Solvent Engineering for High Performance Glucose Sensors with an n-type Organic Electrochemical Transistor


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Abstract

Organic electrochemical transistors (OECTs) exhibit strong technological potential for various applications in bioelectronics, especially as miniaturized, point-of-care biosensors because of their efficient transducing ability. To date, however, the majority of reported OECTs rely on the use of p-type (hole transporting) polymer mixed conductors, due to the limited number of n-type (electron transporting) materials suitable for operation in aqueous electrolytes and the low performance of existing ones. Here, we show that a simple solvent engineering approach boosts the performance of OECTs comprising an n-type, naphthalenediimide based copolymer in the channel. The addition of acetone, a rather bad solvent for the copolymer, into the chloroform-based polymer solution used to cast the film leads to a 3-fold increase in OECT transconductance, as a result of the simultaneous increase in volumetric capacitance and electron mobility in the channel. The enhanced electrochemical activity of the polymer film allows to build high performance glucose sensors with a detection limit at 10 nM of glucose and a dynamic range of more than 8 orders of magnitude. The approach proposed here introduces a new tool for improving, concurrently, the conduction of ionic and electronic charge carriers in polymer mixed conductors and can be utilized for a number of bioelectronic applications that rely on efficient OECT operation.
1. Introduction

Ever since its first demonstration by Wrighton and colleagues,[1] the organic electrochemical transistor (OECT) has attracted great interest for a variety of applications including biosensors,[2] printed logic circuits[3] and neuromorphic computing.[4] These transistors operate in aqueous electrolytes and transduce, as well as amplify, low-magnitude ionic fluctuations into electronic signals, more efficiently than any other transistor technology to date.[5] The OECT channel comprises of organic mixed conductors, i.e., typically polymeric materials that support simultaneous electronic and ionic charge transport through their bulk.[6] Alongside their inherent ability to undergo reversible electrochemical reactions, their fuzzy/soft surfaces facilitate interactions with biological molecules, rendering the OECT a particularly suitable device for transducing biological signals.[7] For example, polymeric materials applied at the channel or as a coating on the gate electrode promote adsorption of catalytic proteins on the active area, transforming these high gain transistors into electrochemical metabolite sensors.[8]

In fact, the early examples of OECT based biochemical sensors revealed the great potential of these devices to invade the biosensor industry which has an estimated market size of US$ 13 billion annual turnover.[11][12]

The organic mixed conductor of choice for OECTs has been the conducting polymer poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS, because of its commercial availability, charge storage/transport capability, and biocompatibility. As a result of its two-component nature, PEDOT:PSS films contain distinct ion and electron transport pathways, where the water-borne dopant (PSS) phase is physically separated from PEDOT and enables the conduction of hydrated ions. [13][14] More recently, the use of hydrophilic p-type polymer semiconductors in OECTs has been demonstrated, with transconductance values competing with that of PEDOT:PSS. These mixed conductors contain hydrophilic side chains that facilitate...
the penetration/transport of hydrated ions and their interactions with the conjugated backbone.\textsuperscript{[15]} \textsuperscript{[16]} The concept of tethering ion-transporting side chains along the backbone has also been applied to their n-type counterparts, which are predominantly based on napthalenediimides (NDIs),\textsuperscript{[17]} and have led to the development of n-type OECTs with decent performance and stable operation in aqueous media.\textsuperscript{[18]} N-type OECTs are essential for the fabrication of low cost and large area complementary circuits but they also open up an avenue for applications, relying on electron transfer.\textsuperscript{[19]} For instance, we have recently reported, for the first time, the use of an n-type OECT as a fast and sensitive metabolite sensor.\textsuperscript{[8]} Due to its electron transporting properties, the n-type channel accepts electrons formed upon the enzymatic reaction and acts as a series of redox centers transmitting the detected bio-signal. Despite the recent progress, the reported transconductance values of the best performing n-type OECTs are still ~3 orders of magnitude lower compared with that of the p-type counterparts.\textsuperscript{[17]} The benefits of these devices are thus hampered due to their low performance.

OECTs operate in depletion or accumulation mode depending on the type of the material used in the channel and follow one principle: application of a gate bias ($V_G$) drives ions into the OECT channel that electrostatically compensate for the electronic charges, modulating the drain current ($I_D$).\textsuperscript{[20]} The electrochemical doping/de-doping occurs over the entire volume of the polymer channel, as opposed to a thin interfacial region typical in thin-film transistors.\textsuperscript{[7]} As such, the gain of OECTs, i.e. the transconductance ($g_m = \partial I_D / \partial V_G$) is record high. The $g_m$ is a steady-state property describing qualitatively how efficient the ion-to-electron coupling is and depends on both the ion-induced charge storage capacity (expressed as the capacitance) and the electron mobility of the channel.\textsuperscript{[21]}

Our current understanding of what makes a material an efficient mixed conductor is mostly built upon studies with PEDOT:PSS, suggesting that ion-to-electron coupling depends on thin
film microstructure and morphology. These studies demonstrate the need of a material with equally high electronic mobility and volumetric capacitance and different morphologies to support these. Even though strategies for enhancing the electron mobility of conjugated polymers via control of morphology are relatively more established, doing so while increasing capacitance is a new design challenge. Moreover, the sensitivity of organic semiconductors to small changes in morphology requires characterizing film morphology/structure during device operation. [22] Recent studies with these polymers evidence a significant, voltage dependent, distortion of the polymer lattice/nano-structure upon ionic doping, which influences the electronic charge transport and thus the performance of OECTs. [23] Another factor to consider is the water that is coupled to the dopant ions penetrating into the films, modifying the film morphology and affecting the electronic charge transport. The latter has not been a concern for PEDOT:PSS films which contain a large water swollen phase in contrast to single component, un-doped semiconducting polymers. [24] With an understanding of mixed transport-morphology relationships, it would be possible to rationally design semiconducting materials and choose processing conditions to target to a film with optimized transport properties.

Research efforts in the field of solution processed organic electronics have shown us that the electronic properties of conjugated polymers films can be greatly enhanced via modifications in processing, e.g. by use of simple solvent engineering concepts. [25] For instance, casting a polymer film from a mixture of two solvents with extreme differences in their volatility properties can result in optimum film morphology relevant to the end application. [26] Sirringhaus and coworkers reported that high boiling point solvents in the polymer casting solution promote the formation of highly ordered microcrystalline structures in poly(3-hexylthiophene) (P3HT), significantly improving the charge carrier mobility. [27] Chang et al demonstrated that a small amount of a “bad” solvent added into the “good” solvent of the polymer solution can improve the crystallinity of the resulting films, enhancing the charge
carrier mobility. Such approaches have not yet been utilized for co-optimization of ionic and electronic transport in semiconducting polymers.

Here we show that when an n-type mixed conductor film is cast from a mixture of a bad solvent (i.e. acetone) and a good solvent (i.e. chloroform), the OECT transconductance increases more than 3 times, as a result of the simultaneous increase of electron mobility ($\mu$) and volumetric capacitance ($C^*$). X-ray scattering and atomic force microscopy studies reveal dynamic structural and morphological differences between the films cast from different solvent mixtures and suggest that film drying kinetics govern molecular ordering of the n-type polymer chains, leading to an optimal morphology that maximizes $\mu$ alongside $C^*$. Conducting grazing incidence wide angle X-ray scattering of electrolyte-swollen and electrochemically reduced states of the film, we conclude that ions more extensively penetrate into the crystalline domains of the films coated from the solvent mixture as well as improve the structural order therein. The enhanced electrochemical activity of the n-type polymer achieved with solvent engineering is leveraged to build mediator-free, enzymatic glucose sensors with a dynamic range between 10 nM and 10 mM of glucose and double the sensitivity of the pristine devices. The approach proposed here introduces a new tool for improving the simultaneous conduction of ions and electrons in polymer mixed conductors, as well as the performance of devices relying on mixed conduction.

2. Results and Discussion

The random copolymer of N,N'-bis(7-glycol)-naphthalene-1,4,5,8-bis(dicarboximide) and N,N'-bis (2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide), copolymerized with bithiophene, known as P-90, is an electron transporting, random copolymer that has been synthesized based on an existing protocol (see Figure 1 for chemical structure). We used photolithography to fabricate OECTs with micron-scale channel dimensions and spin coated P-
90 films from five different acetone:chloroform mixtures which contain concentrations of acetone ranging from 0 to 20 vol.% of the total solution. Hereafter we will refer to these devices that contain films cast from 0, 5, 10, 15 and 20 vol.% acetone as the pristine, 5 %, 10 %, 15 % and 20 %- device, respectively. In all cases, the polymer channels are in direct contact with the aqueous electrolyte, NaCl\(_{(aq)}\) 0.1 M, into which an Ag/AgCl gate electrode is immersed, as depicted in Figure S1a.

**Figure 1.** a) Chemical structure of the n-type copolymer, P-90. b) Drain current \((I_D)\) and c) transconductance \((g_m)\) versus gate voltage \((V_G)\) of P-90 OECTs prepared from chloroform:acetone mixtures. d) OECT peak transconductance measured at \(V_D= 0.6\) V, f) electron mobility \((\mu_{\text{OECT}})\) extracted at \(V_D=0.6\) V and \(V_G=0.45\) V and e) volumetric capacitance \((C^*)\) of P-90 film as a function of acetone formulation content. Error bars in d-f represent standard deviations calculated from measurements of 3 devices for each solvent mixture.

Upon application of a positive gate voltage \((V_G)\), Na\(^+\) ions from the electrolyte solution are injected into the P-90 channel, electrochemically doping the polymer and leading to an increase of the channel conductance and the OECT drain current \((I_D)\) (Figure S1b-f). Figure 1b shows
that $I_D$ increases with increasing $V_G$, consistent with the accumulation mode operation of transistors. All the devices under study switch ON at $V_G = \sim 0.2$ V. Importantly, with increasing the acetone percentage in P-90 casting solution, the ON current increases, with the highest $I_D$ measured for the 15 % -device (i.e., 1.25 μA at $V_D = V_G = 0.6$V), while for the 20 % -device, the current drops (Figure 1b). Overall, the 15 % -devices exhibit a 3-fold increase in channel current compared with the pristine-devices. The OECT transconductance ($g_m$) also follows this trend (Figure 1c-d). The $g_m$ is 4.7 μS for the 15 % -device compared with 1.5 μS of the pristine device measured at $V_G = 0.45$ V. These results show that a simple modification of the polymer solution used to cast the film drastically improves the performance of the n-type OECTs. As reported by Rivnay et al.,[29] the transconductance of the OECTs is determined by the product of the electronic mobility ($\mu$) and the volumetric capacitance ($C^*$) defined mathematically in the following equation: $g_m = \frac{W}{L}d \mu C^*(V_T - V_G)$, where $V_T$ is the threshold voltage and $W$, $L$, and $d$ represent the channel geometry (width, length, and thickness, respectively). From the square root of $I_D$ vs. $V_G$ (Figure S2), we find that the $V_T$ is identical for all the devices studied ($V_T \sim 0.2$ V) and thus has no contribution to the differences observed in $g_m$. The impact of solvent engineering is thus on the product of the electronic mobility and volumetric capacitance ($\mu \cdot C^*$).

To decouple this product into $\mu$ and $C^*$ and verify which property is affected, we first use the previously reported impedance matching method to determine the electronic carrier transit time,[30] and consequently the $\mu$. Figure 1e shows that the electron mobility of the film increases from ca. $0.85 \times 10^{-4}$ to ca. $1.85 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, when the casting solution contains 15 vol. % acetone. In parallel, we calculate $C^*$ via electrochemical impedance spectroscopy (EIS) measurements at the OECT channels (Figure S3). We found that acetone enhances the charge storage capacity of the film: $C^*$ is 217 F/cm$^3$ and 317 F/cm$^3$ for the pristine device and 15 % -device, respectively, accounting for ca. 1.5 times increase (Figure 1f). The product of $\mu$ and $C^*$ is more than 3 times higher for the 15 % -device (0.057) compared with the pristine device
The OECT output characteristics and materials figure of merit for each of the device under study are summarized in Table S1. These results evidence that the increase in the current and transconductance values recorded for the 15 \% device is due to simultaneous increase of the capacitance and electron mobility, suggesting enhanced electrochemical activity of the polymer film. Moreover, regardless of the mixture used to cast the solution, the P-90 OECTs have excellent operational stability. Stability measurements show no degradation of the OECT channels when tested for 2 hours under continuous redox-cycling in the aqueous electrolyte (Figure S4). Although in this study we use acetone as a solvent additive for the P-90 solution in chloroform, different solvent mixtures can be explored. For instance, casting films from a mixture of chloroform with a small amount of high boiling point solvents (e.g. chlorobenzene and ethylene glycol) also improves the OECT performance, i.e., we record an increase in the drain current above the threshold voltage as well as in the maximum transconductance (Figure S5). Such solvents are postulated to change the conjugated polymer film morphology by a change in the film formation kinetics during drying as well by forced aggregation in the solution state.\footnote{31} We also found that the proposed solvent engineering concept is applicable to p-type polymer mixed conductors. By adding different amounts of acetone into chloroform, we observe a clear increase in the OECT performance and electrochemical activity of a top performing p-type polymer (a polythiophene copolymer with grafted glycol side chains)\footnote{23,24} as shown in Figure S6.

Taking advantage of this enhanced electrochemical activity, we employ the 15 vol.\%- OECT for electrochemical sensing of glucose in aqueous media. Recently, P-90 based OECTs have been reported as an efficient platform for enzymatic detection of lactate in bodily fluids.\footnote{8} The interactions between the enzyme and P-90 bring the protein in close proximity to the film, enabling the transfer of electrons generated during the enzymatic reaction to the conjugated polymer.\footnote{8} As P-90 has the ability to stabilize electrons on its backbone, the net effect of the
enzymatic reaction in the electrolyte is an increase in the conductivity of P-90, thereby turning the device ON. We incubated the device active area (the channel and the gate, Figure S7a) in a PBS solution containing the enzyme, glucose oxidase (GOx). The electrocatalytic reactions occurring between GOx and glucose are depicted in Figure S7b. As shown in Figure 2a and b, with each addition of glucose into the electrolyte, the current of the channel (cast from 0 or 15 vol.% acetone solution, respectively) increases stepwise while the biasing conditions remain constant. When we wash glucose away from the solution by rinsing the device with PBS, the drain current reverts to its original value. As a pre-determined amount of glucose is once more added to the measurement solution, followed by a second rinsing step, the sensor responds with a good degree of reversibility, evidencing its reusability (Figure S8). Both OECTs have excellent sensitivity with a low detection limit at about 10 nM and a wide dynamic range (8 orders of magnitude). Remarkably, the chronoamperometric response of the 15 % device to real-time additions of increasing concentrations of glucose shows higher resolution and is better defined than that of the pristine device. Calibration curves deduced from these measurements demonstrate that the sensitivity of 15 % device is ca. 2 times higher than that of the pristine device for low glucose concentrations (10 nM < c < 0.1 M). In the low concentration range, the slope is calculated to be $0.027 \pm 2.28 \times 10^{-3}$ ($R_1=0.97$) for the 15 % device and $0.011 \pm 7.35 \times 10^{-4}$ ($R_1=0.98$) for the pristine device. Both sensors exhibit high sensitivity for higher concentrations of glucose (> 0.1 M). In this concentration regime, the linear fits yield a slope of $0.93 \pm 8.44 \times 10^{-3}$ ($R_2=0.99$) and $0.73 \pm 8.7 \times 10^{-2}$ ($R_2=0.99$) for the 15 % device and the pristine one, respectively. In the higher gain OECT, the channel is able to generate more current when the enzyme oxidizes glucose. This increases the quality of the readout signal, i.e., the signal to noise ratio. A higher gain also translates into faster response of the biosensor. We observe that with each addition of glucose, the current of the 15 % device reaches a saturation value faster than that of the pristine device (Figure 2d).
Figure 2. Real-time response of glucose biosensors as successive amounts of glucose is added into the PBS solution. GOx was drop cast on top of the active area which contains the P-90 channel \( (L = 10 \, \mu m, \, W = 100 \, \mu m, \, d = 50 \, nm) \) and P-90 coated Au electrode \( (500 \, \mu m \times 500 \, \mu m) \) used as the gate. P-90 is cast from a) pure chloroform solution and b) mixture with 15 vol.% acetone. After addition of 20 mM of glucose, the devices were rinsed with PBS. The zoomed-in areas represent the response of the corresponding sensor to low amounts of the analyte \( (10 \, nM \, to \, 250 \, \mu M) \). c) Normalized response (NR) of the pristine (black) and 15 %-OECT (red) to glucose at the low concentration regime. The error bars were derived from recordings with 3 channels. The slopes for two linear regions were calculated with a linear fit with the corresponding error. For all measurements, \( V_D = 0.3 \, V \) and \( V_G = 0.5 \, V \).

The results above show that our solvent engineering concept improves the OECT performance and the electrochemical activity of the P-90, allowing for the realization of highly sensitive glucose biosensors. To understand the origin of this enhancement, we performed a number of electrochemical measurements, as summarized in Figure 3. The cyclic voltammetry (CV) curve of pristine P-90 films contain features that become sharper and more intense as the concentration of acetone increases up to 15 vol.%, while a further increase reduces the current,
in particular of the reduction peak at ca. -0.75 V (Figure 3a). For the 20 vol.% film, we observe that the peak at ca. -0.5 V disappears, which may be attributed to the reduction of the neutral species via the formation of a radical anion).\[^{32}\] These observations indicate faster electron charging and discharging processes within the polymer films cast from solutions containing acetone ≤ 15 vol.%.\[^{33, 34}\] Further evidence for acetone-enhanced electrochemical activity comes from the spectroelectrochemistry measurements where we monitor the changes in the UV-VIS spectrum of the films as they undergo electrochemical doping with electrolyte ions.

First, we investigate the spectra of the dry P-90 films before any exposure to the electrolyte (Figure 3b). The spectra of all films contain two main absorption bands, one around 400 nm, known to arise from the $\pi - \pi^*$ transition of the thiophene rings, and a broader feature with a maximum at around 725 nm which has been attributed to the intramolecular charge transfer complex. Upon increasing the acetone percentage in the P-90 solution, the NDI-related absorption peak at 725 nm shifts slightly to higher wavelengths (i.e., to 736 nm for 20 vol. % acetone) and a shoulder appears at ca. 800 nm with a slight increase in the overall absorbance intensity. These results suggest an increase in the planarization, hence the backbone conjugation length, and the formation of aggregates, triggered by the addition of acetone into the polymer solution in chloroform.\[^{28}\] Importantly, this aggregation starts already in the solution. While the absorbance spectrum of the P-90 in chloroform exhibits one maximum at ca. 600 nm, upon addition of acetone into the solution, a shoulder appears at ca. 750 nm, which evolves to be the most dominant peak in the spectrum with a further increase in the acetone content of the solution (Figure S9). The red shifted absorbance feature indicates the formation of aggregates in the solution as the ratio of bad solvent to good solvent increases.

When we immerse these films in NaCl\(_{\text{(aq)}}\) 0.1 M and start applying doping potentials, we observe a reduction of the intensity of low energy absorption at 725 nm and a simultaneous increase in the intensity of a new absorption feature at 450 nm (Figure S10). These changes are
in agreement with the previously reported electrochemical doping studies of the n-type analogue polymer p(gNDI-gT2),\(^{[35]}\)\(^{[17]}\) indicating that all the films switch from a neutral to a reduced state via the formation of new optical transitions. As shown in Figure 3c, when the film is cast from a solution containing acetone, its spectrum exhibits larger changes in the intensity of the \(\pi-\pi^*\) and polaron related absorption features upon electrochemical doping. The charge recorded at each system follows this trend: 15 vol.% film generates the highest amount of charge when doped at 0.6 V vs Ag/AgCl electrode in the electrolyte (Figure 3d). This is another indication of enhanced electrochemical activity for the P-90 films cast from 15 vol.% acetone. 

In order to evaluate the stability of these films subject to n-type doping in aqueous solution, we performed spectroelectrochemical stability measurements (Figure S11). For all the P-90 films under study, we found that upon 5 consecutive doping-dedoping voltage pulses, the spectral changes are identical between the 1\(^{st}\) and the 5\(^{th}\) doping cycle. This is in agreement with the OECT operational stability studies (Figure S4), evidencing that the films, regardless of the solvent that they are cast from, preserve their structure against repeated redox switching in aqueous electrolytes. Enhanced electrochemical activity of the P-90 achieved by solvent engineering is thus resilient to continuous operation.

Finally, we use electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) to quantify, simultaneously, the mass (ions and water) taken-up by the polymer films and the amount of charge generated during the electrochemical doping.\(^{[13]}\) First, we measure the passive swelling of two selected P-90 films on QCM-D sensors, one that is cast from pure chloroform and another from 15 vol.% acetone containing solution, when they are immersed in NaCl\(_\text{(aq)}\) 0.1 M. The pristine film swells to 39\% ± 2 \% of its initial mass in the electrolyte while the swelling is 46\% ± 2 \% for the one cast from 15 vol.% acetone solution, suggesting facile diffusion of water and hydrated ions therein (Figure S12). Upon application of a doping potential, the 15 vol.% film takes up more mass compared to the pristine one: the
mass accumulating inside the film at the end of the doping pulse is 295 ng/cm$^2$ and 186 ng/cm$^2$ for the 15 vol.% film and the pristine film, respectively (Figure 3e). Furthermore, the charge recorded from these films in-situ upon electrochemical doping with Na$^+$ ions is calculated to be $2.6 \times 10^{-3}$ C for the 15 vol.% film, while it is $6.1 \times 10^{-4}$ C for the pristine one. These values are well in line with the volumetric capacitance calculated from the electrochemical impedance spectra of films recorded from the OECT channels (Figure 1f) and demonstrate the improvement in the ionic charging of the P-90 films as a result of solvent engineering.

Figure 3. a) Cyclic voltammetry curves of P-90 films measured in NaCl$_{\text{aq}}$ 0.1 M with a scan rate of 50 mV/s. The arrow indicates the scanning direction. b) UV-VIS spectra of the dry films. c) The absolute changes in the intensity of the absorption peaks and d) the charge recorded simultaneously as a function of applied potential in NaCl$_{\text{aq}}$ 0.1 M. e) Electrochemical quartz crystal microbalance with dissipation monitoring (QCM-D) analysis for P-90 films casted from 0 (black lines) and 15 vol.% acetone containing solution (blue). The applied voltage pulse is -0.45 V vs. $V_{OC}$ in NaCl$_{\text{aq}}$ 0.1 M. The doping induced changes in the mass of the films as well as the charge extracted are higher for the 15 vol.% film compared to the pristine one.

We find that both the electron mobility as well as the volumetric capacitance of the polymer films increase simultaneously when the films are cast from acetone bearing solutions. The treatment, also, slightly improves the water/ion uptake capacity of the film. We predict that acetone affects the microstructure and morphology of the P-90 film in a way that facilitates
both ionic charging (ion penetration and transport) as well as electronic charge transport. To elucidate the structural effects underlying device improvement, peak performing films (cast from chloroform with 15 vol.% acetone) and pristine films (cast from neat chloroform) were investigated using grazing incidence wide angle X-ray scattering (GIWAXS). Figure S13 shows the 2-D scattering patterns of these two films in three conditions 1) as cast, 2) after successive *ex situ* electrolyte exposure and 3) after *ex situ* electrochemical reduction in NaCl solution. The all alkylated analogue P(NDI2OD-T2) presents a predominately face on structure, with lamellar and backbone ordering parallel to the substrate,[36] however, here P-90 presents a continuum of face-on to edge-on ordering, independent of solvent that is cast from. Scattering from side chain lamellae and π-stacking occurs both in and out of the plane of the sample, while backbone ordering remains parallel to the substrate. In-plane (Figure 4 a and c), both as cast films show a low $q$ lamellar peak, (100) around ~0.25 Å$^{-1}$, and backbone peaks representing two polymorphs, (001) at ~0.46 Å$^{-1}$ and (001)' at ~0.89 Å$^{-1}$. Both films also display a second order backbone peak due to the second polymorph, (002)' at ~0.89 Å$^{-1}$. Expected in-plane π-stack peaks, (010) around 1.6 Å$^{-1}$, are weak in the films cast with 15 vol.% acetone and unresolvable in the pristine film. Out of plane (Figure 4 b and d), the as cast films both display a low $q$ lamellar peak (100) around ~0.29 Å$^{-1}$ with weak second (200) and third (300) order shoulders, and π-stack peaks, (010) around ~1.6 Å$^{-1}$. These patterns are in line with previous GIWAXS investigations of both P-90[17] and the all glycolated homopolymer.[18]
Figure 4. a) In-plane and b) out-of-plane line cuts from 2-D grazing incidence wide angle X-ray scattering patterns of P-90 films cast from neat chloroform. c) In-plane and d) out-of-plane line cuts from 2-D grazing incidence wide angle X-ray scattering patterns of P-90 films cast from chloroform with 15 vol.% acetone. In all plots, green indicates as cast, blue indicates electrolyte (NaCl(aq) 0.1 M) exposed, and red indicates electrochemically reduced state (-0.6 V vs Ag/AgCl) of the films. Line cuts offset in intensity for the sake of clarity.

From the as cast films, there is little reason to argue that the films cast from either pristine chloroform or a chloroform acetone mixture should display better performance in an OECT based device than the other. However, successive ex situ electrolyte exposure and electrochemical reduction reveal dynamic structural differences. Pristine films cast from chloroform show limited in-plane structural change upon electrolyte exposure and electrochemical reduction (Figure 4a). Whereas, the film cast from 15 vol.% acetone mixture shows a much larger decrease in lamellar scattering with electrolyte exposure, followed by a marked increase in backbone scattering upon electrochemical reduction (Figure 4c). Out of plane, both types of films display a disruption to the lamellar ordering upon electrolyte exposure.
With further electrochemical reduction, the lamellar disruption persisted in the pristine chloroform cast film but was partially reversed with a significant increase in the low order out of plane lamellar scattering.

It is expected that ion penetration into the polymer crystallites occurs amongst the side chains, disrupting lamellar ordering and decreasing lamellar scattering. Thus, the dynamic structure in the case of the pristine P-90 is interpreted as a preferential ion penetration into the side chains of the edge-on oriented crystallites, with more limited ion penetration in the face-on crystallites. On the contrary, the larger degree of in-plane lamellar disruption in the 15 vol.% acetone cast P-90 implies more extensive ion penetration into face-on crystallites. From this increased extent of ion intercalation for the film cast from 15 vol.% acetone, it is reasonable expect a higher volumetric capacitance. Equally important is the strong enhancement of backbone scattering present only in the electrochemically reduced 15 vol.% acetone cast P-90 film. This suggests improved in-plane backbone ordering, which should lead to improved intra-molecular charge transport, and thus improved in-plane charge transport which is pertinent to planar OECT devices.

We also employed atomic force microscopy (AFM) to investigate the surface morphology of the P-90 films on the OECT channels after they have been gated in NaCl(aq.) 0.1 M. These films show distinct differences in their surface topography when cast from different solvent mixtures (Figure S14). For instance, with 15 vol.% acetone in the casting solution, the surface of the P-90 films is rougher (3.23 nm) than that of the pristine P-90 film (1.78 nm). 15 vol.% film also exhibits distinctly more hills and valleys on its surface compared with the pristine film and these structures seem to be wider than those found in films cast from other mixture ratios. We envisage that such a surface may facilitate ion penetration inside the film, enhancing the accessibility of the backbone to doping ions, the result of which is the volumetric capacitance.
maximized for this film. In contrast, the surface topography of the 20 vol.% film shows an extreme heterogeneity and discontinuity. By pre-aggregating the chains in solution, the final microstructure enables a more extensive ion transport as well as an uncluttered surface for facile ion injection responsible for the enhancement of the volumetric capacitance.

3. Conclusion
We reported a simple solvent engineering approach to improve the performance of an n-type, accumulation mode OECT. By including a low amount of “bad” solvent (acetone) in the “good” solvent (chloroform) of the polymer, we improved the steady-state performance of the OECTs more than 3-times. The improvement of the OECT transconductance is because of the simultaneous increase in volumetric capacitance and OECT mobility, as verified by device physics analysis, electrochemical impedance spectroscopy, spectroelectrochemistry and EQCM-D measurements. GIWAXS and AFM measurements show distinct differences of the structure and surface morphology of the films cast from different acetone:chloroform mixtures, as a result of the different evaporation rates of these solvents and their interactions during film formation. While the ions seem to preferentially intercalate into the edge-on oriented crystallites of the pristine film, for the acetone treated film, ion penetration is more effective, spread into the side chains of all crystallites, regardless of their orientation. Moreover, doping leads to improved backbone ordering for the electrochemically reduced 15 vol.% acetone cast P-90 film, which is not observed for the pristine one. The optimum morphology/structure for mixed transport is achieved when incorporating 15 vol.% acetone in the chloroform-based polymer solution. This film has pronounced features on its surface, enhanced interactions with electrolyte ions and improved charge transport down the polymer chain, and thus improved in-plane charge transport which is pertinent to planar OECT devices. The increase in OECT gain is reflected in the improved sensitivity of glucose biosensors based on P-90 OECTs. The
approach described here utilizes fundamental principles that could be used to identify solvent systems suitable for other polymer semiconductors and to improve the performance of electrochemical devices which rely on organic mixed conductors.

4. Experimental Section

Materials: P-90 was synthesized as described previously. All the other chemicals were purchased from Sigma Aldrich and used as received. The P-90 solutions were prepared by keeping the polymer concentration constant at 5 mg/ml in chloroform with varying the added amount of acetone from 0 to 20 vol.%. 

OECT fabrication: OECTs were fabricated using photolithography process described previously, with slight modifications. The substrates were cleaned by sonication, first by immersion 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 bilayer photoresist structure was spun in order to facilitate the lift-off process, achieved by coating LOR 5B (Microchem) and S1813 (Shipley), which was exposed to UV light using the EVG 6200 mask alignment system and developed in MF-319 developer. A 10 nm thick layer of Cr, followed by a 100 nm layer of Au were deposited via magnetron sputtering (Equipment Support Company Ltd. ESCRD4) and lifted off with appropriate solvents. Surface activation was done in an O₂ plasma etcher. A Parylene C film was vaporized using a SCS Labcoater 2 to a final thickness of 1.7 µm and was fixed on substrates using 3-(trimethoxysilyl)propyl methacrylate as an adhesion promoter. A second Parylene C layer, acting as a sacrificial layer for polymer patterning, was used. AZ9260 (Microchemicals) served to pattern the areas of Parylene C to be removed by dry etching after exposure and development with AZ developer. Reactive ion etching (Oxford Instruments Plasmalab 100 - ICP 380) was lastly employed to expose both the gate and the channels for
polymer deposition, as well as the contacts. The polymer solutions in different acetone:chloroform mixtures were deposited onto the substrates 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 (NI-PXI) with custom-written control code in LabVIEW. All measurements were performed using an Ag/AgCl pellet (2 mm × 2 mm – Warner instruments) as the gate electrode. The electrolyte was contained in a PDMS well on top of the OECT active area and the electrolyte volume was constant at 100 μL for all measurements. Mobility of the polymer channel ($\mu_{OECT}$) was determined by applying a constant drain bias to the channel ($V_D = 0.6$ V) and a sinusoidal voltage pulse at the gate electrode ($\Delta V_G = 50$ mV) with a pre-set offset ($V_G = 0.45$ V, offset) and at varying frequencies ($f$). The frequency domain relation between the measured gate current ($\Delta I_G$) and drain current ($\Delta I_D$) is:[30]

$$\text{eq. 1: } \Delta I_G (f) = 2 \pi f \tau_e \Delta I_D (f)$$

Matching the gate current and drain current derived impedance yields electron transit time in the channel ($\tau_e$), as detailed by Rivnay et al.[28] Using the $\tau_e$, the channel length ($L$), and the $V_D$, $\mu_{OECT}$ can be estimated as:

$$\text{eq. 2: } \mu_{OECT} = \frac{L^2}{\tau_e V_D}$$

Electrochemical analysis: Cyclic voltammograms were recorded using an Autolab potentiostat with 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. The measurements were carried in 0.1 M NaCl aqueous solution at a scan rate of 50 mV/s. Electrochemical impedance spectroscopy (EIS) was performed with the same three-electrode configuration using a potentiostat (Metrohm Autolab) and spectra were recorded from 10 kHz
to 0.1 Hz. The measurements were performed either at $V_{oc}$ or at a DC offset potential (doping) with an AC amplitude of 10 mV. The capacitance-frequency plots of each film were constructed by using the complex impedance formula as described in equation 3:

\[
Z = \sqrt{R^2 + \frac{1}{\omega^2 C^2}}
\]

where $C$ is the capacitance, $R$ the resistance and $\omega$ the angular frequency.

**Spectroelectrochemistry:** Spectroelectrochemical analysis was performed using an Ocean Optics HL-2000-FHSA halogen light source, Ocean Optics QE65 Pro Spectrometer, OceanView software, Keithley 2602A sourcemeter and a sample holder purchased from redox.me (i.e. MM SPECTRO-EFC). The polymer solutions in different acetone:chloroform mixtures were deposited on ITO substrates by spin coating for 30 seconds, at 1000 rpm with 500 rpm/s acceleration. An Ag/AgCl electrode (redox.me - Ag/AgCl 30mm) was inserted into the sample holder, which was then filled with 1.3 mL of 0.1 M NaCl solution. A blank ITO was placed into the chamber, with the light source and spectrometer fibers attached to the chamber. The setup was then calibrated for absorbance measurements in OceanView software. The blank ITO was then replaced with a polymer-coated ITO. The Keithley was connected to the Ag|AgCl electrode and to the ITO surface. Unless stated otherwise, using a custom-made LabVIEW code, the Keithley was configured to provide a voltage ramp from -0.2 V (de-doping voltage) to 0.6 V (doping voltage) with a step of 0.1 V lasting for 40 seconds. The absorbance was recorded at the 30th second of every voltage step, until the cycle rolls over from 0.6 V to -0.2 V, and absorbance of the reversed polymer state is recorded as well.

**Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D):** We performed EQCM-D measurements using a Q-sense analyzer (QE401, Biolin Scientific). Swelling measurements were performed as follows. First, we recorded the QCM-D response of the bare Au sensors in the air, followed by injection of NaCl$_{aq.}$ 0.1M solution into the chamber. This resulted in large shifts in $f$ and $D$, due to the density differences between the two media.
which must be excluded from the swelling percentage calculation. The measurements were then
stopped, the sensors were removed and P-90 layers were cast directly on the same sensors. The
absolute \( f \) value for each polymer coated sensor was obtained both in air and in \( \text{NaCl}_{(aq.)} 0.1 \text{M} \),
after the \( f \) signal was perfectly flat (i.e., \( f < 0.5 \text{ Hz}/2 \text{min} \)) assuring that the system is in equilibrium.
We then compared the absolute difference in \( f \) for multiple overtones between the bare sensor
and the polymer coated sensors, both in air and in the electrolyte, by using the function “stitched
data” of Q-soft software. This function compares the selected datasets based on the raw
frequencies measured and excludes the effect of the different densities between the two media
(Figure S12). Thus, the difference of the \( f \) values of the stitched data is directly analogous to
the thickness of the polymer in both media, which is calculated by using the Sauerbrey equation
quantifying the mass (\( m \)), using one overtone as:

\[
\text{eq. 4:} \quad \Delta m = \frac{-17.7}{n} \Delta f_n
\]

For the EQCM-D measurements, we coupled the Q-sense electrochemistry module comprising
the three-electrode setup with the Autolab PGstat128N potentiostat. Since the films become
soft and uptake a significant amount of water under doping potentials, we used the Kelvin-
Voigt viscoelastic model to fit the data. To quantify the mass correctly, we used the \( f \) and \( D \)
data of three different overtones (5\textsuperscript{th}, 7\textsuperscript{th} and 9\textsuperscript{th}). The good quality of the fits guaranteed the
accurate mass calculation accumulated within the films upon applied potentials. A Kelvin-
Voigt element has a complex shear modulus as described in equation 5:

\[
\text{eq. 5:} \quad G^* = \mu + 2\pi f \eta
\]

where \( G^* \) is the complex shear modulus, \( \mu \) is elasticity (kgm\(^{-1}\)s\(^{-2}\)), \( \eta \) is viscosity (kgm\(^{-1}\)s\(^{-1}\)) and
\( f \) is the frequency. Q-Tools and D-find software were used for the modeling and data analysis.

\textit{Grazing incidence wide angle scattering studies (GIWAXS):} 2-D GIWAXS patterns were
collected from P-90 films spun from chloroform and chloroform/acetone (15 vol\% acetone) 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 ($\lambda = 1.135$ Å) synchrotron radiation with a 0.14° incident angle and measured with a Pilatus 1M hybrid pixel array detector during 5 second exposures. All data analysis was carried out with GIXSGUI Matlab toolbox.[37] 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 -0.6 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.

Atomic force microscopy (AFM): The topography and the roughness of the polymer films were investigated using a Dimension Icon SPM-IAC AFM (Bruker) in tapping mode in air. The measurements were performed on the surface of the best performing OECT channels for each case.

Chronoamperometric sensing measurements: For the sensing experiments, GOx in PBS (1 mg/mL) was drop-casted on the device active area and left for 30 minutes to adsorb in ambient conditions. Glucose was dissolved as stock solutions in PBS and stored at 4°C until use. Current-voltage characteristics of the devices were recorded using a Keithley 2602A dual source meter. The OECTs were constantly biased at $V_D = 0.3$ V and $V_G = 0.5$ V, using the planar P-90 coated gold gate electrode (580 µm x 580 µm). After a steady $I_D$ baseline was obtained (current at zero analyte concentration = $I_0$), changes in $I_D$ in response to incremental additions of glucose solutions into the electrolyte were monitored as a function of time. In these experiments where we successively increased glucose concentration that the sensor was exposed to, we presumed that upon the addition of a new glucose concentration into the measurement solution, the previous amount has been mostly consumed by the enzyme. When $I_D$ reached saturation at a given glucose concentration, the next glucose concentration was
We evaluated the saturation time of each sensor as the time needed for the $I_D$ to reach 90% of its maximum steady-state value at a given glucose concentration. The volume of the solution was kept constant at 40 μL. The calibration curves were obtained by normalizing the change in the current response of the channel to a particular glucose concentration ($I_D - I_0$) with the maximum current that the channel generates ($I_{\text{max}}$):

$$ NR = \left| \frac{I_D - I_0}{I_{\text{max}}} \right| $$

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

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