Supplementary Information

## Impact of oxidation-induced ordering on the electrical and mechanical properties of a polythiophene co-processed with bistriflimidic acid

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**Molecular Dynamics Simulations.** The solid-state nanostructure was modelled by the following procedure in which all MD simulations were performed with a 1.0 fs timestep: (1) equilibration of the initial box at 800 K for 2 ns in a microcanonical ensemble (NVE) with a Langevin thermostat<sup>1, 2</sup> (damping parameter = 3800 fs), (2) equilibration at 800 K and 1 atm for 5 ns in an isoenthalpic-isobaric ensemble (NPH) with Nose-Hoover barostat and Langevin thermostat, (3) equilibration for 2 ns in an isothermal-isobaric ensemble (NPT) with Nose-Hoover thermostat and barostat,<sup>3-5</sup> (4) a cooling step from 800 to 300 K at a rate of 50 K ns<sup>-1</sup> in a NPT ensemble with a Nose-Hoover thermostat and barostat, and (5) equilibration for 5 ns at 300 K and 1 atm in a NPT ensemble. The initial chemical structure and partial atomic charges of the g42T-T repeat unit and TFSI anions for MD simulations were obtained from Density Functional Theory (DFT) simulations with  $\omega$ B97XD functional<sup>6</sup> and 6-31G(d) basis set<sup>7</sup> using Gaussian 09 Revision D.01.



**Fig. S1.** (a) UV-vis spectra of films of  $p(g_42T-T)$  co-processed with 40 mol% H-TFSI and aged for 2 days at ambient conditions (red) and then reduced by immersing the film into a solution of KOH:DMSO:H<sub>2</sub>O (15:35:50 wt%) for 3 hours at room temperature, washed in acetonitrile and dried at 40°C (blue; insets: photographs of the doped and dedoped film). (b) Chloroform solutions in which reduced films of  $p(g_42T-T)$  co-processed with 4, 18, 25 or 40 mol% H-TFSI were immersed at 40 °C.



Fig. S2. GIWAXS patterns of  $p(g_42T-T)$  co-processed with different mol% of H-TFSI.



**Fig. S3.** (a) Snapshots of films obtained from MD simulations with respect to oxidation level. Note that oligomers and TFSI anions are illustrated in blue and green, respectively, and the side chains of oligomers are omitted. (b) Radial distribution function  $g_{T-C}(r)$  after MD equilibration of the distance r between the center of mass of thiophene rings and TFSI anions at different oxidation levels. (c) Average end-to-end distance  $D_{end-to-end}$  of oligomer chains.



**Fig. S4**. FTIR spectrum of  $p(g_42T-T)$  co-processed with 18 mol% H-TFSI.



**Fig. S5.** FSC heating scans of neat  $p({}^{g}_{4}2T-T)$ .



Fig. S6. FSC heating scans of as-cast and aged samples of  $p(^{g_4}2T-T)$  co-processed with 4, 7, 10, 18, 25 or 40 mol% H-TFSI.



**Fig. S7**. Fragility plots of  $-\log q$  vs.  $T_{f,ref}/T_f$  of as-cast (open triangles) and aged samples (solid circles) of p( $g_{42}$ T-T) co-processed with 4, 7, 10 mol% H-TFSI.  $T_f$  was determined with FSC for q = -0.1 to -1000 K s<sup>-1</sup> and  $T_{f,ref}$  was measured with DSC for q = 0.17 K s<sup>-1</sup>.



**Fig. S8**. Fragility plots with  $-\log q$  vs.  $T_{f,ref}/T_{f}$  of as-cast (open triangles) and aged samples (solid circles) of p( $^{g}$ 42T-T) co-processed with 18, 25 or 40 mol% H-TFSI.  $T_{f}$  was determined with FSC for q = -0.1 to -1000 K s<sup>-1</sup> and  $T_{f,ref}$  was measured with DSC for q = 0.17 K s<sup>-1</sup>.

**Table S1.**  $T_{f,ref}$  of as-cast and aged samples of neat p( $g_{42}$ T-T) and p( $g_{42}$ T-T) co-processed with 4, 7, 10, 18, 25 or 40 mol% H-TFSI.

mol% H-TFSI	$T_{f,ref}$ (K), as-cast	$T_{f,ref}$ (K), aged
0	219.7	219.7
4	219.5	219.5
7	219.3	219.3
10	220.1	220.1
18	221.9	224.2
25	229.4	232.9
40	234.2	240.2



**Fig. S9.** (a) Electrical conductivity  $\sigma$  and Seebeck coefficient  $\alpha$  of  $p(g_42T-T)$  as a function of mol% H-TFSI. (b) Seebeck coefficient of  $p(g_42T-T)$  as a function of conductivity.



**Figure S10.** (a) Stress-strain curves recorded at room temperature during tensile deformation of as-cast free-standing samples of neat  $p(g_42T-T)$  (black) and the polymer co-processed with different mol% of H-TFSI (blue).

## References

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