

Supporting Information

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Increasing the Strength, Hardness, and Survivability of Semiconducting Polymers by Crosslinking

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1. Experimental Methods

1.1 *Synthesis of 4Bx.*

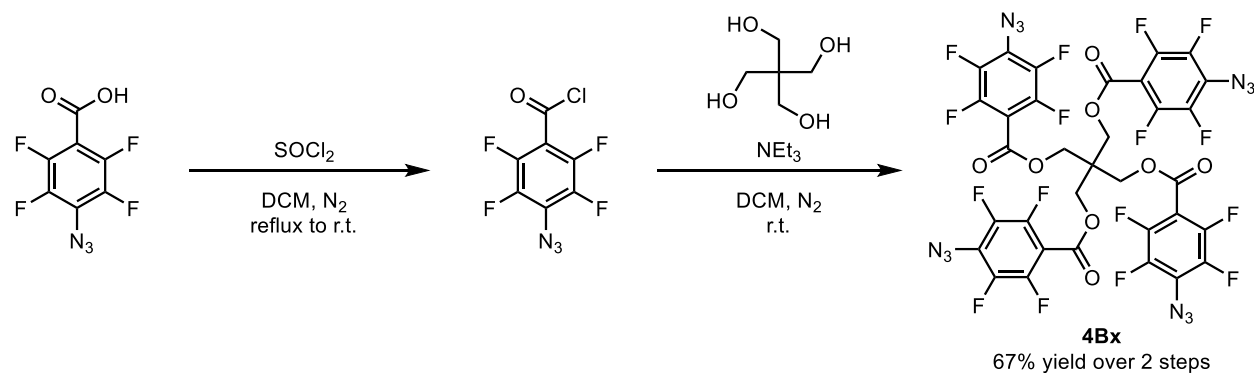
1.1.1 *Materials for Synthesis.*

Dichloromethane (DCM, Fisher Chemical) was degassed with argon and dried on a solvent purification system (JC Meyer) equipped with activated alumina columns before use. Ethyl acetate (Fisher Chemical) and hexanes (Fisher Chemical) were purchased and used as received. Triethylamine (NEt₃, Sigma-Aldrich) was passed through a column of activated alumina and stored over 4 Å molecular sieves for 24 h before use. Pentaerythritol (Sigma-Aldrich) was finely ground and dried in vacuum oven at 50 °C overnight before use. 4-azido-2,3,5,6-tetrafluorobenzoic acid (TCI Chemicals) and sulfurous dichloride (Sigma-Aldrich) were used as received.

Thin layer chromatography was performed on glass-backed silica TLC plates (SiliaPlate) with F254 indicator and analytes were visualized with a UV-C lamp. Flash chromatography was performed using a Teledyne ISCO CombiFlash NEXTGEN chromatography system with Siliaflash P60 Silica (40-60 µm) as the stationary phase.

NMR spectra were collected on a Bruker Avance-III 300 spectrometer operating at 300 MHz and 282 MHz for ¹H and ¹⁹F acquisitions, respectively.

1.1.2 *Synthesis of 2,2-bis(((4-azido-2,3,5,6-tetrafluorobenzoyl)oxy)methyl)propane-1,3-diyl bis(4-azido-2,3,5,6-tetrafluorobenzoate) (4Bx).*



The synthesis of **4Bx** was adapted from the procedure described by Kim et al.¹ A flame-dried Schlenk flask containing a magnetic stir bar was charged with 4-azido-2,3,5,6-tetrafluorobenzoic acid (192 mg, 5.18 eq., 818 μ mol) and purged with nitrogen. DCM (6 mL) and sulfurous dichloride (150 μ L, 13.1 eq., 2.07 mmol) were added under nitrogen via syringe. The flask was equipped with a reflux condenser and heated to reflux with stirring. After 24 hours, the reaction mixture was cooled to ambient temperature and stirred for an additional 24 hours. Volatiles were removed *in vacuo* to yield the crude acyl chloride as a light yellow oil. The residue was dissolved in 4 mL DCM and transferred via cannula to a separate flame-dried Schlenk flask containing a solution of 2,2-Bis(hydroxymethyl)propane-1,3-diol (pentaerythritol, 21.5 mg, 1.00 eq., 158 μ mol) and triethylamine (114 μ L, 5.18 eq., 818 μ mol) in DCM (4 mL). The resulting mixture was stirred at ambient temperature for 48 hours. Water (10 mL) was added to quench the reaction, and the organic phase was separated. The aqueous phase was extracted with DCM (3 x 10 mL), and the combined organic phases were washed with 30 mL brine, dried over magnesium sulfate, and concentrated *in vacuo*. The crude residue was purified by chromatography on silica gel with an eluent of hexanes/ethyl acetate (4:1, v/v; R_f = 0.52), followed by recrystallization from warm ethyl acetate/hexanes (ca. 4 mL and 35 mL,

respectively) to yield **4Bx** as colorless needles in 106 mg (67% yield). ^1H and ^{19}F NMR data matched the literature values.¹

1.2 Preparation of Substrates.

Glass substrates were used as purchased (25mm $\times$ 25mm, 1.1 mm thickness, purchased from Biotain Crystal Company) or cut using a diamond-tipped scribe (37.5 mm $\times$ 25 mm, 1.1 mm thickness) from 75 mm $\times$ 25 mm glass substrates (Fisherbrand, purchased from Fisher Scientific). Silicon substrates were purchased from WaferPro (100 mm N/PH (1-0-0), C04002) and diced into 25 mm $\times$ 25 mm squares. Glass, silicon, and unpatterned ITO substrates (25 mm $\times$ 25 mm, 100 nm of ITO deposited on top of a 1 mm glass substrate, purchased from Ossila) were cleaned by sonicating in Alconox and water, deionized (DI) water, acetone, and isopropyl alcohol (IPA) for 10 min each. Before deposition of the polymer solution, substrates were dried using compressed air and plasma treated in air (10 min, $\sim$ 500 mTorr) to increase the wettability of the substrate.

1.3 Preparation of Polymer Solutions and Film Formation.

J51 (1-Material, $M_n \sim$ 25 kDa, PDI $\sim$ 3), PTB7-Th (Ossila, $M_n \sim$ 29 kDa, PDI $\sim$ 1.95), N2200 (Ossila, $M_n \sim$ 90.9 kDa, PDI $\sim$ 2.2), PTB7 (Ossila, $M_n \sim$ 83 kDa, PDI $\sim$ 2.52), TQ1 (Ossila, $M_n \sim$ 61.5 kDa, PDI $\sim$ 2.44), 2DPP-2CNTVT (1-Material, $M_n \sim$ 24 kDa, PDI $\sim$ 2.5), PZ1 (1-Material, $M_n \sim$ 16.7 kDa, PDI $\sim$ 3), P3HpT (Rieke Metals, $M_n \sim$ 26.4 kDa, PDI = 2.2, RR = 93%), IDTBT (synthesized by H.C. and I.M.,^{2,3} $M_n \sim$ 38 kDa, PDI $\sim$ 2.8), DPP-C3 (synthesized by X.L. and J.M.,⁴ $M_n \sim$ 9.4 kDa, PDI $\sim$ 1.3), and DPP-C9 (synthesized by X.L. and J.M.,⁴ $M_n \sim$ 13.9 kDa, PDI $\sim$ 1.4) were dissolved in chlorobenzene (anhydrous for device fabrication) at a concentration of 10–15 mg mL⁻¹. For J51:N2200 and PTB7-Th:N2200 blends, the ratio of donor

polymer to acceptor polymer was 1:2 and 2:1 for each 12 mg mL⁻¹ solution, respectively. 4Bx was dissolved in anhydrous chlorobenzene at a concentration of 15 mg mL⁻¹. 4Bx (1–3 wt% with respect to the polymer) and 1,8-diiodooctane (DIO) (purchased from Sigma-Aldrich and used as received) (2–3 vol%) were added to each polymer solution as needed. All solutions were prepared in a nitrogen environment (<0.05% oxygen, ~20% RH). After preparation, polymer solutions were left inside the nitrogen environment to stir overnight (~12–16 h) at 60 °C before use. For polymer films subject to mechanical testing or morphological characterization, films were spun outside of the glove box in atmosphere. The polymer solution was deposited on top of a glass substrate with a syringe fitted with a 0.2 µm Nylon filter. Then, the polymer film was formed by spin coating the sample at 1000–2000 rpm (with a ramp half that of the spin speed, i.e., 500–1000 rpm s⁻¹) for 90 s followed by a 2000 rpm (1000 rpm s⁻¹) step if needed. To initiate crosslinking, polymer films were annealed at 150 °C for 90 min or 175 °C for 60 min on a hot plate in atmosphere. After annealing, the hot plate was turned off in order to let the films slowly cool to room temperature.

1.4 Preparation of Polymer Films for Cohesive Fracture Testing and Compressive Mechanical Testing

For fracture testing samples, glass substrates were cut using a diamond-tipped scribe and cleaned as previously described in **Section 1.2**. A layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), purchased from Heraeus (Clevios PH1000), was deposited on top of the glass substrate using a 1 µm glass fiber syringe filter (Chromspec) and spun at 4000 rpm (2000 rpm s⁻¹) for 60 s. Next, a 70–90 nm film of J51:N2200 (3 vol% DIO, 0–1 wt% 4Bx) or PTB7-Th:N2200 (2 vol% DIO, 0–1 wt% 4Bx) was spin coated on top of the PEDOT:PSS at a spin speed of 1800 rpm (1200 rpm s⁻¹) for 90 s

followed by 2000 rpm (1200 rpm s^{-1}) for 30 s in atmosphere. All films were annealed at 175°C for 60 min in atmosphere to initiate crosslinking for polymer blends that included 4Bx as the crosslinker. After annealing, 5 nm of Cr was deposited by thermal evaporation followed by 200 nm of Al by sputter deposition to form an encapsulation layer on top of the polymer film. Finally, a clean glass slide of the same size ($37.5 \text{ mm} \times 25 \text{ mm}$) was adhered to the top of the Al layer using Loctite E-20NS HYSOL epoxy. The final fracture testing sample was cured under nitrogen for 12 h at room temperature before use.

For samples used for compressive mechanical testing (i.e., nanoindentation), silicon substrates were diced and cleaned as described in **Section 2.2**. A solution of J51:N2200 (3 vol% DIO, 0–2 wt% 4Bx) or PTB7-Th:N2200 (2 vol% DIO, 0–2 wt% 4Bx) was drop cast ($\sim 0.4 \text{ mL}$) on top of silicon substrate in a fume hood. A glass crystallization dish (diameter = 125 mm, height = 65 mm) was used to cover the substrates. The polymer samples were allowed to dry over 48 h to form a solid film (J51:N2200 $\sim 4 \text{ }\mu\text{m}$, PTB7-Th:N2200 $\sim 12 \text{ }\mu\text{m}$). After drying, all polymer films were annealed at 175°C for 60 min in atmosphere to initiate crosslinking.

1.5 Mechanical Testing

1.5.1 Pseudo-Free Standing Tensile Tests (“Film-on-Water”)

For FOW tensile tests, a water-soluble sacrificial layer was first deposited on top of the glass substrate before the conjugated polymer film. For the sacrificial layer, a poly(acrylic acid) (PAA) film was used. PAA (purchased from Sigma Aldrich, $M_w = 100 \text{ kDa}$, 35 wt% in water) was diluted in DI water at a ratio of 1:15 to form a 2.3 wt% solution. The PAA solution was filtered using a $1 \text{ }\mu\text{m}$ glass fiber syringe filter (purchased from Chromatographic Specialties Inc.) before being deposited on top of the glass substrate. PAA sacrificial layers were spun at 500 rpm

(250 rpm s⁻¹) for 60 s followed by 2000 rpm (1000 rpm s⁻¹) for 30 s before the conjugated polymer film was deposited using spin conditions described in **Section 2.3**. All films were annealed at 150 °C for 90 min (for J51, PTB7-Th, and N2200) or 175 °C for 60 min (for J51:N2200 and PTB7-Th:N2200). For films containing 4Bx, this annealing step resulted in crosslinking. The polymer films were then scored into a dogbone geometry (length = 1.5 cm, center width = 0.4 cm) using a 3D-printed stencil. The thickness of each polymer film was measured using a Dektak XT stylus profilometer, operated with a force of 3 mg.

To conduct a film-on-water (FOW) tensile test, a dogbone-shaped polymer film was first floated off the glass substrate and onto the surface of water by dissolving the underlying PAA layer. The film was then aligned and adhered to polydimethylsiloxane (PDMS) (Sylgard 184, 1:20 crosslinker to elastomer base ratio) slabs, which were taped to the 3D-printed grips of a Mark-10 linear actuator connected to a 0.5 N force gauge. Films were uniaxially strained at a rate of $6.67 \times 10^{-4} \text{ s}^{-1}$ (0.4 mm min⁻¹) until fracture. The resulting force-displacement curve was converted into a stress-strain curve using the dimensions of the dogbone-shaped film as previously described.⁵

1.5.2 Cohesive Fracture Testing

Double Cantilever Beam testing (DCB) was performed in ambient conditions using a thin-film cohesion testing system (Delaminator DTS, Menlo Park, CA) which measured load, P , versus displacement, Δ . The initial displacement speed was set to $1 \text{ } \mu\text{m s}^{-1}$, which was increased linearly to accommodate the increasing crack length. The critical fracture energy, $G_c \text{ (J m}^{-2}\text{)}$, was then calculated from equation 1:⁶

$$G_c = \frac{12P_c^2 a^2}{b^2 E' h^3} \left(1 + 0.64 \frac{h}{a}\right)^2 \quad (1)$$

Where P_c is the critical load at which crack growth occurs, a is the crack length, E' is the plane-strain elastic modulus, and b and h are the width and half-thickness of the substrates, respectively. The crack length was estimated from elastic compliance ($d\Delta/dP$) using equation 2:

$$a = \left(\frac{d\Delta}{dP} \times \frac{bE'h^3}{8} \right)^{1/3} - 0.64h \quad (2)$$

1.5.3 Nanoindentation

Nanoindentation samples were prepared as described and glued to a steel substrate in order to secure the samples in the grips of the indenter. Nanoindentation measurements (quasistatic⁷ and dynamic⁸⁻¹³) were performed using an ultra-nanoindentation tester (UNHT³, Anton Paar) in ambient conditions. An acoustic isolation chamber and piezo vibration isolation table were used to dampen any surface or acoustic vibrations. Indentations were made using a Berkovich tip (total angle = 141.9°). The projected contact area was $A_C = 24.5 h_C^2$, where h_C is the contact depth of the indenter at maximum load P_{max} .¹⁴ The area shape function A_C was calibrated using a standard silica glass reference prior to testing. Protocol parameters were tuned using pilot tests to ensure accurate surface detection and to determine the loading protocol. For all tests, $P_{max} = 0.06$ mN was used. The maximum indentation depth (h_{max}) was less than 10% of the sample thickness to reduce the effect of the silicon substrate on the indentation measurement.¹⁵ A minimum of 30 indents were performed on each J51:N2200 sample, while a minimum of 60 indents were performed on PTB7-Th:N2200 samples due to the higher scatter.

In quasistatic testing, samples were loaded in force control up to P_{max} . At P_{max} , the load was held constant for 2 s and was then unloaded quickly. The time to maximum load was chosen

such that the maximum load was reached in a minute. The hold and unloading time were set at 1.8s to avoid any time dependent effects while still measuring the unloading curve, down to at 40% P_{max} (as sufficient to calculate the initial unloading slope, S). The output from the measurement was a load (P) versus load point displacement (h) curve at each indentation point, from which Young's modulus (E) and indentation hardness (H_{IT}) was calculated (**Figure S13**). Hardness (i.e., resistance of the material to permanent deformation) was calculated as by dividing P_{max} by the 2D projected contact area (A_c) between the sample and the indenter. The modulus was calculated using the unloading curve (i.e., where it is assumed that only elastic strain energy is being released). Both E and H_{IT} were calculated using the Oliver and Pharr Method encoded in the software provided with UNHT³ using the following equation, where ν is the Poisson ratio (assumed to be 0.35, as for poly(3-hexylthiophene)¹⁶).¹⁴

$$\frac{1 - \nu^2}{E} = \frac{2\sqrt{A_c}}{\sqrt{\pi} S} - \frac{1 - \nu_i^2}{E_i} \quad (3)$$

In dynamic testing (i.e., the continuous stiffness method), the protocol from the quasistatic testing was modified to include superimposed small harmonic oscillations in the force signal during loading in order to measure the viscoelastic properties of the material (e.g., storage modulus (E'), loss modulus (E''), and phase shift (δ)). The amplitude of force oscillation (F_0) and frequency (f) were set to be 0.01 mN and 10 Hz, respectively.⁹ The force amplitude was chosen such that the displacement amplitude (h_0) is much smaller than the indentation depth (h). Dynamic indentation tests generated curves of P vs h , from which the viscoelastic properties were calculated using the following equations encoded in the UNHT³ software (**Figure S13**).

$$\frac{E'}{1 - v^2} = \frac{\sqrt{\pi}}{2\beta\sqrt{A_c}} \left(\frac{F_0}{h_0} \cos \delta + m\omega^2 - K_i \right) \quad (4)$$

$$\frac{E''}{1 - v^2} = \frac{\sqrt{\pi} \omega}{2\beta\sqrt{A_c}} \left(\frac{F_0}{\omega h_0} \sin \delta - D_i \right) \quad (5)$$

Here, β is the constant depending on the indenter geometry (1.034 for a Berkovich tip), F_0 and h_0 are the force and displacement amplitudes, m is the mass of the indenter, $\omega = 2\pi f$ (where f is the harmonic frequency), K_i is the stiffness coefficient, and D_i is the damping coefficient. This model considers the indenter tip-sample interaction as a spring and dashpot system in parallel.⁹ The viscoelastic behavior of each sample can be expressed as $E = E' + iE''$, with the phase shift expressed by $\tan \delta = E''/E'$.

1.6 Fabrication and Measurement of EGaIn Solar Cells

EGaIn solar cells (ITO/PEDOT:PSS/BHJ/EGaIn), were fabricated by first depositing poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), purchased from Heraeus (Clevios PH1000), on top of an unpatterned ITO substrate to form a hole-transport layer (HTL). PEDOT:PSS was deposited using a 1 μm glass fiber syringe filter (Chromspec) and spun at 4000 rpm (2000 rpm s⁻¹) for 60 s to form a 35–45 nm film. Following deposition, a third of the PEDOT:PSS layer was wiped away using a foam swab and DI water in order to allow for contact to the ITO electrode. The PEDOT:PSS film was annealed at 120 °C for 30 min in atmosphere before being allowed to cool slowly to room temperature by turning off the hot plate. To form the bulk heterojunction, a 70–90 nm film of J51:N2200 (3 vol% DIO, 0–2 wt% 4Bx) or PTB7-Th:N2200 (2 vol% DIO, 0–3 wt% 4Bx) was spin coated on top of the ITO/PEDOT:PSS inside a

nitrogen environment ($<0.05\%$ oxygen, $\sim 20\%$ RH) at a spin speed of 1800 rpm (1200 rpm s^{-1}) for 90 s followed by 2000 rpm (1200 rpm s^{-1}) for 30 s. Following deposition, same third of the BHJ layer was wiped away using a foam swab and chloroform, again, to allow for contact to the ITO electrode. The bulk heterojunction was annealed at 175°C for 60 min in the glove box to 1) crosslink the BHJ and 2) remove DIO, which can act as a photoacid within the bulk heterojunction. In a solar cell with evaporated contacts, the DIO is generally removed as a consequence of the thermal deposition process, i.e., under high vacuum. For such devices, crosslinking can be initiated at lower temperatures ($100\text{--}150^\circ\text{C}$) for 90–120 min. After annealing, the ITO/PEDOT:PSS/BHJ structure was allowed to slowly cool by turning off the hot plate. After reaching room temperature, a bare copper wire was attached to the bare ITO region using carbon paint. To ensure good contact, mounting tape (3M) was placed on top of the copper wire after the carbon paint dried. Following this step, solar cells were transferred into the antechamber of a glove box and left under vacuum overnight to remove any residual moisture. Solar cells were tested one day after fabrication in a nitrogen glove box environment ($<0.5 \text{ ppm O}_2$, $<0.5 \text{ ppm H}_2\text{O}$).

To form the eutectic gallium-indium (EGaIn) electrode, a bare copper wire was wrapped and adhered to the luer tip of a 2 mL plastic syringe using silver paint as previously described.¹⁷ EGaIn (purchased from Sigma Aldrich and used as received) was drawn into the plastic syringe. The bare copper wires attached to the ITO and EGaIn-filled syringe were connected to alligator clips that were attached to a Keithley 2400 Sourcemeter in a 2-point measurement format.

To form a solar cell, the plunger of the EGaIn-filled syringe was gently tapped to dispense a droplet of EGaIn on top of the bulk heterojunction to form a complete device stack (ITO/PEDOT:PSS/BHJ/EGaIn). The active area of each cell was measured using a camera

below the device before each measurement (cell area $\sim 0.2\text{--}0.65\text{ cm}^2$). The photovoltaic (i.e., current density versus voltage) characteristics were measured using an ABET Sun 2000 solar simulator (150 W Xe short-arc lamp, AM 1.5G filter) with an irradiance of 100 mW cm^{-2} . A purpose-written LabView program controlling the Keithley 2400 Sourcemeter, sweeping from - 0.2 V to 0.7 V with a voltage scan rate of 10 mV s^{-1} was used to control current density (J) versus voltage (V) measurements, as well as extract the photovoltaic properties (J_{sc} , V_{oc} , FF, PCE). The spectral intensity of the solar simulator was calibrated before each set of measurements using a Si reference cell.

1.7 Degradation Testing of EGaIn Solar Cells

1.7.1 Accelerated Thermal Degradation

After fabrication, J51:N2200 solar cells were heated on hot plate set at $60\text{ }^{\circ}\text{C}$ in a nitrogen glove box environment ($<0.5\text{ ppm O}_2$, $<0.5\text{ ppm H}_2\text{O}$) and periodically tested (every 25 h up to 100 h, then every 50 h up to 200 h, then every 100 h up to 400 h) as described in **Section 2.5**. Before testing, cells were allowed to cool to room temperature slowly by turning off the hot plate. To maximize the measurements that could be obtained from each cell, three measurements were taken at each time interval on the same location on the device by gradually increasing the size of the EGaIn droplet (e.g., from $\sim 0.2\text{ cm}^2$ to $\sim 0.45\text{ cm}^2$ to $\sim 0.6\text{ cm}^2$). For each time interval, a new location on the cell was measured (i.e., to avoid any EGaIn residue remaining from previous measurements from interfering with subsequent measurements). Thus, approximately 9 locations on each device were measured.

1.7.2 Chloroform Exposure

Solar cells containing crosslinked and non-crosslinked PTB7-Th:N2200 bulk heterojunctions were submerged into a beaker of chloroform in a nitrogen environment for 1 s before being annealed on a 100 °C hot plate for 30 min. Following this process, cells were transferred back into the antechamber of the glove box (under vacuum) overnight to remove any residual moisture from the film. J-V measurements were repeated the next day using the EGaIn process as described in **Section 2.5**. This chloroform exposure treatment was repeated twice more for each cell for longer time intervals (10 s, 30 s). For longer exposures, the solar cells were submerged and unperturbed (i.e., no agitation, stirring, or mixing) for the duration of the treatment.

1.7.3 *Physical Agitation using Sonication*

J51:N2200 films (3 vol% DIO, 0-1% 4Bx) were first spun onto 25 mm × 25 mm glass substrates in atmosphere as described in **Section 2.3** at a spin speed of 1800 rpm (1200 rpm s^{-1}) for 90 s followed by 2000 rpm (1200 rpm s^{-1}) for 30 s. After deposition, all films were annealed on a hot plate in atmosphere at 175 °C for 60 min and allowed to cool slowly back to room temperature. The films were then photographed (Nikon D3300) inside a light box, held upright using 3D-printed stands. After being photographed, each film was measured using a UV-vis spectrophotometer as described in **Section 2.7.2**. To qualitatively observe the effect of crosslinking on the abrasion resistance of non-crosslinked and crosslinked films, a Branson 2510 bath sonicator (40 kHz, 120 V) was used to physically abrade the films. J51:N2200 films were placed into glass staining dishes and covered in DI water before being placed in the bath sonicator and sonicated for 5 min. After sonication, the films were carefully removed and gently dried using compressed air, before being photographed and measured using the UV-vis spectrophotometer. To ensure good measurements, the position of the beam (circular, $d \sim 1 \text{ mm}$)

was carefully marked on a clean glass substrate when operating the Cary 60 UV-vis in Zero Order mode (i.e., white light). These UV-vis measurements were repeated 5 times per sonication interval, adjusting the position of the substrate such that the spectrophotometer beam measured regions of intact film. This process was repeated in 5 min intervals up to 10 min, and then 10 min intervals up to 1 h.

The change in film thickness for crosslinked and non-crosslinked films were calculated by comparing the peak absorbance at each time interval to the peak absorbance prior to sonication. The surface coverage of the film was quantified from the photographs of the polymer films using image analysis. For each photograph, the image was exported into Adobe Photoshop and cropped to only display the 25 mm $\times$ 25 mm sample. Color thresholding was conducted by selecting the polymer film using the Magic Wand selection tool (tolerance of 35) to determine the proportion of the glass substrate still covered by the polymer film (relative to the total surface area of the substrate). The number of pixels identified using the Magic Wand selection tool was identified by the total number of pixels defining the size of the substrate to approximate the fraction of film coverage remaining. To estimate the total volume of film lost after each sonication step, we assumed that the polymer film still covering the glass substrate remained uniform in thickness. Thus, the change in film volume was approximated by multiplying the fractional surface coverage by the change in film thickness at each time interval.

1.7.4 *Physical Abrasion using Sponge*

Generic non-scratch scrub sponges (cellulose, 114 mm $\times$ 68 mm $\times$ 15 mm) were purchased from Target Corporation and dried in a desiccator chamber overnight. The sponge was then cut such that the width of the sponge (~40 mm) was slightly greater than the width of each solar cell substrate (25 mm). The sponge was then attached to a 10 N force gauge connected to a

Mark-10 linear actuator using 3D-printed grips. Solar cells with J51:N2200 bulk heterojunctions (3 vol% DIO, 0–1 wt% 4Bx) were fixed onto a lab jack using strips of mounting tape. J51:N2200 devices were chosen due to the significant increase in mechanical robustness when crosslinked with 1 wt% 4Bx (**Figure 3**). The height of the lab jack was adjusted such that the solar cells could be gently grazed by the rough side of the sponge (dark blue). Then, a 20 g weight was placed on the loose end of the sponge. The sponge, pressed down onto the surface of the bulk heterojunction layers from the 20 g weight, was dragged over the solar cells to induce damage from physical abrasion at a velocity of 60 mm min^{-1} . Following abrasion, optical microscopy images of the surfaces of each solar cell were obtained using a Leica DM2700M microscope under bright-field illumination ($50\times$ magnification). The cells were then transferred into the antechamber of the glove box overnight under vacuum to remove any residual moisture before the photovoltaic properties were measured as described in **Section 2.6**. This process was repeated two more times, with the height of the lab jack, position of the sponge, and position of the 20 g weight remaining unchanged between each abrasion treatment.

1.7.5 Accelerated Degradation in 50 °C / 50% RH Chamber

To observe the degradation of our devices under humid environments (e.g., representing no encapsulation), solar cells with PTB7-Th:N2200 bulk heterojunctions (0-3 wt% 4Bx) were put into a testing chamber set at 50 °C and 50% relative humidity (RH). The humidity was controlled by a PID controller regulating the flow of water vapor into the chamber from an attached humidifier. The chamber was relatively small, containing two rows in which samples could be placed. Due to the arrangement of this setup, the 0-2 wt% cells were placed in the row furthest from the water vapor inlet valve, while the 3 wt% cell was placed in the row closest to the valve. After 24 h, the cells were removed and annealed on a hot plate in atmosphere at 100

°C for 30 min before being allowed to slowly cool to room temperature. The cells were then placed into an antechamber under vacuum overnight to remove any residual moisture before being measured the following day as described in **Section 2.5**. This accelerated degradation treatment was then repeated for another 24 h for a total of 48 h in the degradation chamber.

1.8 Morphological Characterization

1.8.1 Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-vis measurements (e.g., absorbance relative to wavelength) were acquired using an Agilent Cary 60 UV-vis spectrophotometer (300–800 nm, 1 nm increments). For P3HpT, H-aggregation was calculated using a purpose-written script in Matlab R2021b.

1.8.2 X-ray Photoelectron Spectroscopy (XPS)

Survey scans (0–1000 eV) were performed on the DCB fracture testing samples (**Section 1.6.2**) with X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra 165 Hybrid Photoelectron Spectrometer) using monochromatic Al K α x-ray radiation at 1486.6 eV to determine the composition of chemical species at the surface of the fractured samples after DCB testing. The side of the fractured sample adhered to the slide glued with epoxy is referred to as the “Epoxy side” and the other side is referred to as the “Glass side.” The binding energies associated with silicon, sulfur, fluorine, oxygen, nitrogen, and carbon are highlighted. In particular, the peaks associated with silicon were used to determine presence of the glass substrates, while the peaks associated with fluorine (common only to J51 or PTB7-Th) were used to determine if there was any remaining bulk heterojunction film on the sample surface.

1.8.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was used to qualitatively observe crosslinking (i.e., the disappearance of the azide peak at 2160-2120 cm^{-1}). A Nicolet6700 FTIR spectrophotometer (ThermoFisher) fixed with a MCT detector was used alongside a diamond ATR attachment. Polymer films were deposited on top of glass substrates, compressed onto the diamond tip, and scanned at a resolution of 2 cm^{-1} for 128 scans per measurement.

1.9 Statistical Analysis

EGaIn measurements were conducted at least 5 times on each fabricated solar cell and each data set was used to generate box plots in Matlab R2021b. Tensile measurements were conducted at least 3 times on each polymer film. Compressive measurements were conducted at least 30 times on each polymer blend. Debonding measurements were conducted at least 6 times on each polymer blend. UV-vis measurements were conducted 5 times on each polymer film during abrasion testing between each sonication step and for the aggregation measurements. Reported values in the manuscript are calculated from the mean of each data set, while the error is calculated as the standard deviation. All calculations were conducted in Matlab R2021b or Microsoft Excel.

Supplementary Figures

Table S1. Summary of tensile properties of J51, PTB7-Th, and N2200 with 4Bx crosslinker.

Polymer(s)	4Bx Loading [wt %]	Elastic Modulus [MPa]	Tensile Strength [MPa]	Resilience [MJ m ⁻³]	Toughness [MJ m ⁻³]	Linear Elasticity [%]	Fracture Strain [%]
J51	0	367 ± 151	8.19 ± 1.41	0.09 ± 0.02	0.10 ± 0.03	2.53 ± 0.71	2.53 ± 0.71
	1	440 ± 118	12.09 ± 1.57	0.18 ± 0.02	0.18 ± 0.02	3.16 ± 0.43	3.16 ± 0.43
PTB7-Th	0	578 ± 63	27.16 ± 0.39	0.51 ± 0.15	2.61 ± 0.16	4.13 ± 0.87	12.62 ± 0.54
	1	409 ± 85	31.05 ± 0.99	1.16 ± 0.42	2.99 ± 0.17	7.51 ± 2.13	13.96 ± 0.41
N2200	0	477 ± 84	19.03 ± 1.12	0.37 ± 0.01	3.38 ± 0.09	3.91 ± 0.28	21.24 ± 2.00
	1	485 ± 71	23.01 ± 1.74	0.41 ± 0.13	4.46 ± 0.61	4.44 ± 0.54	24.27 ± 1.99
J51:N2200 (1:2)	0	501 ± 151	23.82 ± 0.99	0.55 ± 0.28	2.23 ± 0.22	4.70 ± 1.85	12.40 ± 0.69
	1	463 ± 55	30.60 ± 0.63	0.76 ± 0.16	3.88 ± 0.84	5.73 ± 0.95	17.11 ± 3.01
	2	582 ± 133	27.44 ± 1.91	0.65 ± 0.20	1.63 ± 0.42	4.80 ± 1.39	8.58 ± 1.44
PTB7-Th: N2200 (2:1)	0	512 ± 109	30.98 ± 0.74	0.84 ± 0.17	4.35 ± 0.17	5.70 ± 1.32	18.22 ± 0.81
	1	585 ± 3	32.87 ± 0.66	0.73 ± 0.18	4.29 ± 0.64	4.85 ± 0.56	16.76 ± 1.81
	2	629 ± 70	37.03 ± 1.57	0.79 ± 0.18	3.37 ± 0.19	4.92 ± 0.89	12.89 ± 0.73
	3	698 ± 99	38.28 ± 2.68	0.86 ± 0.19	3.69 ± 0.24	4.93 ± 0.92	13.24 ± 0.66

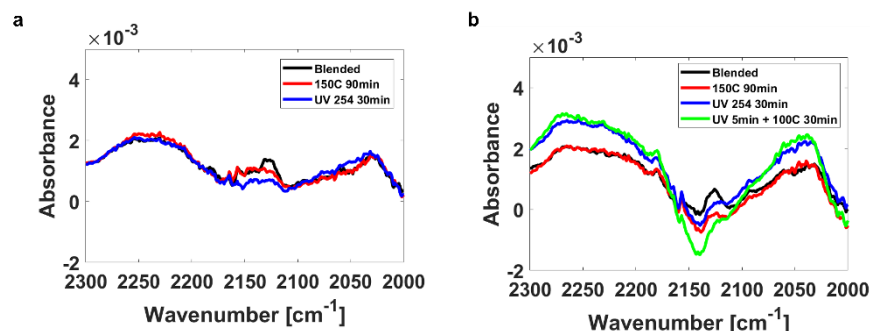


Figure S1. Crosslinking of 4Bx was qualitatively determined using FTIR for (a) J51:N2200 and (b) PTB7-Th:N2200. Films blended with 1 wt% 4Bx showed a peak corresponding to the azide functional group between 2120–2160 cm^{-1} . After crosslinking using 254 nm wavelength UV light or thermal annealing, FTIR spectra of crosslinked films showed a disappearance of this azide peak.

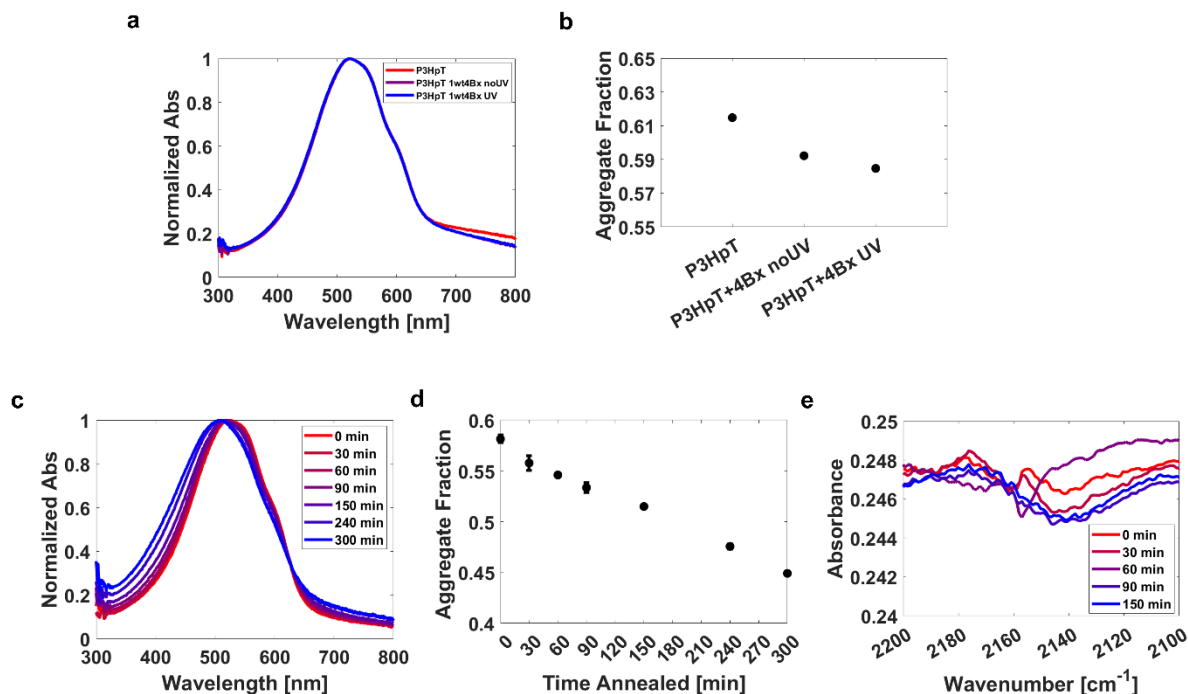


Figure S2. (a) UV-vis spectra of P3HpT films as-cast (red), blended with 1 wt% 4Bx (purple), and crosslinked with 4Bx (blue). (b) The aggregate fraction was determined from the respective UV-vis spectra using a model developed by Spano and coworkers,¹⁸ and show that crosslinking P3HpT with 4Bx reduces the aggregation in the amorphous domains. To determine the onset of crosslinking with thermal annealing, P3HpT films blended with 1 wt% 4Bx were annealed at 100 °C for between 0–300 min with (c) UV-vis spectra taken for each sample, showing a blue shift with increasing annealing time. (d) Similarly, these P3HpT samples show a continuous decrease in aggregation relative to annealing time (i.e., as more 4Bx reacts). (e) FTIR measurements suggest that the azide peak mostly disappears after approximately 60 min when annealed at 100

°C. Slight differences between the 60 min spectra and the other spectra are present due to the 60 min sample being prepared separate from the others.

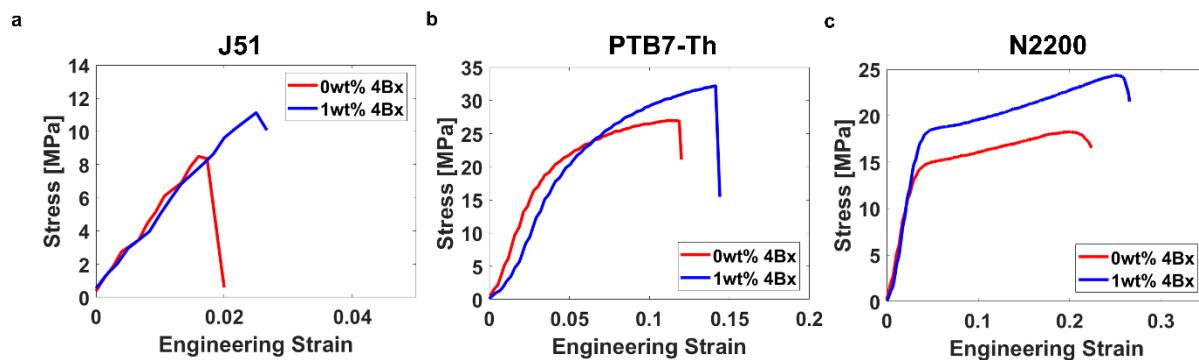


Figure S3. Representative stress-strain curves of **a)** J51, **b)** PTB7-Th, and **c)** N2200 thin films as measured using pseudo-free standing tensile tests.

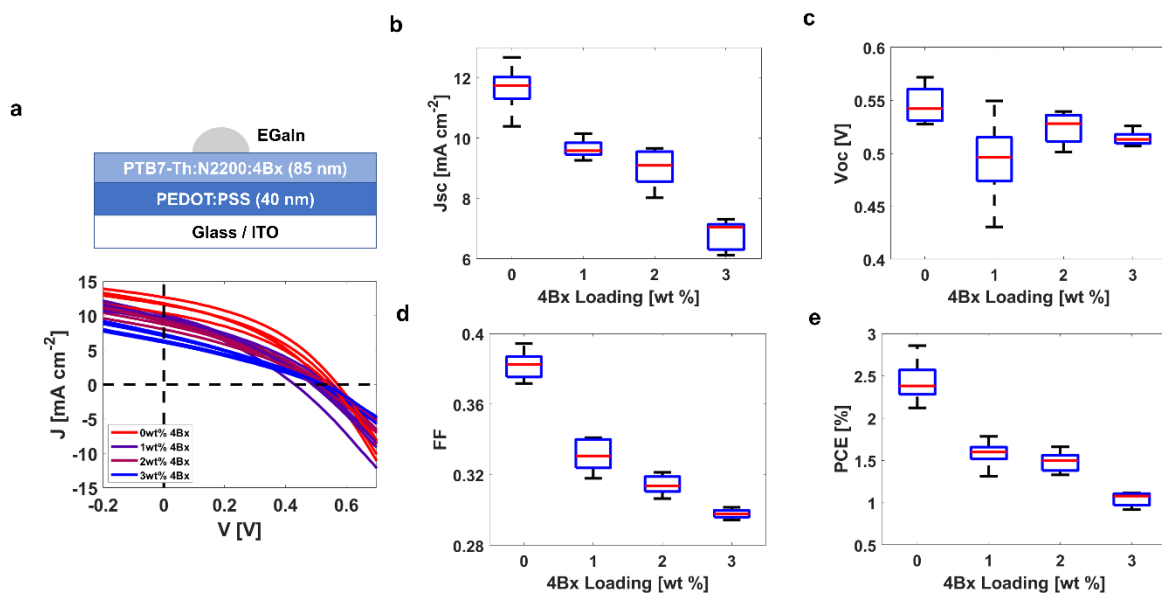


Figure S4. (a) J-V curves of PTB7-Th:N2200 devices (without DIO) relative to increasing 4Bx loading. The (b) J_{sc} , (c) V_{oc} , (d) FF, and (e) PCE are extracted from the J-V curves.

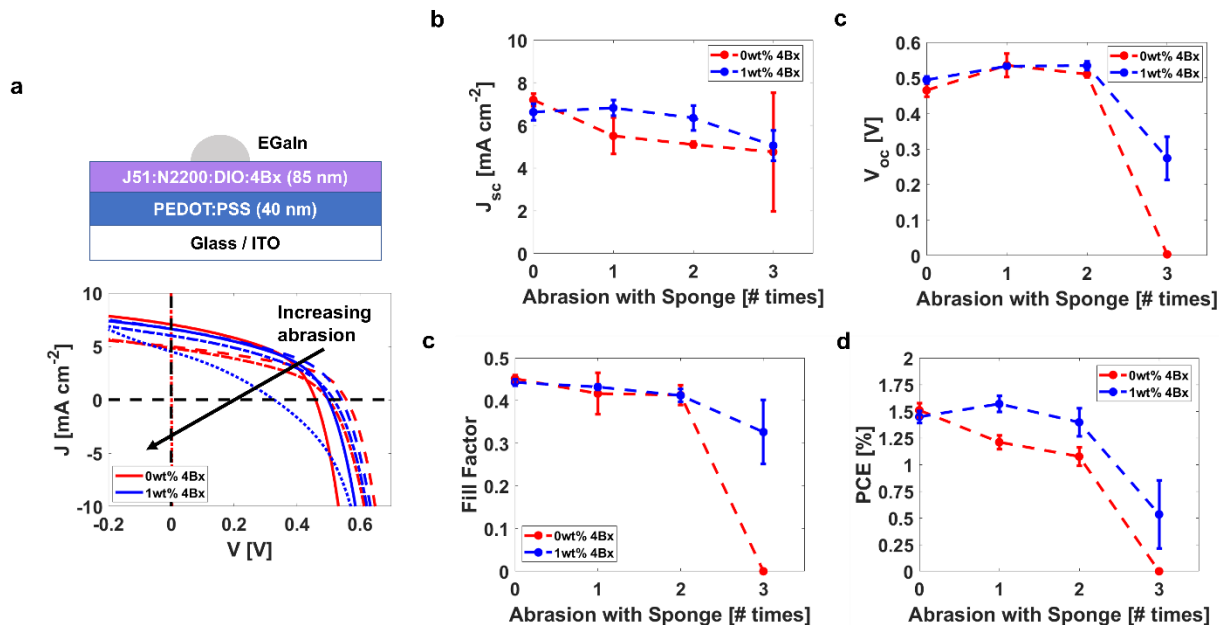


Figure S5. (a) EGaIn solar cells with J51:N2200 bulk heterojunctions were fabricated and subject to abrasion tests using a standard kitchen sponge (where increasingly dotted lines represent greater abrasion). Continuous abrasion resulted in gradual damage to both active layers, resulting in J-V curves with decreasing (b) J_{sc} , (c) V_{oc} , (d) FF, and (e) PCE (where increasingly dotted lines represent greater abrasion) relative to increasing abrasion. However, the solar cell with the crosslinked J51:N2200 active layer (blue) showed greater survivability in comparison to its non-crosslinked counterpart (red).

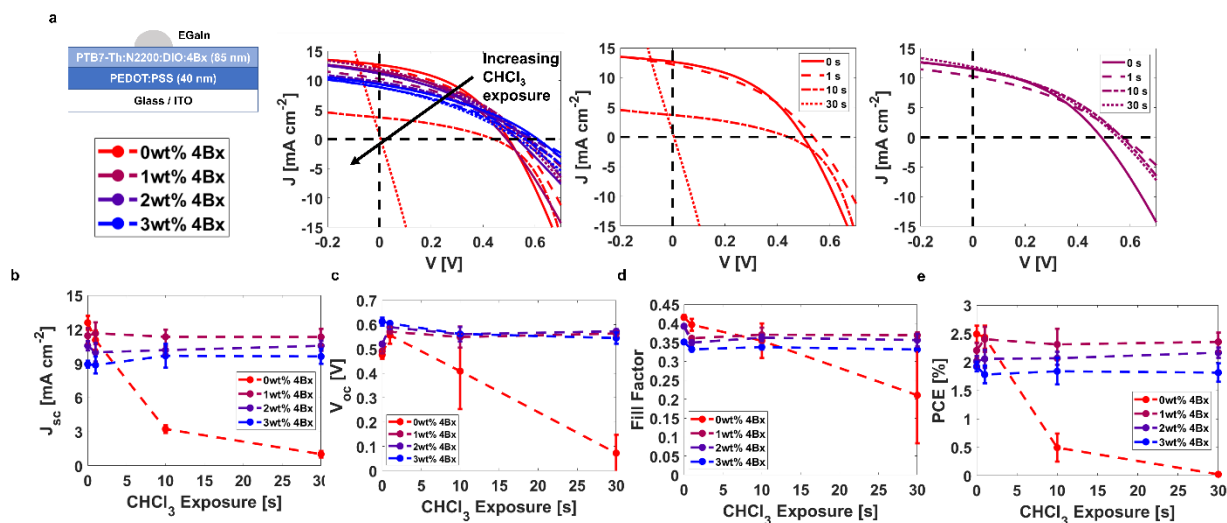


Figure S6. (a) J-V curves of EGaIn solar cells with non-crosslinked and crosslinked PTB7-Th:N2200 bulk heterojunctions relative to greater amounts of direct chloroform exposure. The loading of 4Bx crosslinker ranged from 0–3 wt%. An increasing number of dots in the J-V curve refers to an increasing amount of chloroform exposure. The J-V curves for the 0 wt% (red) and 1

wt% (purple) devices are plotted separately to emphasize the change in degradation. The (b) J_{sc} , (c) V_{oc} , (d) FF, and (e) PCE are extracted from their respective J-V curves.

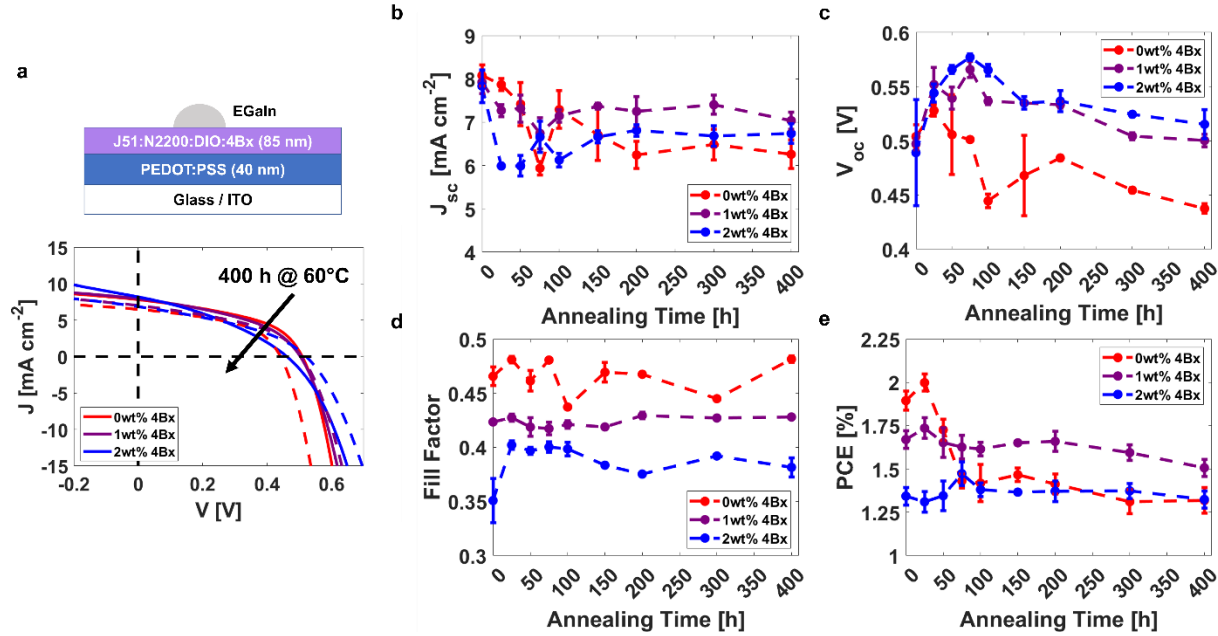


Figure S7. (a) The thermal stability and lifespan of crosslinked (1–2 wt%) and non-crosslinked (0 wt%) J51:N2200 EGaIn solar cells were measured using thermal ageing. Devices were thermally annealed over the course of 400 h at 60 °C in order to accelerate degradation. Dotted J-V curves show a representation of the photovoltaic properties of each device after 400 h, while solid lines refer to a pristine device (0 h anneal). The (b) J_{sc} , (c) V_{oc} , (d) FF, and (e) PCE are extracted from their respective J-V curves.

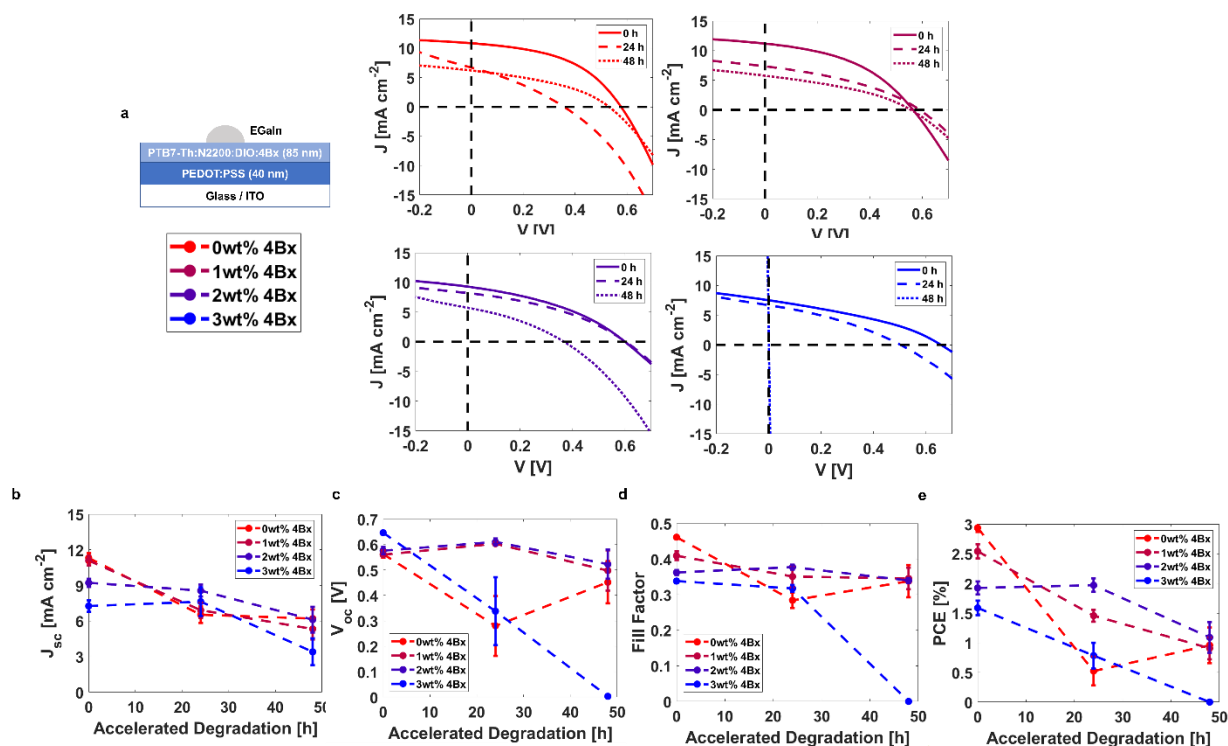


Figure S8. (a) EGaIn solar cells with non-crosslinked and crosslinked PTB7-Th:N2200 bulk heterojunctions were fabricated and degraded in a 50 °C and 50% relative humidity (RH) chamber. The loading of 4Bx crosslinker ranged from 0–3 wt%. An increasing number of dots in the J-V curve refers to a greater amount of time spent in the 50/50 degradation chamber. The 3 wt% device (blue) was placed closest to the water vapor inlet, likely resulting in the device shunting after 48 h. In comparison, the 0 wt% device (red) was placed furthest away. The (b) J_{sc} , (c) V_{oc} , (d) FF, and (e) PCE are extracted from their respective J-V curves.

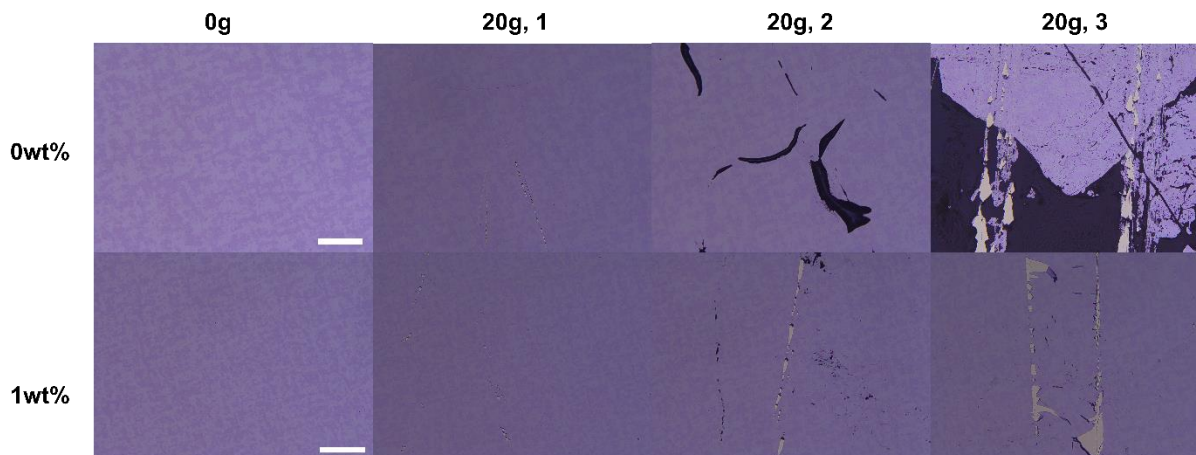


Figure S9. Optical microscopy (bright-field) images taken of J51:N2200 (0–1 wt% 4Bx) EGaIn cells subject to abrasion tests using a standard kitchen sponge. The sponge was weighed down with a 20 g weight in order to make contact with each device. Three abrasion tests (1–3) were done on each device. Dark spots in the images show areas containing EGaIn residue (e.g., filling in any scratches).

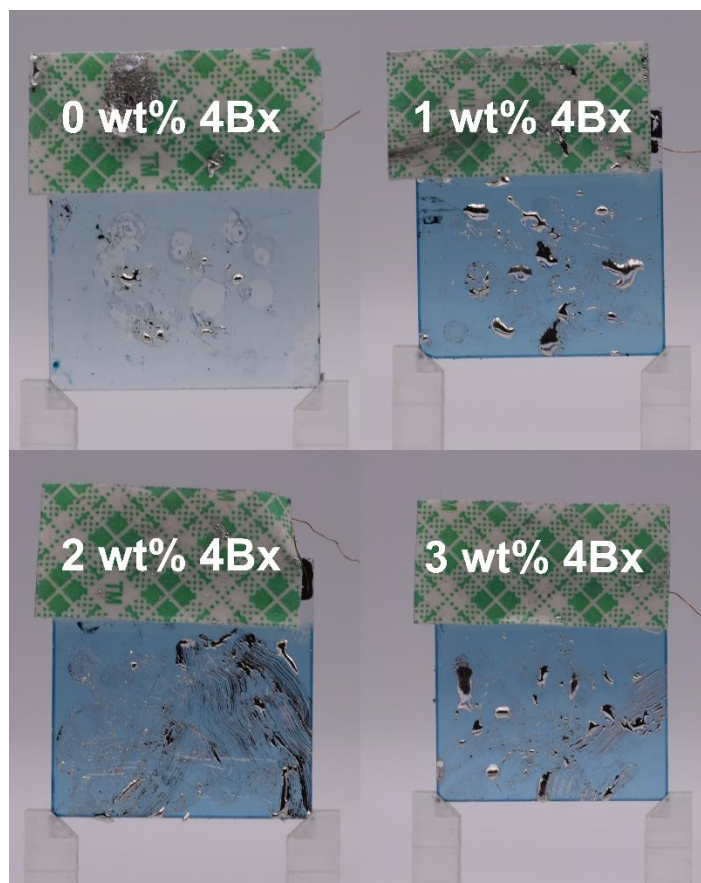


Figure S10. Photographs of PTB7-Th:N2200:4Bx EGaIn solar cells with 0–3 wt% 4Bx after 30 s of direct chloroform exposure. The contrast in color shows a complete removal of the non-crosslinked bulk heterojunction, while the other bulk heterojunctions remained intact.

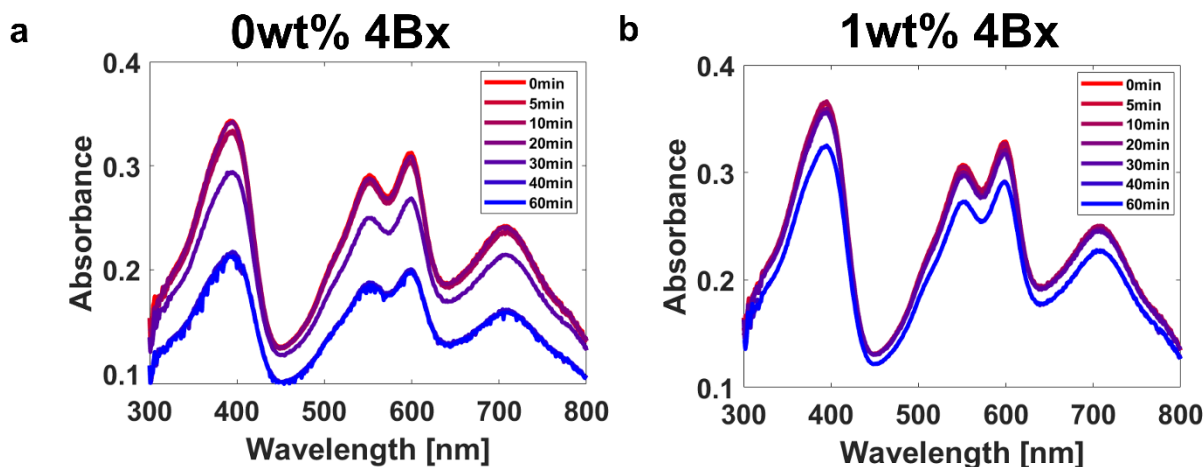


Figure S11. Representative UV-vis spectra of (a) non-crosslinked and (b) crosslinked J51:N2200 films (2 vol% DIO) taken after each sonication step. Five UV-vis measurements were taken after each sonication in order to approximate the thickness of the remaining regions of polymer film.

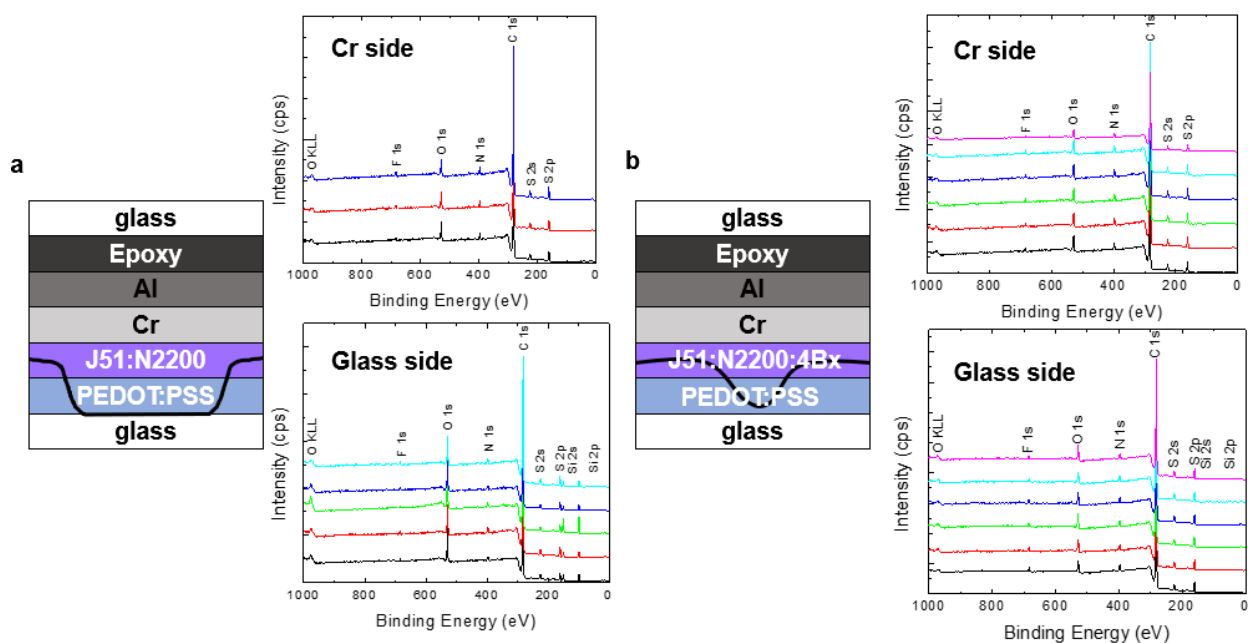


Figure S12. XPS measurements taken after fracture testing of (a) J51:N2200 (1:2, 3 vol% DIO) and (b) J51:N2200:4Bx (1:2, 1 wt%, 3vol% DIO) sample stacks in order to determine the interface of fracture.

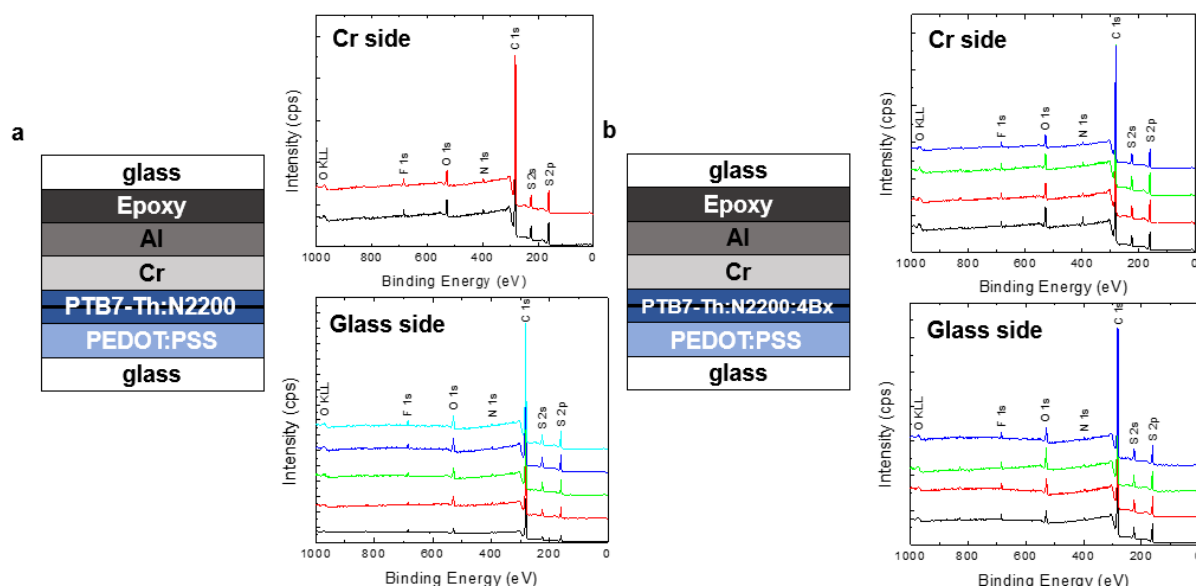


Figure S13. XPS measurements taken after fracture testing of (a) PTB7-Th:N2200 (2:1, 3 vol% DIO) and (b) PTB7-Th:N2200:4Bx (2:1, 1 wt%, 3vol% DIO) sample stacks in order to determine the interface of fracture.

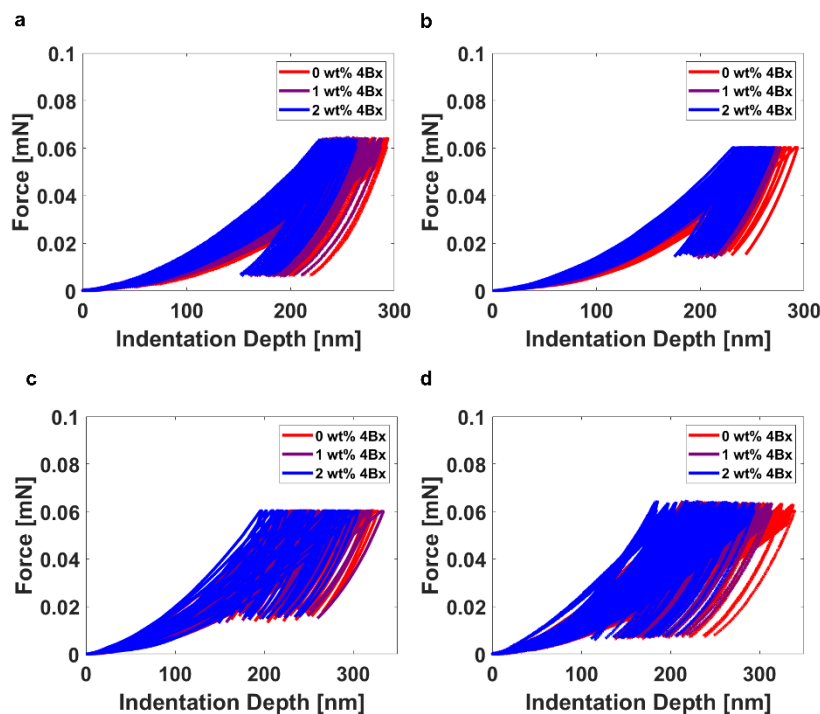


Figure S14. (a) Quasi and (b) sinus load-unloading curves of J51:N2200 with 0–2 wt% 4Bx collected by nanoindentation. (c) Quasi and (d) sinus load-unloading curves of PTB7-Th:N2200 with 0–2 wt% 4Bx collected by nanoindentation.

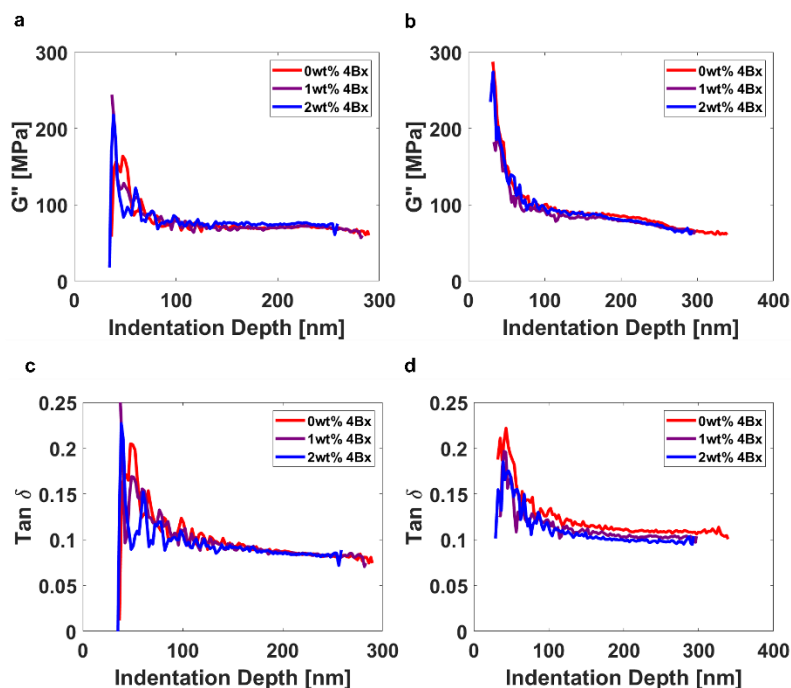


Figure S15. Viscoelastic properties were extracted from sinus measurements using nanoindentation. The (a) loss modulus and (b) $\tan \delta$ (i.e., ratio between loss modulus and storage modulus) are shown relative to indentation depth for J51:N2200 relative to increasing 4Bx loading. Likewise, the (c) loss modulus and (d) $\tan \delta$ are extracted for PTB7-Th:N2200.

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