SUPPORTING INFORMATION

Isomeric cationic ionenes as n-dopant agents of poly(3,4-ethylenedioxythiophene) for *in situ* gelation

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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 LiClO₄, analytical reagent grade, from Aldrich, was stored in an oven at 80 °C before using it in the electrochemical trials. *Orto-*, *meta-*and *para-*phenylenediamine, 4-(chloromethyl)benzoyl chloride and 1,4diazabicyclo[2.2.2]octane (DABCO) were purchased from TCI Europe.^{S1}

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 °C. The cell was filled with 10 mL of a 10 mM monomer solution in acetonitrile with 100 mM LiClO₄. Steel AISI 316 sheets with an area of 1 cm² and 2 cm² were employed as working and counter electrodes, respectively. Before each trial, electrodes were cleaned with acetone and dried in a nitrogen-flow. The reference electrode was an Ag|AgCl electrode containing a KCl saturated aqueous solution (E° = 0.222 V vs. standard hydrogen electrode at 25 °C), which was connected to the working compartment through a salt bridge containing the electrolyte solution.

The polymerization time was adjusted to obtain PEDOT electrodes with a polymerization charge of 0.960 C (480 mC/cm²). The mass of PEDOT deposited onto the working electrode 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 ionenes 1-3

1-3 were synthesized as previously reported^{S1} via a two-step reaction sequence. Briefly, the first step consisted in the amidation of *x*-phenylenediamine (x = ortho- / *meta-* / *para-*) with 4-(chloromethyl)benzoyl chloride in the presence of Et₃N in CH₂Cl₂ to afford the corresponding bis-benzamide monomer upon recrystallization (87-96% yields). Subsequent step-growth copolymerization with DABCO under equimolar conditions in DMF at 80 °C yielded the desired polymers within 3 days (69-98% yields) after a simple filtration, washing and drying protocol. ¹H-NMR (D₂O, 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 °C; 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.

1: ¹H-NMR (D₂O, 300 MHz) δ (ppm) = 7.86–7.26 (m, 6H), 4.54–4.18 (m, *J* = 6.7 Hz, 1H), 3.93–3.66 (m, *J* = 28.2, 12.4 Hz, 4H), 3.42–3.18 (m, *J* = 15.8, 6.9 Hz, 2H), 3.13–2.94 (m, *J* = 12.7, 6.7 Hz, 2H). 1·TFSA: ¹H-NMR (DMSO-*d*₆, 300 MHz) δ (ppm) = 10.15 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 2H), 7.69–7.51 (m, 3H), 7.33 (s, 1H), 4.77 (s, 2H), 3.79 (s, 4H), 3.28 (bs, 1H), 3.02 (bs, 1H). M_w = 8.1 × 10³ 10 3 Da; M_n = 3.9 × 10³ Da; D_M = 2.1; *n* = 7.

2: ¹H-NMR (D₂O, 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). **2**·**TFSA:** ¹H-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 × 10⁴ Da; *M_n* = 5.0 × 10³ Da; *D_M* = 2.4; *n* = 7.

3: ¹H-NMR (D₂O, 300 MHz) δ (ppm) = 7.88 (s, 2 H), 7.72–7.39 (m, 4H), 4.67–4.23 (m, 1H), 3.82 (bs, 4H), 3.33 (bs, 2H), 3.05 (bs, 2H). **3·TFSA:** ¹H-NMR (DMSO-*d*₆, 300 MHz) δ (ppm) = 10.37 (d, *J* = 4.7 Hz, 1H), 8.12 (q, *J* = 11.2 Hz, 2H), 7.75 (d, *J* = 11.3 Hz, 2H), 7.64 (dd, *J* = 15.5, 8.2 Hz, 2H), 4.70 (d, *J* = 74.8 Hz, 2H), 3.84 (s, 4H), 3.31–3.29 (m, 1H), 3.05 (m, 1H). M_w = 1.7 × 10⁴ Da; M_n = 5.9×10³ Da; D_M = 2.9; *n* = 10.

Dedoping and redoping assays

Dedoping and redoping assays were performed using the equipment, cell and electrodes described above. Dedoping of electropolymerized p-doped PEDOT was carried out applying a fixed potential of -1.30 V during 145 s in a 10 mM LiClO₄ water solution, while redoping experiments were conducted using aqueous solutions with 10 mM ionene (**1**, **2** and **3**) or 10 mM TMA and applying a reduction potential of -0.50, -0.70, -0.90 or -1.10 V during 150 s. After redoping experiments, PEDOT films were submerged one time in acetonitrile to clean n-dopant molecules from the surface (*i.e.* removal of ionene molecules non-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. ^{S2} All experiments were conducted considering five independent replicas (n= 5), numerical values of the different electrochemical parameters being provided as the average ± standard deviation.

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 μ m. 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.

Raman spectroscopy

Samples were characterized by micro-Raman spectroscopy using a commercial Renishaw inVia Qontor confocal Raman microscope. The Raman setup consists of a laser (at 785 nm with a nominal 100 mW output power) directed through a microscope (specially adapted Leica DM2700 M microscope) to the sample after which the scattered light is collected and directed to a spectrometer with a 1200 lines mm⁻¹ grating. The exposure time was 10 s, the laser power was adjusted to 1% of its nominal output power and each spectrum was collected with 3 accumulations.

Specific capacitance

The specific capacitance (SC; in F/g referred to the mass of PEDOT) of the active materials in the electrode was calculated as:

$$SC = \frac{Q}{\Delta Vm} \tag{1}$$

where Q is voltammetric charge, which is determined by integrating either the oxidative or the reductive parts of the cyclic voltammogram curve, ΔV is the potential window and m is the mass of PEDOT on the surface of the working electrode. The latter is derived from the productivity current and polymerization charge.^{S2} The *SC* values provided in text corresponds to the average \pm standard deviation, considering five replicas (n=5).

Thermal stability

The thermal stability was studied by thermogravimetry (TGA) at a heating rate of 20 °C/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 °C.

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 samples using a micrometric syringe with a proper metallic needle (Hamilton 500 μ L). 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, fifteen drops were examined and. The values provided in text correspond to the average ± standard deviation.

Atomic Force microscopy (AFM)

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.

Scanning electron microscopy (SEM)

SEM studies were performed to examine the surface morphology of PEDOT:ionene 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.

Electrical conductivity

The electrical conductivity (σ ; S/cm) of p-doped PEDOT, dedoped PEDOT and ndoped PEDOT:ionene films was determined by the two-probe procedure using the following relation:

$$\sigma = \frac{L}{R \cdot S} \tag{2}$$

where L is the distance between two silver terminals, R is the electrical resistance measured between the terminals, and S is the cross-sectional area of the film.

Computer simulations

MD trajectories were conducted using the scalable computer program NAMD 2.9.^{S3} The energy was calculated using the AMBER all-atom force-field.^{S4} All parameters, including the equilibrium parameters and the partial charges of the EDOT^{-0.2} repeating unit, were taken from previous studies in which parameters compatible with the AMBER force-field were developed.^{S1,S5}

Each of the three simulated systems (m1, m2 and m3, 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 each model were equilibrated by applying a two-step process, which was repeated ten times consecutively. The first step 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 run of the second-step: a 1.0 ns NPT-MD trajectory at 298 K and 1 bar. As a consequence of the ten-times repetition, the equilibration of each model took 5 and 10 ns of NVT-MD and NPT-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.^{S6} 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).^{S7}

For the equilibration and production runs, both temperature and pressure were controlled by the Nose-Hoover pistons^{S8} combined with the piston fluctuation control of temperature implemented for Langevin dynamics.^{S9} 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.

REFERENCES

- S1. J. Bachl, D. Zanuy, D. E. López-Pérez, G. Revilla-López, C. Cativiela, C. Alemán and D. Díaz Díaz, *Adv. Funct. Mater.*, 2014, 24, 4893.
- S2. C. Ocampo, R. Oliver, R. Armelin, C. Alemán and F. Estrany, J. Polym. Res., 2006, 13, 193.

- S3. J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kale and K. Schulten, *J. Comput. Chem.*, 2005, 26, 1781.
- S4. W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson,
 D. C. Spellmeyer, T. Fox, J. W. Cadwell and P. A. Kollman, *J. Am. Chem. Soc.*,
 1995, 117, 5179.
- S5. D. Zanuy and C. Alemán, Soft Matter, 2013, 9, 11634.
- S6. H. C. Andersen, J. Comput. Phys., 1983, 52, 24.
- S7. T. Darden, D. York and L. Pedersen, J. Chem. Phys., 1993, 98, 10089.
- S8. Y. Duan, C. Wu, S. Chowdhury, M. C. Lee, G. M. Xiong, W. Zhang, R. Yang, P. Cieplak, R. Luo, T. Lee, J. Caldwell, J. M. Wang and P. Kollman, *J. Comput. Chem.*, 2003, 24, 1999.
- S9 G. J. Martyna, D. L. Tobia and M. L. Klein, J. Chem. Phys., 1994, 101, 4177.



Figure S1. Comparison of the Raman spectra recorded for PEDOT:1 films obtained by redoping p-doped PEDOT electropolymerized using charges of 30 and 480 mC/cm². Both the latter polymerization charge and the removal of PEDOT:1 from the steel support damaged the peak resolution.



Figure S2. Contact angle of water measured for PEDOT redoped with (a) **1**, (b) **2** and (c) **3** as a function of the reduction potential (*i.e.* -0.50, -0.70, -0.90 and -1.10 V).



Figure S3. Height (left) and phase (right) AFM images $(20 \times 20 \ \mu m^2)$ of (a) PEDOT:1, (c) PEDOT:2 and (e) PEDOT:3 prepared using a reduction potential of -0.50 V. The root mean square surface roughness (R_q) and the corresponding standard deviation is also displayed for each PEDOT:ionene system.



Figure S4. SEM micrographs (magnification: 10 KX) of (a,b) PEDOT:1, (c,d) PEDOT:2 and (e,f) PEDOT:3 prepared using a reduction potential of (a,c,e) -0.50 V and (b,d,f) -1.10 V. Scale bar: 2 μ m.



Figure S5. SEM micrographs (magnification: 100 KX) of (a,b) PEDOT:1, (c,d) PEDOT:2 and (e,f) PEDOT:3 prepared using a reduction potential of (a,c,e) -0.50 V and (b,d,f) -1.10 V. Scale bar: 200 nm.



Figure S6. Cross section SEM micrographs of PEDOT:1 after 10 min in an oven at 60 °C under acid wetting conditions. Magnification: (a) 30 KX; (b) 50 KX; and (c) 100 KX. Films were redoped using a reduction potential of–1.10 V.



Figure S7. SEM micrographs of (a) PEDOT:1 and (b) PEDOT:3 after 10 min in an oven at 60 °C under acid wetting conditions. Films were redoped using a reduction potential of–1.10 V.



Figure S8. SEM micrograph and photograph (left and right respectively) of (d) PEDOT:**1** and (e) PEDOT:**3** slices obtained after ionene gelation by scratching the substrate.



Figure S9. Geometry of the (a) **m1**, (b) **m2** and (c) **m3** models used as starting point for productive MD simulations. Ionene molecules **1**, **2** and **3** are displayed in (a) red, (b) blue and (c) green, respectively, while PEDOT molecules are represented in black.