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SUPPLEMENTARY MATERIAL

Cationic ionene as n-dopant agent of poly(3,4-ethylenedioxythiophene)

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METHODS

Materials

3,4-Ethylenedioxythiophene (EDOT) and acetonitrile of analytical reagent grade were purchased from Aldrich. Tetramethylammonium chloride (TMA; 98%) was purchased from Across. Anhydrous $LiClO_4$, analytical reagent grade, from Aldrich, was stored in an oven at 80 ºC before using it in the electrochemical trials. *Meta*-phenylenediamine, 4-(chloromethyl)benzoyl chloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from TCI Europe.

Preparation of PEDOT films

Oxidized PEDOT films were prepared by chronoamperometry (CA) under a constant potential of +1.40 V. Electrochemical experiments were conducted on a PGSTAT204 AUTOLAB potentiostat–galvanostat connected to a PC computer controlled through the NOVA 1.6 software using a three-electrode two-compartment cell under nitrogen atmosphere at 25 ºC. The cell was filled with 10 mL of a 10 mM monomer solution in acetonitrile with 100 mM $LiClO_4$. Steel AISI 316 sheets with an area of 1 cm^2 and 2 cm^2 were employed as working and counter electrodes, respectively. Before each trial, electrodes were cleaned with acetone and dried in a nitrogen-flow. No polishing of the sheets was necessary because of the low roughness of steel AISI 316.[S1] The reference electrode was an Ag|AgCl electrode containing a KCl saturated aqueous solution (E^o = 0.222 V *vs.* standard hydrogen electrode at 25 ºC), which was connected to the working compartment through a salt bridge containing the electrolyte solution. The electrodes used for synthesis of p-doped PEDOT films were also employed for dedoping and redoping experiments.

The polymerization time was adjusted to obtain PEDOT electrodes with a polymerization charge of 0.960 C (480 mC/cm^2). The mass of PEDOT deposited onto the WE was determined as the weight difference between coated and uncoated steel sheets using a CPA26P Sartorius analytical microbalance with a precision of 10^{-6} g. The exact amount of electrochemically polymerized PEDOT onto the electrode was $m_{pol} = 0.84 \pm 0.13$ mg.

Preparation of *m*PI

*m*PI was synthesized as previously reported[S2] via a two-step reaction sequence. Briefly, the first step consisted in the amidation of *meta*-phenylenediamine with 4-(chloromethyl)benzoyl chloride in the presence of Et_3N in CH_2Cl_2 to afford the corresponding bis-benzamide monomer upon recrystallization (87% yield). Subsequent step-growth copolymerization with DABCO under equimolar conditions in DMF at 80 ºC yielded the desired polymer within 3 days as off-white slight brownish solid (69% yield) after a simple filtration, washing and drying protocol. ^{1}H-NMR (D_2O, 300 MHz) δ (ppm) = 8.00–7.18 (m, 6H), 4.44 (s, 1H), 3.91 (s, 4H), 3.34 (d, J = 6.6 Hz, 2H), 3.05 (d, J = 6.2 Hz, 2H). In order to achieve adequate solubility and mobility for GPC/SEC, counteranion exchange of chloride by bis(trifluoromethanesulfonyl)amide (TFSA) anions was carried out using LiTFSA in hot water. SEC data were obtained using a YL GPC instrument equipped with a refractive index detector (temperature of column oven = 50-60 ºC; eluent = DMF including 30 mM of LiTFSA; flow rate = 0.5 mL min^{-1}). Solution of the sample was filtered through 0.2 mm filter before injection into the 10 mm column. Calibration was carried out using poly(methyl methacrylate) standards. *m*PI·TFSA: ^{1}H-NMR (DMSO-d_6, 300 MHz): δ (ppm) = 10.43 (d, J = 5.8 Hz, 2H), 8.42 (s, 1H), 8.25–7.98 (m, 2H), 7.67 (d, J = 6.3 Hz, 4H), 7.49 (t, J = 7.9 Hz, 2H), 7.35 (t, J

= 8.0 Hz, 1H), 4.83 (s, 2H), 3.85 (s, 8H), 3.30 (d, J = 7.7 Hz, 2H), 3.03 (d, J = 6.9 Hz, 2H). $M_w = 1.2 \times 10^4$ Da; $M_n = 5.0 \times 10^3$ Da; $Đ_M = 2.4$; $n = 7$.

Dedoping and redoping assays

Chronopotentiometric and chronoamperometric assays were performed using the equipment, cell and electrodes described above. Dedoping assays of electropolymerized p-doped PEDOT were carried out using water with 10 mM $LiClO_4$ as electrolyte solution, while redoping experiments were conducted using aqueous solutions with 10 mM *m*PI or 10 mM TMA. After redoping experiments, PEDOT films were submerged one time in acetonitrile to clean superficial *m*PI or TMA not electrostatically bounded to the polarons and bipolarons of PEDOT. In all cases, samples were softly washed with the solvent of the solution before the cyclic voltammetry (CV) assays.

X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed in a SPECS system equipped with a high-intensity twin-anode X-ray source XR50 of Mg/Al (1253 eV/1487 eV) operating at 150 W, placed perpendicular to the analyzer axis, and using a Phoibos 150 MCD-9 XP detector. The X-ray spot size was 650 µm. The pass energy was set to 25 and 0.1 eV for the survey and the narrow scans, respectively. Charge compensation was achieved with a combination of electron and argon ion flood guns. The energy and emission current of the electrons were 4 eV and 0.35 mA, respectively. For the argon gun, the energy and the emission current were 0 eV and 0.1 mA, respectively. The spectra were recorded with pass energy of 25 eV in 0.1 eV steps at a pressure below 5×10^{-9} mbar. These standard conditions of charge compensation resulted in a negative but perfectly uniform static charge. The C 1s peak was used as an internal reference with a binding energy of

284.8 eV. High-resolution XPS spectra were acquired by Gaussian–Lorentzian curve fitting after s-shape background subtraction. The surface composition was determined using the manufacturer's sensitivity factors.

Morphological and topographical characterization

Scanning electron microscopy (SEM) studies were performed to examine the surface morphology of as prepared, dedoped and redoped PEDOT films. Dried samples were placed in a Focussed Ion Beam Zeis Neon 40 scanning electron microscope operating at 3 kV, equipped with an energy dispersive X-ray (EDX) spectroscopy system.

Atomic force microscopy (AFM) images were obtained with a Molecular Imaging PicoSPM using a NanoScope IV controller under ambient conditions. The tapping mode AFM was operated at constant deflection. The row scanning frequency was set to 1 Hz. AFM measurements were performed on various parts of the films, which provided reproducible images similar to those displayed in this work. The statistical application of the NanoScope Analysis software was used to determine the root mean square roughness (R_q), which is the average height deviation taken from the mean data plane.

Contact angle

Measurements were carried out using the sessile drop method at room temperature on an OCA 15EC with SCA20 software (Data-Physics Instruments GmbH, Filderstadt, Germany). The solvent used for these experiments was deionized water, contact angle being determined for the first drop. For measurements, the sessile drop was gently put on the surface of sample discs using a micrometric syringe with a proper metallic needle (Hamilton 500 μL). The ellipse method was used to fit a mathematical function to the measured drop contour. This procedure consists on approximate the drop contour to the line of an ellipse, deviations from the true drop shape being in the range of a few percent. The ellipse method provides accurate measure of the contact angle and holds the advantage that it is extremely fast. For each sample, no less than fifteen drops were examined.

Thermal stability

The thermal stability was studied by thermogravimetry (TGA) at a heating rate of 20 ºC/min (sample weight *ca.* 5 mg) with a Q50 thermogravimetric analyzer of TA Instruments (New Castle, DE, USA) and under a flow of dry nitrogen. Test temperatures ranged from 30 to 600 ºC.

Molecular dynamics (MD) simulations

All MD trajectories were generated using the scalable computer program NAMD.[S3] The energy was calculated using the AMBER all-atom force-field.[S4] All parameters, with the exception of the equilibrium parameters and the partial charges of the EDOT repeating unit, were taken from previous studies in which parameters compatible with the AMBER force-field were developed.[S2,S5] Atomic electrostatic parameters for redoped EDOT units (*i.e.* $EDOT^{-0.2}$) were derived using the Restrained Electrostatic Potential (RESP) method[S6] using $(EDOT)_5^{-1}$ (*i.e.* considering a doublet electronic state). The resulting charges are displayed in Figure S1. Equilibrium parameters for $EDOT^{-0.2}$ units were taken from quantum mechanical calculations at the UB3LYP/6-31G(d,p) level.

All MD simulations were performed using the NAMD 2.9 program.[S7] Each of the two simulated systems (**M1** and **M2**, which are described in the main text) was subjected to 20000 steps of energy minimization (Newton Raphson method) before any

MD trajectory was run in order to relax conformational and structural tension. The temperature and pressure of **M1** were equilibrated by applying two MD runs. The first consisted on an NVT-MD simulation at 298 K for 0.5 ns. The resulting atom velocities and coordinates were used as starting point for the second run: a 1.0 ns NPT-MD trajectory at 298 K and 1 bar. For **M2** this process was repeated ten times consecutively, the equilibration taken 5 and 10 ns of NVT-MD and NVT-MD, respectively, distributed in 10 different runs each one. The last step of the equilibration run was the starting point of the productive trajectories presented in this work (298 K and 1 bar pressure).

Bond lengths involving hydrogen atoms were kept at their equilibrium distances using the RATTLE algorithm.[S8] Atom pair distance cutoffs were applied at 14.0 Å to compute the van der Waals interactions. To avoid discontinuities in this energy component, the van der Waals energy term was forced to slowly converge to zero by applying a smoothing factor from a distance of 12.0 Å. Electrostatic interactions were extensively computed by means of Ewald summations. The real space term was defined by the van der Waals cutoff (14.0 Å), while the reciprocal space was computed by interpolation of the effective charge into a charge mesh with a grid thickness of 5 points per volume unit (particle mesh Ewald).[S9]

For the equilibration and production runs, both temperature and pressure were controlled by the Nose-Hoover pistons[S10] combined with the piston fluctuation control of temperature implemented for Langevin dynamics.[S11] Pressure was kept at 1.01325 bars, the oscillation period was set to 1 ps while the piston decay time was set to 0.001 ps. The piston temperature was set to the same value as the thermostat control, 298 K, which used a damping coefficient of 2 ps. The integration step was 2 fs in all simulations.

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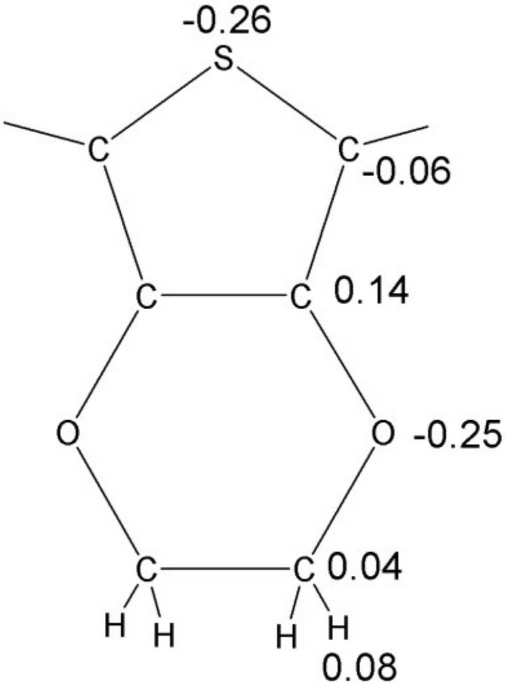

Figure S1. RESP charges calculated for n-doped EDOT unit.