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Smaller counter cation for better transconductance in anionic conjugated polyelectrolytes

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Conjugated polyelectrolytes (CPEs) are in focus of research as they combine their inherent electrical conductivity and the ability to interact with ions in aqueous solutions or biological systems. Still it is not understood to which degree the counter ion in CPEs influences the properties of the CPE itself and the performance of electronic transducers. In order to investigate this, we synthesized three different conjugated polyelectrolytes PTHS^-X^+ , which had the same polythiophene backbone, but different X^+ counter ions; the bulky tetrabutylammonium (TBA^+), tetraethylammonium (TEA^+) and the smallest tetramethylammonium (TMA^+). At the interface with biological systems, thin CPE films have to be stable in aqueous environment and should allow the inward and outward flow of ions from the electrolyte. Since the studied PTHS^-X^+ are differently soluble in water, we additionally investigated the optical properties of pristine PTHS^-X^+ as well as of cross-linked PTHS^-X^+ via UV-Vis absorption spectroscopy. $\text{PTHS}^-\text{TMA}^+$ exhibits better aggregation, fast inter-diffusion of ions and fast recovery from the oxidized state. Additionally,

spectroelectrochemical and cyclic voltammetric as well as electrochemical capacitance investigations showed that $\text{PTHS}^-\text{TMA}^+$ could be oxidized to a higher degree. This leads to a better performance of $\text{PTHS}^-\text{TMA}^+$ based organic electrochemical transistors (OECTs).

1. Introduction

Water-soluble conjugated/conducting polymers are very interesting for applications in biological systems. Heeger et al. obtained solubility of these polymers in water through implementation of ionic sidechains on the conjugated backbone.^[1] As ionic groups, either negatively charged sulfonates, carboxylates, phosphates or positively charged groups like tetraalkylammonium have been reported for the synthesis of conjugated polyelectrolytes (CPEs).^{[1][2]} In addition to the water compatibility, these CPEs are able to interact with ions or charged biological compounds, like DNA.^{[3],[4],[5]} Moreover, CPEs can be used to record electrically the changes in ionic atmosphere when integrated in organic electrochemical transistors (OECTs). In these devices, the current flow in a CPE film can be controlled by a gate voltage applied via an electrode immersed in an aqueous electrolyte in direct contact with the CPE film.^[6] CPEs are highly sensitive to the ion motion between the electrolyte and the polymer film, which strongly influences the performance of OECTs. Still the role of the used counter ion in CPEs is not completely understood regarding their influence on the properties of CPEs as well as the OECTs. It is generally assumed that the optical and electronic properties are controlled by the conjugated backbone.^[7] For example, Yang et al. reported that cationic polyelectrolytes based on poly([(9,9-bis-(6'-N,N,N-trimethylammonium)-hexyl)fluorene] with different counter ions showed almost identical absorption spectra in solution. Nevertheless, they obtained different optical and electrical properties in film.^[8] On the contrary, McCullough et al. showed in carboxylated polythiophenes in aqueous solution that by choosing large counter cations the aggregation of the backbones due to π -stacking can be disrupted, whereas small counter cations promote aggregation of the polymers.^[9] Typical-

ly, high degree of π -stacking of the backbones is favorable for a lot of applications, since the charge transport mobility increases with the degree of aggregation/crystallization of the polymer chains.^[10] For polyelectrolytes with the same backbone but different counter ions, different ionization potentials and electron affinities were reported by Nguyen et al. using ultraviolet photoelectron spectroscopy (UPS) studies.^{[11],[12]}

Many of the reported CPEs were synthesized by oxidative methods in a non-controlled fashion. However with poly(6-(thiophen-3-yl)hexane-1-sulfonate) tetrabutylammonium, we have recently reported a well-defined CPE exhibiting a high bulk charge transport mobility, which led to OECTs operating in accumulation mode with high transconductance.^{[13],[14]} To further investigate electrochemical and optical properties of CPEs with the same backbone but different counterions, we synthesized three different poly(6-(thiophen-3-yl)hexane-1-sulfonate)s (PTHS⁻X⁺) with tetrabutylammonium (X⁺=TBA⁺), tetraethylammonium (X⁺=TEA⁺) and tetramethylammonium (X⁺=TMA⁺) as counter ion. Via absorption measurement in solution and films, we examined the optical behavior in dependence of the counter cation sizes. As thin films have to be stable in aqueous environment for biological applications, we stabilized them with a cross-linker against dissolution and analyzed how the optical properties are influenced through cross-linking. Using spectroelectrochemistry, we investigated the redox behavior of the CPE films after cross-linking in order to understand the influence of inter-difusion of ions. Cyclic voltammetry gave information about the ionization potentials of the synthesized CPEs and the reversibility of the oxidation of the conjugated backbones. Via impedance spectroscopy, we determined the intrinsic wet capacitance of the CPE films before and after oxidation. A quartz crystal microbalance was used to test the swelling capability in aqueous media, which enhance the drift mobility of ions in the film. All the PTHS⁻X⁺s were tested in OECTs to compare and elucidate the impact of the different counterions on device performance.

2. Results and Discussion

2.1. Synthesis and solubility

In this work, we synthesized three different anionic PTHS⁻X⁺ varying in their counter cation size from tetrabutylammonium over tetraethylammonium to the smallest tetramethylammonium cation. All the CPEs were obtained from the precursor polymer, poly(3-(6-bromohexyl) thiophene) (P3BrHT), whose synthesis was reported in a previous work.^[15] One third of a newly synthesized P3BrHT (Size Exclusion Chromatography, M_n : 18 kg mol⁻¹, PDI: 1.14) was converted to poly(6-(thiophen-3-yl)hexane-1-sulfonate) tetrabutylammonium (PTHS⁻TBA⁺),^[15] one third to poly(6-(thiophen-3-yl)hexane-1-sulfonate) tetraethylammonium (PTHS⁻TEA⁺), and the last third to poly(6-(thiophen-3-yl)hexane-1-sulfonate) tetramethylammonium (PTHS⁻TMA⁺) via polymer analogous substitution of the bromine group by reacting with the respective tetraalkylammonium sulfite salts. For all three compounds, the same P3BrHT was used with an average of 75 repeating units (calculated from MALDI-TOF) and a PDI of 1.14 (obtained by Size Exclusion Chromatography). Thus, any detected difference in characteristics between PTHS⁻TBA⁺, PTHS⁻TEA⁺ and PTHS⁻TMA⁺ can be attributed to the change in cation size. **Figure 1** shows a scheme of the synthesis.

PTHS⁻TBA⁺ and PTHS⁻TEA⁺ show very good solubility in water (2.5 wt % soluble), whereas PTHS⁻TMA⁺ is not very soluble (~ 1 wt% solubility). TMA⁺ itself is known as a hydrophilic cation referring to the standard molar Gibbs energy of transfer.^[16] With increasing size of the alkyl chain, the hydrophobicity usually increases, which in turn should lead to a decrease of solubility in water. Otherwise, water molecules and counterions can diffuse between the hydrocarbon arms of TBA⁺ ions, whereas the small TMA⁺ ions cannot be penetrated.^[17] Thus, the attractive forces between the positively charged nitrogen of tetraalkylammonium and the negatively charged sulfonate group on the hexyl side chains should be the strongest for TMA⁺, as the center of the

charge is less shielded due to bulky alkyl chains and diffusing water molecules. This leads to a decreased solubility of PTHS⁻TMA⁺ in water compared to the other two polyelectrolytes with bulkier tetraalkylammonium counter cations.

2.2. UV-Vis/IR absorption in aqueous solution and film

To examine the influence of the counter ion on the optical properties, we performed UV-Vis absorption measurements of the three synthesized polyelectrolytes in aqueous solution (**Figure 2a**). All the samples exhibit features of in-situ doping (absorption in the range of 650 – 1100 nm) as obtained after synthesis. We observed a red-shift of the absorption maximum for PTHS⁻TEA⁺ (λ_{max} : 542 nm) and PTHS⁻TMA⁺ (λ_{max} : 549 nm) in comparison to PTHS⁻TBA⁺ (λ_{max} : 529 nm). Furthermore, the polyelectrolytes show a shoulder at around 580 nm, which is most pronounced for PTHS⁻TMA⁺. The normalized absorption spectra of thin films spin-coated from aqueous solution also feature the vibronic fine structure (mainly for PTHS⁻TEA⁺ and PTHS⁻TMA⁺) and the trend of the absorption maxima: PTHS⁻TBA⁺ (λ_{max} : 499 nm) < PTHS⁻TEA⁺ (λ_{max} : 540 nm) < PTHS⁻TMA⁺ (λ_{max} : 549 nm) (**Figure S1**). For PTHS⁻TBA⁺, a distinct red-shift of 30 nm of the λ_{max} in solution (λ_{max} : 529 nm) is obtained compared to in film (λ_{max} : 499 nm).

The excitonic-vibronic coupling causing fine structure of absorption and emission, obtained in solution as well as in film, is complex for polymers with π - π -stacking.^[18] In polymer assemblies, intrachain through-bond interactions lead to J-aggregate behavior, whereas interchain Coulombic interactions lead to H-aggregate behavior. The photophysics of common emissive conjugated polymer films is determined by a competition between intrachain, J-favoring interactions and interchain, H-favoring interactions.^[19] TMA⁺ ions are less bulky than TEA⁺ and TBA⁺ ions. Consequently, the π - π -stacking of the hydrophobic polythiophene backbones in PTHS⁻TMA⁺ may be less hindered which leads to a stronger aggregation compared to PTHS⁻TEA⁺ and PTHS⁻TBA⁺. A red-shift of the absorption maxima due to the exchange of the bulkier TBA⁺ ions to the less steri-

cally hindered TMA^+ ions was also reported by McCullough et al. for a 2,5-poly(thiophene-3-propionic acid)^[9] and by Hostnik et al. for an aqueous poly(thiophen-2-ylacetic acid) solution.^[20]

2.3. UV-Vis/IR absorption of cross-linked polyelectrolyte films

Since devices for biological applications have to be long-term stable in aqueous environment, we need to stabilize the highly water-soluble PTHS^-X^+ films with a cross-linker. Therefore, we added (3-glycidyloxypropyl)trimethoxysilane (GOPS) (1 wt%) as cross-linker to a solution of PTHS^-X^+ in deionized water. Including GOPS in PEDOT:PSS dispersions is a common strategy to prevent the dissolution and delamination of films in an aqueous media.^{[21],[22],[23]} Moreover, as we have already shown in a previous work that ethylene glycol (EG) improved the OECT performance of a $\text{PTHS}^-\text{TBA}^+$, we also prepared films spin-coated from a solution containing 5 vol% EG.^[13] Unfortunately, the addition of additives may change the aggregation behavior of conjugated backbones. Since a larger volume of ordered conjugated polymer chains leads to a higher charge carrier mobility, the degree of aggregation is important for most applications.^{[24],[25],[26],[27]} To evaluate the effect of the addition of GOPS and EG on the aggregation behavior of PTHS^-X^+ , we compared the UV-Vis absorption spectra of thin films containing GOPS and containing both GOPS and EG, with the ones of pristine PTHS^-X^+ films. In **Figure 2b** the absorption spectra for the $\text{PTHS}^-\text{TMA}^+$ films are shown as a typical example. The respective spectra for $\text{PTHS}^-\text{TBA}^+$ and $\text{PTHS}^-\text{TEA}^+$ can be found in the supporting information (**Figure S2**). By adding GOPS to the spin-coating solution, the absorption spectra of the films of all PTHS^-X^+ are blue-shifted. $\text{PTHS}^-\text{TBA}^+$ is shifted by 45 nm, $\text{PTHS}^-\text{TEA}^+$ by 48 nm and $\text{PTHS}^-\text{TMA}^+$ only by 8 nm due to addition of the cross-linker. Still $\text{PTHS}^-\text{TMA}^+$ is red-shifted in comparison to $\text{PTHS}^-\text{TEA}^+$ and $\text{PTHS}^-\text{TBA}^+$. A closer examination of the spectra for $\text{PTHS}^-\text{TMA}^+$ and $\text{PTHS}^-\text{TEA}^+$ containing GOPS reveals that there is still a tiny shoulder visible around 600 nm. $\text{PTHS}^-\text{TBA}^+$ does not show a

shoulder any more. The supplemental addition of EG does slightly shift the absorption maxima further in the blue region ($\Delta\lambda_{\text{max}}$: 6-15 nm).

The blue-shift of the absorption spectra by adding GOPS indicates that the cross-linker changes the nature of the aggregation of the polythiophene backbones. In aqueous environment GOPS is forming methanol and (3-glycidyloxypropyl)trimethoxysilanol, which build at elevated temperature siloxane bonds with each other or with a methoxy group of another GOPS molecule during drying.^{[28],[29]} In this way a cross-linked network is built. Furthermore, the epoxy group of GOPS is unstable in water and could react to a diol, which can interact with an acidic sulfonic group of PSS or in our case a sulfonate group on a hexyl side-chain of PTHS⁻X⁺.^{[30],[31]} Due to the formed network and the hydrogen bonds to the polymer, the solubility of the film is decreased. Nevertheless, the aggregation of the polythiophene backbones may be simultaneously changed.

2.4. Spectroelectrochemical measurements

To determine whether the hydrated ions interact with the conjugated backbone in our polyelectrolyte films, we proceeded with testing the electroactivity of the cross-linked films in presence of electrolytes.^[32] An electroactive material is able to record the influence of the ions in the surroundings on its electrical signal. Thus this material transduces ionic to electronic signals. For this, ions should be penetrating and drifting inside the thin film. By applying a varying bias (0 mV to 600 mV in steps of 100 mV) between the CPE film casted on ITO substrate and a Pt-counter electrode, while both are immersed in a 0.1 M NaCl_{aq} electrolyte solution, oxidation of the polyelectrolyte is induced. These processes can be simultaneously monitored with UV-Vis spectrometer as the charges formed on the polymer backbones lead to a structural and electronic distortion and consequently to a change in the spectra.^[33] **Figure 3a** shows the resulting plot for cross-linked PTHS⁻TMA⁺ as a typical example. Similar spectra for PTHS⁻TBA⁺ and PTHS⁻TEA⁺ are given in the supporting information (**Figure S3 a and c**, respectively). To render the results

even more comparable, the relative difference between the spectra achieved by applying a bias and the initial spectrum without applied bias (Δ_{Abs}) is also plotted (**Figure S3 b, d, f**).

For all cross-linked PTHS X^+ films, similar trends were observed. On increasing the applied bias, the absorption maxima of the films decrease and get slightly blue-shifted. Furthermore, two additional bands appear, one between 650 nm and 1100 nm, and a second one starting at 1100 nm and extending beyond 1300 nm. Due to the absorption of the ITO substrate at higher wavelengths than 1300 nm, we were not able to measure this peak at higher wavelength range. When the applied bias was reversed stepwise back to 0 mV, the absorption at higher energies once more became dominant and the whole spectrum shifted back to the initial version at 0 mV (not shown). Thus, the two additional absorption bands due to oxidation at 650 nm and 1100 nm bleached. For each of the polyelectrolyte films, an isosbestic point exists, through which all their spectra pass through ($\lambda_{\text{isosbestic}}$: 584 nm for PTHS TBA^+ , $\lambda_{\text{isosbestic}}$: 603 nm for PTHS TEA^+ , $\lambda_{\text{isosbestic}}$: 625 nm for PTHS TMA^+). The appearance of clear isosbestic points are hints for the formation of a new species due to oxidation and also for the reversibility of the oxidation.^[34] For comparison, the spectra obtained at 0 mV are normalized (to avoid inaccuracies due to possible thickness variations) and differential spectra for each applied voltage with respect to the respective normalized spectra are plotted in **Figure S3**. The easiness and degree of oxidation can be evaluated by comparing either the decrease in absorption maximum of the unbiased samples or the increase in radical cation absorption (650-1100 nm). If the differential spectra are compared at absorption maxima of the pristine samples ($\lambda = 500$ nm), it is obvious that PTHS TMA^+ favors the fastest oxidation. On the other hand, if the absorption maxima for the radical cations are considered, the difference in oxidizability between PTHS TEA^+ and PTHS TMA^+ is small. Anyhow, PTHS TBA^+ seems to get oxidized very slowly (**Figure S3**).

A similar behavior in spectroelectrochemical measurements is well-known for poly(3-hexylthiophene) (P3HT).^{[33],[35]} As the electronic and optical properties are mainly determined by the conjugated backbone,^[7] this is hardly surprising. The two simultaneously arising absorption bands, seen for all three polyelectrolyte films, represent the oxidized polythiophene backbone with polarons as charge carriers.^[33] This was demonstrated for P3HT experimentally as well as via quantum chemical calculations.^{[33],[36]} The conversion of the undoped sample into the oxidized species, is denoted by the isosbestic point.^[33] As the polythiophene backbone is an electron donor, a positive bias has to be applied to obtain a change in the absorption spectrum. In contrast, PEDOT:PSS, which is a wide-spread material for bioelectronics, is a doped system. Thus, a negative bias (with respect to the reference electrode) has to be applied to induce dedoping of PEDOT:PSS and to observe a change in the absorption spectrum. Overall, bulk electrical oxidation was proven for all three polyelectrolytes by spectroelectrochemical measurements. All the films containing GOPS were stable in the aqueous electrolyte, even with applied bias. Furthermore, oxidation of the films was reversible and within the electrochemical window of aqueous solutions, which is important for bioelectronic applications utilizing devices such as OECTs.

To get a deeper insight in the electroactivity of the three polyelectrolytes and also in their stability over time, we applied 600 mV bias on thin films dipped in an electrolyte for one hour and examined the extent of oxidation by measuring the absorption at the wavelength of the respective ground state maximum (PTHS⁻TBA⁺ at 482 nm, PTHS⁻TEA⁺ at 497 nm and PTHS⁻TMA⁺ at 545 nm, **Figure 3b**). All three polymers show immediately a decrease in absorption maxima under the applied bias. Most pronounced is the oxidation for PTHS⁻TMA⁺, for which absorption is reduced to 38 % of the initial value within three minutes and is decreasing further to 35 % over time. The absorption of PTHS⁻TEA⁺ is reduced to 53 % and the one of PTHS⁻TBA⁺ to 56 %. When we applied 0 mV, the ground state absorption started recovering. PTHS⁻TMA⁺ is the only

one of the examined polyelectrolytes which exhibits a fast and efficient oxidation followed by re-covering fully to its initial absorption maximum. PTHS⁻TEA⁺ reached 93 % of its initial absorption maximum, whereas PTHS⁻TBA⁺ only 85 %. For the recovery, as PTHS⁻TBA⁺ reached a plateau after around 20 minutes with no applied bias, PTHS⁻TEA⁺ and PTHS⁻TMA⁺ continue increasing till the measurement was ended after 60 minutes.

These results clearly indicate that in PTHS⁻TMA⁺ more thiophenes are oxidized than in PTHS⁻TEA⁺ or PTHS⁻TBA⁺ for the same applied voltage and duration of oxidation. The radical cations created by electrochemical oxidation seem to be stable over time to a certain degree, as the reduction at zero voltage was relatively slow. The maximum degree of oxidation of PTHS⁻TMA⁺ seems to be completed in about 10 minutes (reduction of absorption at 545 nm to 40%) and after that it continues monotonously during the whole 60 minutes, reaching 35% of the original absorption. Also the recovery was at a slow rate reaching 100% after 60 minutes. PTHS⁻TBA⁺, on the other hand, shows a fast recovery to reach a stable re-reduction level at only about 85%. Thus, the degree of oxidation and its recovery are the best for PTHS⁻TMA⁺, which shows the most packed structure among all the discussed polyelectrolytes (see **Figure 2**).

2.5. Cyclic voltammetry

To study the reversibility of the redox reactions and the electrochemical behavior of PTHS⁻X⁺, we performed cyclic voltammetry (CV) measurements. The polyelectrolyte films spin-coated on ITO served as working electrodes. **Figure 3c** shows the obtained cyclic voltammograms. PTHS⁻TBA⁺, PTHS⁻TEA⁺ and PTHS⁻TMA⁺ exhibit reversible oxidation behavior. Values calculated from the half-wave potential of the oxidation are often inappropriately referred to as highest occupied molecular orbital (HOMO).^[37] As suggested by Bredas, we are using the term ionization potential (IP) here.^[37] To calculate the IP values, ferrocene was used as standard and the influence of the solvent was taken into account.^{[38],[39]} The half-wave potentials used for calculation

are averages of several measurements to minimize the inaccuracy. Hereby, we obtained an IP of -5.52 eV for PTHS⁻TBA⁺, -5.50 eV for PTHS⁻TEA⁺ and -5.43 eV for PTHS⁻TMA⁺. The polyelectrolyte with the smallest counterion, PTHS⁻TMA⁺, is therefore relatively easier to be oxidized. IP values obtained from CV measurements should be taken with caution for their absolute values, since they give approximations based on calculations assuming the HOMO value of ferrocene system.^[37] It is interesting to note that Nguyen et al. reported for cationic polyelectrolytes with different counter anions the same trend for IP values as determined by ultraviolet photoelectron spectroscopy (UPS) in solid state.^[11]

2.6. Electrochemical impedance spectroscopy

The result of the ion uptake of a redox-active material could be quantified by the electrochemical capacitance.^[40] Since the ions are able to penetrate the films in aqueous media, we compared the volumetric capacitance as reported by Rivnay et al.^[41] We recorded the electrochemical impedance spectra of the films cast on gold substrates (635 x 635 μm) in a frequency range of 1 Hz and 100 kHz. The spectra were acquired as the film was exposed to a DC voltage of 0 and 550 mV with respect to the reference electrode (**Figure 3d** and **Figure S4**). We modelled the data using an established equivalent circuit comprising serially connected impedance elements; the resistance of the electrolyte and the impedance of the polymer represented by a resistor and a capacitor, C , in parallel.^[42] As the films get doped with the applied bias, the impedance, below 1000 Hz decreases, with an increase in the extracted capacitance values (**Figure 3d** and **S4**).^[43] The films can be assumed to have bulk doping, therefore, it is reasonable to assume a volumetric interaction of ions with the polymer. A clear trend in the obtained volumetric capacitances ($C^*=C/V$, V (volume)) for the three polyelectrolytes was recognized: By decreasing the size of counter ion on the polymer backbone, the C^* increases considerably (**Table 1**). The volumetric capacitance of PTHS⁻TEA⁺ at $V= 550$ mV (5 Fcm^{-3}) is ca. four times larger than for the most

bulky PTHS⁻TBA⁺ (22 Fcm⁻³), whereas for PTHS⁻TMA⁺, the CPE with the smallest counter ion, it is the highest (82 Fcm⁻³). Taken together with the fast and efficient switching of the spectral properties under applied bias, PTHS⁻TMA⁺ constitutes a CPE having the highest potential for ion response.

2.7. Swelling capability

To a large volumetric capacitance, the capability of a film to take up water and swell also contributes.^[41] We, therefore, examined the swelling capacity of the CPEs using quartz crystal microbalance (QCM). **Figure S5** shows the changes in QCM signals (immediate drop in oscillation frequency (f) and increase in dissipation (D)) for the quartz crystals coated with the polymers as the films are exposed to deionized water (DI) water and NaCl solution. This change in f accompanied with an increase in dissipation D with the inflow of water/NaCl solution is translated into an increase in the mass of the film, i.e., swelling due to uptake of water/hydrated ions. We treated our data with Sauerbrey model which directly correlates the change in f to swelling (see the Experimental Section).^[44] When we calculate the swelling percentages, we see that for PTHS⁻TMA⁺, PTHS⁻TEA⁺, PTHS⁻TBA⁺ is 2 %, 2 %, 3 % in DI water, and 3.4 %, 3.5 %, 6.3 % in NaCl respectively as shown in **Table S1**. With the addition of EG, swelling of the three polymers does not seem to be affected. Previous studies have shown that swelling of OECT materials is correlated with ion mobility and/or OECT performance.^[45] Our current findings demonstrate that the CPEs swell less than PEDOT based materials, presumably due to the lack of a polyionic phase. Although swelling is limited, the capacitance measured at the oxidation potential is higher for PTHS⁻TBA⁺ than for PEDOT:PSS, indicating the ease of ion access to the conjugated backbone in the former.^[43]

2.8. Performance in OECTs

OECTs are electronic transducers that also enable studies of mixed (ionic and electronic) transport of redox-active films. The counterion effect on mixed transport could be finally studied using the CPEs in the channel of OECTs. A cross-sectional schematic of the used structure is shown in **Figure 4a**. The channel length was 10 μm and the width 100 μm . We prepared OECTs from six different solutions: PTHS⁻TBA⁺, PTHS⁻TEA⁺ and PTHS⁻TMA⁺ containing GOPS as cross-linker as well as the same CPE solutions containing EG as the co-solvent. For all solutions, the same spin-coating conditions were used, resulting in thin layers of 10 to 20 nm. A series of drain (V_D) and gate voltage steps (V_G) were applied at room temperature, while recording the resulting drain current (I_D). The transfer characteristic for such an OECT is shown in **Figure 4b** as a typical example. All the output characteristics are shown in the SI (**Figure S6** devices without EG and **Figure S8** devices with EG). The transfer characteristics and corresponding transconductance of PTHS⁻TBA⁺ and PTHS⁻TEA⁺ devices are also shown in SI (**Figure S7** without EG and **Figure S9** with EG). Upon applying a negative voltage at the gate electrode, the current between the source and the drain electrode increases, showing that the channel is p-type doped (**Figure 4b**). The negative bias triggers the doping of the polymer via oxidation (along with possible ejection of the counter cation and/or injection of the Cl^- of the electrolyte), which increases the current flowing in the channel and switches the device ON.^[46] Since we use an aqueous electrolyte, the gate potentials to be applied are limited due to the possible electrolysis (at 1.23 eV at pH 0) and a lack of stability of the oxidized CPE in water.^[47] Such accumulation mode transistors are in fact attractive for sensing applications as they consume low power.^[13]

When defining the performance of OECTs, an important parameter is the transconductance ($g_m = \frac{\partial I_D}{\partial V_G}$), quantifying the magnitude of a change in I_D as a small V_G is applied at the gate. Table 1 summarizes the OECT characteristics and the crucial thin film parameters for our CPEs. Comparing the three polymers of similar thicknesses, we see that when PTHS⁻TMA⁺ is in the

channel, the device exhibits the best performance compared to other films: highest values of g_m (ca. $45.5 \mu S$), I_D ($-350 \cdot 10^{-2} \mu A$) and ON/OFF (250) with the fastest switching speed (0.2 s). These results are in good agreement with the observed rate of oxidation and its reversibility in SEC measurements.

Devices with EG treated samples showed in general higher ON/OFF ratios than their respective devices without EG. Addition of EG improves the performance of PTHS⁻TBA⁺ based devices (g : $2.30 \mu S$, I_D : $-28.1 \cdot 10^{-2} \mu A$). This improvement with EG is similar to that reported in a previous work.^[13] In the earlier report, fiber-like features were observed in AFM images of the EG-treated films, whereas the films without EG exhibited no such features.^[13] In contrary, PTHS⁻TEA⁺ (g : $1.16 \mu S$, I_D : $-8.79 \cdot 10^{-2} \mu A$) and PTHS⁻TMA⁺ (g : $36.9 \mu S$, I_D : $-276 \cdot 10^{-2} \mu A$) based devices perform worse when containing EG compared to the ones without. However, PTHS⁻TMA⁺ is the best performing CPE among the three polymers independent of the co-solvent additive.

In order to determine the temporal response of the devices; I_D was recorded while the voltage is pulsed at the gate electrode. The pulses were 15 second-long with amplitude of -600 mV, and applied with an interval of 45 seconds. The ON response time (τ_{ON}) is defined as the time required to reach 90 % of the maximal I_D of the resp. pulse.^[46] PTHS⁻TMA⁺ shows the fastest response with 0.2 seconds, followed by PTHS⁻TEA⁺ and PTHS⁻TBA⁺ which have a τ_{ON} of 3.8 and 3.3 seconds, respectively. Repeating the pulses several times, we noticed that temporal response stays the same for each applied pulse (not shown). However, the current does not reach the maximum value obtained for the first pulse. Here, PTHS⁻TMA⁺ shows the best stability, while PTHS⁻TEA⁺ and PTHS⁻TBA⁺ degrade with time. Moreover, as with steady state characteristics, EG improves the response time of the PTHS⁻TBA⁺ based devices. For the case of PTHS⁻TEA⁺ and PTHS⁻TMA⁺, on the other hand, there was almost no difference in the response time, induced by the co-solvent. As mentioned above, the accumulation mode transistors are switched ON by doping the

polymer in the channel due to application of a positive (n-type, reduction) or like in our case, negative (p-type, oxidation) gate bias.^[48] Negative gate bias can induce the oxidation of a polyelectrolyte followed by either ejection of counter ions (here TBA⁺, TEA⁺ and TMA⁺) or by injection of electrolyte anions (here chloride anions) or both to have charge balance.^{[46],[13]} As TMA⁺ is the smallest and less sterically hindered counter ion among the polymers tested, its ejection might be much easier than the bulky TBA⁺ cation. This could hint the fastest temporal response and stability of TMA. Response time and the stability of the OECT might be related to the mobility of ions inside the polymer film, which is governed by the swelling behavior. Our results, however, do not show any trend between the two, presumably due to the response times not ranging widely. In addition to the C*, the charge carrier mobility (μ) is another material related parameter governing the g and can be determined using the following equation for OECT:^[41]

$$g = \frac{W \cdot d}{L} \cdot \mu \cdot C^* \cdot (V_T - V_G) \quad (1)$$

where W is the channel width, d the film thickness, L the length of the channel and V_T the geometry-independent threshold voltage.^[41] When C^* values extracted from electrochemical impedance spectra are plugged into this equation, we find that the hole mobility of PTHS-TMA⁺ ($267 \cdot 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is orders of magnitude higher than the other two films (for PTHS-TBA⁺, μ : $8.18 \cdot 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; and for PTHS-TEA⁺, μ : $8.21 \cdot 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Although, these values are just rough approximations calculated at one V_G and using a C^* extracted from one impedance plot, the trend is clear and correlates with the aggregation behavior of the polymers revealed by UV-Vis absorption measurements: as PTHS-TMA⁺ shows the most aggregation and with that the densest π - π stacking, it is expected to have a higher hole mobility than the less aggregated PTHS-TEA⁺ and PTHS-TBA⁺. The mobility values for PTHS-X⁺ may be less than for neutral polythiophenes, if the aggregation is hindered due to the incorporation of charged units on side chains.^{[49],[50],[51]} Moreover, the addition of cross-linker disturbs the aggregation of the conjugated backbones. This

also can lead to a decrease of electronic coupling and consequently to lower electronic charge mobility. Garcia et al. obtained a similar effect by adding PEG to an anionic CPE.^[51] A drop in electrical conductivity due to addition of GOPS is well known for PEDOT:PSS, as well.^{[23], [29], [42], [52]}

3. Conclusion

In conclusion, we showed that the selection of counter ion in CPEs plays an important role in determining the thin film characteristics and OECT performance. We synthesized three different CPEs from the same precursor polymer which differ only in the size of counter ions. The used counter ions varied in size from the bulky tetrabutylammonium, over tetraethylammonium to the smallest tetramethylammonium ion. According to UV-Vis absorption studies in aqueous solution as well as in thin films, the CPE with the smallest counter ion showed the highest degree of aggregation. Cross-linking of the materials with GOPS hindered the aggregation of the conjugated backbones independent of the used counter cation. Spectroelectrochemical investigations revealed that the CPE with the smallest counterion can be oxidized to a higher degree than the CPEs with bulkier counter ions. As evidenced by CV and electrochemical impedance spectroscopy measurements, the CPE with the smallest counter ion was able to convert more dopant ions to electrical charges. These results have a direct implication on the performance of an OECT utilizing the CPE in the channel, as the CPE with the smallest counter ion led to best performing devices.

4. Experimental Section

The salts tetra-n-butyl, tetraethyl and tetramethyl ammonium sulfite were prepared by adding 1 equivalent dimethyl sulfite to a solution of 2 equivalents of tetra-n-butyl, resp. tetraethyl, resp. tetramethyl ammonium hydroxide in methanol. All other chemicals were received from commercial suppliers. The synthesized polyelectrolytes were analyzed via ¹H-NMR using a Bruker Avance 250 spectrometer at 300 MHz. For calibration of the spectra the respective solvent signal

was used. Matrix assisted laser desorption ionizations spectroscopy with time-of-flight detection mass spectroscopy (MALDI-TOF MS) of the precursor polymer P3BrHT was measured on a Bruker Reflex III in linear mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as matrix and a matrix to PTHS ratio of 1000:1.

Size exclusion chromatography of P3BrHT was performed utilizing a Waters 515 HPLC pump with stabilized THF as the eluent at a flow rate of 0.5 mL/min. Into a column setup consisting of a guard column (Varian, 50×0.758 cm, ResiPore gel, particle size $3 \mu\text{m}$) and two separation columns (Varian, 300×0.758 cm, ResiPore gel, particle size $3 \mu\text{m}$) $20 \mu\text{L}$ of a P3BrHT solution (concentration of approximately 1 mg/mL) was injected. With a Waters 2489 tunable UV detector at 254 nm the polymer size distribution was monitored. For calibration Polystyrene was used as external and 1,2-dichlorobenzene as an internal standard.

Synthesis

The syntheses of the precursor polymer P3BrHT and $\text{PTHS}^-\text{TBA}^+$ are already published.^[15] The molecular weight of P3BrHT was analyzed by MALDI-TOF MS ($M_n = 18.5 \text{ kg mol}^{-1}$, $M_w = 18.9 \text{ kg mol}^{-1}$, average 75 repeating units) and Size Exclusion Chromatography: $M_n = 18.2 \text{ kg mol}^{-1}$, $M_w = 20.8 \text{ kg mol}^{-1}$, PDI: 1.14).

$\text{PTHS}^-\text{TEA}^+$ was prepared according to the procedure reported for $\text{PTHS}^-\text{TBA}^+$.^[15] Instead of tetra-*n*-butyl ammonium sulfite tetraethyl ammonium sulfite (0.83 mol L^{-1} in MeOH, 11 mL, 9.13 mmol) was used. NMR: δ_{H} (300 MHz; DMSO- d_6) 1.06-1.20 (12 H, t, $\text{N}^+(-\text{CH}_2-\text{CH}_3)_4$), 1.30-1.47 (4 H, m, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$), 1.50-1.75 (4 H, m, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$), 2.37-2.48 (2 H, m, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$), 2.69-2.90 (2 H, m, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$), 3.12-3.27 (8 H, q, $\text{N}^+(-\text{CH}_2-\text{CH}_3)_4$), 7.14-7.26 (1 H, s, H_{arom}).

PTHS⁻TMA⁺ was also prepared according to the procedure reported for PTHS⁻TBA⁺[15] using a solution of 0.14 g of poly(3-(6-bromohexyl)-thiophene) (0.008 mmol) in 38 mL dry THF. Instead of tetra-n-butyl ammonium sulfite tetramethyl ammonium sulfite (1.29 mol L⁻¹ in MeOH, 6 mL, 7.72 mmol) was added. NMR: δ_H (300 MHz d-THF/D₂O: 2/1) 1.30-1.46 (4 H, m, CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-S), 1.55-1.69 (4 H, m, CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-S), 2.63-2.85 (4 H, m, CH₂-CH₂-CH₂-CH₂-CH₂-S), 3.07-3.19 (12 H, s, N⁺(-CH₃)₄), 6.95-7.07 (1 H, s, H_{arom}).

Absorption Measurements

The polyelectrolyte films were prepared from 2.5 wt% solutions of PTHS⁻TBA⁺ and PTHS⁻TEA⁺, and 1 wt% solution of PTHS⁻TMA⁺ in ultrapure water (Milli-Q). Before spin-coating the solutions on cleaned quartz substrates, the solutions were filtered using polyamide syringe filters. For the cross-linked films a solution of 1 wt% polyelectrolyte in ultrapure water (Milli-Q) was prepared and 1 wt% GOPS was added. For the films containing EG 5 vol% of this solvent was added. After filtration and spin-coating of the solutions on quartz substrates, the films were annealed at 90 °C for 1.5 h.

The films for spectroelectrochemical measurements were prepared like the ones for absorption measurements but on ITO substrates. Spectroelectrochemical measurements were performed in a 1 cm quartz cuvette containing 0.1 M NaCl_{aq} and using a platinum wire as counter electrode. The film and the platinum wire were connected to a source meter to apply bias. Every bias was applied for seven minutes, consisting of five minutes waiting time and two minutes for recording the spectra. The bias was changed by steps of 100 mV. For the time dependent measurements, the extent of oxidation was recorded by measuring the absorption at the wavelength of the respective ground state maximum. First, a bias of 600 mV was applied for one hour. Afterwards, the bias was removed and the associated changes in the spectra were recorded for one hour. All absorption spectra were recorded using a Jasco V670 spectrophotometer.

Cyclic voltammetry

The cyclic voltammetry measurements were performed using a standard three electrode assembly under nitrogen with a scanning rate of 100 mV s^{-1} . The assembly was connected to a potentiostat model 263A from EG&G Princeton Applied Research. The measurements were performed in a 0.1 M tetra-butylammonium hexafluorophosphate solution in dichloromethane. A platinum wire in a 0.1 M tetra-butylammonium hexafluorophosphate solution in dichloromethane served as counter electrode, whereas an Ag wire in a 0.1 M AgNO_3 solution in acetonitrile was used as reference electrode. The working electrode was the polyelectrolyte film spin-coated on an ITO substrate. The measurements were calibrated with ferrocene/ferrocenium as external standard. Considering the solvent effects the IP values were calculated as already published.^[38]

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was performed using a in aqueous NaCl solution (0.1 M) using an impedance spectrometer (potentiostat/galvanostat, Metrohm Autolab B.V.) with a three electrode configuration. The polymer-coated gold electrode ($4.03 \cdot 10^{-3} \text{ cm}^2$) was the working electrode, a Pt mesh was the counter, and Ag/AgCl is used as a standard reference electrode. EIS was performed over a range of 1 Hz- 100 kHz—with an AC 10 mV sine wave, and a DC offset of 550 mV and 0 V (the potential on the working electrode with respect to the reference). In order to extract capacitance (C) and volumetric capacitance (C^*) the spectra of doped films (DC offset=at 550 mV) were fit to an (RC) equivalent circuit using NOVA software.

QCM

The swelling of the thin polymer films was studied using QCM-D (Q-Sense, from Biolin Scientific). The polymer solutions were spun cast on clean plasma activated gold-coated Q-sensors. They were kept under vacuum overnight to ensure complete drying of the film. Filtered DI water and afterwards aqueous NaCl solution (0.1 M) were flown over the samples at 24°C at a flow

rate of $50\text{--}100\ \mu\text{L}\cdot\text{min}^{-1}$ controlled by a peristaltic pump. The adsorbed mass (Δm) was estimated from Δf using the Sauerbrey equation $\Delta m = -C \frac{\Delta f_n}{n}$ where C is the mass sensitivity constant ($17.7\ \text{ng}\cdot\text{cm}^{-2}\ \text{Hz}$ at $f = 5\ \text{MHz}$) and Δf_n is the change in resonance frequency at n th overtone.^[44] The 3rd, 5th, and 7th overtones were used for the calculations. Given the initial thickness of the dry films, the water and NaCl uptake could be estimated. The error was due to variation in the measurement of the films thickness.

OECT performance

OECT devices were prepared as described previously, fabricated photo lithographically using a parylene-C lift-off process.^[13] The patterned channels of the transistors had a width of $100\ \mu\text{m}$ and a length of $10\ \mu\text{m}$. 1 wt% CPE was dissolved in deionized water and 1 wt% GOPS was added. Films containing EG had 5 vol% of the co-solvent. The films were spin-coated at 1500 rpm for 30 sec. Afterwards, the substrates were annealed at $90\ ^\circ\text{C}$ for 1.5 h. Thickness measurements of the polyelectrolyte films were performed using a Dektak profilometer. All measurements were performed using an Ag/AgCl wire (Warner Instruments) as the gate electrode and NaCl solution (0.1 M) as the electrolyte. The steady-state measurements of the OECT (output and transfer curves) and the pulsed gate experiments were performed using a Keithley 2612A with customized LabVIEW software.

Supporting Information

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

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Figure 1. Scheme of Kumada catalyst transfer polycondensation for the synthesis of the precursor polymer, poly(3-(6-bromohexyl) thiophene) (P3BrHT) and its post polymerization reaction to obtain poly(6-(thiophen-3-yl)hexane-1-sulfonate) PTHS-X⁺ with tetrabutylammonium (X⁺ = TBA⁺), tetraethylammonium (X⁺ = TEA⁺) and tetramethylammonium (X⁺ = TMA⁺) as counter ions as well as the reactions to obtain the corresponding ammonium salts from dimethylsulfite.

Figure 2. a) Normalized absorption of PTHS-TBA⁺, PTHS-TEA⁺ and PTHS-TMA⁺ in aqueous solution (concentration of $8.30 \cdot 10^{-7} \text{ mol L}^{-1}$) and b) in thin films spin coated on quartz substrates from aqueous solutions of PTHS-TMA⁺, PTHS-TMA⁺ with 1 wt% GOPS and PTHS-TMA⁺ with 1 wt% GOPS and 5 vol% EG. Comparable spectra for PTHS-TBA⁺ and PTHS-TEA⁺ films can be found in **Figure S2**.

Figure 3. a) Normalized (with respect to λ_{max} at 0 mV) spectra of a PTHS-TMA⁺ film (+ 1 wt% GOPS) due to electrochemical oxidation (doping) by applying a varying bias from 0 mV to 600 mV in steps of 100 mV (Spectra of all CPE films containing GOPS can be found in **Figure S3**). b) Monitoring of change in absorption at the wavelength of the respective ground state maximum (PTHS-TBA⁺ at 482 nm, PTHS-TEA⁺ at 497 nm, and PTHS-TMA⁺ at 545 nm). For this measurement 600 mV was applied for one hour, followed by 0 mV for an additional hour for all the samples. c) Cyclic voltammogram of cross-linked PTHS-TBA⁺, PTHS-TEA⁺ and PTHS-TMA⁺ films cast on ITO substrates measured in DCM. d) Bode plot (impedance vs. frequency) of a thin cross-linked PTHS-TMA⁺ film recorded with and without 550 mV applied bias (The same plots for PTHS-TBA⁺ and PTHS-TEA⁺ films are shown in **Figure S4**).

Figure 4. a) Cross-sectional schematic of an OEET. b) Transfer characteristics and corresponding transconductance (g_m) of a cross-linked PTHS-TMA⁺-based device at $V_D = -500$ mV. Output and transfer characteristics for all CPEs are given in **Figure S6 – S9**.

Table 1. The OEET characteristics and materials figure of merit for the PTHS-X⁺ films studied in this work. Transconductance (g_m), drain current (I_D) at $V_G = -600$ mV and $V_D = -500$ mV, ON/OFF ratio and response time (τ_{ON}) at $V_G = -600$ mV and $V_D = -400$ mV. All the OEET parameters are averaged values obtained from two to five devices. All films contain GOPS (1 wt%). Also given is the volumetric capacitance (C^*) calculated at an offset potential vs Ag/AgCl of 550 mV, and the hole mobility (μ) calculated using Equation 1. Note that μ and C^* are extracted from single samples and under one biasing condition and might therefore be prone to error because of ion accumulation at the film/electrolyte interface and V_G dependent channel mobilities.

sample	OEET				C^* [F/cm ³]	μ [10 ⁻⁹ cm ² V ⁻¹ s ⁻¹]
	g_m [μS] ^{a)}	I_D [10 ⁻² μA] ^{a)}	$I_D^{a)}/I_{D,0}$	τ_{ON} [s] ^{b)}		
PTHSTBA ⁺	0.13	-2.56	3.72	3.3	5	8.18
PTHSTEA ⁺	2.16	-14.50	87.50	0.8	22	8.21
PTHSTMA ⁺	45.50	-350	250	0.2	82	267
PTHSTBA ⁺ +EG	2.30	-28.10	19	1.4	15	288
PTHSTEA ⁺ +EG	1.16	-8.79	170	0.8	13	53.7
PTHSTMA ⁺ +EG	36.9	-276	523	0.4	-	-

^{a)} average at $V_G = -600$ mV and $V_D = -500$ mV; ^{b)} at $V_D = -400$ mV, for a step of $V_g = 0$ mV to $V_g = -600$ mV.

Supporting Information

Smaller counter cation for better transconductance in anionic conjugated polyelectrolytes

Martina M. Schmidt, Mohammed ElMahmoudy, George G. Malliaras, Sahika Inal, and Mukundan Thelakkat**

Figure S1. Normalized absorption of thin films spin coated on quartz substrates from aqueous solutions of PTHS-TBA⁺, PTHS-TEA⁺ and PTHS-TMA⁺.

Figure S2. Normalized absorption of thin films spin coated on quartz substrates from aqueous solutions of pristine PTHS-X, with 1 wt% GOPS and with 1 wt% GOPS and 5 vol% EG for a) PTHS-TBA⁺ and b) for PTHS-TEA⁺.

Figure S3. a), c), e) Normalized spectral changes and b), d), f) relative difference between the spectra recorded with bias (0 mV to 600 mV in steps of 100 mV) and the initial spectrum without bias of a PTHS-TBA⁺ (a and b), a PTHS-TEA⁺ (c and d) and a PTHS-TMA⁺ (e and f) film containing GOPS

Figure S4. Impedance measurements of thin cross-linked a) PTHS⁻TBA⁺ and b) PTHS⁻TEA⁺ film with 0 and 550 mV applied bias against the reference electrode.

Figure S5. a) 5th overtone frequency and dissipation curves of cross-linked PTHS⁻TBA⁺, PTHS⁻TEA⁺, and PTHS⁻TMA⁺ films, as well as of a pristine reference sensor using QCM-D, and b) swelling percentage of cross-linked PTHS⁻TBA⁺, PTHS⁻TEA⁺, and PTHS⁻TMA⁺ in both deionized water (in black) and NaCl (in red).

Table S1. Summary of the change in thickness (Δd) and corresponding swelling values in deionized (DI) water and NaCl, with standard deviation based on three different thickness measurements.

Material	Initial thickness (d) [nm]	Δd (DI water) [nm]	Δd (NaCl) [nm]	Swelling (DI water) [%]	Swelling (NaCl) [%]
PTHS ⁻ TBA ⁺	16.7 ± 1,3	0.5 ± 0,22	1.05 ± 0,4	2.9 ± 0.2	6.3 ± 0.5
PTHS ⁻ TEA ⁺	18.3 ± 2,4	0.36 ± 0,06	0.6 ± 0,2	2 ± 0.3	3.5 ± 0.5
PTHS ⁻ TMA ⁺	66 ± 10,7	1.3 ± 0,7	2.2 ± 0,4	2 ± 0.3	3.4 ± 0.5
PTHS ⁻ TBA ⁺ + EG	42,2 ± 5,6	2,2 ± 1,2	2,2 ± 1,3	4.6 ± 1.7	5.2 ± 0.6
PTHS ⁻ TEA ⁺ + EG	79,3 ± 57,6	2,6 ± 1,5	3 ± 1,6	5,8 ± 2,5	6 ± 3,4
PTHS ⁻ TMA ⁺ + EG	144, 7 ± 11,6	2,9 ± 1,6	3,1 ± 1,6	2,3 ± 0,5	2,1 ± 0,2

Figure S6. Output characteristics of cross-linked PTHS-TBA⁺ (a), PTHS-TEA⁺ (b), and PTHS-TMA⁺ (c) based device with V_G of 0 mV, 400 mV, 500 mV and 600 mV.

Figure S7. Transfer characteristics and corresponding transconductance of a cross-linked PTHS-TBA⁺ (a) and PTHS-TEA⁺ (b) based device at $V_D = -500$ mV.

Figure S8. Output characteristics of cross-linked PTHS-TBA⁺ (a), PTHS-TEA⁺ (b), and PTHS-TMA⁺ (c) based devices prepared with EG containing solutions, measured at V_G of 0 mV, 400 mV, 500 mV and 600 mV.

Figure S9. Transfer characteristics and corresponding transconductance of cross-linked PTHS[−]TBA⁺ (a), PTHS[−]TEA⁺ (b), and PTHS[−]TMA⁺ (c) based devices prepared with EG containing solutions, measured at $V_D = -500$ mV.