# On the Unexpected Cation Exchange Behavior, Caused by Covalent Bond Formation between PEDOT and Cl⁻ Ions: Extending the Conception for the Polymer−Dopant Interactions

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Ⓢ Supporting Information
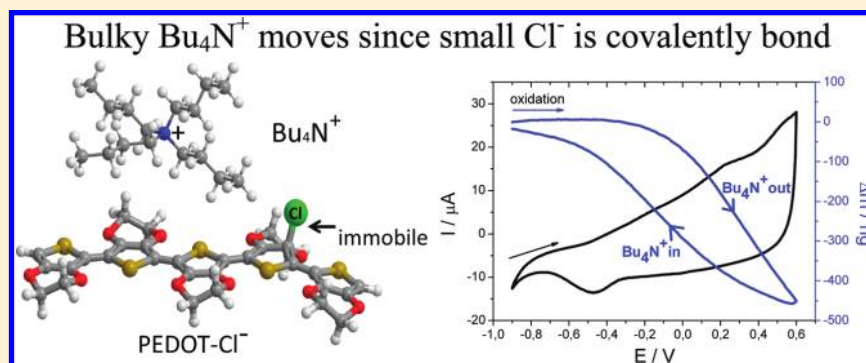
ABSTRACT: The ionic motion in connection with the redox transformation of poly(3,4−ethylenedioxythiophene) (PEDOT) conjugated polymer have been studied by both experimental—electrochemical (electrochemical quartz crystal nanobalance, EQCN) and spectroscopic (infrared spectroscopy, IR−ATR)—and theoretical methods. The observations have been completed by direct, semiquantitative analytical data, provided by energy dispersive X−ray (EDX) microanalysis. The EQCN results suggested an anomalous behavior, since only cationic movements have been observed for films deposited from chloride solutions. Chloride ions were proved to be immobile also when bulky tetrabutylammonium (Bu₄N⁺) cations were substituted with even larger (hexadecyltrimethylammonium) cations. Since PEDOT films synthesized in the presence of other spherical, not too large anions—such as perchlorate and tetrafluoroborate—endowed mixed ion exchange behavior together with the Bu_4N^+ cation, the possibility of a special interaction between chloride and the polymeric chain has been assumed. Semiempirical and DFT calculations indicated that chloride ions interact with the α carbon atoms of the thiophene rings of the oxidized EDOT oligomers, creating sp³ type perturbations in the polymer chain. FTIR−ATR spectra evidenced the appearance of C−Cl bonds. Elementary analysis, performed by EDX spectroscopy with eight polymer samples at different doping levels clearly showed the permanent presence of constant amount of chlorine, independently of the oxidation state of the PEDOT layer. Finally, the presented observations call attention to the fact that unique dopant−polymer interactions during the electrochemical polymerization are of prime importance, being able to rule over conventions for the charge compensation of conjugated polymers, often solely based on steric parameters.

1. INTRODUCTION

The study of the redox transformation of conducting polymers is in the focus of interest since their discovery in 1977.[1] Detailed knowledge on the accompanied ionic and solvent movements is indeed important, since many of the application of such materials rely on these processes.[2,3] During the past decades a large number of studies demonstrated that electrochemical quartz crystal nanobalance (EQCN) can be competently used in the investigation of surface processes and for studying the ionic and solvent exchange at the polymer/electrolytic solution interface.[4−25] These studies revealed that although anion incorporation is the simplest phenomenon in the charge compensation during the oxidation of conjugated polymers, the process may involve also cation and solvent motion, depending on the conditions (e.g., electrode potential) applied during the electrodeposition.[5,6] As for the involvement of cations, a general picture has formed, according to which bulky organic anions may become immobilized in the layers, endowing them with cation exchange behavior. However, a number of recently performed studies indicated a complex picture, namely that larger ions can also move due the redox process in the film,[7,8] and most of the polymer films can be forced to behave as both anion and cation exchangers.[9−11] The background of ion transport properties can also be explained,

and sometimes maybe even predicted by theoretical calculations. However, the phenomenon seems to be complicated, since—beyond the size—also special interactions between the polymeric chain and the ions may affect the overall properties, not speaking about the effect of the solvent, also dependent on the hydrophilic–hydrophobic character of the film.

During the past decade, PEDOT became one of the most intensively studied thiophene type conducting polymers, due to its various favorable properties, such as high conductivity, durability and easy processability. In general, practical applications[12−15] of PEDOT are dominantly based on its redox activity, being closely related to ionic and solvent movements, involved in the charge compensation. Motivated by this fact, counterion incorporation and ion exchange properties of PEDOT was widely investigated,[16−30] and very similar conclusions can be drawn to those presented before for CPs in general. The dominancy of anion flux was evidenced in the presence of generally used, relatively small anions (ClO_4^-, NO_3^-, citrate, SO_4^{2-}, BF_4^-, PF_6^-), while significant cationic contribution was only observed at the negative end of the applied potential regime.[16−20] In contrast, when PEDOT was electrodeposited in the presence of large (sometimes macromolecular) anions, they could be immobilized in the polymeric matrix, and then PEDOT acted as cation exchanger.[21−24] Some reports call attention to the role of solvent, more precisely that beyond the obvious effect of solvation of the electrolyte ions, ionic movements are usually accompanied by solvent expulsion (during doping) and solvent incorporation (during undoping).[18,25] Direct analytical tools have been also deployed to study the doping process of PEDOT. XPS was employed to identify the dopant ion *ex situ*, when PEDOT layers were electrogenerated in various mixtures of conducting electrolytes.[26−28] According to these studies, the Hofmeister series cannot explain the affinity of the polymer toward the different ions completely. Scanning electrochemical microscopic (SECM) studies[29,30] provided controversial data on the involvement of different ions, even compared to results obtained from other techniques. However, it has to be clearly emphasized that in these experiments very thick polymeric layers (up to 13 μm) were investigated, which is significantly different from those studied by EQCN or other techniques.

Despite the above listed achievements, there are still many uncovered aspects, mainly related to the interactions between the counterion and the polymeric backbone. In spite of the large number of studies on the charge compensation process, the mobility of ions has been thought to be governed mainly by their size and charge, while unique interactions were almost neglected. In this paper, we report on the unexpected behavior of the chloride ion doped PEDOT, which result is about to change former perceptions. Scarce studies on PEDOT/Cl systems with various cations reported contradictory results in this respect.[26−30] As demonstrated in the present paper, a strong interaction between the polymer and this anion leads to a film, exhibiting perfect cation exchange property, which is against the general expectations. Moreover, this observation points further than the present system, since it calls attention to the fact that beyond the evident steric factors, specific dopant–polymer interactions are of prime importance from the ion-exchange perspective.

2. EXPERIMENTAL SECTION

2.1. Materials. 3,4-Ethylenedioxythiophene (EDOT) (kind donation from Bayer AG), tetrabutylammonium chloride

(Bu$_4$NCl), tetrabutylammonium fluoride (Bu$_4$NF), hexadecyltrimethylammonium chloride (cetyl-Me$_3$NCl), acetonitrile (AN) (Sigma-Aldrich), sodium chloride (NaCl) (VWR International), tetrabutylammonium-perchlorate (Bu$_4$NClO$_4$), tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (Fluka) were used as received. The aqueous solutions were prepared with ultrapure deionized water (Millipore).

2.2. Methods. All electrochemical measurements were performed on a PGSTAT 302 (Autolab) instrument, in a classical three-electrode electrochemical cell. The reference electrode was an Ag/AgCl/3 M NaCl electrode, having a potential 0.200 V vs the standard hydrogen electrode (SHE).

Poly(3,4-ethylenedioxythiophene) (PEDOT) films were prepared potentiostatically at the potentials properly chosen accordingly to the different solvents ($E = 1.10$ and 1.30 V, in water and acetonitrile respectively), as it is depicted in Figure 1.
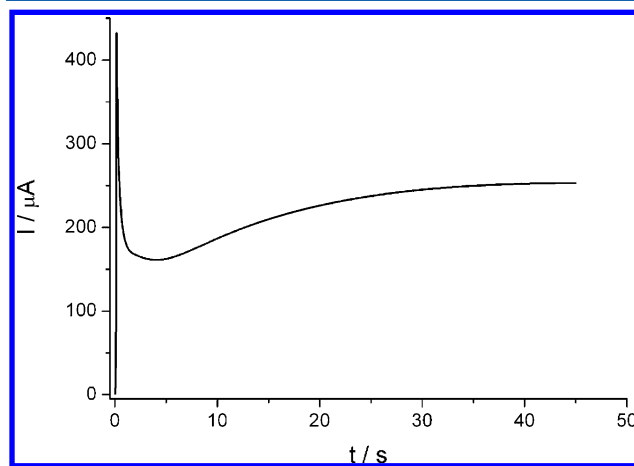

Figure 1. Typical chronoamperometric polymerization curve of PEDOT in 0.05 M Bu$_4$NCl in water at $E = 1.1$ V.

The polymerization solutions contained 0.01 M of the EDOT monomer and either 0.05 M Bu$_4$NCl or 0.025 M Bu$_4$NBF$_4$, or 0.1 M NaCl in water and 0.1 M Bu$_4$NClO$_4$ in AN. The polymerization charge was controlled, and charge density was limited in each case to 50 mC/cm^2, to fulfill the requirements to avoid viscoelastic effects, when EQCN measurements were also performed.[31] The spectral behavior was investigated by FT−IR spectroscopy, while for the elementary analysis, EDX measurements have been used. For these methods, thicker layers have been synthesized, with a deposition charge density of 300 mC/cm^2. In this case, the Pt working and counter electrode surfaces were 2 cm^2.

Cyclic voltammetric curves have been registered at different sweep rates between 10 and 100 mV/s in the solutions containing 0.05 M Bu$_4$NCl, 0.025 M Bu$_4$NBF$_4$, 0.1 M cetyl-Me$_3$NCl in water, and 0.1 M Bu$_4$NClO$_4$ in AN, respectively. During the multiple potential step experiments, the layers were conditioned at −1.0 V for 60 s, then the potential was stepped to −0.8/−0.6/−0.4/−0.2/+0.0/+0.2/+0.4/+0.6 V and was kept there for 60 s in all cases, in order to modify the oxidation level stepwise.[32] For clarity, the composition of the solutions and their notation are summarized in Table 1.

EQCN measurements have been carried out by using a quartz crystal resonator and analyzer EQCM-Oscillator (Autolab module). The crystals ($f_0 = 6$ MHz) were gold coated, and had an overall diameter of 1.36 cm, while the piezoelectrically active area (identical with the geometric area)

Table 1. Composition of the Polymerization Solutions and Their Notation throughout the Text

solution containing	system notation
0.05 M Bu_4NCl in water	PEDOT/Bu_4NCl/aqueous
0.1 M Bu_4NClO_4 in acetonitrile	PEDOT/Bu_4NClO_4/AN
0.025 M Bu_4NBF_4 in water	PEDOT/Bu_4NBF_4/aqueous
0.1 M cetyl-Me_3NCl in water	PEDOT/cetyl-Me_3NCl/aqueous

of the Au working electrode was 0.352 cm^2. The EQCM system was calibrated by electrochemical deposition of lead, using the standard procedure, and the value of −5.04 ng/Hz calibration constant was obtained.

Both the oxidized and the reduced states have been investigated by FT−IR spectroscopy using a Bio-Rad Digilab Division FTS-65A/896 Fourier transform infrared spectrometer equipped with a Harrick's Meridian SplitPea single-reflection diamond attenuated total reflectance (ATR) accessory. All infrared spectra were recorded between 4000 and 400 cm^{-1}, at 4 cm^{-1} optical resolution, by averaging 256 interferograms.

Hitachi S-4700 scanning electron microscope coupled with EDX unit (Röntec QX2) was used to obtain direct data for the elemental composition of the layers. EDX measurements were performed with polymeric films deposited onto Pt electrodes. After the polymerization, the films were transferred into a solution containing 0.05 M aqueous Bu_4NCl solution, and (after a conditioning step described above) reoxidized to various doping levels. Then, they were immediately removed from solution, washed with water, dried, and the elemental analysis was performed. All data presented in the related figures have been obtained by averaging the results measured at three different areas on the films.

2.3. Computational Information. Computations were performed at two levels of theory—the modern semiempirical parametrization PM6,[33] and density functional theory (DFT) in the flavor of the popular B3LYP[34,35] functional using the standard split valence basis set 6-31+G(d,p) were applied. MOPAC 2009[36] and Gaussian 03[37] software were used. Chloride ion complexes with EDOT pentamer cations of different oxidation states were considered, all the geometries were fully optimized without applying any symmetry or other constraints. Various initial geometries were tried in attempt to describe the potential energy surface by finding the most significant local energy minima.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of the PEDOT Synthesized in Aqueous Bu_4NCl Electrolyte. A typical cyclic voltammogram obtained during EQCN measurements in the presence of Bu_4NCl, at a scan rate of 50 mV/s with the PEDOT film, polymerized in aqueous solution of Bu_4NCl, is presented in Figure 2A. The pattern of the curve indicates a delayed reduction of the film, seeing from the negative current during the first section of the positive going scan. Mass changes, registered in parallel with the electrochemical transformation are also depicted in Figure 2A. They reflect that the mass decreases during the oxidation, and increases during the reduction. It is also proved that the delayed reduction is accompanied by the elongated mass increase, reflecting a slow cation uptake. The dominancy of cationic movements is against any presumptions, since chloride is generally considered as a small and mobile anion. However, bulky Bu_4N^+ cations seem to be relatively more mobile here, leading to the cationic exchanger pattern of this film.

In order to quantify this assumingly cation exchanging behavior, mass change vs. charge curve—obtained after the transformation of the data in Figure 2A—is presented in Figure 2B. The turn-point of the sign of the charge at the potential at $E = -0.41$ V indicates the starting of the removal of the cations. The slope of the Δm vs ΔQ curve gives an estimation of the virtual molar mass of the moving species related to the charge compensation during the redox transformation.[4] This value, derived from the slope of the curve in Figure 2B, is close to the theoretical value of 242 g/mol for Bu_4N^+ ions, evidencing the dominant cationic exchange. In Table 2, the values of the virtual molar masses for the species—expelled from the film upon oxidation at different sweep rates—are summarized. As it can be seen, the slower the scan rate, the closer the theoretical value of 242 is approached—owing assumingly to the better approach to the stationary process.

In order to gain further insight into this unexpected phenomenon, cyclic voltammograms of the system presented in Figure 2 have been recorded—after a solution change—in aqueous solution of Bu_4NBF_4. Investigations in this electrolyte can be indeed informative, since it contains the same cation,
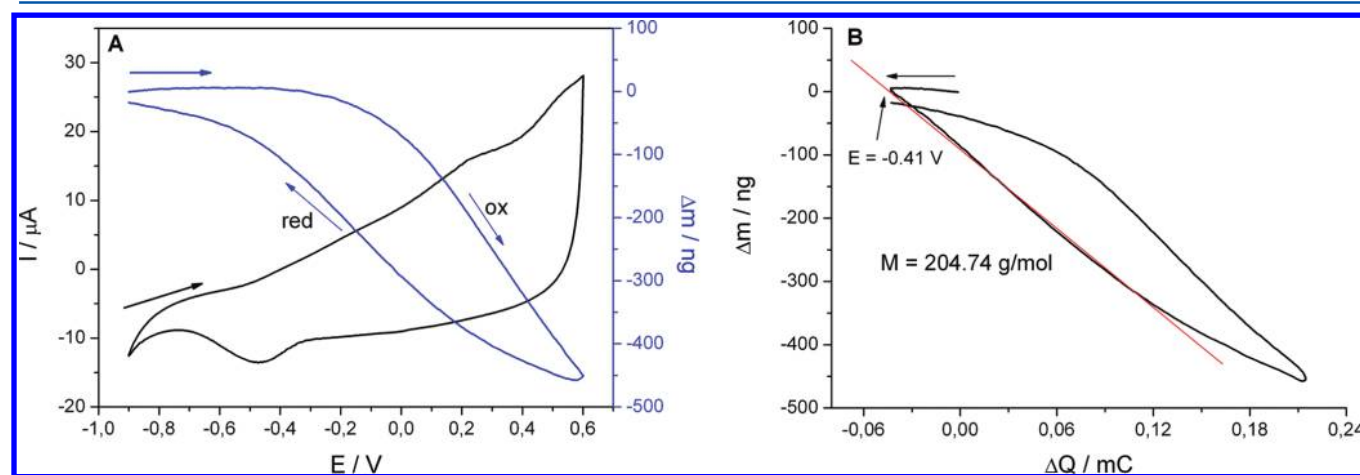

Figure 2. (A) Cyclic voltammogram of PEDOT/Cl measured at a sweep rate of 50 mV/s in 0.05 M Bu_4NCl in water, together with the mass change recorded by EQCN. (B) Mass change vs the integrated charge from the cyclic voltammogram in part A.

Table 2. Virtual Molar Masses of the Moving Species Determined from EQCM Data Measured for the PEDOT/Bu$_4$NCl/Aqueous System in Bu$_4$NCl (Second Column) and Bu$_4$NBF$_4$ (Third Column) Electrolytes

	M (Bu$_4$N$^+$) = 242.4 g/mol	
ν/mV s^{-1}	M/g mol^{-1}	M/g mol^{-1}
10	239.66	322.53
25	229.60	250.54
50	204.74	184.79
100	197.45	147.57

while tetrafluoroborate anion has about the same size[38] as chloride, thus the only difference is the chemical character of the anions. It can be clearly seen in Figure 3A, that both the voltammogram and the mass change curve exhibit a very similar pattern compared to that of recorded in the presence of Cl$^-$ ions (Figure 2A). As for the virtual molar masses derived from Δm vs ΔQ curves (Figure 3B), the similarity, compared to the previously shown system, is evident both in the values and in their trend (see Table 2). This cation exchanging behavior, observed in the presence of BF$_4^-$ is rather surprising, since this anion was proved to be involved in the charge compensation for all the studied systems so far (see the Introduction).

3.2. Electrochemical Behavior of the PEDOT Synthesized in Aqueous Bu$_4$NBF$_4$ Electrolyte. On the ground of the previous observations, we decided to extend our comparative investigation to further PEDOT systems, since the indication of the dominancy of cationic movements is surprising in the light that smaller anions proved to participate easily in the charge compensation process or at least as part of a mixed cationic−anionic exchange.[16−20,39,40] In order to clarify the role of the electrolyte during the electrodeposition, and redox transformation of PEDOT, we performed the mirror experiment of the measurements presented in Figures 2 and 3. More precisely, PEDOT was electrogenerated in the presence of Bu$_4$NBF$_4$ under identical circumstances as its Cl$^-$ ion containing counterpart and was studied in both BF$_4^-$ and Cl$^-$ containing aqueous solutions.

The mixed character of the ionic movements can be visualized on the example of Bu$_4$NBF$_4$ in Figure 4. As is marked in the different sections, the mass changes can be interpreted by considering both anion and cation incorpo-

ration/removal. The inserted comments in the figure indicate the dominant charge compensation process. The complex character of the mass change − transferred charge shows that mixed ionic transport is general during the transformation of PEDOT in the presence of tetraalkyl ammonium tetrafluoroborate in water (Figure 4B), similarly to the behavior observed in acetonitrile with the same electrolyte.[17] We would like to also call attention to the similarity with the PPy/Bu$_4$NBF$_4$/AN system, described recently.[32]

On the other hand, after changing the solution to the Cl$^-$ containing electrolyte (Figure 5), the shape of the nanogravimetric curves are indeed uniform to those obtained in the presence of BF$_4^-$ (Figure 4). The mixed ionic movements are undoubtly visible: with the dominancy of anionic movements in the anodic, and cationic movements cathodic potential regimes, respectively. At the same time, it is also important to call attention to the striking difference in the shape of these curves compared to those presented in paragraph 3.1., which is rather interesting since the experiments have been carried out in the same electrolyte (Figures 2 and 5; Figures 3 and 4), the only difference was the electrolyte being present during the polymerization. This observation suggests that the ion exchange property of PEDOT is predominantly driven by the polymerization conditions, namely the electrolyte in the solution.

Importantly, for both PEDOT films polymerized in the presence of Cl$^-$ ions, EQCN results clearly proved the unexpected cationic exchange behavior of the film by giving an evidence for that Bu$_4$N$^+$ ions are leaving it during the oxidation, so that they are incorporated into the film (Scheme 1). However, the film should be neutral in the reduced state, and hence the negative charges of the immobilized anions must be compensated by an equivalent positive charge within the layer; consequently, cations are also incorporated in there. In order to gain deeper insight into these phenomena, the closer study on the surprising and irregular pattern was decided, and further experiments have been carried out in the presence of other electrolytes.

3.3. Comparison with Other Cl$^-$ Containing Electrolytes: PEDOT/Cetyl−Me$_3$NCl/Aqueous. In order to obtain further confirmation to our hypothesis related to the immobilization of chloride anions, additional studies have been conducted with other systems. It is generally assumed that the irreversible incorporation of ions into the polymers is
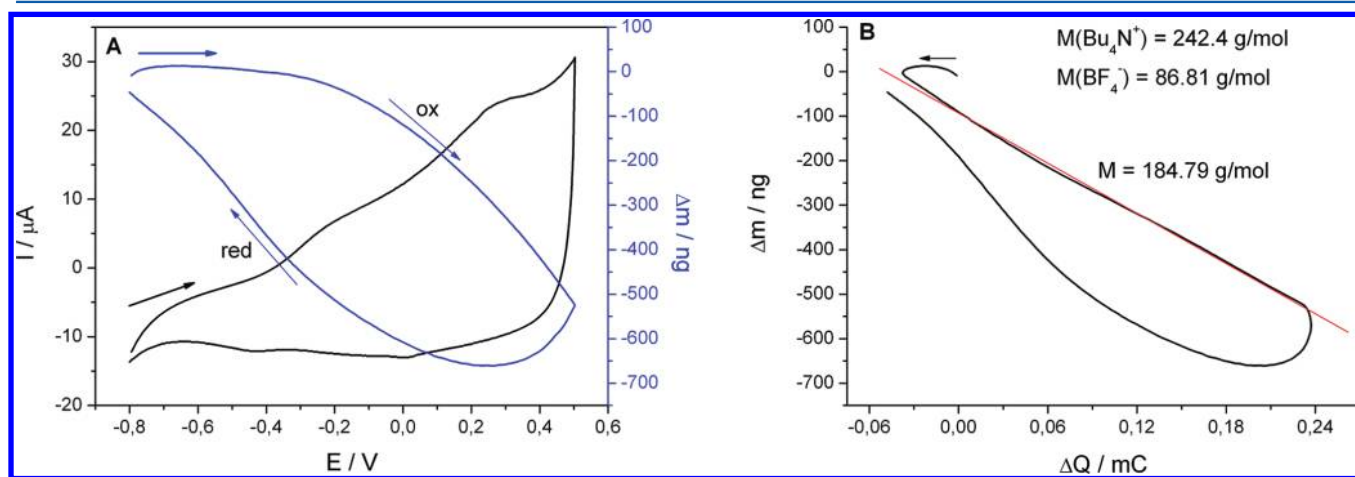

Figure 3. (A) Cyclic voltammogram of PEDOT/Cl measured at a sweep rate of 50 mV/s, in 0.05 M Bu$_4$NBF$_4$ in water, together with the mass change recorded by EQCN. (B) Mass change vs the integrated charge from the cyclic voltammogram in part A.
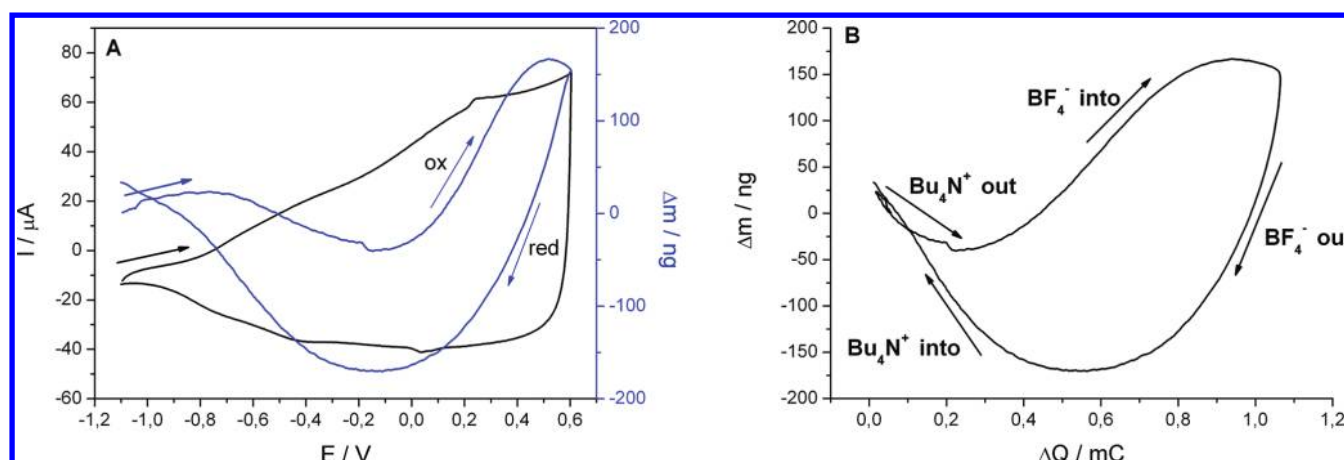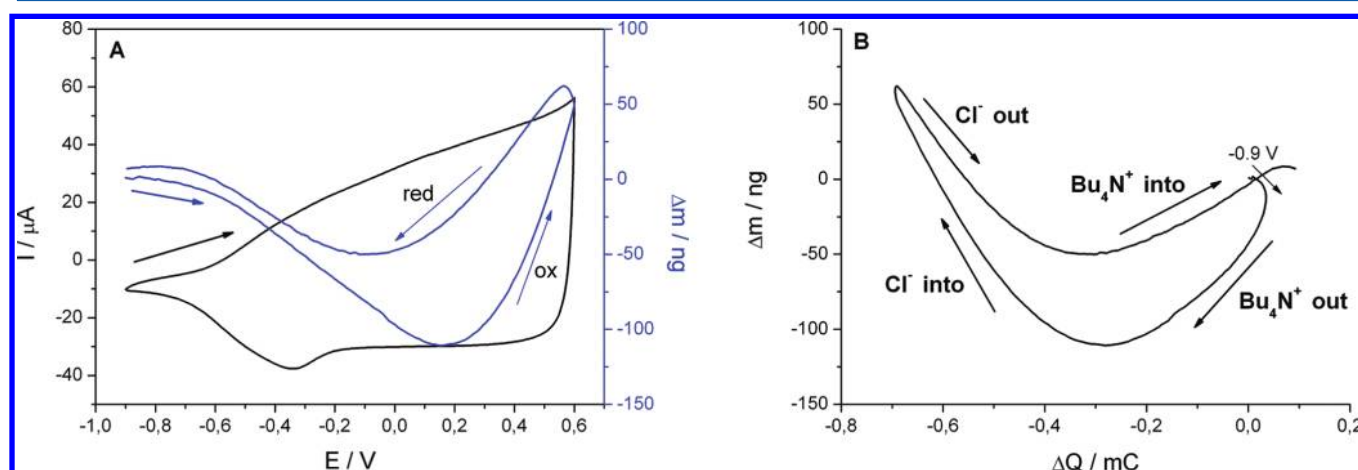
Figure 4. (A) Cyclic voltammogram of PEDOT/BF$_4$ measured at a sweep rate of 50 mV/s in 0.05 M Bu$_4$NBF$_4$ in water, together with the mass change recorded by EQCN. (B) Mass change vs the integrated charge from the cyclic voltammogram in part A.

Figure 5. (A) Cyclic voltammogram of PEDOT/BF$_4$ measured at a sweep rate of 50 mV/s in 0.05 M Bu$_4$NCl in water, together with the mass change recorded by EQCN. (B) Mass change vs the integrated charge from the cyclic voltammogram in part A.

Scheme 1. Cationic Exchange Behavior of the Presented PEDOT/Cl Film: at the End of the Polymerization, after the Reduction, and upon the Re-Oxidation Process[a]
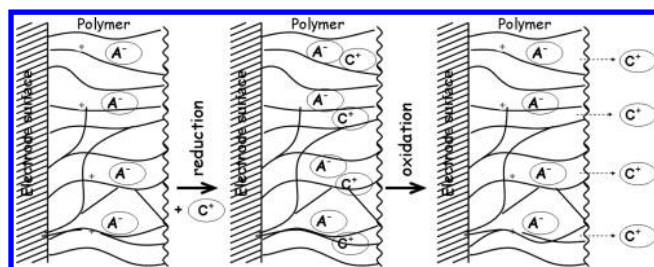
[a]The behavior of moving cations (C$^+$) and the immobile anions (A$^-$) are shown.

related partly to their size. On this basis, similar studies in cetyl−Me$_3$NCl solution have been performed, where the exclusion of the traffic of the cetyl−Me$_3$N$^+$ ion can be presumed, due to its long alkyl "tail" similarly to dodecyl sulfate.[22] However, the polymerization of EDOT in aqueous cetyl−Me$_3$NCl solution proved to be difficult, so another route has been attempted: the polymerization was performed in aqueous NaCl solution, and the polymer was cycled in aqueous

cetyl−Me$_3$NCl solution afterward. This solution change was applied twice.

The results are presented in Figure 6, which has a very similar shape to those shown previously (Figures 2 and 3), where the dominantly cationic movements are clearly visible. The transformation of the EQCN data confirms this behavior. Figure 6B presents one example giving slope values that exceed significantly the mass of Na$^+$ ions. The slope values, obtained at both branches of the scan, summarized in Table 3, show an increase with the decrease in the sweep rate. At the same time, they suggest that there is a gradual change in the virtual molar mass of the moving cation, which is dominantly sodium at first, with the freshly polymerized film, but they are gradually substituted—at least partially—by the cetyl−Me$_3$N$^+$ ions as a result of continuous cycling and repeated solution change.

The intermediate values obtained for the virtual molar mass mean that in case of the PEDOT/cetyl-Me$_3$NCl/aqueous layer, the charge compensation process is the combined movement of cations, proving that chloride is immobile. This conclusion is unexpected, since the small spherical anions are always in a favorable situation, when they are in competition with bulky and more hydrophobic cations.

3.4. Spherical Anion of Similar Size in Nonaqueous Medium: PEDOT/Bu$_4$NClO$_4$/AN. Our control measurement in acetonitrile with PEDOT/Bu$_4$NClO$_4$/AN clearly proved that
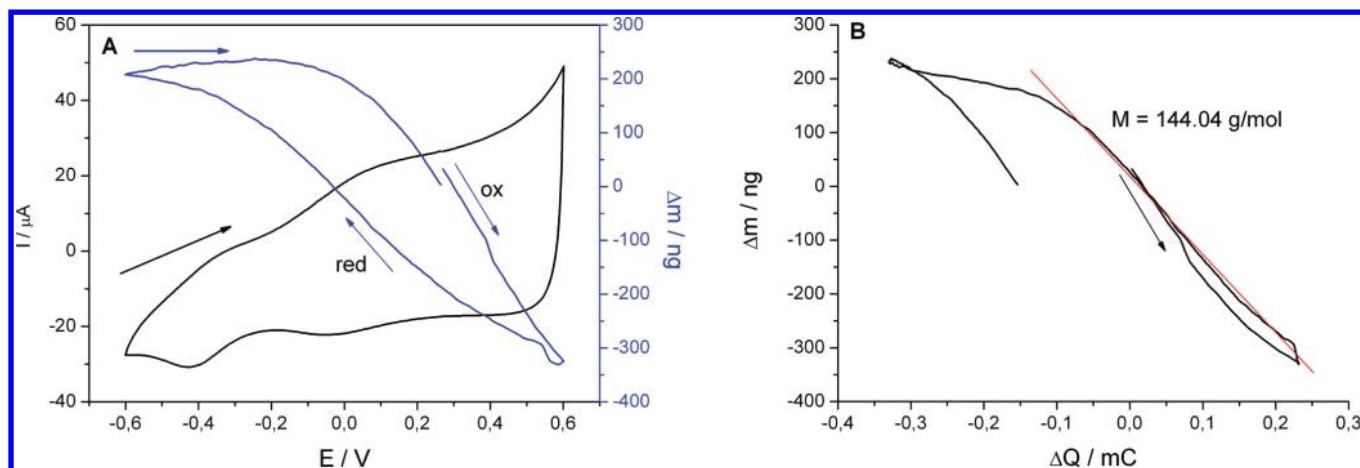
Figure 6. (A) Cyclic voltammogram of PEDOT recorded at 50 mV/s sweep rate in 0.1 M cetyl−Me₃NCl in water, together with the mass change recorded by EQCN. (B) Mass change vs the charge derived from part A.

Table 3. Virtual Molar Masses of the Moving Species Determined from EQCN Data of the PEDOT/Cetyl− Me₃NCl/Aqueous System[a]

	M/g mol^{-1}	
v/mV s^{-1}	first CV measurement	second CV measurement
10	132.03	217.40
25	127.48	192.52
50	105.96	144.04
100	85.34	112.48

[a]M(cetyl−Me₃N$^+$) = 284.2 g/mol.

a spherical anion, such as perchlorate is mobile during the redox transformation of PEDOT (Figure 7), having the same cation in the solution, as in the systems presented before.

The first evident observation we can make is the completely different shape of the $\Delta m-E$ curves, compared to the ones shown before for the Cl$^-$ based samples, and the similarity to those obtained in the presence of BF₄$^-$. For this film, the unambiguously anion exchanging property can be seen between 0 and +1.0 V and +1 and −0.4 V during the oxidation and reduction, respectively. This observation is a further proof of our assumption, namely that the unexpected cation exchanging property can be seen only in case of PEDOT films polymerized

in Cl$^-$ containing electrolytes, but not in case of other small anions (BF₄$^-$, ClO₄$^-$). We may assume that there is an interaction between the oxidized polymer and the Cl$^-$, which makes the anion immobile, and force the polymer to act as cation exchanger, similar to those systems, when large anions are entrapped due to their size.[21−24]

3.5. Semiempirical and DFT Calculations. In order to study the possible interactions between the polymeric backbone and the dopant ion, quantum chemical calculations were performed. According to the results of PM6 semiempirical calculations, the potential energy surface for the location of the chloride anion near the polymer chain at low charges is relatively shallow, with numerous local energy minima near (or above) the sulfur and carbon atoms of the thiophene ring. The polymer chain in these complexes remains mostly unperturbed (more or less planar), with the shortest interatomic distances of 1.6 to 1.85 Å for Cl−S and Cl−C pairs, respectively. This result cannot be used to explain in any way the experimentally observed trapping of chloride anions inside the polymer film. However, if the local (positive) charge density on the PEDOT chain is higher, another lowest energy minimum is found that is somewhat surprising. It appears that the chloride anion can attack the α-carbons of the thiophene ring part or EDOT units (see Figure 8.) and form something close to a covalent bond with the carbon atoms, changing the hybridization of the
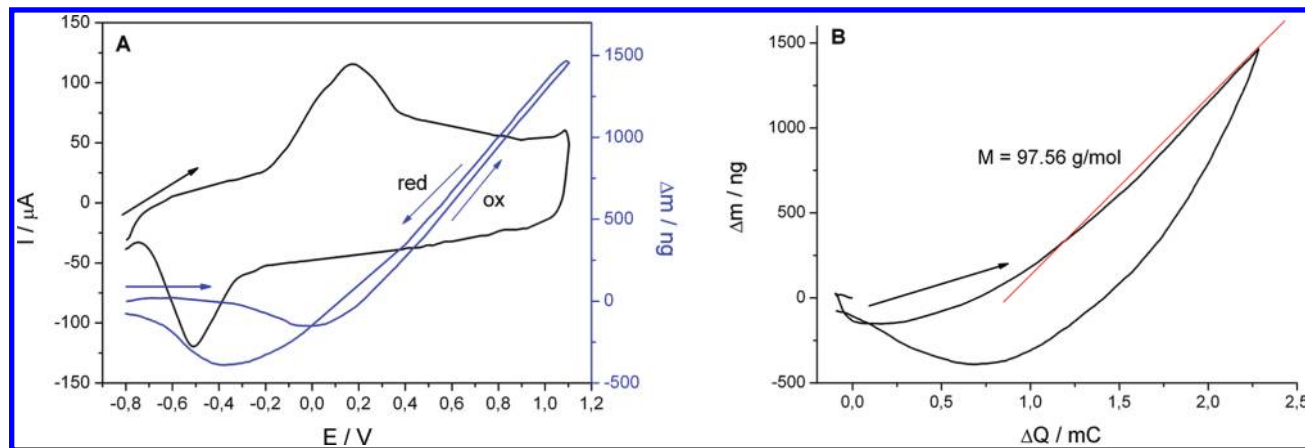

Figure 7. (A) Cyclic voltammogram of PEDOT recorded at 50 mV/s sweep rate in 0.1 M Bu₄NClO₄ in acetonitrile, together with the mass change recorded by EQCN. (B) Mass change vs the integrated charge from the cyclic voltammogram in part A.
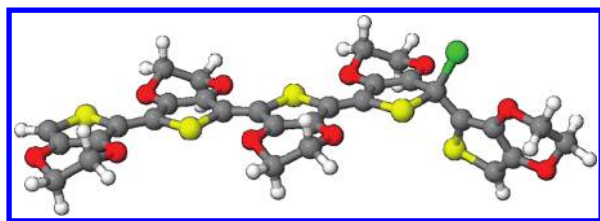
Figure 8. Complex of chloride anion and EDOT pentamer dication, optimized by PM6.

Figure 9. The difference spectrum (a − b) of the reduced (a) and oxidized (b) form of the PEDOT polymer produced in the presence of Bu$_4$Cl, features strong bands in the range of the in-plane vibrational modes of the thiophene ring (1550−1200 cm^{-1}). Most of the other bands can also assigned to the various other modes of the thiophene ring.[41,42]

carbon atom from pure sp^2 to almost sp^3, accompanied by the loss of planarity of the chain. Analysis of partial charges (both Mulliken and fitted electrostatic potential type) indicates that the positive charge on the oligomers is mostly located on these carbons, resulting in a partially unoccupied orbital. This observation is coherent with the previously presented experimental data (parts 3.1 and 3.2), namely that the interaction between Cl$^-$ ions and the oxidized PEDOT is being developed during the polymerization, when significantly higher potential is applied than during the voltammetric studies. As a comparison of the bond character, the corresponding optimized interatomic C−Cl distance (∼1.77 Å) is in between the Cl−C distances in chlorobenzene and 2-chloropropane indicating a much stronger interaction. The gain in potential energy over purely ionic complexes is in the range of 8 to 11 kCal/mol, depending on the position of the ring in chain (largest for terminal units). Similar interactions were also found with the beta carbons of thiophene rings, but with smaller gain in potential energy. The presumably more accurate DFT calculations gave qualitatively very similar results, indicating a local energy minimum with short interatomic distance for C−Cl. Upon reduction, when the oligomer is forced to neutral, in case of PM6 calculations the sigma complex and sp^3 configuration of the carbon remains intact (with some alteration of the dihedral angles bond lengths), while in case of DFT the chloride anion is evicted and the lowest energy (although by just a few kcal/mol) is again found for the planar configuration. The comparison with the experimental situation is quite difficult, as separated polymer fragments do not really describe the configuration of tightly packed chains of chloride-doped PEDOT, where additional steric blocking may not allow the relaxation of the chains and release of the anion, easily reversing the depth of the potential energy minima. Another aspect favoring the result of the PM6 calculations is the fact that if the positive charge on the chains is reduced but not quite to zero, the nonplanar complexes remain favored by both methods. This would correspond to an experimental situation where the tight packing and reduced conductivity of the nonplanar chains does not allow the complete reduction of the polymer.

3.6. Infrared (ATR FT−IR) Spectroscopic Studies.
Infrared spectra of the oxidized and reduced PEDOT polymers, electrodeposited in the presence of Bu$_4$Cl and Bu$_4$F were compared to each other. The spectral subtraction confirmed the destruction of benzoid structure upon oxidation, since the difference spectrum (a − b = red. − ox. see Figure 9) features strong bands in the range of the in-plane vibrations of the thiophene rings, at 1500, 1467, 1432, 1359, and 1071 cm^{-1}, while the very weak bands at 923, 845, 734, and 697 cm^{-1}, could be attributed to further vibrations of the rings, in which there were considerable contribution from the C−S bonds. The
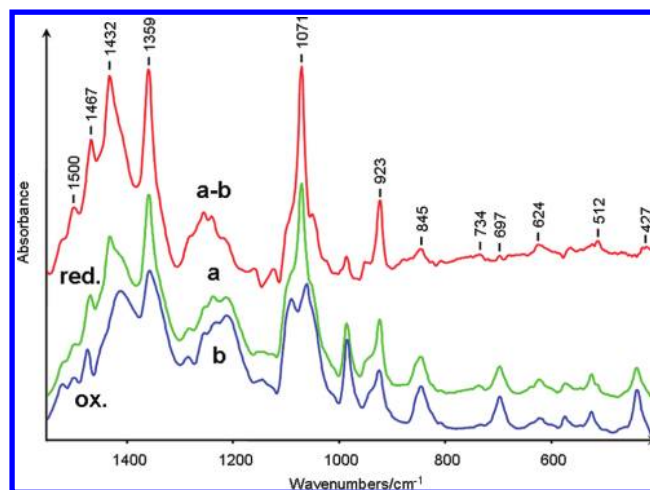
bands at 512 and 427 cm^{-1} were within the range of the out-of-plane vibrations of the fully substituted thiophene ring.[41,42]

It is also possible to characterize the peculiar behavior of the chloride ion revealed by our experiments in detail through molecular spectroscopic investigation. At the same time, these measurements were be able to give an answer to the question, whether the C−Cl interaction were permanent or it was eliminated upon the reduction of the PEDOT, as some of the DFT calculations might suggest. Vibrational spectroscopy was a good choice since the independent chloride ion itself should have no trace in the mid-infrared region, but a covalent carbon-chlorine bond gives rise to a stretching band in the 800−600 cm^{-1} region.[41] On the other hand, however, this region does contain several bands from the fingerprint vibrations of the PEDOT polymer, so reference materials without chlorine content were also needed to identify these bands. The use of tetrabutyl ammonium fluoride salt instead of the corresponding chloride salt was able to provide this possibility; moreover, it had another advantage: the formation of a covalent carbon−fluorine bond also can be identified in the (much higher) mid−IR region (1410−1000 cm^{-1}).[41] The C−Cl stretching vibrational range of the spectra for the oxidized and reduced state of the polymer, prepared by chloride and fluoride salts are given in Figure 10. The most important difference in the above-mentioned region was an additional intensity appearing around 620 cm^{-1} in the chloride containing samples (curves a and b). This weak band overlaps with others, having similar intensities, belonging to the fingerprint bands of the polymer, which were also present in the other fluorine containing samples. Four bands were fitted to this range of the spectra of the fluorine containing samples (curves c and d, see insert in Figure 10. for curves a and c) in order to make it obvious that they were unable to describe the other two spectra. The difference spectrum (a−c) (see insert in Figure 10) showed a broad new band at 624 cm^{-1}, attributed to the stretching mode of the C−Cl covalent bond. The theoretical calculations also predicted the new band between 600 and 650 cm^{-1} (see the Supporting Information, Figure S1).
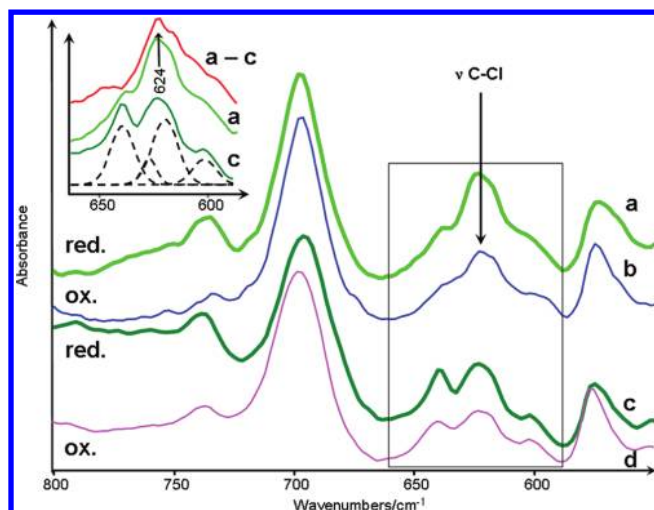
Figure 10. C−Cl stretching vibrational range of the spectra for the oxidized (curves b, d) and reduced states (curves a, c) of the polymers, prepared by chloride (a, b) and fluoride (c, d) salts. The inset shows the C−Cl band at 624 cm^{-1}, in difference spectrum of the reduced forms with the four bands fitted to this range of the spectrum of the fluorine-containing samples (curve c).

Further support was given by the comparison of the stretching range of C−F bond for the same four spectra to our finding. The most prominent differences were between the chlorine and fluorine containing samples, bands at 1148 cm^{-1}, which were assigned as the stretching bands of the C−F bond (see Figure 11, curves c and d), present either in the oxidized or in the reduced sample.
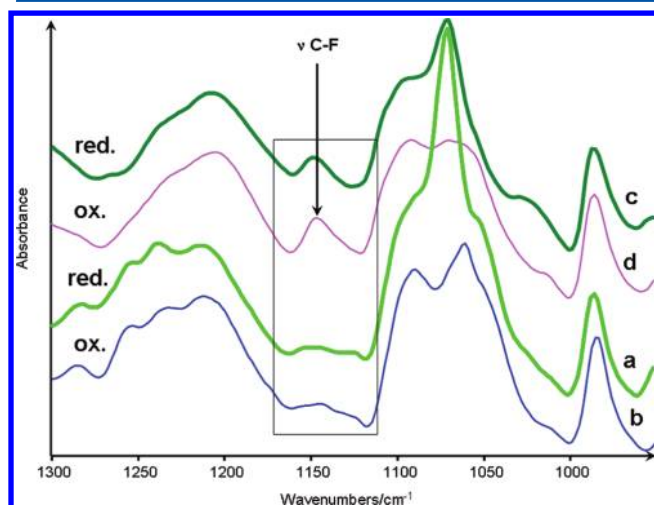

Figure 11. The carbon−fluorine stretching range and the spectra of the polymers in different oxidation states: oxidized states (b, PEDOT/Bu$_4$NCl film; d, PEDOT/Bu$_4$NF film) and reduced states (a, PEDOT/Bu$_4$NCl film; c, PEDOT/Bu$_4$NF film).

The low intensities of both carbon−halogen stretching bands suggested the presence of covalently bonded halogen in a low proportion, since these bands inherited high molar absorbance, due to the strong polarization of the carbon−halogen bond. On the other hand, a slight variation in the intensity of the corresponding bands between the oxidized and reduced state of the polymer (see Figure 9 a band at 624 cm^{-1} in the difference spectrum), did not mean that the bonding of the halogens was

reversible, since the much less polarized carbon−carbon and carbon−sulfur bonds forming the ring produce much stronger bands on rearrangement of the conjugated backbone.

3.7. Elementary Analysis of PEDOT/Bu$_4$NCl Layers by EDX Spectroscopy. In order to confirm the assumptions and conclusions, made on the basis of the experimental and theoretical results, direct elementary analysis was performed with eight individually but identically polymerized PEDOT/Bu$_4$NCl/aqueous layers. Reproducible redox behavior, and thus the comparability of the samples can be seen in the Supporting Information (Figure S2). The various layers have been conditioned at 8 different potential values, and EDX measurements have been performed with layers being at the different oxidation states.

A typical EDX spectrum is presented in Figure 12, showing the signals originating from the substrate electrode (Pt), the
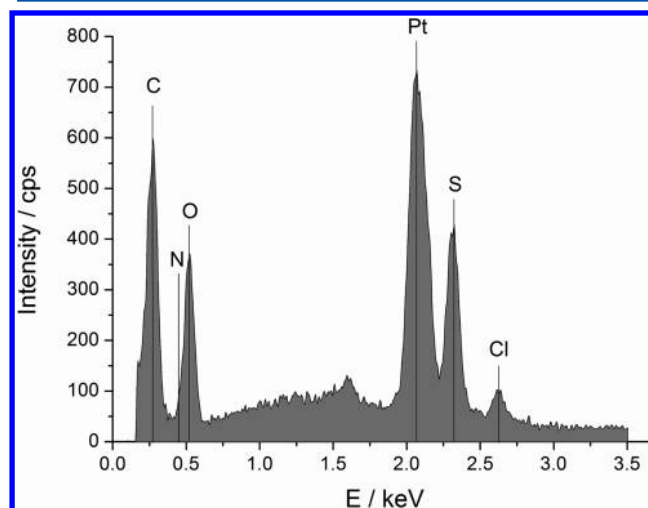

Figure 12. Sample EDX spectrum of a PEDOT layer synthesized potentiostatically in 0.05 M Bu$_4$NCl in water for a charge density of 300 mC/cm^2, and conditioned at the potential of E = +0.6 V.

polymer (C, S, O), and the Bu$_4$NCl electrolyte. Unfortunately the appearance of the Pt substrate is unavoidable, since we wanted to study layers with at least similar thickness to those investigated electrochemically. After the evaluation of the spectra, semiquantitative data can be obtained for the relative amounts of different elements in the sample. In order to avoid any uncertainties arising from the quantification, the *ratio* of the amounts of sulfur over chlorine was calculated, which can be used as the *ratio* between the monomeric units and the incorporated anion.

The results obtained for the eight samples are presented in Figure 13. The first thing which can be clearly seen is that the ratio is independent of the potential of conditioning, i.e., of the oxidation state of the films. The error bars refer to the dispersion of the data calculated from the quantification of 3 spectra acquired at 3 different areas of the samples. Thus, Figure 13 directly provides evidence that the monomer/anion ratio does not change with the doping level. This unambiguously confirms our previous assumption, namely that Cl$^-$ ions are not involved in the ionic movements. It is even worth having a look at the value of these ratios, since they evidence that one chlorine/∼six monomer units remains immobile during the redox transformation.
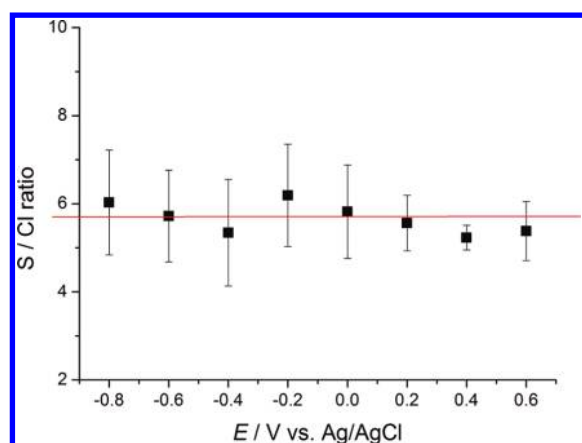
Figure 13. Relative amount of the monomeric unit over the dopant chloride as the S/Cl ratio for the PEDOT layers conditioned at eight different potentials.

Figure 14. Comparison of doping levels for each PEDOT samples presented in Figures 2−6. The annotations on the axis refer to the polymerization electrolyte, while the anions on the bars reflect the anion being present during the voltammetric studies.

3.8. Consequences of the Interaction between the Polymeric Backbone and Cl⁻ Ions. The fact that the amount of the chloride ion is constant, independently from the oxidation state of the polymer, is in perfect accordance with the EQCN results, indicating only cationic movements during the redox transformation of the PEDOT/Bu$_4$NCl/aqueous film. This feature must mean that the charge of the oxidized polymer is compensated by the actual amount of the anions, while the neutral film contains cationic and anionic charges evidently in equal amounts. The incorporation of the anions has to occur during and after the polymerization, hence the amount of chloride ions does not change afterward. We have to conclude that the anions accumulate during the formation of the film, according to the extra charge consumed for the oxidation of the actual amount of the polymer. The interaction between the polymeric chains and the dopant anions is strong enough for them to be pertained even within the reduced layer. Chloride ions cannot be expelled from the neutralized film, and cations have to be incorporated to compensate the charge of the anions. From all these features it is evident that—upon oxidation in a monomer-free solution—Bu$_4$N$^+$ ions leave the layer, endowing it with the cation exchanger behavior, even in the presence of other small anions.

As the reviewers pointed out, the existence of a covalent bond between the oxidized PEDOT and Cl⁻ results in partial loss of conjugation due to the formation of sp^3 carbon atoms, and consequent loss of planarity. In order to shed further light on this important aspect, it is worth comparing the presented voltammograms and nanogravimetric curves again (Figures 2−7). Beyond the obvious alteration in the ion exchange behavior of the Cl⁻ and non-Cl⁻ polymerized samples, careful investigation of the voltammograms reveals further interesting differences, related to the charge capacity of the films. The much lower current densities, observed for the samples polymerized in the presence of Cl⁻ ions are striking. Moreover, this difference seems to be independent from the electrolyte employed during the voltammetric cycling. This trend can be further quantified by comparing the doping levels[4] of the different systems. Comparison of the value of doping levels calculated from polymerization charge and voltammetric data (presented in Figures 2−6) is depicted in Figure 13. In agreement with our expectations, the difference is clearly visible, since the doping level (Figure 14) for all the samples polymerized in the Cl⁻-containing solution is drastically smaller
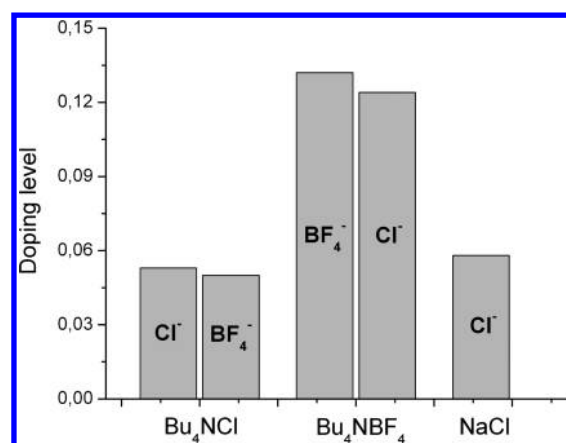
(that is one-third) compared to those polymerized in the BF$_4$⁻-containing solution. This reflects to the weaker electroactivity of these samples, which is not surprising in light of the interaction, and the resulted structural changes described above. Finally, the absolute values of the doping levels look somewhat smaller than those usually observed for conducting polymers, but this may be the consequence of the fact that electro-deposition of PEDOT is more favorable in organic media, or in aqueous micellar solutions.[43]

■ CONCLUSIONS

In this study, the unusual cationic exchange behavior of PEDOT films, electrogenerated in Cl⁻ ion containing media, was demonstrated. On the ground of cyclic voltammetric and nanogravimetric results, the key role of the electrolyte being present during the polymerization was evidenced. The formation of permanent C−Cl covalent bonds as predicted by modeling (DFT and semiempirical) has been revealed by the FT−IR−ATR spectroscopy. Moreover, their existence was proved by discovering C−F bonds within the analogue PEDOT/Bu$_4$NF film. The formation of such bond may decrease the conjugation of the polymeric backbone, which was reflected in the smaller doping levels of the Cl-containing samples. Importantly, we proved that even without utilizing large/macromolecular anions, PEDOT can be forced to act as a cation exchanger. Moreover, this observation calls attention to the fact that dopant−polymer interactions may overwrite former, traditional concepts for the mobility of ions in connection with the charge compensation of conjugated polymers. The evidenced formation of covalent bond between a polymer segment and the dopant enlightens the necessary consideration of even a wide spectrum of individual, eventually less strong interactions. Finally, the special interaction between PEDOT and Cl⁻ ions may open new opportunities in the field of electroanalysis or separation techniques.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

DFT simulated IR spectrum and cyclic voltammograms of PEDOT. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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