Influence of side chains on the n-type organic electrochemical transistor performance

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Abstract

N-type (electron transporting) polymers can make suitable interfaces to transduce biological events that involve generation of electrons. However, n-type polymers that are stable when addressed electrically in aqueous media are relatively scarce, and the performance of the existing ones lags behind their p-type (hole conducting) counterparts. Here, we report a new family of donor-acceptor type polymers based on naphthalene-1,4,5,8-tetracarboxylic-diimide-bithiophene (NDI-T2) backbone where the NDI unit always bears an ethylene glycol (EG) side chain. We study how small variations in the side chains tethered to the acceptor as well as the donor unit affect the performance of the polymer films in the state-of-the-art bioelectronic device, the organic electrochemical transistor (OECT). First, we show that substitution of the T2 core with an electron withdrawing group (i.e., methoxy) or an EG side chain leads to ambipolar charge transport properties and causes significant changes in film microstructure revealed by x-ray scattering studies, which overall impairs the n-type OECT performance. We thus find that the best n-type OECT performer is the polymer that has no substitution on the T2 unit. Next, we evaluate the distance of the oxygen from the NDI unit as a design parameter by varying the length of the carbon spacer placed between the EG unit and the backbone. We find that the distance of the EG from the backbone affects the film order and crystallinity, and thus, the electron mobility. As such, we develop the best performing NDI-T2 based n-type OECT material to date, i.e., the polymer bearing a 6-carbon spacer between the EG and the NDI units. Our work provides new guidelines for the side chain engineering of n-type polymers for OECTs and insights on the structure-performance relationships for mixed ionic-electronic conductors, crucial for devices where the film operates at the aqueous electrolyte interface.

Keywords: organic bioelectronics; n-type polymers; side-chain; electron mobility; organic electrochemical transistor
Introduction

Organic mixed ionic-electronic conductors (OMIECs) are increasingly used in electrochemical devices operating in aqueous electrolytes because of their ability to transport ionic and electronic charges simultaneously.\(^1\)\(^2\) OMIECs, unlike conventional silicon-based electronics, can be processed at low temperatures and soluble in organic or aqueous solvents. They are compatible with printing techniques that enable the mass production of organic electronic devices.\(^3\) Among these devices, organic electrochemical transistors (OECTs) have technological significance, particularly because of their ability to detect weak biological signals better than any other transistor technology to date.\(^4\)\(^5\) OECT applications include monitoring of in vitro barrier tissue integrity,\(^6\)\(^7\) lipid bilayer property and ion channel activity,\(^8\)\(^9\) recording neuronal signals,\(^10\)\(^11\) tracking metabolites,\(^12\)\(^13\) proteins,\(^14\)\(^15\) or ions\(^16\) and, recently, neuromorphic devices.\(^17\)\(^18\) OECTs use OMIECs in the channel and in direct contact with the biological medium. The operation relies on the injection of ions from an aqueous electrolyte into the polymer channel, consequently changing the OMIEC doping state and modulating the channel conductance.\(^19\) Ion-electron interactions occur in the volume of the channel, as opposed to organic field effect transistors (OFETs) where the charge generation is limited to electrolyte/channel interface. The “bulk” doping of OMIECs leads to record high transconductance \((g_m)\) values at the saturation regime for OECTs, which scales with the channel thickness, according to the following equation:

\[
g_m = \frac{Wd}{L} \cdot \mu \times C^* \times (V_{TH} - V_G)
\]

where \(W\) and \(L\) are the width and length of the device channel, respectively, \(d\) is the film thickness, \(\mu\) is the charge carrier mobility, \(C^*\) the volumetric capacitance, and \(V_{TH}\) is the threshold voltage.\(^20\) We proposed the \(\mu C^*\) product in this equation as the material-system figure of merit.\(^20\) As such,
materials with the highest value of \( \mu C^* \) product promise for OECTs with high steady-state performance.

The flagship of OECT channel materials is without a doubt poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS).\(^1\) During OECT operation, PEDOT:PSS is de-doped by hydrated cations injected by the positive potential applied between the gate electrode, immersed in aqueous electrolyte, and the source electrode. By de-doping PEDOT:PSS channel, the source-drain current of the transistor is reduced drastically; hence this operation mode is known as depletion-mode. With applications in mind that are not feasible or efficient with such PEDOT:PSS OECTs,\(^{10, 12, 21-22}\) various materials have been devised to expand the library of OECT materials, with emphasis on enhancing the charge carrier mobilities (ionic and electronic) as well as the \( C^* \).\(^{23}\) A common strategy to improve the \( C^* \) has been tethering hydrophilic ethylene glycol (EG) side-chains to the undoped conjugated backbones.\(^{24-25}\) The EG chains facilitate hydrated ions to penetrate the polymer bulk, allowing their transport therein. The ions compensate for the charges introduced in the backbone, leading to drastic changes in drain current upon a few mVs of gate voltage applied, enabling OECT operation in accumulation-mode.\(^{22}\) One prime example of such an OMIEC is the p-type p(g2T-TT), a polythiophene derivative with EG side-chains, with high \( \mu C^* \).\(^{20, 26}\) Modifications in the distribution of EG chains tethered to these backbones further enhanced the device performance.\(^{27}\) Addition of EG side chains, however, typically came at the expense of a reduction in \( \mu \),\(^{25}\) thus, specific design rules related to side chains, e.g., how they are attached to the backbone, their length, and or branching, are parameters that warrant further inquiry.
While most of the recent achievements in OMIECs for organic bioelectronics concern p-type materials, n-type candidates are sparse.\textsuperscript{23, 28} The first n-type OECT material has been developed only recently, by implementing the EG side-chain strategy to a backbone based on the highly electron-deficient 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic diimide (NDI) monomer copolymerized with the electron-rich bi-thiophene (T2) unit.\textsuperscript{25} The development of n-type OMIECs has enabled new technological opportunities for OECTs such as complementary logic circuits with high gain and low power consumption for on-site amplification.\textsuperscript{29} We have recently shown that an n-type accumulation mode OECT can be used as a high precision enzymatic sensor for metabolites\textsuperscript{12, 21} or to detect cation fluxes\textsuperscript{8}, and that the n-type OMIEC combined with redox enzymes operates as the anode of an aqueous fuel cell running on glucose.\textsuperscript{12} However, the n-type mixed conduction performance limits the impact of these applications. For OECTs, the $g_m$ is about three orders of magnitude lower than the p-type counterparts.\textsuperscript{23, 28} A possible strategy to improve the n-type OECT performance is to introduce a bad solvent into the polymer solution, forcing the chains to aggregate already in solution, leading to a higher $\mu C^*$.\textsuperscript{30} Another approach is to lower the contact resistance and enhance the wetting of the film on the source-drain contacts.\textsuperscript{31} N-type dopants were also shown to improve the transconductance of n-type OECTs by up to 10 fold.\textsuperscript{32} The need for high-performance n-type OMIEC, however, extends beyond OECTs, where applications such as energy storage or thermoelectric generators need to pair n-type and p-type materials with similar performance for maximum efficiency.\textsuperscript{33-34}

One key reason for the low performance of n-type OMIECs is the electronic charge instability.\textsuperscript{35} The injection of an electron into the n-type OMIEC interfacing an electrolyte leads to electrochemically reduced units. The injected electrons are likely to react with $O_2$ and $H_2O$ if the
redox potential of the O$_2$/H$_2$O$_2$ couple is close to LUMO of the polymer,\textsuperscript{36} trapping or neutralizing the charge.\textsuperscript{35, 37-38} The electrolyte can thus be an interferent that inhibits the reversible oxidation/reduction processes and lowers the number of electrons that can be extracted, while producing side products leading to material degradation. For reversible charging, the reduction potential of n-type materials is therefore suggested to be below $\approx-4$ eV.\textsuperscript{36, 39-40} However, as the LUMO increases, so does $V_{TH}$, negatively impacting the $g_m$ and power requirements of OECTs, while increasing the chance of electrochemical reduction of other species in biological media. Furthermore, ions injected from the aqueous electrolyte drags water molecules into the polymer film, leading to irreversible morphological changes in the channel that impairs electron mobility.\textsuperscript{41-42} A rigid and planar polymer backbone would promote charge transport, and this can be controlled by the length and composition of EG side chains.

In this work, we identify the optimal position of the EG side-chains in the NDI-T2 based n-type OMIECs and their optimum distance from the backbone for high-performance OECTs. To do so, we designed two polymer series. In the first series, we investigated the effect of side chains tethered on the bi-thiophene (T2) unit on device characteristics. We found that the substitution of the T2 core with a methoxy group or an EG side chain led to ambipolar charge transport, severely hindering the n-type device performance. The impaired performance stemmed from an increase in $V_{TH}$, accompanied with a decrease in the electron affinity (EA), and a drop in $\mu$, despite a moderate increase in $C^*$. 2-D Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) analysis revealed significant changes in the polymer structure with T2 substitution, i.e., a decrease in backbone ordering and a more random orientation. Having identified that the best OECT performance was obtained for the unsubstituted T2 polymer, we next designed a second series to understand the
effect of the EG chain distance from the NDI unit on the n-type OMIEC characteristics. We found that $\mu$ increased with increasing the carbon spacer length between the backbone and the EG side chains, up to 6 carbon spacers, representing the “sweet-spot” for the OECT performance. Structural characterization showed that the microstructural order was optimized for the 6-carbon spacer polymer, corroborating the polymer’s high OECT performance. Notably, in contrast to high performance p-type polymers showing large structural transformations ($\pi$-$\pi$ contraction and lamellar expansion) upon electrolyte exposure and electrochemical doping, the best performing n-type materials showed no structural change upon electrolyte exposure and electrochemical doping. Our findings led to OECT performances on par with the best reported for the ladder-type n-type polymer (poly(benzimidazobenzophenanthroline), BBL.29 This result suggests that along with their exciting redox properties and solution processability, NDI backbones can exhibit efficient electron transport and high electrochemical capacitance. Our work provides synthetic design guidelines for n-type OMIECs with target applications in OECTs and insights on the general structure-performance relationships for polymer films operating at the electrolyte interface.

Materials and Methods

Synthesis of the polymers: The detailed synthetic route of the polymers is reported in the Supporting Information.

Optical characterization: The polymer solutions prepared in chloroform (15 mg/mL) were coated on glass substrates. UV-Vis absorption spectra were recorded on Carry 5000 UV-VIS NIR spectrometer ($\lambda_{\text{max}}$=3300 nm). Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.3. Samples for PESA were prepared on glass substrates by spin-coating polymers
from a 10 mg/mL solution in chloroform (1000 rpm for 30s). Note that we assumed that the ionization potential (IP), measured by PESA, was similar to the HOMO of the polymers. The optical band gap of each polymer was extracted from the onset of the absorption spectra. The electron affinity (EA) was then deduced from the IP and band-gap values. Similarly, we assumed here that the EA was comparable to the LUMO of the polymer.

**Molecular weight determination:** Matrix-assisted laser desorption/ionization time of flight spectrometry (MALDI-TOF) spectrometry was conducted in positive linear mode on a Micromass MALDI-TOF with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]- malononitrile (DCTB) as the matrix.

**Electrochemical measurements:** All characterizations were performed in 0.1 M NaCl(aq.). Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) measurements were recorded using a potentiostat-galvanostat (Autolab, PGSTAT128N). CVs were recorded using a standard three-electrode setup with polymer films cast on gold substrates (580 x 580 μm) as the working electrode, a Pt mesh as the counter and an Ag/AgCl reference electrode. All measurements were carried out at a scan rate of 50 mV/s. EIS was performed to determine the volumetric capacitance of the films, with the same three-electrode configuration, using a potentiostat (Metrohm Autolab). Spectra were recorded from 100 kHz to 0.1 Hz. The measurements were performed with an AC amplitude of 10 mV at open circuit conditions or a DC offset potential ensuring maximum doping. Capacitance was calculated according to equation (2):

\[
C = \frac{1}{2\pi f \cdot |Z_{\text{img}}|} \tag{2}
\]
where $C$ is the capacitance, $f$ is frequency, and $|Z_{\text{img}}|$ is the magnitude of the impedance imaginary part. The volumetric capacitance ($C^*$) was obtained from the slope of the capacitance values extracted at $0.1 \text{ Hz vs. film volume plot.}$

**Device fabrication and characterization:** Organic field effect transistor (OFETs) were fabricated with a bottom-contact top-gate (BCTG) architecture. Gold source and drain contacts were evaporated on cleaned glass substrates, after which the substrates were immersed in an ethanol solution of 2,3,4,5,6-pentafluorothiophenol -PFBT (1 µL/mL) for 10 minutes. The devices were then extensively washed with ethanol and dried in air at $150 \degree \text{C}$ to remove excess PFBT. The active material was then spin-coated on the substrate in a glovebox at 1000 RPM for 30s from a 15mg/mL polymer solution in chloroform, followed by the deposition of CYTOP™ as dielectric at 2000 RPM (average thickness around 900 nm with a capacitance of 2.1 nF/cm²). Samples were then annealed at $50 \degree \text{C}$ for a couple of hours. Channel length and width are 30 and 1000 µm, respectively. Finally, silver top gate was evaporated (average thickness around 100 nm). Measurements were then performed in a glovebox. For the OECT fabrication, glass wafer substrates were cleaned by sonication, firstly immersed in a diluted soap solution and then in an acetone/isopropanol solution. A final cleaning step was performed by applying an O₂ plasma (Nanoplas DSB 6000) for a short amount of time. In order to define the channels, pads and leads of the transistor, standard photolithographic procedures were used. A S1813 (Shipley) photoresist layer was deposited followed with exposure to UV light using an EVG 6200 mask alignment system and further developed in MF-319 developer. A 10 nm thick layer of Cr and a 100 nm layer of Au were deposited via magnetron sputtering (Equipment Support Company Ltd. ESCRD4) and lifted off with appropriate solvents. A parylene C film was vaporized using a SCS Labcoater 2 with a thickness of 1.7 µm and was adhered on substrates using 3-(trimethoxysilyl)propyl
methacrylate. A second parylene C layer, acting as a sacrificial layer for polymer patterning, was casted. AZ9260 (Microchemicals) photoresist and AZ developer were used to pattern the areas of parylene C. Reactive ion etching (Oxford Instruments Plasmalab 100 - ICP 380) was employed to expose both the channels and the pads for polymer deposition. The polymer films were cast from solutions in chloroform (15 mg/mL) by spin coating for 30 seconds at 1000 rpm with 500 rpm/s acceleration. All the channels studied in this work had the same geometry with a width of 100 µm and length of 10 µm. The channel and gate electrode thicknesses were measured by Dektak stylus profilometer.

**OECT characterization:** OECTs were characterized using a dual-channel source-meter unit (Keithley 2602-A) controlled by a custom-written code in LabVIEW. All measurements were performed using an Ag/AgCl pellet (2 mm × 2 mm – Warner instruments) as the gate electrode. The electrolyte (0.1 M NaCl) was contained in a PDMS well fixed on top of the OECT active area and the electrolyte volume was constant (200 µL) for all measurements.

**X-ray characterization:** 2-D Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) patterns were collected from films spin coated (600 rpm for 60 seconds) from chloroform on P⁺ doped Si wafer substrates with resistivity of ca. 1-100 Ohm/cm. Scattering was carried out at the Advanced Photon Source at Argonne National Laboratory on beam line 8-ID-E at room temperature under vacuum with 10.92 keV (λ = 1.135 Å) synchrotron radiation with a 0.14° incident angle and measured with a Pilatus 1M hybrid pixel array detector during 5 second exposures. Multiple exposures were summed and 2D images with different detector z-position were stitched together to fill in the vertical gaps between detector chips. All data analysis was carried out with GIXSGUI Matlab toolbox. Ex situ electrolyte exposure of GIWAXS samples was accomplished by covering the film with a large droplet of 0.1 M NaCl for ~30 minutes, then
rinsed, and blown dry. Ex situ electrochemical reduction was carried out in a similar fashion except with -0.66 V vs Ag/AgCl potential applied between the film (contacted via a silver paste back contact) and an Ag/AgCl pellet in contact with the electrolyte drop.

Results and discussion

1. Synthesis of the NDI-T2 polymers

In this work, we designed two sets of NDI-based polymers identified by the substitution on the donor unit. In the first series, the NDI monomer (NDI-C_x, x = 4) was polymerized with three different co-monomers: a bi-thiophene (T2), a methoxy-bi-thiophene (T2-OMe) and a bi-thiophene containing three EG units linked to the monomer with alkyl spacers of different lengths (T2-C_y-EG, y = 0, 2, and 4). In the second series, we varied the EG spacer length on the NDI monomer and these monomers (NDI-C_x, x = 2, 4, 6, 8) were polymerized with a T2. The chemical structure of the monomers and resulting polymers -p(C_x-T2), p(C_4-T2-OMe) and p(C_4-T2-C_y-EG)- are presented in Scheme 1.
Scheme 1. The polymers developed in this work. p(C_x-T2) series, p(C_4-T2-OMe) and p(C_4-T2-C_y-EG) series are based on the common NDI monomer (NDI-Br_2-C_x) copolymerized with T2 units that contain -H, methoxy-OMe and tri-EG-R substitution.

The synthetic route of the NDI-Br_2-C_x (x = 2, 4, 6, and 8) monomers is reported in Figure S1-S5. Briefly, the methyl end-capped tri-ethylene glycol chain with an amine end group were prepared
starting from tetra-ethylene glycol monomethyl ether for NDI-Br₂-C₂ and from dibromo-alkyl and tri-ethylene glycol monomethyl ether for NDI-Br₂-Cₓ (x = 4, 6, and 8). In the final step, diimide formation of NDA-Br₂ and the corresponding amines spacer was achieved in refluxing acetic acid, according to literature procedures. The synthesis of the substituted T2 monomers (T2-OMe-Tin and T2-Cₓ-Tin) from commercial unsubstituted T2 monomer is presented in Figure S6-S8. T2-OMe-Tin was prepared from stannylation of 3,3'-dimethoxy-2,2'-bi-thiophene coupled from 3-methoxy-thiophene according to reported protocol. T2-Cₓ-Tin monomer was synthesized from 3-methoxy-thiophene. The methyl end-capped tri-ethylene glycol adjacent to the alkyl spacer chain with an alcohol end group was prepared starting from tri-ethylene glycol monomethyl ether and the corresponding diol. The obtained alcohol was then used to make single thiophene containing the desired spacer via transetherification catalyzed by p-toluene sulfonic acid (PTSA). The bromination was thus carried out for Kumada coupling. Final monomers were then obtained following a stannylation procedure. The polymerization for p(Cₓ-T2) polymer series was carried out via Stille coupling using the catalyst Pd(PPh₃)₄ in an oil bath to obtain the highest molecular weight possible for each polymer without compromising their solubility. The polymerization for p(C₄-T2-OMe) and p(C₄-T2-Cₓ-EG) also used Stille coupling, yielding comparable molecular weight for all polymers. The later was measured by matrix-assisted laser desorption/ionization time of flight spectrometry (MALDI-TOF) (see Table 1) as polymers tend to aggregate due to the presence of EG chains, rendering the determination of the molecular weight by gel permeation chromatography impossible. Table 1 summarizes the optical and physical properties of selected polymer series.

**Table 1.** Material characteristics of the NDI-T2 based polymers: p(Cₓ-T2), p(C₄-T2-OMe) and p(C₄-T2-Cₓ-EG). The ionization potential (IP) was measured by photo-electron spectroscopy in
air (PESA), while the band gap was evaluated by the absorption onset of the polymers. The electron affinity (EA) was then deduced from the values of the band gap and IP.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_a$ (kDa)</th>
<th># of repeat units</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(C$_2$-T2)</td>
<td>18.8</td>
<td>23</td>
<td>5.5</td>
<td>4.1</td>
<td>1.4</td>
</tr>
<tr>
<td>p(C$_4$-T2)</td>
<td>11.3</td>
<td>13</td>
<td>5.5</td>
<td>4.1</td>
<td>1.4</td>
</tr>
<tr>
<td>p(C$_6$-T2)</td>
<td>25.0</td>
<td>27</td>
<td>5.6</td>
<td>4.2</td>
<td>1.4</td>
</tr>
<tr>
<td>p(C$_8$-T2)</td>
<td>14.9</td>
<td>15</td>
<td>5.6</td>
<td>4.2</td>
<td>1.4</td>
</tr>
<tr>
<td>p(C$_4$-T2-OMe)</td>
<td>13.0</td>
<td>14</td>
<td>5.0</td>
<td>3.8</td>
<td>1.2</td>
</tr>
<tr>
<td>p(C$_4$-T2-C$_0$-EG)</td>
<td>15.5</td>
<td>13</td>
<td>5.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>p(C$_4$-T2-C$_2$-EG)</td>
<td>10.7</td>
<td>8</td>
<td>5.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>p(C$_4$-T2-C$_4$-EG)</td>
<td>13.2</td>
<td>10</td>
<td>5.1</td>
<td>4.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

2. The effect of bi-thiophene substitution – NDI-C$_4$ series

**Optical and structural properties**

We will first focus on the effect of T2 substitution on the n-type OECT performance and optical and electrochemical properties of the polymer films. We chose to link the NDI monomer that incorporates 4 carbon spacers at its glycolated side chain to 1) an unsubstituted T2, 2) a methoxy-T2, and 3) a tri-EG unit conjugated T2s, leading to p(C$_4$-T2), p(C$_4$-T2-OMe), and the series of p(C$_4$-T2-C$_{3}$-EG), respectively (Figure 1a). The UV-Vis absorption spectra of these polymers are shown in Figure 1b. All polymers exhibit typical dual-band absorption of donor-acceptor backbones, including intramolecular charge-transfer absorption (ICT) (low energy absorption feature, 700-1000 nm) and $\pi$–$\pi^*$ transition (high energy absorption feature, 395-450 nm). For the unsubstituted polymer p(C$_4$-T2), a small shoulder can be identified around 800 nm, typically attributed to the presence of form I aggregates. For NDI-T2 polymers, form I refers to the cofacial registration where the NDI and T2 units are stacked in segregated columns in the $\pi$–$\pi$ stacking
direction. Alternatively, form II refers to a mixed stacking of NDI units with adjacent T2 units in the \(\pi-\pi\) stacking direction.\(^4^7\) The \(p(C_4\text{-}T2\text{-}OMe)\) spectrum does not display any new peaks compared to that of \(p(C_4\text{-}T2)\). However, introducing an O-substituent on the T2 results in a 150 nm red-shift of the ICT band and a 38 nm red shift of the T2-absorption peak with a decrease in its intensity. The reduced intensity of the \(\pi-\pi^*\) absorption is common to all T2-substituted polymers, attributed to an increase in the general film disorder compared to \(p(C_4\text{-}T2)\).\(^4^8\) The ICT region now has two distinguishable contributions, a peak at ca. 800 nm before the maximum intensity peak of the band at 873 nm. The new contribution before the maximum peak absorbance is typically attributed to the presence of form II aggregates,\(^4^7\) as opposed to \(p(C_4\text{-}T2)\) that seems to display form I aggregates predominantly. These changes also indicate a significant reduction of the optical energy gap for \(p(C_4\text{-}T2\text{-}OMe)\) (1.1-1.2 eV, \textbf{Table 1}). The presence of an oxygen atom directly bonded to the thiophene ring is known to reduce the ionization energy of a conjugated polymer.\(^4^9\)-\(^5^0\) The energy gap reduction stems here from a decrease of the HOMO (ca. 5.0 eV) due to the electron donating ability of the oxygen atoms conjugated to the T2 core, which outweighs the shallower LUMO (see \textbf{Table 1}). 2-D Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) of polymer thin films reveal clear differences in the structure of \(p(C_4\text{-}T2\text{-}OMe)\) and \(p(C_4\text{-}T2)\) (\textbf{Figure 1c, 1d} and \textbf{Table S1}). \(p(C_4\text{-}T2)\) seems quite textured with lamellar stacking (h00) occurring predominantly out-of-plane and \(\pi-\pi\) stacking (0k0) and backbone ordering (00l) predominantly occurring in-plane, indicating a preferential edge-on orientation. The (001) presence is a fingerprint of the segregated stacking of the NDI and T2 units (form I),\(^4^7\) correlating with the UV-Vis spectrum. However, we observe the presence of the (002)' peak (\textbf{Figure 1d}), which suggests the co-presence of form II aggregates in the polymer film, not apparent from the UV-Vis spectrum. In the case of \(p(C_4\text{-}T2\text{-}OMe)\), the lamellar spacing is expanded by 2.7 Å, while
the π-π spacing is decreased by 0.27 Å with the methoxy group substitution on the T2. The film is no longer highly oriented, displaying π-π and lamellar peaks both in- and out-of-plane (Figure 1b, 1c and Figure S10). The polymer backbone remains ordered in-plane, though p(C4-T2-OMe) only displays the (001)’ and (002)’ peaks and lacking the (001) peak, characteristic of form II aggregates in the film.47

![Figure 1](image_url)

**Figure 1.** a) Chemical structures of the polymers in NDI-C4 series; b) Thin film UV-VIS absorption spectra of the polymers normalized to the ICT maximum absorption. c) out-of-plane ($q_z$) and d) in-plane ($q_r$) line cuts of the polymers in NDI-C4 series as a function of bi-thiophene substitution. The line-cuts presented here represents polymer thin films as cast. The corresponding 2D-GIWAXS plots are plotted in Figure S9, S10 and S11 for the p(C4-T2), p(C4-T2-OMe), and the p(C4-T2-Cy-EG) series, respectively.

For p(C4-T2-Cy-EG) series, the π-π* absorption peak displays an increase in intensity compared to p(C4-T2-OMe), possibly due to a modified π-π stacking or molecular alignment.46, 51 We
observe a blue shift in peak position for p(C₄-T₂-C₄-EG). The most significant effect of EG side chains is on the ICT species. We note a 100 nm red shift and a much broader band in the region around 980 nm for p(C₄-T₂-C₀-EG). For this film, we also observe a shoulder at ca. 1115 nm, absent for the other glycolated polymers of the series with 2 and 4 carbon spacers. The structuring of ICT band suggests order in the film and implies the presence of form I aggregates. Increasing the alkyl spacer in the side chain causes a blue-shift in the ICT band, which could imply a decrease in the aggregate content. GIWAXS data provide more cues on the packing behavior of these polymers. While the general (h00) lamellar, (0k0) π-π, and (00l)’ backbone peaks are present in all the p(C₄-T₂-Cₙ-EG) polymers, this series presents a decidedly different and more complicated case (Figure 1c and 1d). Most obvious is the presence of lamellar, π-π scattering both in- and out-of-plane with significant ring-like isotropic character (Figure S11). This supports the presence of crystallites with a distribution of orientation ranging from edge-on to face-on. Lamellar ordering produces two orders of scattering peaks in-plane and three orders out-of-plane, though the out-of-plane peak intensities are low compared to the background along the specular ridge. The lamellar d-spacings are much larger (+5.5 to +7.5 Å) than the possibly interdigitated p(C₄-T₂) lamellar d-spacing, with the in-plane lamellar spacings roughly 1 Å narrower than out-of-plane. Further, there is no systematic variation of the as-cast lamellar d-spacings with increasing alkyl spacers on the T₂ unit. This would suggest that the varied length of the thiophene side-chain is not the determining factor for lamellar d-spacing in the p(C₄-T₂-Cₙ-EG) series polymers. The d-spacing of the (010) π-π stack scattering peaks vary little between in- and out-of-plane and are similar to that of p(C₄-T₂), although p(C₄-T₂-C₄-EG) has a somewhat expanded π-π spacing compared to p(C₄-T₂-C₀-EG) and p(C₄-T₂-C₂-EG). The (001) peak is only present in p(C₄-T₂-C₀-EG) (Figure 1c and 1d), implying the presence of form I aggregates as observed in its UV-Vis spectrum (Figure
The (001) peak is present across the p(C4-T2-Cy-EG) series, while for p(C4-T2-C2-EG) and p(C4-T2-C4-EG) the first order (100) peak intensity is diminished and the second order (002) peak is absent. On a whole, increasing alkyl spacer length appears to decrease the order along the direction of the polymer backbone.

**n-type OECT performance**

All polymers were spin-coated on micro-fabricated OECTs with standard channel dimensions (W = 100 μm, L = 10 μm) and measured in an aqueous electrolyte (0.1M NaCl(aq.)) using an Ag/AgCl gate electrode. The calculated OECT figures of merits, namely the transconductance \( g_m \) (here normalized by the channel thickness (about 160-200 nm), \( V_{TH} \), and the \( \mu C^* \) product, as a function of the T2 substituent, are shown in Figure 2a. The output and transfer curves as well as the \( V_G \) dependent \( g_m \) plots of p(C4-T2), p(C4-T2-OMe) and p(C4-T2-Cy-EG) series are shown in Figure S12, Figure S13, and Figure S14, respectively. It should be noted that the polymers have a comparable molecular weight (i.e., \( M_n \approx 12 \) kDa, see Table 1). Figure 2a shows that the top OECT performer is the polymer with the unsubstituted T2 unit, that is p(C4-T2), exhibiting 0.63 S/cm of thickness normalized \( g_m \), as well as the lowest \( V_{TH} \) (i.e., 0.2 V) and the highest \( \mu C^* \) (i.e., 0.28 F/cmVs). A clear decrease in \( g_m \) is observed when the T2 unit is substituted with a functional group. This is a result of an increase in \( V_{TH} \) and a drop in the \( \mu C^* \) product. The increase in \( V_{TH} \) can be attributed to the slightly lower EA of the T2 substituted polymers. For example, introducing an oxygen on the T2 increases the \( V_{TH} \) from 0.2 V to 0.45 V (EA of (p(C4-T2) is 4.1. eV and EA of p(C4-T2-OMe) is 3.8 eV, Table 1). When the T2 functional group is changed from OMe to EG (i.e., p(C4-T2-Cy-EG), \( y = 0, 2 \) and 4), the \( V_{TH} \) decreases from 0.45 V to ca. 0.3 V (related to an increase of the EA), but remains higher than that of the p(C4-T2).
Figure 2. (a) OECT figures of merit: maximum transconductance ($g_m$) normalized by the channel thickness (top panel), threshold voltage (middle panel) and $\mu C^*$ product (bottom panel) as a function of bi-thiophene substitution in NDI-C4 series; (b) Cyclic voltammogram of the NDI-C4 series performed on polymers coated on Au electrodes (580x580 µm²). The current has been normalized to the volume of the polymer. Arrow indicates the scan direction. Scan rate is 50 mV/s; (c) OECT transfer curve for n-type and p-type transport. The current has been normalized to the channel thickness. Error bars represent the standard deviation out of 6 different devices (W = 100 µm, L= 10 µm).

To identify material properties responsible for the $\mu C^*$ (hence, $g_m$) values measured, we estimated the OECT mobility and the volumetric capacitance of these polymers. Table 2 summarizes the $\mu$
and C* values along with OECT figures of merits. C* was determined from impedance measurements at doping potentials which lead to maximum transconductance for each film. The \( \mu \) was then deduced using equation (1). Note that the OECT mobility of these polymers are generally too low to be measured accurately experimentally, such as via the impedance matching method. Decoupling \( \mu \) and C* reveals that the \( \mu \) is the main factor limiting the OECT transconductance, as the C* of most polymers in this series have similar values. The change in \( \mu \) with T2 substitution follows the same trend as the \( g_m \). For example, the two top OECT performers, i.e., (p(C4-T2) and p(C4-T2-C0-EG), are also those that have the highest \( \mu \). This finding is supported by the more apparent crystalline and ordered nature of these polymers, as observed in the x-ray scattering and UV-Vis spectra in Figure 1. For example, the p(C4-T2-OMe) GIWAXS data suggest diminished edge-on orientation and disruption of backbone order, both expected to undermine intra- and inter-chain charge transport in the plane of the film, which was reflected in decreased drain currents and \( \mu \). Secondly, the increase in C* with T2 substitution is not enough to balance the sharp decrease in \( \mu \), resulting overall in a drastic drop in \( g_m \). For example, when the EG side chains are moved further away from the polymer backbone by the introduction of 4 alkyl spacers, the \( V_{TH} \) does not change, C* improves, but \( \mu \) decreases, which results in lower \( g_m \) values.

**Table 2.** The OECT performance characteristics of the NDI based polymers, p(C4-T2), p(C4-T2-OMe) and p(C4-T2-C0-EG) series. The \( g_m \) values recorded for each OECT were not necessarily obtained at the same \( V_G \). \( V_{TH} \) of each OECT was calculated from the square root of the drain current \( (I_D) \) vs \( V_G \) plot as the point the linear fit intersects the \( V_G \) axis. \( \mu C^* \) product was extracted using equation (1). The capacitance was determined from impedance measurements of thin films with varying geometry. The C* was then extracted from the slope of the capacitance vs film volume curve. \( \mu \) was calculated using the measured \( \mu C^* \) product and C* values.
In Figure 2b, we show the cyclic voltammograms of these polymers in NDI-C₄ series recorded in 0.1 M NaCl(aq.). All films present two quasi-reversible redox couples, associated with a two-fold reduction process to the di-anion via a radical anion intermediate, similar to previously reported NDI-T2 based systems.⁵⁵⁻⁵⁶ We notice a general increase of the overall current with the introduction of a substituent on the T2, suggesting an increase in the film capacitance. At the same time, we notice a delay in the onset reduction potential, following the trend of the $V_{TH}$ of OECTs as discussed above. Interestingly, T2-substituted polymers present electrochemical activity also in the p-type region (≥-0.6 V vs Ag/AgCl). The p-type currents are generated as anions are injected into the films, correlating with the ambipolar charge transport observed in the corresponding OECTs, as illustrated in Figure 2c. On the contrary, p(C₄-T2) (and the rest of the p(Cₓ-T2) series, Figure 4b) do not exhibit any activity in the p-type window. As shown in Table 1, the substitution on the T2 unit led to a decrease in the IP. This lowers the hole injection barrier height and enables hole transport within the material.³⁵ Giovannitti et al. observed a similar behavior when comparing the CV curves of two NDI-T2 based polymers which differ by the EG substitution on the donor unit.²⁵ The narrower bandgap polymer (the one with EG on the T2) had a lower IP, and oxidation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{TH}$</th>
<th>$g_m$</th>
<th>$C^*$</th>
<th>$\mu$</th>
<th>$\mu C^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$(C₄-T2)</td>
<td>0.27±0.004</td>
<td>0.63</td>
<td>158</td>
<td>1.90E-03</td>
<td>0.30±0.0003</td>
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<td>$p$(C₄-T2-OMe)</td>
<td>0.46±0.030</td>
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<td>170</td>
<td>3.87E-04</td>
<td>0.07±0.011</td>
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<tr>
<td>$p$(C₄-T2-C₀-EG)</td>
<td>0.32±0.007</td>
<td>0.31</td>
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<td>1.16E-03</td>
<td>0.22±0.016</td>
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<tr>
<td>$p$(C₄-T2-C₂-EG)</td>
<td>0.30±0.003</td>
<td>0.02</td>
<td>200</td>
<td>4.99E-05</td>
<td>0.01±0.002</td>
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<tr>
<td>$p$(C₄-T2-C₄-EG)</td>
<td>0.33±0.009</td>
<td>0.01</td>
<td>116</td>
<td>5.34E-05</td>
<td>0.006±0.001</td>
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(p-type doping) took place at relatively low positive voltages. However, this polymer also had a higher EA, which is in contrast to the trend we see in EA when introducing EG substitution on the T2. Introducing side chains on the T2 is responsible for the ambipolar transport, but, in our work, this comes at the expense of n-type OECT performance. When we change the substituent on the T2 unit from OMe to EG in p(C4-T2-C0-EG), we observe a slight recovery of the n-type transport and a drop in the p-type performance. However, the n-type regime onset for these polymers is pushed to more positive voltages compared to that of p(C4-T2), while the p-type transport occurs slightly earlier. When moving the EG chains further from the backbone, i.e., p(C4-T2-C2-EG) and p(C4-T2-C4-EG), OECT performance in both regimes decreases significantly. Finally, these devices showed poor shelf life stability (Figure S15) and their response times were characterized with a spike-recovery type behavior, in agreement with low electronic mobilities (Figure S16).

Taken together, it appears that in general, substitution of the bi-thiophene unit in NDI-T2 based polymers significantly reduces the order along the direction of the polymer backbone and disrupts film texture, correlating with poorer electron transport and thus lower device performance. The substitution of the bi-thiophene unit in these polymers is also responsible for ambipolar charge transport in OECTs. Overall, the best n-type OECT performer is the polymer with unsubstituted bi-thiophene units, that is, p(C4-T2).

3. The effect of carbon spacer of the EG side chain on the NDI – NDI-Cx-T2 series

Optical and structural properties

With the studies above, we have identified that for the best n-type OECT performance, the backbone requires no substitution on the T2 unit while the NDI needs to have EG side chains. The next question we asked thus concerned the EG side chains on the NDI unit. Placing alkyl spacers between the backbone and oligo EG side chains has been shown to increase the OFET mobility of
NDI based copolymers upon formation of more interconnected crystalline grains and increase in long-range order.\textsuperscript{57} In addition to the p(C\textsubscript{4}-T2) investigated above, we therefore synthesized three other NDI-C\textsubscript{x}-T2 based polymers with varying length of the carbon spacer (2, 6, and 8 carbons) between the NDI unit and the tri-EG side-chain (Figure 3a). All polymers exhibit typical dual-band absorption, the ICT transition around 700 nm, and the \(\pi-\pi^*\) peak around 395 nm (Figure 3b).\textsuperscript{46} Increasing spacer length on the NDI unit leads to a red-shift in the ICT maximum. We also observe a shoulder around 800 nm, more prominent when going from p(C\textsubscript{2}-T2) to p(C\textsubscript{8}-T2), suggesting an enhancement in form I aggregation.\textsuperscript{47} When we tested the performance of these polymers in OFETs, we found an increase in electron mobility with the spacer length (Table S3), suggesting a better structural order with increasing spacers. PESA revealed that the polymers have similar IP values, and combined with the bandgap values of 1.4 eV, EA was determined to be around 4.1-4.2 eV, which indicates superior air stability of these polymers.\textsuperscript{58}
We next perform GIWAXS studies to understand how film microstructure is affected by the length of alkyl spacers on the NDI unit (Figure 3c, d and S9). The p(C<sub>x</sub>-T2) series present similar scattering patterns, irrespective of alkyl spacer length. The films are quite textured with lamellar stacking (h00) occurring predominately out-of-plane and π-π stacking (0k0) and backbone
ordering (00l) predominately occurring in-plane, indicating a preferential edge-on orientation. The presence of the alkyl spacer drives a high degree of edge-on orientation that is unique compared to the more face-on orientation of previously reported glycolated NDI-T2 based OECT materials.$^{30,58}$ As seen in the line cuts (Figure 3d), the out-of-plane lamellar scattering is the strongest for p(C₄-T2) and p(C₆-T2), displaying four orders of (h00) peaks, while p(C₂-T2) and p(C₈-T2) display three and two orders, respectively. Lamellar d-spacing (Table S1) trends linearly with spacer length, ranging from 16.6 to 22.4 Å, consistent with side-chain interdigitation. In-plane scattering displays a π-π stack scattering peak (010) and two populations of backbone scattering, (00l) and (00l’), representing the form I and form II aggregates (Figure 3d).$^{47,59}$ The (001) and (001’) backbone peaks are clear in the spectrum, indicating d-spacings of 14 and 7 Å, respectively. Across the series, the π-π d-spacing is nominally identical, ranging from 3.81 to 3.85 Å as well as the backbone spacings. The second order (00l) peak is expected at the same $q_r$ as the (001’) peak, thus the two peaks, (002) and (001’), are indistinguishable. However, the (002’) peak is clearly present and a weak shoulder at a $q_r$ consistent with (003). Very weak in-plane (100) peaks are discernable in the case of p(C₄-T2) and p(C₈-T2), though lower in intensity than the π-π stacking and backbone peaks, suggesting a minority population of face- or end-on oriented crystallites.

Of the series, p(C₆-T2) appears the most ordered as exemplified by the presence of mixed index peaks in the p(C₆-T2) 2D GIWAXS plot (Figure S9a). This was further quantified with the Scherrer coherence lengths estimated from scattering peak widths (Table S2). From the (100) peak, p(C₆-T2) clearly displays the longest lamellar coherence of the series. The form I aggregate backbone coherence length extracted from the (001) tracks the UV-Vis data as it increases with spacer length. The form II aggregate backbone coherence length extracted from the (001)’
increases and saturates for the C6 and C8 spacer. The π-π stacking coherence length has a reverse trend, decreasing with spacer length.

**n-type OECT performance**

*Figure 4a* summarizes the OECT figure of merits (i.e., $g_m$, $V_{TH}$ and $\mu C^*$) of the NDI-C$_x$-T2 series. The devices show negligible hysteresis and remarkable shelf-life stability when stored in vacuum for 2.5 years (*Figure S17*). We observe a substantial influence of the alkyl spacer on $g_m$ which increases with the length of the carbon spacer up to 6 units (p(C$_6$-T2)) and then drops for the 8-carbon spacer (p(C$_8$-T2)). The $\mu C^*$ product follows the same trend as the $g_m$: it is maximized for p(C$_6$-T2) and decreases for the p(C$_8$-T2). Furthermore, the gate voltage that leads to the highest $g_m$ shifts towards more positive potentials with increase in the number of carbon spacers (*Figure S12* and S17). $V_{TH}$ starts increasing after p(C$_4$-T2) and is the highest for p(C$_8$-T2). Lastly, similar to what was observed for the p(C$_4$-T2) above, all the polymers in NDI-C$_x$-T2 series display only n-type behavior (*Figure 4 b-c*). The reduction onset potential becomes more negative when the spacer length increases and follows the same trend as the $V_{TH}$ of the OECTs (*Figure 4b*). These devices showed a characteristic switching ON time of ca. 9.7 ± 3.4 ms (*Figure S18*).
Among all the polymers tested in this study, we show that p(C$_6$-T2) is the best performer. p(C$_6$-T2) outperforms other reported n-type OECT materials,$^{25,58}$ approaching the state of the art values of BBL OECTs, reported as the currently best performing n-type OMIEC for OECTs.$^{29}$ This is a result of a dramatic increase in the OECT mobility, which shows a linear increase with the increasing alkyl spacers up to 6 carbons (Table 3). The p(C$_6$-T2) OECTs are also stable against multiple I-V cycles and during operation for 10000 seconds with pulsed gate voltages ($V_G$= 0.4 V,
10 second duty cycle, Figure S19) Structurally, the high p(C$_6$-T2) mobility may be the result of a balance of the opposing backbone and π-π stacking ordering trends, along with an improved lamellar ordering. Likewise, the high p(C$_6$-T2) mobility may in part be the result of its greater molecular weight. Thus, it is interesting to note that despite the vastly different OECT mobilities of p(C$_6$-T2) and p(C$_8$-T2) and factor of two difference in molecular weight, the two polymers display nearly identical UV-vis profiles and OFET mobilities (Figure S20, Table S3). However, OECT operation is governed by the bulk properties, whereas OFET performance depends on the interfacial properties that might differ from the bulk. Besides the lower order of p(C$_8$-T2) compared to p(C$_6$-T2), the exact reason for the drop in OECT mobility of p(C$_8$-T2) remains unclear, as we also do not observe significant structural changes for either of the polymers upon electrochemical doping (see GIWAXS discussion below).

**Table 3.** OECT performance characteristics of the NDI-C$_x$-T2 series. The maximum transconductance ($g_m$) values recorded for each OECT were not necessarily obtained at the same $V_G$. $V_{TH}$ of each OECT was calculated from the square root of the drain current ($I_D$) vs $V_G$ plot as the point the linear fit intersects the $V_G$ axis. $\mu C^*$ product was extracted using equation (1). The capacitance was determined from impedance measurements of thin films with varying geometry. $C^*$ was extracted from the slope of the capacitance vs film volume curve. $\mu$ was calculated using the measured $\mu C^*$ product and $C^*$ values.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{TH}$ (V)</th>
<th>$g_m$ (S/cm)</th>
<th>$C^*$ (F/cm$^3$)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
<th>$\mu C^<em>$ (F/cmV$^</em>$)</th>
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<tr>
<td>p(C$_2$-T2)</td>
<td>0.27±0.004</td>
<td>0.40</td>
<td>492</td>
<td>3.97E-04 ±3.05E-05</td>
<td>0.20±0.015</td>
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<td>p(C$_4$-T2)</td>
<td>0.24±0.002</td>
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<td>158</td>
<td>1.90E-03 ±1.88E-06</td>
<td>0.30±0.0003</td>
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<tr>
<td>p(C$_6$-T2)</td>
<td>0.30±0.003</td>
<td>2.28</td>
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<td>1.29±0.117</td>
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<tr>
<td>p(C$_8$-T2)</td>
<td>0.37±0.002</td>
<td>0.15</td>
<td>342</td>
<td>3.76E-04 ±2.17E-04</td>
<td>0.13±0.074</td>
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</table>
4. *Ex situ GIWAXS studies*

In order to investigate the effect of electrochemical doping on the possible structural changes of the polymer films, and to correlate with the device data, GIWAXS measurements were performed of thin films exposed to electrolyte and then reduced in 0.1 M NaCl at -0.66 V vs Ag/AgCl. Unexpectedly, when ex situ exposed and reduced, no significant structural changes (peak positions, widths, relative intensities) are apparent in the GIWAXS data of the p(Cx-T2) series (Figure S9, Table S1 and S2). This is in contrast to the previous reports of the NDI-T2 copolymer analogue (p(NDI-T2) backbone with EG side-chains on the NDI without any alkyl spacer) which displayed changes in relative peak intensities upon electrolyte exposure and electrochemical reduction.30 The GIWAXS results indicate that the mere presence of alkyl spacers on the EG side chains produces more oriented and more robust crystallites that are stable during electrochemical exposure and charging, and lead to improved charge transport.

While the p(Cx-T2) series showed minimal structural change following electrolyte exposure and electrochemical reduction, the p(C4-T2-Cy-EG) series was sensitive to both (Figure 5). Perplexingly, the (h00) lamellar in-plane and out-of-plane peaks show opposite behavior. Upon electrolyte exposure and electrochemical reduction, the in-plane (h00) d-spacing expands ~1 Å for p(C4-T2-C0-EG) and p(C4-T2-C2-EG) but is essentially unchanged for p(C4-T2-C4-EG). Conversely, the out-of-plane (h00) d-spacing contracts ~1 Å for p(C4-T2-C2-EG) and p(C4-T2-C4-EG) but remains the same for p(C4-T2-C0-EG). To the authors’ knowledge, such anisotropic structural change due to electrolyte exposure and electrochemical reduction has not been observed before. Due to the broadness and low intensity of the (010) peaks, the trends of d-spacing changes of the π-π stack across the series are less confident, however it is safe to say that with electrolyte exposure and electrochemical reduction, π-π stack d-spacing are maintained or slightly expanded,
but not contracted. The (001) peak, present only in the p(C₄-T2-C₀-EG), is insensitive to electrolyte exposure, but is nearly suppressed upon electrochemical reduction. The (001)’ peaks do not change upon electrolyte exposure or electrochemical reduction. The seemingly independent behavior of the (001) and (001)’ peaks highlights the distinct sources of these scattering (i.e. form I and II aggregates). On a whole, we conclude that the structural sensitivity of the thiophene substituted series to electrolyte exposure and reduction correlates with the reduced charge transport properties of these polymers, compared to the unsubstituted, p(Cₓ-T2) series. This result is noteworthy as high performance p-type polymers tend to show large structural transformations (π-π contraction and lamellar expansion). The sensitivity of charge transport to structural change is likely due to the higher degree of charge carrier localization in NDI polymers and the increased importance of intrachain charge transport compared to (electro)chemically doped p-type polymers.
Figure 5. Line cuts of the p(C₄-T₂-Cₓ-EG) series polymers. (a), (c) and (e) represent the out-of-plane $q_z$ line-cut of p(C₄-T₂-C₀-EG), p(C₄-T₂-C₂-EG) and p(C₄-T₂-C₄-EG) respectively; (b), (d) and (f) represent and in-plane ($q_r$) line cuts of p(C₄-T₂-C₀-EG), p(C₄-T₂-C₂-EG) and p(C₄-T₂-C₄-EG) respectively. The color shade, from light to dark, represent the line cuts of thin films.
measured as cast, ex situ exposed to aqueous 0.1 M NaCl, and ex situ electrochemically reduced to -0.66 V vs Ag/AgCl in the same electrolyte respectively.

**Conclusion**

In this work, we investigated the effect of two distinct EG side chain engineering strategies on the electrochemical performance of NDI-T2 based polymers. We varied 1) the side-chain substitution of the T2 unit, and 2) the distance of the EG side chains from the NDI unit. Introducing a substituent (methoxy group or EG side chains) on the T2 unit decreased the EA of the polymers and increased the $V_{TH}$ of their OECTs. With T2 substituted polymers, OECTs performed poorly. The poor performance is mainly due to a decrease in the electronic charge mobility despite a moderate increase in the volumetric capacitance. GIWAXS analysis revealed significant changes in the polymer structure with T2 substitution: a decreased backbone ordering leading to impaired charge transport, and a change from a predominantly edge-on orientation to a mixture of face-on and edge-on chain orientation. Structural changes upon electrolyte exposure and electrochemical doping, manifested as increased backbone disorder, further correlated with disrupted electron transport. While hindering n-type transport, the T2 substitution led to ambipolar operation because of a decrease in IPs.

As we identified the best OECT performer to be the unsubstituted T2 polymer, our study focused on the side chains on the NDI unit. We varied the distance of the EG side-chain from the NDI unit using carbon spacers. Increasing the spacer index, i.e., moving the EG further away from the backbone, led to a general improvement of the electronic charge mobility and, therefore, device performance. GIWAXS studies showed that backbone order was optimized for the polymer with 6-carbon spacer, corroborating with its high device performance. We found that there is a sweet-
spot between the distance of the EG units from the backbone, as p(C8-T2) was not performing as well as p(C6-T2). These results suggest that besides the distance of the hydrophilic unit from the backbone, the length of the side chain can be an important parameter to optimize. We also found that the polymers in this series showed no structural change upon electrolyte exposure and electrochemical doping correlating with their higher performance compared to T2 substituted ones. Overall, our work shows that the n-type OECT performance was governed by the electron mobilities rather than volumetric capacitances, which was affected by side chain architecture and the subsequent backbone disorder. This work provides new guidelines towards the development of high-performance n-type OECT materials, as well as insights on the general structure-performance relationship for OMEICs operating at the electrolyte interface. A combination of interesting redox properties with efficient charge transport and high capacitance poises NDI-T2 based polymers as essential materials for bioelectronics, but also for other applications such as energy generation and storage. While the performance of the n-type OMIECs developed is behind their p-type counterparts, we believe that the side-chain design strategies introduced in our work would inspire other approaches that focus on improving backbone planarity and push further the performance of n-type OMIECs.

Acknowledgements

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supported by King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. OSR-2016-CRG5-3003 and OSR-2018-CRG7-3709.

**Supporting Information**

Detailed synthetic route and NMR spectra, GIWAXS profiles, calculated d-spacing and estimated Scherrer coherence lengths the polymers, output curves, transfer curves, response times, shelf-life and operational stability of OECTs, and OFET mobilities.

**References**


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