Effects of cationic species in salts on the electrical conductivity of doped PEDOT:PSS films

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Abstract Graphic

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Figure 1. Chemical structure of PEDOT:PSS and ionic salts used in this work.

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Figure S6. Dynamic light scattering (DLS) data of PEDOT:PSS and salt-mixed PEDOT:PSS dispersions.

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Effects of cationic species in salts on the electrical conductivity of doped PEDOT:PSS films

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Abstract

The influence of chemical composition of the doping salts on the conductivity of the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films was studied in this work. A series of salts with different cations but the same anion were mixed with PEDOT:PSS. We found out that doping salts of small-size cations led to better conductivity due to the improved crystalline ordering of PEDOT, as revealed by the grazing-incidence wide-angle X-ray scattering (GIWAXS) data. This phenomenon can be rationalized with the fact that small-size cations can dissociate the PSS from PEDOT due to stronger Coulomb interactions, leading to rearrangement of the PEDOT. These findings will help to develop new recipes based on the PEDOT:PSS/salt composite towards the applications for printed flexible electronics, portable displays and flexible energy storage devices.

In the past decade, the stretchable flexible electronics have developed fast as essential parts of the popular electronic devices.\cite{1,2,3} In these applications, conductive polymers have received tremendous attention as ideal electrodes to replace the traditional indium tin oxide (ITO) ones due to their excellent mechanical properties (i.e., flexibility) and solution
processability. In particular, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is recognized as the most promising candidate owing to its mechanical flexibility, visible-light transmittance, biocompatibility, solution processability and good environmental stability.\textsuperscript{4-6} However, untreated PEDOT:PSS film displays poor electrical conductivity as low as about 1 S cm\textsuperscript{-1}, limiting its practical application in popular electronic devices. The low conductivity is mainly attributed to the existence of insulating PSS chains that wrap the conductive PEDOT core and inhibit the formation of PEDOT conductive network.\textsuperscript{7-9} To solve this issue, secondary doping agents like acids,\textsuperscript{10,11} surfactants,\textsuperscript{12} organic solvents\textsuperscript{13-15} and recently the ionic salts\textsuperscript{16-22} are generally introduced into PEDOT:PSS to achieve conductivity that is comparable to the commercial ITO products. Especially the ionic salts in solid or liquid form have garnished particular interest due to their high thermal stability,\textsuperscript{23} unique structural\textsuperscript{24} and electrochemical properties,\textsuperscript{25} as well as an ability to improve conductivity and stretchability of PEDOT:PSS films.\textsuperscript{20,26}

Recent studies indicate that ionic interaction between salts and PEDOT:PSS promoted microstructure reorganization which resulted in the formation of PEDOT-rich and PSS-rich microdomains. This eased the formation of interconnected PEDOT networks, resulting in higher electrical conductivities.\textsuperscript{27-29} For example, Badre et al.\textsuperscript{19} reported the conductivity of PEDOT:PSS composite with 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) was 2084 S cm\textsuperscript{-1} which derived from the salt-induced charge screening between PEDOT and PSS and was three orders of magnitude higher than that of pristine PEDOT:PSS film. Li et al.\textsuperscript{28} revealed ionic exchange between bis(trifluoromethanesulfonyl)imide lithium salt
(LiTFSI) and PEDOT:PSS (LiTFSI + PEDOT:PSS = PEDOT:TFSI + Li:PSS) induced PEDOT microdomain converged together to form a packed and interconnected net structure, which synergistically enhanced the thermoelectric and mechanical performances. Similar ion exchange process and microstructure reorganization was reported by Kee et al.\textsuperscript{30} in the composite of PEDOT:PSS with a series of EMIM cation based ionic liquids (ILs). For an in-depth structural analysis, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement was employed and disclosed a highly ordered nanofibrillar structures of PEDOT chains that eased the electron transfer. Meanwhile, plenty of recent work have focused on studying the structure-performance relationship in the PEDOT:PSS/salt composites to tune the macroscopic conductivity with molecular designs. It’s generally summarized that chemical composition of the salts had strong influence on the conductivity of the PEDOT:PSS/salt composites. Ambroise et al. have claimed that ion exchange (EMIM:anion + PEDOT:PSS = EMIM:PSS + PEDOT:anion, i.e., anionic effect) released the PEDOT from the coupling with PSS, which provided the PEDOT higher $p$-doping density and improved conductivity.\textsuperscript{31} However, to the best of our knowledge, the influence of the cations on the structure and conductivity of PEDOT:PSS films have not been explored yet.

In order to investigate the effect of different cationic species on the structure and conductivity of PEDOT:PSS (Orgacon Dry, Agfa Gevaert N.V., Belgium), we chose four salts with various cations, including lithium ($\text{Li}^+$), 1-ethyl-3-methylimidazolium (EMIM), (2-ethoxyethyl)triethylphosphonium (PEOE) and (2-(2-ethoxyethoxy)ethyl)triethylphosphonium (P2EOE), but the same
bis(trifluoromethanesulfonyl)amide (TFSI) anion, as demonstrated in Figure 1. For the preparation of PEDOT:PSS/IL composite, 0.05 mmol salt was added into 1000 mg PEDOT:PSS aqueous dispersion (1.6 wt%), under vigorous stirring.

![Chemical structure of PEDOT:PSS and ionic salts used in this work.](image)

**Figure 1.** Chemical structure of PEDOT:PSS and ionic salts used in this work.

We chose TFSI as the anion because it was illustrated to be effective for the improvement of the PEDOT conductivity. The cationic size increases monotonically along this series, \( \text{Li}^+ < \text{EMIM} < \text{PEOE} < \text{P2EOE} \). Meanwhile, these cations were widely used as aqueous electrolyte materials in the previous studies and the self-diffusion coefficients for lithium, EMIM, PEOE and P2EOE cations are \( \sim 10 \times 10^{-11} \), \( \sim 7 \times 10^{-11} \), \( 2.33 \times 10^{-11} \) and \( 2.30 \times 10^{-11} \) m\(^2\) S\(^{-1}\), respectively. Thus, we can infer that small-size cation showed stronger mobility in PEDOT:PSS aqueous dispersion. The fast mobility of cation helps to combine with PSS anion to form the coupled cation:PSS and screens the Coulomb interaction between PEDOT and PSS. It’s expected that salt with small size and high cationic mobility would change significantly the molecular structure and thus the conductivity of PEDOT:PSS/salt in the dried films.
Figure 2. (a) The electrical conductivity result of PEDOT:PSS films doped with different ILs and LiTFSI at a series of concentration. (b) Photo images of LED electrical circuits and the parts for PEDOT:PSS composite deposited on paper are marked with the arrows (left: PEODT:PSS, right: PEDOT:PSS/LiTFSI composite). (c) Thickness influence on the conductivity of PEDOT:PSS film (our work is marked by the arrows). (d) UV–Vis absorption spectra of pristine PEDOT:PSS and PEDOT:PSS/IL dispersion. Notes: PEDOT:PSS/salt is denoted as w/salt, mmol/g represents the stoichiometry of salts in 1.0 g of PEDOT: PSS water dispersion.

To verify our hypothesis, we deposited the sample on glass substrate and measured the conductivity of dried films with a multimeter (ST-2258A, Suzhou Jingge Electronic Co., Ltd.) and four-probe method at ca. 58% relative humidity. By taking the PEDOT:PSS/LiTFSI composite sample as an example, we found that the electrical conductivity of the composite peaked at sample with 0.05 mmol/g salt (Figure 2a) and this hybrid sample was used in the
following work. As shown in Figure 2a, the electrical conductivity of PEDOT:PSS films increased after doping with salts. It should be noted that neat salts did not show detectable electrical conductivity. The pristine PEDOT:PSS sample shows a conductivity of 0.83 S cm⁻¹, while the conductivity values for polymer composite with Li⁺, EMIM, PEOE and P2EOE are 418.06, 220.00 15.50 and 7.63 S cm⁻¹, respectively (cf. Table S1 of the supporting information). The enhanced conductivity through mixing with salts is consistent with the previous reports. In addition, there is an obvious difference in the conductivity for the PEDOT:PSS/salt with different cationic components. The smaller-size cations with faster ion diffusivity (Li⁺ and EMIM) show better conductivity. Recent work about the mixture of PEDOT:PSS and EMIM TCB has demonstrated that the IL triggered the structural reorganization via ion exchange, i.e., cation:anion + PEDOT:PSS = PEDOT:anion + cation:PSS, leading to the formation of highly ordered nanofibrillar structures of PEDOT chains and an enhancement of electrical conductivity. We infer that the small-size cations do ion exchange with PEDOT:PSS that lead to a higher conductivity value in PEDOT:PSS/salt.

To demonstrate the conductivity improvement, we drop casted PEDOT:PSS ink on paper and dried it as a part of the electrical circuit of light-emitting diode (LED), as shown in Figure 2b and Figure S1. We found the LED with a PEDOT:PSS/salt circuit was much brighter than the PEDOT:PSS one, confirming the high conductivity of salt-doped PEDOT:PSS and demonstrating its potential application in printed flexible electronics. Moreover, we figured out that the conductivity value of PEDOT:PSS/LiTFSI in this work is comparable to those of
PEDOT:PSS/salts mentioned in the previous reports, see Figure 2c, Table S2 and Table S3 of the supporting information. Note: some deviations are attributed to the sample preparation method and film thickness because our work (Figure 2c) and the others’ reports show that spin-casted nanometer films has better conductivity than the drop-casted micrometer ones.

Previous studies indicate that ion exchange reaction between PEDOT:PSS and ILs increased the oxidation state of the PEDOT polymer chains and thus the electronic conductivity. We characterized the oxidation level of PEDOT:PSS with a SHI-MADZU UV-3600 spectrophotometer. As shown in Figure 2d, the broad absorption band near 850 nm is attributed to oxidation state of PEDOT, i.e., the single polaron with a positive charge. By referring to this peak, we found that PEDOT:PSS/salts films showed a much stronger absorption than PEDOT:PSS, corresponding to an enhanced oxidation level (i.e., higher \( p \)-doping density) of PEDOT chains. The PEDOT conductivity is primarily dependent on the positive charges located along the polymer backbone. Thus the electrical conductivity of PEDOT is proportional to the level of \( p \)-doping. Indeed, the conductivity descends along the series, PEDOT:PSS/LiTFSI, PEDOT:PSS/EMIM TFSI, PEDOT:PSS/PEOE TFSI, PEDOT:PSS/P2EOE TFSI and pristine PEDOT:PSS, which can be rationalized with a lower \( p \)-doped level. Furthermore, there is an obvious difference on the \( p \)-doped level in PEDOT:PSS/salts. The composite with small cations show high-density \( p \)-doping. This phenomenon is likely derived from the fact that cations with fast mobility are easier to combine with negatively-charged PSS molecules and leave a significant amount of TFSI.
anions for the PEDOT (cf. Figure S2). By referring to the previous reports,\textsuperscript{31,46} we hypothesize that TFSI anions take the role of PSS anions to weaken the screening effects of original PSS anions on PEDOT, thus the oxidized PEDOT$^+$ cations release from the shielding effect of PSS$^-$ and sustain their $p$-doped states. In contrast, the salts with big size and slow cationic mobility such as PEOE and P2EOE could not combine with the PSS$^-$ as efficient as that of Li$^+$ due to the steric effect (cf. Figure S3).

**Figure 3.** Typical two-dimensional GIWAXS patterns of (a) pristine, (b) EMIM TFSI-treated and (c) LiTFSI-treated PEDOT:PSS films. (d) Vertical cake cuts of the initial GIWAXS data of pristine and salt-treated PEDOT:PSS films. (e) Horizontal cake cuts of the initial GIWAXS data of pristine and salt-treated PEDOT:PSS films. (f) GIXRD data of pristine and salt-treated PEDOT:PSS films. Note: PEDOT:PSS/salt is denoted as w/salt.

In the following, we explore the structure-property relationships of PEDOT:PSS/salt composite with a series of complementary tools. The microstructure of PEDOT:PSS composite films was characterized with GIWAXS based on synchrotron light at 1W1A beamline of BSRF, Beijing, China (cf. supporting information). GIWAXS is a
well-established protocol to characterize the surface and interface structures of polymer thin film.\textsuperscript{47-49} including PEDOT:PSS before and after IL doping. For example, Kee et al.\textsuperscript{30} demonstrated a highly ordered nanofibrillar structures of PEDOT and Saxena et al.\textsuperscript{18} reported a shortened $\pi-\pi$ stacking distance between PEDOT molecules upon salts’ doping. Such structure change leads to an enhanced conductivity of the PEDOT hybrid sample. The sample dispersion was deposited on silicon substrate ((100) orientation, PlutoSemi Co., Ltd) and the thickness of the dried film was around 11 μm, measured by an Ambios XP-1 profilometer.

Figure 3a-c show the typical 2D scattering pattern of GIWAXS. In Figure 3a, three characteristic peaks with $q = 0.23 \text{ Å}^{-1}$ (d = 27.3 Å calculated with d=2π/q), $1.26 \text{ Å}^{-1}$ (d = 5.0 Å), and $1.82 \text{ Å}^{-1}$ (d = 3.4 Å) are attributed to alternating stacking of PEDOT and PSS (i.e., PEDOT (100) crystal planes), $\pi-\pi$ stacking of PSS, and $\pi-\pi$ stacking of PEDOT, respectively.\textsuperscript{7,50} The lattice spacing distance of (100) plane ($d_{100}$) for pristine PEDOT:PSS is 27.3 Å, which decreases to 15.0 and 14.6 Å for PEDOT:PSS/EMIM TFSI and PEDOT:PSS/LiTFSI composite films, respectively (Figure 3d). The decreased $d_{100}$ value means a shorter $\pi-\pi$ stacking distance and improved crystalline ordering along the main chain direction.\textsuperscript{51} Additionally, a new peak corresponding to (200) crystal plane of PEDOT is found at $q = 0.87 \text{ Å}^{-1}$ (d = 7.2 Å) (Figure 3b-d), indicating an enhanced long-range order of PEDOT crystals after salt doping.\textsuperscript{52} In addition, we studied the in-plane molecular structure of PEDOT:PSS hybrid film by referring to the horizontal cake cuts (Figure 3e) of the initial GIWAXS data. A shortened PEDOT $\pi-\pi$ stacking distance and an improved PEDOT crystallite size in horizontal direction (cf. Figure S4b and S4c) upon the salt doping further
confirms an enhanced crystalline ordering of PEDOT. In the PEDOT:PSS composite, carrier mobility depends upon the intermolecular charge transfer rate in the $\pi$-$\pi$ stacking direction. Namely, more ordered and densely packed PEDOT crystallites in this direction will aid electron transport thereby improve the conductivity. Indeed, the highest conductivity of LiTFSI-treated PEDOT:PSS can be rationalized with the structure changes disclosed by GIWAXS measurements. Similar diffraction results have been reported in highly conductive PEDOT:PSS by Kim et al. who illustrated that ion exchange between concentrated $\text{H}_2\text{SO}_4$ and PEDOT:PSS generated a highly ordered and densely packed PEDOT:PSS nanofibril structure. Moreover, the salt-mixing induced conductivity change agrees with the large-scale structure change as observed with optical microscope (cf. Figure S5). In general, LiTFSI-treated PEDOT:PSS shows clear interconnected networks, which might serve as conductive path and ease the electron transport. Thus, we summarize that the well-aligned and interconnected PEDOT domains in the PEDOT:PSS/salt composite resulted in a high conductivity compared to that of the pristine PEDOT:PSS.

To illustrate the generality of the relationship between crystalline structure and conductivity in PEDOT:PSS films mentioned above, the crystalline structure of all four PEDOT:PSS/salt composite films were measured with GIXRD (Bruker D8 Advance, Germany). As shown in the Figure 3f, the curve of pristine PEDOT:PSS film shows three characteristic peaks: $2\theta = 3.3^\circ$ ($q = 0.23 \text{ Å}^{-1}$), $17.7^\circ$ ($q = 1.26 \text{ Å}^{-1}$), and $25.8^\circ$ ($q = 1.82 \text{ Å}^{-1}$), which are consistent with the GIWAXS data. In addition, the PEDOT:PSS/salt composites show an additional (200) peak and enhanced scattering intensity, like the GIWAXS results.
Both the GIWAXS and GIXRD results indicate that the improved conductivity of PEDOT:PSS film after doping with salts originates from an enhanced crystalline ordering, agreeing with the previous reports.\textsuperscript{18,20,42,53} We understand the structure change with the facts that the salt anion can play the role of condensing agent for polyelectrolytes such as negatively charged DNA,\textsuperscript{54} i.e., salts hold the $p$-doped PEDOT chains together at a shorter $\pi-\pi$ stacking distance and thus improves the crystalline ordering of PEDOT domains, as demonstrated in Figure 4.

**Figure 4.** Schematic illustration of the structure of polymer composite film: loose lamellar packing of pristine PEDOT:PSS (left) and compacted lamellar packing of PEDOT:PSS/LiTFSI composite (right).

Figure 4 schematically demonstrates the structure change of PEDOT:PSS film before and after salt doping. In the pristine state, conducting PEDOT molecules are surrounded by insulating PSS molecules to form a stable colloidal dispersion in water\textsuperscript{26,29} and a loose lamellar packing with periodicity of 27.3 Å formed in the dried film. With salt doping, the wrapped PEDOT molecules were released by ion exchange with salt to form a larger colloidal structure in water, as confirmed by the dynamic light scattering data (cf. Figure S6), which
resulted in a compacted lamellar packing with periodicity of 14.6 Å after solvent evaporation as indicated by the GISAXS and GIXRD data. These structural change as mentioned above explains the 500-fold increase for the conductivity of PEDOT:PSS after doping with LiTFSI.

In summary, we chose four salts with various cations but the same TFSI anion, to study the effect of different cationic species on the structure and conductivity of PEDOT:PSS. The conductivity measurement results revealed that salts with small-size cations endowed the PEDOT:PSS much better conductivity. This phenomenon can be rationalized with the GIWAXS and UV-Vis results: the molecular interactions among salt and PEDOT:PSS made the structural rearrangement of the PEDOT to form ordered crystals and long-range ordered conductive network, as well as the improved $p$-doped level of PEDOT resulted from introducing secondary doping agents. These findings will provide in-depth knowledge about how to manipulate the conductivity of PEDOT:PSS composite towards the applications in printed soft electronics via molecular design and tuning the molecular assembly.

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