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Gerardo Salinas, Ariana Villarroel Marquez, Maël Idir, Shekhar Shinde, Bernardo Frontana-Uribe, et al.. Sodium-Ion Selectivity Study of a Crown-Ether-Functionalized PEDOT Analog. ChemElectroChem, 2020, 7 (13), pp.2826-2830. 10.1002/celc.202000693 . hal-04396523

HAL Id: hal-04396523

<https://hal.science/hal-04396523>

Submitted on 16 Jan 2024

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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemElectroChem* 10.1002/celc.202000693

Link to VoR: <https://doi.org/10.1002/celc.202000693>

Na⁺ ion selectivity study of a crown ether functionalized PEDOT analog

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Abstract: An electropolymerized ion selective PEDOT analog is presented in this communication. Poly-(2-phenyl-15crown-5-(3,4-ethylene-dioxythiophene)-amine) (PEDOT-Crown15) showed excellent electrochemical stability with a fast electron transfer ($\Delta E_p = 50$ mV). In comparison with unmodified PEDOT, a faster change from isolating to conducting state was observed. This is attributed to the formation of a well-ordered internal polymer matrix, caused by the aniline-Crown15 moiety. *In-situ* electrochemical conductance measurements in the presence of different monovalent cations showed high affinity for Na⁺ ions, as evidenced by the decrease of the conductance of the polymer in comparison with K⁺ and Li⁺. This selectivity is attributed to a limitation of the charge hopping conductance.

Conducting polymers are one of the most interesting electronic materials due to their different applications in batteries,^[1-2] capacitors,^[3-5] organic solar cells^[6] and electrochemical sensors.^[7-10] These materials have gained considerable attention as ionophores, due to their high intrinsic electroactive area, good conductivity and selectivity.^[11-13] The possibility to enhance the ionic selectivity of these materials has been reported by tuning the chemical structures of the monomer. For example, different functionalized polythiophenes have been synthesized with selective moieties targeting anion and cation analysis.^[14-18] Although the previously reported conducting polymers present high selectivity, the majority required the synthesis of dimers and trimers^[14-16] or the use of co-monomers *i.e.* 3,4-ethylenedioxythiophene (EDOT)^[17-18] in order to facilitate electropolymerization. Poly-3,4-ethylenedioxythiophene (PEDOT) is one of the most important conducting polymers due to its high conductivity, chemical and electrochemical stability and interesting electrochromic properties.^[19] EDOT provides stability and enhances the electric conductivity of the formed copolymers. Commonly PEDOT doped with complexing agents has been used for the analytical quantification of metal ions by square wave anodic stripping voltammetry^[20] and potentiometric titration.^[21-22] An interesting alternative is the design of chemically functionalized EDOT monomers in order to target an anion or cation of interest. In this work, we present the electrochemical polymerization of 2-phenyl-15crown-5-(3,4-

ethylene-dioxythiophene)-amine (EDOT-Crown15), the electrochemical characterization of the corresponding polymer (PEDOT-Crown15) and its specific ion selectivity towards Na⁺. The presence of the 15-crown-5 moiety inside the EDOT structure allows targeting selectively Na⁺ cations and the aniline linker decreases eventual polymerization problems due to steric hindrance. Synthesis of EDOT-Crown15 was carried out in our group,^[23] following a one-step reaction of nucleophilic substitution between the chloromethyl-EDOT and the 4'-aminobenzo-15 crown-5 (Scheme S1). Experimental details are described in the supporting information. Sodium (Na⁺) was selected as a monovalent target, due to its importance in many biological processes. For example, the continuous exchange between Na⁺ and K⁺ ions produces electrical signals due to the changes in the transmembrane potential and encodes fundamental physiological information.^[24-27] Problems in the transmission of these signals are at the origin of different pathologies and severe health problems in a number of neuronal or cardiac diseases and even diabetes. In this context, the development of ion selective materials and corresponding electrophysiological sensing devices could help to specifically monitor and evaluate these electrical signals.

Oxidation of EDOT-Crown15 (5 mM in a 0.1 M tetrabutylammonium perchlorate/acetonitrile solution) presents two irreversible peaks ($E_{p1} = 0.73$ V and $E_{p2} = 1.68$ V vs Ag⁰) attributed to the aniline and EDOT oxidation respectively. The latter showed the classical crossline, typically observed during electrochemical polymerization^[28] at the first reverse cycle (Inset Figure 1a). The potentiodynamic polymerization was carried out applying five potential cycles between -0.6 and 1.67 V vs Ag⁰ (Figure 1a). A continuous current increase of the anodic and cathodic signals was observed during the electropolymerization at lower potential values than the aniline oxidation potential. The electrochemical behavior of PEDOT-Crown15 in a monomer-free 0.1 M tetrabutylammonium perchlorate/acetonitrile (TBAP/ACN) solution presents a quasi-mirror voltammetric signal between the anodic and cathodic current at different scan rates (Figure 1b). This is characteristic for a fast electron transfer system indicated by the small peak separation values ($\Delta E_p = 50$ mV) in contrast with the electrochemical behavior of

non-substituted PEDOT.^[29] Similar symmetric voltammetric signals have been observed in other benzyl-substituted poly-3,4-dioxythiophenes^[30] and in highly ordered 3-alkyl-polythiophenes^[31–33] indicating that this behavior can be attributed to a well-ordered internal polymer matrix.

The scan rate analysis of the polymer showed that the anodic and cathodic peak current (i_p) (Figure S1a) followed a linear trend with the scan rate (v), which is consistent with the existence of a well-adhering electroactive film on the surface of the Pt electrode. In order to obtain a better understanding of the diffusion limitations of the counterions inside the PEDOT-Crown15 film, the double logarithmic plot of peak current against the scan rate was evaluated (Inset Figure 1b). The corresponding plot showed a slope of $m \approx 1.3$ for the main charge/discharge peaks, thus, this system undergoes fast electron transfer without diffusional limitations.^[34] The cathodic/anodic charge ratio (Q_c/Q_a) vs cycle number remained constant along the whole experiment and was always close to 1 (Inset Figure S1b, right axis blue dots), at least during 50 charge-discharge cycles. A maximum loss of anodic and cathodic charge of 10 % was recorded over the whole period (Inset figure S1b, left axis black dots), which could be attributed to the loss of soluble electroactive material (*i.e.*, low molecular weight oligomers) or to charge trapping processes due to the formation of σ -couplings. These results strongly indicate that PEDOT-Crown15 films show good electrochemical reversibility and redox stability.

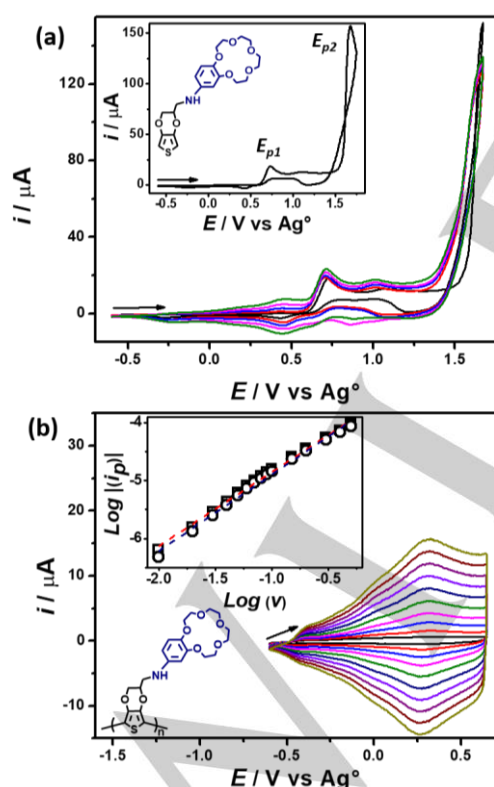


Figure 1. (a) Potentiodynamic polymerization (5 cycles) of EDOT-Crown15 0.005 M, TBAP/ACN 0.1 M, $v = 50 \text{ mV s}^{-1}$, $E_i = -0.6 \text{ V vs Ag}^\circ$, $E_f = 1.68 \text{ V vs Ag}^\circ$. Inset shows the potentiodynamic oxidation of the monomer. (b) Scan rate study of a PEDOT-Crown15 film obtained using the conditions indicated in (a) in a monomer free solution of TBAP/ACN 0.1 M, $E_i = -0.6 \text{ V vs Ag}^\circ$, $E_f = 0.65 \text{ V vs Ag}^\circ$. Inset shows the double logarithmic plot of the peak current vs the scan rate (\square) anodic and (\circ) cathodic peak.

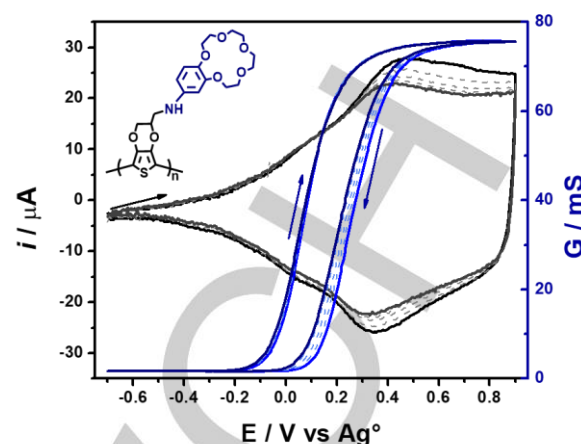


Figure 2. Simultaneous electrochemical (left axis) and conductance (right axis) study of a PEDOT-Crown15 film obtained using the conditions indicated in Figure 1a in a monomer free solution, TBAP/ACN 0.1 M, WE = Pt interdigital microarray electrode (IDMAE), CE = Pt foil, $E_i = -0.70 \text{ V vs Ag}^\circ$, $E_f = 0.9 \text{ V vs Ag}^\circ$, 5 cycles at $v = 50 \text{ mV s}^{-1}$ and a constant potential difference (ΔV) between the IDME branches of 10 mV.

In order to provide more information about this new polymer, *in-situ* electrochemical conductance experiments were carried out.^[35] A characteristic sigmoidal signal for the conductance (G) as a function of the potential was obtained (Figure 2), with a maximum value of $\sim 75 \text{ mS}$. A negligible loss of conductance (0.1 %) in this potential interval was obtained, thus, the decrease of charge can be attributed exclusively to the loss of soluble electroactive material. The full charge/discharge process presented a hysteresis value of 150 mV (ΔE_G) for the conductance signal (evaluated at the half-wave G vs E plot). This ΔE_G value is situated between the unmodified PEDOT^[36] and benzyl-substituted poly-3,4-dioxythiophenes^[30] (500 mV and 70 mV respectively). This observation indicates that a faster change from the insulating to the conducting state is obtained for PEDOT-Crown15 films in comparison with the unmodified PEDOT. Furthermore, this strongly suggests the formation of a well-ordered internal polymer matrix during the electropolymerization, leading to a fast exchange of ions and the formation of internal channels.

The redox stability study of PEDOT-Crown15, carried out by cyclic voltammetry at different inversion potentials (E_i), showed two main anodic peaks (Figure S2). The first signal is a small reversible couple (peaks *Ia/Ic*) and the second reversible couple (peaks *Ila/Ilc*) originates from the main redox doping process of the polymer. When a $E_i \geq 1.3 \text{ V}$ is reached, a third cathodic process was clearly observed at $E = 0.98 \text{ V}$ (*IIIC*), but in contrast to the two first cathodic processes, there was no associated anodic peak. At these potential values, the polymer started to show signs of over-oxidation since the peaks *Ia/Ic* shifted to a more anodic potential. This study was complemented by simultaneous electrochemical-conductance experiments (Figure 3) at different E_i values. At potentials below -0.20 V no conductance was observed; therefore, the reversible redox couple (peaks *Ia/Ic*) found in this potential range involves the formation of non-mobile charges, such as the ones attributed to σ -couplings^[37] formed during electropolymerization.^[38] Although this kind of couplings mainly occurs on the backbone of CPs,

due to the chemical structure of the EDOT-Crown15 monomer, they also might occur on the aniline moiety. Potentiodynamic oxidation of EDOT-Crown15 and the aniline-Crown15 at potentials below the EDOT oxidation (Figure S3) provided support for this hypothesis, because both compounds presented two reduction peaks; E_{red1} around 0.35 V to 0.4 V and E_{red2} between -0.3 V and -0.1 V, which we attribute to the reduction of the dimer aniline and the reduction of the formed σ -couplings, respectively.^[38]

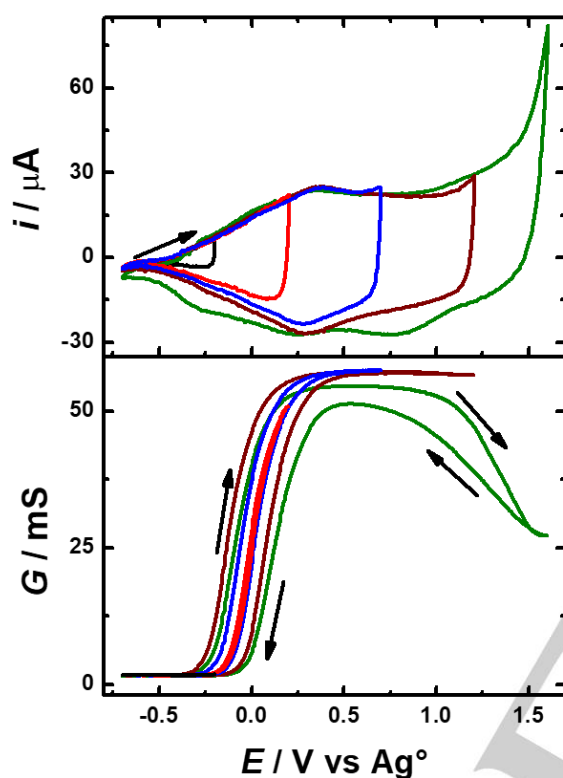


Figure 3. Simultaneous electrochemical (top curve) and conductance (bottom curve) study of a PEDOT-Crown15 film, obtained using the conditions indicated in Figure 1a in a monomer free solution using different E_{Anod} values, TBAP/ACN 0.1 M, WE = Pt IDMAE, CE = Pt foil, $E_i = -0.70$ V vs Ag° , $E_{A1} = -0.20$ V, $E_{A2} = 0.20$ V, $E_{A3} = 0.70$ V, $E_{A4} = 1.20$ V, $E_{A5} = 1.60$ V vs Ag° , $v = 50$ mV s⁻¹ and a constant ΔV of 10 mV between the IDME branches.

Once the maximum conductance has been reached during the simultaneous electrochemical-conductance experiments, a hysteresis gap appeared and increased as the E_A value increased, indicating that the charge/discharge process changes from a fast-reversible system to a slow process controlled by ion mobility. When the E_A value was below 1.1 V the polymer showed a stable redox and conductivity behavior, whereas beyond this potential (1.2 V - 1.6 V) a steep decrease of the maximal conductance occurred, associated with a significant change in the voltammetric signal. This can be attributed to the irreversible over-oxidation of the aniline moiety and the EDOT backbone, which causes a loss in conjugation and limits the movement of charge-carriers along the polymer chains. Thus, PEDOT-Crown15 has a reversible and stable redox behavior in cyclic voltammetry up to a potential value of 1.3 V vs Ag° , which agrees with the reported values for PEDOT.^[39]

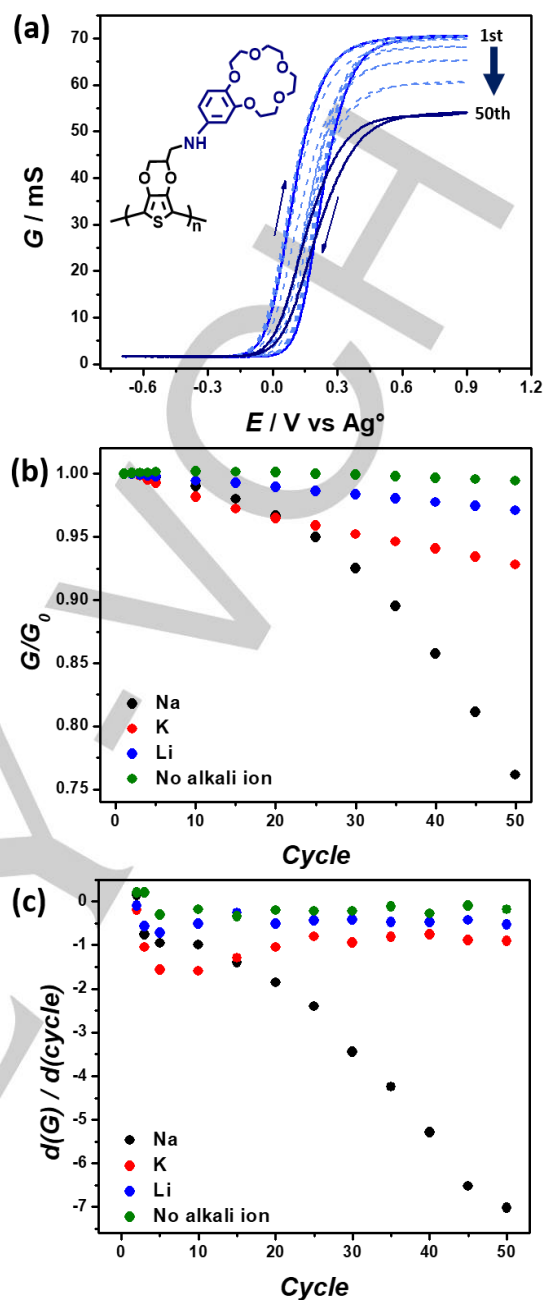


Figure 4. (a) G vs E plot of a PEDOT-Crown15 film obtained using the conditions indicated in Figure 1a in a monomer free solution of TBAP/ACN 0.1 M, NaClO₄ 0.1 mM, 50 cycles, WE = Pt IDMAE, CE = Pt foil, $E_i = -0.70$ V vs Ag° , $E_A = 0.90$ V vs Ag° , $v = 50$ mV s⁻¹ and a constant ΔV between the IDME branches of 10 mV. (b) Relative variation of the conductance as a function of the number of cycles of PEDOT-Crown15 films in the presence of different cations as indicated in the figure. (c) Plot of the conductance derivative as a function of the number of cycles of PEDOT-Crown15 films in the presence of different cations as indicated in the figure.

Finally, in order to test the ion selectivity of PEDOT-Crown15, the conductance behavior of the polymer was evaluated in the presence of different monovalent alkali cations. Conductivity recording was selected as analytical technique, since conductivity is a bulk transport property in conducting polymers, therefore small perturbations of the charge carriers result in high conductivity changes in comparison with variations in potential or current. In the presence of Na⁺, the sigmoidal shape of the

conductance was preserved during the entire experiment (50 charge/discharge cycles), but a very significant change of the maximum conductance value was observed (Figure 4a). Since the ionophore group is not located directly on the backbone of the polymer, we assume that the loss of conductance is due to a limitation of the charge hopping conductance, induced by ion trapping in the crown ether cavity.^[40-41] This is confirmed by the very small change in conductance (3%) obtained with unmodified PEDOT in the presence of Na⁺ (Figure S4). We conclude that the PEDOT backbone does not contribute to the change of conductance of the PEDOT-Crown15 film. The selectivity of PEDOT-Crown15 was evaluated by plotting the relative variation of conductance as a function of the number of cycles for three independent solutions of 0.1 mM Li⁺, Na⁺ and K⁺ (Figure 4b). As can be seen, the conductance of PEDOT-Crown15 in the presence of Li⁺ and K⁺ was reduced by only 3% or 8%, respectively, whereas a 25% loss occurred for Na⁺ as an analyte. Significant differences in the kinetics of conductance changes were also evident for the different ions. Plotting the conductance variation per individual potential cycle for an increasing number of cycles clearly showed a completely different behavior of the polymer in the presence of Na⁺ as opposed to the other alkali cations (Figure 4c). This clearly indicates a preferential and much easier incorporation of Na⁺ ions into the polymer network, in accordance with the crown ether size-matching rule. Finally, the influence of the NaClO₄ concentration on the change in conductance of the films was evaluated (Figure S5). A faster and steeper change of conductance was observed for an increasing sodium ion concentration. This is attributed to a more pronounced complexation of the crown ether cavities inside the polymer, limiting the charge hopping conductance.

In conclusion, the results demonstrate that the present approach allows obtaining electrochemically stable and redox reversible conducting polymers, based on a crown ether functionalized PEDOT with a good selectivity towards Na⁺. The obtained PEDOT-Crown15 films present a fast electron transfer, characterized by its small potential peak separation. The electrochemical experiments coupled with *in-situ* conductance showed a maximal conductance at low and medium values of doping levels with a fast change from the insulating to the conducting state. Although the electrochemical characterization of PEDOT-Crown15 has not yet been carried out in aqueous media, its properties qualify this polymer as an interesting candidate for the elaboration of ion selective organic electrochemical transistors, (OECTs). This opens up promising perspectives for potential applications in the biomedical field and work in this direction is currently in progress.

Acknowledgements

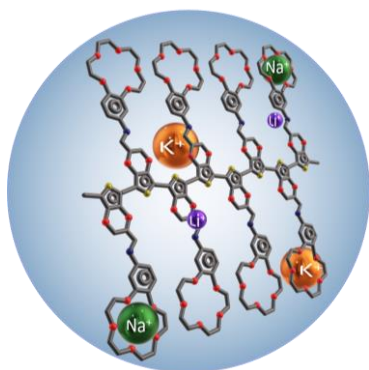
We are grateful for funding from the LabEx AMADEUS-0042 with the help of the French government "Initiative d'excellence" (to EC and JL), from ANR MULTISPOT ANR-17-CE09-0015 (to EC, AK and JL) and the IDEX/CNRS PEPS "MULTISEPT" attributed to M.R. B.A. F-U. acknowledges financial support via PAPIIT-UNAM project IN2028919. G.S. is grateful for support via the ERC Advanced grant ELECTRA (grant agreement no 741251 to AK).

Keywords: PEDOT • Ion selectivity • In-situ Electrochemical-Conductance • EDOT derivative

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Entry for the Table of Contents



Introduction of crown ether functionalities on the backbone of a conducting polymer chain (PEDOT analog) allows conferring ion selective features to the resulting polymer layers. The electrodeposited films are studied by cyclic voltammetry and simultaneous *in situ* conductance measurements, revealing selective interactions with Na^+ ions, compared to Li^+ and K^+ .

1

Supporting information

2

3

Na⁺ ion selectivity study of a crown ether functionalized PEDOT analog

4

Gerardo Salinas, Ariana Villarroel-Marquez, Maël Idir, Shekhar Shinde, Bernardo A.

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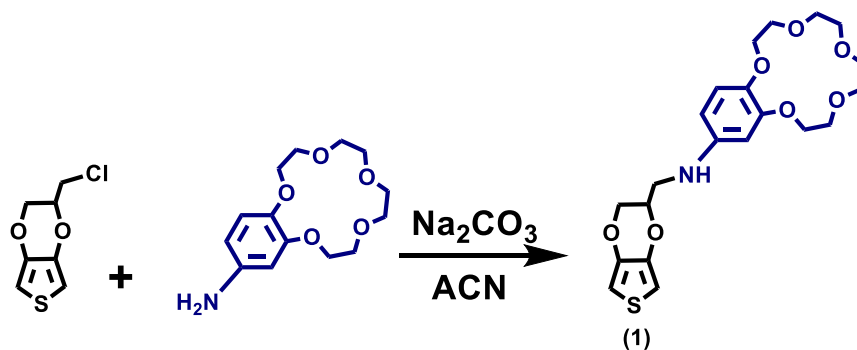
Frontana-Urbe, Matthieu Raoux, Jochen Lang, Eric Cloutet, Alexander Kuhn*

6

7 1. Experimental

8 1.1. Reagents

9 Tetrabutylammonium perchlorate (TBAP, Aldrich, 99.9%), anhydrous ACN (Aldrich,
10 99.9%), LiClO₄ (Aldrich, 99.9%), KClO₄ (Aldrich, 99.9 %), NaClO₄ (Aldrich, 99.9 %),
11 chloromethyl-EDOT (Aldrich, 98%) and 4'-aminobenzo-15-crown-5 (Aldric, 97 %) were
12 used as received. The 2-phenyl-15-crown-5-(3,4-ethylene-dioxythiophene)-amine (EDOT-
13 Crown15) was synthesized in our laboratory (Scheme S1). A three necked round bottom
14 flask, previously flame-dried, and kept under inert conditions was charged with
15 chloromethyl-EDOT (0.3436 g, 1.71 mmol, 1 eq.), 4'-aminobenzo-15-crown-5 (0.5 g, 1.71
16 mmol, 1 eq.) and sodium carbonate (0.5611 g, 5.29 mmol, 3.0 eq.) solubilizing everything
17 with dry and degassed acetonitrile ($v = 40$ mL). The mixture was stirred for 48h at 70°C.
18 The solvent was removed under reduced pressure, and after solubilizing in
19 dichloromethane, the product was washed with water and dried over magnesium sulfate.
20 Solvent was removed after obtaining a brownish oil as product (0,703 g; 90% yield). ¹H-
21 NMR (400 MHz, CDCl₃, 298 K): δ (ppm): 6.72 (d, 1H), 6.36 (q, 2H); 6.28 (d, 1H); 6.23
22 (dd, 1H); 4.36 (m, 1H); 4.26 (dd, 1H); 4.17 (q, 1H); 4.06 (m, 4H); 3.88 (m, 4H); 3.74-3.68
23 (m, 11H). ¹³C-NMR (CDCl₃, 150 MHz, 298 K): δ (ppm)= 150.6; 142.3; 141.3; 140.9;
24 117.5; 107.7; 102.9; 100.3; 77.1; 71.1; 71.0; 70.9; 70.6; 70.1; 69.8; 68.8; 65.8; 41.5. m/z
25 (ESI-HRMS) 460.1 ([MNa⁺] C₂₁H₂₇NO₇SNa requires 460.5).

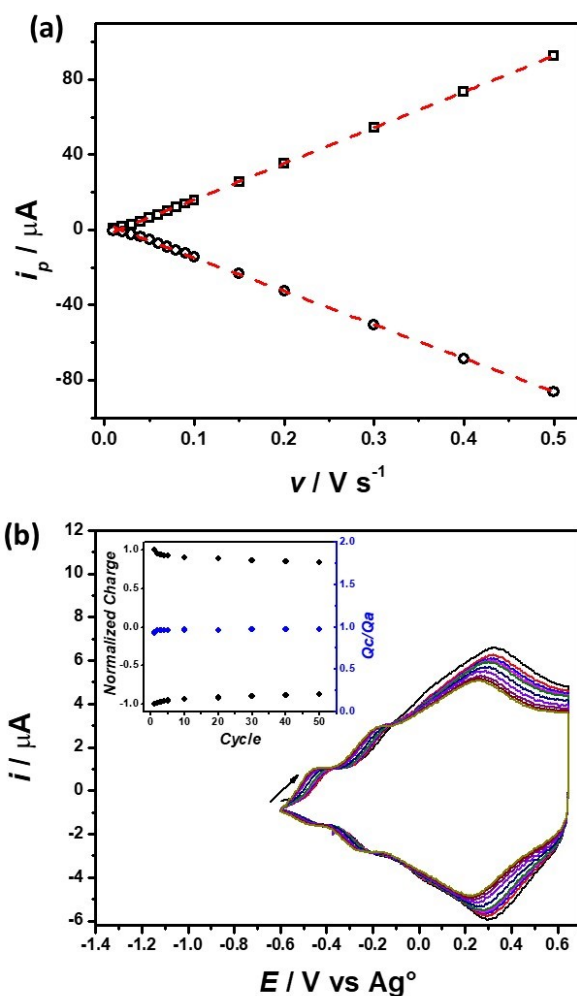


27 Scheme S1. Synthetic route to obtain 2-phenyl-15-crown-5-(3,4-ethylene-dioxythiophene)-
28 amine (EDOT-Crown15).

29

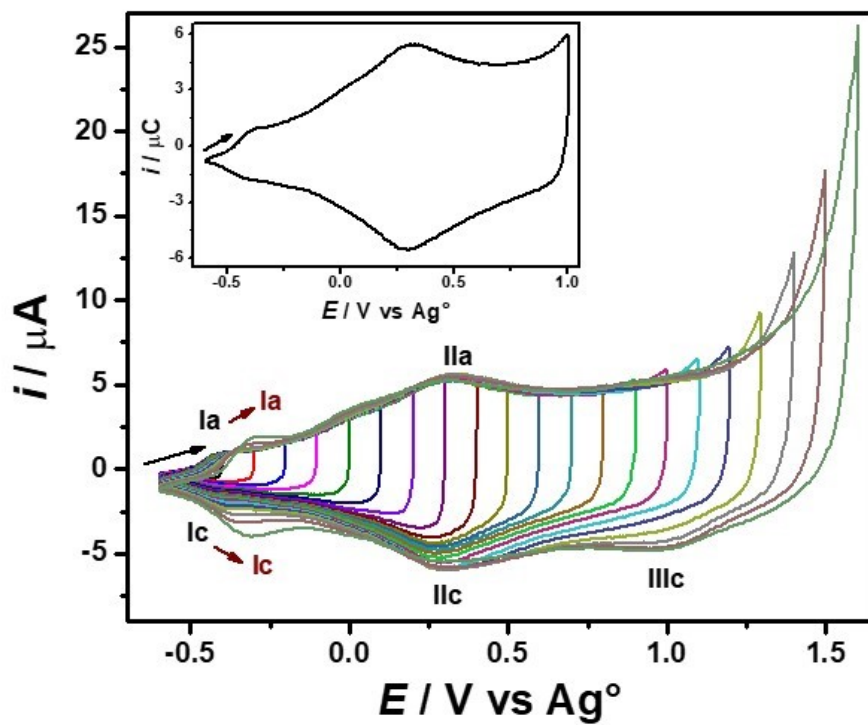
30 1.2. Electrochemical synthesis and characterization of PEDOT-Crown15 films

31 The electrochemical polymerizations and measurements were performed in a three-
32 electrode cell containing anhydrous acetonitrile (ACN) as the solvent and
33 tetrabutylammonium perchlorate as the supporting electrolyte (0.1 M). The monomer
34 concentration used for electropolymerizations was 0.005 M. Cyclic voltammetry
35 experiments were performed by means of a PalmSense4 potentiostat connected to a
36 personal computer. The working electrode was a 1 mm diameter Pt disk electrode. Pt and
37 Ag wires were used as the counter and quasi-reference electrodes, respectively and all
38 determinations were carried out at 25 °C. *In-situ* electrochemical-conductance
39 measurements were carried out using a two potentiostat system, especially built for this
40 application. Interdigital microarray electrodes (IDMAE) of 1 cm x 0.5 cm, featuring
41 separated Pt bands (10 μm) were used as working electrodes. A three-electrode
42 electrochemical cell fitted with a Pt foil counter electrode parallel to the working electrode
43 and of the same size, a quasi-reference electrode (Ag wire) and the IDMAE were used for
44 the studies. A constant potential difference of 10 mV provided by one potentiostat was
45 applied between the IDMAE branches to generate the drain current that circulates through
46 the polymer during conductance measurements. The conductance of the grown films was
47 measured in real time during the cyclic voltammetry experiment in a monomer free solution
48 at 25 °C. Conductance was calculated according to Ohm's Law, which is directly related to
49 the specific conductivity. Even though without an exact thickness value it is not possible to
50 determine the polymer conductivity, the conductance behavior is generally accepted to
51 allow a first indirect insight into conductivity changes as a function of the redox state. More
52 details about this technique and examples of the use of conductance measurements in
53 conducting polymers can be found elsewhere in the literature.^[1]



54

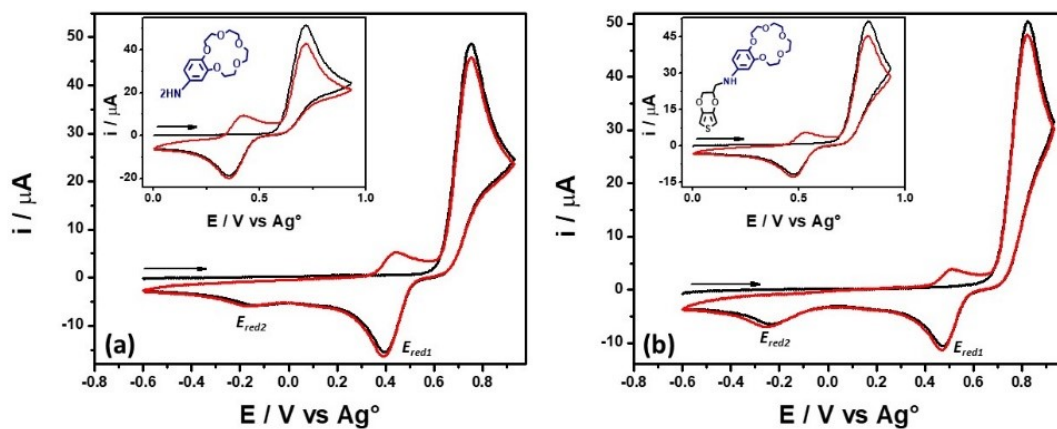
55 Figure S1. (a) I_p vs v graph for the anodic (\square) and cathodic (\circ) peaks from 10 mV s^{-1} to 500
 56 mV s^{-1} . (b) Electrochemical stability of the PEDOT-Crown15 film obtained using the
 57 conditions indicated in Figure 1a in a monomer free solution, ACN/TBAP 0.1M, $E_i = -0.60$
 58 V vs Ag° , $E_\lambda = 0.65 \text{ V vs Ag}^\circ$, $v = 50 \text{ mVs}^{-1}$. The inset shows the variation of the
 59 normalized charge (left axis, black curve: positive is anodic and negative is cathodic) and
 60 the Q_c/Q_a variation (right axis blue curve) both during the 50 cycles.



61

62 Figure S2. $E_{\lambda,Anod}$ study of a PEDOT-Crown15 film obtained using the conditions indicated
 63 in Figure 1a in a monomer free solution, ACN/TBAP 0.1 M, $E_i = -0.60$ V vs Ag° , $\nu = 50$
 64 $mV s^{-1}$. The insert shows the PEDOT-Crown15 response at $E_{\lambda} = 1.0$ V vs Ag° .

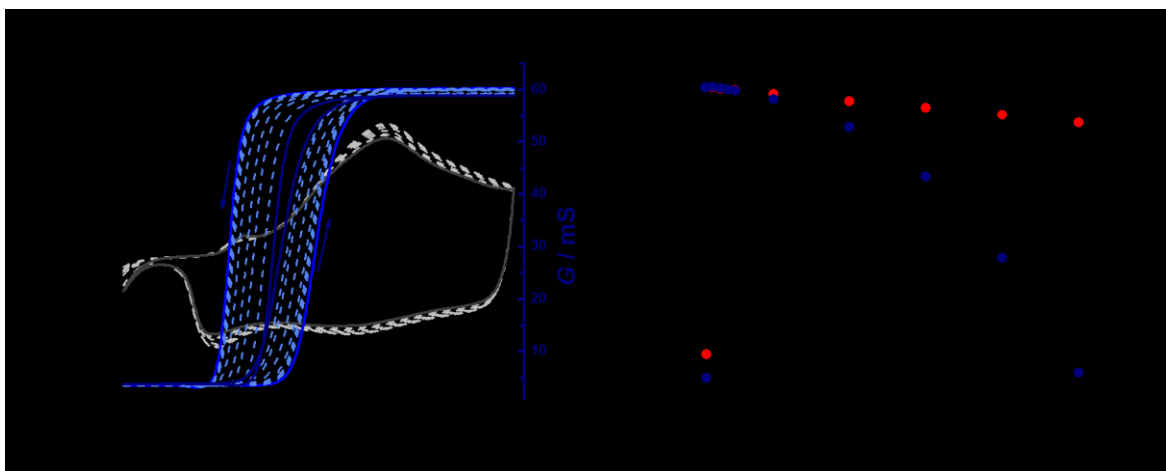
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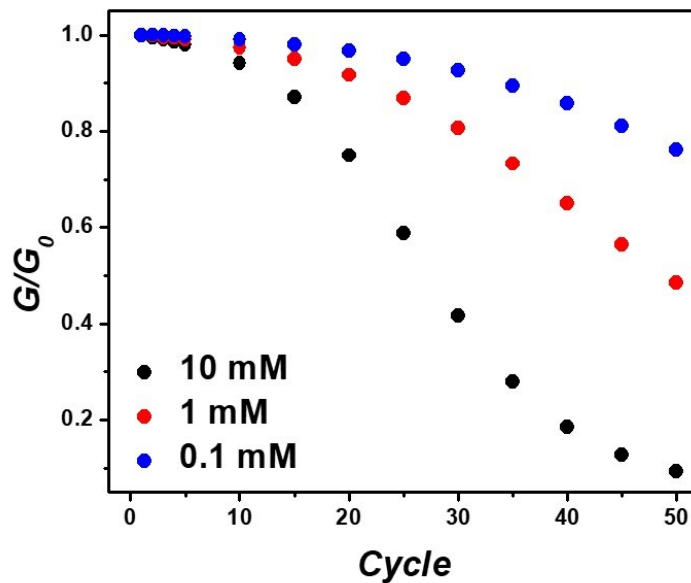
67 Figure S3. Potentiodynamic oxidation of a 5 mM solution of (a) aniline-Crown15 and (b)
 68 EDOT-Crown15 in ACN/TBAP 0.1 M solution, $E_i = -0.60$ V vs Ag° , $\nu = 500$ mV s^{-1} . The
 69 insert shows the same experiments with a $E_i = 0.0$ V vs Ag° .

70



71

72 Figure S4. (a) Simultaneous electrochemical (left axis) and conductance (right axis) study
 73 of a PEDOT film (synthesized from a 5 mM EDOT, 0.1 M TBAP/ACN solution), in a
 74 monomer free solution TBAP/ACN 0.1 M, NaClO₄ 0.1 mM, WE = Pt IDMAE, CE = Pt
 75 foil, $E_i = -1.15$ V vs Ag^o, $E_\lambda = 0.75$ V vs Ag^o, 50 cycles at $\nu = 50$ mV s⁻¹ and a constant
 76 potential difference (ΔV) between the IDME branches of 10 mV. (b) Relative variation of
 77 the conductance as a function of the number of cycles of PEDOT and PEDOT-Crown15
 78 films in the presence of 0.1 mM NaClO₄.



79

80 Figure S5. Relative variation of the conductance as a function of the number of cycles of
81 PEDOT-Crown15 films in the presence of different concentrations of NaClO_4 .

82 2. References

83 [1] G. Salinas, B. A. Frontana-Urbe, *ChemElectroChem* **2019**, *6*, 4105-4117