Conducting Polymers **Hot Paper**

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An Alternative Anionic Polyelectrolyte for Aqueous PEDOT Dispersions: Toward Printable Transparent Electrodes**

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Abstract: *Organic conducting polymers are promising electrode materials for printable organic electronics. One of the most studied conducting polymers is PEDOT:PSS, which is sufficiently conductive and transparent, but which shows some drawbacks, such as hygroscopicity and acidity. A new approach to stabilize PEDOT in aqueous dispersions involves the replacement of PSS with a basic polyanion based on a polystyrene backbone with (trifluoromethylsulfonyl)imide (TSFI) side groups. The PEDOT:PSTFSIK dispersions were obtained by oxidative polymerization of EDOT in an aqueous PSTFSIK solution and were characterized with regard to their composition, morphology, doping, rheological behavior, and optoelectronic performance. The PEDOT:PSTFSIK dispersions showed excellent printability and good optoelectronic performance (238 Ohm sq^{-1} at 91 % transmittance, $\sigma >$ 260 S cm^{-1}) and were successfully integrated as flexible electrodes in OLED and OPV devices.*

Organic conducting polymers are of increasing scientific interest and promising candidates for various applications, such as transparent and flexible electrodes in light-emitting diodes (LEDs),[1,2] photovoltaics (PVs),[3,4] and sensors,[5] as antistatic coatings[6] or as active material in electrochromic devices.[7,8] The main advantages of conducting polymers are their chemical and mechanical stability, their biocompatibility as well as their processability at moderate temperatures and on large areas. One of the most studied conducting polymers is PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate). As a result of its relatively high conductivity and transparency in the doped state, it has been used for a large variety of applications.[1–8] Nevertheless, as mentioned in many reports, it shows some drawbacks, such as hygroscopicity, acidity, and poor wetting behavior on organic layers. Herein, we present a new approach to stabilize PEDOT in aqueous dispersions by replacing the polystyrenesulfonic acid with a basic anionic polymer based on (trifluoromethylsulfonyl)imide (TSFI) side groups attached to a polystyrene backbone. The PEDOT:polyanion systems were characterized regarding their morphology, composition, doping, and optoelectronic performance. Furthermore the effect of polymerization conditions on the conductivity of the resulting PEDOT:polyanion was investigated. These PEDOT:polyanion dispersions showed excellent printability and good optoelectronic performance (238 Ohm sq^{-1} at 91 % transmittance, $\sigma >$ 260 S cm^{-1}) and were successfully integrated in organic LED (OLED) and organic PV (OPV) devices.

Polyelectrolytes, such as the polyanion in this work, are known for their application in lithium batteries,[9] but they can also act as counterion of doped, conducting polymers and therefore stabilize them in aqueous dispersion. In the continuation of our work on PEDOT dispersions,[10,11] we chose to stabilize PEDOT using a poly[4-styrenesulfonyl (trifluoromethyl sulfonyl) imide potassium salt] (PSTFSIK). Even though the synthesis of such polyelectrolytes was pioneered by Armand and co-workers,[9] we developed a controlled polymerization route, using a reversible addition–fragmentation chain transfer (RAFT) process, which resulted in a well-defined, water-soluble polymer in a wide range of molar masses from 20 kDa to 500 kDa together with low dispersity ($Đ < 1.4$; unpublished results).

The PEDOT:polyanion (PEDOT:PSTFSIK) dispersions were obtained by oxidative polymerization of EDOT in aqueous PSTFSIK solution (see the Experimental Section in the Supporting Information). Figure 1 displays the chemical structure of PEDOT:PSTFSIK. For the sake of comparison, a PEDOT:PSS dispersion was synthesized and purified with the same procedure as the PEDOT:PSTFSIK.

As illustrated in Figure 2, the polymerization of EDOT was evidenced by UV/Vis spectroscopy. The concentration and "doping" level of PEDOT in the dispersion can be followed by monitoring the absorption intensities at 500 nm, 900 nm, and above 900 nm, which are generally assigned to neutral, polaronic, and bipolaronic states of PEDOT, respectively.[12,13] At the beginning of the polymerization reaction,

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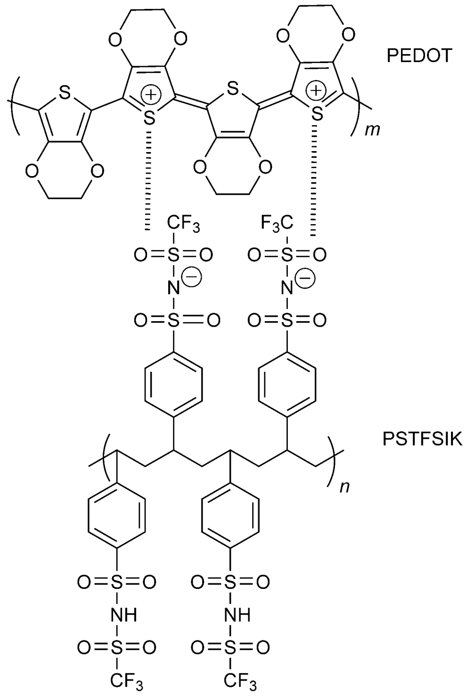

Figure 1. Schematic of the PEDOT:PSTFSIK complex. The negatively charged units of the PSTFSIK stabilize positive charge carriers on the PEDOT chains.

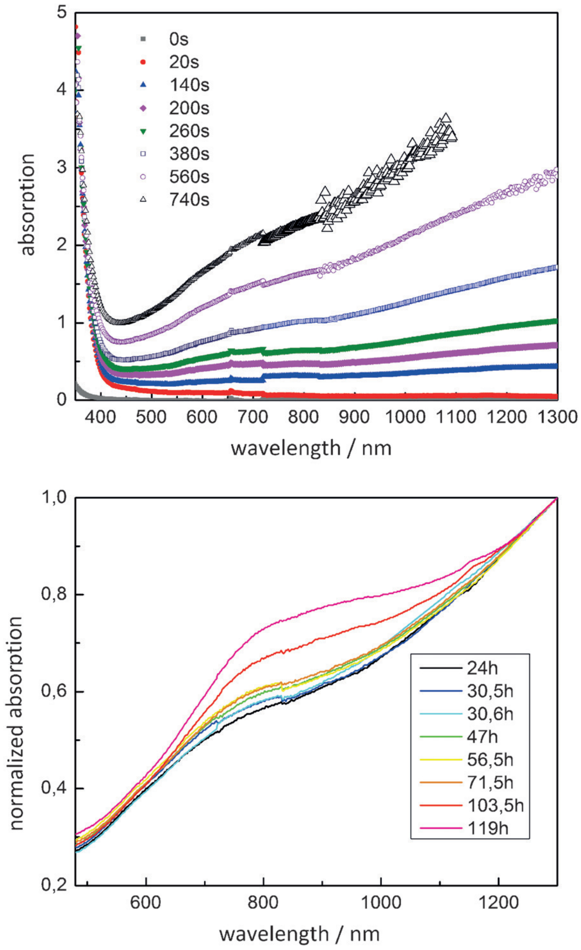

Figure 2. Evolution of the UV/Vis absorption spectrum during the EDOT polymerization over time for 0 s to 740 s (above) and for 24 h to 115 h of synthesis.

the absorption for wavelengths higher than 450 nm increased steadily, indicating a growing concentration of PEDOT in the dispersion. At longer time scales, only the absorption peak at 900 nm kept rising, indicating the continuous formation of polaronic states. This change in the electronic configuration of PEDOT can be experimentally linked to the optoelectronic performance of the dry PEDOT:PSTFSIK films. The influence of the reaction time, along with the effect of the temperature and the pH value on the properties of PEDOT:PSTFSIK have been investigated and will be discussed later in this Communication. After the polymerization, the resulting inks were purified by ultrafiltration to remove remaining reactants and oxidants.

After purification, all samples showed a pH value between 2.1 and 3.5 (home-made PEDOT:PSS pH 2.0) and a concentration of 0.7 wt % in water (see the Experimental Section and Figure S1 in the Supporting Information). Thermal analysis such as TGA and DSC measurements proved that PEDOT:PSTFSIK is stable up to 180 °C and did not show any glass transition or crystallization temperatures (see Figures S2 and S3 in the Supporting Information).

In order to determine the molar ratio of PSTFSIK to PEDOT in the PEDOT:PSTFSIK bulk, fluorine quantification was conducted by ICP-MS analysis. The PSTFSIK to PEDOT ratio was 0.9:1. There are no comparable measurements for PEDOT:PSS, as it does not possess an element that is exclusively present in PSS and that might therefore be easily traceable, such as fluorine in PSTFSIK. A widely used method to determine the PSS to PEDOT ratio on the film surface of PEDOT:PSS is the comparison of the sulfur peaks in the X-ray photoelectron spectroscopy (XPS) S2p spectrum, in which the peaks at energies higher than 167 eV can be assigned to a sulfur in a sulfonate environment (in PSS and PSTFSIK) and the doublet at 163.6 eV to the sulfur in PEDOT. The comparison of the sulfur peaks in the XPS S2p spectrum of home-made and commercial PEDOT:PSS (Clevios PH1000) showed a PSS to PEDOT ratio of 3.0:1 and 2.3:1, respectively. These values are similar to the PSS concentration that was found by XPS measurements for commercial PEDOT:PSS.[14–16] In comparison, the PSTFSIK to PEDOT ratio in PEDOT:PSTFSIK was found to be between 2.6:1 and 3:1 (see XPS S2p spectra in Figure S4 in the Supporting Information). We observed that the PEDOT content in PEDOT:PSTFSIK measured by XPS was systematically lower than the one measured by ICP-MS. Taking into account that XPS is a surface-sensitive method, whereas ICP-MS gives access to the bulk composition, we can state that the PEDOT content on the PEDOT:PSTFSIK film surface is lower than in the bulk. The same behavior is found for PEDOT:PSS films that show a lower PEDOT concentration at the film surface than in the bulk. This behavior is commonly explained by a preferential phase separation of PEDOT and the PSS with the PSS segregating to the film surface.[17]

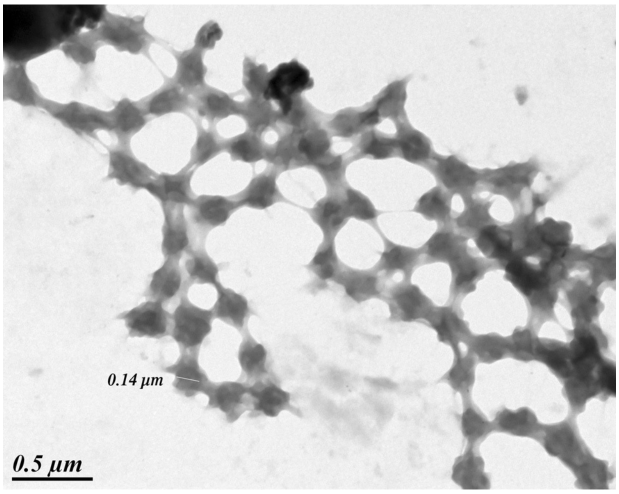

Figure 3. TEM image of PEDOT:PSTFSIK 250 kDa cast from aqueous dispersion of 0.007 wt% in water.

The morphology of PEDOT:PSTFSIK in dispersion was investigated by transmission electron microscopy (TEM; see Figure 3). The TEM image displays a network structure of interconnected particles with an average size of 150 nm. In contrast, home-made PEDOT:PSS shows separated agglomerates with diameters up to 1 µm. Interestingly, the addition of a co-solvent such as DMSO changes the solubility parameters and thus affects the colloidal morphology (see Figure S5 in the Supporting Information).

Further information on the dispersion was obtained by rheological measurements. Already at low concentrations of about 1 wt% in water, the PEDOT:PSTFSIK and the home-made PEDOT:PSS are highly viscous and show shear-thinning behavior (see Figure S6 in the Supporting Information). In comparison, the Clevios PH1000 is less viscous and shows Newtonian behavior at intermediate shear rates. In oscillating shear experiments, PEDOT:PSTFSIK demonstrates the characteristics of a gel ($G' > G''$), whereas Clevios PH1000 shows the behavior of a viscoelastic liquid (see Figure S7 in the Supporting Information). The gel-like behavior, the high viscosity, and the shear-thinning properties of the PEDOT:PSTFSIK inks facilitate the processing through doctor blading or bar coating on large areas.

The optoelectronic properties of the PEDOT:PSTFSIK films were determined by measuring their sheet resistance and transmittance. To allow a valid comparison of the film properties independent of the film thickness, a figure of merit σ_{DC}/σ_{opt} is calculated using the following Equation (1).[18]

$$T(\lambda = 550\text{nm}) = \left(1 + \frac{188.5}{R}\frac{\sigma_{opt}}{\sigma_{DC}}\right)^{-2} \qquad (1)$$

The optoelectronic performance of the different PEDOT systems is presented in Table S1 in the Supporting Information.

The home-made PEDOT:PSS shows similar conductivity as the PEDOT:PSTFSIK (224 ± 20 S cm^{-1} for PSTFSIK of 350 kDa) but a 2.7 times smaller figure of merit. This result is due to a lower absorption coefficient of the PEDOT:PSTFSIK compared to PEDOT:PSS (2×10^{-3} cm^{-1} and 5×10^{-3} cm^{-1}, respectively). Nevertheless, both PEDOT:PSTFSIK (σ ranging from 96 to 224 S cm^{-1} for a series of samples, $\sigma_{DC}/\sigma_{opt} = 13 \pm 3$) and home-made PEDOT:PSS ($\sigma = 229$ S cm$^{-1} \pm 34$ S cm^{-1}, $\sigma_{DC}/\sigma_{opt} = 6$) show lower conductivity and a smaller figure of merit than the Clevios PH1000 ($\sigma = 778$ S cm$^{-1} \pm 116$ S cm^{-1}, $\sigma_{DC}/\sigma_{opt} = 24 \pm 5$). The electronic properties of PEDOT:PSTFSIK films, stored under ambient conditions, were stable over months (see Figure S9 in the Supporting Information).

All the above measured properties were obtained for PEDOT:PSTFSIK dispersions in which 5 wt% DMSO was added. It is well known that the addition of solvents with high boiling points, such as DMSO, to PEDOT:PSS drastically increases the conductivity of the films.[1,19,20] The same effect is observed for PEDOT:PSTFSIK inks. For PEDOT:PSTFSIK, a DMSO concentration of 5 wt% increases the film performance up to 80 times compared to the pristine ink, while higher concentrations of DMSO do not further improve the performance (see Figure S8 in the Supporting Information) and eventually cause the formation of inhomogeneities during film deposition.

The effect of some key polymerization parameters on the optoelectronic performance of the resulting dry PEDOT:PSTFSIK films was studied. Initial experiments indicated that the pH value of the synthesis medium has a significant impact on the polymerization of EDOT and on the conductivity of the resulting PEDOT:PSTFSIK films (see Figure 4). Under acidic conditions, the reaction is accelerated, whereas the addition of a base completely inhibits the polymerization (see the Experimental Section). In aprotic solvents such as DMSO, the polymerization of EDOT does not take place. This observation is in agreement with the mechanism for the oxidative polymerization of thiophenes described by Higashimura et al.[21] in which the transfer of protons to the solvent is a crucial step. The performance of PEDOT:PSTFSIK synthesized in acidified solutions was much lower than the performance of PEDOT:PSTFSIK prepared in the basic PSTFSIK solution.

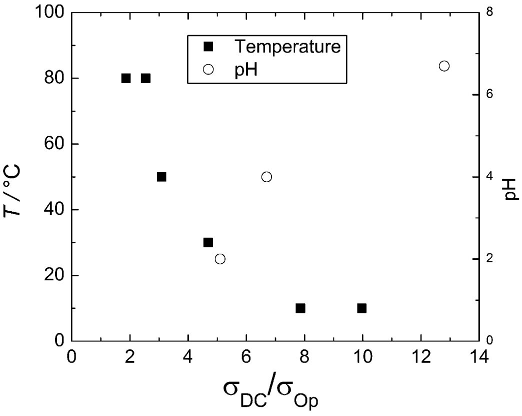

Figure 4. Performance of PEDOT:PSTFSIK films as a function of reaction temperature and as a function of the pH value of the PSTFSIK solution (pH values are controlled by the addition of HCl).

The second important parameter that was studied was the temperature of polymerization. We observed that by lowering the polymerization temperature, the figure of merit of the PEDOT:PSTFSIK films was increased (see Figure 4). A decrease in temperature resulted in slower reaction kinetics, favoring better colloidal stability and good optoelectronic performance.

A study of the relation between polymerization time and the optoelectronic properties of the films showed that the highest performance is obtained after a reaction duration of 50 h at 14 °C (see Figure S10 in the Supporting Information) when an optimum polaron/bipolaron ratio is reached. The relation between polymerization conditions, molar masses, pH value, and performance are under investigation and will be the topic of a forthcoming paper.

In order to demonstrate the potential of these conductive inks as transparent electrodes, flexible orange and white PIN-OLED (PIN: p-doped/intrinsic/n-doped) and organic photovoltaic devices have been studied. Typical LIV (light current voltage) curves of the orange PIN-OLEDs based on PEDOT:PSTFSIK electrodes are presented in Figure 5b. A total number of 40 devices were prepared (yield = 97.5 %) with an average efficiency of 12 ± 1 cd A^{-1} and 14 ± 2 Lm W^{-1} versus a reference device using an ITO anode showing 15 ± 7 cd A^{-1} and 17 ± 9 Lm W^{-1} (measurements at 1000 cdm^{-2}). Lifetime measurements have not yet been performed, but devices encapsulated with barrier foil are stable over several weeks under ambient conditions (relative humidity = 50–80 %, T = 15–30 °C). The white PIN-OLEDs showed efficiencies of 39 ± 5 cd A^{-1} and 25 ± 5 Lm W^{-1}. In comparison, the PEDOT:PSS reference device reached similar efficiencies of 36 ± 4 cd A^{-1} and 24 ± 3 Lm W^{-1}.

Figure 5 a shows typical OPV I–V curves of a device with PEDOT:PSTFSIK electrode (solid line) in comparison to an ITO reference device (dashed line). The difference in V_{oc} is small (5 %), however the PSTFSIK-based electrode is causing a decrease in the I_{sc} (20 %) with respect to the reference. This is most likely a result of the higher light absorption of the polymer anode. For a total of 36 PEDOT:PSTFSIK devices (yield 86.1 %), the average power conversion efficiency was 1.8 %, compared to 2.6 % for ITO OPV reference devices.

In conclusion, a conducting and stable PEDOT:PSTFSIK dispersion was synthesized by using an anionic polymer for the stabilization of PEDOT. The PEDOT:PSTFSIK films show a conductivity of up to 224 S cm^{-1}, which is comparable to the conductivity of home-made PEDOT:PSS, and a figure of merit of up to 16, which is about triple of the value found for our home-made PEDOT:PSS. The gel-like ink is easily processable by doctor blading and the films are stable over several months under ambient conditions. The films were successfully integrated as transparent electrodes in flexible OPV (conversion efficiency of 1.8 %) and OLED devices (39 ± 5 cd A^{-1}, 25 ± 5 Lm W^{-1}). Their performance, together with their intrinsic stability, printability, and compatibility with state-of-the-art OLED and OPV materials, show the potential of PEDOT:PSTFSIK for printable electronics.

Keywords: conducting polymers · electrodes · optoelectronics · polyanions · printed organic electronics

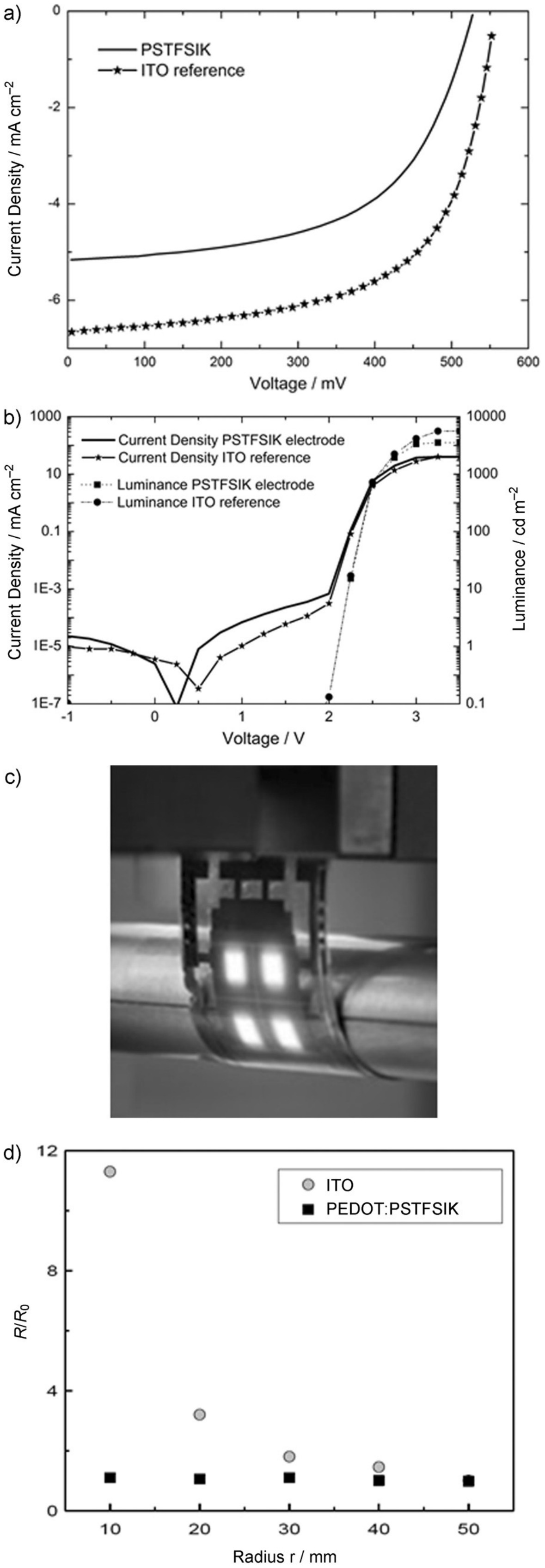

Figure 5. IV characteristics of an OPV (a) and OLED (b) device together with their respective reference. Devices (c, fabricated on 50×35 mm PET foil) withstand flexibility tests down to a bending radius of 10 mm (d).

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