Supporting Information

Thermally activated in-situ doping enables solid-state processing of conducting polymers

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Experimental Section

Materials. Regio-regular poly(3-hexylthiophene) (P3HT) was obtained from SungYoung Int. Ltd. (regio-regularity ~ 95%; $M_n$ ~ 91 kg mol$^{-1}$; dispersity $D$ ~ 1.83); C16-PBT (38 kg mol$^{-1}$; dispersity $D$ ~ 1.78) and p(g4T-T) ($M_n$ ~ 15 kg mol$^{-1}$) were synthesized as previously reported.$^{[1,2]}$ Dodecylbenzene sulfonic acid (DBSA, purity > 95%), ethylbenzene sulfonic acid (EBSA, purity > 95 %) and 2-nitrobenzyl alcohol were purchased from Sigma-Aldrich and used as received, ethylbenzene sulfonyl chloride was purchased from VWR and used as received. Unless otherwise stated, all reactions were done under nitrogen atmosphere. Dodecylbenzene sulfonyl chloride was synthesized according to literature.$^{[3]}

Synthesis

2-nitrobenzyl 4-ethylbenzenesulfonate (EBSAc): In an oven-dried 2-necked round bottom flask, 2-nitrobenzyl alcohol (0.57 g, 3.7 mmol) was dissolved in dry THF (5 mL) and cooled to 0 °C while stirring. Then, trimethylamine (1 mL, 7.4 mmol) and 4-ethylbenzenesulfonyl chloride were added successively and the reagents were shielded from light. Then, a catalytic amount of 4-dimethylamino pyridine (100 mg) was added and the reaction temperature raised to room temperature while reacting overnight. The reaction mixture was extracted with
dichloromethane and water. The organic phase was then washed with a saturated sodium bicarbonate solution and brine. The organic phase was dried on anhydrous magnesium sulfate, filtered and evaporated to dryness. The crude material was taken up in a small amount of acetone, precipitated in demineralized water and filtered. The cream-colored residue was then washed with cold methanol until a white solid remained, which was dried at RT while shielded from light. After a second recrystallization from methanol, the title product was obtained as white crystals. (710 mg, 57%). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.12 (m, 1H), 7.94 – 7.81 (m, 2H), 7.77 (m, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 7.0$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 5.49 (s, 2H), 2.75 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H).

Figure 1. $^1$H-NMR of EBSAc
2-nitrobenzyl 4-dodecylbenzenesulfonate, mixed isomers (DBSAc): The same reaction procedure as for EBSAc was used, with 2-nitrobenzyl alcohol (0.424 g, 2.7 mmol), THF (5 mL), trimethylamine (900 mL, 7.4 mmol), 4-dodecylbenzenesulfonyl chloride (1 g, 2.73 mmol) and 4-dimethylamino pyridine (100 mg). The title compound was purified by column chromatography using silica that was pretreated with 95:5 v/v hexanes:triethylamine, using 85:15 v/v hexanes:DCM as the eluent. The compound was isolated as a very light-yellow colored viscous oil (1.26 g, 96% yield) that slowly solidified upon prolonged storage at 4 °C. 

$^1$H NMR (400 MHz, Chloroform-d) δ 8.11 (m, 1H), 7.85 (m, 2H), 7.76 (m, 1H), 7.67 (m, 1H), 7.56 – 7.42 (m, 1H), 7.42 – 7.29 (m, 2H), 5.62 – 5.41 (m, 2H), 2.92 – 2.35 (m, 1H), 1.83 – 1.44 (m, 6H), 1.35 – 0.96 (m, 16H), 0.95 – 0.69 (m, 6H).
Figure 3. $^1$H-NMR of DBSMe

Figure 4. $^{13}$C-NMR of DBSMe
**Thermal decapping in d-DMSO solution:** A solution of DBSAc or EBSAc in d-DMSO (1 g L\(^{-1}\), 0.5 mL) was charged into an NMR tube, one for each performed decapping time, which was subsequently sealed. Then, the tube was immersed in an oil bath (140 °C) for either 0.5, 1 or 3 minutes, after which the decapping reaction was quenched by immersing the NMR tube in an ice-water bath. Finally, an H-NMR spectrum was recorded to assess the extent of decapping.

**Sample preparation. Thin films:** P3HT, C16-PBTT and p(g₄2T-T) were dissolved in chloroform (6 g L\(^{-1}\)) at 80°C and stock solutions of the dopants EBSA, DBSA, EBSAc and DBSAc of 10 g L\(^{-1}\) in chloroform were prepared. After admixing of the respective amount of dopant stock solution to the polymer solution, the dopant-polymer mixture was rapidly drop-cast onto PET foil and dried on a hotplate at 40°C under ambient conditions. Decapping was performed by annealing of the films for various times on a hotplate at 140°C under N\(_2\) atmosphere. To study the influence of air on the doping, all polymer solutions (6 g L\(^{-1}\) at 80°C) as well as the dopant stock solutions (10 g L\(^{-1}\)) were prepared under Ar and in degassed chloroform. Appropriate amounts of the respective polymer and dopant solutions were admixed under Ar to yield mixtures with a molar ratio of dopant to thiophene unit of 1:3. The polymer-dopant mixtures were then rapidly drop cast onto glass slides, either in air or in an Ar chamber, and dried in air or under Ar flux at 40°C. The films prepared under Ar were then stored under Ar and exposure to air was limited to the time that was needed to measure the sheet resistance. **Pressed films:** For each sample, 25 mg P3HT was dissolved in 2.5 mL chloroform after which EBSA or EBSAc were added with a molar ratio of 0.66 with regard to the average mass of one aromatic moiety. This procedure was also followed for neat P3HT to have the same processing history as the other samples. Then, the solvent was evaporated and the solids collected as neat P3HT, P3HT+EBSA and P3HT+EBSAc. 10 mg of each material was taken and pressed at 70 °C for 30 seconds at a maximum pressure of 5 bar. The samples
ended up being \(\sim 130-150 \text{ \(\mu\text{m}\)}\) in thickness. **Qualitative and quantitative decapping experiments and aging experiments:** 5 mg mL\(^{-1}\) solutions of either p(g42T-T):EBSAc or P3HT:EBSAc with varying latent dopant concentration (0.1, 0.2, 0.33 and 0.66 molar ratio) were prepared by mixing appropriate amounts of polymer or EBSAc stock solutions (chlorobenzene) to a total amount of 1 mL. Each solution was cast on a pre-weighed glass slide and dried at 40 °C shielded from light under a nitrogen blanket. The net deposited weight (6 decimal balance, Mettler Toledo) was recorded to know the exact amount of deposited polymer and EBSAc. For the decapping step, the glass slide was calibrated with a temperature probe to record the delay in reaching the required decapping temperature (140 °C). 30 seconds were added to the decapping time of p(g42T-T):EBSAc \((t_{\text{decap, total}} \sim 0.5 + 0.5 \text{ min})\) and P3HT:EBSAc \((t_{\text{decap, total}} \sim 0.5 + 3 \text{ min})\). After decapping, the initial electrical resistivities of each sample were recorded and left for 16 hours to record the electrical resistivities that were used to determine the charge carrier concentration and charge carrier mobility. After extraction for the \(^1\text{H}-\text{NMR}\) sample preparation, the electrical resistivity of each sample was recorded for up to two weeks for stability studies. **Qualitative and quantitative \(^1\text{H}-\text{NMR}\) experiments:** Extraction of the formed molecular species was performed by washing each film with approximately 10 mL of diethyl ether (subsequent extraction with diethyl ether, acetone and methanol did not provide additional extracted material, verified by \(^1\text{H}-\text{NMR}\)). Evaporation of diethyl ether and drying under vacuum offered the \(^1\text{H}-\text{NMR}\) samples, which were dissolved in 1 mL of CDCl\(_3\) with \(\sim 1 \text{ mg mL}^{-1}\) 1,4-dinitrobenzene as internal standard. The concentration of free EBSA and EBSAc was determined via:

\[
\frac{M_x}{M_y} = \frac{I_x}{I_y} \cdot \frac{N_y}{N_x}
\]
Where $M$ is the concentration, $I$ the integral and $N$ the number of nuclei giving rise to the signal for compound $x$ and $y$. The concentration of bound EBSA was then calculated by subtracting the concentration of free EBSA and EBSAc from the starting concentration of EBSAc.

**NMR spectroscopy.** NMR spectra have been recorded on an automated Agilent (Varian) MR 400 MHz spectrometer (equipped with "one-probe") with CDCl$_3$ or d-DMSO as the solvent. In all cases, the peak values were calibrated relative to the residual solvent signals (CDCl$_3$, 7.26 ppm and d-DMSO, 2.50 ppm). For the quantitative NMR experiments, a 90° pulse calibration was performed, an equilibration time of 5 minutes was selected used prior to starting each NMR experiment and a relaxation delay of 30 seconds to ensure full relaxation of all protons and obtain correct integrals.

**Thermal stability.** Thermal stability measurements were performed by Thermal Gravimetric Analysis (TGA) combined with Differential Scanning Calorimetry (DSC) with a Mettler Toledo TGA / DSC 3+ under a 20 mL min$^{-1}$ nitrogen or air flow at a scan rate of 10 °C min$^{-1}$.

**Electrical resistivity.** The electrical resistivity was measured with a four point probe setup from Jandel Engineering (cylindrical probe head, RM3000) using co-linear tungsten carbide electrodes with equidistant spacing of 1 mm and held down with a constant weight of 60 g. Care was taken to not approach the edges when performing the resistivity measurements as the edges would interfere with the field lines of the probes. The in-line 4-point probe for films gives a measure of the sheet resistance, $r_s$, with the equation $r_s = \frac{\pi}{\ln(2)} \cdot V/I$, where $\pi/\ln(2)$ is a correction factor ($\pi/\ln(2) = 4.53$) for when the probes are placed on a film where the distance between the probes is much smaller than the distance between the probes and the edge of the film. One must then multiply the thickness, $t$, of the sample by $r_s$ to attain $\rho$, and inverse to attain $\sigma$:
\[ \sigma = \frac{1}{t \cdot r_z} \]

**Charge carrier concentration and Charge carrier mobility.** The charge carrier concentration was calculated from the film thickness and the ratio of polymer:bound EBSA that was determined by the quantitative \(^1\)H-NMR experiment. The charge carrier mobility was calculated for each polymer:EBSA ratio by using the calculated charge carrier concentration and the corresponding electrical conductivity according to:

\[ \mu = \frac{\sigma}{N \cdot e} \]

where \( \mu \) is the charge carrier mobility, \( \sigma \) the electrical conductivity, \( N \) the charge carrier concentration and \( e \) the elementary charge.

**Film thickness.** The film thickness of dropcast films was measured on a KLA Alphastep Tencor D-100 profilometer.

**UV-vis absorption spectroscopy.** Absorption measurements were performed with a PerkinElmer Lambda 900 spectrophotometer on films with polyethylene terephthalate (PET) as the substrate. Due to the polymer:TAG dopant blends being inhomogeneous in thickness as a result of the drop-casting process, and random variations in absorption intensity before and after activation, the uncorrected UVVis/NIR spectra were used.

**Dynamic mechanical analysis (DMA)** was performed using a Q800 (TA Instruments) in tensile mode. The film samples were subjected to a dynamic 0.02% strain at a frequency of 1 Hz, while ramping the temperature at 3 °C min\(^{-1}\) from -100 °C to +70 °C. The reported glass transition temperature of each sample was taken as the peak of the loss modulus.
Figure 5. DSC and corresponding TGA thermograms of EBSAc (blue trace) and DBSAc (black trace)
Figure 6. $^1$H-NMR spectra of DBSAc (b) for various decapping times at $T_{\text{decap}} = 140 \ ^\circ C$
Figure 7. Relative electrical conductivity of p(g_42T-T) doped with EBSA or DBSA (molar ratio ~0.1) after prolonged exposure at various elevated temperatures (T_{anneal} = 120, 140 and 160 °C). $\sigma_0$ is ~ 50 S cm$^{-1}$ for both EBSA and DBSA-doped p(g_42T-T).
Figure 8. UV-Vis-NIR spectra of a) p(g$_{42}$T-T):EBSAc, b + c) C16-PBT$^+$TT:EBSAc and d) P3HT:EBSAc with 0.1, 0.2, 0.33 and 0.66 molar ratio latent dopant/thiophene unit before (filled) and after (open spectra) thermal activation.

Figure 9: $^1$H-NMR spectra (zoomed in on the aromatic region) of samples extracted from P3HT (a) and p(g$_{42}$T-T) films with varying concentrations of EBSAc dopant (0.1, 0.2, 0.33 and 0.66 molar ratio of EBSAc/polymer repeating unit after thermal activation ($T_{act} = 140$ °C and $t_{act} = 0.5$ min or 3 min for p(g$_{42}$T-T) and P3HT, respectively). Dashed lines indicate the compound-specific proton signal that was used for the integration to
determine the concentration of 1,4-dinitrobenzene (internal standard), EBSAc and free EBSA. Spectra were normalized by the peak height of the internal standard, 1,4-dinitrobenzene, at 8.43 ppm.

Figure 10. Molar ratio of EBSA dopant, removed EBSA and unreacted EBSAc found in either P3HT (a) or p(4,2T-T) (c) after thermal activation at 140 °C for different molar ratios of added EBSAc. For each concentration of EBSA dopant and the electrical conductivity the charge carrier concentration and the charge carrier mobility could be calculated, respectively, for P3HT (b) and p(4,2T-T) (d).

Figure 11. a) Relative electrical conductivity ($\sigma_{\text{air}} / \sigma_{\text{Ar}}$) of dropcast p(4,2T-T), P3HT and C16-PBTTT films doped with EBSAc, DBSAC, DBSA and EBSA (0.33 molar ratio dopant/thiophene unit) that were processed either in air ($\sigma_{\text{air}}$) or argon ($\sigma_{\text{Ar}}$) atmosphere. The dashed line represents the case where $\sigma_{\text{air}} = \sigma_{\text{Ar}}$, i.e. no difference in the electrical conductivity when performing doping of polymers in air or argon. In case of DBSAc-doped p(4,2T-T), we used the device detection limit (500 MΩ/cm²) for $\sigma_{\text{Ar}}$ as we could not record a resistivity value. b) Relative electrical conductivity of p(4,2T-T) films doped with DBSA (0.33 molar ratio...
dopant/thiophene unit) processed under different conditions, relative to processing under inert and dry conditions.

Figure 12. Electrical conductivity of p(g_4T-T) and P3HT films after thermal activation of the EBSAc dopant at 140 °C with varying concentrations of EBSAc (0.66, 0.33, 0.2, 0.1 molar ratio EBSAc/thiophene unit) as function of exposure time to ambient atmosphere.

Figure 13. WAXS azimuthal plot of pure P3HT (a) and P3HT:EBSA, 0.66 molar ratio EBSA/repeating unit (b) after 0.25 min. annealing (top) and 5 min. annealing (bottom) at 140 °C
References

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