Supplementary Information for

Self-Healing of Defects in Uniaxially Aligned Semiconducting Polymer Crystals via Molecular Doping: Insights into Crystallization from Transient vs. Settled Amorphous Phases

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Experimental

Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT, M_w = 70,000 g/mol) was purchased from Rieke Metals Inc. 1,3,5-Trichlorobenzene (1,3,5-TCB, 99%) and acetonitrile were obtained from Sigma Aldrich, while 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ, >98%) was sourced from Tokyo Chemical Industry Korea.

Device Fabrication & Sequential Doping Process

To fabricate the P3HT_{EFT} films, a eutectic pencil was prepared. P3HT and the 1,3,5trichlorobenzene (1,3,5-TCB) were mixed in a 1:1 weight ratio and completely dissolved in chloroform. The solution was filtered through a PTFE syringe filter (0.2 μ m pore size) and dried at room temperature for 4 hr. The resulting powder was then ground and compressed under a pressure of ~600 MPa to form a pellet, which was subsequently cut and inserted into a pencil for EFT writing. The P3HT_{EFT} films were fabricated by rubbing the eutectic pencil at a speed of 3500 mm/min, applying a pressure of 0.2-0.3 MPa on a glass substrate or on a silicon wafer at a moderate temperature (55 °C). The F4TCNQ doping solution was prepared at various concentrations (0.1 mg/mL, 0.3 mg/mL, 0.5 mg/mL, 1.0 mg/mL, 1.5 mg/mL, 2.0 mg/mL, 2.5 mg/mL, 3.0 mg/mL) in acetonitrile. 200 μ l of the solution was applied to the P3HT_{EFT} film for 10 s, followed by spin-coating to remove excess solution. Gold electrodes (thickness: 100 nm and length: 0.5 mm) were deposited on the P3HT_{EFT} film by thermal evaporation.

Characterizations

All measurements were obtained using instruments located at the Center for Polymers and Composite Materials (CPCM), Hanyang University, Korea, unless otherwise specified. Optical and polarized optical microscope images were recorded on an Olympus BX51 TR-N33MU. UV-VIS absorptions were measured by Agilent Technologies 8453 UV spectrophotometer equipped with polarizers (Edmund Optics). Raman spectra were recorded using a RamanRxn1 (Kaiser Optical Inc.) equipped with a 785 nm laser. Grazing incidence X-ray diffraction (GIXD) and polarized FT-IR mapping experiments were conducted at the Pohang Accelerator Laboratory (PAL). GIXD measurements were conducted using a wavelength of 1.12 Å, a sample-to-detector distance of 224.4 mm, and an incident angle of 0.12°, with sucrose as a reference. Electrical conductivity was measured with a probe station (MS TECH) equipped with a Keithley 4200A-SCS parameter analyzer using a two probe system.



Figure S1. Polarized optical microscopy (POM) micrographs of (a) the P3HT_{SC} film and (b) the d-P3HT_{SC} film when the drawing direction is aligned parallel to the light polarization.



Figure S2. Polarized UV-VIS absorption spectra recorded at various polarizer angles for (a) $d-P3HT_{EFT}$ film and (b) $d-P3HT_{sc}$ film.



Figure S3. (a) Optical microscopy image of the d-P3HT_{SC} film, showing the polarized FT-IR mapping area. (b) Polarized FT-IR spectra of the d-P3HT_{SC} film under polarized conditions. The red and solid lines correspond to the rotation angle at 0° and 90°. FT-IR mapping micrographs of d-P3HT_{SC} using (c, d) the doping-induced mode of P3HT ($\tilde{\nu} = 1350 \sim 1000 \text{ cm}^{-1}$) and (e, f) the F4TCNQ anion vibronic band ($\tilde{\nu} = 2188 \sim 2180 \text{ cm}^{-1}$) at the rotation angle of (c, e) 0° and (d, f) 90°.



Figure S4. The GIXD patterns of (a, b) P3HTsc and (c, d) d-P3HTsc films at the rotation angles of (a, c) 0° and (b, d) 90°.



Figure S5. Changes in the full width at half maximum (FWHM) of the (a, c) (100) crystal peak and (b, d) (010) crystal peak upon doping for (a, b) P3HT_{EFT} and d-P3HT_{EFT} and (c, d) P3HT_{SC} and d-P3HT_{SC} films.



Figure S6. Comparison of electrical conductivities between $d-P3HT_{sc}$ and $d-P3HT_{EFT}$ films.