



HAL
open science

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

Gerardo Salinas, Ariana Villarroel Marquez, Maël Idir, Shekhar Shinde, Bernardo A Frontana-Urbe, Matthieu Raoux, Jochen Lang, Eric Cloutet, Alexander Kuhn

► **To cite this version:**

Gerardo Salinas, Ariana Villarroel Marquez, Maël Idir, Shekhar Shinde, Bernardo A Frontana-Urbe, et al.. Na⁺ ion selectivity study of a crown ether functionalized PEDOT analog. *ChemElectroChem*, 2020, 7 (13), pp.2826-2830. 10.1002/celc.202000693 . hal-02869565

HAL Id: hal-02869565

<https://hal.science/hal-02869565>

Submitted on 16 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Gerardo Salinas^{‡[a]}, Ariana Villarroya Marquez^{‡[b],[c]}, Maël Idir^[b], Shekhar Shinde^[b], Bernardo A. Frontana-Uribe^{[d],[e]}, Matthieu Raoux^[c], Jochen Lang^[c], Eric Cloutet^[b], Alexander Kuhn^{*[a]}

[a] Dr. G. Salinas, Prof. A. Kuhn

Univ. Bordeaux, ISM, CNRS UMR 5255, Bordeaux INP, F-33607 Pessac, France.

[b] Dr. A. Villarroya Marquez, Maël Idir, Dr. Eric Cloutet

Univ. Bordeaux, LCPO, CNRS UMR 5629, Bordeaux INP, F-33615, Pessac, France

[c] Dr. A. Villarroya Marquez, Dr. Matthieu Raoux, Prof. Jochen Lang

Univ. Bordeaux, CBMN, CNRS UMR 5248, Bordeaux INP, F-33600, Pessac, France

[d] Dr. Bernardo A. Frontana-Uribe

Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Km 14.5 Carretera Toluca-Atlatomulco, 50200, Toluca, México

[e] Dr. Bernardo A. Frontana-Uribe

Instituto de Química, UNAM, Circuito Exterior Ciudad Universitaria, 04510, CDMX, México.

‡ Gerardo Salinas and Ariana Villarroya-Marquez contributed equally.

* corresponding author: kuhn@enscbp.fr

Supporting information for this article is given via a link at the end of the document.

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 (ν), 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.

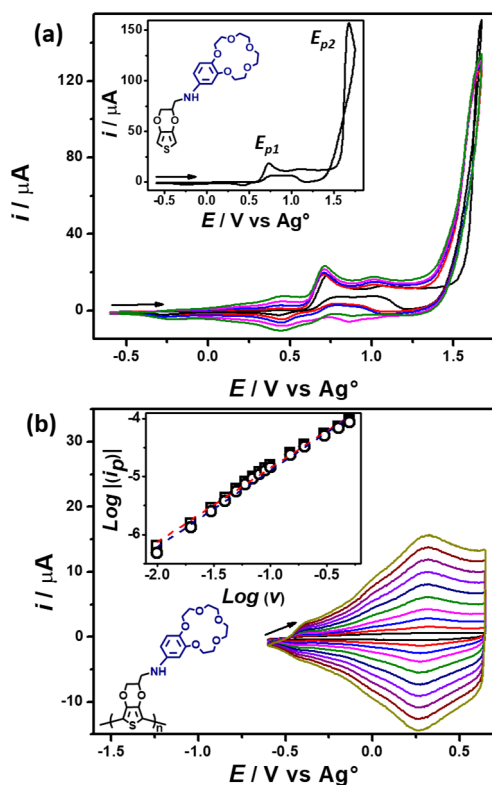


Figure 1. (a) Potentiodynamic polymerization (5 cycles) of EDOT-Crown15 0.005 M, TBAP/ACN 0.1 M, $\nu = 50 \text{ mV s}^{-1}$, $E_i = -0.6 \text{ V vs Ag}^\circ$, $E_A = 1.68 \text{ V vs Ag}^\circ$. Inset shows the potentiodynamic oxidation of the monomer. (b) Scan rate study of a PEDOT-Crown15 film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

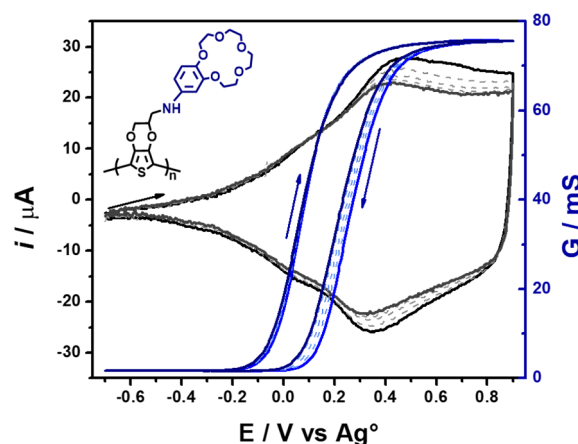


Figure 2. Simultaneous electrochemical (left axis) and conductance (right axis) study of a PEDOT-Crown15 film obtained using the conditions indicated in Figure 1a in a monomer free solution, TBAP/ACN 0.1 M, WE = Pt interdigital microarray electrode (IDMAE), CE = Pt foil, $E_i = -0.70 \text{ V vs Ag}^\circ$, $E_A = 0.9 \text{ V vs Ag}^\circ$, 5 cycles at $\nu = 50 \text{ mV s}^{-1}$ 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_A), showed two main anodic peaks (Figure S2). The first signal is a small reversible couple (peaks I_a/I_c) and the second reversible couple (peaks I_a/I_c) originates from the main redox doping process of the polymer. When a $E_A \geq 1.3 \text{ V}$ is reached, a third cathodic process was clearly observed at $E = 0.98 \text{ V}$ (I_{IIc}), 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 I_a/I_c shifted to a more anodic potential. This study was complemented by simultaneous electrochemical-conductance experiments (Figure 3) at different E_A values. At potentials below -0.20 V no conductance was observed; therefore, the reversible redox couple (peaks I_a/I_c) 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]

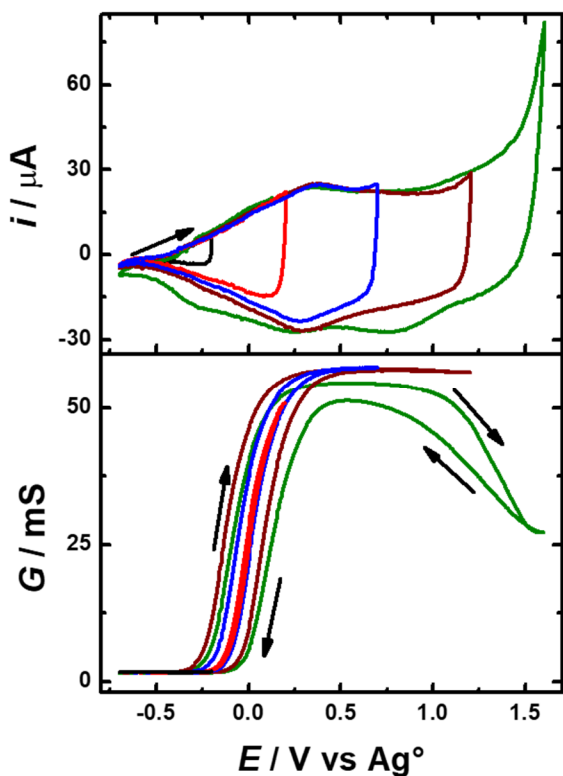


Figure 3. Simultaneous electrochemical (top curve) and conductance (bottom curve) study of a PEDOT-Crown15 film, obtained using the conditions indicated in Figure 1a in a monomer free solution using different $E_{\lambda anod}$ values, TBAP/ACN 0.1 M, WE = Pt IDMAE, CE = Pt foil, $E_i = -0.70$ V vs Ag° , $E_{\lambda 1} = -0.20$ V, $E_{\lambda 2} = 0.20$ V, $E_{\lambda 3} = 0.70$ V, $E_{\lambda 4} = 1.20$ V, $E_{\lambda 5} = 1.60$ V vs Ag° , $\nu = 50$ 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_λ 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_λ 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]

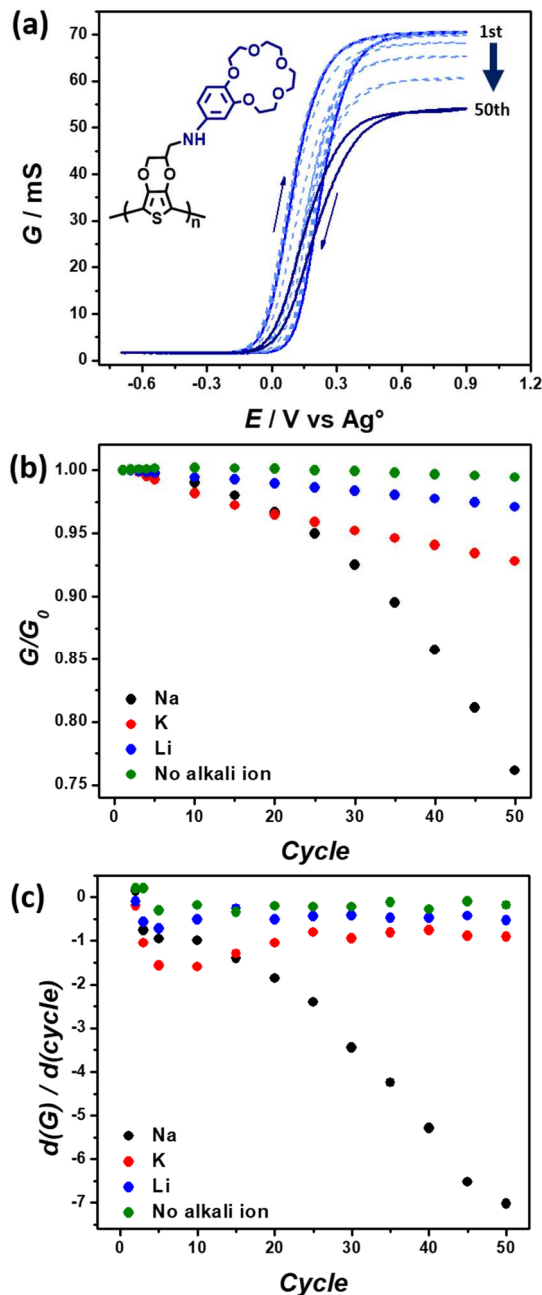


Figure 4. (a) G vs E plot of a PEDOT-Crown15 film obtained using the conditions indicated in Figure 1a in a monomer free solution of TBAP/ACN 0.1 M, NaClO₄ 0.1 mM, 50 cycles, WE = Pt IDMAE, CE = Pt foil, $E_i = -0.70$ V vs Ag° , $E_\lambda = 0.90$ V vs Ag° , $\nu = 50$ mV s⁻¹ and a constant ΔV between 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

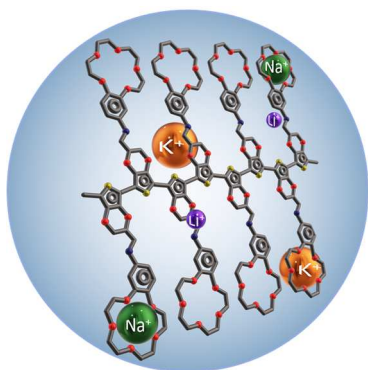
We are grateful for funding from the LabEx AMADEUS-0042 with the help of the French government "Initiative d'excellence" (to EC and JL), from ANR MULTISPOT ANR-17-CE09-0015 (to EC, AK and JL) and the IDEX/CNRS PEPS "MULTISEPT" attributed to M.R. B.A. F-U. acknowledges financial support via PAPIIT-UNAM 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

- [1] D. Aradilla, F. Estrany, F. Casellas, J. I. Iribarren, C. Alemán, *Org. Electron.* **2014**, *15*, 40-46.
- [2] T. J. Simons, M. Salsamendi, P. C. Howlett, M. Forsyth, D. R. MacFarlane, C. Pozo-Gonzalo, *ChemElectroChem* **2015**, *2*, 2071-2078.
- [3] G. Ye, J. Xu, X. Ma, Q. Zhou, D. Li, Y. Zuo, L. Lv, W. Zhou, X. Duan, *Electrochim. Acta* **2017**, *224*, 125-132.
- [4] G. Ye, D. Zhu, Q. Zhou, D. Li, Y. Zuo, X. Duan, W. Zhou, J. Xu, *ChemElectroChem* **2018**, *5*, 1130-1136.
- [5] G. Ye, Q. Zhou, D. Li, Y. Zuo, X. Duan, W. Zhou, J. Xu, *New J.Chem.* **2018**, *42*, 4824-4834.
- [6] S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324-1338.
- [7] J. G. Ibanez, M. E. Rincon, S. Gutierrez-Granados, M. Chahma, O. A. Jaramillo-Quintero, B. A. Frontana-Urbe, *Chem. Rev.* **2018**, *118*, 4731-4816.
- [8] J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.* **2008**, *108*, 329-351.
- [9] E. Stelmach, B. Kaczmarczyk, K. Maksymiuk, A. Michalska, *Talanta* **2020**, *211*, 120663.
- [10] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537-2574.
- [11] U. Lange, N. V. Roznyatovskaya, V. M. Mirsky, *Anal. Chim. Acta* **2008**, *614*, 1-26.
- [12] A. Rostami, M. S. Taylor, *Macromol. Rapid. Commun.* **2012**, *33*, 21-34
- [13] G. Salinas, B. A. Frontana-Urbe, S. Reculosa, P. Garrigue, A. Kuhn, *Anal. Chem.* **2018**, *90*, 11770-11774.
- [14] D. Demeter, C. Lar, J. Roncali, I. Grosu, *Tetrahedron Lett.* **2013**, *54*, 1460-1462.
- [15] A. Berlin, G. Zotti, S. Zecchin, G. Schiavon, *Synth. Met.* **2002**, *131*, 149-60.
- [16] D. Demeter, P. Blanchard, M. Allain, I. Grosu, J. Roncali, *J. Org. Chem.* **2007**, *72*, 5285-5290.
- [17] A. Aydogan, A. Koca, M. K. Sener, J. L. Sessler, *Org. Lett.* **2014**, *16*, 3764-3767.
- [18] S. Wustoni, C. Combe, D. Ohayon, M. H. Akhtar, I. McCulloch, S. Inal, *Adv. Funct. Mater.* **2019**, *29*, 1904403.
- [19] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481-494.
- [20] P. Manisankar, C. Vedhi, G. Selvanathan, P. Arumugam, *Microchim. Acta* **2008**, *163*, 289-295.
- [21] Z. Mousavi, J. Bobacka, A. Lewenstam, A. Ivaska, *J. Electroanal. Chem.* **2009**, *633*, 246-252.
- [22] M. Jeszke, K. Trzcinski, J. Karczewski, E. Luboch, *Electrochim. Acta* **2017**, *246*, 424-432.
- [23] E. Cloutet, J. Lang, A. Kuhn, G. Hadziioannou, M. Raoux, A. Villarroel, M. Abarkan, Nouveaux polymères et leur utilisation pour la détection de flux ioniques. Deposited December 14th, 2018, FR1873085. Conductive polymers transistor for ion channel flux analysis. December 17th, 2019.
- [24] P. Rorsman, F. M. Ashcroft, *Physiol. Rev.* **2018**, *98*, 117-214.
- [25] M. D. Fox, M. E. Raichle, *Nat. Rev. Neurosci.* **2007**, *8*, 700-711.
- [26] D. A. Koutsouras, R. Perrier, A. Villarroel-Marquez, A. Pirog, E. Pedraza, E. Cloutet, S. Renaud, M. Raoux, G. G. Malliaras, J. Lang, *Mater. Sci. Eng. C* **2017**, *81*, 84-89.
- [27] J. Rivnay, R. M. Owens, G. G. Malliaras, *Chem. Mater.* **2014**, *26*, 679-685.
- [28] J. Heinze, A. Rasche, M. Pagels, B. Geschke, *J. Phys. Chem. B* **2007**, *111*, 989-997.
- [29] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electroanal. Chem.* **1994**, *369*, 87-92.
- [30] G. Salinas, J. A. Del-Oso, P. J. Espinoza-Montero, J. Heinze, B. A. Frontana-Urbe, *Synth. Met.* **2018**, *245*, 135-143.
- [31] T. Johansson, W. Mammo, M. Svensson, M. R. Andersson O. Inganäs, *J. Mater. Chem.* **2003**, *13*, 1316-1323
- [32] M. Trznadel, M. Zagorska, M. Lapkowski, G. Louarn, S. Lefrante, A. Pron, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1387-1393

- [33] F. Wang, M. S. Wilson, R. D. Rauh, P. Schottland, J. R. Reynolds, *Macromolecules* **1999**, *32*, 4272-4278.
- [34] Z. Pomerantz, M. D. Levi, G. Salitra, R. Demadrille, A. Fisyuk, A. Zaban, D. Aurbach, A. Pron, *Phys. Chem. Chem. Phys.* **2008**, *10*, 1032-1042.
- [35] G. Salinas, B. A. Frontana-Urbe, *ChemElectroChem* **2019**, *6*, 4105-4117.
- [36] H. J. Ahonen, J. L. Ukkari, J. Kankare, *Macromolecules* **2000**, *33*, 6787-6793.
- [37] J. Heinze, H. John, M. Dietrich, P. Tschuncky, *Synth. Met.* **2001**, *119*, 49-52.
- [38] M. Pagels, J. Heinze, B. Geschke, V. Rang, *Electrochim. Acta* **2001**, *46*, 3943-3954.
- [39] A. Zykwincka, W. Domagala, B. Pilawa, M. Lapkowski, *Electrochim. Acta* **2005**, *50*, 1625-1633.
- [40] M. J. Marsella, R. J. Newland, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1995**, *117*, 9842-9848.
- [41] H.-h. Yu, A. E. Pullen, M. G. Buschel, T. M. Swager, *Angew. Chem. Int. Ed.* **2004**, *43*, 3700-3703.

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⁺.