

Supporting Information for

**Solvent-Resistant Organic Transistors and Thermally-
Stable Organic Photovoltaics Based on Crosslinkable
Conjugated Polymers**

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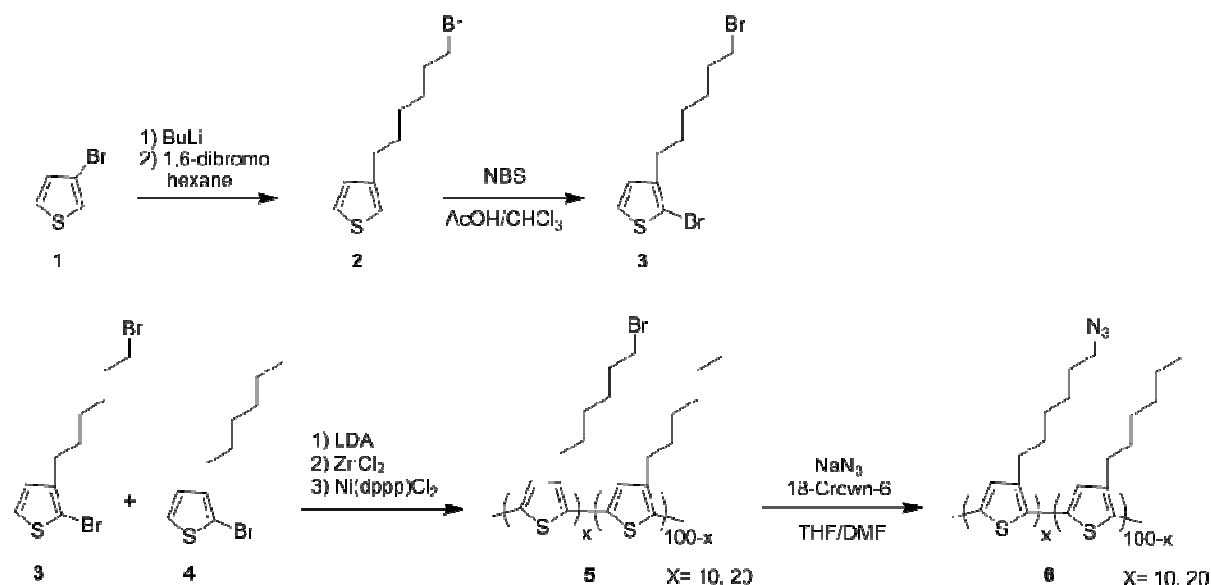
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Synthesis of P3HT-azidecopolymers



Scheme S1. Synthesis of P3HT-azide copolymers (P3HT-azide10 and P3HT-azide20)

Materials: Unless otherwise noted, commercially available reagents were used without further purifications. Column chromatography was carried out on 70~230 mesh. Analytical thin-layer chromatography (TLC) was performed using Merck Kieslgel 60 F₂₅₄ precoated plate with a fluorescent indicator and visualized with UV light (254 nm). All NMR spectra were measured in CDCl₃ with TMS or solvent signals as the standards. Pristine P3HT was purchased from Rieke Metals, Inc.

3-(6-Bromohexyl)thiophene (2): 3-Bromothiophene (5.0 g, 30.67 mmol) was dissolved in dry hexane (60 mL), under an argon atmosphere and cooled to -78 °C. Then, *n*-BuLi (2.5M in hexane, 12.3 mL, 30.67 mmol) was added dropwise to the stirred solution. Dry THF was then added dropwise until the white 3-lithiothiophene salt precipitated. The solution was then stirred for 1 h at -78 °C, and allowed to warm to 0 °C. 1,6-Dibromohexane (18.9 mL, 22.68 mmol) were then added and the reaction mixture was stirred at room temperature for 2 h. The resulting mixture was diluted with hexane (120 mL). The separated organic layer was washed with water, brine, dried over MgSO₄, and concentrated in vacuo. Excess remained 1,6-dibromohexane in crude product was removed by vacuum distillation, and then product was

purified by column chromatography using hexane as the eluent. 3-(6-Bromohexyl)thiophene (**2**) was obtained as a colorless oil (3.11 g, 41%). ¹H NMR (500 MHz, CDCl₃) δ 7.23 (dd, *J* = 7.85, 2.95 Hz, 1H), 6.92–6.94 (m, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.83–1.89 (m, 2H), 1.61–1.67 (m, 2H), 1.44–1.50 (m, 2H), 1.33–1.39 (m, 2H).

2-Bromo-3-(6-bromohexyl)thiophene (3): 3-(6-Bromohexyl)thiophene (**2**) (3.11 g, 2.58 mmol) was dissolved in CHCl₃ (80 mL) and acetic acid (40 mL). The solution was cooled in an ice bath, and *N*-bromosuccinimide (NBS) (2.35 g, 13.21 mmol) was added and the mixture was stirred at room temperature for 2 h. The reaction was monitored by TLC to establish completion. The resulting mixture was diluted with CHCl₃, washed with saturated aq Na₂S₂O₃, 2.0 M aq NaOH, water, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography using hexane as the eluent to afford 2-bromo-3-(6-bromohexyl)thiophene (**3**) as a light-yellow oil (2.95 g, 72%). ¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, *J* = 5.6 Hz, 1H), 6.78 (d, *J* = 5.6 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.84–1.90 (m, 2H), 1.55–1.62 (m, 2H), 1.44–1.50 (m, 2H), 1.32–1.38 (m, 2H).

P3HT-Br10 copolymer (5): Lithium diisopropylamide (LDA) was generated by addition of *n*-BuLi (2.5 M in hexane, 4.47 mL, 11.17 mmol) to a solution of dry diisopropylamine (1.98 mL, 1.40 mmol) in dry THF (20 mL) at -78 °C. The solution was stirred at this temperature for 1 h. The freshly generated LDA solution was added dropwise to the mixture of 2-bromo-3-(6-bromohexyl)thiophene (**3**) (0.38 g, 1.17 mmol) and 2-bromo-3-hexylthiophene (**4**) (2.62 g, 10.59 mmol) in dry THF (60 mL) at -78 °C. After 1 h reaction at -78 °C, ZnCl₂ (1.89 g, 13.85 mmol) was added portionwise to the mixture, which was stirred for 30 min and then warmed slowly to room temperature. Polymerization initiated by addition of Ni(dppp)Cl₂ (25.61 mg, 0.047 mmol) to the mixture was carried out at room temperature for overnight. The solution was quenched by 2 mL of 1.0 N aq HCl in order to stop the polymerization. The polymer was precipitated with methanol (450 mL) containing 7N NH₃ (6 mL) to neutralize it, and the resulting precipitate was then filtered. Oligomers and impurities in the product were removed by soxhlet extractions with methanol and hexane, followed by chloroform extraction. The resulting solid was dried under vacuum to yield the product (**5**). ¹H NMR (500 MHz, CDCl₃) δ 6.98 (s, 1H), 3.42 (t, *J* = 6.5 Hz, BrCH₂, 2H (10%)), 2.81 (t, *J* = 7.5 Hz, CH₂, 2H), 1.65–1.76

(m, CH₂, 2H), 1.40-1.50 (m, CH₂, 2H), 1.26-1.40 (m, CH₂CH₂, 4H), 0.92 (t, $J = 6.5$ Hz, CH₃, 3H (90%)).

P3HT-azide10 copolymer (6): P3HT-Br10 copolymer (**5**) (200 mg) was dissolved in THF (50 mL). The NaN₃ (60 mg, 0.91 mmol) and 18-crown-6 (240 mg 0.91 mmol) was dissolved in DMF (10 mL) and sonication was applied to obtain homogeneous solution. DMF solution was added to THF solution and then refluxed for 8 h under nitrogen atmosphere. The polymer was precipitated with methanol and the resulting precipitate was then filtered. Residual NaN₃ was removed by soxhlet extractions with methanol for 8h. The resulting solid was dried under vacuum to yield the product (**6**). ¹H NMR (500 MHz, CDCl₃) δ 6.98 (s, 1H), 3.28 (t, $J = 6.5$ Hz, N₃CH₂, 2H (10%)), 2.81 (t, $J = 7.5$ Hz, CH₂, 2H), 1.65-1.76 (m, CH₂, 2H), 1.40-1.50 (m, CH₂, 2H), 1.26-1.40 (m, CH₂CH₂, 4H), 0.92 (t, $J = 6.5$ Hz, CH₃, 3H (90%)).

Characterization of P3HT-azide copolymers

Size exclusion chromatography (SEC) measurement: Molecular weights (M_n) and polydispersities (PDI) of the P3HT-azide copolymers were analyzed by SEC (Waters 2414) using UV and RI detectors, which are calibrated by polystyrene standards.

Table S1. Characterization of two different P3HT-azide copolymers

Polymer	Azide unit in copolymer [mol %] ^[a]	M_n [g·mol ⁻¹]	Polydispersity [PDI]
P3HT-azide10	10.21	46,000	1.66
P3HT-azide20	19.92	28,000	1.44

[a] measured by ¹H NMR

FT-IR measurement: FT-IR measurement were obtained using Alpha FT-IR spectrometer (Bruker Optics) P3HT-Br10, P3HT-azide10 and P3HT-azide20 were dissolved in CB (10 mg mL⁻¹) and then, drop casted onto Si substrates. Thick films were taken off from the substrate and measured the transmittance.

Crosslinking behavior of P3HT-azide copolymers

Table S2. Mobility differences as a function of UV exposure time for P3HT-azide copolymers.

UV exposure time	Mobility [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]			
	0min	0.5min	1min	5min
P3HT-azide10	2.92×10^{-2}	3.10×10^{-2}	2.05×10^{-2}	2.38×10^{-2}
P3HT-azide20	3.45×10^{-2}	2.72×10^{-2}	1.52×10^{-2}	2×10^{-2}

UV/visible absorption spectra: UV/vis absorption spectra of P3HT, P3HT-azide10 (before crosslinking) and P3HT-azide10 (after crosslinking by UV 5 min) were obtained using a Carey 50 Conc UV/visible spectrophotometer. Thin films of P3HT and P3HT-azide10 were produced by spincoating from their solution in CB (10 mgmL^{-1}).

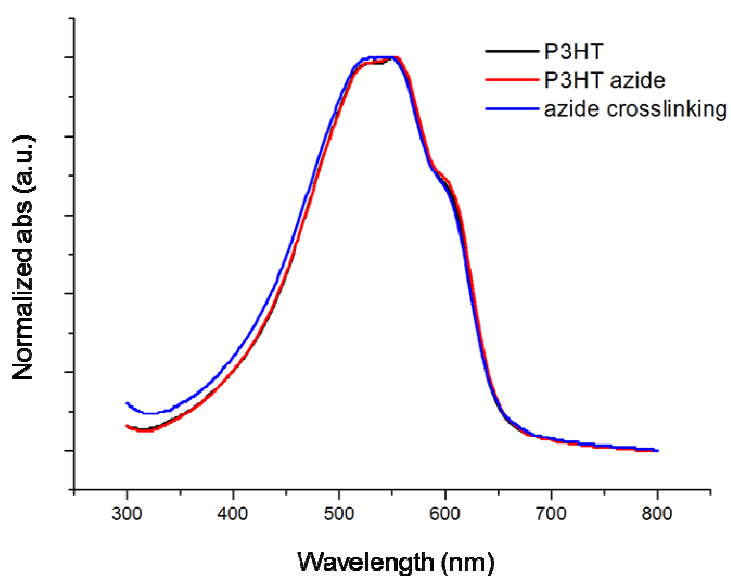


Figure S3. Normalized UV/vis absorption spectra for pristine P3HT (black line), P3HT-azide10 (red line) and 5 min UV treated P3HT-azide10 copolymer (blue line).

GIWAXS measurements: For GISAXS measurements, to produce identical surface conditions as samples for device measurement, a thin layer (20-30 nm) of PEDOT:PSS was spun onto silicon substrates. Two different films of P3HT-azide10 copolymers were produced by spincoating on top subsequently. Only one of them was exposed to UV 30min for its crosslinking. GISAXS measurements were performed on beamline 11.3 in the Stanford Synchrotron Radiation Laboratory. X-rays with a wavelength of 0.9752 Å were used. Incidence angle ($\sim 0.1^\circ$) was carefully chosen to allow for complete penetration of X-ray into the polymer film. The scattering spectra were collected as the 2-D image map that can be divided into a component in the plane of the substrate (q_x) and a component perpendicular to the substrate (q_z).

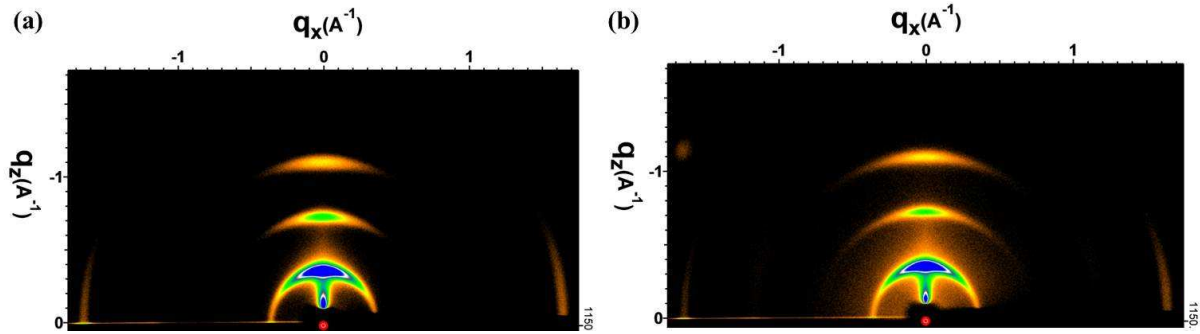


Figure S4. GIWAXS patterns of P3HT-azide10 films. All samples were first annealed at 150 °C for 30 min. (a) as prepared, and (b) after crosslinking by UV 30 min.

Solvent resistance of crosslinked P3HT-azide OTFT

Table S3. OTFT characteristics of P3HT and crosslinked P3HT- azide20 after washing with CB

	Before washing		After washing ^[a]	
	Mobility[cm ² V ⁻¹ s ⁻¹]	On/off ratio	Mobility[cm ² V ⁻¹ s ⁻¹]	On/off ratio
P3HT	3.01×10 ⁻²	3.2×10 ⁵	-	-
Azide 20	2.15×10 ⁻²	1.5×10 ⁵	1.53×10 ⁻²	2.3×10 ⁴

[a] P3HT film could not be measured due to lift-off of the electrode

Flexible OTFT and its solvent resistance behavior

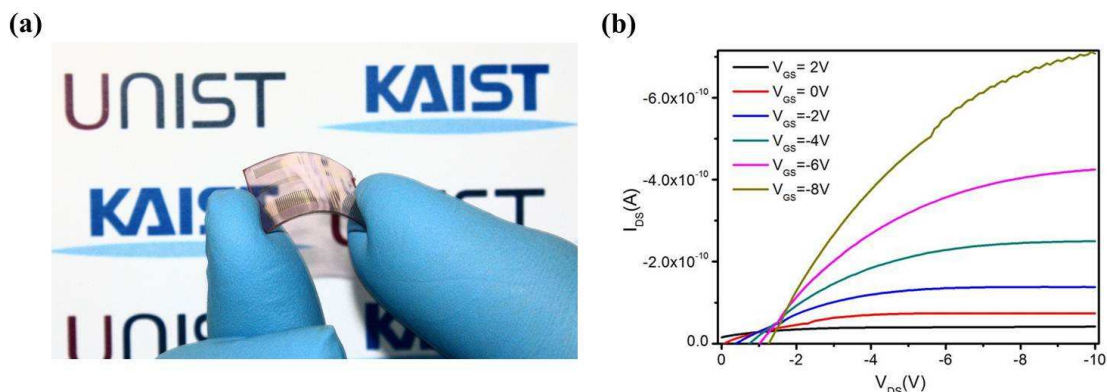


Figure S5. (a) Photographic image of flexible OTFTs of P3HT-azide copolymers. Flexible OTFT were fabricated using ITO-coated PEN substrate and PVP-HDA dielectric layer. (b) Output characteristics of P3HT-azide copolymers exhibiting field effects and good current modulation. The flexible OTFTs are prepared with top-gate bottom-contact geometry.

Flexible OTFT fabrication: PVP dielectric was deposited twice on PEN substrate coated with ITO to get proper thickness and reduce gate leakage which is induced by pinhole defect of polymer dielectric. PEN substrate coated with ITO was rinsed with isopropyl alcohol and blown with nitrogen stream. Poly-4-vinylphenol (PVP, Sigma-Aldrich) and crosslinking agent 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (HDA, Aldrich) were dissolved in propylene glycol monomethyl ether acetate (PGMEA) with ratio of 100 mgmL^{-1} and 10 mgmL^{-1} respectively for the first layer of polymer dielectric. The second layer of polymer dielectric was prepared by the same method but with a different concentration, dissolving with a ratio of 50 mgmL^{-1} and 5 mgmL^{-1} for PVP and HAD, respectively. We spin coated the first layer with 7000 rpm for 1 min. We annealed the substrate on a hot plate at 100°C for 1 h under ambient conditions and cooled down naturally. And then the second polymer dielectric layer was spin coated with the same condition as the first layer, then annealed at 100°C for 4 h and cooled down naturally. P3HT and P3HT-azide10 were dissolved in chloroform with ratio of 2 mgmL^{-1} and stirred to dissolve the compounds completely at 40°C . The semiconductor layer was prepared by spin coating with 3000 rpm for 30 sec and dried with for 12 h in a vacuum oven. After drying, they were annealed on a hot plate at 100°C for 1 h. Photo-crosslinking of azide copolymers was conducted using UV light ($\lambda = 254 \text{ nm}$) for 5 min in nitrogen atmosphere. Then, approximately 40 nm Au was thermally evaporated on the substrates with $50 \mu\text{m}$ channel length (L) and 20 of W/L ratio.

Air stability measurement of P3HT and P3HT-azide10 copolymers in OTFTs

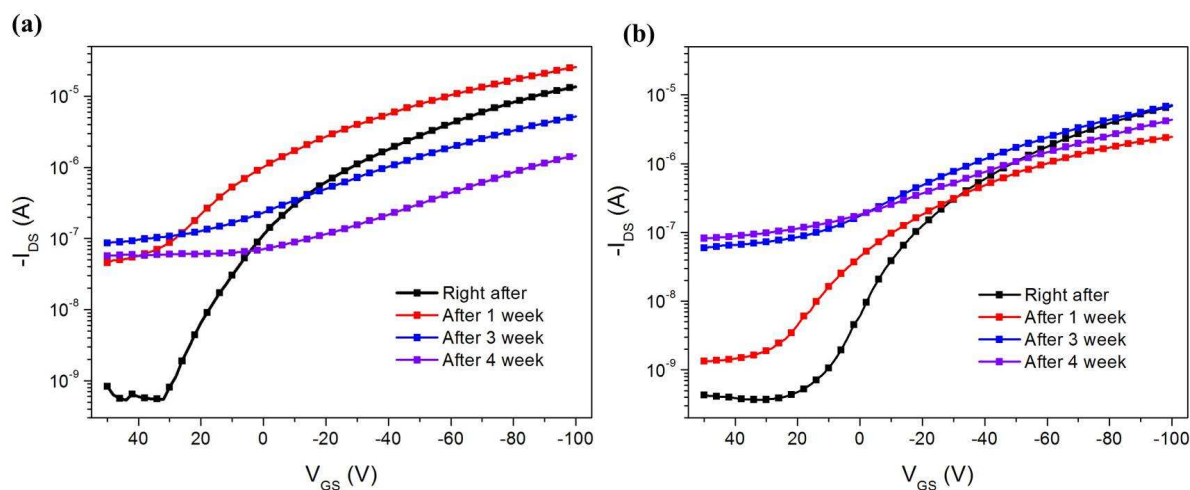


Figure S6. Changes of transfer characteristics of (a) P3HT and (b) crosslinked P3HT-azide10 as a function of exposure time to ambient condition.

Thermal stability of P3HT/PCBM OPVs with in-situ compatibilizer

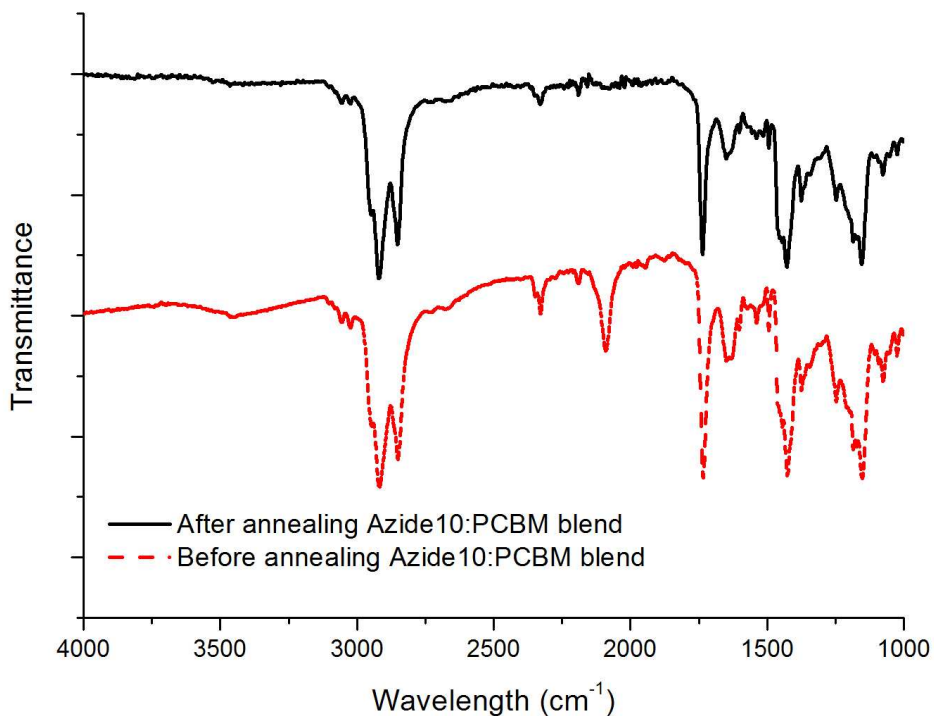


Figure S7. FT-IR data for P3HT-azide10 copolymer blended with PCBM (w/w = 1:1) before (black line) after annealing for 30 min at 150 °C (red dot line). Azide peak (2100 cm⁻¹) was disappeared after annealing, indicating the reaction of azide groups in P3HT-azide with PCBM.

