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Well-defined electrochemical switching of amphiphilic glycolated poly(3,4-ethylenedioxythiophene) $\ddagger$

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The approach of using polyether, aka glycol, side chains to afford amphiphilicity to conducting polymers has recently emerged as a powerful technique for next-generation materials for bioelectronics and electrochemical devices. Herein we apply this synthetic logic to the archetypical conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, to generate a glycolated PEDOT analogue, G-PEDOT. We report on the electropolymerization of this material, and its electrochemical properties: including spectroelectrochemistry, electrochemical capacitance, and operation of microelectrodes and electrochemical transistors. While in many respects performing like PEDOT, G-PEDOT has electrochemical switching within lower potentials with complete de-doping at lower potentials, affording transistors with higher on/off ratios than PEDOT, and electrochromic switching within a smaller electrochemical window. Overall, G-PEDOT emerges as a useful, functional alternative to other PEDOT derivatives, and could be a building block in copolymers.

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1. Introduction

Conducting polymers are a class of multifunctional electronic materials possessing hybrid electronic and ionic conductivity, chemical synthetic tunability, and unique electrochemical, catalytic, and optoelectronic properties. Conducting polymers can be divided into two families: hydrophobic and hydrophilic. The former is synthesized and processed from organic solvents such as toluene, chloroform, *etc.* Thin films of such polymers can be used in many solid-state devices like light-emitting diodes and photovoltaic cells. The other class of conducting polymers are hydrophilic and are processed and often used in aqueous conditions. This class is practically relevant in bioelectronics, biosensors,^{1,2} and electrolytic capacitors.³ Recently, amphiphilic conducting polymers have emerged, featuring polyether-based side chains commonly referred to as glycol side

chains.^{4–6} Glycol side chains afford hydrophilicity, but also affinity for organic solvents such as chloroform. The balance between hydrophilicity and hydrophobicity can be therefore tuned using glycol side chains, or combinations of glycol and alkyl side chains.^{6,7} This principle of tailoring the processability (from organic or aqueous solvent systems) and wettability using glycol side chains has been applied to yield next-generation conducting polymers for electrochemical transistors, ECTs,⁸ as well as electrochromic devices.⁹ Both applications rely on reversible electrochemical redox reactions to modulate the doping of the polymer, and require good ion mobility and efficient exchange of ions between the aqueous surroundings and the polymer film. Side chains play an important role in running wettability and ionic transport. ECT devices are used for biosensing applications, and as transducers for amplifying biopotential signals.^{10,11} High-performance implantable neural recording arrays based on ECT pixels are a major area of research.¹² ECTs require fast and reversible electrochemical redox reactions to modulate the conductivity of the polymer, simultaneously, the polymers must maintain good electrical conductivity and robustness with respect to dissolution or delamination. Poly(3,4-ethylenedioxythiophene), PEDOT, has become one of the most widespread and successful conducting polymer materials, and dominates in ECT research and applications. Most commonly it is deployed with the polyelectrolyte poly(styrene sulfonate) acting as the counter ion, to yield the composite PEDOT:PSS. While many glycol-containing homo- and heteropolymers have begun to compete with PEDOT in

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$\ddagger$ This paper is dedicated to Prof. Adam Proń on occasion of his 70th birthday.

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2.1. Materials

2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl methanol (hydroxymethyl EDOT), copper(I) iodide, 1-(2-bromoethoxy)-2-(2-methoxyethoxy)ethane, potassium *tert*-butoxide, dry pyridine, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (3–4 wt% dispersion in

H₂O), iron(III) chloride anhydrous, acetonitrile, ammonia, hydrazine, dimethylformamide were purchased from Aldrich. Preparative column chromatography was performed on a glass column with Merck silica gel, 230–400 mesh.

The investigated EDOT derivative containing oligo(oxyethylene) substituent, abbreviated as G-EDOT was prepared by modified Ullmann coupling¹⁷ between 2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-2-yl methanol (HO-EDOT) and 1-(2-bromoethoxy)-2-(2-methoxyethoxy)ethane, using a modification of the procedure previously reported.¹⁸ (see Fig. 1a). HO-EDOT can be prepared starting from inexpensive thiodiglycolic acid¹⁹ but recently it has become commercially available. The detailed synthetic protocol for G-EDOT, containing spectroscopic characterization data, can be found below.

Synthesis of 2-(2,5,8,11-tetraoxadodecan-1-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (G-EDOT). A solution of hydroxymethyl EDOT (OH-EDOT) (2.13 g, 12.37 mmol) and CuI (0.47 g, 2.47 mmol) in dry pyridine (40 mL) was purged with argon for 20 min. The 1-(2-bromoethoxy)-2-(2-methoxyethoxy)ethane (4.21 g, 18.54 mmol) and *t*-BuOK (2.36 g, 21.03 mmol) were added and the mixture was stirred for 20 hours at 100 °C under an argon atmosphere. After cooling down, water (20 mL) was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over

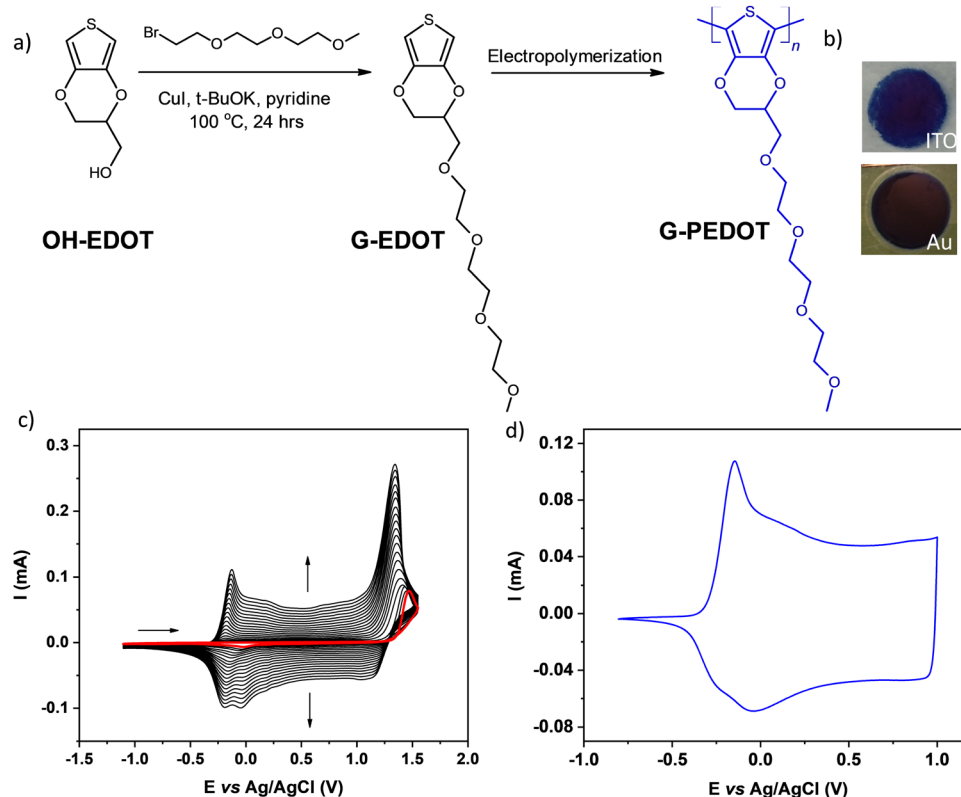


Fig. 1 (a) Synthetic route for the preparation of G-EDOT and G-PEDOT. (b) Photographs of 1 cm² areas of G-PEDOT polymerized on ITO and gold-coated PET substrates. (c) Potentiodynamic electropolymerization of G-EDOT on a platinum electrode immersed in 0.1 M TBAPF₆/CH₃CN electrolyte containing 5 × 10^{−3} M of the monomer, first scan is red. Scan rate 100 mV s^{−1}. (d) CV scan of a thin film of G-PEDOT electropolymerized on a Pt electrode. Electrolyte 0.1 M TBAPF₆/CH₃CN, scan rate 100 mV s^{−1}.

3.1 Electropolymerization and spectroelectrochemistry

For preliminary CV characterization G-PEDOT layers were deposited on a platinum disk. In the investigated potential range during the first scan, red colored in Fig. 1c, the irreversible peak is observed at 1.57 V and one reduction wave at 0.02 V in the reverse scan. This voltammogram was very similar to that reported for EDOT,²¹ however, its anodic peak maximum is shifted towards higher potentials reflecting slightly more difficult oxidation of G-EDOT. A representative cyclic voltammogram of G-PEDOT on the platinum electrode (Fig. 1d), prepared by potential scanning, consists of the principle oxidative peak in the anodic part at -0.14 V. In the cathodic part of the voltammogram the broad reduction peak is observed at -0.04 V. The introduction of the oligo(oxyethylene) chain on the poly(3,4-ethylenedioxythiophene) backbone leads to CV shape changes compared to the ones reported for PEDOT.^{22,23} In particular for G-PEDOT, at cathodic potentials < 0 V currents become very low, indicating it is electrochemically depleted, while PEDOT retains significant currents in this potential region.¹⁶ This comparison will become more apparent in aqueous electrochemistry differences seen during ECT characterization. Consistent with this electrochemical switching, G-PEDOT shows marked electrochromic color changes of the deposited polymer film of G-PEDOT cycled between reduced and oxidized forms,

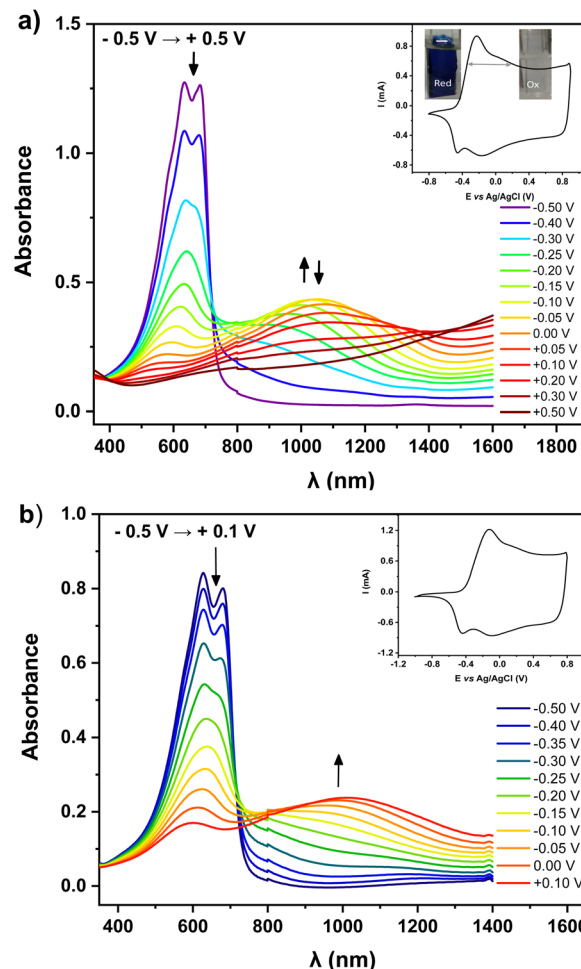


Fig. 2 CV scans and UV-vis-NIR spectra of thin films of G-PEDOT deposited on an ITO substrate, recorded for increasing electrode potential vs. Ag/AgCl pseudo-reference wire, under an inert atmosphere of argon. (a) Electrolyte: 0.1 M TBAPF₆/CH₃CN; (b) electrolyte: 0.1 M KCl/H₂O.

from deep-blue (reduced state) to transparent (oxidized state) (Fig. 2).

To quantify optical changes in detail, *in situ* spectroelectrochemistry was applied. Spectroelectrochemical measurements of the polymer film deposited on indium tin oxide (ITO) are shown in Fig. 2a and b, for organic and aqueous electrolyte conditions, respectively. UV-Vis-NIR spectral changes of G-PEDOT in acetonitrile using 0.1 M TBAPF₆ as an electrolyte and in 0.1 M KCl aqueous solution, induced by the oxidation process, are compared (see Table 1). In the first case, the polymer film was biased at different potentials from $E = -0.5$ V to $E = +0.5$ V vs. Ag/AgCl. As seen in Fig. 2a, G-PEDOT film exhibit a dual band with a maximum of 634 nm and 683 nm in the reduced form ($E = -0.5$ V). Upon electrochemical oxidation, the intensity of these peaks is gradually lost, while a new broad band at about 1028 nm at $E = -0.1$ V indicating the formation of charge carriers starts to appear and intensify. At the potential of $E = +0.5$ V, the featureless absorption tail can be observed, extending towards the NIR part of the spectrum.

Table 2 Summary of the electrochemical capacitance determination for G-PEDOT, deposited onto ITO (active area of 0.05 cm²) by galvanostatic electropolymerization from aqueous solution (3.14 mM of monomer, 0.1 M HClO₄)

Deposition time (s)	Thickness (nm)	Areal capacitance (μF cm ⁻²)	Volumetric capacitance (F cm ⁻³)
0 (= bare ITO)	0.0	10	N/A
75	38.5	181	47.2
150	72.6	351	48.3
225	114	588	51.5
300	157	815	52.0

comparable films synthesized with the same passed charge (samples were prepared with 2 or 4 μC total passed charge). Cyclic voltammetry of the resultant microelectrodes shows essentially the same behavior and electrochemical capacity for both PEDOT and G-PEDOT (Fig. 4a and b). The microelectrodes demonstrate stability over 4000 cycles. Electrochemical impedance of the microelectrodes (Fig. 4c and d) reveals that modification with electropolymers significantly reduces impedance with respect to the metal microelectrode, and that the impedance traces for both PEDOT and G-PEDOT are essentially the same. An impedance around 4 kΩ at 1 kHz is a relatively competitive value for a microelectrode of this size,³² and compares favorably with other examples of PEDOT-coated microelectrodes.³³ The addition of the glycol chain therefore does not significantly affect the performance in this application with respect to the unfunctionalized PEDOT. All samples were subjected to an accelerated aging test at 60 °C over 41 days, and

PEDOT and G-PEDOT remained comparably stable. ESI† Fig. S5 and S6 show the measurements from more days during the same aging test shown in Fig. 4, and results from thinner films prepared with 2 μC total passed charge.

Next, ECTs were fabricated according to the vertical geometry introduced by Donahue *et al.*,³⁴ featuring a channel length of 1 μm. This vertical geometry is beneficial for deposition by electropolymerization as the insulating distance between source and drain contacts is minimized compared to planar geometries. This makes it easier for an electropolymer to “bridge” the source–drain channel distance. This design is convenient for comparing electropolymerized active polymers, but it should be said that due to relatively large, exposed source–drain contact regions the parasitic capacitance makes their modulation speed limited. To deposit PEDOT or G-PEDOT by electrochemical polymerization, both source and drain electrodes were shorted together as a working electrode and a constant amount of current was passed in each case. We found better and more reproducible results with respect to good adhesion and channel forming, using ClO₄[−] as a counter ion as opposed to PF₆[−]. The resultant ECTs were characterized using an AgCl pellet gate electrode (pseudo-reference electrode), and the transfer curves are plotted in Fig. 5, including gate currents and transconductance values. Both polymers provide similar “ON” currents, indicating that the conductivity of both polymers in their doped forms is similar. However, the depletion mode switching off is different. While scanning to positive gate voltages electrochemically de-dopes both materials, by +800 mV the PEDOT channel conductivity

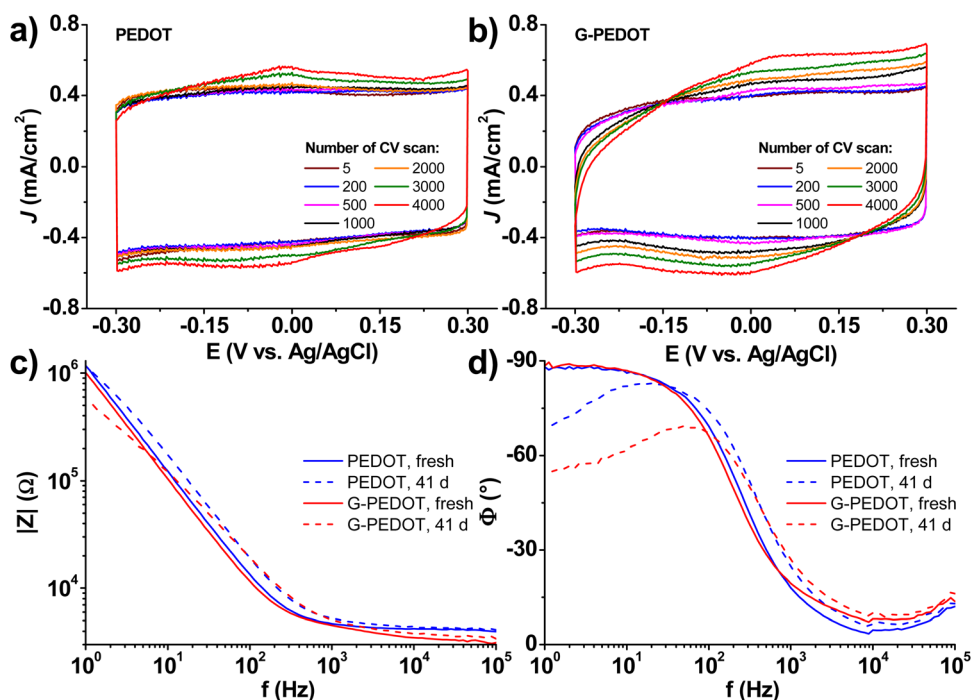


Fig. 4 Electrochemistry of PEDOT and G-PEDOT microelectrodes (50 × 50 μm) prepared by galvanostatic electropolymerization (2 μC: 20 nA, 100 s) (a and b): selected cyclic voltammograms (scan rate = 100 mV s^{−1}) over 4000 cycles (electrochemical stability test); (c and d): electrochemical impedance spectra (bode plots, averaged over 2–3 different specimens) as prepared and after 41 days of accelerated aging test (60 °C, PBS solution).



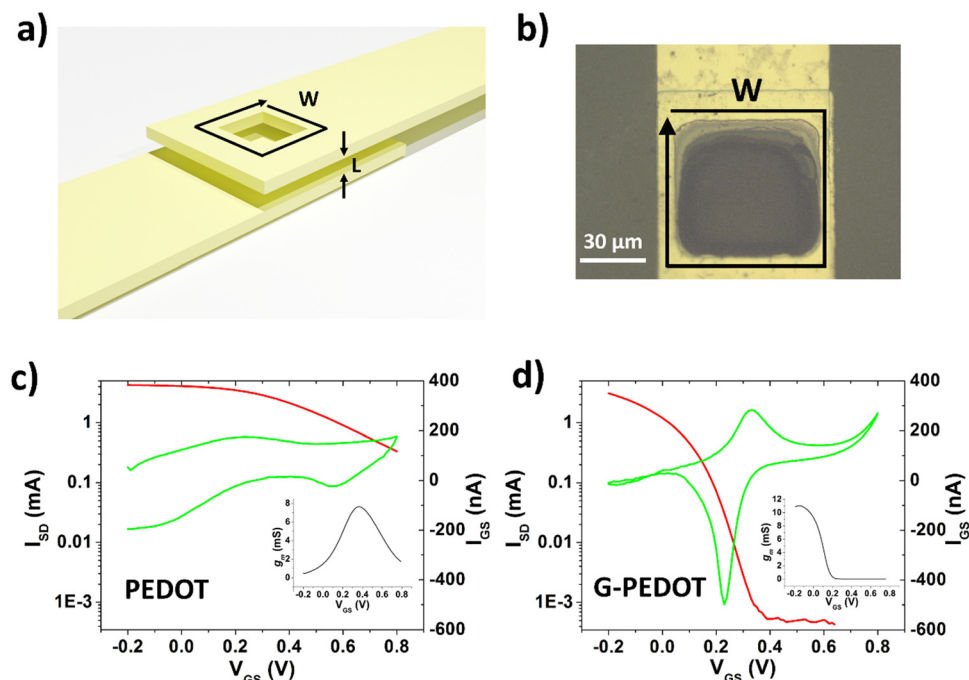


Fig. 5 Vertical electrochemical transistors (vECTs). (a) General schematic of a vECT structure, where the channel length is defined by the thickness of an insulator layer (parlylene-c, $L = 1 \mu\text{m}$). (b) Top-view photograph of electropolymerized G-PEDOT vECT. (c and d) transfer curves, $V_{\text{SD}} = -0.6 \text{ V}$. Red traces are the source–drain current (left y-axis), green represents the gate currents (right y-axis). (c) Electropolymerized PEDOT, compared under the same conditions with electropolymerized G-PEDOT. (d) Three CV cycles were used to complete the channel.

declines by roughly a factor of 50. G-PEDOT, in contrast, by +400 mV is clearly completely depleted and conductivity drops to a low value. As a consequence, the on/off ratio of the G-PEDOT ECT is significantly higher (4 orders of magnitude), within a smaller voltage window than PEDOT. This difference in electrochemical doping and dedoping is very evident when comparing the gate current traces. Whereas the G-PEDOT trace features clear, narrow, doping/dedoping peaks, the peaks in the case of PEDOT are wide and poorly defined. This complete depletion of G-PEDOT at relatively low voltages was anticipated already from the CV curve in organic electrolyte shown in Fig. 1d. We verified this difference between PEDOT, PEDOT:PSS and G-PEDOT by measuring CV as well (Fig. S7a and b, ESI†). The general shape of the recorded voltammograms is very similar and shows a typical pseudo-capacitive response of quasi-rectangular form. On the other hand, finding, the pinch-off mentioned before in G-PEDOT electrochemistry at negative voltages is observed, whereas PEDOT is still doped at these voltages. The G-PEDOT film was fully reduced by applying a potential at least 400 mV less negative than in PEDOT and PEDOT:PSS cases. This correlates with comparing the spectroelectrochemistry between G-PEDOT and PEDOT (see Section 3.1).

4. Conclusions

Glycolation is a frequently used tool to make conducting polymers which are synthetically manipulatable in organic solvents, yet still hydrophilic enough to function in applications

where ionic exchange from water is necessary. In this study, we have endeavored to critically evaluate the effects of glycolation on the archetypical conducting polymer PEDOT. In many respects, G-PEDOT gives properties, such as electrochemical capacitance, very similar to PEDOT. The most significant difference is that electrochemical switching occurs in a smaller voltage window, which is apparent in the ECT application and also in the electrochromic effect. In effect, G-PEDOT is easier to dedope than PEDOT. The higher on/off ratio and smaller voltage window for G-PEDOT ECTs shows that this derivative could be a better choice for some ECT applications than using PEDOT. Nevertheless, our results have been limited to electropolymerization. We have spent considerable effort to conduct bulk electropolymerization and chemical oxidative polymerization, followed by reduction and rinsing of electrolyte or oxidant, respectively, to then re-uptake the polymer in a suitable solvent for solution processing. While this approach works in principle, it is difficult to implement. Our efforts were hampered by very low solubility of these electro- and chemically synthesized and reduced polymers, therefore pure G-PEDOT may be impossible to solution process in a useful way. However, this finding together with the results on interesting electrochemical properties suggest that the glycolated EDOT unit may be a useful component to incorporate into copolymers.

Conflicts of interest

There are no conflicts to declare.



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