Supplementary Information: Photocrosslinking Polymeric Ionic Liquids *via* Anthracene Cycloaddition for Organic Electronics

Bhooshan C. Popere,^{1,†,§} Gabriel E. Sanoja,^{1,3,†,‡} Elayne M. Thomas,² Nicole S. Schauser,² Seamus D. Jones,¹ Joshua M. Bartels,¹ Matthew E. Helgeson,¹ Michael L. Chabinyc,² and Rachel A. Segalman^{1,2,*}

¹Department of Chemical Engineering and ²Materials Department, University of California,

Santa Barbara, California, 93106, United States

³Department of Chemical and Biomolecular Engineering, University of California, Berkeley,

California, 94720, United States

*Email address: segalman@ucsb.edu

 $\dagger = Equal \ contribution$

1. Materials

All reagents were obtained from commercial sources and used as received without further purification, unless otherwise specified. N-acryloxysuccinimide (NASI) was purchased from TCI America and recrystallized from diethyl ether/methanol prior to polymerization. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic (DDMAT), acid 1 - (3 aminopropyl)imidazole, anhydrous DMF, 9-chloromethylanthracene, bromohexane, lithium bis(trifluoromethylsulfonyl)imide $(LiNTf_2)$ purchased from Sigma-Aldrich. were Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and recrystallized from methanol prior to use. RAFT polymerization of NASI was performed under oxygen-free conditions. Poly(3-hexylthiophene) was purchased from Merck and used as received.

2. Instrumentation

Gel permeation chromatography (GPC) was performed on a Waters Alliance HPLC System (2695 Separation Module) using a refractive index detector (Waters 2414 Differential Refractometer) and two Tosoh TSKgel Super HM-M columns. DMF (0.01 % of LiBr) at 40 °C was used as the mobile phase with a flow rate of 0.3 mL.min⁻¹. ¹H NMR spectra were collected on a 600 MHz Varian NMR spectrometer using the residual proton resonance of the solvent as an internal reference. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. UV-vis absorption spectra were collected on an Agilent Technologies Cary 60 UV-vis spectrometer. Differential scanning thermograms were determined on a Perkin-Elmer DSC 8000 using hermetically sealed aluminum pans. Thermo-Gravimetric Analysis (TGA) was performed in a TA Discovery Thermo-Gravimetric Analyzer operating under dry argon flow. Electrochemical impedance spectroscopy was performed using a Bio-Logic VSP 300 potentiostat in a nitrogenfilled glovebox. Stress relaxation and frequency sweeps were performed on a TA Instruments ARG2 rheometer with either 8 mm or 20 mm stainless steel parallel plates. Polymers were photocrosslinked with a 6W 365 nm UVP handheld UV lamp in a nitrogen-filled glovebox.

3. Detailed Synthetic Procedures

a. Poly(N-acryloxysuccinimide) (PNASI)



N-acryloxysuccinimide (10.0 g, 59.2 mmol), DDMAT (112 mg, 0.153 mmol) and recrystallized AIBN (5 mg, 0.0153 mmol) were dissolved in anhydrous DMF (60 mL) in a Schlenk flask. The solution was degassed using three freeze-pump-thaw cycles. After the third cycle, the flask was filled with dry nitrogen, immersed in a pre-heated oil bath maintained at 70°C, and allowed to react under vigorous stirring for 12 h. After cooling to 25°C, the polymer was precipitated in methanol, filtered, dried in ambient conditions, dissolved in DMF and re-precipitated from methanol. The polymer was filtered and dried under a vacuum at 60°C for 24 h to yield a pale yellow powder (9.4 g). ¹H NMR (600 MHz, DMSO- d_6) δ 3.13 (1H, br), 2.80 (4H, br), 2.05 (2H, br).

b. Poly(1-(3-aminopropyl)imidazolyl)acrylamide (PIm)



PNASI (9.0 g, 53.2 mmol) was dissolved in anhydrous DMF (50 mL) at 25°C in a 100 mL round bottom flask. A solution of 1-(3-aminopropyl)imidazole (8.2 g, 63.8 mmol) in anhydrous DMF (10 mL) was added dropwise to the vigorously stirring polymer solution (Note: an exotherm was

observed during addition) and the reaction was allowed to proceed at 25°C for 12 h. The polymer was precipitated from ethyl acetate, dissolved in methanol and re-precipitated from diethyl ether. The polymer was isolated by centrifugation and dried under a vacuum at 60°C for 12 h to yield a pale yellow brittle solid that softened upon exposure to air presumably due to moisture-uptake (9 g). ¹H NMR (600 MHz, DMSO- d_6) δ 7.64 (1H, br), 7.13 (1H, br), 6.88 (1H, br), 3.90 (2H, br), 2.92 (2H, br), 1.98 (1H, br), 1.76 (2H, br), 1.58 (2H, br).

c. Poly[1-((3'-(9"-anthracenyl)chloride-(3-aminopropyl))imidazolyl]acrylamide-*random*-poly[1-((3'-hexyl)bromide-(3-aminopropyl))imidazolyl]acrylamide (PIL-Cl/Br)



Poly(1-(3-aminopropyl)imidazolyl)acrylamide (PIm) (7.0 g, 39.06 mmol) was dissolved in anhydrous DMF (20 mL) at 25°C. To this solution was added 9-chloromethylanthracene (0.885 g, 3.906 mmol) and the reaction mixture was maintained at 70°C for 12 h. After cooling the solution to 25°C, the polymer was precipitated from diethyl ether, dissolved in methanol, re-precipitated from diethyl ether, and dried under a vacuum at 60°C for 12 h. The dried polymer (5.7 g, 31.8 mmol) was dissolved in anhydrous DMF (15 mL) at 25°C. To this solution was added 1-bromohexane (6.3 g, 38.16 mmol) dropwise and the reaction mixture was maintained at 70°C for 12 h. After cooling the solution to 25°C, the polymer was precipitated from diethyl ether, and dried under a vacuum at 60°C for 12 h. The dried polymer (5.7 g, 31.8 mmol) was dissolved in anhydrous DMF (15 mL) at 25°C. To this solution was added 1-bromohexane (6.3 g, 38.16 mmol) dropwise and the reaction mixture was maintained at 70°C for 12 h. After cooling the solution to 25°C, the polymer was precipitated from diethyl ether, dissolved in methanol, and re-precipitated form diethyl ether by duplicate. The polymer was isolated by centrifugation, dried under a vacuum at 60°C for 12 h to yield a yellowish brown sticky solid (7.5 g). The polymer was used as such without further purification.

d. Poly[1-((3'-(9"-anthracenyl)-(3-aminopropyl)))imidazolyl]acrylamide-*random*-poly[1-((3'-hexyl)-(3-aminopropyl))imidazolyl]acrylamide bis(trifluoromethylsulfonyl)imide (PIL-NTf₂) $c_{12H_{25}} s_{1} s_{1$



To a stirring solution of PIL-Cl/Br (7.4 g, 21.55 mmol) in methanol (15 mL) was added LiNTf₂ (19.47 g, 53.9 mmol) at 25°C. After 24 h, the polymer was precipitated from DI water, dissolved in methanol and re-precipitated from DI water. The isolated polymer was further washed with copious amounts of DI water to remove residual LiNTf₂. The polymer was then dried under a vacuum at 80°C for 24 h to yield a deep amber colored sticky solid (10 g).

4. Detailed Experimental Procedures

a. Molecular Characterization



Figure S 1. Gel Permeation Chromatography of 300PNASI calibrated against polystyrene standards. The polydispersity ($D = M_n/M_w$) was approximately 1.2. This is consistent with the controlled nature of the RAFT polymerization of N-(acryloxysuccinimide).



Figure S 2. ¹H NMR of 300PNASI in DMSO-d₆. End-group analysis yields the number of repeat units of N-(acryloxysuccinimide) P(NASI)₂₇₉. Inset illustrates the methyl peak. This spectrum is collected at a polymer concentration of 60 mg.mL⁻¹ with 128 scans and a pulse delay time of 5 s.

From the presented ¹H NMR, the number of repeat units in PNASI are given by:

$$n = N_{NASI} = \frac{I_{methyl}}{3} * \frac{I_{NASI}}{4} = \frac{3.0}{3} * \frac{1116}{4} = 279 \approx 300$$

The resulting polymer is then P(NASI)₂₇₉ which for simplicity is denoted in Table 1 as 300PIL.

A similar analysis yields P(NASI)₁₀ (Data not shown).



Figure S 3. ¹H NMR of 300PIL with NTf_2^- counteranion. Anthracene content is determined from the ratio of peak integrations between 6.5 ppm and 4.1 ppm.

The presented ¹H NMR allows for quantification of the anthracene content in the PIL. The

number of repeat units in 300PIL is given by

$$x = N_{Anth} = N * \left(\frac{\frac{I_{6.5}}{2}}{\frac{I_{6.5}}{2} + \frac{I_{4.1} - I_{6.5}}{4}}\right) = 279 * \left(\frac{0.07}{0.07 + \frac{2 - 0.07}{2}}\right) = 19$$
$$m = N_{Hex} = N * \left(\frac{\frac{I_{4.1} - I_{6.5}}{4}}{\frac{I_{6.5}}{2} + \frac{I_{4.1} - I_{6.5}}{4}}\right) = 279 * \left(\frac{\frac{2 - 0.07}{2}}{0.07 + \frac{2 - 0.07}{2}}\right) = 260$$

The resulting polymer then has 8 mol% anthracene as denoted in Table 1. A similar analysis yields 22 mol% anthracene for 10PIL (Data not shown)

b. General Procedure for Photocrosslinking

Analytical samples were crosslinked by exposure to a low power hand-held UV lamp. All crosslinking reactions in solid state were performed in a nitrogen-filled glovebox wherein the samples were placed at a distance of \sim 5 cm from the UV source in a container lined with aluminum foil for varying durations. Due to the low power of the UV source, the temperature of the samples did not increase significantly during the course of the experiments.

c. UV-Vis spectrometry

Thin-film samples for UV-vis spectrometry were prepared by spin coating a 20 wt% polymer solution in anhydrous acetonitrile at 1000 rpm on pre-cleaned fused quartz discs. The average ellipsometric thickness of the as-cast films was determined to be $\sim 1 \mu m$. The samples were annealed under vacuum at 60°C for 12 hours prior to measurements. In order to minimize exposure to oxygen, a cleaned quartz disc was then placed on top of the sample in an inert atmosphere. The adherence between the quartz and the sample was optimized with a subsequent thermal annealing step under vacuum at 60 °C for 2 h. Samples were further exposed to UV light (365 nm) and the absorption spectra immediately recorded under a stream of nitrogen. The absorbance of the peak

at 370 nm at 0 min exposure time was taken as reference and all subsequent absorbance spectra for different exposure times were normalized to this peak.

d. Stress Relaxation

Samples for stress relaxation were prepared in a nitrogen-filled glove box by shaping two samples of 10PIL into 8mm Teflon molds followed by heating under vacuum at 70 °C to remove microscopic bubbles from the PIL pellets. After degassing, one sample was cross-linked *via* irradiation to 365 nm light for 3 hours. Samples were approximately 1 mm thick. Constant strains of 1% and 0.1% were applied to the un-crosslinked and cross-linked samples, respectively, at a measurement temperature of 50 °C. These values are within the linear viscoelastic regime of the materials. Due to limitations in the instrument torque sensitivity, data for the un-crosslinked 10PIL was disregarded after ~10 seconds when the material had essentially fully relaxed.

e. Rheology

Samples for rheology were also prepared in a nitrogen-filled glovebox by casting 300PIL directly into 20 mm stainless steel parallel plates. Dynamic frequency sweeps were performed over a range of temperature, frequency, and strain amplitude respectively of 10 °C to 70 °C, 0.1 rad.s⁻¹ to 100 rad.s⁻¹, and 0.1% to 10%. Strain sweeps at 10 rad.s⁻¹ confirmed that measurements were performed in the linear viscoelastic regime. The reference temperature used for time-temperature superposition was 70 °C and master curves were generated horizontal shift factors.

f. Electrochemical Impedance Spectroscopy

Samples for ionic conductivity were prepared by drop casting the polymer from a 20 wt% solution prepared from anhydrous acetonitrile. The solution was drop cast onto pre-cleaned ITO/glass electrodes into Kapton wells (thickness = $150/250 \mu m$, diameter = 0.65 cm). The films were cast at 40°C in ambient and then annealed under a vacuum at 60°C for 12 h. The samples were then

transferred into a nitrogen-filled glovebox. Another polished ITO/glass electrode was placed on top of the dried polymer, and the assembly was subsequently annealed for 2 h. Connections were made to both electrodes and the cell was sealed inside the glovebox. Impedance spectra were recorded at frequencies from 1 MHz to 100 mHz with a sinusoidal voltage amplitude of 20 mV. Real (*Z'*) and imaginary (*Z''*) parts of the complex impedance were used to calculate the real part (σ') of the complex conductivity as follows:

$$\sigma' = \frac{Z'}{k(Z'^2 + Z''^2)}$$

where, k = area/thickness is the cell constant.

Capacitance was calculated from impedance spectra according to literature protocols.¹ The average capacitance of the PIL from 0.1 - 1 Hz is ~ 1 μ F.cm⁻² at 25 °C and independent of crosslinking time (Figure S4).



Figure S 4. (a) Capacitance-frequency curves of the 300PIL before and after crosslinking. The capacitance averaged in the low frequency regime (0.1 - 1 Hz) (b) remains unchanged as a function of crosslinking time. Error bars represent 68% confidence intervals.

5. PIL Transistor Fabrication

All transistor measurements took place in a nitrogen-filled glovebox. Top-gate-bottom-contact (Top-gate) devices were fabricated by spin coating poly(3-hexylthiophene) (50 mg/ml, chlorobenzene) onto patterned source-drain contacts (width = 2.7 mm, length = 150μ m) and

annealing at 150 °C for 10 minutes. Crosslinked 300PIL (thickness = 88 μ m) was then laminated onto the channels. The gate contact was deposited by placing a clean gold foil on top of the PIL. Top-contact-bottom-gate (bottom-gate) devices were fabricated by crosslinking a 300PIL (thickness = 5 μ m) on Au-coated Si, followed by laminating a P3HT film onto the 300PIL *via* a well-established PDMS transfer method.² Gold electrodes with identical channel dimensions as the Top-Gate devices were thermally evaporated on P3HT.

6. Patterning Procedure

A 6 wt % PIL solution in anhydrous acetonitrile was drop cast on Si/SiO_2 substrates and annealed at 70 °C overnight under vacuum. The films were patterned by aligning the samples with a photomask printed on transparency film, followed by exposure to 365 nm UV for 45 minutes. The films were subsequently washed with methanol to remove the uncrosslinked precursor and blown dry with air.

7. Kinetic Model

The mechanism of anthracene photodimerization has been investigated as early as 1905 by Luther and Weigert and reviewed extensively upon formulation of the Woodward-Hoffmann rules for concerted processes in photochemically activated cycloaddition reactions. For intermolecular photodimerization, the singlet state ($^{1}A^{*}$) is considered to be the reactive species and the following mechanism has been proposed:

$$A \xrightarrow{k_E, h\nu} A^*$$

$$A \xrightarrow{k_{dim}} A^*$$

$$A^* + A \xrightarrow{k_{dim}} A_2$$

$$A^* + A \xrightarrow{k_{CQ}} A + A$$

$$A^* \xrightarrow{k_F} A$$

$${}^{1}A^{*} \xrightarrow{k_{NR}} A$$

Where k_{E_s} , k_{dim} , k_{CQ} , k_F , and k_{NR} correspond respectively to rate constants of excitation, dimerization, concentration quenching, fluorescence, and other non-radiative processes (*e.g.* intersystem crossing). The reaction rate is then given by

$$\frac{d[A_2]}{dt} = -\frac{1d[A]}{2 \ dt} = k_{dim} [{}^1A^*][A]$$

And the steady-state concentration of the singlet, short-lived species

$$[{}^{1}A^{*}]_{SS} = \frac{k_{E}I_{0}\varphi[A]}{k_{F} + k_{NR} + (k_{dim} + k_{CQ})[A]}$$

Thus, the resulting first-order ordinary differential equation is

$$-\frac{1d[A]}{2 dt} = k_{dim} \left(\frac{k_E I_0 \varphi[A]}{k_F + k_{NR} + (k_{dim} + k_{CQ})[A]} \right) [A]$$

with initial condition $[A](t = 0) = A_0$. Integration by separation of variables yields the following non-linear rate law describing the reaction kinetics over the entire range of conversion

$$(k_F + k_{NR}) \left(\frac{1}{[A]_0} - \frac{1}{[A]} \right) + (k_{dim} + k_{CQ}) \ln \left(\frac{[A]}{[A]_0} \right) = -2k_{dim} k_E I_0 \varphi t$$

Previous work³ on the mechanism of the photodimerization of anthracenes in solution has demonstrated that $k_F + k_{NR} \ll k_{dim} + k_{CQ}$. Assuming that this observation is still valid in a polymer matrix results in a simplified rate law

$$\frac{[A]}{[A]_0} = \exp\left(-\frac{2k_{dim}k_E I_0\varphi}{k_{dim} + k_{CQ}}t\right) = \exp\left(-\frac{k_{eff}t}{k_{eff}}t\right)$$

where $k_{eff} = \frac{2k_{dim}k_E I_0 \varphi}{k_F + k_{NR}}$. Note that k_{eff} represents an overestimate of the timescale of anthracene photodimerization, as fluorescence and other non-radiative processes provide a pathway to regenerate anthracene groups over the course of the reaction. Fitting the experimental data (Figure 1a) to this kinetic model yields a time constant for anthracene dimerization on the order of 800 s.

This value is significantly longer than the 1 ns estimated for small molecules dissolved in aromatic solvents.³

Though the presented reaction mechanism yields an approximate analytical solution suitable to fit the experimental data and get an estimate of the reaction timescale, it neglects reversibility enabled by the photochemical cleavage of dianthracene. Accounting for this elementary step yields the following system of coupled differential equations

$$\frac{d[A_2]}{dt} = k_{dim} [{}^{1}A^{*}][A] - k_{cle} [A_2]$$

$$\frac{d[A]}{dt} = -k_E I_0 \varphi[A] - k_{dim} [{}^{1}A^{*}][A] + k_{cle} [A_2] - k_{CQ} [{}^{1}A^{*}][A] + (k_F + k_{NR}) [{}^{1}A^{*}]$$

$$\frac{d[{}^{1}A^{*}]}{dt} = k_E I_0 \varphi[A] - k_{dim} [{}^{1}A^{*}][A] + k_{cle} [A_2] - k_{CQ} [{}^{1}A^{*}][A] - (k_F + k_{NR}) [{}^{1}A^{*}]$$

The time-dependent solution can be obtained by numerical integration but it is outside the scope of this work. However, this set of equations serves to illustrate that the long-time concentrations of [A], $[{}^{1}A^{*}]$, and [A₂] are finite and governed by thermodynamic equilibrium, a prediction consistent with the incomplete conversion revealed in Figure 1b.

$$K = \frac{k_{dim}}{k_{cle}} = \frac{[A]_{eq}}{[A]_{eq}[A^*]_{eq}}$$

8. Thermal Characterization



Figure S 5. Differential Scanning Calorimetry of (a) 10PIL and (b) 300PIL reveal that the T_{gs} are respectively 19 °C and -7 °C. These values were determined using the half-height step in heat capacity of the second heating curve at 20 °C.min⁻¹.



Figure S 6. Thermo-Gravimetric Analysis of 10PIL reveals that the onset of polymer degradation is approximately 270 °C, a temperature significantly higher than the experimentally investigated region. This trace was obtained using a heating rate of 20 °C.min⁻¹ from 20 - 600 °C.

9. Linear Viscoelastic Response

The non-covalent π - π interactions between anthracene moieties physically crosslink the PIL and play a key role in the viscoelastic properties. The linear viscoelastic response before exposure to UV (Figure S6a) is characteristic of an associated polymer with a plateau modulus at high frequencies, a crossover of the storage G' and loss G'' moduli, and terminal relaxation with characteristic liquid scaling of G' ~ ω^2 and G'' ~ $\omega^{1.6}$ The regime at intermediate frequencies with G' and G'' ~ $\omega^{2/3}$ is probably due to ionic interactions and similar to that observed in analogous associating polymers (*e.g.*, ionomers,⁷ hydrogen-bonded polymers,⁸ small molecules,⁹ and coiledcoil protein gels¹⁰). After irradiation with UV, the π - π stacked anthracenes undergo a cycloaddition reaction that chemically crosslinks the PIL and changes the linear viscoelastic response to that of a polymer network near the critical gel point.¹¹ Throughout the entire frequency window, G" \approx G' (*i.e.*, tan(δ) \approx 1) demonstrating the highly viscoelastic nature of the photo-crosslinked material (Figure S6b). Although a crossover of G' and G" is apparent at very low frequencies, the resulting value of G' is relatively small and indicative of a very lightly crosslinked polymer network.



Figure S 7. The master curves of the storage and loss moduli shifted relative to 70°C for the anthracene containing 300PIL suggest a change in polymer microstructure due to photocrosslinking. 300 PIL a) before (green triangles) and b) after (red circles) exposure to 365nm UV radiation for 60 min. Exposure to 365nm UV radiation results in the development of a highly dissipative material (G' \approx G"). These observations suggest formation of a lightly crosslinked polymer network. The inset images illustrate the change from a viscous liquid to a soft solid film.



Figure S 8. Storage and loss moduli for the anthracene containing 300PIL (a) before and (b) after exposure to 365 nm UV radiation for 60 min.

10. Network Elasticity

The elasticity of a PIL network can be considered within a phantom network model, where the ends of network strands are joined at crosslink junctions that can fluctuate. The shear elastic modulus is then given by

$$G = \nu kT \left(1 - \frac{2}{f}\right)$$

Where v, k, T, and f correspond respectively to the number density of elastically active strands,

Boltzmann constant, absolute temperature, and crosslink functionality.

Solving for the number density of elastically active strands yields

$$\nu = \frac{Gf}{kT(f-2)}$$

The plateau modulus obtained for the photocrosslinked 10PIL by stress relaxation is 1.7 kPa, which corresponds to a concentration of elastically active strands of 0.41 M or 0.00025 crosslinks

 nm^{-3} ($N_c = 2800$). This low value serves as quantitative validation of the formation of a very lightly crosslinked polymer network upon irradiation with UV.



11. Sweep-Rate Dependence of FETs

Figure S 9. Dependence of transfer characteristics on sweep rate of a bottom-contact P3HT/PIL device. Increasing sweep rate decreases the degree of hysteresis, output current, and turn-on voltage. Further improvements could be made by decreasing the dielectric thickness or increasing the operating temperature to facilitate ion transport to the active layer. For each curve, $V_{DS} = -1$ V.

References

- 1. H. Lee Keun, S. Kang Moon, S. Zhang, Y. Gu, T. P. Lodge and C. D. Frisbie, *Adv. Mater*, 2012, **24**, 4457-4462.
- 2. M. L. Chabinyc, A. Salleo, Y. Wu, P. Liu, B. S. Ong, M. Heeney and I. McCulloch, *J. Am. Chem. Soc*, 2004, **126**, 13928-13929.
- 3. H. Bouas-Laurent, A. Castellan, J.-P. Desvergne and R. Lapouyade, *Chem. Soc. Rev*, 2001, **30**, 248-263.
- 4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca and London, 1953.
- 5. P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca and London, 1979.
- 6. Z. Zhang, Q. Chen and R. H. Colby, *Soft Matter*, 2018, 14, 2961-2977.
- 7. Q. Chen, G. J. Tudryn and R. H. Colby, J. Rheol, 2013, 57, 1441-1462.
- 8. C. L. Lewis, K. Stewart and M. Anthamatten, *Macromolecules*, 2014, 47, 729-740.
- 9. C. Gainaru, R. Figuli, T. Hecksher, B. Jakobsen, J. C. Dyre, M. Wilhelm and R. Böhmer, *Phys. Rev. Lett*, 2014, **112**, 098301.
- 10. S. Tang, M. Wang and B. D. Olsen, J. Am. Chem. Soc, 2015, 137, 3946-3957.
- 11. H. H. Winter and F. Chambon, J. Rheol, 1986, **30**, 367-382.