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Highly Conductive Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Films Using 1-Ethyl-3-methylimidazolium Tetracyanoborate Ionic Liquid

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Highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films are obtained using ionic liquids as additives. Upon adding 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) to the conducting polymer, the conductivity increases to 2084 S cm^{-1}; this is attributed to the phase separation of PSS leading to a structural change in the film. A comparative study with 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIM BF_4) shows that EMIM TCB gives higher conductivity and transmittance and can be regarded as one of the most promising additives for the preparation of indium tin oxide (ITO)-free organic devices using PEDOT:PSS/EMIM TCB as electrodes.

1. Introduction

In recent years, significant progress has been achieved in the development of materials with a remarkable combination of high electrical conductivity and optical transparency. These materials are important components of many electronic and optoelectronic devices such as organic light-emitting diodes (OLEDs), organic photovoltaic devices (OPVs), radio frequency identification (RFID) tags, and many others.[1] This trend is driven by the demand for materials that can replace tin-doped indium oxide (ITO) and this need is driven by three factors: First, the limited availability of indium sources impacts drastically the price of the material, causing potentially expensive fluctuations in the cost of devices. Second, bending a substrate covered by an ITO layer highly decreases the sheet resistance of the layer thereby limiting the use of ITO in devices that require mechanical flexibility. Third, deposition of ITO requires a high temperature process that is mainly done by sputtering deposition; this process limits the use of ITO on common plastic substrates. To respond to these needs, numerous solutions of processable and printable candidates have been investigated. For example, carbon nanotubes, metal nanowires, and conductive polymer formulations have been proposed to replace ITO.[1–3]

Here, we find that conducting polymers combined with ionic liquids can be used to make films with conductivities comparable to ITO. Conducting polymers (CP) are finding increasing use in organic electronic and optoelectronic applications. They are an attractive class of materials because they combine the properties of organic polymers with the electrical conductivity of semiconductors or metals. Poly(3,4-ethylenedioxythiophene) (PEDOT) is among the most promising CP and it has been well investigated due to its numerous properties including low bandgap (1.6–1.7 eV), good environmental stability, high optical transparency, low redox potential, etc. PEDOT is used in a variety of applications, for example as a hole injection layer in OLEDs and as a flexible, transparent electrode in lighting applications.[4]

PEDOT is polymerized from ethylenedioxythiophene (EDOT) monomers and is not soluble in water.[4] To improve the processability, PEDOT is coupled with polystyrenesulfonate (PSS), resulting in material that can be dispersed in water. In an aqueous dispersion of PEDOT:PSS, PEDOT chains are surrounded by a thin PSS-rich surface layer. However, PEDOT:PSS suffers low conductivity typically 10^{-5} to 10 S cm^{-1} for commercial solutions provided by Heraeus (Clevios).[5] The need to enhance the conductivity of PEDOT:PSS has been recognized by many researchers and continues to be a topic of ongoing work.[4] Many techniques have been proposed to enhance the conductivity of PEDOT:PSS. For example, modifying the ratio of PEDOT to PSS can lead to a large variation in conductivity.[4,5] Decreasing the pH of the PEDOT:PSS dispersion can also increase the conductivity of the film. Many secondary dopants, commonly called conductivity enhancement agents, such as polyols, alcohols, surfactants, salts, acids, and organic solvents have been widely used to enhance PEDOT:PSS conductivity.[6] The addition of water miscible high boiling solvents to a PEDOT:PSS dispersion typically increases the conductivity. To date, some of the highest conductivities reported are obtained with dimethylsulfoxide.[4,7–9] Upon heating the films and removing the solvent, an increase in the conductivity up to 1418 S cm^{-1} is reported.[10]

We report the use of a new family of non-volatile ionic liquids to enhance PEDOT:PSS conductivity. Ionic liquids (ILs) are organic/inorganic salts with unique properties such as good chemical stability, low flammability, and negligible vapor

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pressure.[11,12] ILs have been employed in the synthesis of some conducting polymers[12,13] and are used as electrolytes in electrochromic and electromechanical actuator devices by in combination with specific conductive polymers.[14]

Recently, Dobbelin et al. have investigated the effect of several ionic liquids on the conductivity of PEDOT:PSS.[15] They reported a value of 136 S cm^{-1} with the addition of 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIM BF_4) to PEDOT:PSS. Lee et al.[16] have used ionic materials, i.e., pyridinium salts, to enhance the conductivity of PEDOT:PSS films. After adding 1 wt% of pyridinium p-toluene sulfonate to a PEDOT:PSS dispersion, they measure a conductivity of 23 S cm^{-1}.

We investigate the effect of addition of 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) on the conductivity of a PEDOT:PSS dispersion. Imidazolium cations generally impart ionic liquids with the lowest viscosities and highest conductivities, small anions with delocalized charges such TCB are known to increase conductivity.[17] Here, we demonstrate that the addition of EMIM TCB to PEDOT:PSS formulations increases the conductivity up to 2084 S cm^{-1}, exceeding any value we have found in the literature. These results are very promising to replace ITO in the flexible electronics market where the price and brittleness of this electrode material are two major drawbacks.

2. Results and Discussions

2.1. Conductivity Enhancement of the PEDOT:PSS Films

We investigate the effect of the addition of ionic liquids on PEDOT:PSS dispersions. EMIM TCB is used for this purpose and added to a dispersion of PH1000 Clevios (using the approach, A_1, as described in the experimental section). **Figure 1** shows the chemical structure of EMIM TCB.

In our experiments, EMIM TCB drastically decreases the sheet resistance of films containing PH1000. As clearly seen in **Figure 2**a, the pristine PEDOT:PSS (PH1000) yields a high sheet resistance (≈280 KΩ sq^{-1}) with a transmittance of 98% at 550 nm. Doping PH1000 with different amounts of EMIM TCB results in a decrease in the sheet resistance. The lowest sheet resistance value 31 Ω sq^{-1} is obtained when the amount

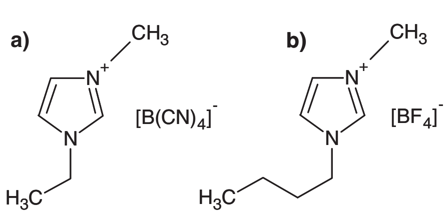

Figure 1. Chemical structures of a) EMIM TCB and b) BMIM BF_4.

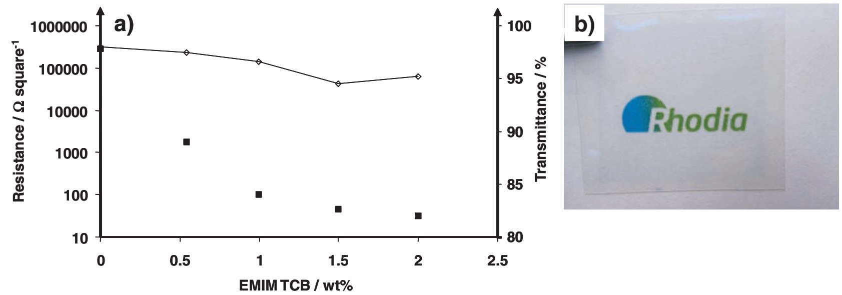

Figure 2. a) Sheet resistance (■) and transmittance (◊) variations versus the concentration of EMIM TCB wt% in solution. b) Picture of a PH1000 film prepared from a dispersion containing 1.5 wt% EMIM TCB.

of EMIM TCB reaches 1.99 wt% in solution. At this concentration and any other typically >2 wt%, the dispersion becomes viscous and is difficult to spin coat. It is important to note that the transmittance value remains higher than 95% at all EMIM TCB concentrations (Table S1 in the Supporting Information) and as evidenced in Figure 2b, a picture of the prepared transparent film on polyester (PET) substrate is shown.

When compared to a PEDOT:PSS PH 1000 film prepared from a solution containing 5 wt% dimethyl sulfoxide (DMSO) as suggested by the supplier (Heraeus/H.C.Starck),[5] PEDOT:PSS/DMSO films showed a resistance value of 199 Ω sq^{-1} and a transmittance 95% at 550 nm.

In order to calculate the films conductivities, we spin coated PEDOT:PSS/EMIM TCB films on glass substrates. **Figure 3** shows the variation of the conductivity of PEDOT:PSS films with respect to the amount of EMIM TCB in solution. Thickness and transmittance values are indicated for each concentration and plotted on the same figure (Table S2 in the Supporting Information). The pristine PEDOT:PSS shows an electrical conductivity of 0.68 S cm^{-1}. After addition of EMIM TCB, the conductivity dramatically increases and reaches a maximum of 2084 S cm^{-1} at 1.57 wt%. It is clearly shown that the thickness of the film increases with the increasing amount of EMIM TCB in the film, it reaches 96 nm at ≈1.57 wt%, the transmittance slightly changes and remains as high as 96.07% at such concentration. As the minimum optical and electrical requirements

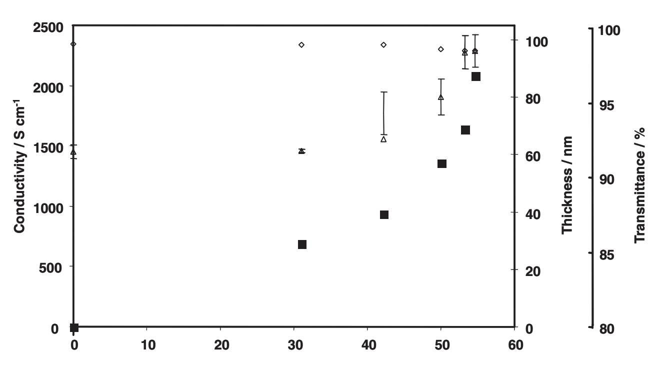

Figure 3. Conductivity (■), film thickness (Δ), and transmittance (◊) variations versus the concentration of EMIM TCB in solution. The films are prepared using A_1, where A_1 designates the approach that was used to prepare the dispersion.

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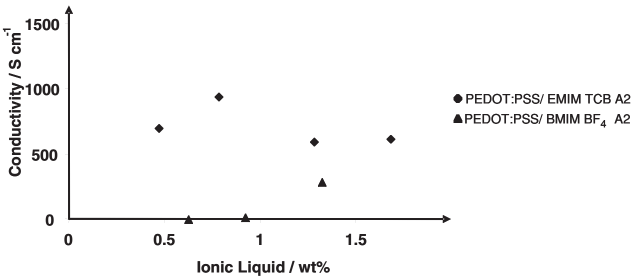

Figure 4. Variation of the electrical conductivity of PEDOT:PSS films with the concentration of ionic liquid using A_2.

for transparent electrodes are $T > 90\%$ and sheet resistance $R_s < 100\ \Omega$ per square. In addition to measuring the sheet resistance, thickness and optical properties of the film, the ratio $\frac{\sigma_{dc}}{\sigma_{op}}$ was calculated for each film based on the following equation:

$$T = \left(1 + \frac{Z_0}{2R_s}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2}$$

where T is the transmittance, $Z_0 = 377\ \Omega$ is the impedance of free space, and σ_{op} and σ_{dc} are the optical and dc conductivities, respectively. The experimental data for all the films prepared at different contents of EMIM TCB give a ratio higher than the minimum industry standard value >35 (data given in Table S1 to S3 in the Supporting Information). The highest value 243.90 is obtained with a film prepared from a dispersion containing 1.99 wt% EMIM TCB. On glass substrates, this value is 185.19. The ratio values obtained with EMIM TCB compete with any other value in the literature[10,18] highlighting once again the unique characteristics of PEDOT:PSS/EMIM TCB films as alternatives to ITO material and their possible applications as transparent electrodes.

A comparative study with a second IL has been conducted, here the BMIM BF_4 is added to PEDOT:PSS and the sheet resistance of the films are compared to the PEDOT:PSS/EMIM TCB films. It has been shown that doping PEDOT:PSS with BMIM BF_4 (Figure 1b) improves the conductivity of PEDOT:PSS films up to 136 S cm^{-1} when the film contains 62.5 wt% IL.[15]

For this work, we use the same pristine PEDOT:PSS dispersions with both ILs so our reported enhancement factors give an exact measure of the quality of each additive as a conductivity enhancement agent. Adding BMIM BF_4 directly into a vial containing PH1000 even at low concentrations is not possible due to the aggregation of PEDOT:PSS. To this end, we have developed an approach (A_2) in which the BMIM BF_4 is added to PH1000 under agitation. No aggregation is observed even at high concentrations and homogeneous films are obtained after spin coating the dispersions on glass substrates. **Figure 4** shows the evolution of the electrical conductivity of PEDOT:PSS films with the addition of BMIM BF_4. PEDOT:PSS/EMIM TCB composite films are also prepared according to approaches A_2 on glass substrates and plotted for comparison.

The pristine PEDOT:PSS shows an electrical conductivity of 0.68 S cm^{-1}. After addition of both ILs, the conductivity increases and reaches a maximum of 941.17 S cm^{-1} and 286.77 S cm^{-1}, respectively, with 0.78 wt% EMIM TCB and 1.32 wt% BMIM BF_4. A film prepared from a dispersion containing 1.28 wt% EMIM TCB showed a decrease of the conductivity (Table S3 in the Supporting information), a trend that has previously been observed when more than 1.5 wt% BMIM BF_4[15] is added to PEDOT:PSS. The conductivity of a PEDOT:PSS/DMSO film prepared on glass substrates was measured to be around 575 S cm^{-1}. It is interesting to note that the thickness of PEDOT:PSS/ILs layers prepared according to A_2 show higher values than those prepared following A_1, i.e., the thickness measured on a PEDOT:PSS/EMIM TCB A_1 film prepared from 1.48 wt% EMIM TCB is 95.5 nm, a similar film (1.68 wt% EMIM TCB) prepared using A_2 shows a thickness of 235 nm, while a PEDOT:PSS film prepared from a concentration of 1.32 wt% BMIM BF_4 has a thickness 317 nm (Table S4 in the Supporting Information). The transmittance of PEDOT:PSS/BMIM BF_4 films are also lower than PEDOT:PSS/EMIM TCB films. The transmittance decreases from 91.24% (concentration of BMIM BF_4 = 0.62 wt%) to 85.49% (concentration of BMIM BF_4 = 1.32 wt%). The transmittance is higher than 96% for all the PEDOT:PSS/EMIM TCB films on glass substrates (Table S2 and S3 in the Supporting Information).

According to our data, the thickness is an important parameter that influences the conductivity of the PEDOT:PSS film. A critical thickness value is required in order to enhance the conductivity of PEDOT:PSS PH1000 film. This value is around 107 nm. When this value is exceeded, we have seen that the conductivity decreases even though the sheet resistance values remains low (Table S1, S2, S3 in the Supporting Information).

2.1.1. Characterization of PEDOT:PSS/EMIM TCB Films

To further explore the conductivity enhancement and to understand the role of EMIM TCB, atomic force microscopy (AFM) characterization was conducted on several films containing different amounts of ionic liquid. AFM images of **Figure 5** clearly show a morphological change occurs in the films when EMIM TCB is added. Bright regions in the phase image can be assigned to PEDOT, while darker regions are assigned to low conductive PSS regions.[7] Increasing the amount of IL in the

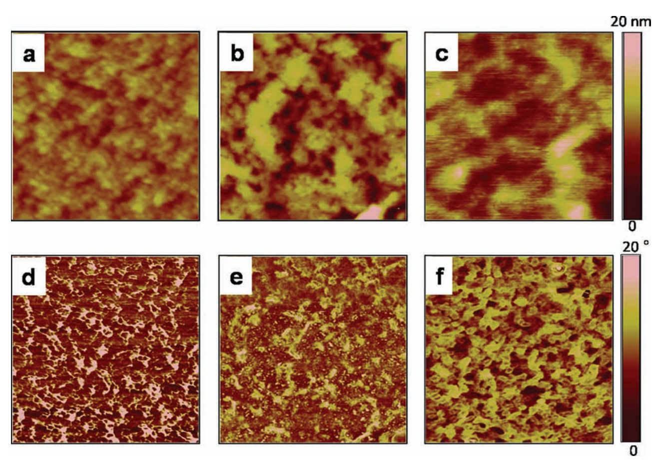

Figure 5. Topography (a–c) and phase images (d–f) of PEDOT:PSS films (a,d), PEDOT:PSS film prepared with 0.59 wt% EMIM TCB (b,e), and PEDOT:PSS film prepared with 1.57 wt% EMIM TCB (c,f).

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film induces phase separation and swells the PSS domains. The disconnected bright regions of PEDOT in pristine PEDOT:PSS films (Figure 5a,d) are better interconnected and form larger areas with the addition of IL in the film (Figure 5b,c,e,f). The depletion of insulating PSS leads to a 3D conducting network of highly conductive PEDOT, resulting in an increase of the conductivity up to 2084 S cm^{-1}. Adding IL to PH1000 results in the ordering of PEDOT segments in the film, this leads to a pathway of very high conductivity. These pathways are only created if the additive is present long enough to allow thermodynamically driven order to occur, in our case, the EMIM TCB is non-volatile and remains in the films to bridge the PEDOT together and remove the insulating PSS chains. Our results are consistent with other results reported in the literature.[19,20]

AFM images on films prepared with more than 1.57 wt% IL are difficult to obtain because the films are thick and rough, clouds of liquid are distinguished on the images, which we attribute to an excess of ionic liquid in the film resulting in a disconnected PEDOT network witnessed by inhomogeneity in the films and a decrease in the conductivity.

AFM images with previous results clearly show together that the conductivity enhancement is not only a surface effect in our case. Addition of EMIM TCB to PEDOT:PSS affects the whole PEDOT:PSS film imparting it with both high conductivity and transmittance.

We perform Fourier transform infrared (FTIR) measurements on the PEDOT:PSS/EMIM TCB films. **Figure 6** shows the FTIR spectra of a bare PH1000 film, PH1000 films containing different amounts of EMIM TCB, and pure EMIM TCB. The FTIR spectra clearly show that EMIM TCB is present in the film, two peaks originally observed in the pure EMIM TCB situated at 931 (C–N–C) and 1166 (C=C, C=N) cm^{-1} are observed in both PEDOT:PSS films prepared with 0.59 and 1.57 wt% of EMIM TCB. Other peaks at 725 (C–H), 827 (C–H), 1724 (C=C), 2987 (–C–H), and 3157 cm^{-1} (=C–H) are also associated with the peaks of EMIM TCB and show that the IL is retained in the film.[21] The peak at 2221 cm^{-1} can be attributed to the tetracyanoborate anion.[22] The films show some water content at 3500 cm^{-1}, this is caused by the sample fast water uptake from the atmosphere due to PSS acidity and the KBr pellets hygroscopy.

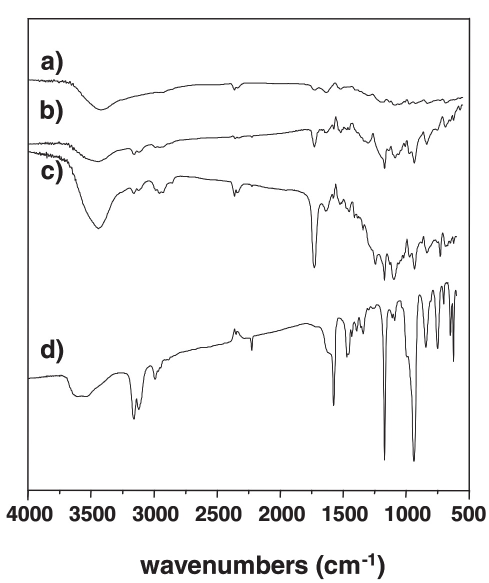

Figure 6. FTIR spectra of a) bare PEDOT:PSS film, b) PEDOT:PSS film prepared with 0.59 wt% EMIM TCB, c) PEDOT:PSS film prepared with 1.57 wt% EMIM TCB, and d) pure EMIM TCB.

3. Conclusions

In summary, we have demonstrated that ionic liquids such as EMIM TCB are one of the best additives for PEDOT:PSS. Single layer PEDOT:PSS films with a sheet resistance of 31 Ω sq^{-1} have been prepared. These highly conductive films maintain a transmittance higher than 96% and compare well to similar films reported in the literature. When compared with a commonly used ionic liquid, the PEDOT:PSS/EMIM TCB films show a conductivity of 2084 S cm^{-1} compared to 287 S cm^{-1} of PEDOT:PSS/BMIM BF_4 films and 575 S cm^{-1} of PEDOT:PSS/DMSO films. Our films are very promising to replace ITO in devices where highly conductive, transparent, and flexible electrodes are required. The detailed study of the conductivity enhancement mechanism is underway.

4. Experimental Section

Materials: Highly conductive grades of PEDOT:PSS or PH1000 were purchased from Heraeus/H.C.Starck and used in this work. DMSO (ACS reagent ≥99.9%) was purchased from Sigma Aldrich. Two ionic liquids were tested: EMIM TCB (ultrapure grade) was purchased from EMD chemicals and used as received; BMIM BF_4, ≥98.5%, was provided by Sigma Aldrich and used as received.

Preparation of PEDOT:PSS Films: PEDOT:PSS/IL films were prepared by two approaches. A_1 Ionic: Liquids were added directly into the vial containing the PEDOT:PSS PH1000 and stirred afterwards. A_2 PEDOT:PSS PH1000 was weighed in a vial. The vial was stirred on a vortex genie 2 (VWR) and the ionic liquid was added directly into the stirred PEDOT:PSS dispersion.

In both cases, highly conductive PEDOT:PSS films were obtained by spin coating. The spin speed was fixed at 4000 rpm for 60 s. All films were prepared by spin coating a 100 µL formulation of PEDOT:PSS containing different amount of ionic liquids on plastic sheets and glass substrates. The glass substrates were sonicated in acetone, ethanol, water, and pretreated in oxygen plasma for 15 min. All films were then annealed at $T >$ 120 °C for at least 15 min before any further characterization. The films were also freeze dried for some characterizations in order to remove excess water, if present.

Characterization of PEDOT:PSS Films: AFM images of the PEDOT:PSS films were obtained in tapping mode using a Veeco/Digital Instruments Nanoscope III. The films were spin coated on glass substrates and used for this purpose.

The thickness measurements were carried out with an alpha-SE ellipsometer (J.A. Woollam Co., Inc.) measuring about 180 separate wavelengths between 380 and 900 nm. The PEDOT:PSS films were spin-coated onto glass substrates. The back side reflection was removed by taping the glass substrate (an example of the model used is detailed in the Supporting Information).

The sheet resistance of the PEDOT:PSS films were measured by applying the technique used by H.C.Starck/Heraeus[23] and by using a four point setup, a Jandell Instrument connected to a RM3-AR unit. On each sample, at least four regions were measured and averaged. The values obtained with the two methods compare well.

FTIR measurements were done on a Tensor 27 (Bruker Optik Gmbh) Instrument. Transmittance measurements were obtained using a Cary 100 (Varian) and the values reported were measured at the wavelength

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of 550 nm. They were corrected by the substrate (plastic or glass) compared to a bare plastic or glass substrate and the incident beam went straight through the sample.

Supporting Information

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

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