Controlling Electrochemically Induced Volume Changes in Conjugated Polymers by Chemical Design: from Theory to Devices

Maximilian Moser,*‡ Johannes Gladisch,† Sarbani Ghosh,† Tania Cecilia Hidalgo, James F. Ponder Jr., Rajendar Sheelamanthula, Quentin Thiburse, Nicola Gasparini, Andrew Wadsworth, Alberto Salleo, Sahika Inal, Magnus Berggren, Igor Zozoulenko,* Eleni Stavrinidou* and Iain McCulloch

M. Moser, Dr A. Wadsworth, Prof. I. McCulloch
University of Oxford, Department of Chemistry, Oxford, OX1 3TA, United Kingdom

Corresponding authors: maximilian.moser@chem.ox.ac.uk, igor.zozoulenko@liu.se and eleni.stavrinidou@liu.se

J. Gladisch, Dr S. Ghosh, Prof. M. Berggren, Prof. I. Zozoulenko, Prof. E. Stavrinidou
Linköping University, Department of Science and Technology, Laboratory of Organic Electronics, Norrköping, SE-60174, Sweden

Dr S. Ghosh
Birla Institute of Technology and Science (BITS), Department of Chemical Engineering, Pilani, 333031, India

J. Gladisch, Prof. M. Berggren, Prof. I. Zozoulenko, Prof. E. Stavrinidou
Wallenberg Wood Science Center, Department of Science and Technology, Linköping University, Norrköping, SE-60174, Sweden

T. C. Hidalgo, Prof. S. Inal
King Abdullah University of Science and Technology (KAUST), Biological Sciences and Engineering Division, Thuwal, 23955-6900, Saudi Arabia

Dr Q. Thiburse, Prof. A. Salleo
Stanford University, Department of Materials Science and Engineering, Stanford, CA 94305, United States of America

Dr J. F. Ponder Jr.
George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

Dr R. Sheelamanthula, Prof. I. McCulloch
King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, Thuwal, 23955-6900, Saudi Arabia

Dr N. Gasparini
Imperial College London, Department of Chemistry and Center for Plastic Electronics, London, W12 0BZ, United Kingdom

*†These authors contributed equally
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Abstract

Electrochemically induced volume changes in organic mixed ionic-electronic conductors (OMIECs) are particularly important for their uses in dynamic microfiltration systems, biomedical machinery and electronic devices. Although significant advances have been made to maximize the dimensional changes that can be accomplished by OMIECs, there is currently limited understanding of how changes in their molecular structures impact their underpinning fundamental processes and their performance in electronic devices. Herein, a series of ethylene glycol functionalized conjugated polymers was synthesized, and their electromechanical properties evaluated through a combined approach of experimental measurements and molecular dynamics simulations. As demonstrated, alterations in the molecular structure of OMIECs impact numerous processes occurring during their electrochemical swelling, with sidechain length shortening decreasing the number of incorporated water molecules, reducing the generated void volumes and promoting the OMIECs to undergo different phase transitions. Ultimately, the impact of these combined molecular processes is assessed in organic electrochemical transistors (OECTs), revealing that careful balancing of these phenomena is required to maximize device performance.

Introduction

The last decade has witnessed a tremendous increase in interest in organic mixed ionic-electronic conductors (OMIECs), for use in a number of diverse research areas, including next-generation energy storage and bioelectronic applications.\[^1\]–\[^4\] In OMIECs, ionic conduction is facilitated by the inclusion of hydrophilic sidechains that are either ionic, such as alkyl sulfonate sidechains,\[^5\]–\[^7\] or highly polar yet nonionic, such as ethylene glycol (EG) moieties,\[^8\]–\[^10\] while electronic conduction occurs along the conjugated polymer backbones. Generally, OMIECs can be classified into two groups depending on whether their conjugated polymer backbone is doped in their as cast state, such as in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), or undoped. Recently, undoped semiconducting polymers have received considerable attention, due to their excellent performance in several electronic devices and application areas, including electrochemically triggered actuators,\[^8\] organic electrochemical transistors,\[^10\]–\[^13\] biomolecule sensors,\[^14\]–\[^16\] circuit elements for neuromorphic computing,\[^17\] amongst many others.

Electrochemically triggered actuators represent a particularly interesting application area of OMIECs given the importance of actuators towards soft robotics, artificial muscles,
prosthetics, microvalves, etc.\textsuperscript{[18,19]} In electrochemically triggered actuators the organic semiconductor can undergo doping level induced (\textit{i.e.} voltage dependent) reversible volumetric changes, which arise from a complex interplay of several parallel processes, including ion and solvent exchange between the semiconductor and the electrolyte, conformational changes in the conjugated polymer backbone and electrostatic repulsions between like-charged conjugated polymer backbones.\textsuperscript{[20–23]} This behavior has been studied for several types of conjugated polymers, most notably for polypyrrole (PPy),\textsuperscript{[24–26]} but also for others, \textit{e.g.} polyaniline (PANI),\textsuperscript{[27]} polyalkylthiophenes\textsuperscript{[21,22,28]} and PEDOT:PSS.\textsuperscript{[29]} While several metrics determine the performance of electrochemical actuators in devices, the most fundamental one is the maximum deformation or strain that can be accomplished upon electrochemical biasing. Typically, the reversible volumetric (bulk) expansion of conjugated polymers during electrochemical addressing in aqueous electrolytes is limited to a few percent, with PPy incurring some of the highest deformations (up to 40%), in both thin film and cylindrical actuator configurations.\textsuperscript{[8,25,30,31]} Therefore in electrochemical actuators significant focus has been given to amplify the small strain to a larger bending motion using bi- or multilayer structures, which have however limited applications. Achieving large dimensional changes in electrochemical systems is, however, particularly relevant for several novel applications going beyond the bending motion, including dynamic microfiltration, microfluidic valves and electronic release of large molecules. Recently, we reported an EG functionalized polythiophene based conjugated polymer (\textbf{p(g3T2)} - whereby the number three stands for the number of EG repeat units on each thiophene moiety) that can reversibly expand and contract by about 300\% and irreversibly up to 1000-10000\%, thus significantly exceeding the values that can be reached by PPy.\textsuperscript{[8]} Molecular Dynamics (MD) revealed that a solid to gel transition was responsible for the large volume change in the doped state. Although the development of \textbf{p(g3T2)} represents a significant improvement in terms of device performance in electrochemically triggered actuators, currently there is limited understanding of how changes in the molecular structure impact actuating performance, with most studies focusing on optimizing either the \textit{i)} device architecture,\textsuperscript{[32–36]} \textit{ii)} synthetic parameters during electropolymerization (\textit{e.g.} by variation of the electrolyte choice,\textsuperscript{[37]} use of co-surfactants\textsuperscript{[38]} or substitution of the counterion\textsuperscript{[39]} or \textit{iii)} operating conditions (\textit{e.g.} by variation of the electrolyte concentration\textsuperscript{[40]} or nature of the electrolyte\textsuperscript{[41]}).

With this in consideration, we herein developed a series of EG functionalized polythiophenes based on the \textbf{p(g3T2)} backbone, in which we have changed the length of the pendant EG sidechains, comprising the all-diethylene glycol substituted polymer, \textbf{p(g2T2)}, the
alternating diethylene-triethylene glycol substituted polymer, \( \text{p(g2T2-g3T2)} \), and the reference all-triethylene glycol substituted polymer, \( \text{p(g3T2)} \). The chemical structures of the polymers are presented in Figure 1a. By varying the overall length of the pendant EG sidechains, we were able to gradually modulate the reversible volumetric expansion that can be achieved between 27-245%. Importantly, we also conducted MD simulations to provide a fundamental insight into the origins of the different dimensional changes reported across the polymer series. Recent MD simulations have demonstrated the predictive power of this method showing not only qualitative, but remarkable quantitative agreement between the simulated and experimental values for various conductive polymer/electrolyte systems, most notably for PEDOT:PSS,[42,43] but also in an EG functionalized thiophene-based conducting polymer.[44] Ultimately, our MD simulations show that changing the polymers’ chemical structures directly impacts several factors affecting their electromechanical properties and in turn also their performance in electronic devices.
Figure 1. Volume change performance. a) Chemical structures of the investigated polymers. b) Visual representation of the employed setup. c) p(g3T2) coated fiber in the pristine and d) expanded state at the 100th electrochemical cycle. e) Volume change of the polymers relative to their pristine state during their first CV cycle (voltage range: -0.8 V to +0.8 V, scan rate 10 mV s⁻¹). f) Relative polymer volume increase with respect to the pristine state (ΔV/ΔV_{pristine,0}) after application of +0.5 V (n = 4 for p(g2T2) and p(g2T2-g3T2), n = 10 for p(g3T2)). g) Stability of the relative polymer volume increase (ΔV/ΔV_{contr,n-1}) over 300 cycles (voltage range: -0.2 V to +0.5 V, duration of a single switching cycle: 30 s). h) Relative polymer volume increase (ΔV/ΔV_{contr,n-1}) at the 100th electrochemical cycle. i) Passive polymer volume increase monitored over 12 h. j) Retention of the polymers’ expanded state over 5 h.
after their 101st electrochemical expansion. All experiments were performed in an aqueous 0.01 M KCl supporting electrolyte and error bars calculated from a minimum of three repetitions.

**Polymer Synthesis and Characterization**

The synthesis of the polymers is described in the supporting information (S.I.). A combination of cyclic voltammetry (CV), UV-vis absorption spectroscopy and spectroelectrochemistry was used to evaluate the optoelectronic properties of the materials. The polymers’ onset of oxidation in aqueous media \( E_{\text{ox,ag}} \) was calculated to be between -0.17 V and -0.14 V, see Figure S1. Their onset of oxidation in organic media \( E_{\text{ox,org}} \), was comparable with values between -0.20 V and -0.17 V for all three polymers, see Figure S1. Varying the overall length of the pendant EG chains did therefore not have any substantial effects on the electrochemical properties of the polymers. This was further highlighted by the similar optical gaps \( E_{\text{opt}} \) ~1.63 eV that were obtained for the three polymers in thin film, see Figure S2.

The electrochromic properties and doping ability of the polymers were evaluated by spectroelectrochemical measurements and were performed in both an aqueous and organic supporting electrolyte, see Figures S3-S8. As shown in Figures S3-S8, each of the polymers was partially doped under ambient conditions, requiring a negative potential to be applied to fully dedope the films. The thin film UV-vis absorption spectra recorded for the fully dedoped state of \( p(g2T2-g3T2) \) and \( p(g3T2) \) showed no significant differences, with both polymers featuring two maximum absorption wavelengths \( \lambda_{\text{max}} \) at ~700 nm and ~640 nm with a higher energy shoulder ~590 nm. On the other hand, the \( \lambda_{\text{max}} \) of the fully dedoped \( p(g2T2) \) was significantly blue-shifted and appeared ~590 nm. The thin film absorption spectrum of \( p(g2T2) \) also did not afford pronounced absorption shoulders, but only a low intensity one occurring ~700 nm. This suggested a lower degree of order to be present in the solid-state fully dedoped form of \( p(g2T2) \) compared to the other two polymers of the series, which is in agreement with the grazing incidence wide-angle X-ray scattering (GIWAXS) data recorded for as-cast films of the polymers, see Figure S9. As can be seen, all of the polymers oriented themselves in a predominantly edge-on texture, however, while both \( p(g2T2-g3T2) \) and \( p(g3T2) \) gave rise to three orders of out-of-plane lamellar scattering (100), \( p(g2T2) \) only afforded one order of out-of-plane lamellar scattering. Despite a certain degree of morphological differences, all of the polymers were able to be doped reversibly and to a similar degree in both media, see Figures S3-S8, thus suggesting good electrochemical cycling stability.
Electrochemically Induced Volume Change Characterization

In order to determine the volumetric change of the polymers upon electrochemical cycling, carbon monofilaments were coated coaxially with the different polymers and used as the working electrode in a three-electrode electrochemical set-up,[8] see Figure 1b-d and Figure S10. The volume change of the materials was then observed and recorded from top view through a stereomicroscope. The acquired micrographs were computationally processed to extract the two figures of merit: i) the relative volume change \( (\Delta V_{\text{rel},n} = V_{\text{exp},n} - V_{\text{contr},n}) / V_{\text{contr},n} ) \), which describes the polymer volume change in the \( n^{\text{th}} \) cycle with respect to the previous contracted state and ii) the volume change relative to initial \( (\Delta V_{\text{rel},0} = (V_{\text{exp},n} - V_{\text{contr},0}) / V_{\text{contr},0}) \), which describes the polymer volume in the \( n^{\text{th}} \) cycle with respect to the polymer volume in the pristine state.

The volume change performance and stability of the various polymers were evaluated by 300 consecutive redox cycles in a 0.01 M aqueous potassium chloride solution, whereby one cycle consisted of applying a doping bias of +0.5 V \( (V_{\text{exp},n}) \) followed by a 30 s dedoping bias of -0.2 V \( (V_{\text{contr},n}) \). The addressing potentials were selected following an initial characterization of the volume change during a voltage sweep between ±0.8 V, see Figure 1e and Figure S11, which demonstrated that the polymers do not show significant volume change above +0.5 V and below -0.2 V. Additionally based on our previous study on \( \text{p(g3T2)} \) we found that this potential range results in both high volume change performance and high stability.[8]

In the first electrochemical cycle, see Figure 1f, the polymers start from a fully contracted state \( (V_{\text{pristine},0}) \) and application of a positive voltage leads to an overall expansion of the polymer film \( (V_{\text{exp},1}) \). For the first cycle, \( \text{p(g3T2)} \) shows a significantly larger polymer volume increase than the other two polymers with an average expansion ~1200% while the maximum expansion reaches 2980%. In contrast \( \text{p(g2T2-g3T2)} \) and \( \text{p(g2T2)} \) expand by only ~100% and ~50% on average respectively. It must be noted that although we performed 9 independent experiments for \( \text{p(g3T2)} \), the values of the first cycle expansion show a large variation ranging from 200-2980%. Subsequent application of a negative potential \( (V_{\text{contr},1}) \) leads to the dedoping of the polymer, which is accompanied by a contraction of the material. The volume of the contracted state of the polymer after the first electrochemical switching cycle \( (V_{\text{contr},1}) \) was however not the same as the volume of the contracted state of the polymer prior electrochemical addressing \( (V_{\text{contr},0}) \). Indeed, up to about the 100th cycle, a clear shift in the total volumes both in expanded and contracted state was observable, see Figure S12. Similar behavior has been commonly observed in various other conjugated polymers, including polyalkoxythiophenes and PPy.[45] This break in effect, can be a result of reorganization of the
morphology due to retention of residual water molecules or charge balancing counterions within the polymer film.\[46\]

The polymers featuring the larger volumetric expansion upon electrochemical addressing, \textit{i.e.,} \textit{p(g2T2-g3T2)} and \textit{p(g3T2)}, showed an initial improvement and subsequent stabilization of their volume change performance by repeatedly addressing the polymers electrochemically, see \textbf{Figure 1g}. In contrast, for \textit{p(g2T2)}, the polymer showing the lowest degree of volumetric expansion in its first swelling cycle, such an effect was not observed. As after 100 expansion-contraction cycles, all polymers had reached a steady state, we compared how changes in the chemical structure of the polymers affect the volume change performance at the 100th expansion-contraction cycle, see \textbf{Figure 1h}.

As is clearly illustrated in \textbf{Figure 1g-h}, increasing the length of the pendant EG sidechains led to a gradual increase in the relative volume expansion \((\Delta V/V_{\text{contr},n-1}})\) and hence volume change ability of the polymers that could be achieved, with \textit{p(g2T2)}, \textit{p(g2T2-g3T2)} and \textit{p(g3T2)} exhibiting a \(\Delta V/V_{\text{contr},n-1}\) of 27\(\pm\)10\%, 160\(\pm\)45\% and 245\(\pm\)21\% respectively. Micrograph images of the fibers coated with the various polymers in the pristine, electrochemically expanded and electrochemically contracted state can be found in \textbf{Figure S13}. The overall trend between chemical structure and volume change ability was also confirmed by e-QCM(D) experiments, see \textbf{Figure S14} and \textbf{Table S1}. To confirm that the recorded volume change trend was not just a reflection of the polymers’ increased hydrophilicity upon increasing the EG chain length, we also recorded the polymers’ passive volume changes \((\Delta V_{\text{passive}})\), \textit{i.e.} those occurring when the materials are immersed in the supporting electrolyte without the application of an external bias. The \(\Delta V_{\text{passive}}\) recorded for each polymer coated fiber when immersed in the supporting electrolyte over a 12 h period, is shown in \textbf{Figure 1i}, while \textbf{Figure S13} in the S.I. shows micrograph pictures of the polymer coated fibers after 12 h of passive swelling. As can be seen from \textbf{Figure 1i}, the polymers’ trend in \(\Delta V_{\text{passive}}\) mirrored the one recorded for their \(\Delta V/V_{\text{contr},n-1}\), with \textit{p(g2T2)}, \textit{p(g2T2-g3T2)} and \textit{p(g3T2)} exhibiting a \(\Delta V_{\text{passive}}\) of 6\(\pm\)2\%, 15\(\pm\)6 \% and 18\(\pm\)5\%. As none of the polymers featured passive swellings that were close in magnitude to their active ones, it followed that the difference in active swelling recorded across the polymers was not just due to differences in the polymers’ hydrophilicities.

For many actuator applications, another important parameter to consider is the retention of the actuator’s state without further application of voltage. We therefore investigated the ability of the polymers to retain their expanded state by disconnecting the polymer coated fibers from the electrical circuit after their 101st electrochemical expansion and
recorded the change in polymer volume relative to its expanded state over five hours. All the polymers retained their expansion well, see Figure 1j, as after 1 h the polymers only lost around 10% of the volume of their maximum expansion. The volumetric retention of the polymers then followed an exponential decay profile, with the polymers only losing around 30% of the volume of their maximum expansion after 5 h. The good retention of the volume expansion indicates that these polymers are promising candidates for applications in which the long-term expansion has to be preserved without addressing, thus also reducing the energy consumption of the system.

**Molecular Dynamics Simulations**

To gain insight into the molecular processes occurring during the electrochemical doping and obtain a fundamental understanding on how variations in the EG sidechain length affect the polymers’ volumetric expansion abilities in an aqueous electrolyte we performed MD calculations. As model systems we chose oligomers of p(2T2) and p(3T2) comprising 20 thiophene rings, whereby this polymer chain length was chosen to reflect both the polymeric nature of the materials without paying an excessive computational cost. To simulate the chemical oxidation of the materials, positive charges were added to the polymer chains, whereby \( n_i \) denotes the number of positive charges placed on each polymer chain. \( n_i \) was then varied between 0, 1, 3 and 6, corresponding to polymer oxidation levels of \( c_{\text{ox}} = 0\% \), 5\%, 15\% and 30\% respectively. An upper limit of \( c_{\text{ox}} = 30\% \) was chosen as this corresponds approximately to the maximum doping level that can be achieved by energetically similar oxygen-substituted thiophene polymers.\(^{[47]}\) Further details surrounding the MD simulations can be found in the S.I.
**Figure 2.** MD Simulations. a) Volume expansion, b) number of uptaken water molecules in the polymer networks and c) average end-to-end distance between the conjugated backbone chain ends \( d_e \) of \( p(g2T2) \) and \( p(g3T2) \) as a function of \( c_{ox} \). Representative MD snapshots of the systems at different oxidation levels, \( c_{ox} \), for d) \( p(g2T2) \) and e) \( p(g3T2) \). Backbones are shown in red, sidechains in light purple, ions in yellow and water molecules in light blue.

The MD simulated swelling of the two polymers \( p(g2T2) \) and \( p(g3T2) \) during oxidation and reduction is shown in **Figure 2**. Swelling was quantified in terms of a percentage volume expansion compared to the initial dry film, see **Figure 2a**. Details of the polymer volume difference calculations can be found in the S.I., see **Figure S16**. For the polymers, swelling was shown to progressively increase with increasing \( c_{ox} \), corroborating the experimental findings, see **Figure 2**. On a fundamental level this can be explained due to several processes occurring in parallel. Firstly, upon doping the polymers, \( \text{Cl}^- \) counterions enter the polymer network from the aqueous environment surrounding the polymers to compensate the excess charges in the polymer chains, see **Figure S17**. Concomitantly to counterion migration, water molecules in the hydration shells of ions also enter the polymer network, causing the polymer film to swell.\(^8\) The number of water molecules taken up by the materials at different oxidation levels is plotted in **Figure 2b**. For the polymers water uptake is directly proportional to the amount of charge injected into the polymer, thus explaining why an increase in swelling of the
polymers upon increasing the oxidation level is observed. The calculated average number of water molecules brought to the film by each ion \(N_w\) is 40 for \(p(g2T2)\) and 140 for \(p(g3T2)\) (it is interesting to note that this is much larger than the \(N_w = 4\) for the conductive polymer PEDOT:PSS, which practically does not swell in similar cyclic voltammetry experiments).[42,48] Upon reduction most water molecules are brought back to the bulk electrolyte, see Figure 2b. Some water molecules, however, remain in the polymers even after complete reduction, which explains why the polymers do not contract back to their initial volume. As will be demonstrated later on, the morphology and lamellar structure of \(p(g2T2)\) and \(p(g3T2)\) are quite similar for \(c_{ox} = 0\). Therefore, after the oxidation cycle when polymers are reduced from \(c_{ox} = 30\%\) to \(c_{ox} = 0\) the volumes of both polymers shrink to approximately the same value, see Figure 2a.

Finally, upon oxidation of the polymer chains, the end-to-end distance \((d_e)\) of the conjugated polymer backbone chain ends also increases, see Figure 2c. This essentially results in the individual polymer chains to assume more planar, elongated and quinoidal structures, which also contributes to the overall expansion of the polymer network. Ultimately, the simulated swelling trends corroborate both previous literature and the experimental data recorded herein, both of which indicate that higher doping levels lead to increased electrochemical expansion and hence actuation of the polymers.[8]

In addition to these molecular processes, the polymers’ conjugated backbones and sidechains undergo additional conformational transformations resulting in further morphological changes. To better understand these processes, we calculated X-ray diffraction (XRD) patterns and interchain radial distribution functions, \(g(r)\), of the polymer films, see Figure S18. As the simulated XRDs have contributions from both the sidechains and the backbones of the polymer, it is difficult to distinguish the individual structural changes occurring in these. Consequently, we also calculated the XRDs of the backbones and sidechains independently and compared the evolution of the individual XRDs with the respective behavior of the radial distribution functions when the oxidation level increases. In what follows, we will focus on the XRD and \(g(r)\) for the polymer backbones, while the corresponding results for sidechains are presented in the S.I., see Figure S18.

Illustrative snapshots of the polymer backbone packing for \(p(g2T2)\) and \(p(g3T2)\) are shown in Figure 3a-b. The XRD plots of the polymers’ backbones in their fully undoped state \((c_{ox} = 0)\) show a broad \(\pi-\pi\) stacking peak centered at \(q \sim 1.65 \text{ Å}^{-1}\), see Figure 3c-d, indicating that changing the length of the pendant EG sidechains does not have a strong impact on the \(\pi-\pi\) stacking distance recorded for the polymers. We note that the morphology of the polymers
on ordered surfaces, such as those employed when studying systems by GIWAXS, can vary significantly compared to those on disordered ones, such as those employed when studying the polymers by MD simulations and swelling experiments, due to the effect of the surface on the molecular ordering.\(^{[49,50]}\) Consequently, this has to be taken into consideration when comparing results from different measurement techniques and can indeed lead to some discrepancies in the obtained results. Nonetheless, the computed π-π stacking distances for the polymers are in relatively good agreement with the experimentally recorded GIWAXS patterns for pristine films of p(g2T2) and p(g3T2), which despite not featuring strong π-π stacking peaks, still displayed a weakly scattering π-π stacking peak around 1.7 Å\(^{-1}\), see Figure S9.

Increasing the oxidation level on the polymer chains led to both a narrowing in the π-π stacking peak and a shift in \(q\) from ~1.65 Å\(^{-1}\) to ~1.75 Å\(^{-1}\). While this behavior fully agrees with previous structural data reported for related glycolated organic polymers,\(^{[46]}\) we herein also describe the origin of this behavior. Specifically, at lower oxidation levels the π-π stacking peaks for the polymers are broader and occur at smaller \(q\) values because the polymer chains are present in a range of coil like structures, which is elucidated from the lower value of \(d_e\), see Figure 2c. At higher oxidation levels, the chains elongate and become more rigid, thus explaining the larger \(d_e\) values, which in turn leads to polymer backbone conformations that can stack more tightly.
Figure 3. Representative snapshots of the different conformational changes occurring in p(g2T2), left panels, and p(g3T2), right panels, upon electrochemical oxidation. a,b) Representative polymer π-π backbone stacking at a) \( c_{\text{ox}} = 0\% \) and b) \( c_{\text{ox}} = 30\% \). c,d) Calculated X-ray diffraction (XRD) patterns. e,f) Lamellar structures with interpenetrating sidechains at \( c_{\text{ox}} = 0\% \). g) Phase transition in p(g2T2) to ion-intercalated lamellar stacks formed at \( c_{\text{ox}} = 30\% \). h) Large pores formed by the elongated polymer chains in p(g3T2) at \( c_{\text{ox}} = 30\% \). Backbones are shown in red, sidechains in light purple, counterions in yellow and water molecules in light blue.
The XRD results are supported by the interchain backbone-backbone radial distribution functions \((g_{b-b}(r))\) of \(p(g2T2)\) and \(p(g3T2)\), see Figure 4a-b respectively. (The radial distribution function defines the probability of finding another particle at the distance \(r\) from a given particle, hence the peaks in the \(g(r)\) correspond to the distances with the highest probability to find the particles, see S.I. for more details.) For all oxidation levels \(g_{b-b}(r)\) show polymer π-π stacking peaks at \(r_{\pi-\pi} \sim 4 \text{ Å}\) (corresponding to \(q \sim 1.6 \text{ Å}^{-1}\)) and several much weaker peaks at multiples of \(r_{\pi-\pi}\). This indicates that most crystallite aggregates consist of two π-π stacked polymer chains. The peak at \(\sim 4 \text{ Å}\) in the \(g_{b-b}(r)\) for both polymers also becomes narrower with increasing \(c_{ox}\), which supports the conclusion from the XRD measurements above about tighter π-π stacking at higher \(c_{ox}\). It is important to stress that for all polymers at all the oxidation levels the π-π stacking among the backbones is preserved. Thus, even in the fully swollen state, the polymers are still connected via their backbones, which holds the polymers together, preventing them from getting dispersed in water, and provides a percolative conductivity network via π-electrons in the backbones.

In addition to documenting the changes occurring within the individual materials upon doping, the MD simulations also showed that \(p(g3T2)\) exhibits a much larger swelling than \(p(g2T2)\), hence corroborating the experimentally determined trend shown in Figure 1. This can be explained due to the different phase transitions, and in particular due to the evolution of significantly different lamellar structures, in the two materials. At lower oxidation levels \((c_{ox} = 0\text{-}15\%)\) the XRDs of both \(p(g2T2)\) and \(p(g3T2)\) show a broad peak between \(q\) values of 0.4 Å\(^{-1}\) and 0.8 Å\(^{-1}\) corresponding to the lamellar stacking of the backbones, see Figure 3c-d. The formation of the lamellar structure also manifests itself as a broad peak in the backbone distribution function \(g_{b-b}(r)\) centered around 8-14 Å, see Figure 4a-b. Representative snapshots in Figure 3e-f illustrate the lamellar structure at lower oxidation levels \((c_{ox} = 0\text{-}15\%)\), where the polymers are kept together by interpenetrating sidechains belonging to neighboring polymer chains. Upon further oxidizing the polymer \((c_{ox} = 30\%)\) the evolution of the lamellar structure is strikingly different for \(p(g2T2)\) and \(p(g3T2)\). In \(p(g2T2)\) at \(c_{ox} = 30\%,\) the lamellar peak shifts to \(q\) values between 0.25 Å\(^{-1}\) and 0.5 Å\(^{-1}\) corresponding to an increased lamellar spacing of 15-24 Å. This is a manifestation of a phase transition of the material, which is caused by Cl\(^-\) counterions intercalating between the polymer sidechains to screen the positive charges on the conjugated backbones at high oxidation levels. These ions “unzip” the lamellar structure of the inter-penetrating sidechains. A representative snapshot of \(p(g2T2)\)’s structure at \(c_{ox} = 30\%\) is shown in Figure 3g, which illustrates the new lamellar structure where the backbones are kept together with the help of ions intercalating in the space between the sidechains. In
addition, the counterions entering the space between the interpenetrating network of the sidechains also reduce the van der Waals interaction between the \( \pi - \pi \) stacked sidechains. This, in turn, reduces the forces keeping the backbones in the lamellar stacking together, facilitating the transformation from the lamellar structure with interpenetrating chains, Figure 3e, to the ion-intercalated lamellar structure, Figure 3g. The effect of ion intercalation is also manifested itself in the evolution of the radial distribution functions between the ions and backbones and ions and sidechains, which show that the probability to find ions close to the backbone and sidechains at higher oxidation levels is higher for \( p(g2T2) \) in comparison to \( p(g3T2) \), see Figure S19. A similar unzipping phenomenon has been reported in a related conductive polymer functionalized with EG sidechains,[44] and theoretically studied by means of MD simulations.[50]

In contrast to \( p(g2T2) \), \( p(g3T2) \) does not undergo the same ion-intercalation phase transition at \( c_{ox} = 30\% \). Instead, large pores are formed across the polymer network. As the polymer is oxidized, the long-range electrostatic repulsions among the like-charged polymer chains help to form pores in the film. The addition of positive charges also elongates the chains, which helps to form large pores where the pore boundaries are defined by interconnected elongated backbones, see Figure 3h. To further highlight this point, we calculated the pore size distribution in swollen polymer networks using the radical Voronoi tessellation method as described in the S.I. A pore is defined as a space inside the film that is not occupied by the atoms of polymers. We plotted the pore size distribution as a function of pore diameter in Figure 4c-d. As can be seen for both polymers, the pore size generally increases as the oxidation level increases. At each oxidation level and importantly at the highest oxidation level (\( c_{ox} = 30\% \)), the pore sizes in \( p(g3T2) \) are significantly larger than those in \( p(g2T2) \), which is consistent with the enhanced swelling in this polymer.

Ultimately, the difference in swelling observed between \( p(g2T2) \) and \( p(g3T2) \), is due to \( p(g2T2) \)’s swelling being hindered at high oxidation levels by the ion-intercalating phase transition, in which the lamellar stacking undergoes a fundamental structural change, see Figures 3g-h. This structure keeps the backbones in the film together preventing further swelling. The formation of the ion-intercalated lamellae is possible for the case of relatively short sidechains. In contrast, the longer sidechains in \( p(g3T2) \) prevent the formation of the intercalated lamellar structure and as a result, its swelling is not hindered.

It is noteworthy that we also performed calculations for polymers with shorter and longer sidechain lengths, namely, \( p(g0T2) \) and \( p(g4T2) \). The degree of swelling is practically the same for \( p(g0T2) \) and \( p(g2T2) \), see Figure S20. It is interesting that despite longer
sidechains, the degree of swelling of \( p(g4T2) \) is smaller than the one for \( p(g3T2) \). We attribute this to the fact that longer sidechains effectively hinder pore formation, as manifested itself in the pore size distribution function, see Figure S20. Therefore, our calculations suggest that \( p(g3T2) \) possesses an optimal chain length required to achieve the maximal degree of swelling.

![Figure 4](image)

**Figure 4.** a,b) Backbone-backbone radial distribution functions and c,d) pore size distribution in \( p(g2T2) \) and \( p(g3T2) \) (left and right columns respectively) for different oxidation levels \( (c_{ox} = 0\%, 5\%, 15\% \text{ and } 30\%) \). The oxidation levels indicated in c) apply to all plots across panels a-d.

**Organic Electrochemical Transistors**

The polymers’ ability to be doped stably and reversibly in an aqueous electrolyte and their ability to retain percolative pathways for charge carrier transport even when in their doped state, made the materials excellent candidates for organic electrochemical transistors (OECTs) channel materials.\(^{[1–4]}\) Consequently, OECTs were fabricated for each polymer following previous literature procedures,\(^{[12,46]}\) with details surrounding their fabrication and characterization available in the S.I. The polymers’ OECT performance is summarized in Table 1.
Table 1. Summary of the polymers’ OECT performance.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(d^a) [nm]</th>
<th>(g_m^b) [mS]</th>
<th>(g_m^c) [S cm(^{-1})]</th>
<th>(\mu_{\text{OECT}}C_p^d) [F cm(^{-1}) V(^{-1}) s(^{-1})]</th>
<th>(\mu_{\text{OECT}}) [cm(^2) V(^{-1}) s(^{-1})]</th>
<th>(C^e) [F cm(^{-3})]</th>
<th>On/off (^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p(g2T2))</td>
<td>65</td>
<td>0.09±0.03</td>
<td>19±6</td>
<td>5.0±1.3</td>
<td>0.03±0.01</td>
<td>187±16</td>
<td>~10(^3)</td>
</tr>
<tr>
<td>(p(g2T2-g3T2))</td>
<td>68</td>
<td>16.0±5.2</td>
<td>2940±955</td>
<td>378±116</td>
<td>2.35±0.72</td>
<td>161±17</td>
<td>~10(^5)</td>
</tr>
<tr>
<td>(p(g3T2))</td>
<td>60</td>
<td>2.0±1.2</td>
<td>587±352</td>
<td>127±62</td>
<td>1.04±0.51</td>
<td>122±4</td>
<td>~10(^4)</td>
</tr>
</tbody>
</table>

a) Determined from profilometry measurements. b) Calculated from the slope of \(g_m\) against \((Wd/L)(V_{Th}-V_G)\). c) Calculated from the transistor saturation mobility and the corresponding \(C^*\) value. d) Determined from electrochemical impedance spectroscopy. 

As can be seen from Table 1 and section 9 in the S.I., devices with similar thicknesses (\(d\) )\(\approx\)65 nm, widths (\(W\)) and lengths (\(L\)) were fabricated for the three polymers, see S.I. for more details. Significantly different maximum transconductances (\(g_m\)) were however recorded for the three polymers, with \(p(g2T2)\) incurring the lowest \(g_m\) of 0.09±0.03 mS, \(p(g3T2)\) a \(g_m\) of 2.0±1.2 mS and \(p(g2T2-g3T2)\) the highest \(g_m\) of 16.0±5.2 mS. While this trend already hinted at \(p(g2T2-g3T2)\) being the highest performing channel material, \(g_m\) has been shown to depend on both a device geometry term and a material dependent term (\(\mu_{\text{OECT}}C^*\), where \(\mu_{\text{OECT}}\) is the electronic charge carrier mobility in the OECT and \(C^*\) the volumetric capacitance). More suitable OECT performance metrics for different channel materials are thus the channel thickness normalized transconductance (\(g_m^c\)) or the product \(\mu_{\text{OECT}}C^*\).[51] As shown in Table 1, evaluation of the polymers’ OECT performance by \(g_m^c\) or \(\mu_{\text{OECT}}C^*\) in this case did not change the overall performance trend recorded for the three polymers. \(p(g2T2)\), \(p(g2T2-g3T2)\) and \(p(g3T2)\) incurred a \(\mu_{\text{OECT}}C^*\) of 5.0±1.3 F cm\(^{-1}\) s\(^{-1}\) V\(^{-1}\), 378±116 F cm\(^{-1}\) s\(^{-1}\) V\(^{-1}\) and 127±62 F cm\(^{-1}\) s\(^{-1}\) V\(^{-1}\) respectively. To obtain a better understanding of the performance difference across the materials, we analyzed their recorded \(\mu_{\text{OECT}}\) and \(C^*\). The polymers’ \(C^*\) were obtained from EIS and all lied between 122-187 F cm\(^{-3}\), which are values on par to those recorded for comparable EG functionalized polythiophenes.[10–12,52–54] Spectroelectrochemical measurements of the polymers in an aqueous electrolyte, see Figures S3-S8, demonstrated that all polymers can be doped to a similar degree (as for all polymers an approx. 80% reduction in the main \(\pi-\pi^*\) transition is observed upon electrochemical doping), in turn suggesting a similar number of charges present within the polymer films. On the other hand, as evidenced both by experimental carbon monofilament swelling measurements and MD simulations, see Figure 1 and Figure 2 respectively, \(p(g2T2)\) undergoes the lowest degree of electrochemically induced
volumetric swelling, while $p(g3T2)$ the highest. Therefore upon going from $p(g2T2)$ to $p(g2T2\text{-}g3T2)$ to $p(g3T2)$ the electronic charge density is diluted and $C^*$ is lowered.

Given the rather small variation in the $C^*$ recorded for the three materials, their steady-state OECT performance difference was likely to be caused mainly by their different abilities to transport electronic charges, which was confirmed by the measured $\mu_{OECT}$. Compared to $p(g3T2)$’s $\mu_{OECT}$ of $1.04\pm0.51$ cm$^2$ V$^{-1}$ s$^{-1}$, an improved $\mu_{OECT}$ of $2.35\pm0.72$ cm$^2$ V$^{-1}$ s$^{-1}$ was recorded for $p(g2T2\text{-}g3T2)$. $p(g2T2\text{-}g3T2)$’s approximately two-fold higher $\mu_{OECT}$ and $\mu_{OECT}C^*$ were expected given that previous literature had already documented a similar two-fold improvement in $\mu_{OECT}$ and overall OECT performance upon halving the volumetric swelling by increasing ion concentration in the supporting electrolyte during doping of a different EG functionalized OECT channel material.$^{[46]}$ Following this trend, $p(g2T2)$ was anticipated to yield even higher OECT performances, nonetheless a $\mu_{OECT}$ of only $0.02$ cm$^2$ V$^{-1}$ s$^{-1}$ was obtained. Based on our understanding of the fundamental physical processes occurring during polymer doping, see MD simulations, we attributed $p(g2T2)$’s low electronic charge carrier mobility to its formation of ion-intercalated structures at high doping levels such as those encountered during OECT operation. In addition, $p(g2T2)$’s lower degree of ordering in the solid state, as evidenced by UV-Vis spectroscopy and GIWAXS, could also contribute to this behavior. Nonetheless, as these measurements do not evaluate the doped state of the polymer, care must be taken when correlating these findings with device data, in which the polymers are found in a highly doped state. Ultimately, this data demonstrates that OECT performance is dependent on numerous interrelated factors and highlights the predictive power that MD simulations can have for the design of future OECT channel materials.

Conclusions

In summary, a series of OMIECs with varying pendant EG chains has been synthesized and their swelling upon electrochemical doping evaluated both by experimental techniques and MD simulations. As evidenced from the experimental measurements, electrochemical charging of the polymers resulted in a volumetric expansion, irrespective of the employed sidechains. Notably, modification of the selected sidechains had a significant effect on the maximum swelling that could be achieved, with expansion percentages increasing from a few tens to several hundred percent by sidechain elongation. MD simulations fully corroborated the experimental trend and were therefore employed to gain further insights into the fundamental processes and underlying reasons giving rise to the observed data. Several commonalities were identified across the polymers irrespective of their molecular structures, including the
formation of lamellar motifs with interpenetrating sidechains at low doping levels and the
generation of more extended and quinoidal conjugated backbones upon electrochemical
addressing. More importantly, however, significant differences were also found. Specifically,
sidechain shortening resulted in decreased water quantities being incorporated into the polymer
network upon electrochemical doping. Sidechain variation also resulted in different phase
transitions upon electrochemical oxidation, with the shorter sidechains promoting ion
intercalation in the sidechains and the longer ones pore formation. This, in combination with
the formation of significantly smaller void volumes, resulted in significantly reduced
volumetric swelling in the shorter EG containing polymer.

To evaluate the importance that each of these underlying processes plays on the
electronic performance of the polymers in devices, organic electrochemical transistors were
fabricated for each polymer. These highlighted that sidechain length shortening can be
beneficial to the recorded steady-state OECT performance due to decreased volumetric
swelling and reduced water uptake. Nonetheless, care must be taken to also consider the
different phase transitions that occur in these polymers, since these can also lead to drastically
lower OECT performances.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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