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"Click"-functionalization of conducting poly(3,4-ethylenedioxythiophene) (PEDOT)†

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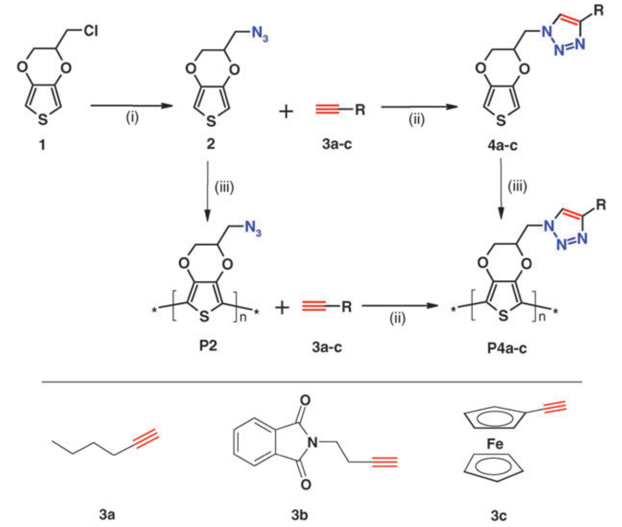
Efficient post-functionalization of conductive polymer films was achieved by Cu$^+$-catalyzed "click"-cycloaddition of novel poly(azidomethyl-EDOT) P2 and various functionalized terminal alkynes under mild heterogeneous conditions with high conversion efficiencies.

Functionalization of conducting polymers offers the attractive possibility of developing novel materials, which in addition to the particular optoelectronic properties of the conjugated backbone incorporate specific properties of the functional group.[1] The general approach to functionalized conducting polymers followed mainly for polypyrroles[2,3] and polythiophenes[3] is the covalent linkage of the functional unit to the corresponding monomers and their subsequent polymerization. Unfortunately, this strategy may fail and the polymerization process is inhibited if, *e.g.*, steric demand or interfering redox chemistry of the functional group come into play.[4] Hence, post-functionalization of conjugated polymers by polymer-analogous chemical reactions represents a viable solution to this problem. Although various protocols using standard coupling reactions have been developed,[5] active ester-functionalized polythiophenes[6] and polypyrroles[7] were introduced to mildly and efficiently couple sensitive functional units, such as, *e.g.*, redox active ferrocenes or enzymes to the conducting polymer.

The use of a clean addition reaction without the release of unwanted side products would be even more advantageous. In this respect, the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes, frequently referred to as "click"-reaction, would represent an ideal post-functionalization reaction and is meanwhile increasingly applied in many fields of chemistry due to its reliability, specificity and biocompatibility.[8] Related to our problem, it has been successfully used, for both, architectural modifications of mainly flexible (co)polymers[9] or immobilizations on surfaces.[10] Only very recently, two examples of side-chain modification of semiconducting polymers have been reported though in solution.[11]

In this communication, we report the first examples of a post-functionalization of conducting poly(3,4-ethylenedioxythiophene), PEDOT, by "click"-reaction. PEDOT has developed to one of the most successful and technologically important conducting polymers,[12] but still the number of functionalized PEDOTs is rather scarce.[13,14] Based on a previous approach,[14] we now develop novel poly(azidomethyl-EDOT) **P2** and demonstrate the versatility of an effective "click"-protocol to modify PEDOT with various types of terminal alkynes. We recently introduced chloromethyl-EDOT **1** as a versatile building block for substituted EDOTs.[14] By nucleophilic substitution with sodium azide, EDOT **1** was easily transformed in 97% yield to corresponding azidomethyl-EDOT (N_3-EDOT) **2** (Scheme 1). In order to obtain functionalized monomeric units, N_3-EDOT **2** was converted to the corresponding 1,2,3-triazolo-substituted EDOTs **4a–c** *via* "click"-reaction with terminal alkynes **3a–c** in 64–84% yield. Alkynes bearing an alkyl chain (**3a**), an electron acceptor (**3b**), and an electron donor (**3c**) were chosen as representative examples.

Potentiodynamic electropolymerization of N_3-EDOT **2** yielded corresponding polymer P(N_3-EDOT) **P2** as a



Scheme 1 Synthesis of azido-functionalized EDOT **2**, corresponding polymer **P2** and "click"-reactions with various alkynes **3a–c** to 1,2,3-triazolo-functionalized EDOTs **4a–c** and PEDOTs **P4a–c**. *Reagents and conditions*: (i) NaN_3/DMF, 120 °C, 97%; (ii) Cu/$Cu(CH_3CN)_4PF_6$/CH_3CN, r.t., 64–84%; (iii) CH_3CN–TBAHFP, $-ne^-/-nH^+$.

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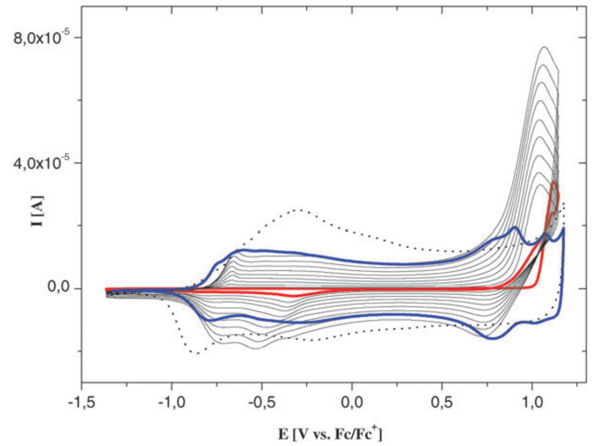

Fig. 1 Electrochemical oxidation of N_3-EDOT **2** in dichloromethane–TBAHFP (0.1 M). 1st scan (red), successive scans, 2nd to 10th (black). Characterization of corresponding P(N_3-EDOT) **P2** in CH_3CN–TBAHPF (0.1 M) (blue). For comparison the CV of PEDOT polymerized from EDOT under the same conditions is shown (dotted black line).

conducting film strongly adhering to the working electrode. In Fig. 1 cyclic voltammograms (CV) for a typical experiment are shown: an irreversible oxidation wave of the monomer at a potential typical for EDOTs (E_p = 1.10 V *vs.* Fc/Fc$^+$) is seen in the first scan (red line). In subsequent scans, the formation and growth of a conducting polymer film is reflected by the appearance of a broad novel redox wave at lower potentials than the monomer oxidation which gradually increases in subsequent potential cycles (black lines). The thickness of the electroactive polymer film is steadily increased and can be controlled by the number of cycles. Azidomethyl-PEDOT film **P2** was electrochemically characterized in an electrolyte free of monomer yielding a CV typical for PEDOTs (blue line). The onset potential for **P2** (E_{onset} = −0.93 V) which marks the beginning transition from the semiconducting to the conducting state is nearly as low as for PEDOT (E_{onset} = −0.97 V, dotted black line). Continuous cycling indicated a high electrochemical stability of P(N_3-EDOT) **P2** (82% electroactivity retained after 100 scans; ESI;† Fig. S1) providing an excellent basis for post-functionalization reactions.

The electrochemical characterization of monomeric triazolo-functionalized EDOTs **4a–c** showed typical irreversible oxidation waves at remarkably higher potentials than parent N_3-EDOT **2** (ΔE > 0.12 V). In general and in contrast to EDOT **2**, trials to electropolymerize EDOTs **4a–c** typically resulted in the passivation of the working electrode by ill-defined and non-conducting precipitates and not in the formation of corresponding conducting PEDOT films. The reason for this failure could come from the interference of triazole units with EDOT radical cations so that polymerization is inhibited.

Nevertheless, post-functionalization of azido-PEDOT **P2** by "click"-chemistry represented a solution to this problem. The following protocol for post-modification of P(N_3-EDOT) films **P2** was developed: Pt-disk electrodes covered with thin films of various thicknesses were treated in vials containing alkynes **3a–c** in acetonitrile as solvent in the presence of catalytic amounts of $Cu^+(CH_3CN)_4PF_6^-$ and elemental copper. Complete reaction to corresponding functionalized PEDOTs **P4a–c** occurred after three days at room temperature. After washing the "click"-functionalized electrodes were characterized electrochemically. This protocol turned out to furnish the best polymer films and led to better results than reaction with the system $CuSO_4/Cu^0$ in aqueous organic solution which resulted in the growth of crystalline copper salts on the polymer surface.

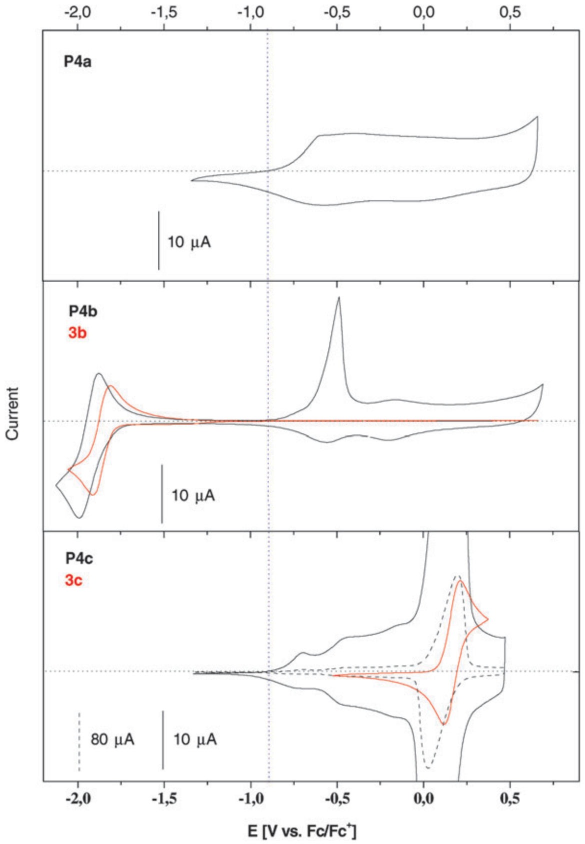

Fig. 2 Cyclic voltammograms of post-functionalized polymers **P4a–c** (black) in comparison to corresponding alkynes **3b,c** (red) in acetonitrile or benzonitrile/TBAHFP (0.1 M), calibrated *vs.* Fc/Fc$^+$. The blue vertical dotted line gives the onset potential of P(N_3-EDOT) **P2**.

The electrochemical characterization for resulting PEDOT films **P4a–c** are shown in Fig. 2 in comparison to corresponding (electroactive) alkynes **3b,c**. The CV of 4-butyl-1,2,3-triazole-substituted PEDOT film **P4a** is typical for PEDOTs showing that electroactivity of the polymer film is maintained despite side-chain modifications (E_{onset} = −0.91 V). More significant for side-chain modification with alkyl groups was a shift in onset (ΔE = 0.37 V) and peak potential (ΔE = 0.44 V) with increasing number of cycles in multiple sweep CV experiments, which is not observed for parent polymer **P2**. We attribute this behavior to irreversible rearrangements in the morphology of the post-modified polymer. Nevertheless, continuous cycling of **P4a**-modified electrodes indicated high electrochemical stability (91% electroactivity retained after 100 scans; ESI; Fig. S2) very similar to the behaviour of original polymer **P2**. FT-IR spectroscopic characterization of rather thick and neutral P(N_3-EDOT) **P2** films prepared on ITO glass before and after "click"-modification with 1-hexyne **3a** and the Cu/Cu$^+$ system revealed a high conversion of *ca.* 95% azido to 1,2,3-triazole groups indicated by the nearly complete disappearance of the strong azido band at 2098 cm^{-1} in **P2** and the appearance of the C–C double bond stretching vibration of the triazole ring at 1514 cm^{-1} in **P4a** (ESI;† Fig. S3).

The CVs of PEDOTs **P4b,c** which were "clicked" with electroactive alkynes **3b,c** clearly showed reversible waves and redox transitions of the phthalimide acceptor at potentials where the PEDOT backbone is semiconducting (E° = −1.94 V) and of the ferrocene donor (E° = 0.12 V) which is superimposed to the response of the conjugated backbone and lies in the conducting regime. These redox potentials well coincided with those of the free alkynes **3b,c** (E° = −1.87 V and E° = 0.16, respectively; Fig. 2) and triazolo-EDOT monomers **4b,c** (E° = −1.89 V and E° = 0.09 V, respectively). High current stability of the corresponding redox waves in multiple cycling experiments manifested the covalent immobilization of the alkynes to the polymer by the cycloaddition reaction. The broad redox activity of the PEDOTs is retained after "click"-functionalization which is documented by their nearly identical onset potentials (**P4b**: E_{onset} = −0.95 V; **P4c**: E_{onset} = −0.94 V). This transition from the semiconducting to the conducting state is in the same regime compared to parent polymer **P2**.

These experiments gave clear proof that efficient post-functionalization of conductive polymer films was achieved by Cu$^+$-catalyzed "click"-cycloaddition of novel poly(azidomethyl-EDOT) **P2** and various functionalized terminal alkynes under mild heterogeneous conditions. Facile immobilization of neutral (alkyl), electron-accepting (phthalimide) and electron-donating (ferrocene) units was obtained with high conversion efficiencies. Critical redox active groups such as ferrocene were easily bound to a conducting polymer which is typically not possible by polymerization of corresponding monomers and show redox transitions overlaid with this of PEDOT. Even at very negative potentials where the PEDOT backbone is not electroactive and semiconducting, specific redox transitions of electron-accepting pendant groups were well identified. These results now offer the perspective to immobilize further moieties of interest to PEDOTs, such as catalysts or biologically active molecules which could open the way to novel amperometric (bio)sensors.

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