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An easy functionalizable oligo(oxyethylene)- and ester-substituted poly(3,4-propylenedioxythiophene) derivative exhibiting alkali metal ion response

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ABSTRACT

A new poly(3,4-propylenedioxythiophene) (PProDOT) derivative combining ion complexing oligoether units and a reactive ester group in the side chain obtained by oxidative chemical and electrochemical polymerization of the corresponding ProDOT monomer is described. The P(ProDOT-EO-ester) chemically synthesized after dedoping reveals a strong UV blue shift in THF in the presence of Na^+ and K^+, respectively, indicating conformational disordering and a substantially decreased conjugation of the polymer chain induced by ion complexation. Post-polymerization functionalization can be achieved by treatment with hydrazine hydrate leading to partial hydrazinolysis of the ester group. The electrogrowth process of the polymer onto ITO is carried out using Bu_4NClO_4 or $LiClO_4$ as supporting electrolyte resulting in the formation of conductive thin films. Cyclic voltammetry reveals a slight shift of the redox peaks to lower potentials in the presence of Li^+.

1. Introduction

Polythiophenes represent an important class of conducting polymers widely used as advanced materials for the fabrication of organic transistors[1,2], organic light emitting diodes[3-5], organic solar cells[6,7], supercapacitors[8], sensors[9,10] and other types of devices. These materials can be synthesized directly either by chemical[11] or electrochemical oxidative polymerization[12] of a thiophene bearing suitable substituents in 3- and 4-position in order to adjust the polymer properties and to prevent undesired side-coupling during chain propagation. Using thiophenes carrying alkyl groups or polar modified alkyl substituents metal-mediated polymerization techniques have been elaborated leading to polymers of high regioregularity[13-16].

A milestone in polythiophene chemistry has been the commercial launch of PEDOT[17-19], prepared from 3,4-ethylenedioxythiophene (EDOT)[20]. In this monomer two electron-donating oxygen atoms are connected via an ethylene bridge leading to a relatively rigid polymer structure showing reasonable conductivity due to efficient π-conjugation. PEDOT exhibits unique physical and chemical properties such as low oxidation potential, moderate band gap, good stability in the oxidized and reduced state, reversible switching and formation of transparent thin films, which has led to various applications[21]. By polymerizing EDOTs bearing heteroatoms a number of functionalized PEDOT derivatives have been developed[22-27].

For expanding the synthetic flexibility of EDOT a further carbon atom quaternary blocked by alkyl groups has been introduced into the ether bridge[28] giving access to a huge number of derivatives of 3,4-propylenedioxythiophene (ProDOT). The corresponding poly(3,4-propylene-dioxythiophene)s (PProDOTs)[29] bearing an alkyl-substituted ether bridge have been employed successfully for color tuning of electrochromic devices[30-32], and for optimising of capacitive behaviour[33,34], as well as for tailoring of charge-transporting materials in solar cells[35-38], the preparation of electroluminescent materials[39] and electro-optic chromophores[40] and as conducting layers in actuators[41], respectively. Further modification of the alkyl substituents in ProDOT by bromine atoms[42] or a hydroxyl group[43] gives synthetic access to functionalized ProDOTs[44-48] which can be transformed into the related PProDOTs including polymers bearing reactive groups in the side-chain[49-51], useful for designing complex molecular architectures[52,53] and the synthesis of PProDOT hybrid materials[54,55], respectively.

Dioxyethylene units have been introduced as substituents in thiophenes in order to enhance the solubility of the monomer and the corresponding polythiophene in polar organic solvents and aqueous media[56-60] as well as for improvement of the ionic conductivity[61,62] and for adjustment of the oxidation potential and the band gap of the polymer[63], respectively. Oligo(oxyethylene) side chains in polythiophenes are able to coordinate cations of various size in solution[64-66] and in solid state[67] influencing the electrochemical[68,69] and optical properties[70] of the polymer. Thus a number of cation-sensing ether-functionalized polythiophenes have been developed[71].

Ester groups have been incorporated in the substituents of thiophenes[72-75] for protection of the carboxylic acid function during the polymerization and its deprotection in the polythiophene for chemosensing application[76,77] or its transformation into activated esters which are useful for the immobilization of proteins and other biomolecules[78-80].

Since all these polythiophenes exhibit interesting optical properties and several derivatives are useful for colourimetric sensing[81] intense research is dealing with fine tuning of the polymeric structures in order to optimize application behaviour. The colour changes in the presence of an analyte seem to be related to a conformational transition of the polymer backbone between a planar and nonplanar form induced by adequately functionalized and responsive side chains[82]. Thus side chain engineering[83] is one main direction in the development of new polythiophenes. In the present work we combine oligoether units and an aromatic ester group in the side chain of a ProDOT derivative in order to introduce an ion coordinating structural element with the option of further functionalization[84,85] of the corresponding PProDOT structure synthesized by electrochemical and chemical polymerization, respectively. Beside some electrochemical data the optical properties of the new PProDOT derivative in the presence of selected cations are reported.

2. Experimental section

Details of the synthesis of monomeric ProDOT-EO-ester **2**, its chemical and electrochemical polymerization and post-polymerization functionalization of the P(ProDOT-EO-ester) as well as the corresponding spectroscopical data can be found in the *Supporting Information*.

The infrared (FTIR) spectra were recorded with a FT-IR Bruker Vertex 70 Spectrophotometer in reflexion mode.

Average-molecular weight of P(ProDOT-EO-ester) was determined by gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with refraction and UV photodiode array detectors and Shodex column. Measurements were carried out with polymer solutions having 2 % concentration, and by using DMF/0.1 mol $NaNO_3$ as solvent and eluent, with a rate of 0.6 mL/min. Polystyrene standards of known molecular weight in solution of DMF/0.1 mol $NaNO_3$ were used for calibration. The average molecular weight value, M_w, was 81200 Dalton, the number average molecular weight, M_n, was found to be 48800 Dalton, and the polydispersity M_w/M_n was calculated to 1.66.

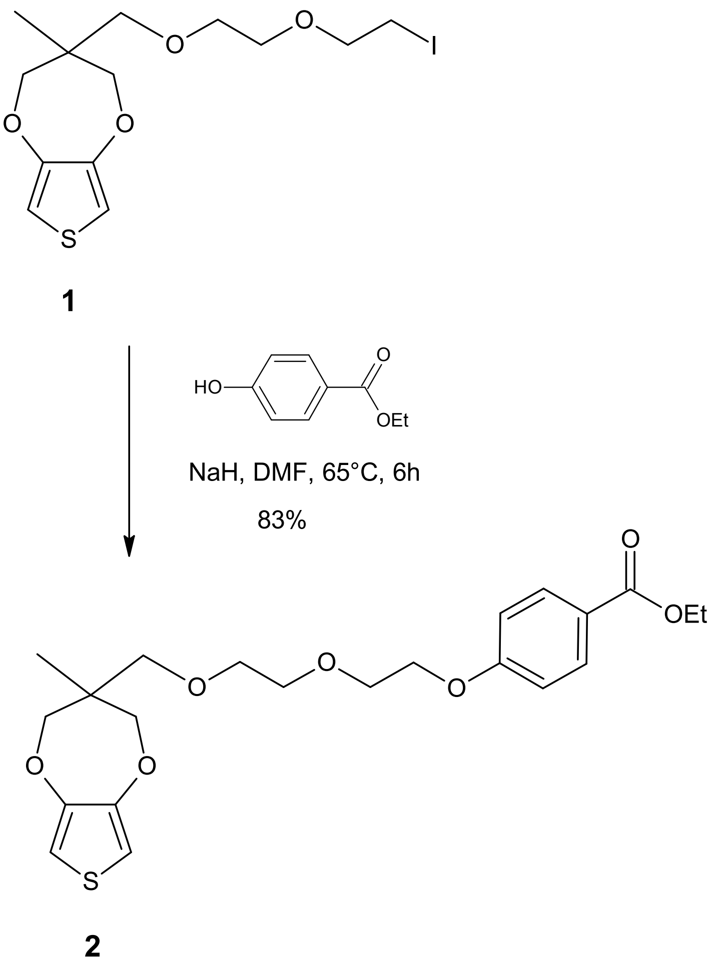
The UV-vis absorption spectra were recorded with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, using diluted polymer solutions with concentration of about 5×10^{-5} M (based on the average molecular weight of one repeat unit) and very thin films.

For investigation of the cation complexing behavior the polymer concentration was below 1×10^{-5} M, in order to keep the values of absorbance always less than 0.1. For the preparation of polymer-salt mixtures, LiCl, NaI, KI, NH_4SCN were previously dissolved in DMF or THF in order to obtain different concentrations. Identical volumes of a salt solution and the polymer solution were mixed in order to keep a constant polymer concentration.

3. Results and discussion

*3.1. Synthesis of monomeric ProDOT-EO-ester **2***

ω-Iodo functionalized thiophenes[86] and polythiophenes[87,88] are known as intermediates in the Williamson type reaction with nucleophiles allowing the introduction of various molecular structures into the side chain. Following this strategy the ProDOT-EO-ester **2** was synthesized in good yield from the ProDOT-dioxyethylene-iodo derivative **1**[89] by O-alkylation of Ethyl 4-hydroxybenzoate in the presence of sodium hydride in DMF[90] (Scheme 1).



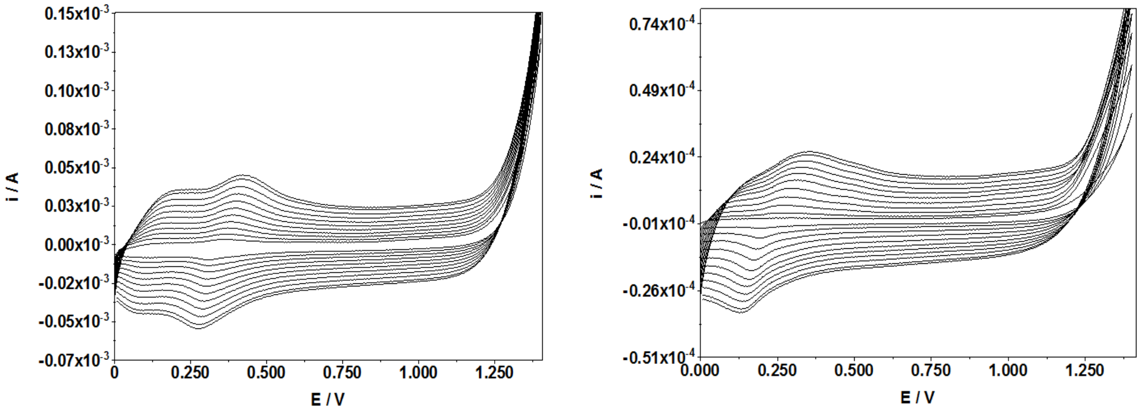
Scheme 1. Synthesis of ProDOT-EO-ester **2**

The structure of **2** was confirmed by its ^{1}H- and ^{13}C-NMR data (Fig. S1, *Supporting Information*) showing similar chemical shifts like two adjacent dioxyethylene units attached in 4-position of the aromatic ring of benzoic acid[91].

*3.2. Electropolymerization of ProDOT-EO-ester **2***

The electrochemical polymerization of ProDOT-EO-ester **2** onto ITO was carried out from a 0.02 M solution in acetonitrile (ACN) in the presence of 0.1 M Bu_4NClO_4 (Fig. 1a) or 0.1 M $LiClO_4$ (Fig. 1b) as supporting electrolyte by scanning the potential between 0 and +1.40 V with a scan rate of 100 mV/s.

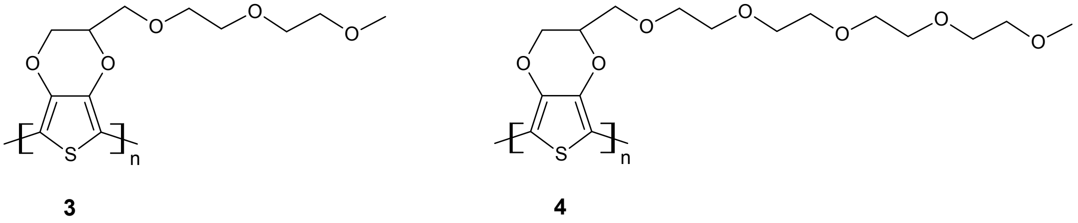
Fig. 1. Cyclic voltammograms (CVs) of electrodeposited P(ProDOT-EO-ester) in (a) 0.1 M Bu_4NClO_4/ACN and (b) 0.1 M $LiClO_4$/ACN at a scan rate of 100 mV/s



(a) b)

In both cases the increase of the current density with each cycle indicates the electrogrowth process resulting in the formation of a thin film of the conducting polymer. When Bu_4NClO_4 is used as electrolyte the intensity of peak currents is higher in comparison to $LiClO_4$. Also with Bu_4NClO_4 the peak potential separation for the polymer is $\Delta E \approx 60$ mV, while with $LiClO_4$, the peak potential separation is higher than 59 mV, indicating the quasi-reversible redox behaviour of the depositing polymer.

Unlike to the CV of PEDOT derivative **3** (scheme 2)[92] which remains unchanged using $LiClO_4$ as electrolyte during the electropolymerization of ProDOT-EO-ester **2** an obvious shift of the redox peaks to lower potentials can be noticed, indicating that the electropolymerization of **2** is strongly affected by the electrolyte employed, especially by the electrolyte cation. The slight negative shift of the main oxidation peak induced by Li^+ may be explained by conformational changes[64] due to complexation of the cation leading to a more effective conjugation of the polymer rather than obtained with Bu_4N^+. As reported previously in the case of polythiophenes and poly(3,4-ethylenedioxythiophene)s bearing an oligo(oxyethylene) chain the complexation of cations from the electrolyte exerts a considerable influence on the peak potential associated with the oxidation of the polymer[64,68,93]. This behavior of the P(ProDOT-EO-ester) is opposite to that of the PEDOT derivative **4** (scheme 2)[93] functionalized by a very long dioxyethylene side chain wherein a considerable negative shift of the main oxidation peak is induced by Bu_4N^+ compared to Li^+.



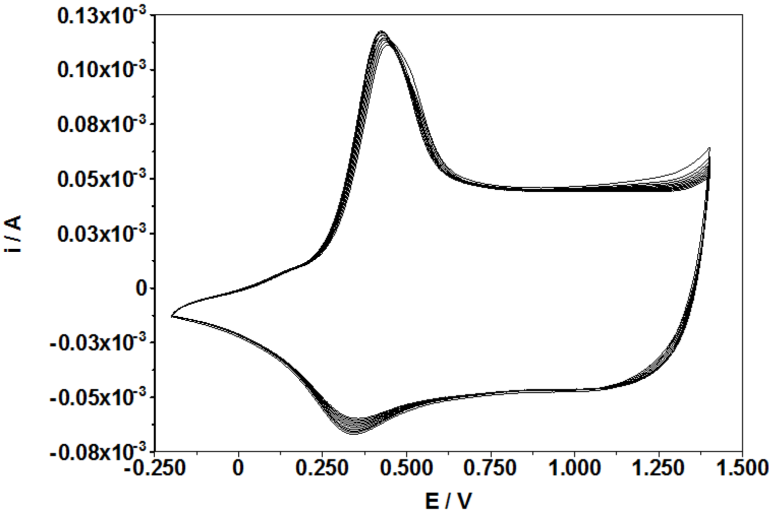
Scheme 2. Ether-functionalized PEDOT structures **3** and **4**

The CV of the P(ProDOT-EO-ester) in a monomer-free medium in the presence of Bu_4NClO_4 was carried out by repetitively sweeping the potential between –0.25 V and +1.40 V at a scan rate of 100 mV/s *vs.* Ag/AgCl (Fig. 2). The oxidation peak of the polymer electrodeposited onto ITO is sharp and centered at +0.42 V and accompanied by a less high reduction peak around +0.34 V. The intensification of the main oxidation peak has been observed previously in the CVs of different polythiophenes functionalized by oligoether side chains[66,69,87].

*3.3. Chemical polymerization of ProDOT-EO-ester **2***

The chemical polymerization of **2** was initiated by iron(III)-chloride in chloroform using aqueous ammonia for dedoping of the polymer (scheme 3).

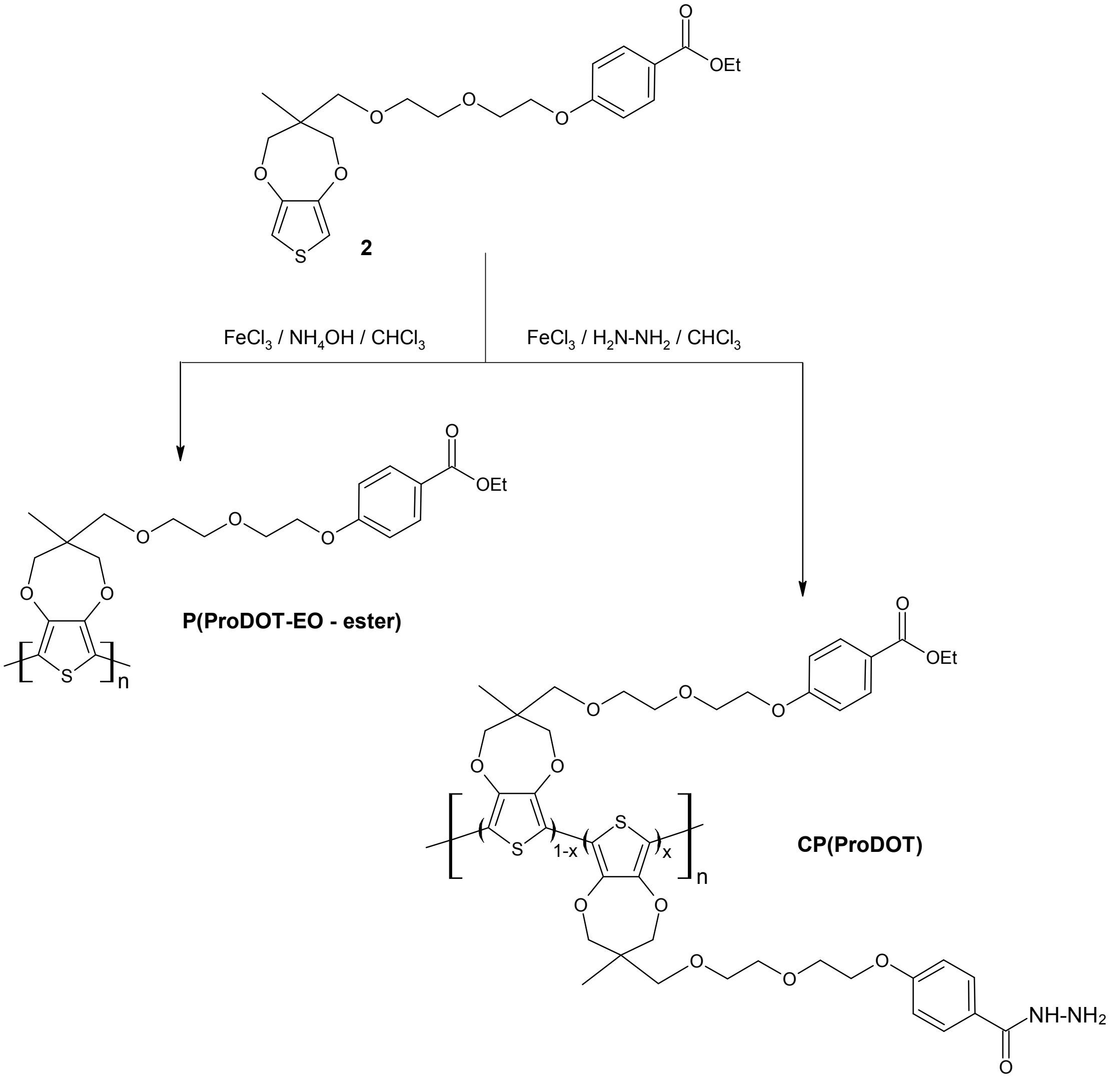
Fig. 2. CV of P(ProDOT-EO-ester) in 0.1M Bu_4NClO_4/ACN monomer free solution at the scan rate of 100 mV/s (40 scans)



The polymer structure was confirmed by ^{1}H-NMR data due to the absence of the thienyl proton signal which was observed for the monomer at 6.46 ppm whereas absorptions of the aromatic and dioxyethylene protons still appear in the same spectral region although as unresolved signals (S2, *Supporting Information*).

Further evidence for P(ProDOT-EO-ester) was given by infrared data showing the absence of the thienyl C-H stretching frequency at 3108 cm^{-1} and a shift of the aromatic C=C stretching vibration from 1484 cm^{-1} which is characteristic for a monomeric thiophene to 1470 cm^{-1} in the polythiophene as a result of successful polymerization. The C=O stretching band at 1707 cm^{-1} typical for the ester functional group of the monomer showed a slight shift to 1704 cm^{-1} in the polymer demonstrating that no saponification or degradation of the ester function took place during polymerization (Fig. 3a).

Using hydrazine hydrate for dedoping of the P(ProDOT-EO-ester) synthesized by chemical polymerization of **2** led to partial hydrazinolysis of the ester group in the side chain to give the copolymer CP(ProDOT) bearing both hydrazide and ester functional groups (scheme 3).

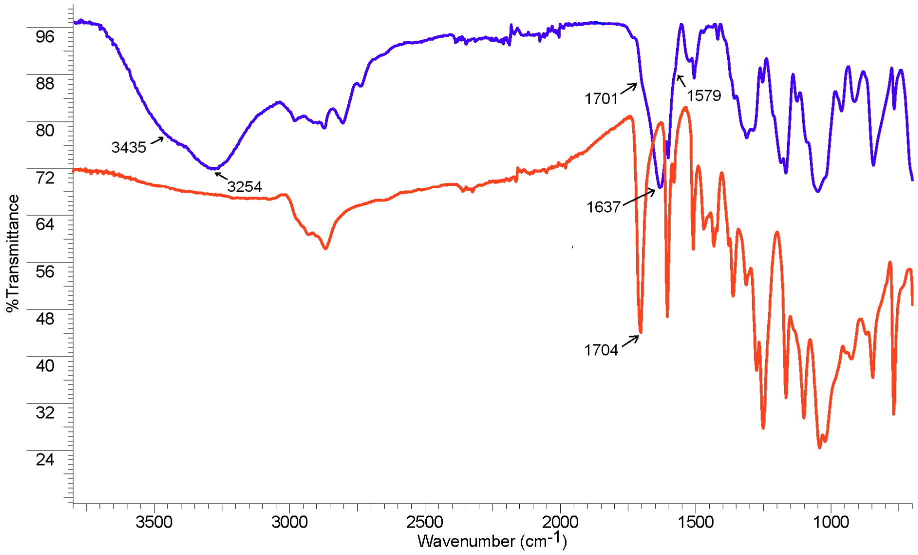


Scheme 3. Chemical polymerization of **2** and partial hydrazinolysis of P(ProDOT-EO-ester)

The formation of CP(ProDOT) was evidenced by its infrared spectrum showing bands typical for both functional groups. The presence of hydrazide is indicated by absorptions at 3435 cm^{-1} (N-H stretching) and 3254 cm^{-1} (NH_2 stretching), respectively, and additional bands appearing at 1637 cm^{-1} and 1579 cm^{-1}, associated with C=O stretching of the $CONHNH_2$ group and N-H deformation, respectively. (Fig. 3b).

Since the CP(ProDOT) was less soluble in chloroform and other solvents any attempt to obtain ^{1}H-NMR spectra sufficiently resolved for structural analysis was unsuccessful.

Fig. 3. FTIR spectra of P(ProDOT-EO-ester) before (a) and after (b) partial hydrazinolysis

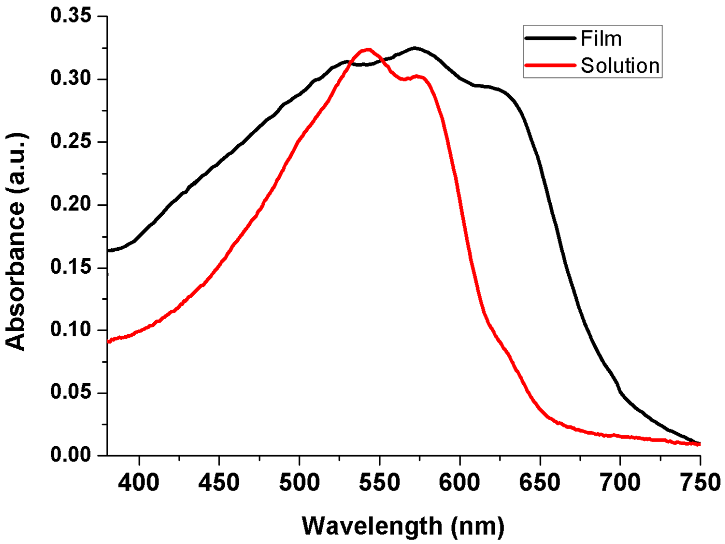


3.4. *Optical properties and cation complexing behavior of the P(ProDOT-EO-ester)*

The UV-vis spectrum of the P(ProDOT-EO-ester) revealed absorptions at lower energies in comparison to monomer **2** (254 nm), clearly proving conjugation of the polymer chain (Fig. 4). In DMF solution absorption peaks at 542 nm and 575 nm, respectively, were observed together with a shoulder at 625 nm. The main peaks can be associated to a twisted (less conjugated) form of the polymer backbones and to a more planar conjugated form[94], respectively. The shoulder at 625 nm may be attributed to aggregate formation of P(ProDOT-EO-ester) in DMF solution.

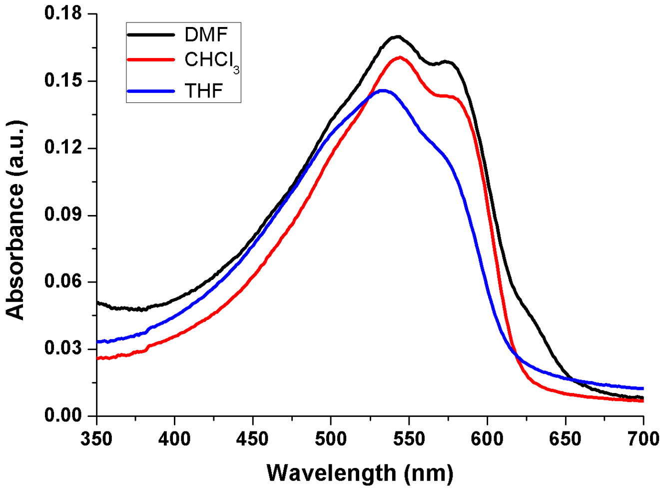
In solid state UV-vis absorptions of P(ProDOT-EO-ester) showed a broadening compared to solution with three maxima at 527, 573 and 631 nm. The first two maxima are blue-shifted with 15 nm and 2 nm, respectively, compared with the absorption of isolated molecules. The polymer film exhibited only a 6 nm red shift of its long wavelength absorption peak compared to the solution.

Fig. 4. UV-vis absorption spectra of P(ProDOT-EO-ester) in DMF and as film on quartz glass



The solvatochromic behaviour of P(ProDOT-EO-ester) was investigated at room temperature in THF, chloroform and DMF (Fig. 5).

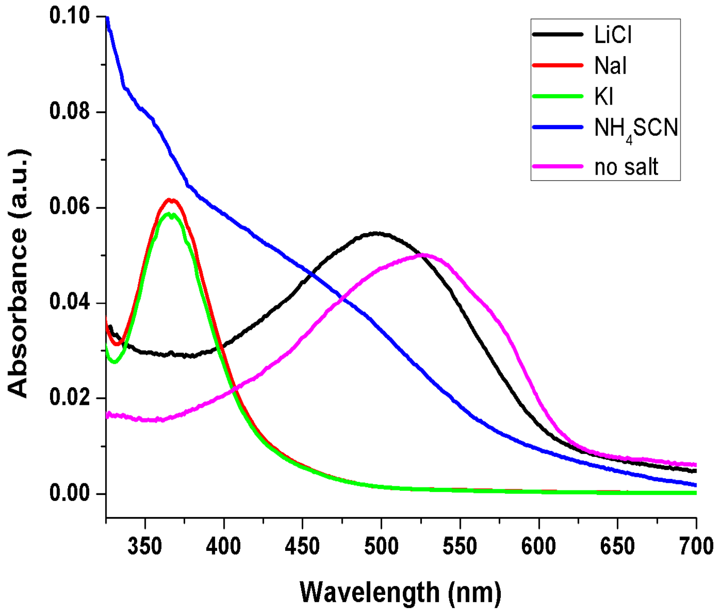
Fig. 5. UV-vis spectra of P(ProDOT-EO-ester) in THF, chloroform and DMF

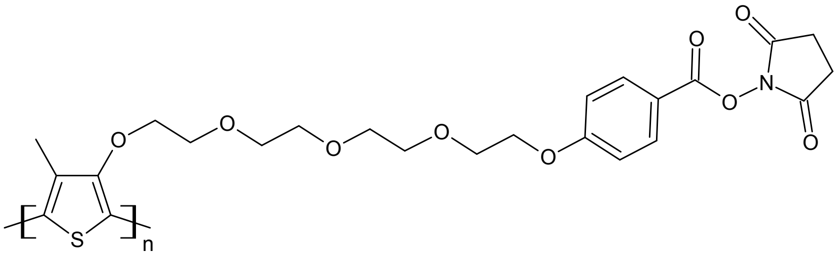


Dissolving of P(ProDOT-EO-ester) in THF as a good solvent produced a pink-purple coloured solution exhibiting a UV maximum at 532 nm, indicating that the polymer mainly adopted the twisted form. The shoulder at 575 nm accounted for the presence of planar forms of the polymer backbones in THF as well. In chloroform and DMF the maximum of absorption was shifted to higher wavelengths proving that the polymer backbones gained higher conjugation in these solvents. Simultaneously the UV absorption associated with the twisted conformation was red-shifted showing that the polymer chains were less disordered and consequently have a higher conjugation length in chloroform and DMF than in THF. The difference between the UV-vis spectra of the polymer dissolved in chloroform and DMF consisted in the different ratio of the main peak intensities and the presence of an additional shoulder at 625 nm in DMF. Similar conformational transitions of the polymer backbones between a planar and a non-planar form were also observed for PProDOT derivatives quaternary blocked by branched alkyl chains with resolved chiral center in xylene/DMF mixtures[95] and other polythiophenes bearing oligoether side chains[79], respectively.

The introduction of 10^{-3} M of sodium iodide into a solution of P(ProDOT-EO-ester) in THF spontaneously turned the color from pink-purple to yellow-orange. A similar effect was observed after the addition of potassium iodide whereas ammonium thiocyanate produced light yellow color and lithium iodide only changed slightly the shade of color of the solution. The UV-vis spectra of the polymer/salt solutions demonstrated a blue-shift of about 166 nm for Na^+ and K^+, respectively and of 67 nm for NH_4^+ and of only 28 nm for Li^+, respectively (Fig. 6). The occurrence of UV-shifts in solution was already observed for polythiophene derivatives bearing a crown ether unit at adjacent thiophene moieties upon addition of alkali metal ions. The effect was explained by adoption of a twisted conformation of the polymer backbone due to ion complexation[96]. A blue-shift of comparable size as found here for Na^+ and K^+ was detected previously only with regioregular poly(3-[2,5,8-trioxanonyl]thiophene)[97] dissolved in chloroform coordinating Pb^{2+} or Hg^{2+} as cations[13,98]. Interestingly, the related polythiophene derivative **5** (scheme 4) in THF exhibited no chromic effects in the presence of alkali metal salts[79].

Fig. 6. UV-vis spectra of P(ProDOT-EO-ester) in THF in the presence of different cations.





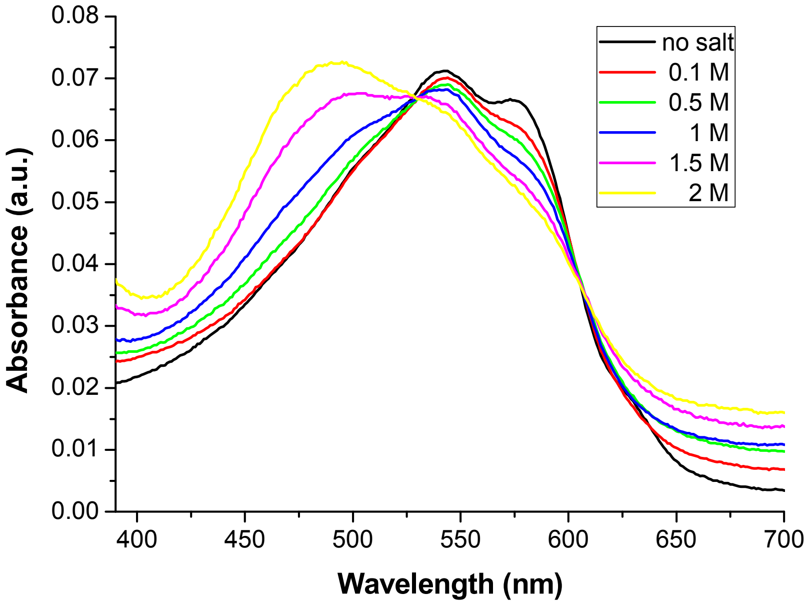
5

Scheme 4. Poly[3-(N-succinimido-p-phenylcarboxylate(tetraethoxy)oxy)-4-methylthiophene **5**

In THF, in which the polymer prefers the twisted form, the chromic effect may be attributed to the adoption of a crown-ether like conformation of the side chain with participation of the three oxygen atoms from the dioxyethylene chain and of one oxygen atom from the ester group and presumably also of one oxygen from the thiophene ether bridge. Such a conformation creating a disordered polymer backbone may imitate an arrangement similar to 15-crown-5 forming stable complexes with Na^+ and K^+, respectively. Such chromic features induced by cationic stimuli through a possible crown-ether like conformation were explained by Leclerc et al.[99-101] for polythiophene derivatives bearing flexible oligo(oxyethylene) side chains in terms of planar and non-planar transition of the polymer backbones, although these colour changes could also be rationalized by better solubilisation of the polymer upon salt addition as a solvatochromic effect. In both cases the non-covalent interactions between oxygen atoms and cations were responsible for the chromic response.

On the other hand, in DMF solution in which the polymer adopted mostly a planar or nearly planar conformation, the complexation effect measured with 0.1 M salt concentration was detected only for NH_4^+. As shown in Fig. 7, the addition of various concentrations of NH_4SCN induced a cooperative twisting of the main chain with increasing salt concentration, the effect was much more visible at a salt concentration higher than 1.0 M. The presence of two isosbestic points accounted for the coexistence of three conformational related to planar/non-planar (left) and aggregate/planar (right) transitions (Fig. 7). The absence of any chromic effect in DMF compared to THF for Na^+ or K^+, respectively, may be explained by the impossibility for the oligo(oxyethylene) side chain to adopt a crown-ether like conformation for ion interactions and only a very high concentration of NH_4^+ was able to disturb the planar conformation of the polymer backbones.

Fig. 7. UV-vis spectra of P(ProDOT-EO-ester) in DMF with different NH_4SCN concentrations



The chromic effect of P(ProDOT-EO-ester) observed in THF solution in the presence of Na^+ and K^+, respectively, may be useful to detect these physiologically important ions with high selectivity[102].

4. Conclusions

We have developed for the first time a bifunctional poly(3,4-propylenedioxythiophene) (PProDOT) derivative combining alkali metal ion coordinating oligoether units and a reactive ester group in the side chain. The new polymer (P(ProDOT-EO-ester) was synthesized by oxidative chemical and electrochemical polymerization of the corresponding monomer. The electropolymerization was achieved from acetonitrile using Bu_4NClO_4 or $LiClO_4$ as electrolyte to give conductive thin films onto ITO. Cyclovoltammetric analysis of the electrodeposited material indicated a small shift to lower oxidation potentials when using lithium salt as supporting electrolyte. The neutral P(ProDOT-EO-ester) obtained by chemical initiation in THF solution exhibited a strong UV-blue-shift of about 166 nm in the presence of Na^+ and K^+, respectively, indicating a tremendous conformational disordering and decreased conjugation of the polymer backbone. The specific ion complexing ability of the polymer in THF presumably arose from the formation of a crown ether like conformation of the side chain. In DMF solution smaller UV-blue shifts induced by NH_4^+ were observed with increasing salt concentration. The possibility of post-polymerization functionalization of the material was proved by partial hydrazinolysis of the ester group during dedoping of P(ProDOT-EO-ester) with hydrazine hydrate. The new polymer will provide further opportunities for creating powerful ion sensors based on environmentally stable poly(3,4-propylenedioxythiophene)s.

Acknowledgements

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