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

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ABSTRACT

Three isomeric ionene polymers containing 1,4-diazabicyclo[2.2.2]octane (DABCO) and N,N' -(x -phenylene)dibenzamide ($x = ortho-$ / $meta-$ / $para-$) linkages have been used as dopant agents to produce n-doped poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes by reducing already dedoped conducting polymer (CP) films. This work focuses on the influence of the ionene topology in both the properties of n-doped PEDOT:ionene electrodes and the success of the *in situ* thermal gelation of the ionene inside the CP matrix. The highest doping level is reached for the *para*-isomeric ionene-containing electrode, even though the content of *ortho*- and *meta*-topomers into the corresponding n-doped PEDOT:ionene electrodes is greater. Thus, many of the incorporated ionene units are not directly interacting with CP chains and, therefore, do not play an active role as n-dopant agent but they are crucial for the *in situ* formation of ionene hydrogels. The effect of the ionene topology is practically inexistent in properties like the specific capacitance and wettability of PEDOT:ionene films, and it is small but non-negligible in the electrochemical and thermal stability. In contrast, the surface morphology, topography, and distribution of dopant molecules significantly depend on the ionene topology. *In situ* thermal gelation was successful in PEDOT films n-doped with the *ortho*- and *para*-topomers, even though this assembly process was much faster for the former than for the latter. The gelation considerably improved the mechanical response of electropolymerized PEDOT film, which was practically non-existent before it. Molecular dynamics simulations prove that the strength and abundance of PEDOT...ionene specific interactions (*i.e.* π - π stacking, N-H...S hydrogen bonds and both N^+ ...O and N^+ ...S interactions) are higher for the *meta*-isomeric ionene, for which the *in situ* gelation was not achieved, than for the *ortho*- and *para*-ones.

INTRODUCTION

Cationic polyelectrolytes bearing quaternary ammonium in the backbone constitute an important group of highly charged polymers, named ionenes, with potential uses in the biomedical¹⁻³ and catalytic applications.⁴⁻⁷ The synthesis of new ionene polymers (Scheme 1) containing 1,4-diazabicyclo[2.2.2]octane (DABCO) and N,N'-(*x*-phenylene)dibenzamide (*x*= *ortho*- / *meta*- / *para*-) was described and their gelation capacity in aqueous media was reported by some of us.^{8,9} It was found that the topology of this polymers plays a fundamental role in their self-assembly properties in pure water⁸ and in aqueous solutions with different acidic pH and ionic strength.⁹ The properties of hydrogels formed by the *ortho*-ionene (**1**) were superior to those of the *meta*- and *para*-isomeric analogues (**2** and **3**, respectively) in all cases. Specifically, **1** showed the highest gelation efficiency, lower critical gelation concentrations, higher gel-to-sol transition temperature, thermosreversibility, thixotropic behavior, and dispersion ability when combined with single-walled carbon nanotubes.^{8,9}

Scheme 1

In this work we focus our interest on the use of ionenes for applications related with energy storage. More specifically, we put our focus on the preparation of capacitive n-doped electrodes using ionenes as polycationic dopants of poly(3,4-ethylenedioxythiophene) (PEDOT), an important conducting polymer (CPs) frequently employed for the fabrication of supercapacitors.¹⁰⁻¹⁵ Although the literature about p-doped PEDOT electrodes prepared using polyanionic dopants, as for example poly(styrenesulfonate) (PSS), is very abundant,¹⁶⁻²² the number of studies on n-doped PEDOT is very scarce.²³⁻²⁶ Moreover, these studies were focused on the spectroscopic, electrical and electrochemical properties of negatively charged PEDOT prepared using very small tetraalkylammonium cations as electrolyte, as for example tetramethylammonium (TMA).²³⁻²⁵

In a very recent study we considered a cationic polyelectrolyte as n-dopant agent of PEDOT.²⁶ Specifically, the electrochemical conditions required for the n-redoping of PEDOT films, previously dedoped, using **2** as reducing agent, were examined. The advantages and disadvantages of **2** as n-dopant agent with respect to conventional TMA were deeply analysed and discussed. Thus, films redoped with **2** showed higher hydrophilicity and thermal stability than those redoped with TMA. However, the use of ionenes with hydrogel-forming capability, as **1** and **3**, as n-dopant agents has not been attempted until now. It is worth noting that the different characteristics of these ionenes at both molecular (*i.e.* topology) and supramolecular (*i.e.* hydrogel) levels, which are defined by ionene...ionene interactions, can be altered by ionene...PEDOT interactions, affecting in turn the CP properties.

As the development of polymeric n-doped electrodes is an unresolved need so far, in this work, we investigate the abilities of the three different DABCO-containing ionenes as reducing agents. The properties of the resulting n-doped PEDOT films, hereafter

denoted PEDOT:**1**, PEDOT:**2** and PEDOT:**3**, respectively, exhibit a non-negligible improvement with respect to TMA, which is the most used reducing agent so far. Discussion of the results has been focused on the influence of the ionene topology in the preparation and properties of n-doped PEDOT. Furthermore, the challenging hydrogelation of the ionenes once incorporated into the PEDOT matrix has been attempted considering thermally-induced aggregation phenomena in acidic conditions. The effects of such *in situ* hydrogelation on the properties of the films have been experimentally evaluated, while the impact of the gelator-topology in PEDOT···ionene interactions have been understood through computational Molecular Dynamics (MD) simulations.

RESULTS AND DISCUSSION

Preparation of n-doped PEDOT:ionene films

p-Doped PEDOT films were deposited onto steel electrodes by anodic polymerization in acetonitrile, using a constant potential of +1.40 V and adjusting the polymerization charge to 480 mC/cm². These films were subsequently dedoped applying a potential of −1.30 V during 145 s in a 10 mM LiClO₄ aqueous solution. After this, the electrochemical n-redoping of the dedoped films was performed by chronoamperometry using a constant reduction potential (−0.50, −0.70, −0.90 or −1.10 V), which was applied during 150 s, and a 10 mM ionene (**1**, **2** or **3**) aqueous solutions. Details about the experimental conditions used for the preparation of p-doped, dedoped and redoped PEDOT films are provided in the Supporting Information.

Control assays (blank) were conducted applying identical experimental conditions using bare steel electrodes (*i.e.* in absence of dedoped PEDOT). For a given reduction potential, the neat redoping charge (Q_{rdop}^{neat}) was estimated as the difference between the

chronoamperometric charges determined for the redoped PEDOT:ionene films (Q_{rdop}) and the corresponding blanks (Q_{blank}):

$$Q_{rdop}^{neat} = Q_{rdop} - Q_{blank} \quad (1)$$

Figure 1a displays the absolute values of Q_{rdop}^{neat} obtained for **1-3** with the four tested reduction potentials. The value of Q_{rdop}^{neat} , which reflects the charge of PEDOT normalized by repeat unit after the redoping process, becomes more negative with the reduction potential. However, the response of the ionenes to the reduction potential clearly depends on their molecular topology. Thus, **3** is sensitive to the redoping potential in the whole studied range, **1** is sensitive to the redoping potential in the range from -0.50 to -0.70 V, and **2** exhibits similar and relatively low Q_{rdop}^{neat} values for all reduction potentials with exception of -1.10 V (*i.e.* **2** exhibits low sensitivity to the potential in the range of -0.50 to -0.90 V). For the -1.10 V potential, the absolute value of Q_{rdop}^{neat} grows as follows: **3** > **2** > **1**. This suggests that under such conditions the PEDOT...ionene interactions are more effective for the *para*-isomeric topomer. The moles of ionene repeating units ($N_{\#}$ with $\# = \mathbf{1}, \mathbf{2}$ or $\mathbf{3}$) incorporated during the redoping process were estimated using the values of Q_{rdop}^{neat} for each reduction potential (Eqn 2):

$$N_{\#} = \frac{Q_{rdop}^{neat}}{2F} \quad (2)$$

where F is the Faraday's constant and includes two positive charges of every ionene repeat unit. The resulting values were combined with the moles of EDOT repeat units in the CP chains (N_{EDOT} ; Eqn 4) to calculate the doping level of each ionene ($dl_{\#}$ with $\# = \mathbf{1}, \mathbf{2}$ or $\mathbf{3}$) at a given reduction potential, which expresses the percentage (in %) of dicationic ionene unit per EDOT unit:

$$dl_{\#} = \frac{N_{\#}}{N_{EDOT}} \times 100 \quad (3)$$

$$N_{EDOT} = \frac{(Q_{pol} - Q_{ddop})}{2F} \quad (4)$$

where Q_{pol} is the charge consumed during the polymerization process of p-doped PEDOT films and Q_{ddop} is the charge consumed during the dedoping process for elimination of ClO_4^- counterions.

Figure 1b, which represents the $dl_{\#}$ values obtained for each reduction potential, proves the successful incorporation of ionene molecules during the redoping process. As it was expected, $dl_{\#}$ increases with the absolute reduction potential, even though the dependence on the ionene topology is not clear. When the reduction potential decreases from -0.50 V to -1.10 V, $dl_{\#}$ increases by $1.9\% \pm 0.4\%$, $3.5\% \pm 0.2\%$ and $2.8\% \pm 0.5$ for **1**, **2** and **3**, respectively ($n=5$ in all cases). However, the values of $dl_{\#}$ obtained using -1.10 V are practically identical for **2** and **3**, which in turn are higher than that achieved for **1**. For the sake of completeness, Figure 1 includes the Q_{rdop}^{neat} and the $dl_{\#}$ obtained for PEDOT films redoped with TMA obtained using reduction potentials of -0.50 and -1.10 V. Considering that a TMA molecule involves one positive charge rather than the two positive charges of ionene repeat units, the doping levels of the two species are comparable.

The maximum doping level achieved for PEDOT:**1**, PEDOT:**2** and PEDOT:**3** corresponds to one dicationic ionene unit for every ~ 28 , ~ 20 and ~ 20 EDOT units, respectively. The doping level achieved for monocationic TMA using identical experimental conditions was reported to be $dl_{TMA} = 8.9 \pm 0.3\%$ ($n=5$), indicating that one cationic TMA molecule has been incorporated every ~ 31 EDOT units.²⁶ Accordingly,

the n-doping capacity of the TMA is lower than that DABCO-containing ionenes, even though the mobility of former is greater than that of the cationic polyelectrolytes.

Chemical characterization of PEDOT:ionene films

The success of the redoping process and the structural changes of PEDOT chains as a function of the ionene were investigated using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, respectively. Results derived from XPS analyses, which were performed considering PEDOT:ionene films prepared by applying a reduction potential of -1.10 V, are displayed in Table 1. The apparition of N 1s demonstrates the incorporation of the ionene into the PEDOT matrix. However, the variation of the atomic content of N 1s, $2 > 1 > 3$, is not consistent with the variation of $dl_{\#}$ (Figure 1b), $2 \approx 3 > 1$. Thus, the S / N ratios derived from the XPS atomic percent compositions for samples redoped with **1**, **2** and **3** suggest the presence of one dicationic ionene unit for approximately every 9, 5 and 13 EDOT units (*i.e.* each ionene unit contains four nitrogen atoms, while there is one sulfur per EDOT unit). The difference between the electrochemical and XPS doping levels has been attributed to the fact that many of the incorporated ionene units are not directly interacting with PEDOT chains and, therefore, do not play a role as active n-dopant agents. This may represent an advantage for the *in situ* hydrogelation of PEDOT:ionene films since polycationic chains could form stable gels without affect the electrochemical performance of n-doped PEDOT.

Figure 2a displays the Raman spectra obtained for p-doped PEDOT (as prepared), PEDOT:**1**, PEDOT:**2**, PEDOT:**3** and PEDOT:TMA. Worth mentioning that the Raman spectra were obtained using PEDOT samples electropolymerized at $+1.40$ V but adjusting the polymerization charge to 30 mC/cm^2 rather than the 480 mC/cm^2 used for all assays. This was because, although the latter polymerization charge produced films

of higher thickness, their roughness did not allow us to obtain a good peak resolution. This feature is illustrated in Figure S1, which compares the spectra recorded for PEDOT:1 films that were redoped using p-doped PEDOT obtained using polymerization charges of 30 and 480 mC/cm².

The Raman fingerprints of PEDOT were reported in previous studies.²⁷⁻²⁹ The main vibrational modes of this CP are located at 1490 cm⁻¹, 1424 cm⁻¹, 1371 cm⁻¹ and 1261 cm⁻¹, which correspond to asymmetric C_α=C_β stretching, symmetric C_α=C_β stretching, C_β=C_β stretching and C_α-C_{α'} inter-ring stretching vibrations, respectively. Other important bands are located at 438, 700, and 991 cm⁻¹, assigned to the deformation of C-O-C, symmetric C-S-C and oxyethylene ring, respectively.

Comparison between dedoped PEDOT and n-doped PEDOT:ionene and PEDOT:TMA samples (Figure 2a) shows the appearance and disappearance of several bands. Some interesting remarks are:

- Both types of samples present different Raman shift and width of the peak centered at 1424 cm⁻¹.
- The band located at 1261 cm⁻¹ splits into two peaks in the presence of the ionenes.
- The peak at 1490 cm⁻¹ disappears.

Changes in the characteristic band at 1424 cm⁻¹ are related with a variation in the electronic structure of PEDOT chains that affects to the C_α=C_β stretching.^{30,31} This peak, which is pointed at 1424 cm⁻¹ for dedoped PEDOT, shifts to 1416 cm⁻¹ for n-doped samples, indicating that this vibration mode is sensitive to the reduction caused by the n-dopant agent. More specifically, this red shift has been associated with ionene-induced benzenoid-to-quinoid conversion of PEDOT chains, which is consistent with earlier theoretical studies.³²

Cho *et al.*³³ reported that the width of the characteristic band of $C_{\alpha}=C_{\beta}$ can be correlated with the resonant structure of PEDOT: narrower peaks correspond to a higher content of quinoid structure. Figure 2a reflects that this peak becomes narrower for all PEDOT:ionene films, even though this is slightly more evident for PEDOT n-doped with **2** and TMA than with **1** and **3**. The width of the $C_{\alpha}=C_{\beta}$ stretching peak can be also related with the crystallinity: narrower peaks associated with more crystalline samples.³⁴ Accordingly, Figure 2a suggests that the crystallinity is higher for PEDOT:**2** and PEDOT:TMA than for PEDOT:**1** and PEDOT:**3**. This feature, together with the fact that the quinoid structure is more expanded and rigid than the benzoid one, suggest that PEDOT:**2** presents stronger PEDOT...ionene interactions than PEDOT:**1** and PEDOT:**3**. Thus, the more extended the PEDOT chains are (*i.e.* the aromatic rings organize in a trans disposition when the electronic structure is quinoid), the delocalized negative charges along them are more accessible to the positive charges of the ionenes. The crystallinity has been reported to exert an important effect on the gelation capacity,³⁵ being lower or even completely absent when the crystallinity of the sample is too high. In this case, the width of the $C_{\alpha}=C_{\beta}$ stretching peak (Figure 2a) is consistent with the *in situ* gelation capacity of the ionenes in the examined PEDOT:ionene samples that, as it is described below, was higher for **1** and **3** than for **2**.

The $C_{\alpha}-C_{\alpha'}$ inter-ring stretching at 1261 cm^{-1} (Figure 2a) is also connected with the percentage of benzoid and quinoid structures.³⁶ After redoping with the ionene, this peak becomes broader and splits into two bands located at 1249 and 1268 cm^{-1} . The observed Raman shifts and reduction in the intensity are ascribable to the variation of $C_{\alpha}-C_{\alpha'}$ and $C_{\beta}=C_{\beta'}$ to $C_{\alpha}=C_{\alpha'}$ and $C_{\beta}-C_{\beta'}$, respectively, suggesting the conversion from the benzoid to the quinoid electronic structure, in agreement with the interpretation of the changes in the peak at 1424 cm^{-1} . On the other hand, the peak at 1371 cm^{-1} , which

is related with $C_{\beta}=C_{\beta'}$, decreases in intensity in the presence of ionenes, confirming its conversion to $C_{\beta}-C_{\beta'}$. Furthermore, the disappearance of the peak centered at 1490 cm^{-1} , which corresponds to the asymmetric $C_{\alpha}=C_{\beta}$ stretching, could be also related with the reduction of the double bond character due to the benzoid-to-quinoid conversion.

Figure 2b displays optical images taken with the Raman confocal microscope of dedoped PEDOT and PEDOT:ionene prepared using a polymerization charge of 30 mC/cm^2 . Interestingly, PEDOT:**1** and, especially, PEDOT:**3** shows dark and large agglomerates homogeneously distributed onto the surface. These agglomerates have been attributed to regions in which the n-dopant agents, **1** and **3**, are segregated from the CP forming a micrometric ionene phase. The presence of the latter suggests that the balance between PEDOT...ionene and ionene...ionene interactions is regulated by the ionene topology, which is expected to play a very important role in the properties of such n-doped films.

Physical characterization of PEDOT:ionene films

Figure 3a displays the variation of the specific capacitance (SC), as determined by cyclic voltammetry (CV), for PEDOT:ionene against the reduction potential. As it is expected, the resulting SC s values, which express the ability to store charge of n-doped films referred to the PEDOT mass, are very low (*i.e.* SC ranged from 3.0 ± 0.1 to $6.1\pm0.5\text{ F/g}$, considering $n=5$ in all cases) with respect to p-doped PEDOT ($SC=56\text{ F/g}$ doped with ClO_4^-)³⁷ and PEDOT-nanocomposites involving MoO_3 , RuO_2 , carbon nanotubes, MnO_2 , and clays (SC varying between 96 and 375 F/g).³⁷⁻⁴³ These differences are associated to the low doping level n-doped PEDOT, which in general is significantly smaller than that of p-doped, and to the fact that negative polarons are the only charge carriers in n-doped PEDOT, as proved by Ahonen and co-workers.⁴⁴ These observations

are consisted with the *SCs* obtained for PEDOT films redoped with TMA, which ranged from 3.9 ± 0.2 to 4.7 ± 0.4 F/g ($n= 5$ in all cases) depending on the reduction potential (Figure 3a),²⁶ and with the fact that the *SCs* of PEDOT:ionene films are relatively independent of the polycation topology. Thus, the *SCs* obtained for the three ionenes are very similar with exception of the films redoped at -0.50 V with **3**, which exhibits slightly higher values.

The cyclic stability of PEDOT:ionene electrodes was evaluated by CV. After 100 consecutive oxidation-reduction cycles, which were applied using -0.50 V as initial and final potentials and -1.10 V as reversal potential (scan rate: 50 mV/s), the *SC* of films redoped with **1** and **3** decreases around $\sim 50\%$, independently of the reduction potential (Figure 3b). However, PEDOT:**2** shows a higher dependence on the redoping potential, the reduction of the *SC* ranging between 40% (-0.90 V) and 70% (-0.50 V). Although the electrochemical stability of films doped with ionenes is apparently low, it should be remarked that this behavior is similar to that observed using TMA as n-dopant agent.²⁶ Thus, the *SC* of PEDOT redoped with TMA decreases $\sim 60\%$ and $\sim 50\%$ when the reduction potential is -1.10 and -0.50 V, respectively (Figure 3b).

On the other hand, considering that PEDOT is a thermoelectric,^{45,46} photothermal,⁴⁷ and biocompatible^{48,49} material, understanding of both the thermal stability and hydrophilicity of electrodes derived from this CP is necessary for future biomedical applications (*e.g.* fabrication of biocapacitors). Thermogravimetric analyses (Figure 4) showed that the topology of the ionene has a small but non-negligible effect in the thermal stability of n-doped PEDOT. Inspection of differential thermogravimetric analysis (DGTA) curves of redoped PEDOT:ionene indicates that solvent evaporation starts at around $45\text{--}50$ °C. After this, all systems exhibit a pronounced degradation step, the maximum temperature (T_{max}) being at 345 °C, 350 °C and 360 °C for PEDOT:**1**,

PEDOT:2 and PEDOT:3, respectively. These values are higher than those observed for dedoped PEDOT ($T_{\max} = 340\text{ }^{\circ}\text{C}$) but similar to those observed for PEDOT redoped with TMA²⁶ ($T_{\max} = 350\text{ }^{\circ}\text{C}$). The temperature at a 50% weight loss ($T_{50\%}$) increases as follows: dedoped PEDOT ($T_{50\%} = 371\text{ }^{\circ}\text{C}$) < PEDOT:3 ($T_{50\%} = 403\text{ }^{\circ}\text{C}$) < PEDOT:1 ($T_{50\%} = 410\text{ }^{\circ}\text{C}$) < PEDOT:2 ($T_{50\%} = 427\text{ }^{\circ}\text{C}$). Although the order is preserved, differences among $T_{50\%}$ values increase at a 70% weight loss ($T_{70\%}$): 449 (dedoped), 469 (PEDOT:3) 480 (PEDOT:1) and 518 $^{\circ}\text{C}$ (PEDOT:2), respectively. According to these results and by comparison with TMA ($T_{50\%} = 403\text{ }^{\circ}\text{C}$, $T_{70\%} = 465\text{ }^{\circ}\text{C}$), ionenes improve the thermal stability of PEDOT, the maximum protection being provide by the *meta*-topomer. This feature suggests that the strength and amount PEDOT...ionene interactions are higher for the *meta*-isomeric ionene than for the *ortho*- and *para*-ones, which is consistent with Raman observations.

Contact angle (θ) measurements were performed to examine the influence of the ionene in the film wettability. As it was previously reported,²⁶ the hydrophilicity of oxidized PEDOT increases significantly upon dedoping (*i.e.* θ decreases from $65^{\circ}\pm 6^{\circ}$ to $37^{\circ}\pm 5^{\circ}$) due to a drastic reduction in the surface roughness (R_q), which decreases from 771 ± 117 to 155 ± 28 nm. The high hydrophilicity of dedoped PEDOT is maintained by the three ionene-containing films (*i.e.* $\theta = 34^{\circ}\pm 8^{\circ}$, $31^{\circ}\pm 6^{\circ}$ and $37^{\circ}\pm 5^{\circ}$ for PEDOT:1, PEDOT:2 and PEDOT:3, respectively; $n = 15$ in all cases). The wettability of redoped PEDOT is not only practically independent of the ionene topology but also of the redoping potential (Figure S2). These results together with the fact that the R_q of the three ionenes is submicrometric and relatively close to that of p-doped PEDOT (see below), suggest that the affinity of PEDOT:ionene films towards water is due to the charged and polar groups contained in the ionene. In opposition, redoping with TMA resulted in a hydrophobic material ($\theta = 101^{\circ}\pm 12^{\circ}$), which was explained by the

formation of a highly hydrophobic TMA layer at the surface of the films.²⁶ Thus, this small organic molecule was found to act not only as n-dopant agent but also as organic coating.

Height and phase AFM images of PEDOT:ionene films obtained using a reduction potential of -1.10 V are shown in Figure 5. As it can be seen, both the surface topography and the distribution of dopant polycations drastically depend on the ionene topology. The R_q of PEDOT:ionene films grows progressively when the ionene topology varies as follows: *ortho* (**1**) > *meta* (**2**) > *para* (**3**) (Figure 5). Thus, the surface topography of the CP redoped with the *ortho*-isomeric ionene consists in a homogeneous distribution of abundant and relatively small PEDOT clusters. This distribution becomes more heterogeneous for films redoped with the *meta*-DABCO containing ionene. In this case, small clusters are accompanied by large aggregates, even though the former ones abound more than the latter ones. Finally, the topography of films containing the *para*-topomer can be described as a heterogeneous distribution of large PEDOT clusters, albeit some small aggregates are still present. In regard to the distribution of the ionene molecules, phase images that are sensitive to the surface stiffness / softness reveal significant differences. Specifically, phase shifts, which are registered as bright and dark regions in phase images, are more abundant and contrasted in samples redoped with **1** and **3** than with **2**. The *ortho*- and *para*-topomers form submicro- and nanometric organizations, respectively, those remain relatively close among them. These microstructures are expected to favor the *in situ* gelation process of **1** and **3**, as will be demonstrated in the next sub-section. In contrast, the presence of the *meta*-isomeric ionene is much less appreciated in films redoped using a reduction potential of -1.10 V (Figure 5b, right).

The roughness, surface topography and phase distributions are also affected by the redoping potential, even though distinctive characteristics that can be only attributed to the ionene topology are still observed. For example, when the reduction potential is -0.50 V, the R_q values determined for PEDOT:1 and PEDOT:3 films are very similar and significantly higher than those of PEDOT:2 (Figure S3). In addition, height images reflect that the size of the CP clusters is significantly lower for films redoped at -0.50 V than at -1.10 V (Figure S3). This is particularly noticeable for PEDOT:2 films, which exhibits a leveled topography formed by a homogeneous distribution of very small PEDOT clusters.

AFM topographic images are fully consistent with representative SEM micrographs. (Figures 6, S4 and S5 for 50 KX, 10 KX and 100 KX magnification, respectively), which reflect the influence of the ionene architecture in the morphology and, especially, the size of globular PEDOT clusters. The globular appearance of n-doped PEDOT:ionene films is similar to that reported for p-doped and dedoped PEDOT.^{26,27} Moreover, the incorporated ionenes preserve the porosity of the films, which is more affected by the reduction potential than by the topology of the n-dopant agent. Thus, the diameter and tortuosity of the pores is higher for the films obtained using -0.50 V than for those redoped at -1.10 V, independently of the ionene topology (Figure 6).

***In situ* thermal hydrogelation of ionenes in n-redoped films**

PEDOT:ionene and PEDOT:TMA (control) films prepared using a reduction potential of -1.10 V (surface area: 1 cm^2), were subjected to thermal hydrogelation tests. After wetting by depositing $80\text{ }\mu\text{L}$ of 0.1 M HCl at each side, supported films were heated in an oven at $60\text{ }^\circ\text{C}$ during a time comprised between 5 and 60 min. The changes in the aspect and texture of PEDOT:1 and PEDOT:3 films (Figure 7a)

suggested the successful gelation of **1** and **3**. In contrast, the thermally-induced gelation was unsuccessful for PEDOT:**2** films and PEDOT:TMA, which did not exhibit any change in their appearance. This was an expected result because of the poor and null gelation capacity of the *meta*-isomeric ionene^{8,9} and TMA, respectively.

It should be mentioned that **1** and **3** efficiently gelled in acidic aqueous solutions at room temperature,⁹ both exhibiting relatively low critical gelation concentrations (22 and 33 g/L, respectively) and gelation times (10 and 50 min, respectively). However, no gelation was observed for PEDOT:**1** and PEDOT:**3** at room temperature, which was attributed to the fact that the concentration of ionene molecules inside the n-doped PEDOT films was too low. However, the kinetics energy provided by increasing the temperature to 60 °C facilitated the approximation of ionene molecules, enabling their assembly. This aggregation phenomenon, combined with the acid wetting, caused the formation of ionene micro/nano-hydrogels inside n-doped PEDOT films.

The topology clearly affected the kinetics of the gelation, which was much faster for **1** than for **3** at all the tested temperatures. For example, the time required to change the aspect and texture of PEDOT:**1** films at 60 °C (10 min) was 5-times shorter than that needed for PEDOT:**3** (60 min). This observation is fully consistent with that reported for the thermal hydrogelation of **1** and **3** from the corresponding aqueous solutions,⁹ even though it should be remarked that the gelation time in PEDOT:ionene films is also influenced by the amount (**1** > **3**, in Table 1) and distribution of the ionene molecules inside the CP matrix (*i.e.* microstructure).

SEM micrographs of gel-containing PEDOT:**1** and PEDOT:**3** films (Figures 7b and 7c, respectively) reveal significant changes with respect to films before the thermal hydrogelation assays (Figure 6). As it can be seen, mild heating combined with acidic wetting conditions gave place to the gradual aggregation of neighboring ionene

molecules, inducing the formation of crosslinked ionene networks and forming gel domains with a smooth texture. Although these newly formed domains are mainly located at the surface of films, cross section SEM micrographs reflect the presence of gel also inside the CP matrix. This characteristic is particularly evident for PEDOT:**1**, as is reflected by the progressively magnified cross section SEM micrographs (Figure S6). Although the gelation kinetics is faster for **1** than for **3**, ionene-forming hydrogel surface domains are more abundant in PEDOT:**3** than in PEDOT:**1** (Figure S7). The latter observation is consistent with the phase AFM images displayed in Figure 5, which show that the *para*-topomer abound more at the surface of films redoped at -1.10 V than the *ortho*-one. These features suggest that the kinetics of self-assembly via facilitated diffusion of the *ortho*-ionene molecules is compensated by the *para*-ionene through the formation of abundant and very stable interactions. MD simulations on representative model systems to provide additional microscopic information about the *in situ* formed hydrogels are discussed in the next sub-section.

The electrical conductivity determined for p-doped PEDOT, $\sigma = 326$ S/cm, is similar to that typically described for PEDOT:perchlorate films⁵⁰ but two orders of magnitude higher than that reported for PEDOT p-doped with PSS ($\sigma = 2$ S/cm).⁵¹ As it was expected, the conductivity of PEDOT decreases drastically after the dedoping, $\sigma \leq 10^{-8}$ S/cm, evidencing the success of the process. However, the conductivity of gel-containing n-doped PEDOT:**1** and PEDOT:**3** films is $4.1 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$ and $3.9 \cdot 10^{-4} \pm 3 \cdot 10^{-5}$ S/cm, respectively. These electrical conductivities are clearly lower than those reported for of p-doped gels based on thiophene-containing molecular gelators,⁵²⁻⁵⁴ which were found to depend on both the chemical nature of the CP and the doping level. For example, the conductivity of oligo(thienylenevinylene) xerogels increases from $4.8 \cdot 10^{-2}$ S/cm to 4.8 S/cm after iodine doping.⁵² This significant difference has been

attributed to the three main reasons: 1) n-doped systems typically present electrical conductivities several orders of magnitude lower than the corresponding p-doped analogues;⁴⁴ 2) the charge mobility attributed to the small dopant ions in gels prepared using doped thiophene-containing gelators is expected to be higher than that of ionene gels; and 3) electron and charge mobility in hybrid systems, in which a hydrogels are immersed into a supported CP film, is expected to be restricted with respect to continuous CP hydrogels.

The *SC* of PEDOT:**1** and PEDOT:**3** films after gelation of the corresponding ionene, $SC = 12.9 \pm 0.4$ and 7.0 ± 0.5 F/g ($n = 5$ in all cases), respectively, were noticeably high in comparison with those discussed above for as prepared redoped films ($SC = 3.8 \pm 0.1$ and 4.1 ± 0.7 F/g, respectively, in Figure 3a). Thus, the gain in the ability for charge storing clearly indicates the ionene hydrogel facilitates the charge mobility. Furthermore, the thermally-induced ionene hydrogel phases formed inside PEDOT film supports that the amount of ionene molecules in PEDOT:ionene is closer to that determined by XPS (Table 1) than to the one reflected by the electrochemical doping level (Figure 1b).

The *in situ* gelation of the ionenes provides important advantages from a mechanical point of view. More specifically, the mechanical response of p-doped PEDOT films prepared by anodic polymerization, as well as of the films dedoped and n-redoped with ionene (before gelation) or TMA, is null. Thus, PEDOT films adhered to the surface of the substrate used as working electrode during the electropolymerization, disintegrate as a powder when they are tried to separate by scratching. Moreover, the mechanical characteristics of films adhered to the substrate are also very poor, tending to undergo cracking when exerted the slightest touch or pressure. In contrast, mechanical failures are much less evident in PEDOT:**1** and PEDOT:**3** after the ionene gelation. Accordingly, ionene nano- and micro-hydrogels act as a cement that prevents the

cracking of the adhered films and, in addition, allows to obtain small slices of films (*i.e.* of millimetric dimensions) by scratching the substrate (Figure S8).

Obviously, in order to extend the applicability of n-doped PEDOT:ionene films, such mechanical response must be further improved, for example by looking for other gelation strategies that would allow a greater incorporation of ionene into the CP matrix. However, a completely different approach based on the integration of the PEDOT:ionene electrodes into a second hydrogel, which acts as a flexible substrate is being considered in our group. In recent studies we used the latter approach for the fabrication of flexible p-doped PEDOT-based electrodes, in which microparticles obtained by breaking a p-doped PEDOT:perchlorate film retained the percolation inside a hydrogel of poly- γ -glutamic acid.⁵⁵ Moreover, the covalent assembly of two of such electrodes through a dielectric layer made with the same hydrogel resulted in a flexible organic supercapacitor able to retain its properties upon drastic compression.⁵⁶ A variation of this strategy could be used to obtain flexible n-doped PEDOT:ionene electrodes.

Computational studies on the self-assembly process

MD simulations were conducted on atomistic models formed by 48 PEDOT chains, each having 40 repeat units, and 32 ionene (**1**, **2** or **3**) chains, each containing 6 repeat units. Hereafter, models for PEDOT:ionene systems involving the *ortho*-, *meta*- and *para*-topomer are denoted **m1**, **m2** and **m3**, respectively. A charge of -0.2 was accounted for each EDOT unit (*i.e.* 10 EDOT units were needed to neutralize each ionene repeat unit). Thus, the ratio between PEDOT and ionene repeat units was close to that determined by XPS (Table 1), which ranged from 5 (PEDOT:**2**) to 13 (PEDOT:**3**). PEDOT and ionene chains were initially distributed in two groups that, in

turn, were arranged in separated blocks (Figure S9) with a density of 1.0 g/cm^3 . After thermalize and equilibrate the starting geometries using the protocol provided in the Electronic Supporting Information, productive trajectories of 100 ns NPT-MD were run at 298 K. During the first half of such trajectories, PEDOT and ionene chains experienced significant re-distributions with respect to the initial geometry. Figure 8a displays the last snapshot of the 100 ns trajectory for **m1**, **m2** and **m3**.

Models **m1**, **m2** and **m3** stabilized at a density of $\rho = 1.34 \pm 0.02$, 1.44 ± 0.04 and $1.44 \pm 0.03 \text{ g/cm}^3$ (averaged over the last 10 ns of each trajectory), reflecting the compression of the simulation box. The experimental density of PEDOT samples redoped with **1**, **2** or **3** at -1.10 V was $\rho = 1.46 \pm 0.03$, 1.55 ± 0.06 and $1.54 \pm 0.05 \text{ g/cm}^3$, respectively, as determined by the flotation method. Thus, theoretical predictions and experimental values differ in $\sim 6\text{-}8\%$ only, showing that MD simulations satisfactorily represent PEDOT...ionene, ionene...ionene and PEDOT...PEDOT interactions.

Although the three examined systems are dominated by the electrostatic interactions between the negatively charged CP and the polycation, specific $\pi\text{-}\pi$ stacking and hydrogen bonds are expected to play also an important role. Figure 8b represents the partial radial distribution functions (RDF) for pairs of centers of masses of aromatic rings of polymeric chains, describing PEDOT...PEDOT ($\text{RDF}_{\text{PEDOT-PEDOT}}$), PEDOT...ionene ($\text{RDF}_{\text{PEDOT-ionene}}$) and ionene...ionene ($\text{RDF}_{\text{ionene-ionene}}$) $\pi\text{-}\pi$ stacking interactions. Previous quantum mechanical studies indicated that the center of masses of two interacting aromatic rings are separated by $\sim 3.7 \text{ \AA}$ and $\sim 5.0 \text{ \AA}$ when they adopt sandwich and T-shaped arrangements, respectively.⁵⁷⁻⁶⁰ The relative disposition of interacting aromatic rings has been examined through the tilting angle, θ , formed by their respective planes (*i.e.* ideally, θ is 0° and 90° for sandwich and T-shaped arrangements, respectively). Figure 8c displays the tilting angle calculated for

PEDOT...PEDOT, PEDOT...ionene and ionene...ionene π - π stacking interactions using cut-off distances extracted from the corresponding RDFs (see below).

The calculated $\text{RDF}_{\text{PEDOT-PEDOT}}$ (Figure 8b, left) is independent of the ionene topology. Thus, the three models present a very intense and sharp peak centered at $r=3.9$ Å and a less intense peak at $r=7.7$ Å. The latter reflects the local order induced by the rigid conformation of PEDOT chains. The distribution profiles of θ , which were calculated using a cutoff distance of 5.0 Å, show a maximum centered at $\sim 15^\circ$, indicating that the stacked rings prefer a slightly distorted coplanar disposition.

PEDOT...ionene π - π stacking interactions are slightly more abundant ($\sim 5\%$) in **m2** than in **m1** and **m3**, as suggested previously discussed experimental results. The $\text{RDF}_{\text{PEDOT-ionene}}$ calculated for **m2** exhibits peaks centered at $r=4.1, 5.1$ and 5.7 Å. Although the peaks at $r=5.1$ and 5.7 Å are maintained in **m1** and **m3**, the peak at $r=4.1$ Å is less intense or practically inexistent in such models. This indicates that PEDOT...ionene interactions are stronger for the *meta*-isomeric ionene than for the *ortho*- and *para*-ones. The θ distribution profiles, calculated considering a cutoff distance of 7.0 Å, evidence the preference towards a distorted T-shape configuration in all cases. The population of pairs with $\theta > 45^\circ$ is 67%, 55% and 66% for **m1**, **m2** and **m3**, respectively, even though the degree of distortion is very variable (*i.e.* θ ranges from 46° to 90° in all cases).

Finally, ionene...ionene π - π stacking interactions are less abundant for **m1** (31%) and **m3** (16%) than for **m2**. The calculated $\text{RDF}_{\text{ionene-ionene}}$ profiles display small and relatively broad peaks at r values comprised between 4 and 6 Å, which have been attributed to the periodicity of the ionene chains (*i.e.* ionenes contain 3 aromatic rings per repeat unit), and a sharp peak at $r \approx 6.5$ Å that actually corresponds to the inter-chain π - π stacking. The preferred arrangement of the interacting rings is the T-shape, even

though a dependence on the ionene topology is clearly observed. Thus, the population of interacting aromatic rings with $\theta > 45^\circ$ grows as 57% (**m3**) < 67% (**m2**) < 71% (**m1**).

On the other hand, specific PEDOT...ionene hydrogen bonds have been analyzed through the RDFs for (N-)H...O and (N-)H...S pairs ($\text{RDF}_{\text{N-H}\cdots\text{O}}$ and $\text{RDF}_{\text{N-H}\cdots\text{S}}$), where N-H, O and S refer to the amide group of ionene chains, the oxygen atom of the dioxane ring and the sulfur atom of the thiophene ring, respectively. The $\text{RDF}_{\text{N-H}\cdots\text{O}}$ indicates that the presence of N-H...O hydrogen bonds is practically null (Figure 9a) since the first peak or shoulder is centered at a distance ($r \approx 4.5 \text{ \AA}$) much larger than those typically found for H...O hydrogen bonds.^{61,62}

Regarding N-H...S hydrogen bonds, the calculated $\text{RDF}_{\text{N-H}\cdots\text{S}}$ reflects a peak centered at $r = 2.75 \text{ \AA}$ for **m1** (Figure 9b), which is consistent with the H...S distance typically found in hydrogen bonds involving the sulfur atom of thiophene rings.^{62,63} This peak is more intense and much broader for **m2** (*i.e.* it extends from 2.6 to $\sim 4.3 \text{ \AA}$), indicating the tendency of *meta*-topomer to form weak PEDOT...ionene interactions through specific N-H...S hydrogen bonds. Finally, the *para*-topomer exhibits the lowest affinity towards the sulfur atom of the thiophene ring.

Finally, the role of intermolecular $\text{N}^+\cdots\text{O}$ and $\text{N}^+\cdots\text{S}$ interactions, which involve the positively charged nitrogen atoms of the ionene chains and the oxygen and sulfur atoms of PEDOT, has been evaluated through the corresponding RDFs, $\text{RDF}_{\text{N}^+\cdots\text{O}}$ and $\text{RDF}_{\text{N}^+\cdots\text{S}}$ (Figures 9c and 9d, respectively). The former profile exhibits a broad peak that extends from 4.6 to $5.4 \text{ \AA}$, suggesting that the strength of $\text{N}^+\cdots\text{O}$ is very variable. Considering cut-off distances of 4 and $7 \text{ \AA}$ for N-H...S and $\text{N}^+\cdots\text{O}$ interactions, respectively, the population of the former is half that of the latter. Moreover, $\text{N}^+\cdots\text{O}$ interactions are more abundant ($\sim 12\%$) in **m2** than in **m1** and **m3**. Besides, $\text{RDF}_{\text{N}^+\cdots\text{S}}$

profiles also exhibit a sharp peak centered at $r = 4.5 \text{ \AA}$ that is more intense for **m2** than for **m1** and **m3**.

Overall, results displayed in Figure 9 indicate that attractive N–H $\cdots$ S, N $^+$ $\cdots$ O and N $^+$ $\cdots$ S PEDOT $\cdots$ ionene interactions are more abundant and stronger for **2** than for **1** and **3**. These specific interactions combined with the fact that ionene $\cdots$ ionene interactions are stronger for **1** and **3** than for **2**, as was demonstrated in previous work,^{8,9} explains that the *in situ* hydrogelation was only successful for PEDOT:**1** and PEDOT:**3**.

CONCLUSIONS

We have prepared novel n-doped PEDOT:ionene modified electrodes by electro-oxidative polymerization of EDOT in acetonitrile with LiClO₄. The obtained p-doped films are dedoped in aqueous medium and subsequently redoped in presence of ionene aqueous solutions by applying a reduction potential. Three DABCO-containing ionene polymers, which differ in the isomeric form of the *N,N'*-(phenylene)dibenzamide linkage (*i.e.* *ortho*, *meta* and *para*) have been compared to investigate the influence of the topology in the properties of the resulting films.

The SCs and electrochemical stability of PEDOT:ionene, which as usual for n-type CPs are low, and the high wettability are relatively independent of the polycation topology. In contrast, the thermal stability provided by the ionene dopants to the CP increases with the strength of PEDOT $\cdots$ ionene interactions, which are stronger for the *meta*-topomer than for the *ortho*- and *para*-ones. Also, the ionene topology has a pronounced effect on the surface topography and microstructure of the films, even though such two properties are also affected by the reduction potential. Interestingly, PEDOT:**1** and PEDOT:**3** films experience *in situ* thermally-induced hydrogelation, forming ionene micro/nano-hydrogels at the surface and inside the CP matrix. After

gelation, PEDOT:1 and PEDOT:3 exhibit a noticeable improvement of the mechanical response and a significant enhancement of the *SC* increases, evidencing that ionene hydrogels act as a cement and facilitate the charge movement.

Classical MD simulations have been conducted to unravel which specific interactions accompany and reinforce the predominant electrostatic interactions between the negatively charged CP and the positively charged ionene. As suggested experimental observations, PEDOT...ionene π - π stacking interactions are more abundant and stronger in PEDOT:2 than in PEDOT:1 and PEDOT:3. Similarly, ionene...ionene π - π stacking interactions are less abundant in PEDOT:1 and PEDOT:3 than in PEDOT:2. On the other hand, N-H...S hydrogen bonds and both N⁺...O and N⁺...S interactions seem to play a decisive role in the stabilization of the PEDOT...2 interactions. More specifically, such three kind of interactions are more abundant and stronger in PEDOT:2 than in PEDOT:1 and PEDOT:3, explaining that the successful *in situ* hydrogelation of the latter two.

Results presented in this work open a new door for the future preparation of self-supported n-doped PEDOT electrodes using the *in situ* hydrogelation approach. Detailed investigations on new strategies to increment the amount of ionene loaded during the redoping process are currently underway in our laboratories.

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REFERENCES

1. A. Strassburg, J. Petranowitsch, F. Paetzold, C. Krumm, E. Peter, M. Meuris, M. Koller and J. C. Tiller, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36573–36582.
2. S. R. Williams, E. M. Borgerding, J. Layman, W. Wang, K. I. Winey and T. E. Long, *Macromolecules*, 2008, **41**, 5216–5222.
3. M. Yoshida, N. Koumura, Y. Misawa, N. Tamaoki, H. Matsumoto, H. Kawanami, S. Kazaouni and N. Minami, *J. Am. Chem. Soc.*, 2007, **129**, 11039–11041.
4. Y. M. A. Yamada and Y. A. Uozumi, *Org. Lett.*, 2006, **8**, 1375–1378.
5. P. Ahamed, Md. A. Haque, M. Ishimoto, Md. M. Parvez, N. Haraguchi and S. Itsuno, *Tetrahedron*, 2013, **69**, 3978–3983.
6. A. T. N. Berlamino, E. S. Orth, R. S. Mello, M. Medeiros and F. Nome, *J. Mol. Catalysis A*, 2010, **332**, 7–12.
7. M. Tiffner, K. Zielke, J. Mayr, M. Häring, D. D. Díaz and M. Waser, *Chem. Select*, 2016, **1**, 4030–4033.
8. J. Bachl, D. Zanuy, D. E. López-Pérez, G. Revilla-López, C. Cativiela, C. Alemán and D. D. Diaz, *Adv. Funct. Mater.*, 2014, **24**, 4893–4904.
9. J. Bachl, O. Bertran, J. Mayr, C. Alemán and D. D. Díaz, *Soft Matter*, 2017, **13**, 3031–3041.
10. D. W. Zhao, Q. Zhang, W. S. Chen, X. Yi, S. X. Liu, Q. W. Wang, Y. X. Liu, J. Li, X. F. Li and H. P. Yu, *ACS Appl. Mater. Interfaces*, **2017**, **9**, 13213–13222.
11. J. F. Sun, Y. Huang, C. X. Fy, Y. Huang, M. S. Zhu, X. M. Tao, C. Y. Zhi and H. Hu, *J. Mater. Chem. A*, 2016, **4**, 14877–14883.

12. Y. Q. Liu, B. Weng, J. M. Razal, Q. Xu, C. Zhao, Y. Y. Hou, S. Sevedin, R. Jalili, G. G. Wallace and J. Chen, *Sci. Rep.*, 2015, **5**, 17045.
13. T. M. Higgins and J. N. Coleman, *ACS Appl. Mater. Interfaces*, 2015, **7**, 16495–16506.
14. B. Anothumakkool, S. N. Soni, S. N. Bhange and S. Kurungot, *Eng. Environ. Sci.*, 2015, **8**, 1339–1347.
15. M. M. Pérez-Madrigal, F. Estrany, E. Armelin, D. D. Díaz and C. Alemán, *J. Mater. Chem. A*, 2016, **4**, 1792–1805.
16. J. E. Lim, S. M. Lee, S. S. Kim, T. W. Kim, H. W. Koo and H. Kim, *Sci. Rep.*, 2017, **7**, 14685.
17. M. Y. Teo, N. Kim, S. Kee, B. S. Kim, G. Kim, S. Hong, S. Jung and K. Lee, *ACS Appl. Mater. Interfaces*, 2017, **9**, 819–826.
18. G. F. Cai, P. Darmawan, M. Q. Cui, J. X. Wang, J. W. Chen, S. Magdassi and P. S. Lee, *Adv. Energy Mater.*, 2016, **6**, 1501882.
19. M. Vosgueritchian, D. J. Lipomi and Z. A. Bo, *Adv. Funct. Mater.*, 2012, **22**, 421–428.
20. J. Huang, P. F. Miller, J. S. Wilson, A. J. de Mello, J. C. de Mello and D. D. Bradley, *Adv. Funct. Mater.*, 2005, **15**, 290–296.
21. A. M. Nardes, M. Kemerink, M. De Kok, E. Vinken, K. Maturova and R. Janssen, *Org. Electron.*, 2008, **9**, 727–734.
22. X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andresson, A. Volodin, C. van Haesendonck, M. Van der Auweraer, W. R.; Salaneck and M. Berggren, *Chem. Mater.*, 2006, **18**, 4354–4360.
23. A. R. Hillman, S. J. Daisley and S. Bruckenstein, *Electrochim. Acta*, 2008, **53**, 3763–3771.

24. H. Gustafsson, C. Kwarnström and A. Ivaska, *Thin Solid Films*, 2008, **517**, 474–478.
25. A. P. Sandoval, J. M. Feliu, R. Torresi and M. F. Suárez, *RSC Adv.*, 2014, **4**, 3383–3391.
26. M. G. Saborio, O. Bertran, S. Lanzalaco, M. Häring, D. D. Díaz, F. Estrany and C. Alemán, *Phys. Chem. Chem. Phys.*, 2018, **20**, 9855–9864.
27. S. Garreau, J. L. Duvail and G. Louarn, *Synth. Met.*, 2002, **125**, 325–329.
28. Y.-K. Han, M.-Y. Chang, W.-Y. Huang, H.-Y. Pan, K.-S. Ho, T.-H. Hsieh and S.-Y. Pan, *J. Electrochem. Soc.*, 2011, **158**, K88–K93.
29. A. A. Farah, S. A. Rutledge, A. Schaarschmidt, R. Lai, J. P. Freedman and A. S. Helmy, *J. Appl. Phys.*, 2012, **112**, 113709.
30. D. Wu, J. Zhang, W. Dong, H. Chen, X. Huang, B. Sun and L. Chen, *Synth. Met.*, 2013, **176**, 86–91.
31. F. Ely, A. Matsumoto, B. Zoetebier, V. S. Peressinotto, M. K. Hirata, D. A. Sousa and R. Maciel, *Org. Electron.*, 2014, **15**, 1062–1070.
32. C. Alemán, D. Curcó and J. Casanovas, *Chem. Phys. Lett.*, 2004, **386**, 408–413.
33. M. S. Cho, Y. Y. Yun, J. D. Nam, Y. Son and Y. Lee, *Synth. Met.*, 2008, **158**, 1043–1046.
34. G. R. Strobl and W.; Hagedorn, *J. Polym. Sci.: Polym. Phys. Ed.*, 1978, **16**, 1181–1193.
35. H. M. Tan, B. H. Chang, E. Baer and A. Hiltne, *Eur. Polym. J.*, 1983, **19**, 1021–1025.
36. S. H. Chang, C.-H. Chiang, F.-S. Kao, C.-L. Tien and C.-G. Wu, *IEEE Photonic Journal*, 2014, **6**, 1–7.

37. D. Aradilla, D. S. Azambuja, F. Estrany, M. T. Casas, C. A. Ferreira and C. Alemán, *J. Mater. Chem.*, 2012, **22**, 13110–13122.
38. L. Chen, C. Yuan, H. Dou, B. Gao, S. Chen and X. Zhang, *Electrochim. Acta*, 2009, **54**, 2335–2341.
39. A. V. Murugan, A. K. Viswanath, G. Gampet, C. S. Gopinath and K. Vijayamohanan, *Appl. Phys. Lett.*, 2005, **87**, 24351.
40. R. Sharma and L. Zhai, *Electrochim. Acta*, 2009, **54**, 7148–7155.
41. P. M. Sen and M. De, *Electrochim. Acta*, 2010, **55**, 4677–4684.
42. B. Babakhani and D. G. Ivey, *Electrochim. Acta*, 2010, **55**, 4014–4024.
43. A. V. Murugan, A. K. Viswanath, C. S. Gopinath and K. Vijayamohanan, *J. Appl. Phys.*, 2006, **100**, 074319.
44. H. J. Ahonen, J. Lukkari and J. Kankare, *Macromolecules*, 2000, **33**, 6787–6793.
45. I. Petsagkourakis, E. Pavlopoulou, G. Portale, B. A. Kuropatwa, S. Dilhaire, G. Fleury and G. Hadziioannou, *Sci. Rep.*, 2016, **6**, 30501.
46. Z. U. Khan, O. Bubnova, M. J. Jafari, R. Brroke, X. J. Liu, R. Gabrielsson, T. Ederth, D. R. Evans, J. W. Andreasen, M. Fahlman and X. Crispin, *J. Mater. Chem. C*, 2015, **3**, 10616-10623.
47. C. M. MacNeill, E. M. Wailes and N. H. Levi-Polyachenko. *J. Nanosci. Nanotechnol.*, 2013, **13**, 3784-3791.
48. L. J. del Valle, F. Estrany, E. Armelin, R. Oliver and C. Alemán, *Macromol. Biosci.*, 2008, **8**, 1144-1151.
49. L. J. del Valle, D. Aradilla, R. Oliver, F. Sepulcre, A. Gamez, E. Armelin, C. Alemán and F. Estrany, *Eur. Polym. J.*, 2007, **43**, 2342-2349.
50. C. Ocampo, R. Oliver, E. Armelin, C. Alemán and F. Estrany, *J. Polym. Res.*, 2006, **13**, 193-200.

51. J. G. Chen, H. Y. Wei and K. C. Ho, *Sol. Energ. Mat. Sol. Cell.*, 2007, **91**, 1472-1477.
52. S. Prasanthkumar, A. Gopal and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2010, **132**, 13206-13207.
53. S. Prasanthkumar, A. Saeki, S. Seki and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2010, **132**, 8866-8867.
54. S. Prasanthkumar, S. Ghosh, V. C. Nair, A. Saeki, S. Seki and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2015, **54**, 946-950.
55. M.C.G. Saborío, S. Lanzalaco, G. Fabregat, J. Puiggali, F. Estrany and C. Aleman, *J. Phys. Chem. C*, 2018, **122**, 1078-1090.
56. M.C.G. Saborío, S. Zukic, S. Lanzalaco, J. Casanovas, J. Puiggali, F. Estrany and C. Aleman, *Mater. Today Commun.*, 2018, **16**, 60-70.
57. S. Tsuzuki, K. Honda, T. Uchimar, M. Mikami and K. Tanabe, *J. Am. Chem. Soc.*, 2002, **124**, 104-112.
58. F. Rodríguez-Ropero, J. Casanovas and C. Alemán, *J. Comput. Chem.*, 2008, **29**, 69-78.
59. S. Tsuzuki, K. Honda and R. Azumi, *J. Am. Chem. Soc.*, 2002, **124**, 12200-12209.
60. R. G. Huber, M. A. Margreiter, J. E. Fuchs, S. von Grafenstein, C. S. Tautermann, K. R. Liedl and T. Fox, *J. Chem. Inf. Model.*, 2014, **54**, 1371-1379.
61. C. Alemán, *J. Phys. Chem. A*, 2001, **105**, 6717-6723
62. C. Alemán, B. Teixeira-Dias, D. Zanuy, F. Estrany, E. Armelin and L. J. del Valle, *Polymer*, 2009, **50**, 1965-1974.
63. D. Zanuy and C. Alemán, *J. Phys. Chem. B*, 2008, **112**, 3222-3230.

CAPTIONS TO FIGURES

Figure 1. Variation of (a) the absolute value of the neat redoping charge (Q_{ndop}^{neat} , Eqn 1) and (b) the doping level ($dl_{\#}$, Eqn 3) against the reduction potential for n-doped PEDOT:1, PEDOT:2, PEDOT:3 and PEDOT:TMA.

Figure 2. (a) Raman spectra of dedoped PEDOT and n-doped PEDOT:ionene and PEDOT:TMA films upon excitation with a laser at 785 nm. Samples were obtained using a polymerization charge of 30 mC/cm^2 . (b) Optical micrographs recorded with the confocal Raman microscope of dedoped PEDOT, PEDOT:1, PEDOT:2 and PEDOT:3.

Figure 3. Specific capacitance (SC) of PEDOT:ionene and PEDOT:TMA (a) as prepared and (b) after 100 consecutive redox cycles, as a function of the reduction potential. Redox cycles were applied by CV using a potential interval from -0.50 to -1.10 V (50 mV/s).

Figure 4. TGA and DTGA (inset) curves for PEDOT reduced at constant potential of -1.30 V , and PEDOT redoped with **1**, **2**, **3** or TMA using a reduction potential of -1.10 V .

Figure 5. Height (left) and phase (right) AFM images ($20 \times 20 \mu\text{m}^2$) of (a) PEDOT:1, (b) PEDOT:2 and (c) PEDOT:3 prepared using a reduction potential of -1.10 V . The root mean square surface roughness (R_q) and the corresponding standard deviation is displayed for each PEDOT:ionene system.

Figure 6. SEM micrographs (magnification: 50 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: 400 nm.

Figure 7. (a) From left to right: a1) Dedoped PEDOT; a2) redoped PEDOT:1 using a reduction potential of -1.10 V (PEDOT:3 is not shown because its aspect is identical to that of PEDOT:1); a3) PEDOT:1 after 10 min in an oven at 60°C under acid wetting

conditions; and a4) PEDOT:**3** after 60 min in an oven at 60 °C under acid wetting conditions. Surface (left and center) and cross-sectional (right) SEM micrographs of (b) PEDOT:**1** and (c) PEDOT:**3** after the *in situ* gelation.

Figure 8. (a) Representation of the last snapshot from the productive 100 ns NPT-MD trajectory for **m1** (left), **m2** (centre) and **m3** (right) models. (b) Radial distribution functions (RDFs) for the pairs of centres of masses of aromatic rings belonging to two different PEDOT chains ($\text{RDF}_{\text{PEDOT-PEDOT}}$; left), to one PEDOT chain and one ionene chain ($\text{RDF}_{\text{PEDOT-ionene}}$; center), and to two different ionene chains ($\text{RDF}_{\text{ionene-ionene}}$; right) for **m1-m3** models. (c) Distribution of the number of pairs of interacting aromatic rings as a function of the tilting angle θ for intermolecular PEDOT...PEDOT (left), PEDOT...ionene (center) and ionene...ionene (right) interactions in **m1-m3** models.

Figure 9. Radial distribution functions used to evaluate the population and strength of specific PEDOT...ionene interactions: (a) (N⁻)H...O ($\text{RDF}_{\text{N-H...O}}$), (b) (N⁻)H...S ($\text{RDF}_{\text{N-H...S}}$), (c) N⁺...O ($\text{RDF}_{\text{N+...O}}$) and (d) N⁺...S ($\text{RDF}_{\text{N+...S}}$) pairs in **m1-m3** models.

Table 1. Atomic percent composition (C 1s , N 1s, O 1s and S 2p) obtained by XPS for PEDOT: p-doped, dedoped, and redoped (n-doped) with **1**, **2** or **3**.

Sample	C 1s	N 1s	O 1s	S 2p
p-doped PEDOT	59.2	0.0	30.2	10.6
dedoped PEDOT	63.3	0.0	25.5	11.2
n-doped PEDOT: 1	69.6	3.7	18.7	8.0
n-doped PEDOT: 2	72.8	4.9	16.3	6.0
n-doped PEDOT: 3	67.2	2.8	20.8	9.1

(a)

(b)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical Abstract