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Supplementary Information

Enhanced charge-carrier mobility in polymer nanofibers realized by solvent-resistant soft nanolithography

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Materials: *n*-type Si (100) wafer with low resistivity (<6 mΩ·cm) and coated by a thermally-grown SiO_2 layer with thickness of 400 nm are provided by Silicon Materials. 5% dimethyldichlorosilane (DMDS) in heptane (silanization solution I) is from Sigma-Aldrich. The 2-hydroxy-2-methylpropriophenone photoinitiator (Darocur 1173) used for fabricating PFPE elements is from Ciba. Regioregular P3HT>99% with an average molecular weight of 87 kg/mol is purchased from Sigma-

Aldrich, and dichlorobenzene is from J. T. Baker. All the samples in this study are prepared by the same active material. Poly(dimethylsiloxane) (PDMS) components (Sylgard 184 Silicone Elastomer Kit) are purchased from Dow Corning (Midland, MI).

Device fabrication: A thin metal film (10 nm/50 nm of Cr/Au) is deposited by a phase vapor deposition system (PVD 75, Kurt J. Lesker) through a shadow mask, using micrometric Cu grids with bars of 25 μm in width and a matrix of 16×16 square holes with side of 100 μm (TAAB Laboratories Equipment Ltd). Thereafter, the samples are treated by DMDS under N_2 atmosphere to make hydrophobic the SiO_2 surface. Two Si master templates, consisting of parallel grooves with a period of 1 μm and 330 nm (height of 300 nm) are realized by electron beam lithography with a Raith 150 equipment and a subsequent CF_4/Ar reactive ion etching. The masters are replicated by molding, starting from a PFPE-prepolymer obtained by mixing the PFPE-urethane dimethacrylate with 4% w/w of photoinitiator, or from a PDMS prepolymer (base and curing agent in a 9:1 w/w ratio). The liquid PFPE is poured onto the master surface and spin-cast at 400 rpm for 40 s. The PFPE polymerization is carried out under UV irradiation (λ ~ 360 nm, delivered by two 6 W lamps for 30 s at a distance of 10 cm from the sample), under nitrogen atmosphere. PDMS prepolymer is instead cured at 140 °C for 15 minutes.

OFETs based on P3HT films (300 nm thick) are realized by spin-coating (1000 rpm for 60 s) a 0.2 mM dichlorobenzene solution. P3HT features are produced by depositing a 1 μL droplet of P3HT solution between the PFPE (or PDMS) mold and the OFET substrate. The P3HT solution does not wet the PFPE surface, remaining highly confined within the recessed features of the mold. After the complete evaporation of the solvent (at 50 °C for 2 hours), the template is peeled-off and an array of spatially isolated features remains on the device, connecting source and drain. On the contrary, PDMS replicas undergo swelling when exposed to the dichlorobenzene solution, with a consequent deformation and loss of conformal contact with the substrate during the lithographic procedure, as

clearly visible in Fig. S1. A layer of P3HT is indeed present underneath the features fabricated by PDMS molds. Thermal annealing of the final devices is carried out at 150 °C for 5 min under N_2 atmosphere.

Optical characterization. Fluorescence microscopy (Olympus IX71) is performed exciting samples with an Hg lamp (U-RFL-T, Olympus, Tokyo, Japan). Confocal microscopy is carried out using an Olympus FV-1000 microscope (Olympus Europa Holding GmbH, Hamburg, Germany), equipped with a 40× objective and an Ar laser source (excitation wavelength 488 nm; VFC SP 2009, CVI Melles Griot, Albuquerque, NM). Polarized absorption spectra are acquired by the UV/Vis/NIR spectrophotometer Lamba950 (PerkinElmer, Waltham, MA, USA), with incident light filtered by a polarizer.

SEM and AFM characterization. SEM is performed by using a Raith 150 electron beam system operating with an acceleration voltage of 5 kV and an aperture size 60 μm and by a Nova NanoSEM 450 instrument (FEI Europe) with an acceleration voltage of 10 kV and an aperture size of 30 μm. Tapping-mode AFM is performed in air, employing a Nanoscope IIIa controller with Multimode head integrated with a E-scanner (Veeco Instruments, Plainview, NY). Phosphorous-doped Si tips are employed with an 8-10 nm nominal curvature radius and a resonant frequency of 270 kHz.

Electrical characterization. A probe station (PH100, Süss Micro TecAG) and a stereomicroscope (MZ16FA, Leica Microsystems GmbH) are used for electrically contacting transistors. The characterization is carried out in air at room temperature, collecting and analyzing signals by means of a semiconductor parameter analyzer (4200 SCS, Keithley Instruments Inc. Cleveland, OH). In Fig. S2a we show the *D-S* current-voltage [$I_{ds}(V_{ds})$] characteristics for gate voltages (V_{gs}) from 0 to -100 V, for devices patterned by PDMS molds with 1 μm periodic grooves. The corresponding transfer characteristics, $I_{ds}(V_{gs})$, and $|I_{ds}|^{1/2}(V_{gs})$ curves (for V_{ds} = -100 V) are displayed in Fig. S2b.

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X-ray diffraction measurements: Grazing incidence wide angle X-ray scattering (GIWAXS) measurements are performed at the X-ray micro-imaging laboratory (XMI-LAB) of the IC-CNR, by a synchrotron class rotating anode X-ray microsource (Rigaku FR-E+ SuperBright) coupled through a focusing high-flux multilayer optics (Cu radiation) to a three-pinhole camera (SMAX-3000). Data are collected using a beam size at the sample position (circular shape) approximately equal to 200×200 μm^2, and a RAXIA image plate detector with off-line read-out unit and 100 µm pixel size. The detector is positioned at ~120 mm from the sample, and the angle of incidence of the x-ray beam on sample surface is 0.8°. The out-of-plane and the in-plane XRD profiles, obtained from the vertical ($Q_r \approx 0$) and horizontal ($Q_z \approx 0$) cuts respectively, taken in the 2D GIWAXS maps, are reported in Fig. S3, for the patterned nanostructures.

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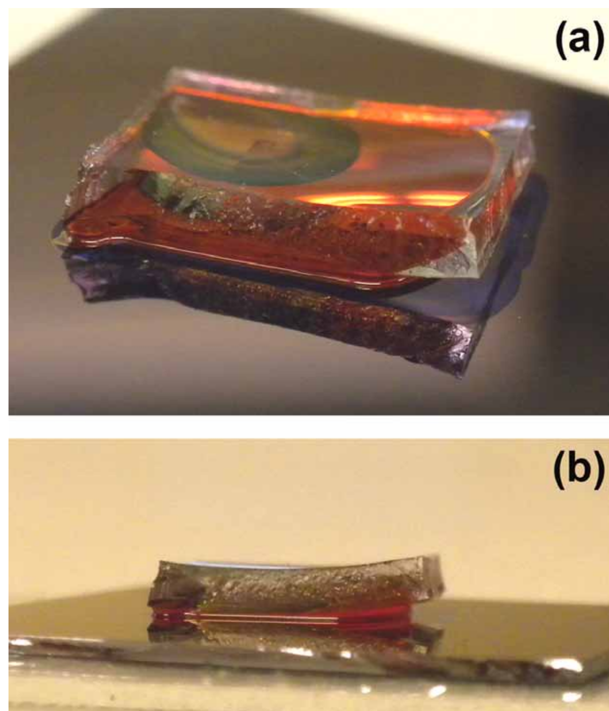

Fig. S1. (a)-(b) Photographs of a PDMS replica placed in contact with the dichlorobenzene solution of P3HT. The bending of the elastomeric element is clearly visible.

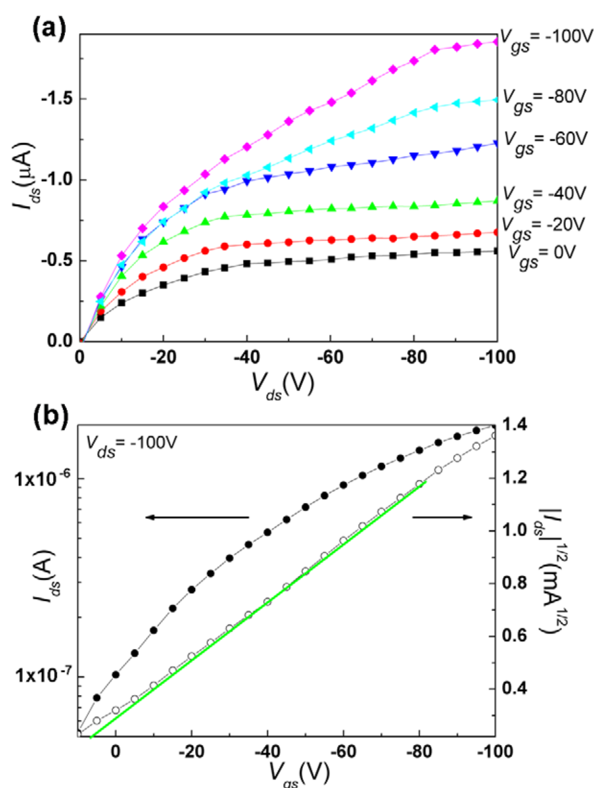

Fig. S2. (a) Output characteristics of OFETs with P3HT features of 270 nm, produced by means of a PDMS replica, for various gate bias, V_{gs} = 0 V (squares), -20 V (circles), - 40 V (upward triangles), -60 V (downward triangles), – 80 V (diamonds), and - 100 V (leftward triangles). (b) Corresponding transfer characteristics $I_{ds}(V_{gs})$ (left vertical scale) and $|I_{ds}|^{1/2}(V_{gs})$ (right vertical scale), for V_{ds}= - 100 V. Continuous line: linear fit to data.

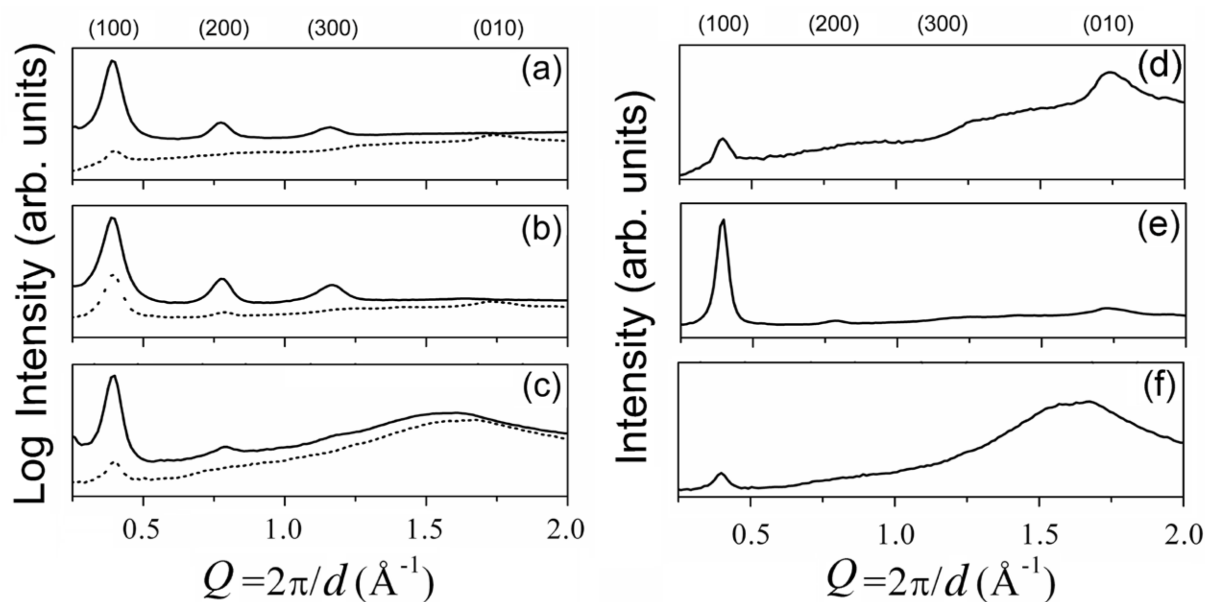

Fig. S3. (a)-(c): Out-of-plane (continuous line) and in-plane (dotted line) cuts extracted from the 2D GIWAXS maps for 270 nm P3HT features obtained by means of PDMS molds, 270 nm P3HT features obtained by PFPE molds, and 80 nm features obtained by PFPE molds, respectively. (d)-(f) Corresponding in-plane cuts plotted in linear scale for sake of better visualization.