Supporting Information

Experimental

Device fabrication. Organic field-effect transistors were fabricated in the bottom gate, bottom contact configuration on heavily doped n-type Si substrates as the gate and a thermally grown 250 nm silicon dioxide as the dielectric layer (Silicon Quest, dry oxide). The source and drain electrodes were patterned using standard photolithography methods and were deposited on the SiO_2 by sputter deposition of ~5 nm of titanium and 50 nm of gold. Channel lengths ranged from 5 to 100 μm, and channel widths from 250 to 1000 μm. Devices were plasma etched (IPC Plasma etcher, 250W, 15 min, temperature reached at least 150°C) and stored in a desiccator until ready for use. Just prior to use, the devices were cleaned by exposure to UV light in air (Novascan PSD-UVT). The substrates were then surface treated with octyltrichlorosilane (OTS, Acros) by immersion in a ~30 mM OTS solution in anhydrous toluene or anhydrous hexadecane at room temperature for 1 to 3 hours, cleansed by rinsing with HPLC grade toluene, and dried with nitrogen flow followed by vacuum for at least one hour. The polymer films were deposited in air by drop casting 5 mL of a 1 mg/ml solution in dry chloroform (passed through alumina columns), and allowed to dry in a covered glass Petri dish that was saturated with chloroform vapor. These conditions assured a slow evaporation rate, which is believed to promote the formation of the nanofibrillar morphology that yields higher mobilities. The polymer solutions were filtered through 0.2 μm PTFE filters prior to film deposition. After film formation, the devices were further dried in a dessicator under vacuum overnight prior to being measured. The films formed ranged from 50 to 250 nm, and were 200 nm on average. Devices were also thermally annealed at 120 or 150°C for 30 minutes.

Electrical measurements were made while the devices were under a flow of Argon using an Agilent 4155C Semiconductor parameter analyzer and a Micromanipulator S6 probe station. The devices were only briefly exposed to air while being set on the probe station. When measuring current-voltage curves and transfer curves, V_G was scanned from -80V to +40V. The field-effect mobilities were obtained from the transfer curves in the saturation regime at V_{DS}=-80V. A line drawn through the linear part of an $I_{DS}^{1/2}$ vs V_G plot allowed extraction of threshold voltage and field-effect mobility using the square-law equation for the saturation regime (Equation 1).[2,12] The median mobility was obtained from measurements from at least four different polymer films, usually cast on different days. All data were obtained over a period of about 11 months and therefore cover a wide range of conditions.

$$I_{DS} = C_i \frac{W}{L} \mu_{eff} (V_G - V_T)^2 \qquad (1)$$

Microstructure Characterization.

Out-of-plane and in-plane x-ray diffraction Out-of-plane and in-plane XRD scans were performed on a Philips X'Pert Pro diffractometer. Copper radiation was used with a poly-capillary lens. The Philips was operated at 45 kV and 40 mA. Incident crossed slits were 4mm wide by 4mm high. The ψ tilt angle was 0 degrees for out-of-plane scans and 88 degrees for in-plane scans. The step size for all scans was 0.1 degrees with a count time of 10 seconds per step except for the range between 19 and 26 degrees two-theta where a 40 second count time was used. Large size (2 × 2 cm^2) silicon wafers were used as XRD sample substrates; thin film samples for XRD analysis were prepared under exactly the same conditions as those used to fabricate P2 FETs.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS): GIWAXS images were taken at the Cornell High Energy Synchrotron Source (CHESS) D1 station. A wide bandpass (1.47%) double-bounce multilayer monochromator supplied an intense beam of 10.006 keV photons. These were impinged onto the sample surface at various incident angles ranging from below the critical angle of the film and above the critical angle of the substrate. The sample was mounted on a sample goniometer, in order to control the incident angle and the sample azimuth. An accurate calibration of the incident angle was performed in-situ by measuring the x-ray reflectivity from the sample using an ion chamber. GIWAXS scattering intensities were recorded with an area detector (Medoptics) with a resolution of 47.19 μm per pixel and a total area of about 50 mm by 50 mm at a distance of 91.6 mm from the sample. The intense scattering in the incident plane was blocked with a 1.5 mm wide tantalum rod. Exposures times under these conditions ranged from 1 sec to 30 sec depending on contrast and sample quality.

Tapping Mode Atomic Force Microscopy: TMAFM studies were carried out with the aid of a Nanoscope III-M system (Digital Instruments, Santa Barbara, CA), equipped with a J-type vertical engage scanner. The AFM observations were performed at room temperature in air using silicon cantilevers with nominal spring constant of 50 N/m and nominal resonance frequency of 300 kHz (standard silicon TESP probes). A typical value of AFM detector signal corresponding to an r.m.s. cantilever oscillation amplitude was equal to ~ 1V and the images were acquired at 2 Hz scan frequency in $2 \times 2\ \mu m^2$ scan areas.

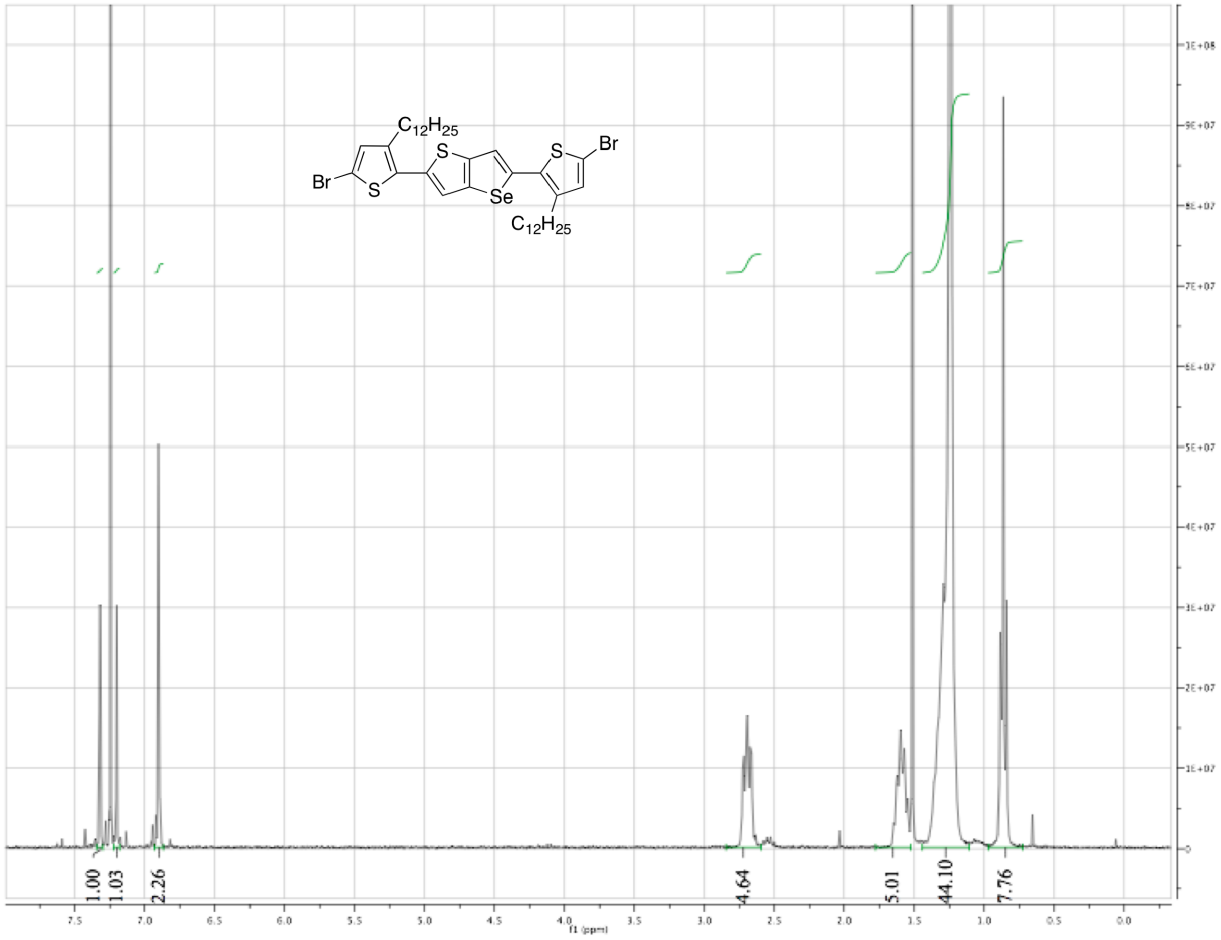

Figure SI1. ^{1}H NMR spectra for monomer.

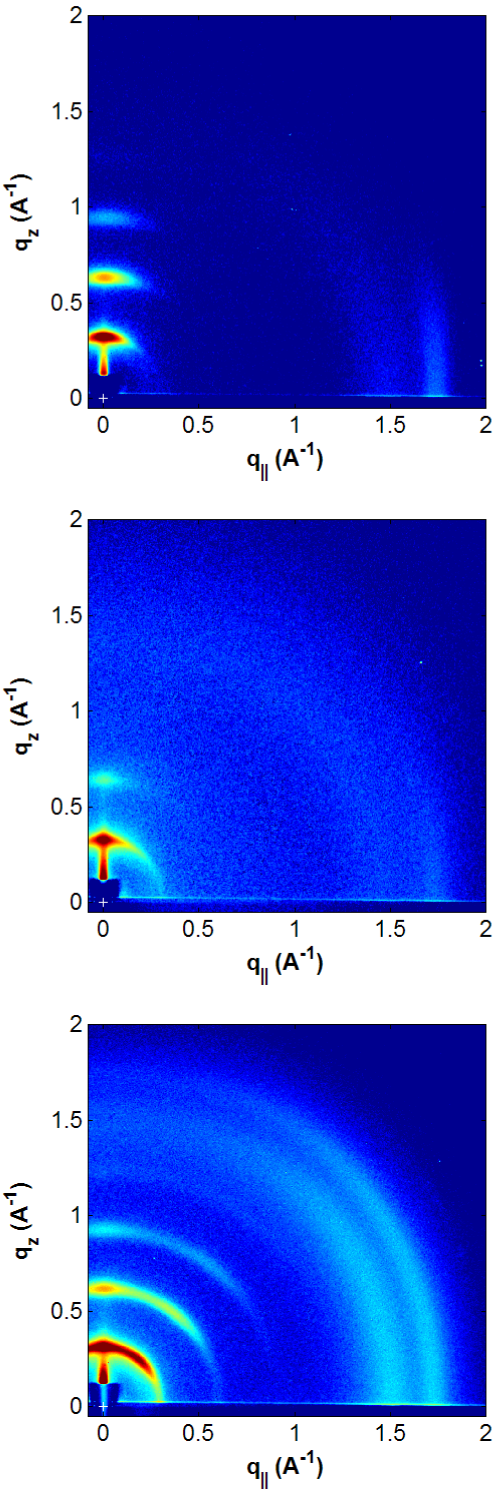

Figure SI2. GIWAXS scatter plots for PMC, PMD and PMG.

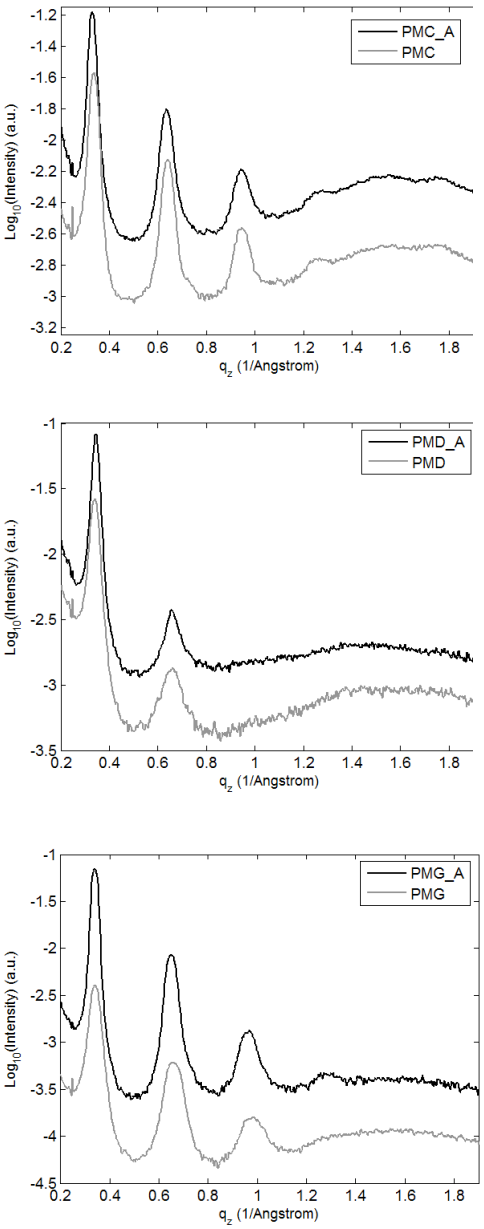

Figure SI3. Out of plane scatter plots before and after annealing for PMC, PMD and PMG.

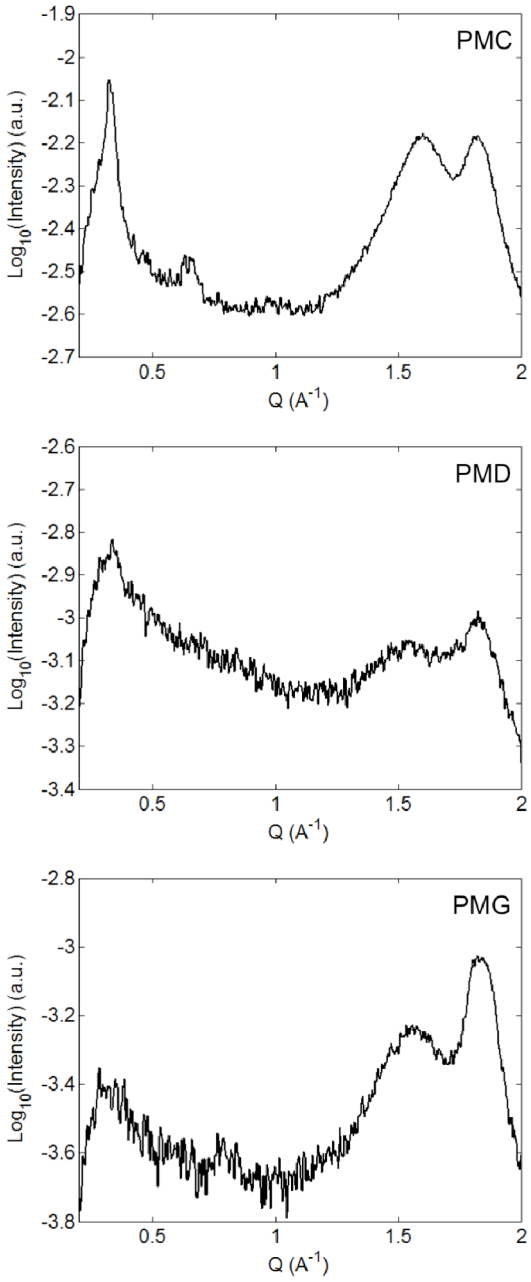

Figure SI4. In plane scatter plots after thermal annealing for PMC, PMD and PMG.

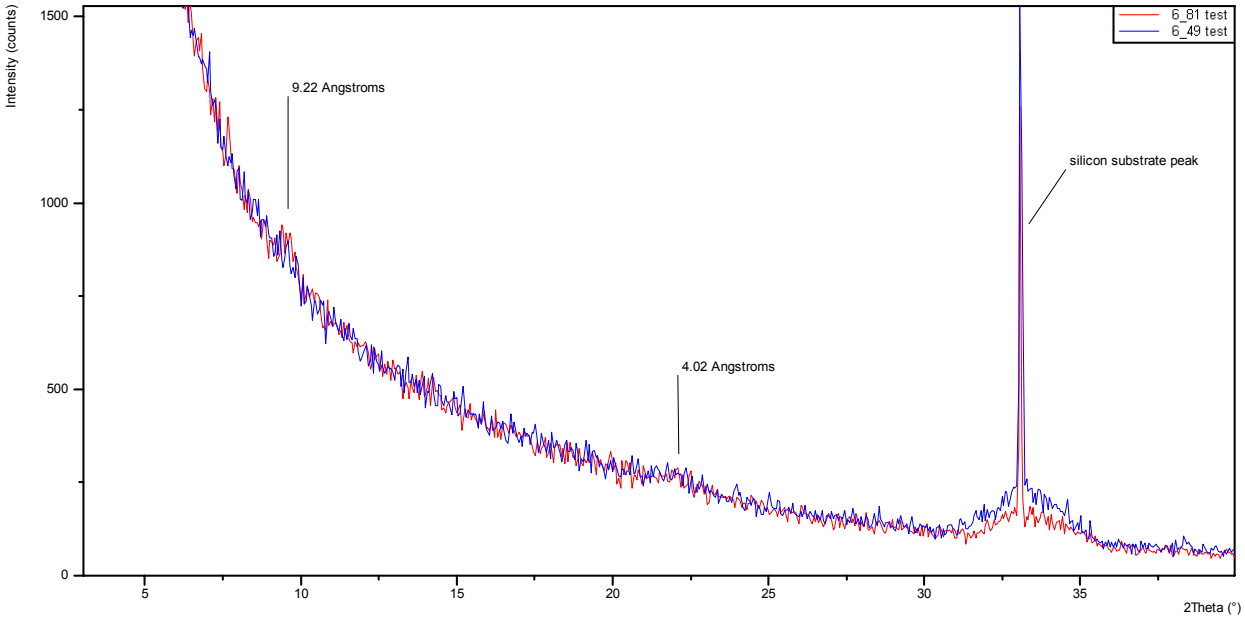

Fig. SI5. Scatter plots for PMA (blue) and PMH (red).

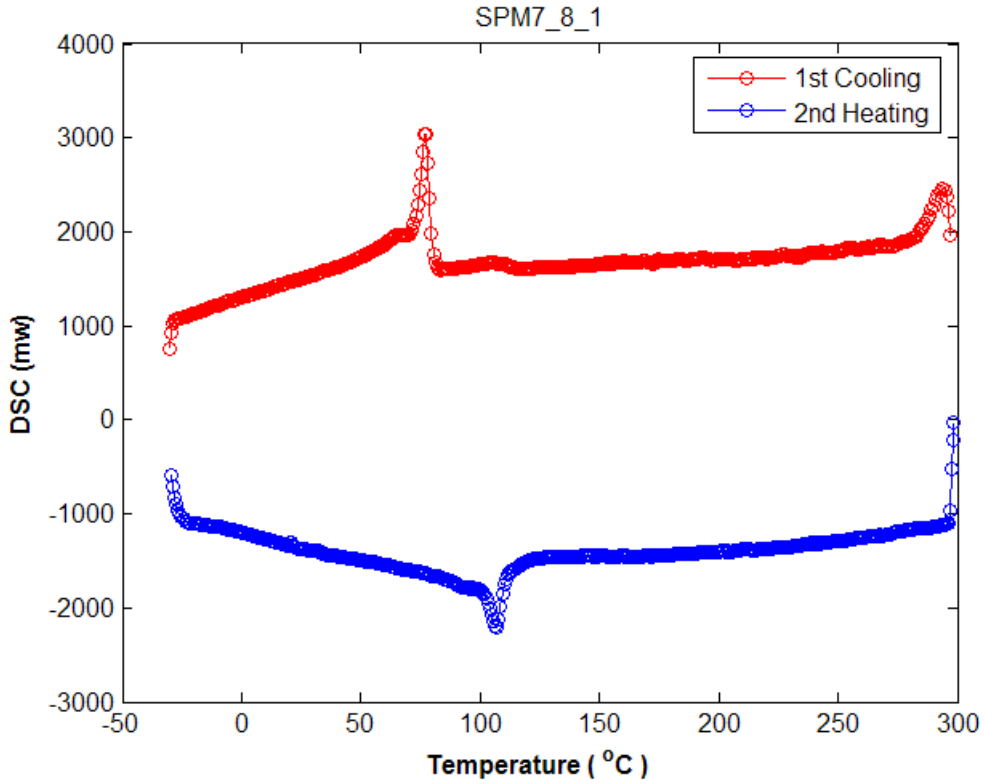

Fig. SI6. DSC curve of a representative polymer sample.