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Supplemental material

Two-dimensional charge transport in disordered organic semiconductors

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Experimental details

Transistor substrates were fabricated on a heavily *n*-doped silicon wafer acting as a common gate electrode. Thermally grown SiO₂ (200 nm) passivated with hexamethyldisilazane (HMDS) was used as gate dielectric. The gate capacitance per unit area was $C_i = 17 \text{ nF/cm}^2$. Au source and drain electrodes were defined using conventional photolithography, using a Ti adhesion layer. To minimize the influence of short-channel effects and contact resistances, channel lengths larger than 10 μm were used.

As a semiconducting polymer, poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) (MDMO-PPV) was used. MDMO-PPV was spin-coated in a N₂ atmosphere from chlorobenzene, subsequently the transistors were annealed at 100 °C in vacuum. Experimental data of spin-coated poly(3-hexylthiophene) (P3HT) transistors and poly(2,5-thienylene vinylene) (PTV) transistors were obtained from the literature [1,2]. The semiconductor film thicknesses as measured with a Dektak 6M Profilometer were 80 nm or more.

Transistors with a semiconducting monolayer were fabricated using self-assembly and by thermal evaporation. Self-assembled monolayer field-effect transistors (SAMFETs) of chloro(11-(5''''-ethyl- 2,2:5',2'':5'',2''':5''',2''''-quinoxethien-5-yl)undecyl) dimethylsilane were self-assembled from a toluene solution, as reported previously [3,4]. Alternatively, a monolayer of α -sexithiophene (T6, Sigma Aldrich) was evaporated at a rate of about 0.6 nm/min onto a substrate at elevated temperature (120 °C).

Electrical characterization was performed in vacuum ($< 10^{-4}$ mbar) and in the dark. Measurements were performed using a Keithley 4200 Semiconductor Measurement System or an Agilent 4155C Semiconductor Parameter Analyzer.

Characterization of T6 monolayers

FIG. S1 Atomic force microscopy image of evaporated T6 in the transistor channel. The first monolayer is fully closed and islands of the next layers start to grow.

The evaporation time of T6 molecules was systematically increased to study the layer growth. Atomic force microscopy (AFM) clearly shows height steps of approximately the molecular length of T6 (~ 2.4 nm), as shown in Fig. S1. The first monolayer is fully closed. Large islands of the second layer, and smaller islands of the next layers, start to form, but are not percolating. Therefore, only the first monolayer contributes to the charge transport, and we consider the sample a monolayer transistor.

Current calculations

Spin-coated film: MDMO-PPV & PTV

FIG. S2 Experimental transfer curves of spin-coated thin-film transistors, measured as a function of temperature at a drain bias of -2 V. The current was described using Eq. 5, based on a carrier density which quadratically decreases with distance from the semiconductor-dielectric interface, Eq. 3. The semiconductor was a film of (a) MDMO-PPV and (b) PTV. The data were described with the following parameters: For MDMO-PPV: $T_0 = 411$ K, $\sigma_0 = 6.2 \times 10^5$ S/m, $\alpha^{-1} = 1.6$ Å, and $V_t = 0$ V. For PTV: $T_0 = 441$ K, $\sigma_0 = 1.8 \times 10^6$ S/m, $\alpha^{-1} = 1.9 \times 10^{-10}$ Å, and $V_t = 1$ V. The MDMO-PPV transistor had a channel width and length of 2500 μm and 10 μm . The PTV transistor had a channel width and length of 20000 μm and 20 μm .

Monolayer semiconductor: T6

FIG. S3 (a) Experimental transfer curves of a T6 monolayer field-effect transistor measured as a function of temperature, at a drain bias of $V_D = -2$ V. The curves calculated according to Eq. 8, based on a step-function carrier distribution, are presented as black lines. The following parameters were used: $W/L = 2500 \text{ } \mu\text{m}/10 \text{ } \mu\text{m}$, $T_0 = 539 \text{ K}$, $\sigma_0 = 7.5 \times 10^5 \text{ S/m}$, $\alpha^{-1} = 4.5 \text{ } \text{\AA}$, and $V_t = 0\text{--}3 \text{ V}$. The semiconductor thickness was taken as 2 nm. (b) The same experimental data as in Fig. S3a plotted on a double logarithmic scale. The red lines are a power-law fit at high gate bias, for each temperature.

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