Electronic Supplementary Information

Post-Deposition Dipping Method for Improving the Electronic Properties of a Narrow Bandgap Conjugated Polymer

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Experimental

Synthesis

Poly[(4,4-didodecyldithieno[3,2-b:2',3'-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl], **P1** has been prepared by following a previous report.[1] For comparison of UV absorption spectra, **P1** samples with various molecular weights were synthesized by controlling the polymerization stoichiometry.

Device Fabrication and measurement

Poly[(4,4-didodecyldithieno[3,2-b:2',3'-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (**P1**) was prepared according to the method described in our previous report.[1] Once the

polymerization was complete, the reaction was quenched with methanol and the product was purified via Soxhlet extraction successively with hexane (4 h), THF (16 h) and acetone (1 h) to obtain **P1** in sufficiently high average molecular weights. After Soxhlet extraction, the number average molecular weight (M_n) and polydispersity index were found to be 25.1 KDa and 2.5 respectively, as measured by using GPC with polystyrene standards. Field-effect transistors with a bottom-gate, top-contact geometry were fabricated by using heavily doped n-type Si wafers as the gate electrodes and a 150 nm-thick thermally grown silicon dioxide (SiO_2) layer (capacitance = 20 nF cm^{-2}) as the gate dielectric. Hexamethyldisilazane (HMDS) was used as the organic interlayer material between the organic active material and the dielectric layer to reduce interface charge trapping, and spin-cast onto the SiO_2 substrate. **P1** chlorobenzene solution (5 mg mL^{-1}) was continuously kept at 100°C to ensure that **P1** was completely dissolved. This solution was spin-cast onto the substrate to fabricate **P1** thin-films with thicknesses of ~17.8 nm at 1800 rpm, which were then dipped into methylene chloride, hexane, and acetone for various dipping times. The gold source and drain electrodes (channel length: 50 μm, width: 1000 μm) were thermally evaporated through shadow masks. The electrical characteristics of the OFETs were measured in the accumulation mode with Keithley 4200 source/measure units at room temperature and under ambient conditions.

Characterization of the P1 thin-film and solution

Solubility test: The solubility of **P1** in chlorobenzene, methylene chloride, hexane, and acetone was determined. The solutions were then stirred for 4 days at room temperature followed by an idle period to allow the solutions to settle. The undissolved particles were filtered and the UV-vis absorption of these solutions was recorded. The concentration in each solvent was calculated by using Beer's law.

Uv-vis analysis: To obtain the UV absorption spectra of the low MW components dissolved in hexane, 50 spin-coated films were dipped into hexane for a few minutes. After dipping, the hexane solution was removed and dried, and then the remaining low MW component was re-dissolved in chlorobenzene. For comparison of the UV absorption spectra, **P1** samples with various MWs were synthesized by controlling the stoichiometric adjustment.[1] Solid and solution state UV-vis absorption spectra were recorded on a Beckman Coulter DU 800 series spectrophotometer at room temperature. Solution absorption studies were conducted in 1 cm

quartz cuvettes.

Grazing-incidence X-ray diffraction (GIXD) measurements were performed for the **P1** thin-films at the 8C1 beamline (wavelength approx. 1.54 Å) at the Pohang Accelerator Laboratory (PAL), Korea.

Film thickness: Film thicknesses were determined with an ellipsometer (M-2000V, J.A. Woollam Co., Inc.). An uncoated Si wafer was first scanned in the ellipsometer. Measurements were performed from 850 to 1000 nm at an angle of incidence of 75˚. The data obtained were fitted to a Cauchy model. The index of refraction was not kept constant while measuring the film thickness.

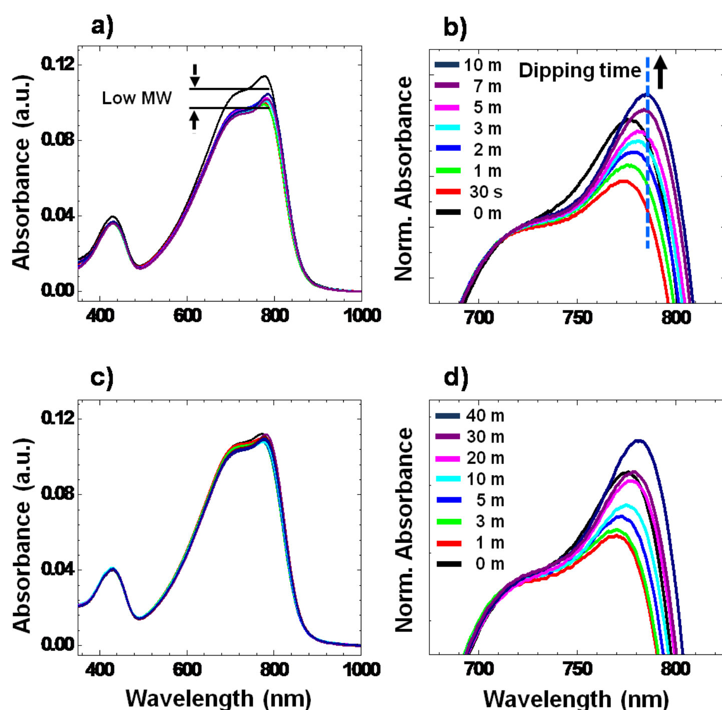

Figure S1. UV-vis absorption spectra of the **P1** thin-films for various dipping times in (a) methylene chloride and (c) acetone. Magnified normalized maximum UV-vis absorption bands of the **P1** thin-films for various dipping times in (b) methylene chloride and (d) acetone. The dipping time increases in the direction of the arrow.

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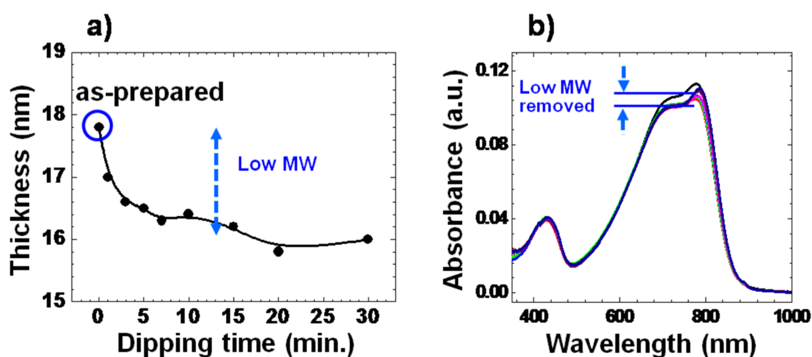

Figure S2. (a) The **P1** thin-films thickness, and (b) UV-vis absorption spectra of the **P1** thin films for various dipping times in hexane.

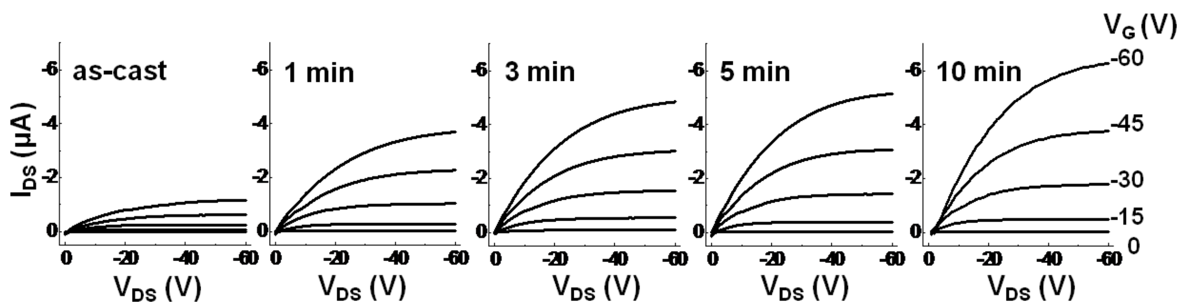

Figure S3. Current-voltage output characteristics of the **P1** FETs. (50 μm long and 1000 μm wide) after various dipping times.: 0, 1, 3, 5, and 10 minutes from left.

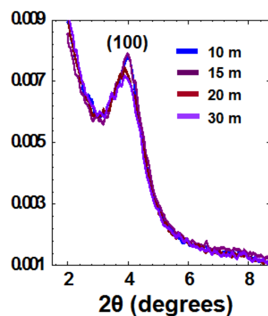

Figure S4. Out-of-plane grazing incidence angle X-ray diffraction intensities as a function of the scattering angle 2θ for **P1** thin-films on SiO_2/Si substrates for various dipping times: 10, 15, 20, and 30 minutes.

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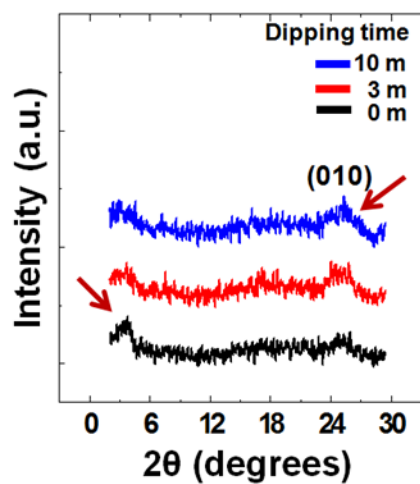

Figure S5. In-plane grazing incidence angle X-ray diffraction intensities as a function of the scattering angle 2θ for **P1** thin-films on SiO_2/Si substrates for various dipping times: 0, 3 and 10.

Reference

[1] R. C. Coffin, J. Peet, J. Rogers, G. C. Bazan, *Nat. Chem.,* 2009, **1**, 657.