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Efficient post-polymerization functionalization of conducting poly(3,4-ethylenedioxythiophene) (PEDOT) via 'click'-reaction

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ABSTRACT

The possibility to functionalize polymers after a successful polymerization process is often an important challenge in macromolecular science. Herein, modified electrodes based on azide-containing potentiodynamically electropolymerized PEDOT derivatives are reported. This reactive coatings are subsequently modified under mild heterogeneous conditions by copper-catalyzed Huisgen 1,3-dipolar cycloaddition with terminal alkynes, the so-called 'click'-reaction. A series of terminal alkynes have been successfully used for the facile immobilization of neutral, electron-accepting and electron-donating units to the conducting PEDOT with high conversion efficiencies showing the broad scope of the strategy. The route is devoid of the limitations generated by the various steric and electronic impacts of the substituents when attached to the monomer before polymerization.

1. Introduction

With the class of polythiophenes a great variety of properties can be realized related to a polyconjugated backbone, their stability, processability, and structural versatility, which are beneficial for applications in organic electronics.[1] In particular, thiophene-based conjugated polymers are receiving widespread attention as active materials in electronic devices, such as light emitting diodes,[2] organic solar cells,[3] field effect transistors,[4] and chemical and biological sensors.[5] Some of these applications are based on the synthesis via electropolymerization of defined thiophene-containing oligo- or monomers resulting in modified electrodes coated with a π-conjugated electroactive polymer.[6] The main feature of electrochemical synthesis is the application of defined potentials to induce a polymerization reaction that allows a rapid growth of polymer films of a few hundred nanometers thickness. Additionally, electropolymerization represents a straightforward method for the elaboration of modified electrodes in which the inherent electrochemical and/or optical properties of the conjugated polymer backbone are associated with specific properties of covalently bound functional groups.[7] Despite its apparent simplicity, the concept fails sometimes due to electronic and steric limitations of the attached functional groups during electropolymerization with the result that electropolymerization is hindered. Thus, easily oxidized groups can interfere with, or even inhibit, the polymerization process. In this regard, co-electropolymerization[8] or the incorporation of additional thiophene units in the monomer[9] are sometimes required for successful polymerization of monomers bearing strong donating substituents.

An alternate approach to obtaining derivatized polymers is post-functionalization of precursor polymers,[10] which has been extensively applied to conventional non-π-conjugated polymers. This strategy has also been applied to poly(pyrrole),[11] poly(aniline),[12] and poly(thiophene)s.[13]

Among conducting polymers, PEDOT has evolved as one of the most important materials because of the unique combination of high stability, high conductivity, and optical transparency in the visible spectral range. The significance and main applications of PEDOT and its derivatives have been discussed at length in recent reviews.[14]

One approach to functionalize PEDOT is to covalently link the functional unit to monomeric EDOT.[15,16] Consequently, the chemistry of the EDOT monomer itself and the modification of the basic structure have been developed in parallel. Very recently, Roncali et al. have reviewed the opportunities offered by the EDOT building block for the design and synthesis of new classes of functional π-conjugated systems.[17]

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The post-polymerization functionalization of PEDOT derivatives has been less explored yet. Besbes et al.[18] reported on functionalization of PEDOT derivatives bearing ω-iodoalkyl or ω-iodo-polyether chains attached at the ethylenedioxy bridges. Lyskawa et al. explored the potential of this strategy to prepare modified electrodes for Pb^{2+} detection.[19] In 2008, Balog et al. introduced a functionalized EDOT derivative bearing a highly nucleophilic thiolate group, which after electropolymerization afforded a functionalizable PEDOT derivative.[20] The electrogenerated polymer could be efficiently functionalized with the strong electron donor tetrathiafulvalene (TTF). In 2009, Bhandari et al.[21] reported the post-polymerization functionalization of a PEDOT film electropolymerized from an aqueous micellar solution encompassing the EDOT monomer and the dopant sodium bis(2-ethylhexyl)sulfosuccinate. The post-polymerization reaction consisted of a photochemical nitrene reaction by the reactive 1-fluoro-2-nitro-4-azidobenzene (FNAB) typically used for biochemical applications. In general, this strategy is devoid of the limitations generated by the various steric and electronic impacts of the substituents when attached to the monomer before polymerization.

In polymer-analogous reactions the formation of side products can be a deficit if their separation is cumbersome. Therefore, the use of a clean addition reaction without the release of unwanted byproducts 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.[22]

In principle, the [3+2] cycloaddition reaction between an organic azide and an acetylene derivative needs rather harsh conditions as described by Huisgen[23] in a review about cycloaddition reactions. However, Sharpless[24] and Meldal[25] found that the activation threshold is dramatically reduced if the reaction is catalyzed by Cu(I), which was generated in early times from Cu(II) in presence of sodium ascorbate. Thus, this reaction has been developed to an efficient coupling method for a large variety of substrates and reagents, which works not only at room temperature (or even lower) but also under environmentally benign conditions, furnishing regioselectively the 1,4-substituted 1*H*-[1,2,3]triazoles. Therefore, this type of reaction fits nicely to the criteria of 'click' chemistry defined by Sharpless et al.

Related to our approach, it has been successfully used, for both, architectural modifications of mainly flexible (co)polymers,[26,27] and immobilizations on surfaces.[28] Very recently, some examples of side-chain modification of semiconducting polymers[29] and a variety of functional soft materials[30] have been reported in solution by means of the click reaction. In 2008, we reported the first example of efficient post-functionalization of an electrochemically polymerized conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), by Cu(I) catalyzed click-addition under mild heterogeneous conditions with high conversion efficiencies.[31] Hvilsted et al. later reported functionalization of a chemically polymerized PEDOT applying click-chemistry also under heterogeneous conditions.[32] The same group has shown, by using alkyne-modified fluoresceine, that post-functionalization of PEDOT via click-chemistry can be performed in micrometer-sized areas.[33]

In this article, we want to report the general scope of our original strategy[31] for the post-functionalization of PEDOT through Cu(I)-catalyzed click-cycloaddition. For this purpose, we have synthesized a family of terminal alkynes substituted with electron donor and acceptor moieties and performed efficient post-functionalization of poly(azidomethyl-EDOT) (**P2**, Scheme 1) under mild heterogeneous conditions with high conversion efficiencies and characterized the functionalized electrodes electrochemically.

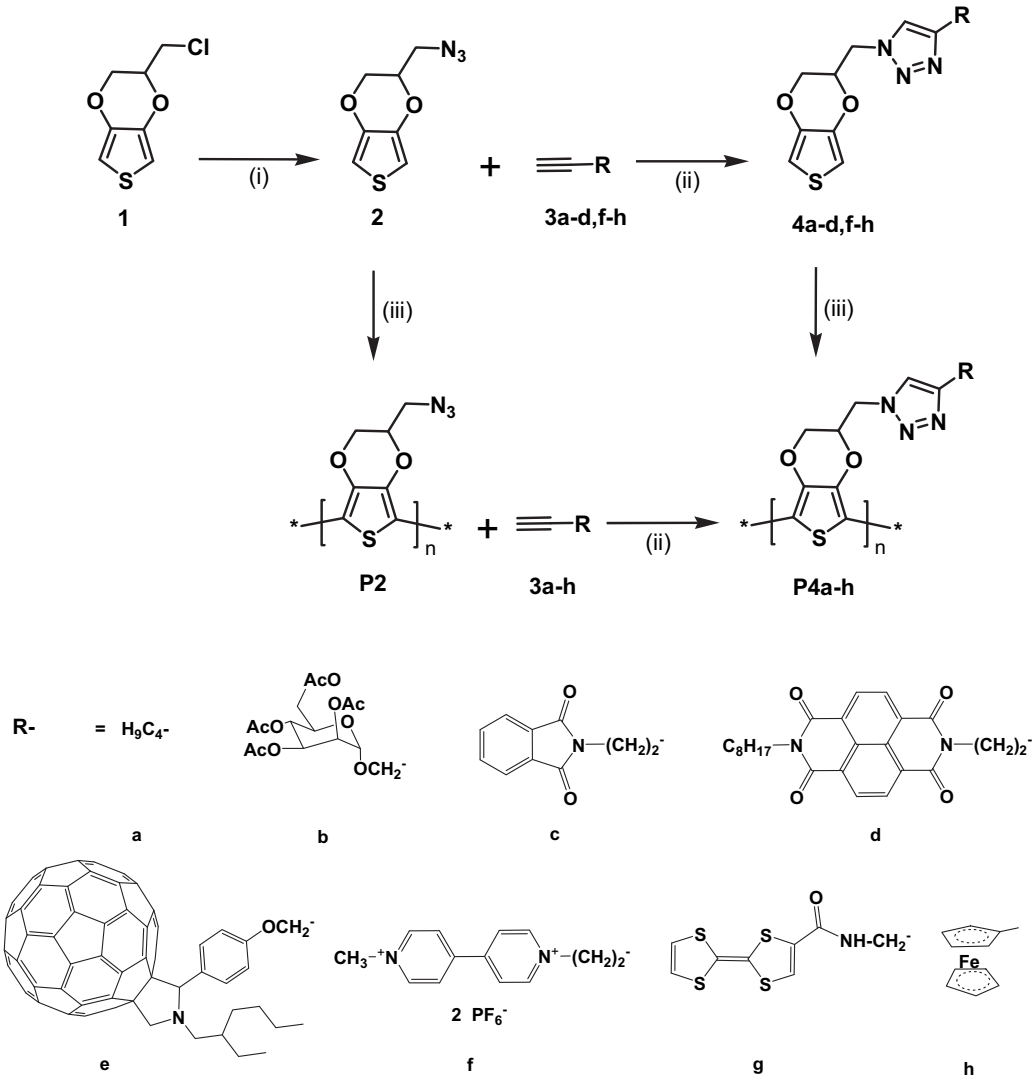
2. Results and discussion

2.1. Synthesis of functionalized EDOTs (4a–d,f,g)

Maintaining the integrity of the PEDOT polyconjugated backbone implies that substitution of an EDOT monomer can only be realized at the ethylenedioxy bridge. Thus, we introduced chloromethyl-EDOT (**1**), which turned out to be a universal building block for a series of further substitution reactions to yield a number of functionalized EDOTs.[15] 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 **4** via click-reaction with a series of terminal alkynes **3**. In order to demonstrate the broad scope of the strategy alkynes bearing neutral moieties (**3a**,**b**), redox active electron acceptors (**3c**–**f**), and electron donors (**3g**,**h**) were chosen and furnished the click-products **4a**–**d**,**f**–**h** in 37–91% yield. In Scheme 1 an overview of our strategy toward post-functionalization of PEDOT via click reactions is presented.

In Scheme 2 the preparation of the new alkynes **3** is summarized, in which the crucial step, starting from literature known or commercially available compounds, is represented. We decided for a rather simple design of **3** with few synthetic steps needed to introduce the alkyne unit at the functional group. Thus, a series of acetylene derivatives with rather short linkers up to two methylene units between the terminal group and the triple bond have been selected.

We subsequently investigated the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of the EDOT monomer **2** and alkynes **3a**–**d**,**f**–**h** first under the conditions previously described in literature, i.e., with $CuSO_4$/sodium ascorbate in a protic polar solvent mixture (mainly *tert*-BuOH–water), at room temperature.[24] In analytical scale reactions the conversion was monitored by TLC and after several hours the cycloaddition product was detected in most cases. However, the conversions were not complete even after a reaction time of more than one day. In order to evaluate the click-reaction in solution more quantitatively, we used 1-hexine **3a** and azidomethyl-EDOT **2** in equimolar amounts in *t*-BuOH–water mixture under Cu(II)/ascorbate catalysis and found a conversion of 11% after 24 h at room temperature. Solubility was also an issue for some acetylenes **3** in the aqueous *t*-butanol medium with the result that no reaction was observed for TTF-derivative **3g**. Similar results were observed by Fokin and Sharpless in the model reaction of phenylacetylene and benzylazide in aqueous *t*-butanol and found a yield of 21% for 1-benzyl-4-phenyl-[1,2,3]-triazole formation catalyzed by $CuSO_4$/Na-ascorbate and of 1% in the catalysis with Cu$(CH_3CN)_4PF_6$ each after 24 h.[34] In this regard, the same authors investigated polytriazoles as Cu(I)-stabilizing ligands and experienced a remarkable acceleration in catalysis of the cycloaddition reaction, later improved by polybenzimidazoles.[35a,b] On the other hand, Leigh et al. showed better results by performing the cycloaddition reaction in non-aqueous organic solvents in presence of catalytic amounts of Cu$(CH_3CN)_4PF_6$ (5 mol %).[36] Thus, we have also tested these reaction conditions with our compounds. In order to avoid oxidation of the Cu(I) catalyst in solution, elemental Cu (powder) was added to the reaction mixture in equimolar amounts. In presence of this Cu(I)-salt, soluble in acetonitrile, 1-hexine **3a** and azidomethyl-EDOT **2** formed EDOT-substituted alkyltriazole **4a** in a 66% conversion after 24 h. Apart from unreacted **2** no further byproducts were detected by NMR. With the intention to develop a universal procedure for the cycloaddition reaction other acetylenes **3** were reacted with azidomethyl-EDOT **2** under very similar conditions just changing the solvent according to the solubility of component **3**. After a reaction time of three days at room temperature, triazoles **4** were isolated in mainly good yields up to 90% after



Conditions: i) NaN_3/DMF, 120°C; (ii) Cu/Cu$(CH_3CN)_4PF_6$/CH_3CN or THF or PhCN, r.t.; (iii) CH_3CN or PhCN/Bu_4NPF_6, -ne$^-$/-nH$^+$.

Scheme 1.

purification by column chromatography or recrystallization. The only exception was TTF-derivative **4g**, which was isolated in only 37% yield, due to solubility problems of the acetylene compound **3g**. Thus, a series of functionalized EDOT derivatives **4** were well available for further electrochemical characterization and polymerization.

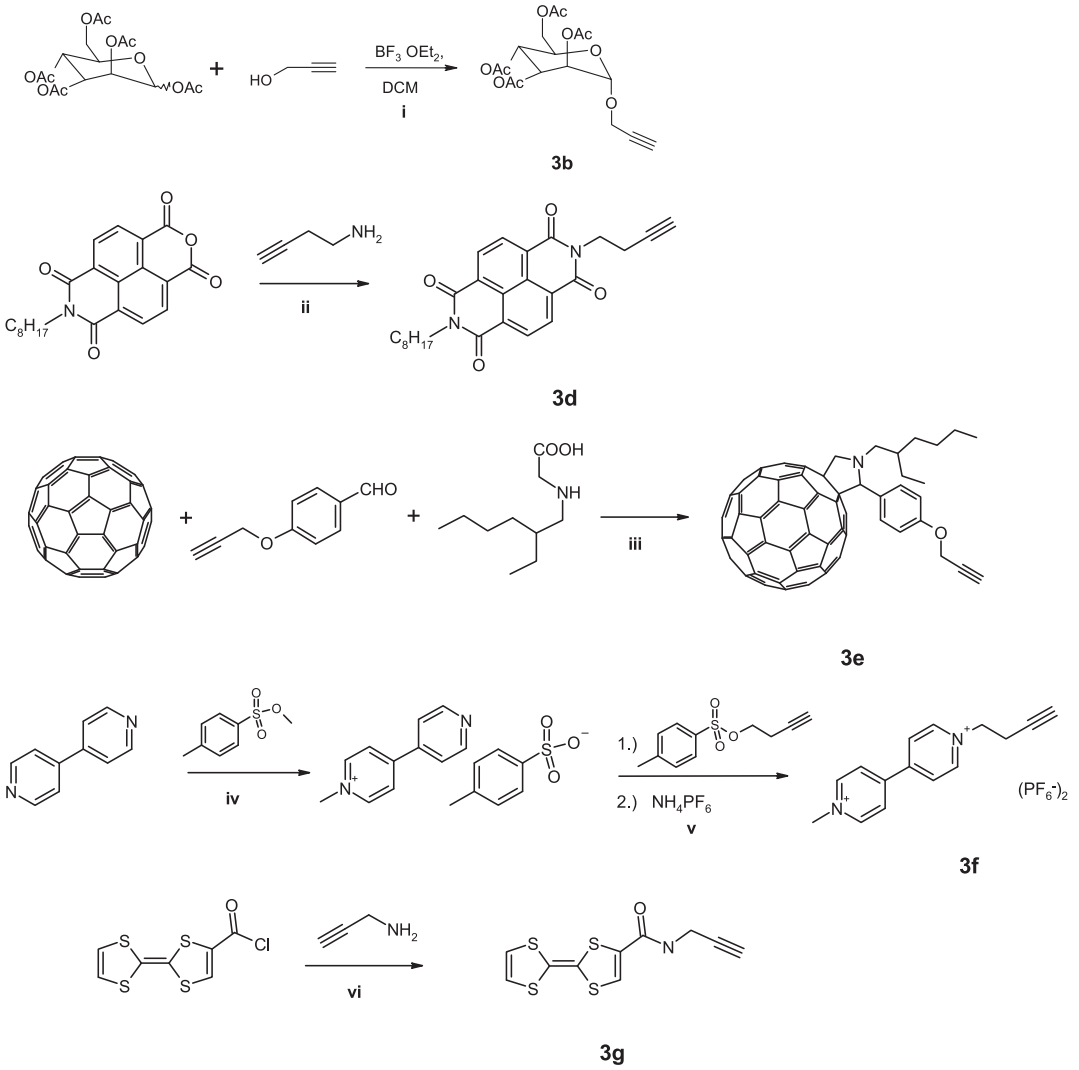
2.2. Electrochemical studies

Starting with the new EDOT derivative N_3-EDOT **2** its electrochemical behavior was investigated by cyclic voltammetry (CV) in dichloromethane (DCM) and tetrabutyl ammonium hexafluorophosphate (TBAHFP) as electrolyte. Reduction and oxidation potentials were measured relative to the internal standard ferrocene–ferricenium (Fc/Fc^+). Thus, single potential scans of electrolytic solutions of N_3-EDOT **2** showed an irreversible anodic peak at ca. 1.07 V corresponding to the formation of the EDOT radical cation (Fig. 1, dashed line). These values are comparable to methyl-substituted EDOT (Me-EDOT), which exhibits an irreversible anodic peak at 1.03 V under identical conditions.[37]

Potentiodynamic electropolymerization of N_3-EDOT **2** yielded the corresponding polymer **P2** as a conducting film strongly adhering to the working electrode. In Fig. 1 the formation and growth of a conducting polymer is depicted, characterized by the appearance of a broad novel redox wave at lower potentials than this of the monomer oxidation, which gradually increases in subsequent potential cycles (solid lines). The thickness of the electroactive polymer film is steadily increased and can be controlled by the number of cycles.

The novel azidomethyl-PEDOT film **P2** was electrochemically characterized in an electrolyte free of monomer (acetonitrile/TBAHPF (0.1 M) (Fig. 2, solid line)). In the CV, a broad redox wave corresponding to the *p*-doping/dedoping of the PEDOT backbone can be observed. The charging of the conjugated backbone, which is concomitant with the transition from the semiconducting to the conducting state, starts at around $E_{lim}=-0.93$ V, which is similar to that recorded for an unsubstituted PEDOT polymerized from EDOT under the same conditions (Fig. 2, dotted line). These results reveal, that the electrochemical behavior of azido-substituted EDOT and PEDOT is practically not much influenced by the substituent.

In order to investigate the stability of azidomethyl-substituted polymer film **P2** under recurrent redox cycling, the second and 100th cycles are compared in Fig. 3. Although a loss of charging capacity of 18% is estimated from these measurements the onset potential of the polymer film stays nearly constant or even shifts to slightly more negative values.



Conditions: i) 16h, reflux (79%),; ii) o-DCB, reflux, 2h (83%); iii) o-DCB, reflux, 8h (34%); iv) MeCN, r.t. - 50°C, 22h (83%); v) 1.) MeCN, 80 °C, 84h (73%), 2.) H_2O, r.t. (quant.); vi) DCM, Et_3N, r.t., 18h (57%). Yields given in paranthesis.

Scheme 2.

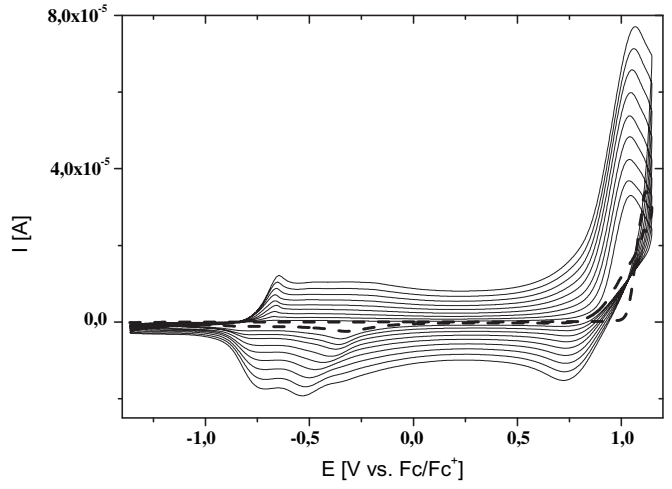


Fig. 1. Electrochemical oxidation of N_3-EDOT **2** in dichloromethane/TBAHFP (0.1 M). First scan (dashed), successive scans second to 10th (solid).

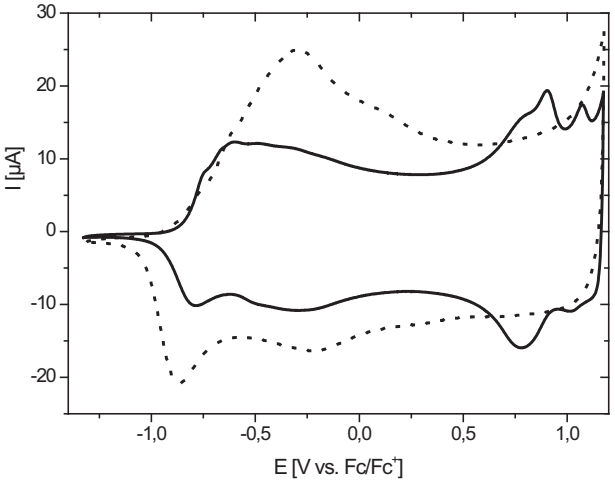


Fig. 2. Characterization of corresponding P(N_3-EDOT) **P2** in acetonitrile/TBAHPF (0.1 M) (solid line). For comparison the CV of PEDOT polymerized from EDOT under the same conditions is shown (dotted line).

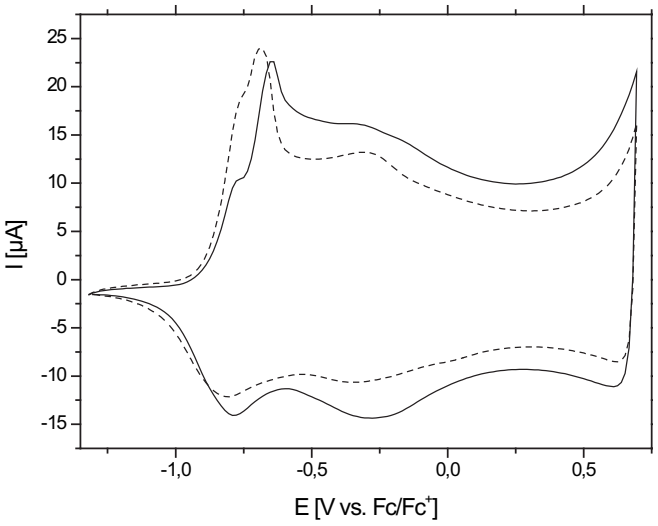


Fig. 3. Electrochemical characterization of **P2** in acetonitrile/TBAHFP (0.1 M), 100 mVs^{-1}, second (solid) and 100th sweep (dashed).

Although the polymerization behavior of functionalized EDOTs can be versatile, almost nothing is known about the electrochemical behavior of 1,4-disubstituted 1*H*-[1,2,3]-triazoles. The oxidation potential of redox active groups attached to this heterocycle experienced a shift to more positive values due to its electron

On the other hand, in presence of redox active groups the polymerization tendency of EDOT is also reported to be problematic and the preparation of the respective polymers is achieved in a post-functionalization reaction of the substituted EDOT after its polymerization.[18] Nevertheless, examples of acceptor-substituted EDOTs are known, which readily polymerize with formation of good electroactive polymer films.[15a,b] From these different observations it is difficult to make reliable predictions with respect to polymerization of redox-functionalized EDOTs.

The electrochemical behavior of triazole-substituted EDOT derivatives (**4a**–**h**) was investigated under conditions similar to that used for N_3-EDOT **2**, just exchanging the solvent by acetonitrile (Fig. 4). Acetonitrile was chosen as the solvent because it can be used to investigate both EDOT and PEDOT derivatives thus allowing a more systematic comparison between the electrochemical behavior of the pendant groups in the monomer and the polymer. In the positive potential regime, the CVs of **4b**–**d**, **f**–**h** showed the typical irreversible anodic peak at potentials higher than 1 V corresponding to the formation of EDOT radical cations. Additionally, the characteristic reversible oxidation waves corresponding to TTF and ferrocene moieties were also observed for **4g** and **4h**, respectively. For electron acceptor-substituted derivatives, a potential scan toward negative potentials showed the characteristic reduction waves corresponding to phthalimide (**4c**), naphtalenebisimide (**4d**), and viologen (**4f**). Attempts to electropolymerize triazole derivatives **4** typically did not result in polymer deposition. The only triazole derivative that could be electropolymerized was hexylsubstituted triazole **4a**.

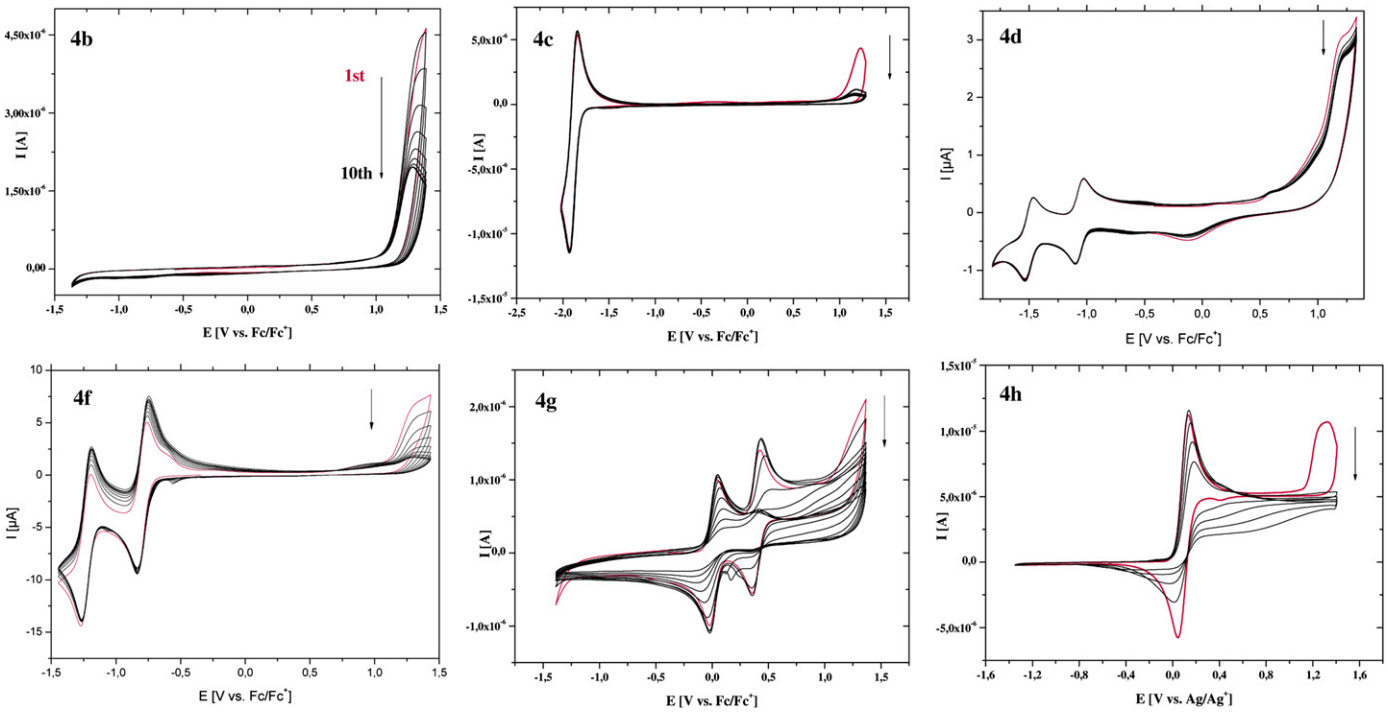


Fig. 4. Electrochemical behavior of triazoles **4** (5 mmol/L) in acetonitrile/TBAHFP (0.1 M).

deficient nature. To give a more quantitative impression, this observation has been exploited to determine the Hammett σ_p value for the 4,5-di(methoxycarbonyl)-1*H*-[1,2,3]-triazol-1-ylmethyl moiety linked to ferrocene.[38] Plotting the oxidation potentials of ferrocene derivatives as function of the substituent parameter σ_p results in a linear correlation for which a value of σ_p=0.56 is determined, lying in between the isocyano-(0.58) and CF_3-group (0.54) but is significant lower than the cyano-substituent (0.66).

Differences in electrochemical behavior and polymerization tendency of triazole **4a** can be observed depending on monomer concentration, which were disclosed by the I–E-curves in Fig. 5 for concentrations of 5 and 50 mmol/L. In contrast to pristine or some functionalized EDOTs, demonstrating their high reactivity in a trace crossing[39] at least in the first scan, the reactivity of the EDOT moiety in **4a** at an oxidation potential of E_p=1.26 V is remarkably diminished. Compared to **2** (E_p=1.12 V) the peak potential is slightly higher, which

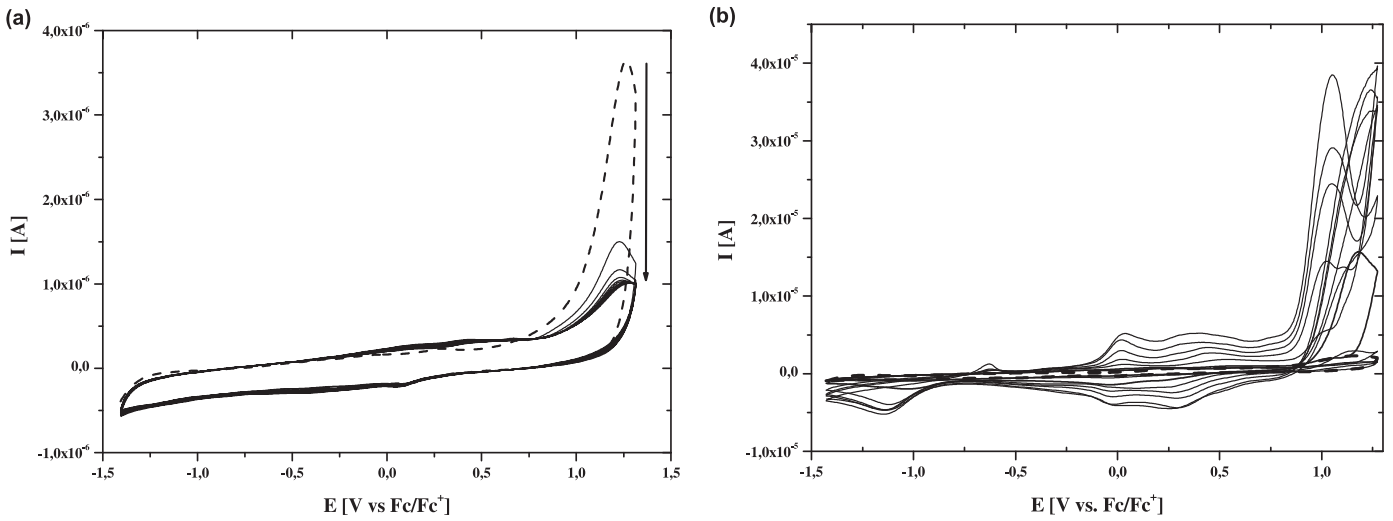


Fig. 5. Electrochemical oxidation of **4a** in acetonitrile/TBAHFP (0.1 M) at two different concentrations; first scan (dashed), successive scans second to 10th (solid). (a) c=5 mmol/L; (b) c=50 mmol/L.

might be attributed to the acceptor ability of the triazole unit. At the lower concentration the peak current drops in successive cycles (Fig. 5 (a)). At higher concentrations and after a delay of about five cycles the peak current of the oxidation step starts to increase with formation of current loops in the last four cycles. Additionally broad redox waves evolve at potentials slightly below 0 V versus Fc/Fc^+ indicating the growth of a redox active polymer film.

The electrochemical response of a freshly prepared film **P4a** after 30 sweeps of potentiodynamic polymerization is depicted in Fig. 6. The onset potential of this polymer is determined at −0.42 V. During a series of successive measurements with different scan speed (25, 50, 100, 150, and 200 mVs^{-1}) and increasing reverse potentials (0.68, 098, and 1.18 V) the polymer significantly looses its initial electroactivity during multiple charging and discharging. Compared to PEDOT or **P2** (Fig. 2) the polymer **P4a** approximates a current plateau of highest redox activity at a remarkably higher potential of around 0.3 V. We assume that the film consists mainly of shorter oligomeric chains, which do not show a tendency of chain elongation in the film during recurrent charging.

These results clearly show that triazole units exert an influence on the electrochemical behavior of attached EDOT moieties remarkably diminishing or even inhibiting their propensity to electropolymerization. The electroactivity of a polymer film, if it is formed, is of minor stability.

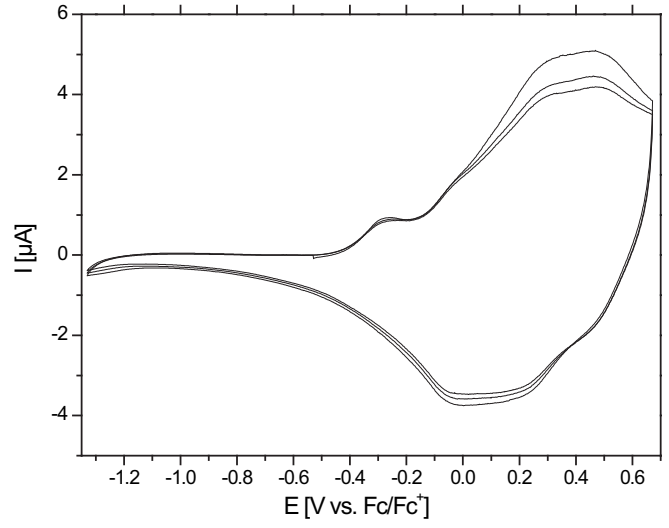


Fig. 6. Polymer characterization of **P4a** (30 cycles) in acetonitrile/TBAHFP (0.1 M), 100 mVs^{-1}.

2.3. Post-functionalization of polymer film P2 via click-reaction with acetylenes 3 and their electrochemical characterization

Taking these observations into account we investigated the possibility to modify azido-substituted EDOT-polymer **P2** in a polymer-analogous heterogeneous click-reaction according to the conversion of monomer **2** in solution. Therefore, electrodes coated with polymer **P2** were treated with terminal acetylenes **3** by dipping the electrode in solutions of **3** in an appropriate organic solvent in presence of catalytic amounts of Cu(I) salt and Cu(0) powder. In the case of hexyne **3a** post-modification of **P2** was alternatively catalyzed by Cu(II) salt plus sodium ascorbate in aqueous *t*-butanol. After three days at room temperature with occasional gentle swirling, the electrodes were electrochemically characterized after copious rinsing to remove reagents and the catalyst from the polymer film. The electrochemical characterization was performed in acetonitrile/TBAHFP (0.1 M).

Changes in the electrochemical behavior of the polymer films are demonstrated in Fig. 7, comparing the initial (**P2**) with the modified one (**P4a**), prepared in the system acetonitrile/Cu$(CH_3CN)_4PF_6$. As no further electroactive moiety is introduced via the reaction with 1-hexyne, a shift in the onset potential of ΔE_{onset}=+120 mV for the product **P4a** (−775 mV) already clearly indicates, that click-reaction also works under heterogeneous conditions at the solid–liquid interface of the polymer film.

This first hint is further supported in the so-called polymer electrochemical stability tests by multiple electrochemical scanning. In Fig. 8 cyclic voltammograms of polymer films modified by 1-hexyne **3a** are depicted, one reaction catalyzed by the system Cu (II)/sodium ascorbate in aqueous alcohol (Fig. 8a) and the other by Cu$(CH_3CN)_4PF_6$ in acetonitrile (Fig. 8b) but under otherwise equal conditions. In both figures the second and 100th cycle is plotted.

From these plots the polymer stability can be determined by integration of the area encircled by the I–V-curve. For the Cu(II)-catalyzed polymer **P4a**(**Cu**(**II**)) a retain of charging/discharging of 93% after 100 cycles is observed. In the case of the modified polymer film catalyzed by Cu(I) **P4a**(**Cu**(**I**)) a similar value of 91% is estimated. Thus, introduction of alkyltriazole units doesn't result in a remarkable loss of PEDOT electroactivity in both samples. On the other hand, the shift in onset potentials during multiple

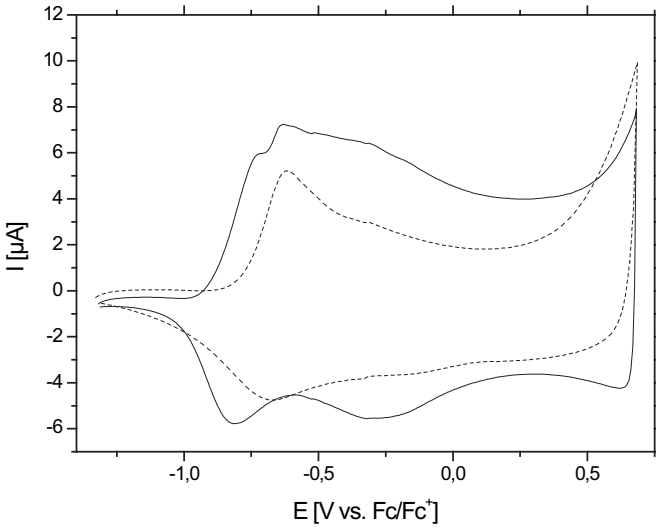


Fig. 7. Typical I–E curves, characterizing polymers **P2** (solid) and **P4a** (dashed); in acetonitrile/TBAHFP, 100 mVs^{-1}.

electrochemical cycling is determined to $\Delta E_{onset} \approx +250$ mV for **P4a** (**Cu**(**II**)), a significant lower value than for **P4a**(**Cu**(**I**)) with +440 mV. In contrast, the starting polymer **P2** doesn't show such a change in onset potential (see Fig. 3). This may be due to the fact that via the post-modification reaction non-polar side chains are introduced in the PEDOT film. In the subsequent multiple cycling experiments a rearrangement of the polymer chains takes place resulting, at least partially, in a phase separation in the polar electrolyte and a change in film morphology. This gives rise to a shift in the onset potential to higher values in agreement with the same trend observed for PEDOT films, electrochemically prepared from EDOT monomer substituted with longer alkyl groups (hexyl) in the 2- and 3-position of the 2,3-dihydro-[1,4]dioxine ring compared to PEDOTs with short chains (methyl) or the unsubstituted one.[32] Taking this explanation into account one can conclude from the results shown in Fig. 8 that the post-modification reaction in pure organic solvent is more effective after the same reaction time than in the aqueous solvent system as was observed for the click-reaction of monomer **2** with hexyne **3a**.

Further and somewhat more quantitative support is given by FT-IR measurements. In Fig. 9 FT-IR spectroscopic characterizations 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**.

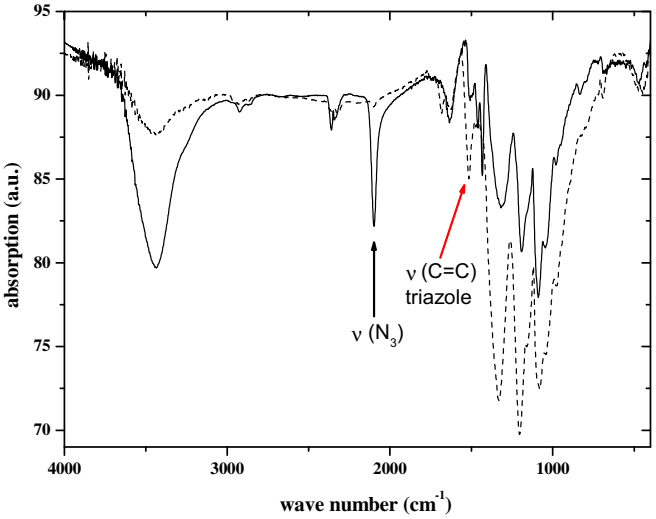


Fig. 9. IR-spectrum of precursor polymer P(N_3-EDOT) **P2** in KBr (dashed line) and 4-butyl-1,2,3-triazole-modified PEDOT **P4a** after derivatization (solid line). The black arrow indicates the strong N_3-absorption at 2098 cm^{-1} in **P2** and the red arrow the C=C-absorption at 1514 cm^{-1} in **P4a**.

A general click-protocol was used to post-functionalize P2-coated electrodes with various alkynes **3b**–**h**. In contrast to other previously post-polymerization strategies used for PEDOT functionalization in which cyanoethylene leaving groups are formed and strong basic medium are required,[18] the use of this click protocol offers the possibility of performing clean addition reactions under mild conditions without the release of unwanted byproducts.

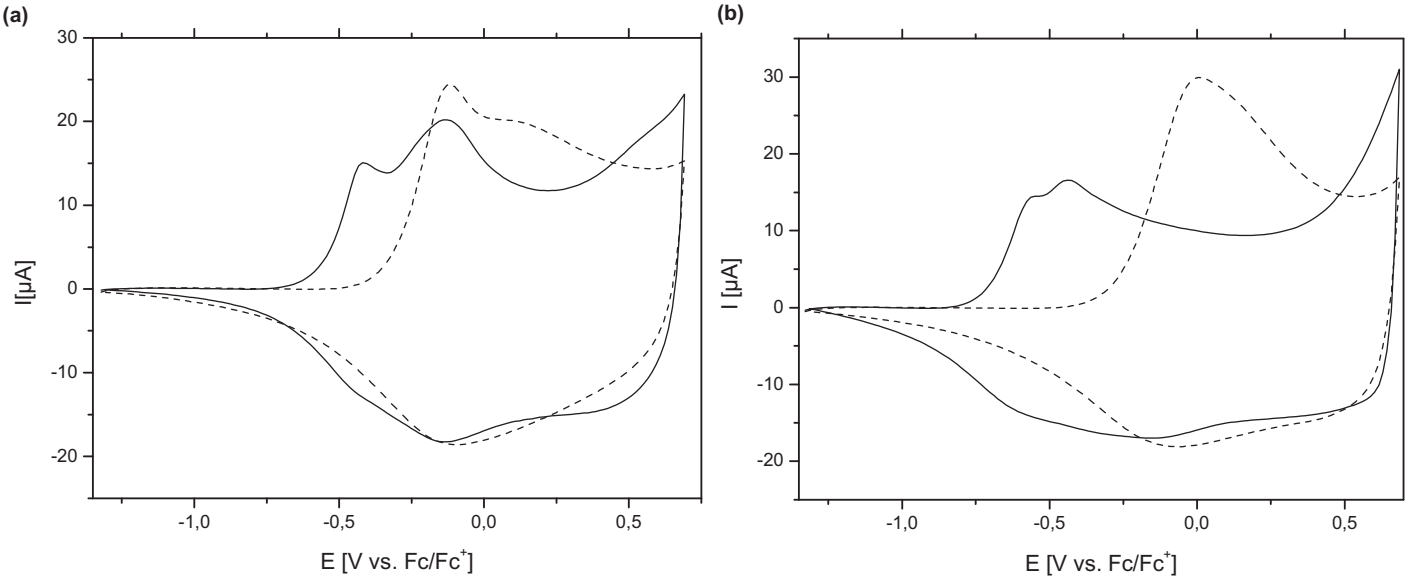


Fig. 8. Cyclic voltammograms of **P2** film after surface modification with **3a** catalyzed by (a) $CuSO_4$/sodium ascorbate and (b) $Cu(acn)_4PF_6$; the second (solid) and 100th cycle (dashed) is plotted.

The resulting PEDOT films **P4b**–**h** were electrochemically characterized and the potential values are summarized in Table 1. In Fig. 10 the CVs of **P4b**–**h** are shown in comparison to corresponding alkynes **3c**–**h** labeled with an electroactive moiety. Except for sugar-modified polymer **P4b**, which revealed an electrochemical behavior quite similar to **P4a**, the CVs of post-functionalized polymers **P4c**–**h** clearly showed the reversible waves and redox transitions of the donor or acceptor groups, which are superimposed to the electrochemical response of the conjugated backbone. Thus, redox systems, which are basically characterized by, e.g., two or multiple successive electron transfer steps retained their behavior after click-functionalization and their redox potentials fairly well coincided (±10 mV) with those of alkynes **3c**–**h** and triazolo-EDOT monomers **4c**,**d**,**f**–**h**. High current stability of the corresponding redox waves in multiple cycling experiments manifested the covalent attachment of the alkynes by the cycloaddition reaction. Compared to parent polymer **P2**, the onset potential of PEDOTs **P4b**–**d** decorated with neutral (sugar) or electron-accepting redox units were shifted positively by 0.3–0.4 V likewise to butyltriazole-PEDOT **P4a** after multiple cycling. On the other hand, the electrochemical characterization of polymers **P4g** and **P4h**, with electron donor groups, show that the contribution of the conducting PEDOT backbone is masked by the oxidation waves of the donor electroactive moieties. This behavior is consistent with that previously reported for other PEDOT derivatives covalently attached to such strong electron-donating moieties as tetrathiafulvalene[20] and ferrocene.[8,40] For polymers **P4e**,**f** E_{onset} could not be determined because the electron transfer of the pendant redox system takes place in the same potential range as the charging of the polymer backbone.

Table 1
Electrochemical data of post-functionalized PEDOTs **P4a**–**h** in comparison to parent P(N_3-EDOT) **P2**. N denotes neutral, Acc acceptor, Do donor, FG functional group and n.d. not determined. Values of corresponding electroactive alkynes **3c**–**h** measured in solution are given in brackets. Potentials versus Fc/Fc^+

PEDOT (type)	E_{onset} [V]	E^1_{FG} [V]	E^2_{FG} [V]
P2 (N)	−0.85	—	—
P4a (N)	−0.78	—	—
P4b (N)	−0.45	—	—
P4c (Acc)	−0.56	−1.94 (−1.87)	—
P4d (Acc)	−0.50	−1.11 (−1.06)	−1.51 (−1.52)
P4e (Acc)	n.d.	−1.08 (−1.04)	−1.48 (−1.45)
P4f (Acc)	n.d.	−0.75 (−0.80)	−1.30 (−1.22)
P4g (Do)	−0.96	0.08 (0.01)	0.50 (0.39)
P4h (Do)	−0.71	0.12 (0.16)	—

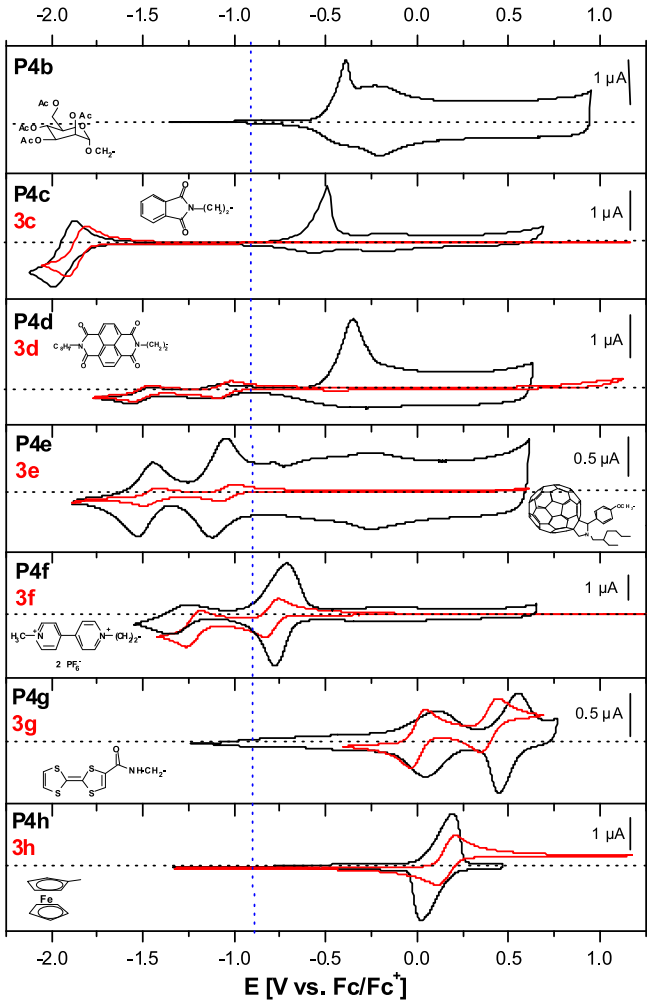


Fig. 10. Cyclic voltammograms of post-functionalized polymers **P4b**–**h** (black) in comparison to corresponding alkynes **3c**–**h** (red) in acetonitrile or benzonitrile/TBAHFP (0.1 M), calibrated versus Fc/Fc^+. The blue vertical dotted line gives the onset potential of P(N_3-EDOT) **P2**.

3. Summary and conclusions

In summary, we have carried out the straightforward synthesis of a versatile azidomethyl-EDOT derivative **2**, which provides easy access to a poly(azidomethyl-EDOT) **P2** by potentiodynamic electropolymerization. We have also carried out the synthesis of a series of terminal alkynes bearing neutral moieties (**3a**, **3b**), redox active electron acceptors (**3c**–**f**), and electron donors (**3g**,**h**) suitable to react with the azide-substituted EDOT and PEDOT by Cu^+-catalyzed 'click'-cycloadditions. The family of alkynes was chosen in order to demonstrate the broad scope of the strategy. Differences in conversion efficiency was observed between catalysis with $Cu(acn)_4PF_6/Cu^0$ in acetonitrile under anhydrous conditions and the often applied $CuSO_4$/sodium ascorbate in aqueous *t*-butanol. In model reactions between hexyne **3a** and N_3-EDOT **2** or P(N_3-EDOT) **P2** we observed better results for the Cu(I)-salt under water free conditions.

N_3-EDOT **2** was converted to the corresponding 1,2,3-triazolo-substituted EDOTs **4** via 'click'-reaction with terminal alkynes **3** in moderate to good yields. However, in the presence of triazole units the propensity to electropolymerization is dramatically diminished or inhibited and the electroactivity of the film, if it is formed, is of minor stability.

On the other hand, we have developed a versatile synthetic protocol for the post-polymerization of poly(azidomethyl-EDOT) **P2** and terminal alkynes under mild heterogeneous conditions. The route is devoid of the limitations generated by the various electronic impacts of the substituents when attached to the monomer before polymerization. The experiments described gave clear proof that efficient post-functionalization of PEDOT films was achieved even with the bulky fullerene moiety. Thus, this strategy may provide a good platform for the functionalization of polymer films with more complex biomolecules, which may pave the way for the development of novel amperometric biosensors.

4. Experimental section

4.1. Materials

2-Chloromethyl-2,3-dihydro thieno[3,4-*b*][1,4]dioxine **1**,[15a,b] 2-propynyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside **3b**,[41] ethynyl-ferrocene **3h**,[42] 7-octyl-2-oxa-7-aza pyrene-1,3,6,8-tetraone,[43] 3-butynylamine,[44] 4-prop-2-ynyloxybenzaldehyde,[45] *N*-(2-ethylhexyl)-glycine,[46] 3-butynyltosylate[47] and tetrathiafulvalene-4-carbonylchloride[48] were synthesized according literature. Hex-1-yne **3a**

and 4,4′-bipyridine were purchased from *Merck*. 2-But-3-ynyl-isoindole-1,3-dione **3c**, 2-propynylamine, 1-octylamine, [60]fullerene and $Cu(CH_3CN)_4PF_6$ were purchased from *Aldrich*.

4.2. Characterization

NMR spectra were recorded on a *Bruker* AMX 400 spectrometer at 25 °C (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) and *Bruker* AC-200 spectrometer at 25 °C (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz). Chemical shift values (δ) are expressed in parts per million using the internal standard tetramethylsilane (^{1}H NMR, δ_H=0.00) or the solvent as reference (^{13}C NMR, δ_C=77.00 for $CDCl_3$, 39.52 for DMSO-d_6 29.84 for acetone-d_6). The following abbreviations reflect the multiplicity of the signals obtained: s=singlet, d=doublet, t=triplet, m=multiplet, combination dd=double of doublets, dt=double of tiplets. Infrared (FT-IR) spectra were recorded on a *Perkin–Elmer* FT-IR Spectrum 2000, absorptions are reported in cm^{-1}. Mass spectra were measured on a *Varian* Saturn 2000. Melting points were determined using a *Büchi* B-545 apparatus. Elemental analyses were performed on an *Elemental Vario* EL (Ulm University). Preparative flash column chromatography was performed using glass columns packed with silica gel 60 (particle size 40–63 μm, *Merck*).

4.3. Synthesis of acetylenes, EDOT-monomers and -polymers

*4.3.1. 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4]dioxine (**2**).* Under an inert atmosphere, 2.42 g (37.2 mmol) sodium azide were added to a magnetically stirred solution of 3.55 g (18.6 mmol) 2-chloromethyl-2,3-dihydro-thieno[3,4-*b*][1,4]dioxine **1** in 180 mL abs DMF. The reaction mixture was heated up to 120 °C for 3 h. After cooling, the solvent was removed by rotary evaporation under vacuum. Then, 200 mL water was added to the residue and the product was extracted three times with 150 mL diethyl ether each. The organic phases were combined, washed with 100 mL water, and dried using $MgSO_4$. Subsequently, the diethyl ether was evaporated yielding 3.56 g (97%) of a nearly colorless oil. ^{1}H NMR ($CDCl_3$): δ=6.36 (AB-system, J_{AB}=3.7 Hz, 2H, Th), 4.30 (m, 1H, CH–O), 4.18 (dd, J_1=11.7 Hz, J_2=2.3 Hz, 1H, CH_2–O), 4.04 (dd, J_1=11.7 Hz, J_2=6.9 Hz, 1H, CH_2–O), 3.56 (dd, J_1=13.1 Hz, J_2=6.0 Hz, 1H, CH_2–N_3), 3.47 (dd, J_1=13.1 Hz, J_2=5.2 Hz, 1H, CH_2–N_3); ^{13}C NMR ($CDCl_3$): δ=141.0, 140.6, 100.21, 100.04, 72.4, 65.7, 50.5; IR (liq.): ν (cm^{-1})=3114, 2926, 2876, 2104, 1674, 1485, 1185, 1023, 763; EI-MS: *m*/*e*=197 (M^+, 100%); elemental analysis: $C_7H_7N_3O_2S$ (M_w 197.2), calcd(%) C 42.63, H 3.58, N 21.31, found C 42.87, H 3.65, N 21.22.

*4.3.2. 2-But-3-ynyl-7-octyl-benzo[lmn][3,8]phenanthroline-1,3,6,8-tetraone (**3d**).* To a stirred solution of 7-Octyl-2-oxa-7-aza-pyrene-1,3,6,8-tetraone (350 mg, 0.92 mmol) in 30 ml of 1,2-dichlorobenzene, 3-butynylamine (253 mg, 3.68 mmol) was added. The solution was refluxed for 2 h and after cooling to room temperature, the solvent was evaporated. The residue was purified by flash chromatography (silica gel, dichloromethane) to yield 328 mg (83%) of **3d** as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ=8.77 (s, 4H, Naphth), 4.43 (t, ^3J=7.1 Hz, 2H, CH_2–N), 4.19 (t, ^3J=7.4 Hz, 2H, CH_2–N), 2.71 (dt, ^3J=7.1 Hz, ^4J=2.7 Hz, 2H, CH_2–C_2), 1.96 (t, ^4J=2.7 Hz, 1H, C_2H), 1.77 to 1.68 (m, 2H, CH_2–), 1.39 to 1.27 (m, 10H, CH_2–), 0.87 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ=162.73 (C=O), 162.70 (C=O), 131.12, 130.91, 126.83, 126.75, 126.70, 126.30, 80.39, 70.18, 41.01, 38.97, 31.78, 29.26, 28.06, 27.06, 22.61, 17.69, 14.06; IR (KBr): ν (cm^{-1})=2924, 2853, 2123, 1703, 1661, 1627, 1468, 1353, 1264, 768; EI-MS: *m*/*e*=430 (M^+, 100%); elemental analysis: $C_{26}H_{26}N_2O_4$ (M_w 430.50), calcd(%) C 72.54, H 6.09, N 6.51, found C 72.21, H 6.15, N 6.57.

*4.3.3. N-(2-Ethylhexyl)-2-(4-prop-2-ynyloxyphenyl)-3,4-fullero-pyrrolidine (**3e**).* A stirred solution of 4-prop-2-ynyloxybenzaldehyde (630 mg, 3.94 mmol), *N*-(2-ethylhexyl)glycine (295 mg, 1.58 mmol), and C_{60} (567 mg, 0.79 mmol) in 100 ml of 1,2-dichlorobenzene was refluxed for 8 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (silica gel, hexane/toluene 8:2) to yield 271 mg (34%) of **3e** as a black solid. ^{1}H NMR ($CDCl_3$): δ=7.73 (d, ^3J=8.7 Hz, 2H, Ph), 7.00 (d, ^3J=8.7 Hz, 2H, Ph), 5.07 (d, ^3J=9.8 Hz, 1H, CH_2–N), 4.99 (s, 1H, CH–N), 4.69 (d, ^4J=2.3 Hz, 2H, CH_2–O), 4.03 (d, ^2J=9.8 Hz, 1H, CH_2–N), 2.98 (m, 1H, CH_2–), 2.51 (m, 1H, CH_2–), 2.43 (m, 1H, CH<), 1.99 (m, 1H, C_2H), 1.25 (m, 8H, CH_2–), 0.95 (m, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ=158.04, 157.17, 154.77, 154.15, 154.14, 147.72, 147.71, 147.26, 146.94, 146.73, 146.72, 146.67, 146.63, 146.56, 146.54, 146.51, 146.35, 146.33, 146.18, 146.17, 146.02, 146.00, 145.97, 145.94, 145.88, 145.73, 145.68, 145.64, 145.60, 145.58, 145.54, 145.13, 145.07, 144.83, 144.81, 143.57, 143.56, 143.52, 143.40, 143.09, 142.99, 142.96, 142.80, 142.78, 142.70, 142.56, 142.54, 142.53, 142.43, 142.41, 142.39, 142.37, 142.22, 142.08, 141.93, 140.57, 140.53, 140.30, 139.91, 137.19, 137.17, 136.93, 136.91, 136.20, 136.18, 136.10, 131.18, 130.85, 115.27, 82.98, 82.95, 78.87, 77.25, 76.00, 69.36, 69.35, 67.69, 67.59, 58.04, 57.95, 56.31, 38.74, 38.32, 33.34, 31.67, 29.92, 25.84, 24.65, 14.59, 12.16; IR (KBr): ν (cm^{-1})=3293, 2924, 2853, 2134, 1609, 1508, 1461, 1217, 1030, 829; MS (FAB) (*m*/*z*): 1006 (M^++1); elemental analysis: $C_{79}H_{27}NO$ (M_w 1006.09), calcd(%) C 94.32, H 2.69, N 1.39, found C 93.98, H 2.40, N 1.28.

*4.3.4. N-(3-Butynyl)-N′-methyl-4,4′-bipyridinium bis(hexafluorophosphate) (**3f**).* Methyl-tosylate (5.39 g, 29 mmol) dissolved in 35 ml acetonitrile, was added to a intensively stirred solution of 4,4′-bipyridine (7.80 g, 50 mmol) in 15 ml acetonitrile at room temperature within 1 h. After 15 h at room temperature and 6 h at 50 °C the solvent was evaporated under reduced pressure and the residue was treated with benzene six times each with 10 ml in an ultra-sonic bath and at slightly elevated temperatures. The solid residue was recrystallized from aqueous acetone (<5% water) affording 1-methyl-4-(4-pyridyl) pyridinium 4-methylbenzene-sulfonate in a total yield of 8.31 g (92%). Mp 185–186 °C. ^{1}H NMR (DMSO-d_6): δ=9.12 (d, ^3J=6.8 Hz, 2H, bipy-H2/H6), 8.86 (dd, ^3J=4.6 Hz, ^4J=1.5 Hz, 2H, bipy-H2′/H6′), 8.60 (d, ^3J=6.8 Hz, 2H, bipy-H3/H5), 8.03 (dd, ^3J=4.6 Hz, ^4J=1.6 Hz, 2H, py-H3′/H5′), 7.47 (d, ^3J=8.0 Hz, 2H, Tos-H2/H6), 7.09 (d, ^3J=8.0 Hz, 2H, Tos-H3/H5), 4.38 (s, 3H, CH_3–N^+), 2.26 (s, 3H, CH_3–Ph); elemental analysis: $C_{18}H_{18}N_2O_3S$ (M_w 342.41), calcd(%) C 63.14, H 5.03, N 8.18, S 9.36, found C 62.90, H 5.33, N 7.89, S 9.66.

1-Methyl-4-(4-pyridyl)pyridinium 4-methylbenzene-sulfonate (1.70 g, 5 mmol) and 3-butynyl-tosylate (2.24 g, 10 mmol) dissolved in 5 ml acetonitrile, were refluxed for 84 h. After cooling, the solvent was evaporated under reduced pressure furnishing viscous oil. The residue was first treated with diethyl ether and acetone three times each with 20 ml, then dissolved in 10 ml acetonitrile and precipitated in 150 ml acetone under vigorous stirring. A colorless oil was formed, which, after removal of the solvent in vacuum, solidifies as colorless foam in 2.08 g (73%) yield. ^{1}H NMR (DMSO-d_6): δ=9.38 (d, ^3J=6.7 Hz, 2H, bipy-H2/H6), 9.25 (d, ^3J=6.7 Hz, 2H, bipy-H2′/H6′), 8.81 (d, ^3J=6.8 Hz, 2H, bipy-H3/H5), 8.74 (d, ^3J=6.5 Hz, 2H, bipy-H3′/H5′), 7.47 (d, ^3J=8.0 Hz, 2H, Tos-H2/H6), 7.09 (d, ^3J=7.9 Hz, 2H, Tos-H3/H5), 4.86 (t, ^3J=6.6 Hz, 2H, CH_2–N^+), 4.44 (s, 3H, CH_3–N^+), 3.10 (t, ^3J=2.5 Hz, 1H, C_2H), 3.03 (dt, ^3J=6.5 Hz, ^4J=2.4 Hz, 2H, CH_2–C_2), 2.27 (s, 6H, CH_3–Ph); ^{13}C NMR (DMSO-d_6): δ=148.90, 147.81, 146.50, 145.93, 145.50, 137.57, 127.97, 126.21, 126.01, 125.36, 78.96, 75.19, 58.64, 47.90, 20.65, 20.25.

To a solution of the intermediate product (2.08 g, 3.7 mmol) in 5 ml water a concentrated aqueous solution of ammonium hexafluorophosphate (1.80 g, 11 mmol) was added at room temperature. A colorless precipitate formed immediately. Heating up the mixture to 90–100 °C dissolves the product, which crystallizes on cooling to room temperature in colorless needles, delivering **3f** in a yield of 1.85 g (98%). ^{1}H NMR (acetone-d_6): δ=9.44 (d, *J*=6.9 Hz, 2H, bipy-

H2/H6), 9.32 (d, J=6.6 Hz, 2H, bipy-H2′/H6′), 8.86 (d, J=6.6 Hz, 2H, bipy-H3/H5), 8.74 (d, J=6.3 Hz, 2H, bipy-H3′/H5′), 5.12 (t, J=6.5 Hz, 2H, CH_2-N^+), 4.72 (s, 3H, CH_3-N^+), 3.18 (dt, J_1=6.4 Hz, J_2=2.5 Hz, 2H, CH_2-C_2), 2.68 (t, J=2.5 Hz, 1H, C_2H); ^{13}C NMR (acetone-d_6): δ=151.49, 150.48, 147.78, 147.11, 127.96, 127.74, 78.97, 74.94, 61.00, 49.38, 21.54; elemental analysis: $C_{15}H_{16}F_{12}N_2P_2$ (M_w 514.23), calcd (%) C 35.04, H 3.14, N 5.45, found C 34.83, H 3.20, N 5.34.

*4.3.5. Tetrathiafulvalene-4-carboxylic acid prop-2-ynylamide (**3g**).* To a stirred solution of tetrathiafulvalene-4-carbonylchloride (200 mg, 0.75 mmol) and propargylamine (184 mg, 3.35 mmol) in 15 ml of anhydrous dichloromethane, was added triethylamine (1 ml, excess) and stirring was continued at room temperature for 18 h. The solvent was evaporated, and the residue was purified by flash chromatography (silica gel, dichloromethane) to yield 122 mg (57%) of **3g** as an orange solid. ^1H NMR ($CDCl_3$): δ=7.15 (s, 1H, Vinyl-H), 6.34 (s, 2H, Vinyl-H), 5.72 (br s, 1H, NH), 4.13 (dd, J_1=5.2 Hz, J_2=2.5 Hz, 2H, CH_2-N), 2.28 (t, J=2.5 Hz, 1H, C_2H); IR (KBr): ν (cm^{-1})=3293, 3035, 2924, 2133, 1703, 1615, 1545, 1410, 1255, 948; EI-MS: m/e=285 (M^+, 100%); elemental analysis: $C_{10}H_7NOS_4$ (M_w 285.41), calcd(%) C 42.08, H 2.47, N 4.91, found C 41.91, H 2.39, N 4.80.

4.4. General procedure for the synthesis of 1,2,3-triazolo-functionalized EDOTs (4a–d,f–h)

Azidomethyl-EDOT **2**, alkyne **3**, and tetrakis(acetonitrile)copper (I) hexafluorophosphate in a molar ratio of 1:1:0.05 (unless otherwise stated) were dissolved in the given organic solvent. One equivalent of copper powder was added and the mixture was stirred for three days at room temperature. Subsequently, the mixture was diluted with dichloromethane, chloroform or THF. After separation of elemental copper by filtration, the solvent was evaporated and the residue was purified by recrystallization or column chromatography on silica gel.

*4.4.1. 4-Butyl-1-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazole (**4a**).* According general procedure, starting from 592 mg (3 mmol) **2**, 247 mg (3 mmol) hex-1-yne **3a**, 56 mg (0.15 mmol) $Cu[CH_3CN]_4(PF_6)$, and 191 mg (3 mmol) Cu-powder in 12 ml acetonitrile. **4a** was isolated as colorless solid in 704 mg (84%) yield by column chromatography (elution with dichloromethane/ethyl acetate, stepwise increasing ethyl acetate up to 25 volume percent). Mp 83 °C. ^1H NMR ($CDCl_3$): δ=7.40 (s, 1H, triazole), 6.39 (AB-system, J_{AB}=3.7 Hz, 2H, Th), 4.63 (m, 2H, CH_2-N), 4.56 (m, 1H, CH–O), 4.27 (dd, J_1=11.9 Hz, J_2=2.1 Hz, 1H, CH_2-O), 3.85 (dd, J_1=11.9 Hz, J_2=6.2 Hz, 1H, CH_2-O), 2.73 (t, J=7.7 Hz, 2H, α-CH_2), 1.67 (m, 2H, β-CH_2), 1.39 (m, 2H, γ-CH_2), 0.94 (t, J=7.3 Hz, 2H, CH_3); ^{13}C NMR ($CDCl_3$): δ=148.8, 140.8, 140.2, 122.0, 100.46, 100.45, 71.9, 65.4, 49.7, 31.5, 25.3, 22.3, 13.8; IR (KBr): ν (cm^{-1})=3111, 3065, 2958, 2927, 2874, 1492, 1202, 1055, 1024, 777; EI-MS: m/e=279 (M^+, 100%); elemental analysis: $C_{13}H_{17}N_3O_2S$ (M_w 279.3), calcd(%) C 55.89, H 6.13, N 15.04, found C 55.70, H 5.99, N 14.91.

*4.4.2. 4-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyloxymethyl)-1-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazole (**4b**).* According general procedure, starting from 115.9 mg (0.3 mmol) **3b**, 59.2 mg (0.3 mmol) **2**, 19.1 mg (0.3 mmol) Cu, and 5.6 mg (15 μmol) $Cu[CH_3CN]_4(PF_6)$, in 1.2 ml acetonitrile. **4b** was isolated as colorless, viscous oil in 143 mg (81%) yield by column chromatography (elution with dichloromethane/ethyl acetate=1:1 v/v). ^1H NMR ($CDCl_3$): δ=7.66 (s, 1H, triazole), 6.37 (d, J_{AB}=3.7 Hz, 1H, Th), 6.31 (d, J_{AB}=3.6 Hz, 1H, Th), 5.26 (dd, J_1=10.1 Hz, J_2=3.0 Hz, 1H, man-H3), 5.23 (t, J=10.3 Hz, 1H, man-H4), 5.175 (dd, J_1=2.8 Hz, J_2=1.4 Hz, 1H, man-H2), 4.90 (d, J=1.7 Hz, 1H, man-H1), 4.80/4.79 (d, J=12.4 Hz, 1H, CH_2-triazole), 4.66/4.64 (d, J=12.5 Hz, 1H, CH_2-triazole), 4.64 (dd, J_1=10 Hz, J_2=4 Hz, 1H, CH_2-N), 4.62/4.61 (dd, J_1=10 Hz, J_2=6 Hz, 1H, CH_2-N), 4.54 (m, 1H, CH–O), 4.23 (dd, J_1=11.9 Hz, J_2=2.3 Hz, 1H, CH_2-O-Th), 4.22 (d, J=12 Hz, 1H, man-H6), 4.04 (br d, J=12 Hz, 1H, man-H6), 4.00 (m, 1H, man-H5), 3.86/3.84 (dd, J_1=11.9 Hz, J_2=6.2 Hz, 1H, CH_2-O-Th), 2.08, 2.05, 1.97/1.96, 1.91 (4s, 12H, CH_3); ^{13}C NMR ($CDCl_3$): δ=170.70, 170.06, 169.91, 169.73 (C=O), 151.65, 140.87, 140.09, 121.03, 100.84, 100.63, 97.00/96.95, 71.82/71.81, 69.54, 69.05, 68.85, 66.19/66.17, 65.50, 62.46, 61.12/61.06, 50.08/50.06, 20.90, 20.72, 20.81, 20.70 (CH_3); CI-MS: m/e=584 (HM^+, 100%); elemental analysis: $C_{24}H_{29}N_3O_{12}S$ (M_w 583.57), calcd(%) C 49.40, H 5.01, N 7.20, S 5.49, found C 49.28, H 5.07, N 7.07, S 5.66.

*4.4.3. 2-{2-[1-(2,3-Dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl]-ethyl}-isoindole-1,3-dione (**4c**).* According general procedure, starting from 59.2 mg (0.3 mmol) **2**, 59.7 mg (0.3 mmol) **3c**, 5.6 mg (15 μmol) $Cu[CH_3CN]_4(PF_6)$, and 19.1 mg (0.3 mmol) Cu-powder in 1.2 ml acetonitrile. **4c** was isolated as colorless solid in 87 mg (73%) yield by column chromatography (elution with dichloromethane/ethyl acetate=1:1 v/v). Mp 159 °C. ^1H NMR ($CDCl_3$): δ=7.78 (m, 2H, Ph), 7.68 (m, 2H, Ph), 7.53 (s, 1H, triazole), 6.37 (d, J_{AB}=3.7 Hz, 1H, Th), 6.34 (d, J_{AB}=3.7 Hz, 1H, Th), 4.62 (d, J=5.4 Hz, 2H, CH_2-triazoleN), 4.51 (m, 1H, CH–O), 4.23 (dd, J_1=11.9 Hz, J_2=2.2 Hz, 1H, CH_2-O), 4.02 (t, J=7.0 Hz, 2H, CH_2-imideN), 3.80 (dd, J_1=11.9 Hz, J_2=6.5 Hz, 1H, CH_2-O), 3.16 (t, J=7.0 Hz, 2H, CH_2-triazole); ^{13}C NMR ($CDCl_3$): δ=168.1, 144.7, 140.9, 140.3, 133.95, 132.0, 123.2, 122.8, 100.6, 100.4, 71.9, 65.4, 49.9, 37.5, 24.85; IR: ν (cm^{-1})=3148, 3116, 2938, 2867, 1770, 1708, 1484, 1188, 757, 723; CI-MS: m/e=397 (HM^+, 100%); elemental analysis: $C_{19}H_{16}N_4O_4S$ (M_w 396.4), calcd(%) C 57.57, H 4.07, N 14.13, found C 57.46, H 4.11, N 13.95.

*4.4.4. 2-[2-(2,3-Dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl-ethyl]-7-octyl-benzo[lmn][3,8]phenanthroline-1,3,6,8-tetraone (**4d**).* According general procedure, starting from 72.4 mg (170 μmol) **3d**, 63 mg (320 μmol) **2**, 4 mg (11 μmol) Cu $[CH_3CN]_4(PF_6)$, and 12.7 mg (0.2 mmol) Cu-powder in 0.5 ml THF. **4d** was isolated as colorless solid in 96 mg (90%) yield, recrystallized from benzene–ethanol (1:1). ^1H NMR (CD_2Cl_2): δ=8.65 (AB-system, J_{AB}=7.5 Hz, 4H, naphth), 7.71 (br s, 1H, triazole), 6.33 (AB-system, J_{AB}=3.6 Hz, 2H, Th), 4.64 (d, J=4.7 Hz, 2H, CH_2-triazoleN), 4.49 (m, 3H, CH_2-imideN, CH–O), 4.23 (dd, J_1=11.8 Hz, J_2=1.6 Hz, 1H, CH_2-O), 4.15 (t, J=7.6 Hz, 2H, CH_2-imide), 3.75 (dd, J_1=11.8 Hz, J_2=6.9 Hz, 1H, CH_2-O), 3.20 (br s, 2H, CH_2-triazole), 1.72 (ddt, J=7.5 Hz, 2H, CH_2-), 1.47 to 1.22 (m, 10H, CH_2-), 0.87 (t, J=6.9 Hz, 3H, CH_3); ^{13}C NMR (CD_2Cl_2): δ=163.21, 163.13 (C=O), 149.46, 141.45, 140.91, 131.16, 131.05, 127.22, 127.06, 126.74, 100.75, 100.57, 72.40, 65.97, 50.39, 41.24, 40.41, 32.23, 29.71, 29.62, 28.42, 27.52, 24.52, 23.06, 14.26; IR: ν (cm^{-1})=3114, 2955, 2925, 2854, 1707, 1663, 1485, 1339, 1243, 1187, 1018, 769; CI-MS: m/e=628 (HM^+, 100%); HRMS (ESI) calcd for $C_{33}H_{34}N_5O_6S$: 628.2224 (HM^+), found 628.2221.

*4.4.5. N-{2-[1-(2,3-Dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl]-ethyl}-N′-methyl-4,4′-bipyridinium bis(hexafluorophosphate) (**4f**).* According general procedure, starting from 59.2 mg (0.3 mmol) **2**, 154.3 mg (0.3 mmol) **3f**, 5.6 mg (15 μmol) Cu $[CH_3CN]_4(PF_6)$, and 19.1 mg (0.3 mmol) Cu-powder in 1.2 ml acetonitrile. The crude product was dissolved in acetone (100 mg/ml) and precipitated by addition of *n*-hexane. During magnetic stirring the viscous oil crystallized yielding **4f** as nearly colorless solid in 179 mg (83%). Mp 180–190 °C (decomposition). ^1H NMR (acetone-*d*6): δ=9.37 (d, J=6.6 Hz, 2H, bipy-H2/H6), 9.35 (d, J=6.6 Hz, 2H, bipy-H2′/H6′), 8.77 (d, J=6.3 Hz, 4H, bipy-H3/H5/H3′/H5′), 7.99 (s, 1H, triazole), 6.47 (d, J_{AB}=3.6 Hz, 1H, Th), 6.43 (d, J_{AB}=3.6 Hz, 1H, Th), 5.32 (t, J=6.5 Hz, 2H, CH_2-N^+), 4.82 (dd, J_1=14.9 Hz, J_2=4.2 Hz, 1H, CH_2-triazoleN), 4.74 (dd, J_1=14.9 Hz, J_2=7.0 Hz, 1H, CH_2-triazoleN), 4.74 (s, 3H, CH_3-N^+), 4.61 (m, 1H, CH–O), 4.34 (dd, J_1=11.9 Hz, J_2=2.2 Hz, 1H, CH_2-O), 3.91 (dd, J_1=11.9 Hz, J_2=7.0 Hz, 1H, CH_2-O),

3.70 (t, J=6.5 Hz, 2H, CH_2−triazoleC); ^{13}C NMR (acetone-d_6): δ=151.1, 150.4, 148.8, 147.76, 147.0, 142.1, 141.5, 127.8, 127.7, 127.6, 101.1, 100.9, 72.9, 66.3, 62.0, 50.8, 49.4, 27.9; HRMS (ESI) calcd for $C_{22}H_{23}F_6N_5O_2PS^+$: 566.12143 (M−$PF_6^-$), found 566.11998, and for $C_{22}H_{23}N_5O_2S^{2+}$: 421.15725 (M−2PF_6^-), found 421.15642.

*4.4.6. Tetrathiafulvalene-4-carboxylic acid 1-(2,3-dihydro-thieno [3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethylamide (**4g**).* According general procedure, starting from 39.4 mg (0.2 mmol) **2**, 28.5 mg (0.1 mmol) **3g**, 1.9 mg (5 μmol) Cu[CH_3CN]$_4$(PF_6), and 6.4 mg (0.1 mmol) Cu-powder in 2.5 ml THF. **4g** was isolated as orange colored crystals in 18 mg (37%) yield after column chromatography by elution with ethyl acetate. Mp 198 °C. ^{1}H NMR (THF-d_8): δ=8.00 (br t, J=5.4 Hz, 1H, CONH), 7.80 (s, 1H, triazole), 7.13 (s, 1H, Vinyl-H), 6.49 (d, J=6.4 Hz, 1H, Vinyl-H), 6.46 (d, J=6.4 Hz, 1H, Vinyl-H), 6.40 (d, J_{AB}=3.6 Hz, 1H, Th), 6.38 (d, J_{AB}=3.6 Hz, 1H, Th), 4.64 (m, 2H, CH_2−triazoleN), 4.55 (m, 1H, CH−O), 4.45 (d, J=5.7 Hz, 2H, CH_2−amideN), 4.26 (dd, J_1=11.8 Hz, J_2=2.2 Hz, 1H, CH_2−O), 3.88 (dd, J_1=11.8 Hz, J_2=6.8 Hz, 1H, CH_2−O); ^{13}C NMR (THF-d_8): δ=159.8, 145.8, 142.4, 141.8, 135.0, 124.7, 120.3, 119.8, 113.0, 108.2, 100.8, 100.5, 73.2, 66.6, 50.3, 36.0; HRMS (EI) calcd for $C_{17}H_{14}N_4O_3S_5$: 481.96695 (M^+), found 481.96609.

*4.4.7. 4-Ferrocenyl-1-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazole (**4h**).* According general procedure, starting from 59.2 mg (0.3 mmol) **2**, 63 mg (0.3 mmol) **3h**, 5.6 mg (15 μmol) Cu[CH_3CN]$_4$(PF_6), and 19.1 mg (0.3 mmol) Cu-powder in 2.5 ml acetonitrile. **4h** was isolated as a pale orange solid in 78 mg (64%) yield, recrystallized from chloroform/*n*-hexane. Mp 172 °C. ^{1}H NMR ($CDCl_3$): δ=7.57 (s, 1H, triazole), 6.40 (AB-system, J_{AB}=3.7 Hz, 2H, Th), 4.72 (m, 2H, Fc), 4.65 (m, 2H, CH_2−triazoleN), 4.61 (m, 1H, CH−O), 4.30 (m, 2H, Fc), 4.29 (dd, J_1=11.9 Hz, J_2=2.1 Hz, 1H, CH_2−O), 4.07 (s, 5H, Fc), 3.89 (dd, J_1=11.9 Hz, J_2=6.1 Hz, 1H, CH_2−O); ^{13}C NMR ($CDCl_3$): δ=147.2, 140.9, 140.2, 120.3, 100.60, 100.53, 75.0, 71.9, 69.6, 68.7, 66.7, 65.5, 49.8; EI-MS: m/e=407 (M^+, 52%), 408 (HM^+, 100%); elemental analysis: $C_{19}H_{17}FeN_3O_2S$ (M_w 407.3), calcd(%) C 56.03, H 4.21, N 10.32, found C 55.90, H 4.22, N 10.29.

4.5. Post-functionalization of azidomethyl-PEDOT P2 films with alkynes 3a–h

Pt electrodes coated with azidomethyl-PEDOT **P2**, obtained by 5 repetitive electrochemical cycles, were dipped into a solution of the alkyne **3** (0.6 mmol) and Cu(CH_3CN)$_4$ PF_6 (5 mol %) in 1.2 mL acetonitrile, THF or benzonitrile (appropriate to dissolve the acetylene **3**) to which copper powder (0.3 mmol) was added. After three days at room temperature with occasional gentle swirling the coated electrodes were steeped and rinsed with acetonitrile, THF or benzonitrile several times, washed with methanol and diethyl ether and dried in vacuum. Finally the polymer film was characterized electrochemically in acetonitrile/0.1 M TBAHFP. **P2** coated ITO electrodes were treated in a similar way. The resulting polymer film was scratched off from the glass to prepare KBr pellets for IR measurement.

4.6. Electrochemistry

Cyclic voltammetry experiments were performed with a computer-controlled *Metrohm* Autolab PGSTAT 30 potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A=0.785 mm^2, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. Alternatively ITO coated glasses were cut into pieces of 1 to 1.5×2 cm^2 and used as working electrodes. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl secondary electrode. A 0.1 M solution of tetrabutyl-ammonium hexafluorophosphate (TBAHFP, Fluka) was used as electrolyte in dichlormethane, distilled over sulfuric acid in an argon atmosphere or deaerated acetonitrile (Lichrosolv, Merck), which were rinsed over highly active, basic alumina prior to use. In electrochemical monomer characterization and polymerizations concentrations of 5×10^{-3} mol L^{-1} of the electroactive species were applied, whereas polymer films were characterized in neat electrolyte solutions free of monomer. All potentials were internally referenced to the ferrocene–ferricenium couple.

4.7. Preparation of poly(azidomethyl-EDOT) films (P2)

Electropolymerization of monomer **2** was carried out by successive potential scanning between −1.0 and +1.5 V (vs reference electrode) in several cycles with the polymer film left in a partially oxidized state applying a final potential of −0.2 V. In the case ITO glasses as electrodes an end potential of −1 V was applied for several seconds, which provides a polymer film in the reduced state. The electrodes were removed, washed with acetonitrile, and dried in vacuum. Finally polymer films of azidomethyl-PEDOT **P2** were characterized electrochemically in acetonitrile/0.1 M TBAHFP or post-functionalized.

4.8. Attempted polymerization of 1,2,3-triazolo-functionalized EDOTs 4a,c,h

Electrolyte solutions of monomers **4a**, **4c**, and **4h** (c=5x10^{-3} M in acetonitrile/0.1 M TBAHFP) in the described electrochemical set-up were subjected to potentiodynamic scanning between −1.0 V and +1.65 V (vs. Ag/AgCl). After 10 cycles ending at a potential of −0.2 V the electrodes were removed without precipitation of a polymer film. In a repeating experiment with **4a** (c=5x10^{-2} M) applying 30 cycles but otherwise same conditions furnished a polymer coated electrode, which was rinsed copiously with acetonitrile, dried in vacuum, and electrochemically characterized.

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