Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Highly stable doping of a polar polythiophene through coprocessing with sulfonic acids and bistriflimide

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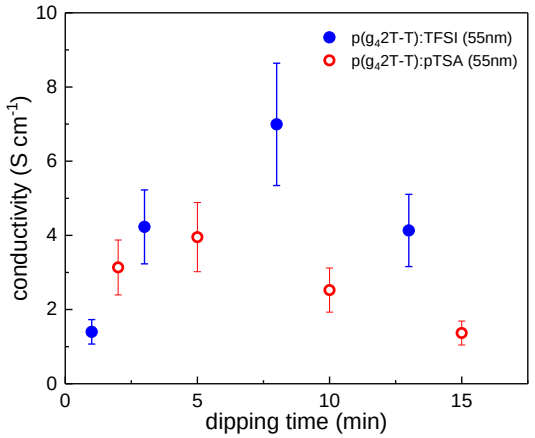

Figure S1: Conductivity of p($g_4$2T-T):TFSI and p(g42T-T):pTSA films with a thickness of 55nm, sequentially doped from solution, as a function of dipping time.

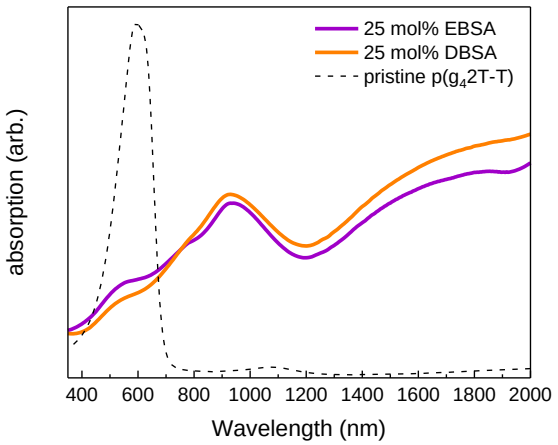

Figure S2: UV/Vis absorption of a pristine p($g_4$2T-T) film and of p($g_4$2T-T) films doped with 25mol% EBSA or DBSA.

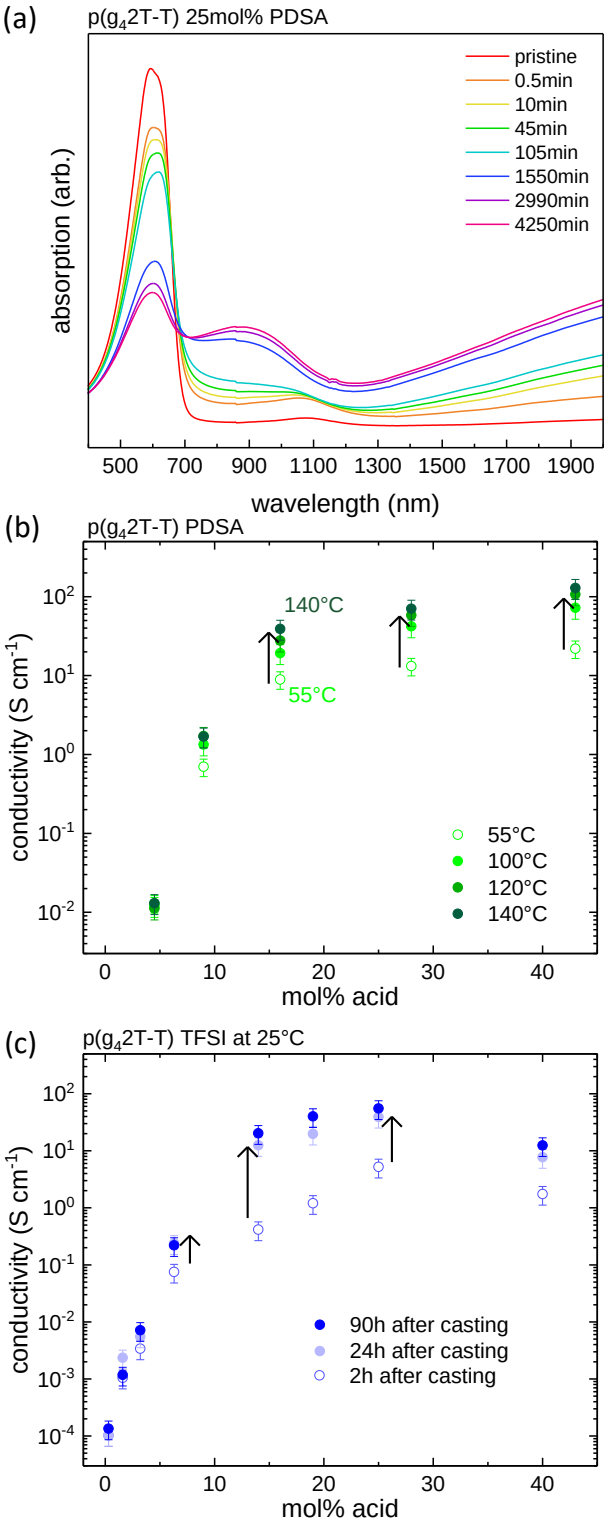

Figure S3: a) UV/Vis absorption of p($g_4$2T-T): PDSA in solution, b) evolution of the conductivity of p($g_4$2T-T):PDSA films upon annealing as a function of dopant concentration and c) evolution of the conductivity of p($g_4$2T-T):TFSI films over time as a function of dopant concentration.

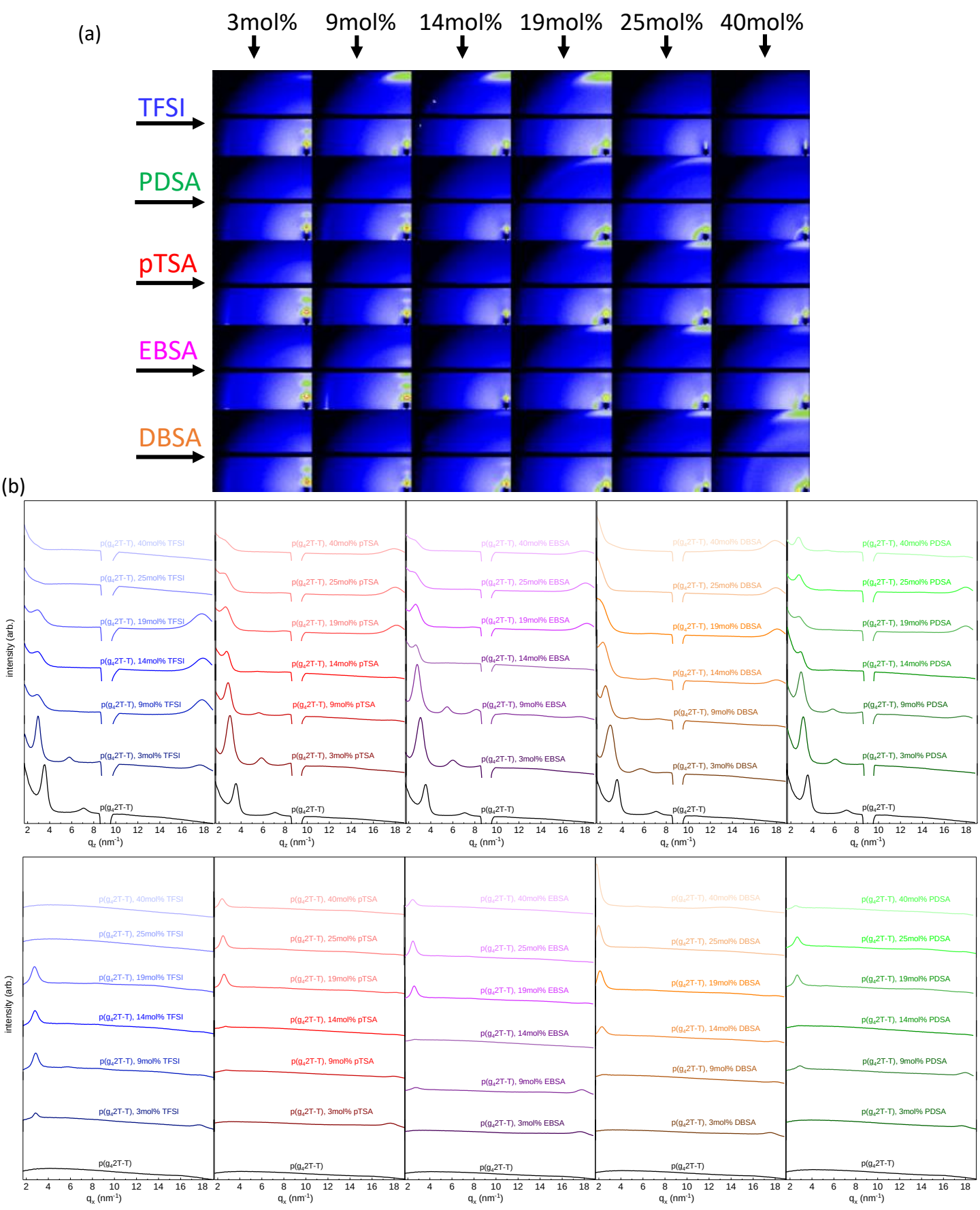

Figure S4: a) GIWAXS spectra and b) integration over the scattering intensity along the q_z and q_z axis of the GIWAXS spectra of p($g_4$2T-T) doped with different concentrations of TFSI, pTSA, EBSA, DBSA and PDSA

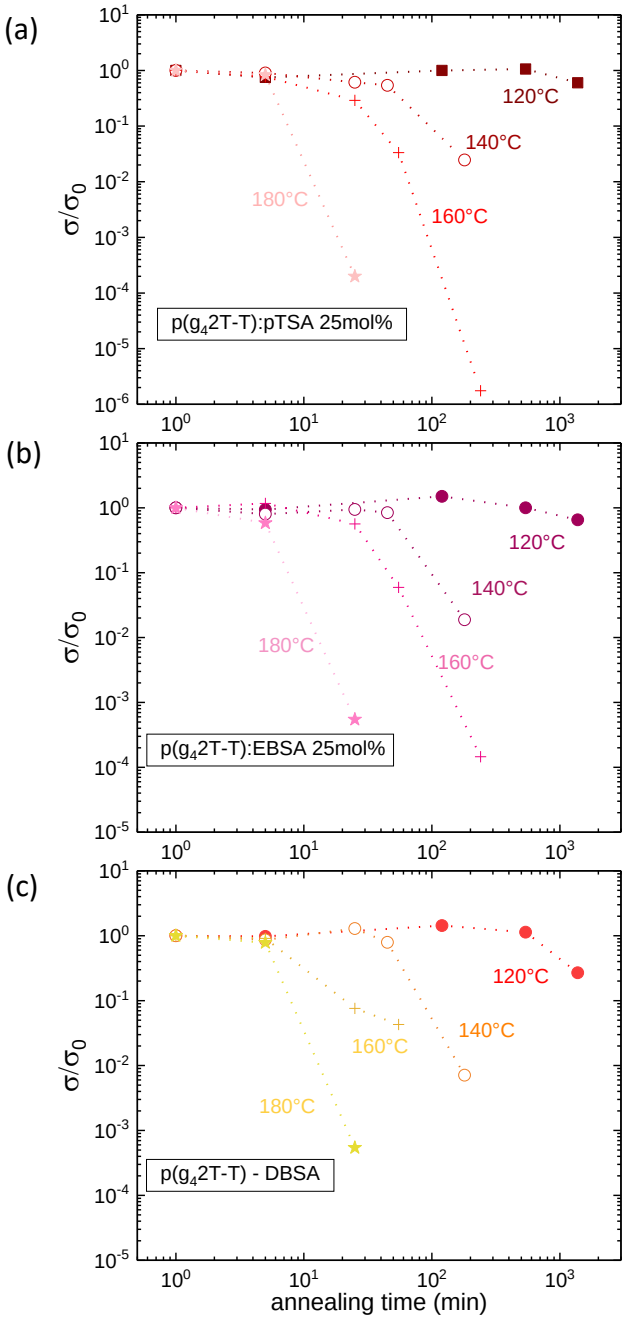

Figure S5: Relative conductivity as a function of annealing time and temperature for p($g_4$2T-T) doped with 25mol% a) pTSA, b) EBSA and c) DBSA.

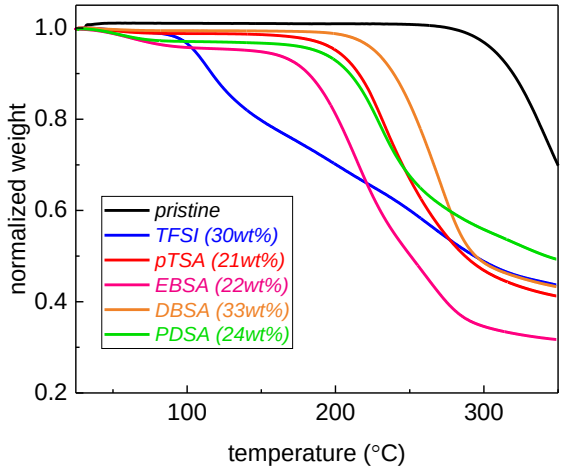

Figure S6: Thermogravimetric analysis of pristine and doped p($g_4$2T-T), containing 20mol% of the respective acid dopant, under N_2. The weight loss of 5% in p($g_4$2T-T):PDSA and of 6% in p($g_4$2T-T):EBSA below 100 °C can be attributed to the evaporation of solvent.

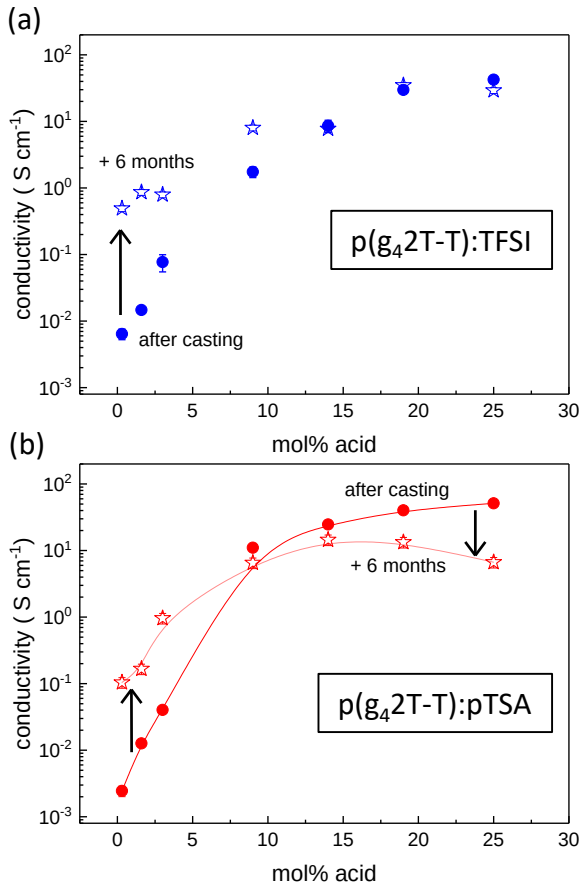

Figure S7: Temporal evolution of the conductivity as a function of dopant concentration for spin coated films of a) p($g_4$2T-T):TFSI and b) p($g_4$2T-T):pTSA.

EXPERIMENTAL

Materials. p($g_4$2T-T) was synthesized according to the previously published synthesis route[1]. p-toluenesulfonic acid monohydrate (pTSA·H_2O), 4-Ethylbenzenesulfonic acid (EBSA), 4-Dodecylbenzenesulfonic acid (DBSA), bis(trifluoromethane)sulfonimide (TFSI) and 1,3-Propanedisulfonic acid (PDSA) (70wt% in H_2O) were purchased from Sigma Aldrich and used as received.

Sample Fabrication. P($g_4$2T-T) was dissolved under magnetic stirring at room temperature with c = 6 g L^{-1} in Chloroform:Acetonitrile (3:2, v:v)). For the preparation of sequentially doped samples p($g_4$2T-T) films were spin-coated onto glass substrates to yield film thicknesses between 50nm to 150nm. For vapour doping a small amount of the acid dopant was put into a glass petri dish, which was then placed onto a hot plate at 80 °C in air. The dry p($g_4$2T-T) films were taped face down to the cover of the petri dish, which was then placed onto the petri dish containing the acid, forming a vapour chamber. The p($g_4$2T-T) films were exposed to vapours until no more increase in the film conductivity were observed. The reported conductivity values are average values of the maximum conductivities of four samples. Solution doped samples were prepared by immersion of dry p($g_4$2T-T) films (thickness 55nm ± 10nm) for the given times in a solution of pTSA (2 g L^{-1}) and TFSI (2.8 g L^{-1}) in acetonitrile, respectively. For co-processing stock solutions of the acid dopants in acetonitrile (c= 10 g L^{-1}) were prepared. The required amount of the respective acid stock solutions was admixed to the p($g_4$2T-T) solution (c = 6 g L^{-1}) in Chloroform:Acetonitrile (3:2, v:v) and the mixture was then drop-cast onto glass or PET substrates and dried at 40°C.
For the preparation of doped films in the absence of air, p($g_4$2T-T) as well as pTSA and TFSI were dissolved in Chloroform:Acetonitrile (3:2, v:v)), which had been degassed with Argon for one hour. After mixing under Argon atmosphere, films were drop cast and dried either under Argon atmosphere or in air at 40°C.
De-doping of acid doped p($g_4$2T-T) was performed by washing of the dry, doped polymer with a solution of KOH:DMSO:H_2O (15wt%:35wt%:50wt%) at room temperature. All experiments were performed under ambient conditions.

UV/Vis absorption spectroscopy. Absorption measurements of liquid and solid samples were performed with a PerkinElmer Lambda 900 spectrophotometer.

Electrical characterization. The electrical resistivity was measured with a four-point probe setup from Jandel Engineering (cylindrical probe head, RM3000). Seebeck coefficients were measured at 300K with an SB1000 instrument equipped with a K2000 temperature controller from MMR Technologies using a thermal load of 1-2 K and a constantan wire as an internal reference. Samples of about 1 mm x 5 mm were cut from drop-cast films and mounted on the sample stage using silver paint (Agar Silver Paint, G302). The film thickness was determined using a KLA Tencor AlphaStep D-100 profilometer.

Grazing-incidence wide-angle X-ray scattering (GIWAXS). Grazing-incidence wide-angle X-ray scattering (GIWAXS) images were obtained at the D-line at the Cornell High Energy Synchrotron Source (CHESS) at Cornell University. A synchrotron radiation of a wavelength of 1.155 Å was used for these measurements. A Pilatus 200K detector with pixel size of 172μm × 172μm was used to collect scattered X-ray from the sample at a sample to detector distance of 169.5 mm.

Thermogravimetric analysis (TGA). Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 3+ STAR System with a heating rate of 10 °C min^{-1} under nitrogen.

1. Kroon, R., Kiefer, D., Stegerer, D., Yu, L., Sommer, M., Müller, C. *Adv. Mater.*, 2017, **29**, 1700930.