“Click”-modification of a functionalized poly(3,4-ethylenedioxythiophene) (PEDOT) soluble in organic solvents†

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A PEDOT-based conductive copolymer soluble in organic solvents was synthesized electrochemically using dihexyl-EDOT and azidomethyl-EDOT as monomers and was successfully post-functionalized by “click”-cycloaddition reaction with a functionalized terminal alkylene under mild heterogeneous conditions.

Poly(3,4-ethylenedioxythiophene)s (PEDOT) exhibit excellent environmental and thermal stability, good mechanical strength as well as ease of preparation.1 PEDOTs also comprise a low band gap2 and excellent transparency in their doped state3 which renders them among the most successful conducting polymers in optoelectronic applications. The extended use of PEDOT is based on the conducting properties of its complex with polyelectrolytic polyanion PSS6 and, as a consequence, present lower conductivity compared to vapor-phase polymerized PEDOTs.7 An additional limitation is that the acidic character of PSS leads to corrosion of ITO electrodes in devices8 or decomposition of PSS.9 Thus, synthesis of processable PEDOT derivatives devoid of the limitations imparted by the presence of the PSS counter ion is of general interest. However, PEDOT and most derivatives are insoluble in most organic solvents which represents a significant limitation in manufacturing processes. Therefore, the search for processable PEDOT derivatives with intact electronic properties is a challenge in the area of printable electronics. In this area novel technologies have been developed for the patterning of conducting polymers including screen10 and inkjet printing,11 which have been used for the fabrication of organic light-emitting diodes (OLED),12 field-effect transistors (OFET),13 and solar cells.14 However, despite the large number of potential applications, only few examples of PEDOT derivatives soluble in water- or organic solvents have been demonstrated.15

A general approach to functionalized PEDOTs is the covalent linkage of functional units to the ethylenedioxy bridge of the corresponding 3,4-ethylenedioxythiophene (EDOT) monomers16 and their subsequent polymerization. Despite its apparent simplicity, the concept sometimes fails due to electronic and steric limitations of the attached functional units which hinder electropolymerization.17

An alternative approach to obtaining derivatized polymers involves the post-functionalization of precursor polymers. In this regard, we recently reported efficient post-functionalization of poly(azidomethyl-EDOT) (P2, Scheme 1)18 by using the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes,19 frequently referred to as “click”-reaction. Nevertheless, the processability of the novel PEDOT derivatives obtained by this procedure is limited by the rigid nature of their conjugated backbones,20 which results in poor solubility in common organic solvents. On the other hand, with the aim to obtain processable PEDOTs we reported

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Scheme 1 Electrochemical polymerization of dihexyl-substituted EDOT 1, azidomethyl-substituted EDOT 2 and copolymerisation of 1 and 2, to yield, respectively, P1, P2, and copolymer P3 and “click” reaction with phthalimide-functionalized alkyn 4 to afford 1,2,3-triazolo-functionalized PEDOT 5. (i) ACN or PhCN/Bu4NPF6, -ne −/nH+; (ii) Cu/Cu (CH3CN), nPF6, ACN, rt.
synthesis of dihexyl-substituted EDOT (Hex2-EDOT, 1, Scheme 1) and its electrochemical polymerization.21 The resultant polymer was found to be soluble in chloroform, dichloromethane (DCM), tetrahydrofuran (THF), toluene, and benzonitrile (BCN) without a polyanion such as PSS. The possibility to combine the post-functionalization strategy with a solution-processable PEDOT would pave the way for the synthesis of soluble and processable PEDOTs endowed with redox- or bioactive functionalities suitable for the formation of homogeneous ultrathin conducting polymer films.

In this communication, we report an example of a PEDOT-based conducting copolymer soluble in organic solvents which can be post-functionalized by means of “click”–reaction. We started with the electrochemical copolymerization of Hex2-EDOT 1 and azidomethyl-EDOT (N3-PEDOT, 2) in a feed ratio of 80/20 mol% to obtain the corresponding copolymer 3 as a conducting film adhering to the working electrode (Fig. 1A and Scheme 1). An irreversible oxidation wave of the monomers typical for EDOTs \( (E_{pa} = 1.12 \text{ V vs. } \text{Fc/Fc}^-) \) appears in the first scan (Fig. 1A, red line). In the second scan, a novel broad redox wave appeared at lower potentials than the first oxidation peak, which gradually increases in the subsequent potential scans as shown in Fig. 1(A) (black lines). The thickness of the electroactive polymer film steadily increased and can be controlled by the number of cycles.

Copolymer film 3 was electrochemically characterized in a monomer-free electrolyte solution, resulting in a CV typical for PEDOTs (Fig. 1B, black line). The onset potential \( (E_{onset}) \) for 3 as well as the first redox process fits very well with those measured for 1 (−0.58 V, Fig. 1B, blue line). On the other hand, \( E_{onset} \) of 2 is observed at a much lower potential (−0.95 V; Fig. 1B, red line). Thus, monomer 1 is dominantly inherited in copolymer 3 sequences, so that the CV response of copolymer 3 resembles that measured for 1.

By comparing the peak area of the azide band in the IR spectra of 3 (Fig. S1, ESI†) and that of N3-PEDOT 218 a composition ratio of ca. 18% of N3-EDOT 2 units in the 3 film has been estimated indicating that the composition ratio of monomer 2 in the 3 film nearly retains the feed ratio of 20 mol% of 2 in the electrochemical copolymerization of 1 and 2. Examination of the solubility of copolymer 3 in common organic solvents (Table 1) showed solubility in THF, toluene, and benzonitrile (BCN). The highest solubilities were observed in DCM, in which 0.14 wt% of copolymer 3 and 0.11 wt% of functionalized copolymer 5 can be dissolved.

UV-Vis-NIR absorption of DCM solutions of copolymer 3 with various concentrations of the oxidant (thianthrenium hexachloroantimonate) has been also investigated (Fig. 2). In the reduced state, the copolymer solution was deep blue in colour and showed a strong absorption throughout the visible region \((400–700 \text{ nm})\) similar to that observed for 1. This absorption is due to the \( \pi \rightarrow \pi^* \) interband transitions of the conjugated chain. The interband transition is split into two distinct peaks at 638 and 586 nm, which are attributed to vibronic coupling due to a high degree of planarity along the copolymer backbone. In the neutral state, PEDOT exhibits an optical band gap \( (E_g) \) of ca. 1.84 eV, as determined from the onset for the \( \pi \rightarrow \pi^* \) absorption at 673 nm.

By increasing the concentration of the oxidant a decrease in the absorption in the visible region was observed and the concomitant growth of a low-energy absorption at 1023 nm due to the formation of a polaronic state. In the highly oxidized state the absorption in the NIR region continuously increased and the solution became pale magenta and transmissive. The variation of the absorption pattern offers a clear proof of the reversible redox activity of the dissolved polymer in the presence of a chemical oxidant.

It is also of interest to check whether the soluble PEDOT derivative 3 keeps its properties when it is processed from solution into films. With this aim, a film of 3 was spin-coated \((800 \text{ rpm for } 200 \text{ s})\) onto a platinum (Pt) disk electrode by using a DCM solution of copolymer 3 and electrochemically

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<th>Table 1</th>
<th>Solubilities of copolymers P3 and P5* in organic solvents of before and after “click”–modification</th>
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<tr>
<td>Polymer content in solvent [wt%]</td>
<td>PEDOT</td>
</tr>
<tr>
<td>P3</td>
<td>0.14</td>
</tr>
<tr>
<td>P5</td>
<td>&gt;0.11</td>
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* Post-functionalized product of P3 with phthalimide 4.
characterized. The CV of the spin-coated P3 film exhibited an $E_{\text{onset}}$ of $-0.62$ V which well accords with that of the electrodeposited P3 film ($E_{\text{onset}} = -0.58$ V, Fig. 1B, black line). The presence of azide groups in the polymer renders P3 suitable for post-functionalization through “click”-reaction yielding a 1,2,3-triazolo-functionalized PEDOT. Thus, Pt disk electrodes covered with P3 thin films were reacted with N-(3-butynyl)-phthalimide 4 by dipping the electrode in acetonitrile solutions containing 4 in the presence of catalytic amounts of Cu$^{+}$ (CH$_3$CN)$_4$PF$_6$ and elemental copper. The formation of the corresponding phthalimide-functionalized PEDOT P5 was completed in three days at room temperature. After copious rinsing to remove reagents and the catalyst from the polymer film, the “click”-functionalized electrode was characterized electrochemically.

The CV of the “clicked” P5 film (Fig. 3, red line) clearly showed redox transitions of the phthalimide acceptor at potentials ($E^o = -1.92$ V) where the PEDOT backbone is semiconducting. This redox potential well coincided with that of the free butyne 4 ($E^o = -1.87$ V) which confirms efficient functionalization of the polymer with phthalimide pendant groups. A nearly identical onset potential is observed for spin-coated P3 and “clicked” P5 films which indicates that the redox activity of the PEDOT backbone is retained after “click”-functionalization. Interestingly, the solubility of copolymer P3 in DCM is almost retained after “click”-functionalization with terminal alkyne 4 (Table 1).

Continuous cycling caused a decrease of the copolymer charging capacity to 53% of the original electroactivity. Nevertheless, the onset potential and the peak potential did not change after the 100th scan ($E_{\text{onset}} = -0.58$ V, $E_{\text{pa}} = -0.17$ V) providing a good electrochemical activity for the post-functionalized polymer (Fig. S2, ESIF). FT-IR spectroscopic characterization of the neutral P3 films prepared on an ITO electrode before (P3) and after the “click”-modification (P5) with phthalimide 4 confirmed the conversion of the azide to triazol moieties endowed with phthalimide units, as evidenced by the nearly complete disappearance of the weak azide band in P3 at 2101 cm$^{-1}$ and the appearance of a medium strong C=O bond stretching vibration of the phthalimide at 1715 cm$^{-1}$ in P5 (Fig. S1, ESIF).

In summary, formation of a PEDOT copolymer soluble in organic solvents has been achieved by electrochemical copolymerization of monomers 1 and 2 in a feed ratio of 80/20 mol%. Even after mechanical processing such as spin-coating the copolymer remained electroactive. In a subsequent post-functionalization step, facile immobilization of electron-accepting phthalimide 4 was achieved by “click”-reaction with high conversion efficiencies. CVs of “click”-derivatized copolymer P5 revealed the specific redox transitions of the immobilized unit. These results now offer perspectives to process ultrathin conductive polymer films, which can be further functionalized with catalytically or biologically active groups opening the way to functional printable organic electronic devices and sensors.

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**Notes and references**