

Influence of Ionic Liquids on the Electrical Conductivity and Morphology of PEDOT:PSS Films

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The field of polymer electronics has been attracting increasing attention in the past decade because of its applications in novel optoelectronic devices such as organic light-emitting diodes and photovoltaic devices.¹ Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), known as PEDOT:PSS, is today probably the most successful conductive polymer in commercial applications.² One of the actual opportunities for conductive polymers is to replace indium tin oxide as transparent conductive layer in transparent electrodes. However, in the field of conductive transparent electrodes the major drawback is the relatively low electrical conductivity of PEDOT:PSS compared with its inorganic counterparts. An enhancement in the conductivity was obtained by adding to the PEDOT:PSS dispersions different organic compounds called secondary dopants or additives, such as several alcohols (diethylene glycol, meso-erythritol 1,2,3,4,-tetrahydroxybutane, 2-nitroethanol, glycerol, or sorbitol) and high-boiling-point solvents (dimethyl sulfoxide, tetrahydrofurane, and dimethylformamide).^{3–10} An increase in conductivity is seen upon removal of the secondary dopant

or additive by evaporation. The goal of this communication is to report a new family of small-molecule nonvolatile additives based on ionic liquids (ILs) as electrical conductivity enhancers in PEDOT:PSS films.




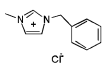

Ionic liquids (ILs) are organic/inorganic salts with a good chemical stability, low flammability, negligible vapor pressure, and high ionic conductivity that are receiving exponential interest due to their applications in many technological fields.¹¹ For instance, ILs are being investigated in the synthesis of self-assembled, highly organized hybrid nanostructures due to their ability as supramolecular solvents.¹² Another example, the combination of ILs with conducting polymers is giving rise to a new materials and devices. For instance, ILs have been used as electrolytes in conducting-polymer-based electrochemical devices,^{13,14} in the electrochemical synthesis of conducting polymers,^{15,16} and in the synthesis of conducting polymer organic dispersions¹⁷ and conducting polymer nanostructures.¹⁸

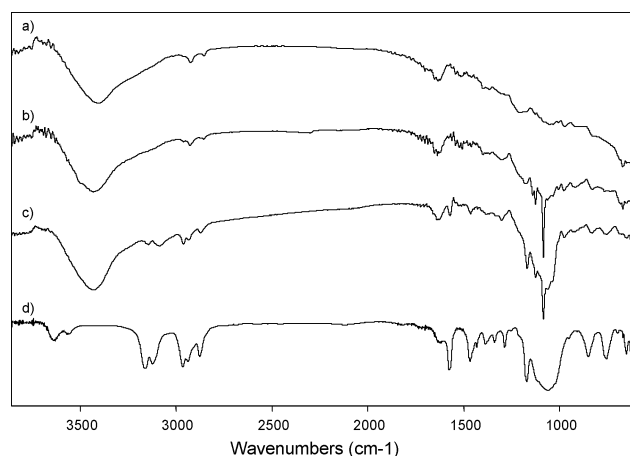
Because of the affinity of ILs with conductive polymers and their ability of supramolecular ordering, we envisaged the use of ILs as additives to increase the conductivity of PEDOT:PSS. For this purpose, we added different percentages of five ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (bmim)BF₄, 1-butyl-3-methylimidazolium bromide (bmim)Br, 1-ethyl-3-methylimidazolium chloride (emim)Cl, 1-benzyl-3-methylimidazolium chloride (bemim)Cl, and 1-butyl-1-methylpyrrolidinium chloride (bmpyr)-Cl to a PEDOT:PSS commercial dispersion (Baytron P-V4, HC Starck). In a classical experiment, ILs were dissolved in deionized water and stirred for 10 min. This mixture was then added into the PEDOT:PSS dispersion and stirred for another 15 min. Films on PET substrates were prepared by casting the PEDOT:PSS/IL mixtures and dried by slowly heating from 50 to 120 °C. Table 1 shows the chemical structure of the ILs investigated and the percentage at which the highest conductivity measured by the four-point method was obtained. Films of pure PEDOT:PSS showed an average

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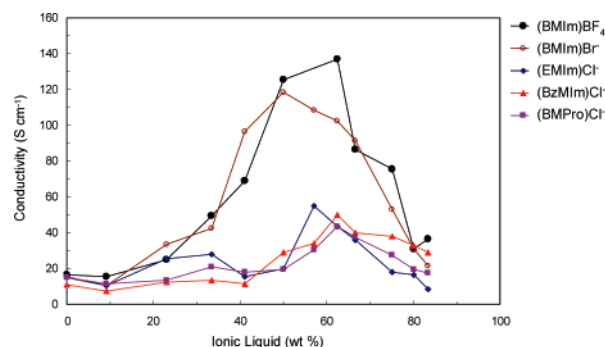
Table 1. Electrical Conductivity of PEDOT/PSS Films Using Different IL Additives

| Name | Chemical structure | IL wt % (solution) | IL wt % (film) | σ (S cm ⁻¹) |
|---|---|--------------------|----------------|--------------------------------|
| 1-Butyl-3-methylimidazolium tetrafluoroborate |  | 1.5 | 62.5 | 136 |
| 1-Butyl-3-methylimidazolium bromide |  | 1.0 | 50.0 | 118 |
| 1-Ethyl-3-methylimidazolium chloride |  | 1.25 | 57.1 | 55 |
| 1-Benzyl-3-methylimidazolium chloride |  | 1.5 | 62.5 | 49 |
| 1-Butyl-1-methylpyrrolidinium chloride |  | 1.5 | 62.5 | 43 |

**Figure 1.** FT-IR spectra of (a) PEDOT:PSS, (b) PEDOT:PSS with 0.7 wt % (bmim)BF₄, (c) PEDOT:PSS with 1.5 wt % (bmim)BF₄ and (d) (bmim)-BF₄.

conductivity of 14 S cm⁻¹, which corresponds to the value range given by the supplier. In all the other cases where ILs were added, an enhancement in the electrical conductivity of the PEDOT:PSS films was observed. A clear influence of the chemical structure of anion and cation is not seen. The highest electrical conductivity value of 136 S cm⁻¹ was obtained in the case of (bmim)BF₄. It is worth noticing that this value is similar to those of some of the best examples of PEDOT:PSS films reported so far in the literature, which average 150 S cm⁻¹.^{6,7,9}

The most clear difference between ILs and the high-boiling-point solvents previously used as additives was that ILs were not volatile and thus remained in the PEDOT:PSS films. Figure 1 compared Fourier transform infrared (FT-IR) spectra of pure PEDOT:PSS, PEDOT:PSS films casted from solutions containing 0.7 and 1.5 wt % (bmim)BF₄, respectively, and pure (bmim)BF₄. The bands associated with both PEDOT:PSS and the IL are clearly seen in the modified films (752, 848, 108, 2962, and 3160 cm⁻¹), showing that the IL is retained in the films. On the other hand, one of the

**Figure 2.** Electrical conductivity versus the amount of IL wt % in the PEDOT:PSS films.

proposed explanations about the increase in conductivity due to secondary doping consists of reducing the coulombic interaction between the charge carriers transported on the PEDOT chains and the negative PSS counterions. However, in this case, although it is possible that such an effect may exist between polyanionic PSS-PEDOT and IL, the FT-IR spectra do not show any clear broadening of the bands, which supports the hypothesis of polar interactions between the three components.¹⁹

Figure 2 shows the electrical conductivity of PEDOT:PSS/IL films as a function of increasing IL concentration. It is noted that the electrical conductivity changes significantly after the addition of IL and a maximum is reached in all the cases between 50 and 65 wt % IL in the solid films. Further addition of IL produces a gradual decrease in conductivity of the films. This trend was previously observed in the case of other remaining or nonvolatile additives for PEDOT:PSS, such as poly(ethylene glycol).²⁰

To understand the conductivity enhancement by the addition of different amounts of ILs, we investigated the surface morphology of selected samples by atomic force microscopy (AFM; Figure 3). Images A and B of Figure 3 show the topography and phase images of a 0.6 × 0.6 μm² area of PEDOT:PSS without ILs. Typical grains (bright phase) were observed on the film surface of a dimension of about 40–70 nm associated with PEDOT domains in a PSS matrix similar to those reported in the literature.^{3,8,20} Images C and D of Figure 3 showed the images of PEDOT:PSS films containing 50% (bmim)BF₄. It seems that the IL swells the PSS domains and induces a phase separation domains with an excess of insulating PSS (black phase) with a dimension of about 40–60 nm surrounded by a phase of merged conducting PEDOT grains (bright phase, Figure 3D). Crispin et al. observed the same effect using DEG as dopant. Their phase image of a DEG-doped PEDOT:PSS surface was similar to our image containing 50 wt % (bmim)BF₄ as dopant. They proposed that a three-dimensional conducting network of highly conducting PEDOT grains was formed

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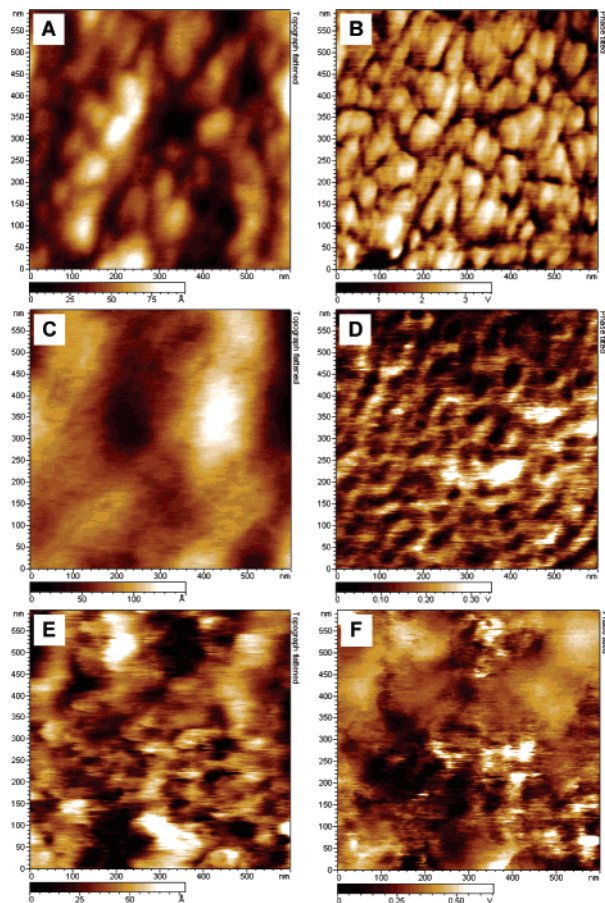


Figure 3. Topography (A,C,E) and phase images (B,D,F) of PEDOT:PSS film (A,B), PEDOT:PSS film containing 50% of (bmim)BF₄ (C,D), and PEDOT:PSS film containing 84% (bmim)BF₄ (E,F).

and was the reason for the enhanced conductivity. On the

other hand, to explain the observed decrease in conductivity at high IL contents, we conducted AFM of a PEDOT:PSS film containing 84 wt % (bmim)BF₄ (images E and F of Figure 3). Cloudy areas at the top of the image were visible. These could be drops of (bmim)BF₄ with a diameter of 0.1–0.2 μm on the surface due to leaching out of the IL. Beneath the drops, a network similar to that in Figure 3D can be seen. However, the network is not homogeneous. The conducting phase of merged PEDOT grains is disconnected in some points. The observed leaching effect and the broken conducting network could explain the observed decrease in electrical conductivity at high IL contents.

In conclusion, we demonstrated that ILs showed very good performances as permanent conductivity enhancers in PEDOT:PSS films. AFM images showed that IL induced the formation of a three-dimensional conducting network with smaller PEDOT domains as observed in the case of other additives such as ethylene glycol. Interestingly, the ionic character of the films is significantly increased because of the presence of ILs, which can be of interest for their performance in optoelectronic devices, including ILs, e.g., electrochromic and electrochemical light-emitting²¹ and solar cells.

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