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Controlling the mode of operation of organic transistors through side chain engineering

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Abstract

Electrolyte gated organic transistors offer low bias operation facilitated by direct contact of the transistor channel with an electrolyte. Their operation mode is generally defined by the dimensionality of charge transport, where a field effect transistor allows for electrostatic charge accumulation at the electrolyte/semiconductor interface, while an organic electrochemical transistor (OECT) facilitates penetration of ions into the bulk of the channel, considered a slow process, leading to volumetric doping and electronic transport. Conducting polymer OECTs allow for fast switching and high currents through incorporation of excess, hygroscopic ionic phases, but operate in depletion mode. Here, we show that the use of glycolated side chains on a thiophene backbone can result in accumulation mode OECTs with high currents, transconductance, and sharp sub-threshold switching, while maintaining fast switching speeds. Compared to alkylated analogues of the same backbone, the triethylene glycol side chains shift the mode of operation of aqueous electrolyte gated transistors from interfacial to bulk doping/transport and show complete and reversible electrochromism and high volumetric capacitance at low operating biases. We propose that the glycol side chains facilitate hydration and ion penetration, without compromising electronic mobility, and suggest that this synthetic approach can be used to guide the design of organic mixed conductors.

Significance Statement:

Side chain engineering is a versatile tool to modify the processability, as well as the physical, electrical and optical properties of conjugated polymers. This approach is used to tailor the operating mechanism of electrolyte gated organic transistors, allowing for facile bulk doping and therefore efficient modulation of transistor channel conductance. Such transistors combine fast response with high current-to-voltage signal transduction necessary for active sensing and low power circuit applications.

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Introduction

Electrolyte-gated transistors offer high current densities and low bias operation. At the most general level, these transistors yield desirable performance characteristics owing to an electrolyte which effectively replaces the gate dielectric. The chosen electrolyte can be in solid, gel or liquid state – the sole requirement being that ions within it can rearrange in response to an external bias. This bias, which is applied at the gate electrode, will lead to an ion-induced modulation of channel conductance. Electrolyte gating has been demonstrated with channels made of bulk and nanoscale materials ranging from semiconducting oxides(1), to carbon nanotubes(2), graphene(3), and small molecule/polymeric semiconductors and conductors(4). Unlike traditional transistors, which reach high performance through the use of ultra-thin, pinhole-free, and high dielectric constant gate dielectrics based on oxides or self-assembled organic layers(5), electrolyte-gated transistors offer relaxed requirements. Solid-state and gel electrolytes can be processed from solution, and allow for the physical placement of the gate electrode to be decoupled from that of the channel. Such devices have thus been used to control active matrix displays(6), electrochromic pixels(7), and have been used for logic circuitry(8). Biosensing in particular, has been a strong beneficiary of the developments in electrolyte gated transistors.(9-11) Nearly all biological analyte and electrophysiology sensing takes place in ion-rich aqueous media. In these cases, a biological event (e.g. an electrophysiological signal, or an enzymatic reaction) modifies the effective gate bias; the inherent gain of the transistor can then be used as an amplifying transducer to enhance the recorded signal(12). Organic electronic materials are particularly interesting active channel materials due to their synthetic tunability, biocompatibility, and soft mechanical properties, readily allowing for integration with cells and biological tissue(13).

The mode of operation of electrolyte-gated organic transistors has garnered significant attention due to the free volume and weak bonding interactions of the channel material. Two disparate operation modes are possible: an interfacial electrostatic operation (which defines a pure electrolyte gated organic field effect transistor, EG-OFET), and a bulk doping operation dominated by volumetric penetration of ions (referred to as an organic electrochemical transistor, OECT). In an EG-OFET, the gate-induced formation of an electrical double layer (DL) at the semiconductor/electrolyte interface, imparts a capacitance (C_{DL}) on the order of 10 µF/cm^2, which electrostatically dopes the semiconductor, forming a 2D conducting channel at that interface.(14) An OECT, on the other hand, allows for facile penetration of ions into the bulk of the channel; this volumetric doping leads to molecular-scale effective surface areas, and thus even higher effective areal capacitance values that depend on channel thickness.(15, 16) The difference between these two modes is the dimensionality of electrostatic doping and electronic transport. The control of the mode of operation can impart aspects of both interfacial and bulk operation that are mutually advantageous (17-20), or can allow one mode to dominate, simplifying analysis and implementation. Interfacial operation can be achieved by eliminating any opportunity for ion ingress into the transistor channel by making the channel material impenetrable (i.e. using an excessively dense channel material), or by selecting large or chemically incompatible ions (i.e. bulky ionic liquids or polyelectrolytes) (4). Bulk OECT operation, conversely, requires facile ion interaction through the volume of a semiconductor, requiring good mixed conduction properties. Since OECT operation involves penetration of ions into the semiconductor, it is presumed to be significantly slower than EG-OFETs, leading to a trade-off between fast response time and high currents.

Most organic transistors gated in a biologically-relevant environments rich in chloride and metal cations should show mixed operation modes dependent on the magnitude and frequency of the gate bias. Pure bulk switching behavior, as in OECTs, has been demonstrated in a limited class of materials where a separate phase or ionic moieties facilitating ion transport are introduced, for example, the conjugated polymer/polyelectrolyte composites based on poly(3,4-ethylenedioxythiophene), PEDOT. OECTs of these materials are considered to be the best performing bulk-gated transistors, but operate in depletion mode: they are ON in the absence of a gate bias.(21, 22) Conjugated polyelectrolytes offer an alternative route to accumulation-mode devices.(17, 23-25) However, ion-free, neutral polymers that utilize the wealth of synthetic knowledge from traditional organic electronics have not been achieved for aqueous (bulk-gated) OECTs. To this end, we show that modification of semiconducting polymer side chains can transform a material exhibiting mixed modes of operation into an entirely bulk-doped OECT when gated in aqueous media. We design a system where alkoxy or ethylene glycol side chains are attached to identical polythiophene scaffolds at the same positions, leading to energetically and conformationally similar conjugated polymer backbones. The glycolated polymer allows for significant enhancement in reversible electrochromism and a large modulation in capacitance. Transistors based on this material behave as true OECTs, with transconductance outpacing that of PEDOT:PSS-based OECTs of the same geometry, and exhibit a subthreshold swing of 60 mV/dec. Notably, no additives or crosslinkers are required to enhance mobility or stabilize the film in aqueous environments. Moreover, these devices show minimal hysteresis, long term constant and pulsed stressing stability, and response times of <1 ms. The nature of the side chain is found to critically affect ion injection and transport. Thus, the approach presented here promises to contribute to the synthetic control of mixed conduction, and to the design of high performance electrolyte-gated transistors.

Results

Materials Synthesis and Characterization. The chemistry of side chains is well understood to influence a number of physical and optoelectronic properties of semiconducting polymers, such as solubility, stability and electrochemical behavior.(26) In order to make a fair comparison, we sought to investigate polymers with the same backbone structure and energy levels that have either alkoxy side chains (tetradecyloxy, $C_{14}H_{29}O$-) or triethylene glycol side chains ($CH_3(OCH_2CH_2)_3O$-). A glycol side chain should allow for swelling of the polymer, and thus more facile ion penetration necessary for electrochemical doping in water. The backbone of the polymers consists of a bithiophene-thienothiophene (2T-TT) unit which is selected due to its rigidity and potential for high hole mobilities(27), and was functionalized with alkoxy or ethylene glycol side chains at the 3,3' position of the bithiophene unit affording poly(2-(3,3'-bis(tetradecyloxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene), p(a2T-TT), and poly(2-(3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene), p(g2T-TT), respectively (Figure 1a). The intramolecular sulfur-oxygen interactions of the head-to-head coupled bithiophene unit is known to induce backbone co-planarity and increase the effective conjugation length of the polymer which should favor efficient charge transport, while decreasing the ionization potential (IP).(28) Utilizing a palladium-catalyzed Stille polycondensation reaction, polymers p(a2T-TT) and p(g2T-TT) were synthesized by reacting 2,5-bis(trimethylstannyl)-thieno[3,2-b]thiophene with equimolar amounts of 5,5'-dibromo-3,3'-bis(tetradecyloxy)-2,2'-bithiophene and 5,5′-dibromo-3,3′-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene, respectively, as further detailed in the Supporting Information. The polymers are moderately soluble in warm chlorinated solvents such as chlorobenzene, 1,2-dichlorobenzene and 1,1,2,2-tetrachloroethane while p(g2T-TT) is also moderately soluble in chloroform and N,N-dimethylformamide. The ionization potentials of the polymers, determined by cyclic voltammetry (CV, Figure S1) and by photoelectron spectroscopy in air (PESA; values in brackets), are 4.4 eV [4.61 eV] for p(g2T-TT), and 4.6 eV [4.76 eV] for p(a2T-TT). The slightly lower IP of p(g2T-TT) can be explained by the different side chain-side chain and side chain-solvent interactions which will affect both microstructure, noted below, and ion penetration. Despite differences in solution aggregation, UV-Vis spectra (Figure S1c) show similar absorption onsets, confirming their similar band gap, which is corroborated by density functional theory calculations (Figure S2). Roughness and film formation of both materials are found to be comparable as determined by atomic force microscopy (AFM; Figure S3). Additionally, comparison of the solid-state microstructure by 2D grazing incidence X-ray scattering (Figure S4, Table S1) reveals that both polymers show similar edge-on texture and backbone repeat distances, but that intermolecular interactions in the π-stacking direction are affected by the side chain engineering, and will thus also influence intermolecular charge transport.

Electrochemical switching characterization. p(a2T-TT) and p(g2T-TT) are used as the active material in capacitor and transistor devices as shown in Figure 1b,c. Devices are fabricated as described in the Methods. Electrochemical cycling, electrochromism, and impedance, are probed with EIS capacitor structures, where the polymers are coated on either gold or indium tin oxide (ITO) electrodes (and operated as in Figure 1b). Monitoring the change in optical absorption as a function of bias (electrochromism) allows to investigate the extent of electrochemical doping that occurs within the bias range allowed by operation in water (to avoid hydrolysis). As shown in Figure 2a, the change in visible absorption of p(a2T-TT) is negligible up until a working electrode bias of, V_{offset}=0.4 V, after which only a modest decrease in π-π* absorption, and an increase in polaronic absorption at high wavelengths can be observed. Above 0.6 V, the π-π* absorption is nearly quenched, indicating a majority of the film is doped, however, the initial state cannot be recovered when the bias is removed or reversed, likely due to a combination of ion trapping and/or physical/chemical modification of the polymer film. Conversely, p(g2T-TT) can be completely and reversibly doped at 0.5 V, with both polaronic (~800-900 nm), and bi-polaronic species (>1100 nm) arising (Figure 2b). The spectroelectrochemical signatures observed are in agreement with the CV behavior of these polymers when cycled in aqueous (Figure S1b).

The capacitive nature of p(a2T-TT) and p(g2T-TT) can be further quantified with electrochemical impedance spectroscopy, as seen in Figure 3 and Figure S5. Figure 3a,b show the effective capacitance (the capacitance per electrode area, see Methods for details) and phase response for the polymers in question. From the phase behavior of the impedance spectra, we can identify whether the channel material is dominated by more resistive ($0° > \varphi > -45°$) or capacitive ($-45° > \varphi > -90°$) character.(17, 29) p(a2T-TT), for example shows a more capacitive nature at low frequency (<100Hz). This trend is true for a majority of the biasing range (-0.3 to 0.4 V), where both phase and effective capacitance are largely unchanged. At a $V_{offset} \geq 0.5$ V, the effective capacitance slightly increases, while application of $V_{offset} > 0.6$ V results in an irreversible modulation in the impedance, in agreement with the spectroelectrochemical measurements of Figure 2a. p(g2T-TT), on the other hand, shows significant and fully reversible electrochemical modulation over a similar offset bias range. At negative working electrode biases, capacitive behavior dominates the 10Hz to >1kHz frequency range, with modest effective capacitance values on par with those of p(a2T-TT). Application of >0V offset results in a saturation of both phase and effective capacitance: the phase shows nearly ideal capacitive behavior ($\varphi \sim 90°$) at low frequency, and a 50-fold increase in the capacitance. Figure 3c shows that not only does p(g2T-TT) accommodate a nearly two order of magnitude modulation in effective capacitance, but that its alkoxylated analogue behaves similar to a bare gold electrode (dominated by the double-layer capacitance typical of an impenetrable interface).

Transistor characteristics and transient response. The electrochemical characterization suggests that over the measurement range dictated by polymer stability and operation in aqueous chloride electrolyte, the two materials operate in different regimes. Transistor performance should therefore reflect this difference, which is imparted by the side chain structure and its interaction with the electrolyte solution.

Figure 4 shows the output and transfer characteristics of p(a2T-TT) and p(g2T-TT) based transistors with the same areal device geometry (W/L=100 µm /10 µm) and operating conditions. p(a2T-TT) exhibits moderate ON currents on the order of 50-100 µA at a gate bias of V_g=-0.6 V, and shows significant hysteretic behavior. p(g2T-TT), on the other hand, reaches currents >1mA at V_g>-0.5V, and shows minimal hysteresis. The I-V characteristics and hysteresis of the same devices at a number of sweep rates are shown in Figure S6, along with the corresponding gate current. p(a2T-TT) shows significant hysteresis for all sweep rates investigated, and does not reach steady-state even at unreasonably slow rates of 0.02 V/s, thus precluding extraction of steady state ON/OFF ratios and mobility characteristics. Conversely, p(g2T-TT) shows nearly identical behavior for sweep rates of 0.2 and 2 V/s.

The glycolated polymer exhibits high performance OECT characteristics. Devices show an ON/OFF ratio of 10^5, with the OFF current exactly matching the leakage gate current of ~10-20 nA. Peak transconductance (g_m=$\partial I_d/\partial V_g$) of the device in Figure 4c,d is 5.4 mS. Varying the polymer channel thickness results in a proportional increase in transconductance, consistent with electrochemical transistors made of PEDOT:PSS.(16) Thicker transistor channels of comparable areal dimensions, W/L, are found to reach a g_m of ca. 27 mS with a current of 9 mA (Figure S7). Remarkably, the geometry-independent transconductance of p(g2T-TT) out-paces PEDOT:PSS-based OECTs, and other high performance OECTs at all channel dimensions (Figure S8).(16) The hole mobility of the material can be extracted using constant current or impedance matching methods previously reported for OECTs (30, 31) which use the hole transit time to determine carrier mobility. This method results in a hole mobility of 0.95 cm^2/Vs, which is in good agreement with the estimate of transistor saturation mobility (using C_i=0.94 mF/cm^2, from Figure 3) of μ_{sat}=1.27 cm^2/Vs.

An intriguing feature of p(g2T-TT)-based OECTs is their desirable sub-threshold characteristics; the devices are capable of a sharp turn-on (Figure 4d). The entire modulation of channel conductance occurs within ~0.5V, a hallmark of electrolyte gated transistors. Moreover, the peak subthreshold slope is 60 mV/decade, among the lowest reported values for organic transistors.(32) PEDOT:PSS OECTs can reach 75 mV/dec for very thin devices, but since they operate in depletion mode, V_g>0.7 V is required to turn the device off.(33) For p(g2T-TT) OECTs, the devices turn on with the same subthreshold slope, at V_g~0 V, regardless of channel dimension or thickness (Figure S8b).

The transient (turn on/turn off) characteristics can further inform the time scales and operation of p(a2T-TT) and p(g2T-TT); the time constants (τ) are estimated from exponential fits. Figure 5 and Figure S9 show that p(a2T-TT) has a multi-stage switching behavior, with a relatively slow turn on time of $\tau_{ON}\approx1.5$ s. The current does not saturate, even while stressing the device for several minutes at $V_g=V_d=-0.6$ V. It is also clear from Figure 5 that the OFF→ON and ON→OFF characteristics are highly asymmetric, with τ_{OFF}=1.3 ms, resulting in $\tau_{ON}/\tau_{OFF}\approx1.1\text{x}10^3$. A lower current regime (1 ms < t < 50 ms) is also observable in Figure 5, with drain currents of 10-100nA, however, the transient characteristics of this regime are not fully accessible given the device geometry and measurement procedure used here. p(g2T-TT), on the other hand, shows significantly faster switching, with exponential rise times of τ_{ON}=420 µs. The asymmetry in the switching characteristics is also significantly reduced with τ_{OFF}=43 µs (τ_{ON}/τ_{OFF}=9.8). These data show that the p(g2T-TT) transistor shows significantly faster high-current switching characteristics compared to that of p(a2T-TT).

The fast electrochemical switching and high transconductance of p(g2T-TT) transistors reveal their potential utility in sensing and circuits, however, long term operational stability is required. The stability of p(g2T-TT) transistors was evaluated by stressing the devices during 10 min of constant biasing. At low and moderate bias, V_d=V_g=-0.1 to -0.4 V, the current is stable at long time points (Figure S10). At V_d=V_g=-0.6 V, the device shows a stretched exponential decay, similar to previous reports,(19) which is irreversible. Currently, it is unclear if this decay is due to polymer degradation or to permanent morphological changes. Long term pulsed cycling (nearly 2 hours, ~700 cycles) at the moderate biasing condition (V_d=V_g=-0.4 V) shows good stability, with only ~25% decrease in on current over the time of the experiment (Figure S11). It is interesting to note that dynamic (50% duty cycle) stressing leads to a more rapid degradation in ON current (~2% reduction over 10 minutes) compared to DC stressing (100% duty cycle), where there is 0.05% deterioration during the same time.

Discussion

Mode of operation. The mode of operation of transistors depends on the bias magnitude and frequency range in question.(17-19) Motivated by operation in aqueous media typical for applications in biosensing, we are restricted to a low voltage operation (due to hydrolysis), with a total potential drop $V_d+V_g < 1.2$ V. The synthetic design of the polymers ensures proper control of the IP, such that operation at $|V_g|<0.6$ V is possible. While both p(a2T-TT) and p(g2T-TT) show some switching characteristics indicative of ion penetration into the bulk, the combined electrochemical characterization and transistor characteristics suggest that p(a2T-TT) behaves as a mixed mode-of-operation transistor material, while p(g2T-TT) is dominated by bulk doping and thus operates as an OECT.

For p(a2T-TT), there is no significant indication of electrochromism when V_{offset}<0.4V (Figure 2a), as the onset of oxidation has not yet occurred (Figure S1b). The effective impedance does not change appreciably (Figure 3a), and maintains a low frequency capacitance of ~10-20 μF/cm^2, on par with that of a gold electrode. This means that, to first approximation, the capacitance in this regime is that of an electrical double layer.(14, 34) As such, at low bias and short time scales (high frequency), p(a2T-TT) devices should behave as an OFET. This regime is not directly observable in the transistor characteristics (Figure 4), owing to the small W/L ratio utilized in these studies (W/L=10) which translates to lower currents compared to that of previous reports using a W/L≈300.(17) At higher V_g, consistent with the onset of oxidation, and longer times (low frequency) the mode of operation transitions towards a bulk-doping regime. The current and capacitance does not reach saturation within the allowable bias range – higher potentials lead to device degradation – thus p(a2T-TT) does not show pure OECT operation.

p(g2T-TT), on the other hand, is an OECT, operating fully within the bulk doping regime. At V_g<0 V (working electrode V_{offset} > 0 V), capacitance saturates at ~1 mF/cm^2 – nearly two orders of magnitude higher than C_{DL}. Taken together with the complete and reversible electrochromic switching behavior, subthreshold switching consistent with electrochemical oxidation, and high transconductance, transistors based on this material behave as OECTs, governed by ion penetration and doping throughout the bulk of the channel.

The comparison of p(g2T-TT) and p(a2T-TT) is ostensibly similar to work of Laiho et al, who compare P3HT and a polyelectrolyte analogue of P3HT in electrolyte gated transistors (17). Therein, the authors find that P3HT devices operate entirely in the interfacial doping regime (OFET), whereas the transistors employing the conjugated polyelectrolyte material can operate in either an interfacial-like regime or a bulk-doped regime (facilitated by self-doping of ionic side groups) where high currents are achievable at the cost of slow switching. However, in ref. (17), the transistors are gated by a solid state polyelectrolyte, while in this work, aqueous chloride salts are used. Here, we show that it is the fully alkoxylated p(a2T-TT) transistors which operate in a mixed interfacial/bulk regime, while the glycolated p(g2T-TT) transistors are bulk-dominated OECTs, and operate significantly faster – yielding both rapid transient response and high current (Figure 5a). Thus, we pose that for electrolyte gated transistors, unless the transistor channel is impenetrable to ions (as is the case with inorganic solid state materials, or with bulky ions), entirely interfacial (OFET) operation is not possible.

The role of side chains. The reason for p(g2T-TT)'s superior performance and extended operation in the bulk doping regime can be attributed to the presence of triethylene glycol side chains, likely facilitating penetration and transport of aqueous Cl^- ions. An initial indicator is the relative agreement of the oxidation onsets from CV of the films examined in acetonitrile (ACN) and in an aqueous electrolyte. The difference between these two onsets (Figure S1) is ΔV=0.06 V for p(g2T-TT); much smaller than the 0.42 V observed for p(a2T-TT). This indicates that for p(g2T-TT), the energetics associated with penetration of PF_6^- ions from ACN solution, and for Cl^- ions from water are comparable. Furthermore, previous studies have shown that swelling of OECT materials is correlated with ion mobility and/or device performance.(35, 36) Compared to its alkylated, hydrophobic counterpart, side chains consisting of oligo-ethylene glycol, much like free poly(ethylene glycol), PEG, should allow for favorable aqueous interaction. Although modest in comparison to PEDOT:PSS, p(g2T-TT) shows ~10% swelling on exposure to water as measured by dissipative quartz-crystal microbalance; a further ca. 10% increase occurs when Cl^- ions penetrate the polymer on application of a doping potential (Figure S12). A lateral electrochromic moving front can also be visualized for p(g2T-TT) films (Figure S13), however proper quantification of ion mobility is precluded due to non-idealities and deviation from the model of ref (36). Nevertheless, the front velocity, i.e. rate of motion of the doped/undoped interface in response to drifting Cl^- ions, is slower than that of cations in PEDOT:PSS films. These findings agree with the observations that p(g2T-TT) swells less than PEDOT-based materials, where significant polyanion content allows for extensive water uptake. (35, 36) Regardless, moderate swelling is sufficient for facilitating reversible aqueous Cl^- ion drift, doping, and thus high effective capacitance. The bulk doping of p(g2T-TT) by hydrated ions allows for extraction of the volumetric capacitance of $C^*=240$ F/cm^3, a value ~6x higher than PEDOT:PSS (16), indicating a higher density of ion accessible sites. Thus, while the lack of a hygroscopic polyionic phase may hurt the swelling and hence ionic mobility in p(g2T-TT), it provides a high density of electronic sites that are made accessible to ions by the presence of ethylene glycol side chains. It has been shown that the materials figure of merit of OECTs is dependent on the product of electronic mobility (μ_e) and volumetric capacitance (C^*). The enhanced OECT performance of p(g2T-TT) compared to PEDOT:PSS (Figure S8) can therefore be attributed to a large C^*, while maintaining a comparable electronic mobility (lower by only a factor of ~2).(16)

The effect of molecular design on swelling may affect the ability of a material to accommodate molecular reorganization in response to the physical penetration/withdrawal (mass transport) of ions. For example, the anisotropy in ON→OFF compared to OFF→ON transients could be explained by such reorganization which dominates lateral hole transport, where the glycol side chains help to accommodate local reorganization in aqueous compared to the alkoxy functionalization. Even so, the enhanced degradation of current in p(g2T-TT) devices due to pulsed biasing compared to constant DC biasing (Figures S10, S11) further suggests that physical penetration/withdrawal of ions leads to permanent morphological changes. Ameliorating such effects may require a balance between hydration and the need for dense morphologies necessary for a high site density (C^*).

Transistors made of the glycolated polymer are able to achieve high ON currents, and to switch in the 0.5 ms time scale, sufficiently fast for most biological applications including environmental/analyte detection and electroencephalography (EEG). It achieves agreeable transconductance values of 5-27 mS, dependent on the thickness of the active layer, with V_d normalized values of ~10-60 mS/V and subthreshold slopes of 60 mV/dec. Sharp subthreshold switching is targeted for low power electronics applications, and may be a promising avenue for some sensing applications, especially given the 0 V bias and comparatively high currents (µA) observed here. The fact that the turn on voltage is independent of device geometry, and that the subthreshold regime ($0.2\ \mathrm{V} > V_g > 0\ \mathrm{V}$) coincides with the range in which effective capacitance increases fifty-fold, suggest that the electrochemical modulation onset is integral to subthreshold switching in OECTs.

It should be noted that simply synthesizing π-conjugated polymers with glycol side chains is not sufficient to yield high performance OECTs. The ionization potential of the conjugated polymer should be within the operation window allowed by the chosen electrolyte, and within the stability window of the polymer in that medium (i.e. stable polaron formation). Furthermore, side chain modification is known to change the processability and morphology of the resulting films, which is observed in the X-ray scattering and the varied solubility of the polymers reported herein. As such, it is not only the local environment offered by glycolated side chains that affects ion penetration, but also the relative modification of the polymer backbone conformation and energetics, interchain π-stacking and meso-structure that influence the ion drift, C^*, stability and electronic mobility.

Conclusions

While a number of routes exist to control an electrolyte gated transistor’s mode of operation, side chain modification can be a fruitful method, especially for biosensing applications where the choice of electrolyte and bias window are constrained. This concept is explicitly demonstrated with alkoxylated and glycolated analogues of a semiconducting polymer with a 2T-TT backbone. While the alkoxylated polymer shows a mix of interfacial and bulk-doping operation depending on bias time and magnitude, the glycolated version acts as an OECT throughout our window of operation. p(g2T-TT) achieves high currents at sub-millisecond time scales, high transconductance, and steep subthreshold switching. The devices based on this material are stable in continuous operation in aqueous media, and show little hysteresis. In addition to these advantages, the material can be processed from organic solvents and yields stable, high performance devices without the need for additives or crosslinkers. This work suggests that for suitably selected organic semiconducting backbones, careful side chain selection can completely transform a field-effect transistor material into one that operates on the principle of bulk doping (an electrochemical transistor). Further modification of side chain characteristics (length, branching, and density) may allow for unprecedented control of ion transport. Since the side chains can ultimately influence both ion injection into the film, and their effectiveness in doping the conjugated chromophores, they are central in the molecular design of mixed conductor materials for high performance transistors.

Methods

Synthesis and characterization. Materials and methods associated with synthesis of p(a2T-TT) and p(g2T-TT) are included in their entirety in the Supporting Information.

Device fabrication. Transistors and electrodes for electrical and electrochemical testing were fabricated as previously reported.(16, 21) Briefly, cleaned glass substrates were photolithographically patterned with Cr/Au interconnects, electrodes, and source/drain contacts. The semiconducting polymer and an insulating parylene C layer were then simultaneously patterned in a second photolithography step followed by a sacrificial peel-off process. The parylene C isolates the Au interconnects, leaving only the semiconducting polymer surface exposed to the electrolyte. The semiconducting polymers are spin cast from organic solvents (as noted) at 5 mg/mL, without the use of solution additives. Solution preparation and film casting were performed under ambient conditions.

Electrochemical characterization. Cyclic voltammograms were obtained using an Autolab PGSTAT101 with a standard three-electrode setup with ITO coated glass slides as the working electrode, a platinum mesh counter electrode and a Ag/AgCl reference electrode calibrated against ferrocene (Fc/Fc^+). The measurements were carried out in 0.1 M aqueous NaCl or in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at scan rates of 100 mV/s. Ionization potentials were obtained using the equation: IP = (E_{ox} – E_{Fc} + 4.8V). All electrochemical and device characterization were performed in ambient.

Spectroelectrochemical measurements were performed with an ITO-coated glass slide with spun cast polymer immersed in a cuvette with 0.1 M aqueous NaCl solution. A UV-1601 UV-Vis spectrometer was used with the beam path passing through the filled cuvette and polymer/ITO/glass sample. A background spectrum with cuvette/electrolyte/ITO/glass was recorded before a potential was applied to the cell. The potential was applied for 5 s before the spectra were recorded.

Electrochemical impedance spectroscopy (EIS) was performed in aqueous NaCl solution (0.1M) on 3.48×10^{-3} cm^2 gold electrodes coated with the semiconducting polymers (working electrode), using the EIS300 module of a Gamry Reference 600 potentiostat with a Pt mesh counter electrode, and Ag/AgCl standard reference electrode (BASi). EIS was performed over a range of 10kHz to 1Hz with an AC 10 mV (RMS) sine wave, and a DC offset of $0.6 \text{ V} > V_{offset} > -0.6 \text{ V}$. Custom MATLAB tools were used for data analysis. Effective capacitance was extracted from $1/(2\pi f \mathrm{Im}(Z))$ where f is the frequency, and Z is the complex impedance, to estimate areal capacitance. In order to extract capacitance (C), and therefore the volumetric capacitance, C^*, the spectra of doped, saturated films were also fit to an $R_s(R_p||C)$ equivalent circuit (Figure S5) where R_s and R_p are the resistance of the electrolyte and the parallel resistance of the polymer film, respectively.

Transistor characterization. Transistor characterization was performed on devices with *W/L* of 100 µm/10 µm, where *W, L* and *d* are the channel width, length, and thickness. The transistors were operated in the common source configuration with a Ag/AgCl pellet electrode (Warner Instruments) immersed in NaCl solution (0.1M). The measurements were performed using a National Instruments PXIe-1062Q system. To obtain output and transfer characteristics, the gate and drain of the OECT were addressed using two channels of a source-measurement unit (SMU) NI PXIe-4145. For transient responses and stability measurements, the gate bias was applied using a NI PXI-6289 modular instrument, and current recorded with either the NI PXI-4145 SMU or a NI PXI-4071 digital multimeter.

Measurements were triggered through the built-in PXI architecture. The recorded signals were saved and analyzed using custom LabVIEW and MATLAB software.

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Figure Legends

Figure 1. a. Molecular structure and schematic of interactions of ions with alkoxylated p(a2T-TT), and glycolated p(g2T-TT). Anions, in this work Cl^- ions, are shown in blue, cations (Na^+) in grey, and holes along the polymer backbone are in white. **b.** Capacitor structure used for electrochemical impedance spectroscopy (EIS), where the semiconductor is deposited on a photolithographically defined gold electrode. A Ag/AgCl electrode and Pt mesh (not shown) is used as a reference and counter electrode, respectively. **c.** Electrolyte gated transistor structure operated in the common source configuration, where the Ag/AgCl electrode is used as the gate.

Figure 2. Spectroelectrochemistry of p(a2T-TT) (**a**), and p(g2T-TT) (**b**) films deposited on ITO. Spectra are normalized to the peak absorption of the neutral spectra. The grey-scale coding denotes the bias at the working electrode (the polymer coated electrode). Dotted lines denote biasing conditions where electrochromism is not spontaneously reversible, owing to ion trapping and/or associated degradation in the p(a2T-TT) film.

Figure 3. The effective capacitance and phase from electrochemical impedance spectroscopy of p(a2T-TT) (**a**), and p(g2T-TT) (**b**) films on Au electrodes (the working electrode). The grey scale denotes working electrode bias (V_{offset}) from negative to positive voltages (black to grey), identical to the voltage values in (**c**). Dotted lines denote biasing conditions that are not reversible. **c.** The effective capacitance at 1 Hz for p(a2T-TT), red, p(g2T-TT), blue, and bare gold, grey, electrodes of the same area, 3.48×10^{-3} cm^2. p(g2T-TT) is 40nm thick, and p(a2T-TT) is 150 nm. Raw impedance spectra can be found in Figure S5.

Figure 4. Transistor current-voltage traces of p(a2T-TT) (**a,b**), and p(g2T-TT) (**c,d**). I_d-V_d, output, curves for $-0.6\ V < V_g < 0\ V$ to (**a,c**), and I_d-V_g, transfer, characteristics at V_d=-0.6 V (**b,d**). Dotted lines show current on a logarithmic scale. All traces show hysteresis measurements with direction indicated with arrows. Transistors are W/L=100 µm/10 µm. Sweep rate is 0.2 V/s.

Figure 5. Transient response of drain current (I_d) to a gate voltage pulse (V_g=0 to -0.6 V), V_d=-0.6V. The transient response is shown on a logarithmic time scale, with t=0 s as the time that the gate bias was turned on (dark colors, closed symbols), or turned off (light colors, open symbols).