Supporting Information

OTFT Performance of air-stable ester-functionalized polythiophenes

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OTFT Results for freshly synthesized polymers

TFT devices were fabricated on Si/SiO_2 wafers in the top contact geometry using 45-50 nm of gold as the electrodes. All device fabrication for the **M1**, **M2**, and **M3** polymers was performed in air except for the final metal deposition step, which was performed under high vacuum.

The polymer layer was applied by spin casting a solution of the freshly synthesized polymer in anhydrous *o*DCB (**M1** 2.5 mg/mL, **M2** 2.0 mg/mL, **M3** 2.0 mg/mL) at 1100 rpm. The **M1** polymer solution was heated to 40 °C and the **M2** and **M3** polymer solutions were heated to 60 °C prior to spin coating to form clear solutions. All solutions were filtered using a 0.2 μm PTFE filter before spin casting. The substrates were heated on a 80 °C hot plate prior to spin coating in order to maintain polymer solubility. TFT devices were annealed in air at 110 °C for 10 mintues.

Inter-digitated source and drain electrodes made of gold (W = 9000 μm, L= 90 μm) with an aspect ratio (W/L) of 100 were deposited on top of the polymer active layer by evaporating a 50 nm thick gold film at 0.5 Å/s through a shadow mask from a resistively heated Mo boat under high vacuum (2.0×10^{-6} torr). The devices were tested in air as p-type TFTs using an Agilent 4155B semiconductor parameter analyzer. Further device testing was conducted one month after fabrication. During storage, the devices were kept in air and protected from light. The source, drain and gate electrodes of the TFT devices were connected to the parameter analyzer using thin pin electrodes. Two test types were conducted with each device, a transfer curve and a set of family curves. Family curves were obtained by measuring the drain current of the transistor compared to the source-drain voltage at different discrete gate voltages. Transfer curves were obtained by measuring the source-drain current while varying the gate voltage at a constant source-drain voltage. At least 6 devices were fabricated using each polymer and the average mobility is presented in this paper

Supplementary information: OTFT Performance of air-stable ester-functionalized polythiophenes

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	Devices constructed using polymers stored in air for 1 year		Devices constructed using newly synthesized polymers	
Polymer	Mobility (cm^2/Vs)	On/off ratio	Mobility (cm^2/Vs)	On/off ratio
M1[a]	3.3×10^{-3} $\pm 5 \times 10^{-4}$	10^5	3.0×10^{-3} $\pm 5 \times 10^{-4}$	10^5
M2[a]	2×10^{-4} $\pm 1 \times 10^{-4}$	10^5	2×10^{-4} $\pm 1 \times 10^{-4}$	10^5
M3[a]	4×10^{-4} $\pm 1 \times 10^{-4}$	10^3	4×10^{-4} $\pm 1 \times 10^{-4}$	10^3

Table S1 TFT Results for polymers **M1**, **M2** and **M3** stored in air for 1 year, and newly synthesized.

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was conducted at room temperature in a typical three-electrode cell with a working electrode (Pt wire), a reference electrode (Ag/Ag^+, referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 50 mV s^{-1} (CV-50W voltammetric analyzer, BAS). A Pt electrode was dipcoated into a polymer solution, and used as the working electrode. The **M1** polymer was annealed at 200 °C, **M2** at 180 °C, and **M3** polymer was annealed at 170 °C. CV measurements were performed in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) in anhydrous acetonitrile. Polymer films were made by dipping a working Pt electrode in a $CHCl_3$ solution of the polymer, then annealing the electrode on a hot plate, under a nitrogen atmosphere for 20 minutes. After bubbling the electrolyte solution with nitrogen gas for 10 minutes, a scan rate of 50 mV s^{-1} was employed for all measurements. Each polymer showed a chemically reversible redox process in the positive direction, with small fluctuations in peak height which stabilized after approximately four scans. The CV of ferrocene was conducted immediately after the polymers were measured, and used as an internal standard. The HOMO level of all three polymers was calculated from the onset potentials determined by the intersection of two tangents drawn at the rising current and background current of the cyclic voltammograms (see supporting information), and using 4.8 eV as the reference energy level of ferrocene compared to vaccum.[1] The reduction reactions during CV measurements of **M1** and **M3** were irreproducible, but shown here for comparison.

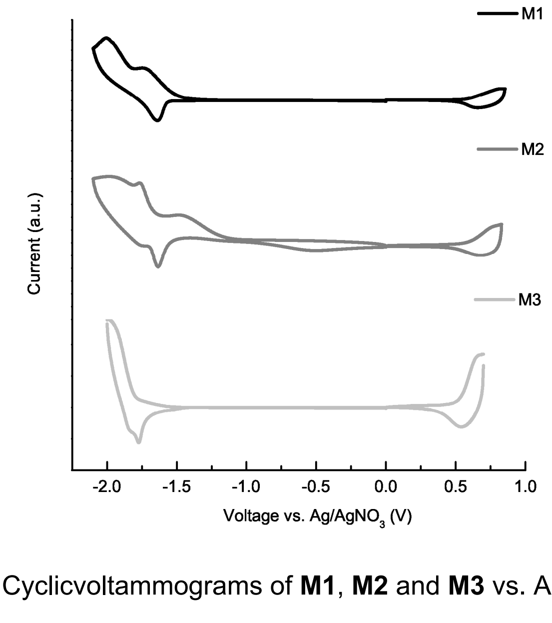

Fig. S1 Cyclicvoltammograms of **M1**, **M2** and **M3** vs. Ag/AgNO$_3$.

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Differential scanning calorimetry (DSC)

Thermal transitions were measured by DSC using a Texas Instruments DSC2010 with a heating and cooling rate of 5 °C min^{-1} under a constant flow of nitrogen.

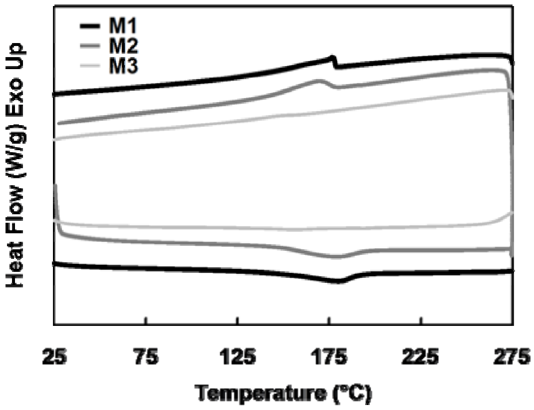

Fig. S2 DSC thermograms of **M1**, **M2** and **M3**.

X-Ray diffraction (XRD)

X-Ray diffraction measurements were performed on a Bruker D8 X-ray diffractometer using an accelerating voltage of 40 kV and a Cu-Kα source. The three polymers were drop cast on Si/SiO_2 wafers (as used in the TFT devices) from *o*DCB solution, and dried in the presence of solvent vapor to produce uniform thick films. The **M1** film was annealed at 200 °C, **M2** at 180 °C, and **M3** at 170 °C.

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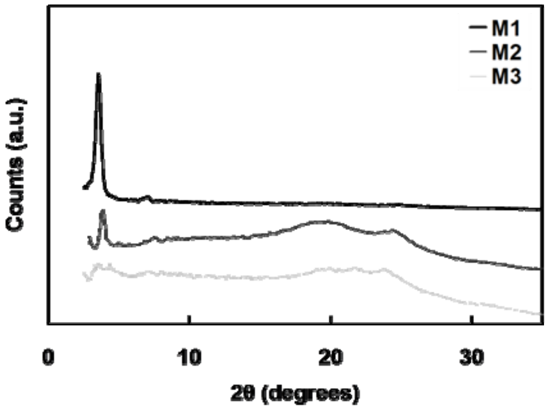

Fig. S3 XRD analysis of **M1**, **M2** and **M3** polymer thick films on Si/SiO$_2$ wafers.

References

1. Y. F. Li, Y. Cao, J. Gao, D. L. Wang, G. Yu and A. J. Heeger, *Synth. Met.*, 1999, **99**, 243-248.