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Supporting Information

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Based on Photocrosslinkable Donor-Acceptor Conjugated
Polymers

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Supporting Information**Long-term thermal stability of high-efficiency polymer solar cells based on photocrosslinkable donor-acceptor conjugated polymers**

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1. Experimental

Materials: All air and moisture sensitive reactions were performed under inert atmosphere with glassware that was oven and flame dried. All organic extracts were dried over powdered MgSO₄ and concentrated under reduced pressure with a rotary evaporator. Flash chromatography was performed using Merck Kieselgel 60 (230 - 400 mesh) silica. Dry tetrahydrofuran (THF) and *N,N*-dimethylmethanamide (DMF) were purchased from Fisher Scientific and passed through two packed columns of neutral alumina, under N₂ pressure. All reagents from commercial sources were used without further purification.

Monomers 2,6-bis(trimethyltin)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-EH) and 1,3-dibromo-5-octyl-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (TPD-o) were synthesized and characterized as previously reported.^[1]

Synthesis of 1,3-dibromo-5-(8-bromooctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione

(TPD-Br): Thiophene-3,4-dicarboxylic acid (20.0 g, 116 mmol), glacial acetic acid (120 mL) and bromine (23.9 mL, 74.3 g, 465 mmol) were combined and heated to 55 °C for 96 h. After cooling the reaction mixture to almost room temperature (RT), excess bromine was quenched with saturated NaHSO₃, until the reaction contents became nearly clear. The mixture was cooled to 4 °C and flakey beige solids crystallized from solution. The crystals were crushed during filtration and were washed with ice water to yield 2,5-dibromothiophene-3,4-dicarboxylic acid as a beige powder (22.0 g, 57 %). ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) = 162.5, 135.9, 115.3. HRMS (EI, *m/z*): calcd. for C₆H₂Br₂O₄S [M]⁺: 329.8020; found, 329.7987.

2,5-Dibromothiophene-3,4-dicarboxylic acid (13.3 g, 40.3 mmol) was combined with acetic anhydride (110 mL) and stirred at 110 °C for 1 h. After cooling the reaction flask to RT, crystallization occurred. Pure crystals were obtained by filtration and washing with hexanes to yield 4,6-dibromothieno[3,4-*c*]furan-1,3-dione as off-white needles (10.9 g, 87 %). ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) = 161.7, 135.0, 114.7. HRMS (EI, *m/z*): calcd. for C₆Br₂O₃S [M]⁺: 311.7914; found, 311.7919.

4,6-dibromothieno[3,4-*c*]furan-1,3-dione (4.00 g, 12.8 mmol) was dissolved in dry THF (12 mL). Ammonia (7.54 mL of a 5.1 M solution in methanol, 38.5 mmol) was added to the flask and the reaction mixture was stirred at RT for 5 min. After removing volatile species in vacuo, water was added to the flask until the organic residue completely dissolved. The organic species was precipitated by dropwise addition of concentrated hydrochloric acid (3 mL) and then filtered to yield 2,5-dibromo-4-carbamoylthiophene-3-carboxylic acid as a white powder (3.68 g, 87 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 13.46 (s, 1 H), 7.86 (s, 1 H), 7.62 (s, 1 H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) = 163.7, 161.9, 140.9, 133.3, 116.2, 109.8. HRMS (EI, *m/z*): calcd. for C₆H₃Br₂NO₃S [M]⁺: 328.8180; found, 328.8179.

Triethylamine (2.23 mL, 1.62 g, 16.0 mmol) and then carbonyldiimidazole (2.72 g, 16.8 mmol) were slowly added to a solution of 2,5-dibromo-4-carbamoylthiophene-3-carboxylic acid (5.26 g, 16.0 mmol) in dry THF (200 mL). After stirring for 12 h at RT, the reaction mixture was extracted with ethyl acetate (150 mL) and washed with 1.0 M aqueous NaHSO₄ (3 x 200 mL). The organic layer was dried, filtered and concentrated to yield 1,3-dibromo-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione as a fine white solid (4.62 g, 93 %). ¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) = 11.57 (s, 1 H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) = 161.0, 136.0, 112.5. HRMS (EI, *m/z*): calcd. for C₆HBr₂NO₂S [M]⁺: 310.8074; found, 310.8080.

1,3-Dibromo-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1.00 g, 3.22 mmol) was dissolved in dry DMF (6 mL) and combined with sodium hydride (0.100 g, 4.18 mmol). The reaction contents were stirred at RT for 1 h and then added dropwise to a 50 °C solution of 1,8-dibromooctane (2.62 g, 9.65 mmol) in dry DMF (10 mL). After stirring for 12 h at RT, the reaction mixture was extracted with ether (50 mL) and washed with water (3 x 50 mL). The organic layer was dried, filtered, concentrated and purified by column chromatography on silica gel with a mixed mobile phase of CHCl₃ and hexanes (80:20). Further purification of the organic extract by recrystallization in methanol and CHCl₃ yielded 1,3-dibromo-5-(8-bromooctyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione as flakey, light yellow crystals (0.534 g, 33%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 3.59 (t, *J* = 7.25 Hz, 2 H), 3.39 (t, *J* = 6.84 Hz, 2 H), 1.83 (m, 2 H), 1.62 (m, 2 H), 1.41 (m, 2 H), 1.32 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 160.5, 134.9, 113.1, 38.9, 34.2, 32.8, 29.0, 28.7, 28.3, 28.2, 26.8. HRMS (EI, *m/z*): calcd. for C₁₄H₁₆Br₃NO₂S [M]⁺: 500.8431; found, 500.8438.

Polymer molecular weight determination: Polymer solutions (1 mg/mL) were prepared using HPLC grade chloroform (CHCl₃). Samples were briefly heated and then allowed to return to room temperature prior to filtering through a 0.45 μm PVDF filter. Size exclusion chromatography (SEC) was performed with HPLC grade CHCl₃ eluent at 1.0 mL/min by

using three PLgel columns (7.5 x 300 mm) with pore sizes of 10^5 , 10^3 , and 500 Å, respectively. The particle size in columns was 5 μm and the columns were thermostated at 35 °C. The SEC system consisted of a Waters 510 pump, a Waters 717 autosampler, a Waters 486 UV-Vis detector, and a Wyatt Optilab DSP differential refractive index detector. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Empower software from Waters.

Representative Synthesis of Copolymers: BDT-EH (200 mg, 259 μmol), TPD-o (91.3 mg, 216 μmol), TPD-Br (21.7 mg, 43.2 μmol), tris(dibenzylideneacetone)dipalladium(0) (7.11 mg, 7.77 μmol) and tri-*o*-tolylphosphine (9.46 mg, 31.1 μmol) were combined and then cycled 3 times with vacuum and nitrogen. The reagents were dissolved in dry chlorobenzene (6.0 mL) and stirred at 110 °C for 36 h. A strong complexing ligand (*N,N*-diethyl-2-phenyldiazene-carbothioamide, 17.0 mg, 76.8 μmol mmol) was added to the reaction mixture to remove residual catalyst before precipitating the reaction contents into methanol (200 mL). The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 2 h with methanol, 2 h with methylene chloride and was finally collected in chlorobenzene. The chlorobenzene solution was then purified by column chromatography on mixed column of silica gel, Celite and neutral alumina with a mobile phase of warm chloroform. The eluted purple solution was finally concentrated in vacuo, precipitated into methanol (200 mL) and filtered to yield PBDTTPD-Br16 as a dark purple solid (179 mg, 96 %). SEC analysis: $M_n = 30.3$ kDa, $M_w = 71.1$ kDa, PDI = 2.35.

2. Experimental procedure to evaluate the extent of photocrosslinking

Photocrosslinking was carried out in a nitrogen-filled glove box by irradiating the polymer films with UV light ($\lambda = 254$ nm) from a low-power hand-held lamp ($2.1 - 2.4$ mW cm⁻²) with exposure times ranging from 0 to 45 min. To evaluate the extent of photocrosslinking, the irradiated polymer films were immersed into chlorobenzene for 5 min, followed by rinsing with acetone for 3 minutes and then dried under a stream of nitrogen. UV-Vis absorption spectra were then recorded on the polymer films after irradiation and solvent washing, and compared to the UV-Vis absorption spectra of the same polymer films prior to irradiation.

3. Device Fabrication

All devices were fabricated on ITO-coated glass substrates (pre-patterned, $R = 20 \Omega \square^{-1}$, Thin Film Devices, Inc.). The substrates were subjected to successive ultrasonication in de-ionized water (20 min), acetone (20 min) and isopropyl alcohol (20 min). The substrates were then dried under a stream of nitrogen. A thin-layer (40 nm) of filtered PEDOT:PSS (Baytron PH) was spin-coated onto UV-ozone treated ITO substrates at 4000 RPM for 40 s followed by baking at 140 °C for 15 min in air. All substrates were then moved to a nitrogen-filled glove box to perform all the following fabrication steps. Solutions of the polymers (15 mg/mL) and PC₇₁BM (40 mg/mL) in *o*-DCB were prepared separately and stirred overnight at 110 °C. The solutions were passed through a 0.45 μ m polytetrafluoroethylene filter, prior to the preparation of the blend solutions. The polymer:PC₇₁BM (TPD-Br16:PC₇₁BM = 1:2 wt/wt, TPD-Br33:PC₇₁BM = 1:2.5 wt/wt) blend solution (24 mg/mL in *o*-DCB) was spin-coated onto the substrate for 40 sec at 1200 RPM followed by 4 sec at 2000 RPM to produce a film with a thickness of 90-100 nm. UV-mediated photocrosslinking was then performed on the TPD-Br16 and TPD-Br33 cast films, by irradiating them with a low-power UV lamp at 254 nm (UV light intensity: $2.1 - 2.4$ mW cm⁻²). The cathode, consisting of Ca (20nm) and Al (100 nm), was then deposited by thermal evaporation under vacuum ($\sim 10^{-7}$ torr) through a

shadow mask defining an active device area of 0.03 cm^2 . The layout of the shadow mask afforded eight independent devices on each substrate. In order to carry out the thermal stability tests, thermal annealing was performed on complete devices on a temperature-controlled hot plate at $150 \text{ }^\circ\text{C}$. Devices were left to cool down to room temperature before testing. The current-voltage (J - V) curves were measured using a Keithley 2400 source-measure unit under AM 1.5G solar illumination at 100 mW cm^{-2} (1 sun) using a Thermal-Oriel 150W solar simulator. During device optimization, different concentrations for the blend solutions and different polymer:PC₇₁BM ratios were tested in order to obtain the optimized process conditions, and the experiments were repeated multiple times to ensure data reproducibility. Eight distinct devices on each substrate were tested.

4. Instrumentation

UV–Vis absorption spectra were recorded at room temperature using a Varian Cary 50 Conc UV-Visible spectrophotometer. The polymers were spin-coated on ITO-coated glass substrates from *o*-DCB solutions (15 mg/ml). The thickness of the thin films was measured by profilometry (Veeco Dektat 150) and determined to be $90 \pm 10 \text{ nm}$. A blank ITO-coated glass substrate was used as reference.

Tapping-mode atomic force microscopy (AFM) was performed on a Veeco Nanoscope V scanning probe microscope using RTESP tips.

5. References

- [1] C. Piliago, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2010**, *132*, 7595.

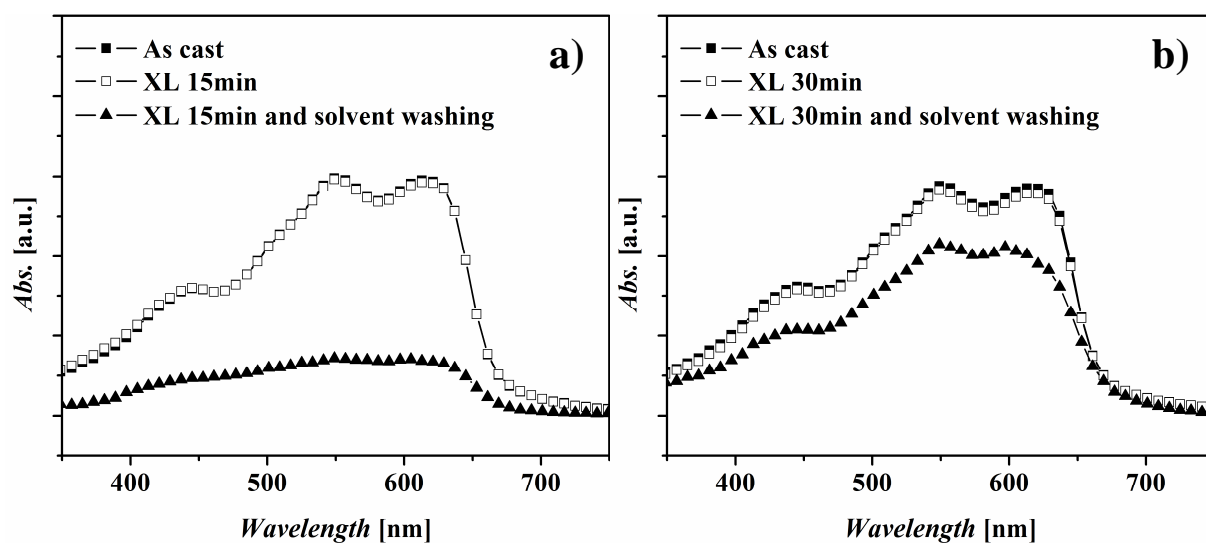


Figure S1. Absorption spectra of TPD-Br16 polymer films at different UV-irradiation times. a) after 15 min of UV-irradiation; b) after 30 min of UV-irradiation.

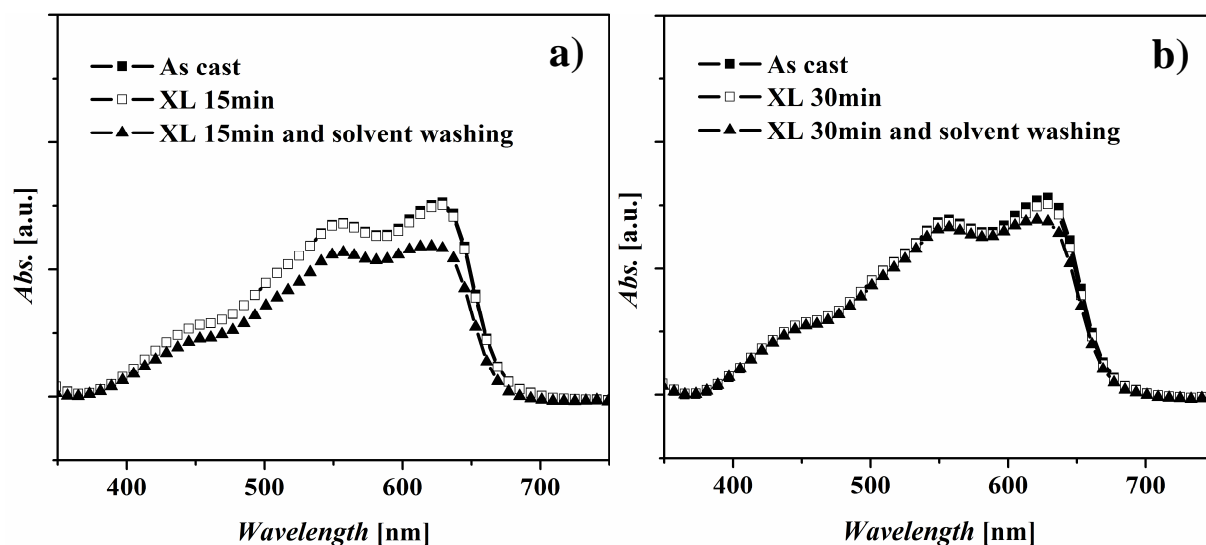


Figure S2. Absorption spectra of TPD-Br33 polymer films at different UV-irradiation times. a) after 15 min of UV-irradiation; b) after 30 min of UV-irradiation.

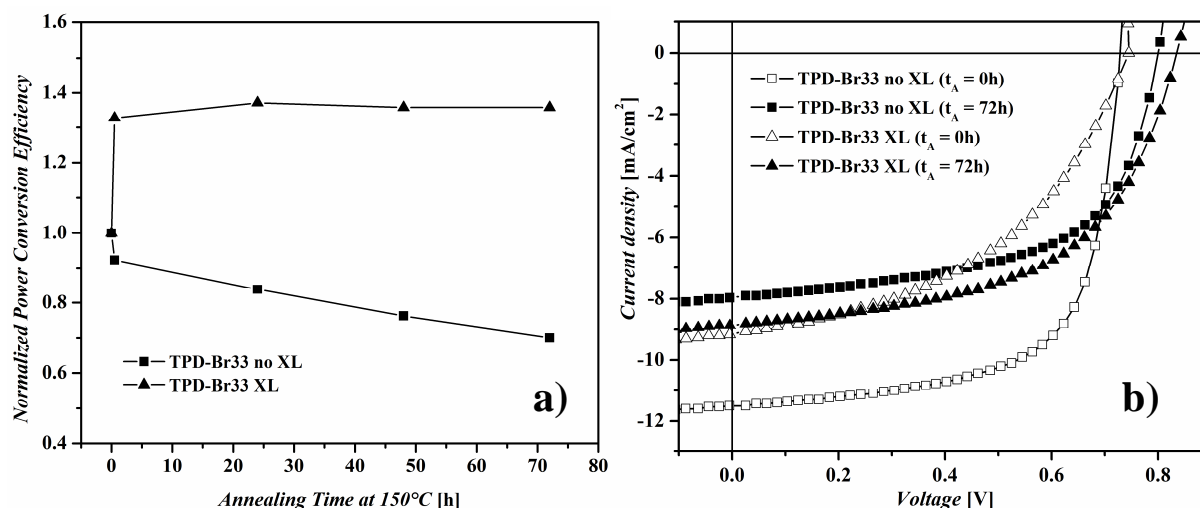


Figure S3. (a) Normalized power conversion efficiencies of non-photocrosslinked TPD-Br33 (no UV-XL ■) and photocrosslinked TPD-Br33 (UV-XL ▲) devices during long-term thermal annealing at 150 °C with PC₇₁BM as n-type material. The efficiency of each device was normalized to its initial efficiency (at annealing time 0 h). The same blend concentration (24 mg/mL in dichlorobenzene) and polymer:PC₇₁BM ratio (1:2.5) was used for all devices. (b) *J*-*V* curves of the best OPV devices before (open symbols, *t*_A = 0 h) and after (full symbols, *t*_A = 72 h) long-term thermal annealing (*t*_A).

Table S1. Characteristic photovoltaic parameters for TPD-Br33:PC₇₁BM devices.

	XL [a]	Annealing Time <i>t</i> _A [h]	<i>J</i> _{sc} [mA/cm ²]	<i>V</i> _{oc} [V]	FF [%]	PCE (PCE _{max}) [%]
TPD-Br33	-	0	-11.6	0.72	66	5.5 (5.6)
TPD-Br33	-	72	-8.1	0.80	59	3.9 (3.9)
TPD-Br33	+	0	-8.8	0.74	45	3.0 (3.1)
TPD-Br33	+	72	-8.7	0.83	55	4.0 (4.1)

[a] Active layers not subjected (-) and subjected (+) to crosslinking under UV-irradiation prior to cathode deposition.

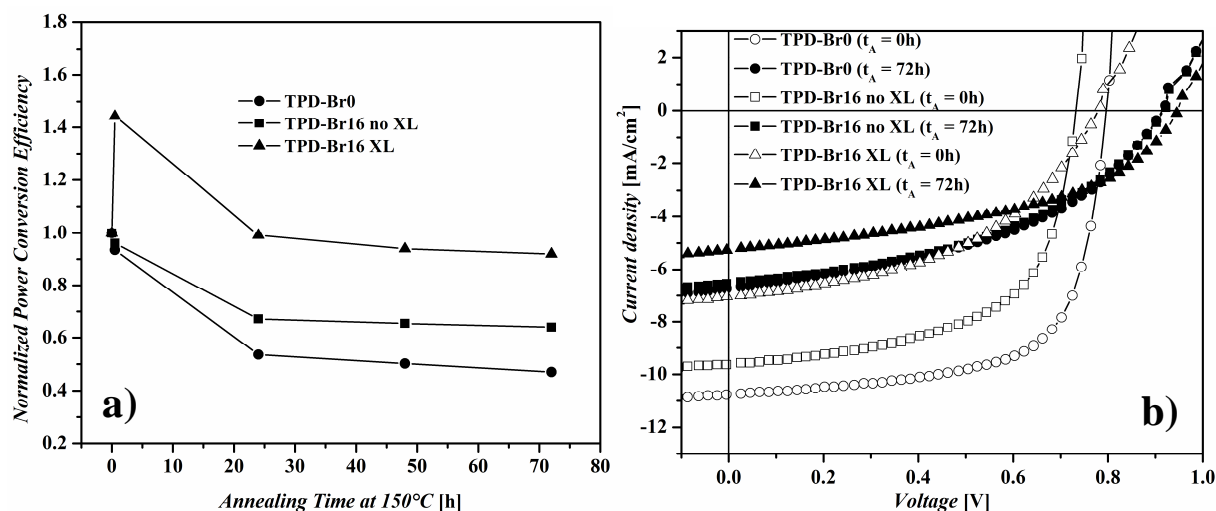


Figure S4. (a) Normalized power conversion efficiencies of TPD-Br0 (●), non-photocrosslinked TPD-Br16 (no XL ■) and photocrosslinked TPD-Br16 (XL ▲) devices during long-term thermal annealing at 150 °C with PC₆₁BM as n-type material. The efficiency of each device was normalized to its initial efficiency (at annealing time 0 h). The same blend concentration (24 mg/mL in dichlorobenzene) was used for all devices. The polymer:PC₆₁BM ratio was 1:2 for TPD-Br0 devices and 1:2.5 for both non-photocrosslinked and photocrosslinked TPD-Br16 devices. (b) *J-V* curves of the best OPV devices before (open symbols, $t_A = 0$ h) and after (full symbols, $t_A = 72$ h) long-term thermal annealing (t_A).

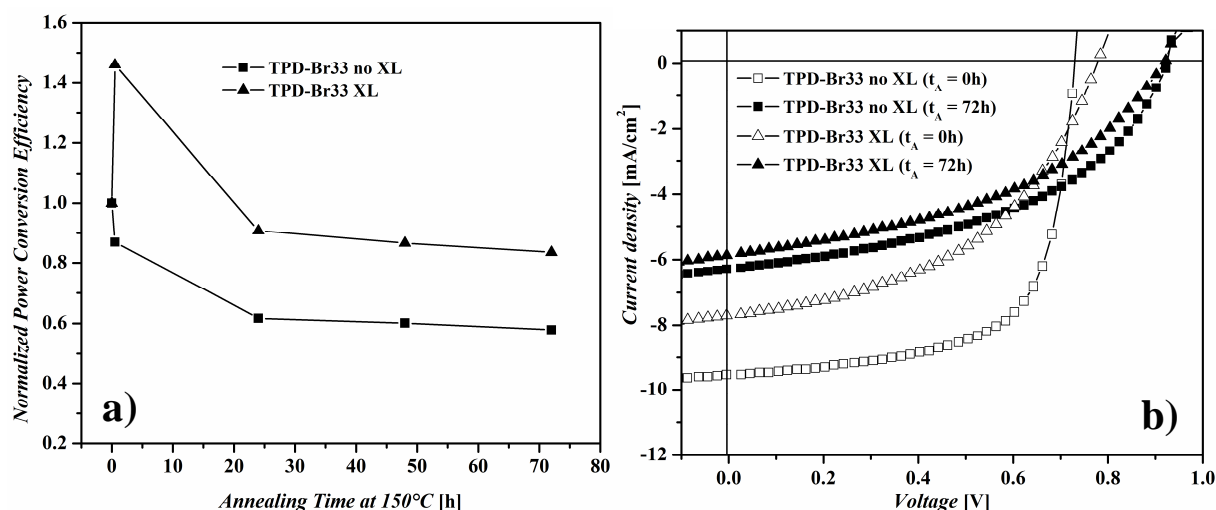


Figure S5. (a) Normalized power conversion efficiencies of non-photocrosslinked TPD-Br33 (no XL ■) and photocrosslinked TPD-Br33 (XL ▲) devices during long-term thermal annealing at 150 °C with PC₆₁BM as n-type material. The efficiency of each device was normalized to its initial efficiency (at annealing time 0 h). The same blend concentration (24 mg/mL in dichlorobenzene) was used for all devices. The polymer:PC₆₁BM ratio was 1:2.5 for all devices. (b) *J-V* curves of the best OPV devices before (open symbols, $t_A = 0$ h) and after (full symbols, $t_A = 72$ h) long-term thermal annealing (t_A).

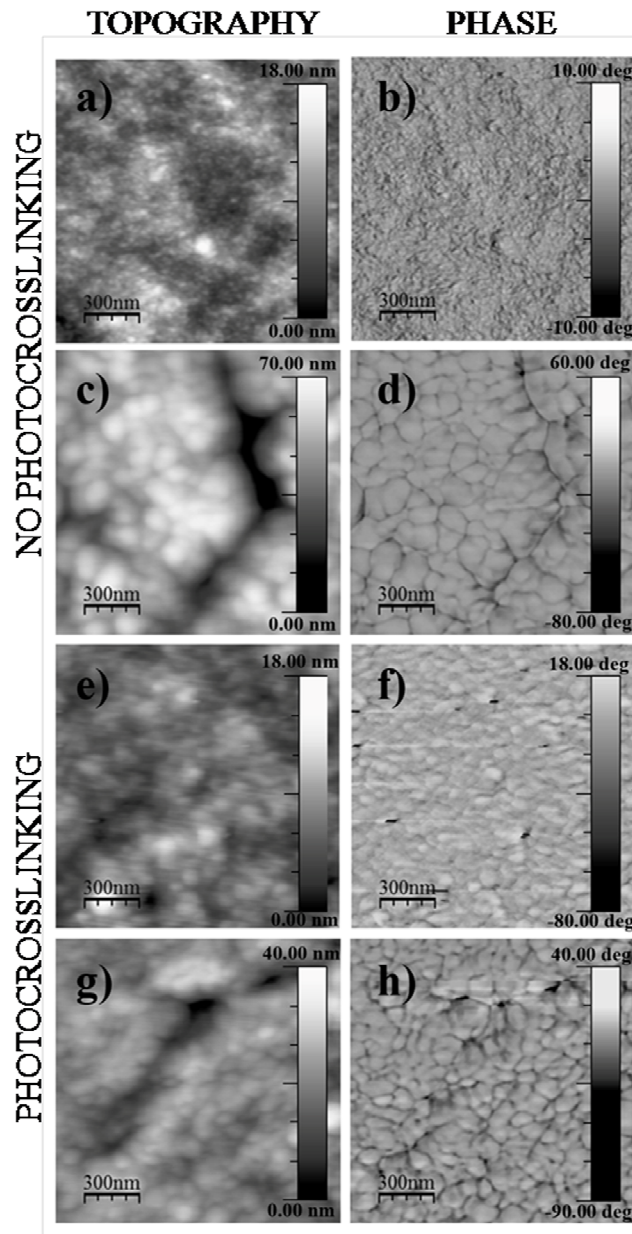


Figure S6. AFM ($1.5 \mu\text{m} \times 1.5 \mu\text{m}$) topography and phase images of TPD-Br16:PC₆₁BM active layers (1:2 wt/wt). The top four images are for the non-crosslinked films (TPD-Br16 no XL), prior to (a, b) and after (c, d) 72 h of thermal annealing at 150 °C. The bottom four images are for the crosslinked devices (TPD-Br16 XL), prior to (e, f) and after (g, h) 72 h of thermal annealing at 150 °C. The values of RMS roughness are as follows: 2.3 nm (prior to annealing) and 10.2 nm (after 72 h of annealing at 150 °C) for TPD-Br16 no XL; 2.1 nm (prior to annealing) and 5.9 nm (after 72 h of annealing at 150 °C) for TPD-Br16 XL.