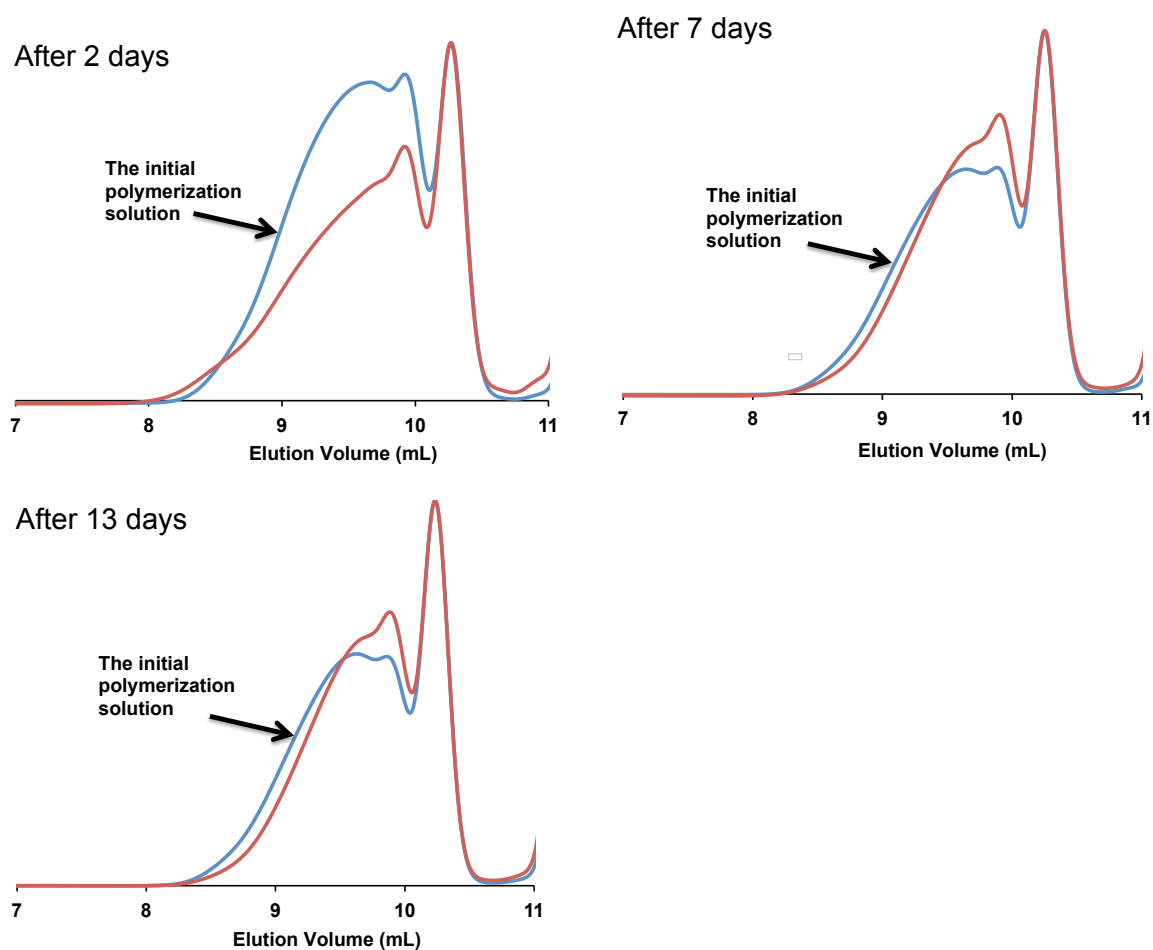


**Figure S7** Weight changes after the film (3.7 mg) was immersed in toluene (3 mL) at room temperature. Insert: Images are optical microscopic images of the films before (A) and after (B) immersing in toluene for 3 days at room temperature (scale bar: 1 mm).

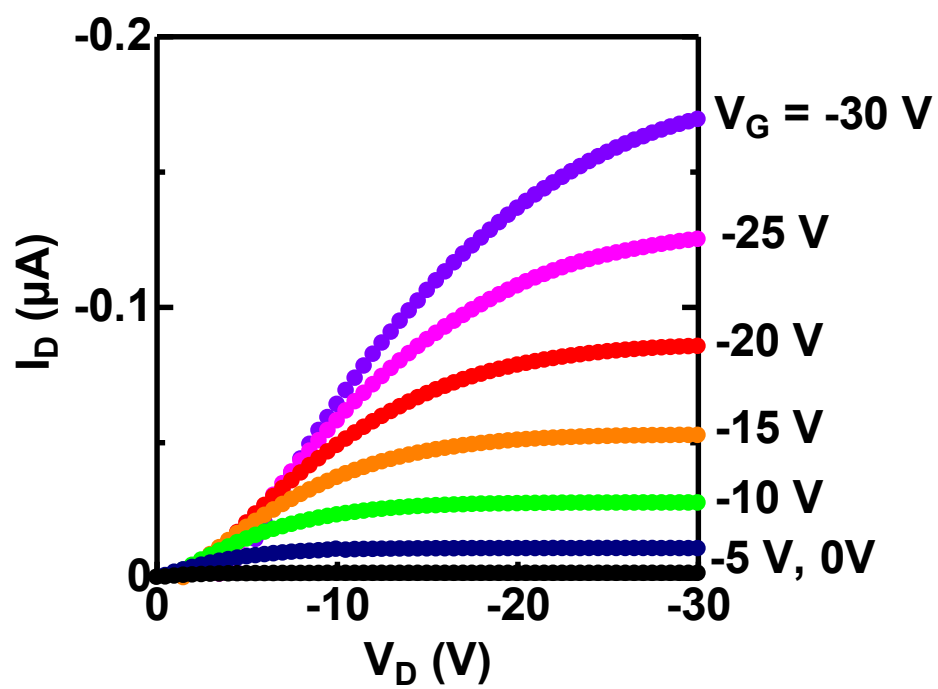




**Figure S8** Optical microscopic images of the films before and after immersing in THF and chloroform for 3 days at room temperature.



**Figure S9** Weight GPC traces of the polymerization solution after the casting film of the polymer (17.1 mg) was added to toluene (3 mL) and stirred at room temperature, measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm.



**Figure S10** Output characteristics of bottom-gate top-contact P3HT OFET using the poly(azomethine) as a gate insulator.