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## **Design of potassium selective mixed ion/electron conducting polymers**

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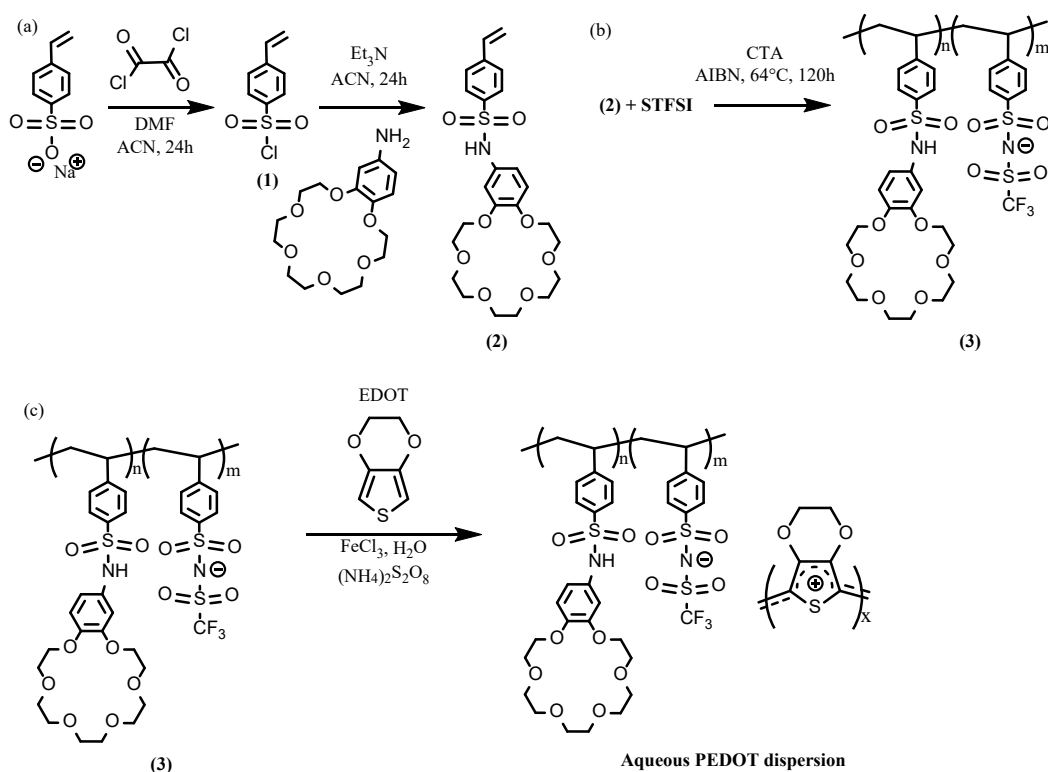
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Keywords: Mixed conducting polymers, PEDOT, crown-ether, ion sensing, coul voltammetry.

An approach providing cation selective PEDOT:polyelectrolyte mixed conductors is presented in this communication, based on the structural modification of this ambivalent (ionic and electronic conductive) polymer complex. First, an 18-crown-6 moiety was integrated into the styrene sulfonate monomer structure as a specific metal cation scavenger particularly targeting  $K^+$  vs  $Na^+$  detection. This newly functionalized monomer has been characterized by  $^1H$ -NMR titration to evaluate the ion selectivity. Aqueous PEDOT dispersion inks containing the polymeric ion-selective moieties have been designed and their electrical and electrochemical properties have been analysed. These biocompatible inks are the first proof-of-concept step towards ion selectivity in view of their interfacing with biological cells and microorganisms of interest in the field of biosensors and physiology.

Mixed conducting polymer films are materials that have gained considerable interest, due to the synergy between the polyelectrolyte, for ionic transport, and the conjugated conducting polymer, for electronic transport.<sup>[1-2]</sup> Poly-(3,4-ethylenedioxythiophene) (PEDOT),<sup>[3]</sup> stabilized by poly(styrene sulfonate) (PSS), is one of the most used mixed conducting polymer system for the development of organic electronics.<sup>[4-6]</sup> PSS has a double role in the blend; it works as the counter ion for the conducting doped PEDOT chains and stabilizes the insoluble charged PEDOT in aqueous suspensions. PEDOT:PSS dispersions have been used to obtain thin film electrodes for different applications such as solar cells (OPV), electrochromic electrodes, flexible screen devices (OLED) and organic electrochemical transistors (OECTs).<sup>[4],[7-8]</sup> In the latter, since mixed conduction occurs in the volume of these devices, the low current resistance of the films allows better electrical recordings with local signal amplification and consequently unprecedented signal detection in biology applications<sup>[9-10]</sup> pH<sup>[11]</sup> and ion monitoring.<sup>[12-13]</sup> An interesting alternative is the enhancement of ion selectivity of these materials by tuning the chemical structures of the conducting polymer or the polyelectrolyte, in order to target an analyte of interest.<sup>[14]</sup> Complex functionalized polythiophenes, with selective moieties targeting anion and cation analysis have been synthesized.<sup>[15-16]</sup> Although these mixed conducting polymers present high selectivity, the poor solubility of the monomer in water imposes the use of non-biocompatible organic solvents during the electropolymerization. A promising approach to improve biocompatibility is the functionalization of the water soluble polyelectrolyte. In this work, we present an approach to confer cation selectivity to a PEDOT:polyelectrolyte mixed conductor. A specific metal cation scavenger particularly targeting K<sup>+</sup> detection, the 18-crown-6 moiety, was integrated into the styrene sulfonate monomer through the modification of the corresponding anion. The 18-crown-6 moiety has been chosen due to its well-known affinity towards the target cation K<sup>+</sup>, based on its size matching, as well as for the commercial availability of its functional derivatives (*i.e.* aminocrown).<sup>[17]</sup> Potassium (K<sup>+</sup>) was selected as a monovalent target among all the possible choices, due to its importance in the generation and

dissipation of electrical cell signals as changes in  $K^+$  efflux from cells play a major role in cell depolarization and repolarization of membrane potentials.<sup>[18]</sup> Incorporation of the ionophore 15-crown-5 in electrodeposited PEDOT for monovalent cations analysis has been previously reported.<sup>[19]</sup> However, the electrodeposition requires the presence of different counter ions (PSS, chloride and perchlorate) to keep the electroneutrality of the charged PEDOT chains.



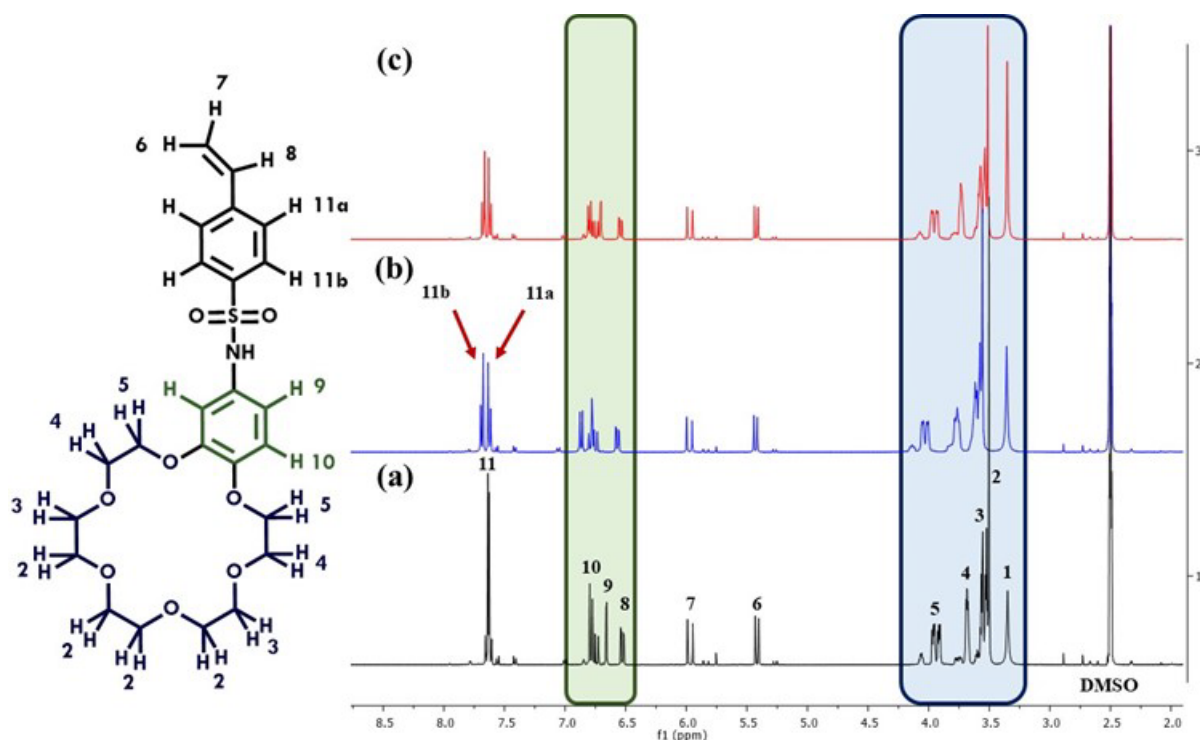
**Scheme 1.** (a) Synthetic route to obtain the 4-styrenesulfonyl(phenyl-18-crown-6) imide monomer (2); (b) RAFT copolymerization of PEDOT counterpart (3) in the presence of CTA: Chain transfer agent 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid, AIBN: Initiator 2,2'-Azobis(2-methylpropionitrile) with m: fraction of 4-styrenesulfonyl (trifluoromethylsulfonyl) imide (STFSI) and n: fraction of monomer (2). (c) Synthesis of ion-sensitive aqueous PEDOT dispersion by oxidative polymerization of EDOT in water in the presence of  $\text{FeCl}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

The newly functionalized monomer (2) was characterized by  $^1\text{H-NMR}$  titration to evaluate its ion selectivity (*i.e.*  $\text{K}^+$  vs  $\text{Na}^+$ ). Aqueous PEDOT dispersion inks containing the ion-selective moieties were then designed and their electrical and electrochemical properties have been

analyzed. Synthesis of the ion selective monomer, copolymerization of the polyelectrolyte and synthesis of the conductive inks are illustrated in Scheme 1. First, the synthesis of (2) has been achieved in a two-step reaction path. The formation of the styrenesulfonyl chloride (1) was followed by reaction with the functionalized amino phenyl-18-crown-6, to obtain the targeted monomer (2). The  $^1\text{H-NMR}$  spectrum of (2) (Figure SI-1) shows the corresponding signals for the styrene aromatic protons at 7.4 ppm and 7.7 ppm. Vinyl protons are evidenced by the presence of the signals at 5.37 ppm and 5.82 ppm. The signal of  $-\text{CH}_2\text{-O-}$  from the crown moiety is assigned at 3.75 ppm. Finally, the multiplet signal at 6.62 ppm corresponds to the aromatic protons of the crown moiety. The corresponding  $^{13}\text{C-NMR}$  spectrum of (2) also confirms the expected monomer structure (Figure SI-2).

Ion selectivity toward  $\text{K}^+$  vs.  $\text{Na}^+$  of newly designed monomer (2) was first investigated via  $^1\text{H-NMR}$  titration at various concentrations of potassium and sodium perchlorate (Figure SI-3 and Figure SI-4). Figure 1 shows for instance the chemical shifts obtained during the NMR study of monomer (2) in the presence of 2 molar equivalents in concentration of potassium and sodium perchlorate, respectively. Thus, in the presence of  $\text{K}^+$ , the signals related to the protons in the proximity of the crown ether cavity (signals 9-10 and 2-5) are shifted, as compared to the  $^1\text{H-NMR}$  spectrum of the pristine monomer (Figure 1b vs. 1a) in the absence of  $\text{K}^+$ . This behavior can be attributed to the formation of a coordination compound between the  $\text{K}^+$  and the crown ether moiety (signals 2-3 in Fig 1b vs 1a). Furthermore, the chemical shifts related to the vinyl protons (signals 6-7) were not affected by the presence of the cation. This confirms that the binding interaction with the monovalent cations occurs as expected through the crown ether moiety. However, when  $^1\text{H-NMR}$  study was performed in the presence of sodium perchlorate at the same concentration as  $\text{K}^+$ , the variation of the chemical shift was negligible (signals 2-3 in Figure 1c vs 1a). From the analysis of the chemical shift as a function of the salt concentration the binding isotherms were obtained (Figure SI-5). Using a 1:1 binding model of the experimental data, the association constants ( $K_a$ ) of (2) with both cations were evaluated ( $K_{a, \text{Na}}$

=  $121.7 \pm 6.9 \text{ M}^{-1}$  and  $K_{a,K} = 1026.2 \pm 118.3 \text{ M}^{-1}$ ). As the  $K_a$  is one order of magnitude higher for potassium in comparison to sodium, these results confirm the high selectivity of (2) for the  $\text{K}^+$  cation in accordance with the crown ether size-matching rule. Finally, saturation of the binding sites was obtained only by the addition of the potassium salt (plateau range in figure SI- 5).



**Figure 1.**  $^1\text{H}$ -RMN Spectra (DMSO- $d_6$ , 400 MHz) obtained for monomer (2) in the absence (a) and in the presence of 2 molar equivalents of (b) potassium perchlorate and (c) sodium perchlorate.

Monomer (2) was then integrated into a polyanion through copolymerization with the monomer 4-styrenesulfonyl (trifluoromethylsulfonyl) imide (STFSI). PSTFSI derivative has been reported by us as an alternative to PSS in PEDOT:PSS materials for further use in transparent organic electrodes.<sup>[8],[20]</sup> The STFSI fraction provides solubility in water, whilst the functionalized monomer (2) confers the ion-sensitive ability. It appears that the dispersity gets larger as the content in monomer (2) is increased, *i.e.* from 5 to 15% (Table 1) due to the statistical distribution of these moieties in the different polymer chains. Moreover, when the

content of the monomer (2) increases up to 40% or 50%, it became complicated to reach the targeted chain length ( $M_w$ ) (Table 1). A copolymer at a ratio of 85 wt. % of STFSI and 15 wt. % of monomer (2) has been taken as a case study from a larger copolymer family (Table 1). A polyanion P(STFSI-*co*-S(18-crown-6)) (3) with an apparent molar mass of 135 kDa was for instance obtained (Figure SI-6, PS standard calibration and DMF solvent) with quite broad distribution which can be attributed to specific interactions with SEC columns. The  $^1\text{H-NMR}$  of the P(STFSI-*co*-S(18-crown-6)) (Figure SI-7) clearly shows broadening of signals as compared to the initial monomers' spectra in accord with the polymer formation. In fact, the  $^1\text{H-NMR}$  chemical shifts from aromatic rings, polystyrene backbone and crown ether moieties could be assigned at  $\delta = 6.59\text{-}7.54\text{ppm}$ ,  $\delta = 1.44\text{ ppm}$  and  $\delta=3.53\text{-}4\text{ ppm}$  respectively.

**Table 1.** Summary of polyanion (3) synthesized, and used for the stabilization of ion-sensitive PEDOT dispersions.  $M_0$ : STFSI monomer; M: functionalized monomer (2);  $n_{M0} / n_M$ : molar ratio between both monomers;  $M_w$ : Weight Average Molar mass (kDa) of the obtained polyanions copolymers<sup>a)</sup> and  $\mathcal{D}$ : Dispersity as obtained from SEC<sup>a)</sup> analysis in DMF using PS standard calibration

Theoretical polyelectrolyte composition [ $M^{\circ}_{WT\%}$ - $M_{WT\%}$ ]	$n_{M0}/n_M$	$M_w$ [kDa] <sup>a)</sup>	$\mathcal{D}$ <sup>a)</sup>
PSS <sub>95</sub> -PS18cr6 <sub>5</sub>	13.6	112	1.3
PSTFSI <sub>90</sub> -PS18cr6 <sub>10</sub>	6.5	127	2.3
PSTFSI <sub>85</sub> -PS18cr6 <sub>15</sub>	4.1	135	2.6
PSTFSI <sub>85</sub> -PS18cr6 <sub>15</sub> (250KDa)	4.1	208	2.8
PSTFSI <sub>70</sub> -PS18cr6 <sub>30</sub>	1.7	144	2.3
PSTFSI <sub>60</sub> -PS18cr6 <sub>40</sub>	1.1	44	1.4
PSTFSI <sub>50</sub> -PS18cr6 <sub>50</sub>	0.7	96	2.3

The ion-sensitive functionalized polyelectrolyte, P(STFSI-*co*-S(18-crown-6)), was subsequently used as a stabilizer/counterpart of aqueous PEDOT dispersions during the oxidative *in-situ* polymerization of EDOT<sup>[21]</sup> in the presence of iron chloride and ammonium persulfate; see Scheme 1c). PEDOT inks were obtained after polymerization for 64h at 10°C

under inert atmosphere, then recovered through purification via ultrafiltration. As illustrative example, an initial copolymer solution (Figure SI-8a) is presented, acting as stabilizer of PEDOT favoring the complex formation and stability of the PEDOT dispersion in water when the polymerization takes place (Figure SI-8b).

Processable and stable aqueous inks were obtained, containing the hydrophobic ion-selective moiety in the polyelectrolyte chains. However, stable PEDOT inks were difficult to obtain when trying to incorporate more than 50% (in weight content) of crown ether modified styrene subunits into the copolymer. In fact, in these cases the dispersion was unstable and the polymer precipitated. Spin-coated PEDOT films presented conductivities from the  $\text{mS cm}^{-1}$  to the  $\text{S cm}^{-1}$  range ( $\sigma < 1.366 \text{ S cm}^{-1}$ ). Although this is less than what is observed for PEDOT:PSS and PEDOT:PSTFSI ( $190 \text{ S cm}^{-1}$  and  $110 \text{ S cm}^{-1}$  respectively), this conductivity range is sufficient for bioelectronics applications.

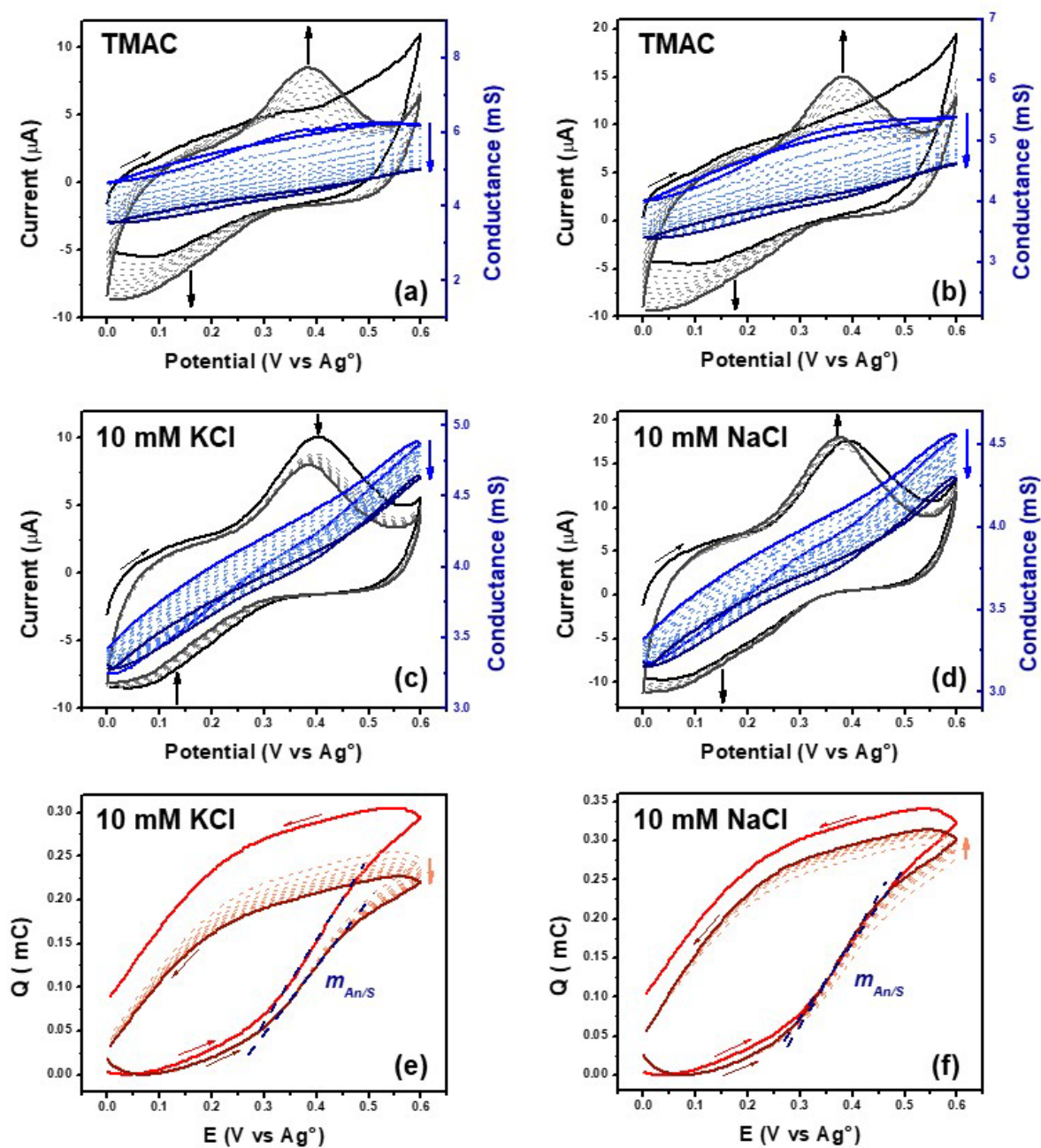
In order to evaluate the electrochemical properties of the films and provide more evidence for the occurrence of ion selectivity of these mixed conducting polymers, *in-situ* electrochemical conductance experiments were carried out.<sup>[22]</sup> The electrochemical characterization of drop casted films was evaluated in an aqueous 0.1 M tetramethyl ammonium chloride (TMAC) solution (Figure 2a and b). Initially, during the first potential sweep, peaks of current were not observed for both films (Fig. 2 (a) and (b)). Subsequently, a peak of current starts to appear, between 0.36 V and 0.38 V vs  $\text{Ag}^\circ$ . This additional anodic reaction is attributed to the oxidation of the aniline moiety attached to the crown ether group along the P(STFSI-*co*-S(18-crown-6)) polyanion. It should be noted that PEDOT:PSS and PEDOT:PSTFSI do not show any anodic peak in this range of potentials. The conductance profile of the films shows no significant variation during the potential sweep, whereas, a decrease of conductance was observed as the cycling proceeds (from  $5.44 \pm 0.75 \text{ mS}$  to  $4.61 \pm 0.37 \text{ mS}$ ). This small decrease is attributed to a conformational rearrangement of the oligomeric chains of the polymer blend and not to a limitation of charge hopping caused by the trapped positive charges formed during the aniline



oxidation.<sup>[23]</sup> In order to provide more evidence of these conformational changes, the charge-potential plots were obtained by integration of the potentiodynamic plots.<sup>[24]</sup> From the coul voltammetric response it is possible to identify changes in structural components driven by electrochemical reactions inside the conducting polymer matrix.<sup>[25-28]</sup> These charge-potential plots have been used by Otero *et al.*, by means of the electrochemically stimulated conformational relaxation model (ESCR) to explain the reversible and irreversible structural changes driven by electrochemical reactions of conducting polymers exchanging cations.<sup>[29]</sup> Since, for mixed conducting materials, composed of conducting polymers and anionic polyelectrolytes, the anion remains inserted in the conducting polymer matrix during the charge/discharge process, exchange of cations occurs. According to the ESCR model, variations in the slope values of the charge-potential plots are attributed to conformational changes of the polymer matrix.<sup>[24]</sup>

The coul voltammetric response of the films, in a 0.1 M TMAC aqueous solution (Figure SI-9a), presents in the first cycle, starting from the minimum of charge, two oxidation processes: an oxidation/shrinking ( $m_{O/S} = 0.48 \text{ mC V}^{-1}$ ) and an oxidation/compaction<sup>[30]</sup> ( $m_{O/C} = 0.78 \text{ mC V}^{-1}$ ), both caused by the release of cations from the polymer matrix. The latter is followed, at the beginning of the cathodic sweep, by some oxidation inertia and two reduction processes: a reduction/relaxation ( $m_{R/R} = 0.16 \text{ mC V}^{-1}$ ) and a reduction/swelling ( $m_{R/S} = 0.50 \text{ mC V}^{-1}$ ), caused by the insertion of tetramethyl ammonium cations. During subsequent scans, the slope value of the oxidation/shrinking and the oxidation/compaction slope decreases (Figure SI-9b,  $m_{O/S} = 0.26 \text{ mC V}^{-1}$ ,  $m_{O/C} = 0.46 \text{ mC V}^{-1}$ ), whilst a new oxidation process appears, between 0.30 V and 0.45 V vs  $\text{Ag}^\circ$ , with a concomitant increase of slope ( $m_{An/S} = 0.81 \text{ mC V}^{-1}$ ). Due to the range of potential where it appears, this is attributed to the positive charge formed during the aniline oxidation<sup>[31]</sup> that, in addition to the oxidation of PEDOT, causes a faster oxidation/shrinking process, hereafter referred to as aniline-oxidation/shrinking. Finally, during the cathodic sweep, a faster reduction/swelling process was observed ( $m_{R/S} = 0.77 \text{ mC V}^{-1}$ ). This may be attributed

to a positive “charge trapping”, which requires a faster exchange of cations and anions inside the polymer matrix to keep electroneutrality.



**Figure 2.** Simultaneous electrochemical (left axis black curves) and conductance (right axis blue curves) study of drop casted PEDOT/ P(STFSI<sub>85</sub>-co-S18cr<sub>615</sub>) films in a 0.1 M TMAC aqueous solution using  $E_{\lambda} = 0.6$  V vs  $Ag^{\circ}$ , 10 cycles,  $\nu = 10$  mV s<sup>-1</sup> and  $\Delta V$  on the WE = 10 mV, WE = Pt IDMAE, CE = Pt foil, in the absence (a and b) and in the presence of (c) 10 mM

KCl and (d) 10 mM NaCl. Charge-potential plots in the presence of (e) 10 mM KCl and (f) 10 mM NaCl.

The ion selectivity was evaluated in a 0.1 M TMAC aqueous solution in the presence of 10 mM potassium or sodium chloride (Figure 2c and d, respectively). In the presence of KCl, a continuous decrease in current of the aniline oxidation peak ( $\Delta i_{p-K} = 2.07 \mu\text{A}$ ) was observed. In contrast, in the NaCl solution, first a small decrease of the aniline oxidation peak was obtained, followed by a slow increase of the peak current ( $\Delta i_{p-Na} = 0.43 \mu\text{A}$ ). A possible explanation for this observation is that potassium ions provide an electron withdrawing effect on the aniline moiety, which causes an anodic shift of the oxidation potential of the aniline. Thus, the amount of aniline present and able to get oxidized at 0.38 V vs  $\text{Ag}^\circ$  decreases as the cycling proceeds. In the presence of sodium, the cation does not fit into the crown ether cavity and it is easier to oxidize the aniline moiety. Finally, for both cations, the conductance profile of the films shows a non-significant variation during the potential sweep, whereas a small decrease of conductance was observed ( $\Delta G_{p-K} = 0.17 \pm 0.01 \text{ mS}$  and  $\Delta G_{p-Na} = 0.28 \pm 0.11 \text{ mS}$ ). Thus, the charge hopping process is not influenced by the presence of different cations.<sup>[23]</sup>

From the charge-potential plots of the films, in the presence of KCl and NaCl (Figure 2e and f, respectively), the change of the maximum oxidation charge ( $\Delta Q$ ) after 10 potentiodynamic cycles was evaluated ( $\Delta Q_{K^+} = 88.70 \pm 1.59 \mu\text{C}$  and  $\Delta Q_{Na^+} = 48.31 \pm 5.65 \mu\text{C}$ ). As the  $\Delta Q$  for potassium is the double in comparison to sodium, these results confirm the selectivity of the films for the  $\text{K}^+$  cation in accordance with the size-matching rule. In addition, the coulometric response presents, for all the cycles, the same oxidation/reduction process as in the absence of the monovalent cations (Figure 2e and f). As the experiment proceed, changes on the slope for all the oxidation/reduction process can be observed. From the charge-potential plots (Figure 2e and f, respectively), it can be seen a higher variation of the slope for the aniline-oxidation/shrinking and the reduction/swelling process. In the presence of  $\text{K}^+$  the aniline-oxidation/shrinking and the reduction/swelling present a decrease in the slope value

( $\Delta m_{An/S\ K} = -0.19\ \text{mC V}^{-1}$ ,  $\Delta m_{R/S\ K} = -0.03\ \text{mC V}^{-1}$ ). However, in the NaCl solution, both processes show an increase in the slope value ( $\Delta m_{An/S\ Na} = 0.08\ \text{mC V}^{-1}$ ,  $\Delta m_{R/S\ Na} = 0.10\ \text{mC V}^{-1}$ ). Since potassium ions, trapped inside the crown ether cavity, are not expelled during the aniline-oxidation/shrinking process, an abrupt rearrangement of the oligomeric chains (between 1<sup>st</sup> and 2<sup>nd</sup> cycle) followed. This may be due to a slow mass insertion/repulsion of ions during the charge/discharge process.

Finally, in order to prepare for a future integration of these new ion-sensitive mixed conducting polymer complexes with biological systems, cell viability was evaluated on such PEDOT films. The quantification of the ratio between dead and total number of cells (dead + alive) grown on these films was comparable to the one in control conditions, suggesting an unchanged growth of  $\beta$  cells on the coverslips covered with films (Figure SI-10). Thus the polymer material does not exhibit a major cytotoxic effect under the conditions tested. These results open up the possibility of interfacing these ion-sensitive polymers with pancreatic  $\beta$ -cells, who play a key role in nutrient homeostasis and in diabetes.<sup>[18],[32]</sup>

In conclusion, a new approach was presented to introduce cation selectivity in a mixed conducting polymer material. A specific metal cation scavenger, particularly targeting  $\text{K}^+$ , was integrated in the PEDOT: PSTFSI complex through the polyanion counterpart by appropriate modification of the styrene subunits. We achieved synthesis and characterization of a functionalized styrene derivative with an ion-selective moiety, *i.e.* 18-crown-6, monomer (2). This monomer was used for the synthesis of a polyanion copolymer, which was then used as a substitute to PSS in the oxidative dispersion polymerization of EDOT in water. All these new compounds have been evaluated for their ability to sense  $\text{K}^+$  metal cations. First, monomer (2) showed a higher affinity for  $\text{K}^+$  compared to  $\text{Na}^+$ . Second, the PEDOT inks composed of such polyanions displayed interesting new electrical and electrochemical characteristics. By *in-situ* electrochemical conductance measurements and the correspondent charge-potential plots, the higher affinity for  $\text{K}^+$  as compared to  $\text{Na}^+$  of these PEDOT materials has been confirmed.

Finally, these materials were not cytotoxic and therefore qualify for applications such as recordings of K<sup>+</sup>-dependent electrical signals in pancreatic  $\beta$ - or other cells via the fabrication of ion selective OECTs.

### Supporting Information

Supporting Information is available from the author.

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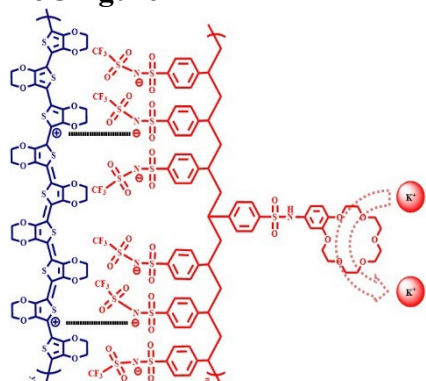
**ToC text:** Differentiating and sensing  $K^+$  cations vs  $Na^+$  through specific functionalization of mixed conducting PEDOT complexes

**Keywords** Mixed conducting polymers, PEDOT, crown-ether, ion sensing, coulombometry

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**Title** Design of potassium selective mixed ion/electron conducting polymers

**ToC figure**





## Supporting Information

### Design of potassium selective mixed ion/electron conducting polymers

*Ariana Villarroel Marquez, Gerardo Salinas, Myriam Abarkan, Maël Idir, Cyril Brochon, Georges Hadziioannou, Matthieu Raoux, Alexander Kuhn, Jochen Lang, Eric Cloutet\**

### Chemicals

4'-aminobenzo-18-crown-6; 4-styrene sulfonic acid sodium salt; 4-vinylbenzyl chloride; azobisisobutyronitrile; oxalyl chloride; potassium carbonate; sodium carbonate; triethylamine and all other products were used as received or according to manufacturer's instructions (Sigma Aldrich, France). N,N-dimethylformamide (DMF) was distilled from calcium hydride (CaH<sub>2</sub>) prior to use. Acetonitrile was distilled prior to use or dried by a solvent dryer machine (MB SPS-800, MBraun). Tetrahydrofurane was distilled from benzophenone/sodium prior to use.

### Techniques and instrumentation

*Nuclear magnetic resonance (NMR) spectroscopy:* <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra for structural characterization and titration experiments were recorded on Bruker Avance (300MHz) and Bruker Prodigy (400MHz) spectrometers, respectively, at 300K and the residual proton signal of the solvent was used as the internal standard. *Size exclusion chromatography (SEC)* was used to determine molar masses and dispersity of the copolymers synthesized. The system (Agilent GPC220HT) is equipped with UV and RI detectors and is equipped with a pre-column GF-1G-7B and two columns Asahipack GF-7MHSi (DMF, 0.1M LiBr, T=75°C, flow rate=0.6mL/min). Polystyrene standards were used for calibration. *Film Deposition:* A Brewer Science 200CBX spin-coater was used for film deposition. Substrates were cleaned with a VWR ultrasonic cleaner. UV-ozone treatment was carried out using a UVO cleaner 42A-220

from Jelight company inc. A Bruker Dektak XT-A profilometer was used to measure film thickness.

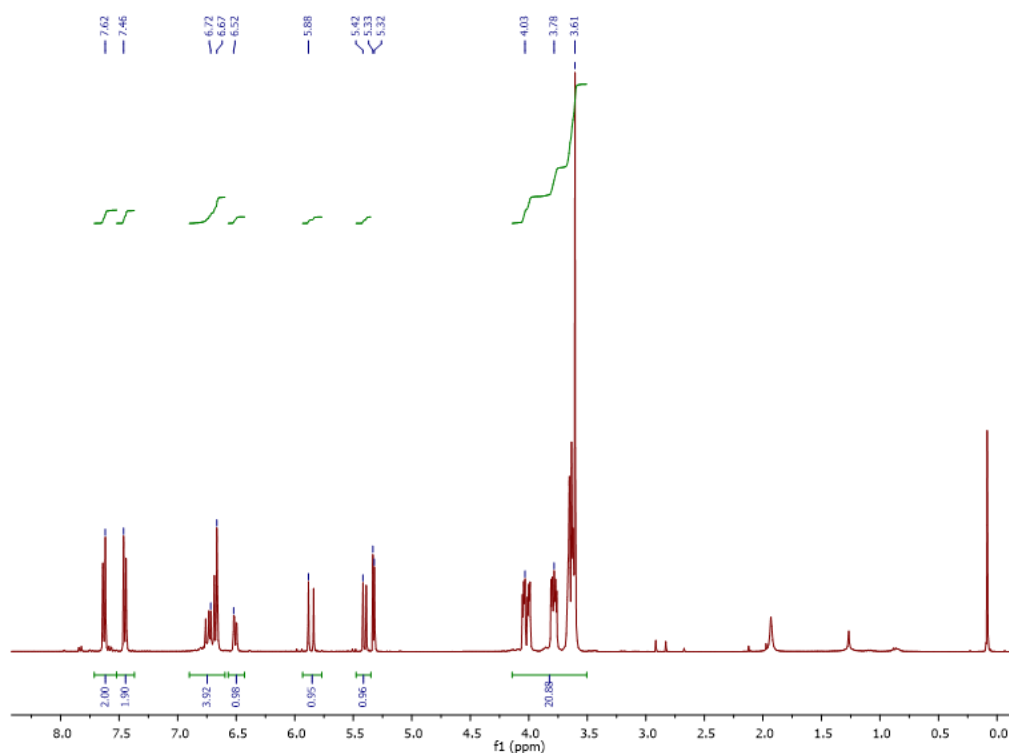
*NMR titrations:* Supramolecular titration experiments have been carried out at constant concentration of the monomer under study (host) and increasing concentrations of the salt. Spectra were recorded for every sample, observing the change in the chemical shift in the case of  $^1\text{H-NMR}$  spectroscopy. Variations in the chemical shift observed in  $^1\text{H-NMR}$  spectroscopy were fitted to a 1:1 binding model using Affinimeter<sup>[1]</sup> software and from these data the global association constants were extracted.

### **Monomer synthesis and spectrochemical characterization**

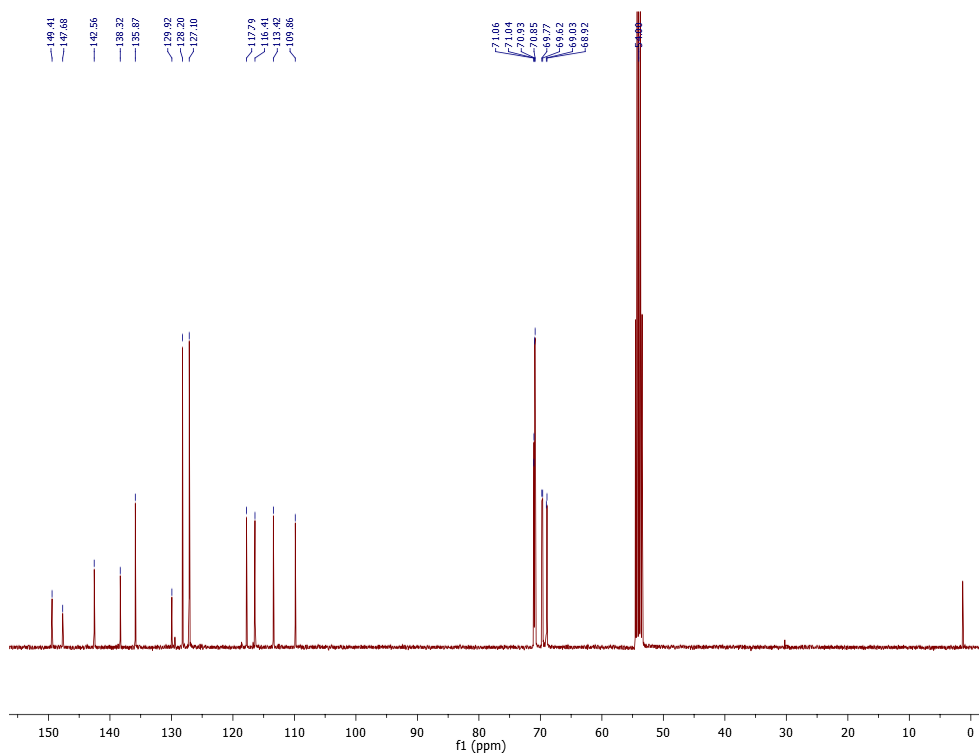
*Step 1- Formation of 4-styrenesulfonyl chloride (1):* A round bottom flask, previously flame-dried, was charged with dry and degassed acetonitrile ( $V=60$  mL). Oxalyl chloride (5.91 g, 46.6 mmol, 1.2 eq.) and DMF were added. This solution was kept under stirring at room temperature to solubilize the reagents and promote the Vilsmaier-Haack complex formation for 4 or 5 hours. Once the characteristic yellow colour of the solution became stable, 4-styrenesulfonic acid sodium salt (8.0 g, 38.8 mmol, 1.0 eq.) was added slowly to the solution under nitrogen atmosphere and at room temperature. After 24h of reaction, the precipitated salt was separated by filtration and the reaction mixture was used in the second step.

*Step 2- Synthesis of 4-styrenesulfonyl(phenyl-18-crown-6) imide (Sph18cr6SI) (2):* In a second flame-dried round bottom flask containing dry and degassed acetonitrile ( $V=50$  mL), triethylamine (4.29 g, 30.2 mmol, 3 eq.) and 4'-aminobenzo-18-crown-6 (3.00 g, 10.1 mmol, 1 eq.) were added and stirred for one hour. During this time, the 4-styrenesulfonyl chloride/acetonitrile solution (formed during Step 1) was cooled at  $0\text{ }^\circ\text{C}$ . Subsequently, the trifluorosulfonamide solution was added in vacuum atmosphere to the former. Finally, the mixture was allowed to warm up to room temperature and the reaction was kept running under

stirring for 16h. Purification was done firstly by removing under low pressure the solvent mixture and solubilizing the monomer in dichloromethane. The product was obtained by extraction with potassium carbonate and a subsequent wash with 1M hydrochloric acid solution. Solvent was removed under low pressure and after drying overnight at 45°C under vacuum, the product was recovered as a brown solid product. (yield=54%). Scheme 1. <sup>1</sup>H-NMR (400 MHz; d-DMSO; 298K): δ(ppm)= 7.79 (d, 2H); 7.61 (d, 2H); 6.80 -6.52(q, s, dd, 4H); 5.99-5.94 (d, 1H); 5.48-5.36 (d, 1H); 3.98 – 3.50 (m, 20H). <sup>13</sup>C-NMR (75 MHz; d-DMSO; 298K): δ(ppm)= 147.9; 145.46; 141.1; 138.4; 135.2; 130.54; 127.9; 127.15; 126.84; 126.63; 117.76; 113.93; 113.14; 107.7; 68.82; 69.74-67.97. m/z (ESI-HRMS) 516.17 ([MNa<sup>+</sup>] C<sub>24</sub>H<sub>31</sub>NO<sub>8</sub>SNa requires 516.57).

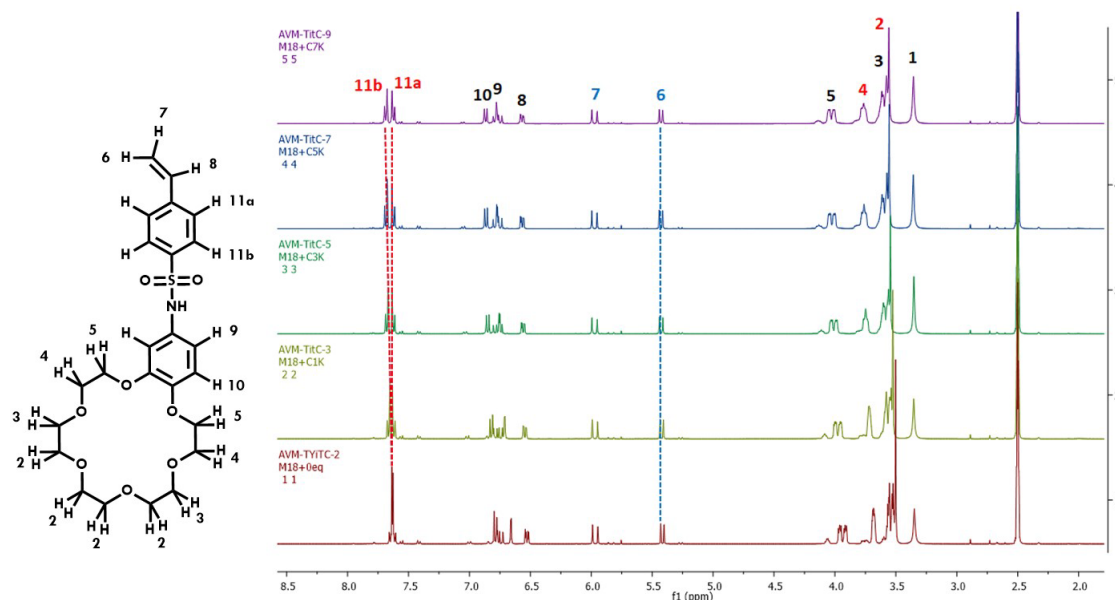


**S1:** <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) of 4-styrenesulfonyl(phenyl-18-crown-6) imide (2).

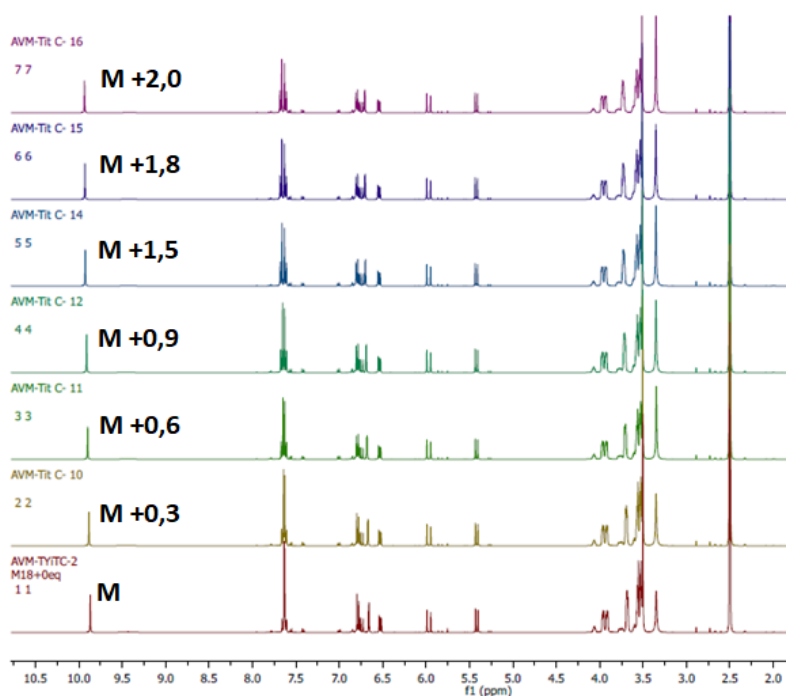


**S2**  $^{13}\text{C}$ -NMR ( $\text{CD}_2\text{Cl}_2$ , 150 MHz) of 4-styrenesulfonyl(phenyl-18-crown-6) imide (2)

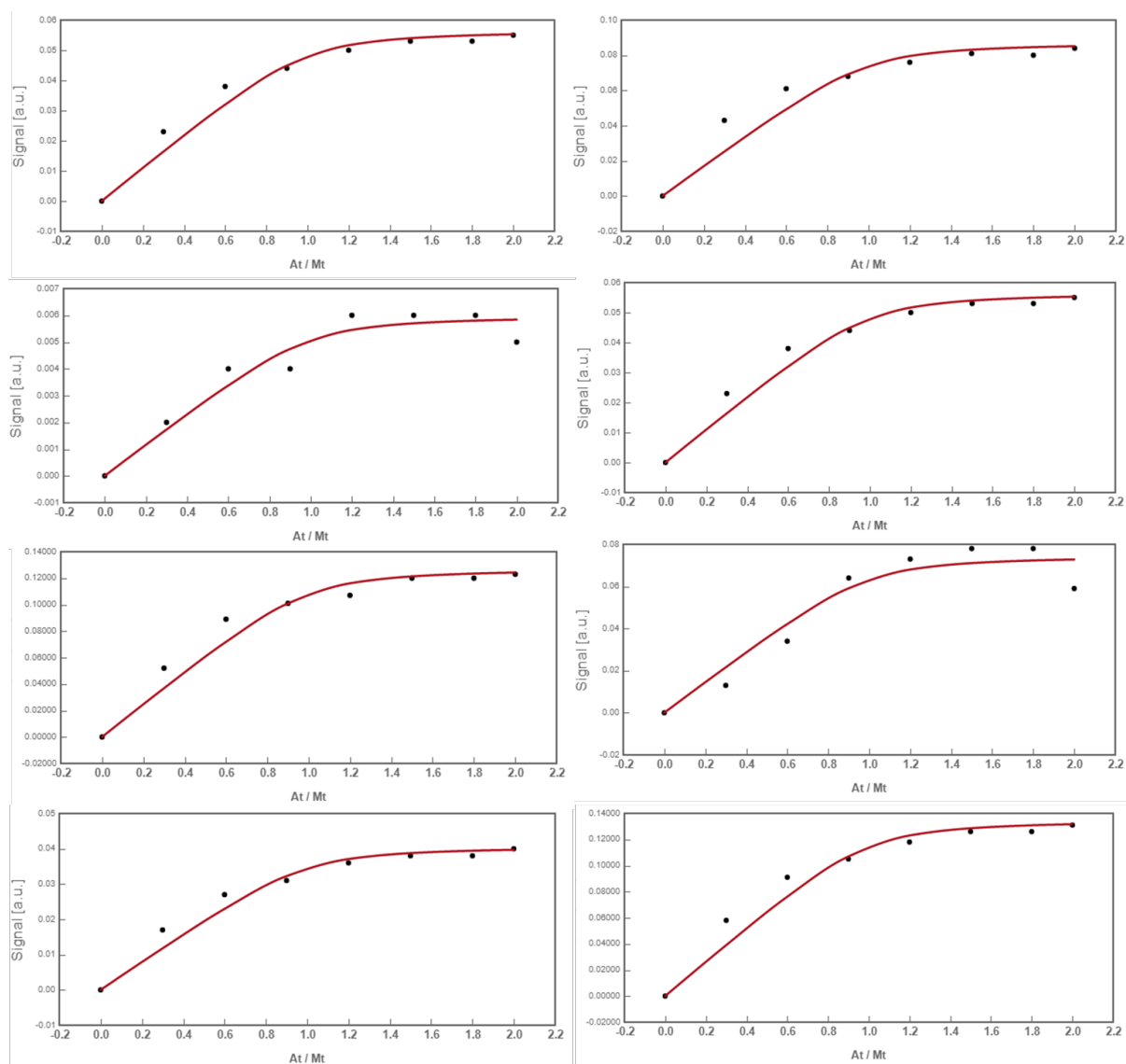
*Binding ability evaluation by  $^1\text{H}$ -NMR titration of monomer (2)*



**S3:**  $^1\text{H}$ -RMN Spectrum (DMSO, 400 MHz) obtained for the titration of the monomer (2) under variable concentrations (from 0 to 2 molar equivalents) of potassium perchlorate.

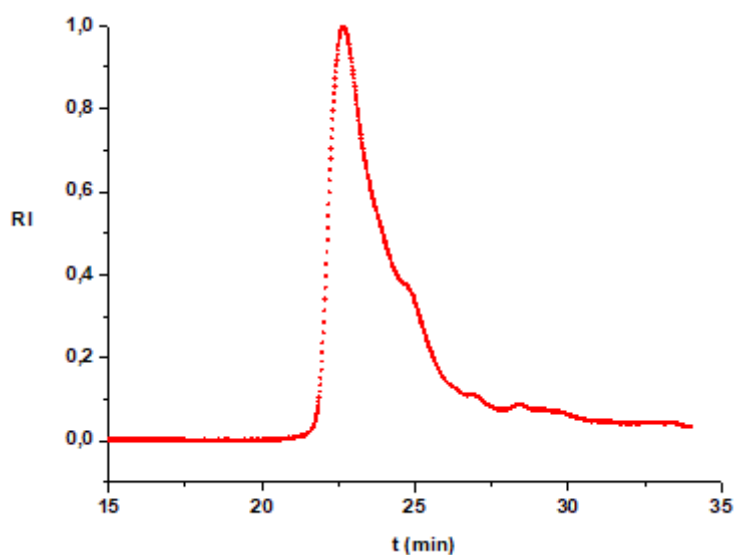


**S4:** <sup>1</sup>H-RMN Spectrum (DMSO, 400 MHz) obtained for the titration of the monomer (2) under variable concentrations (from 0 to 2 molar equivalents) of sodium perchlorate.

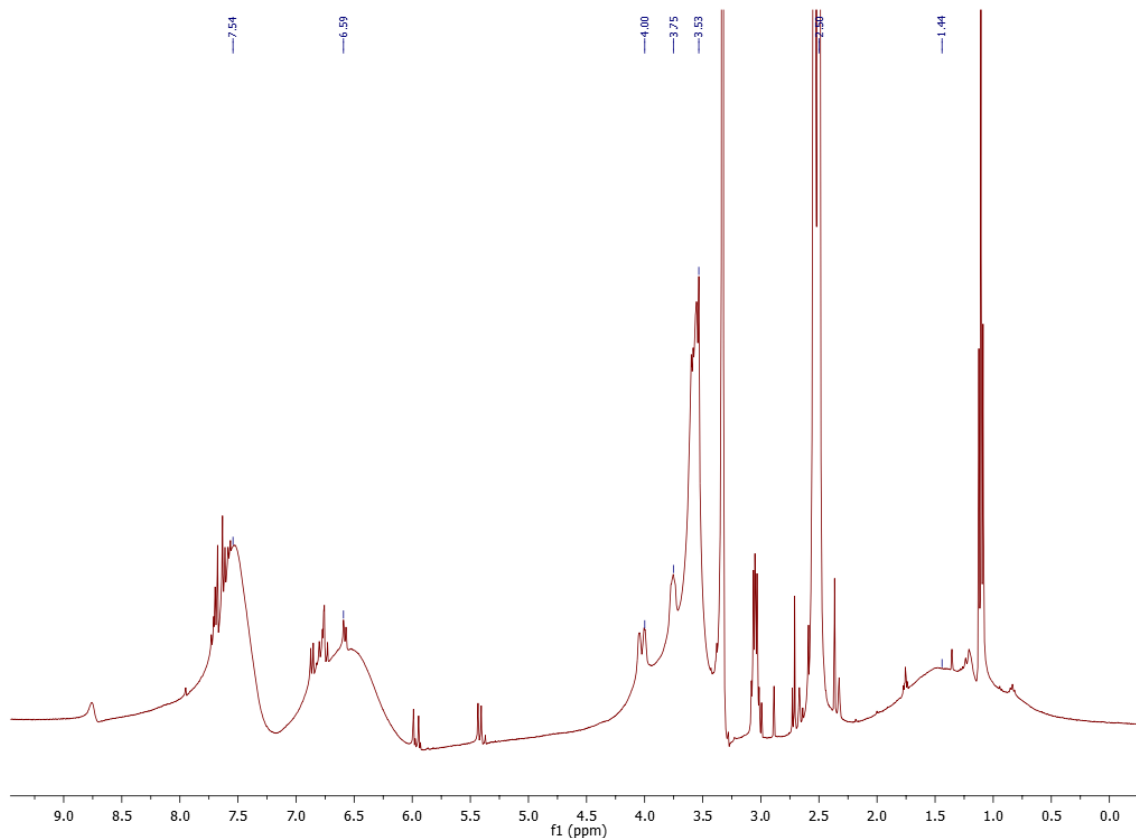


**S5.** Binding isotherms and fitting to a 1:1 binding model of the experimental data from  $^1\text{H}$ -NMR titration of the monomer (2). Scattered dots: Experimental data obtained from the difference in NMR shift (ppm) with respect to initial monomer spectra (y-axis – “Signal”) vs the increasing concentration of  $\text{KClO}_4$ , for a constant monomer concentration,  $M_t$  (x-axis – “At/  $M_t$ ”). Red curves: Fitting to the different binding isotherms with a 1:1 binding model to obtain the global binding constant ( $K_A$ ).

*Radical polymerization and Copolymerization (GENERAL PROCEDURE):* The copolymers between STFSI monomer and ion-sensitive styrene monomer (2) were synthesized by reversible addition-fragmentation chain-transfer (RAFT) radical polymerization by mixing, according to the targeted molar mass and composition, the proper quantity of the STFSI/(2) monomers, chain transfer agent and azobisisobutyronitrile (AIBN) in DMF. After several freeze-thaw cycles, the mixture was left to polymerize at 64°C from several hours to few weeks, depending on the molar mass that should be obtained. The polymer was ready after precipitation in tetrahydrofuran (THF) or the adequate solvent mixture, filtration, washing with THF and drying in vacuum oven at 65°C for at least one day.



**S6:** Size exclusion chromatogram (SEC) of a copolymer between STFSI (wt.% = 85) and monomer (2) (wt.% = 15) showing a main population of 135 kDa. Conditions: Polystyrene standard calibration. DMF, LiBr, 70°C.

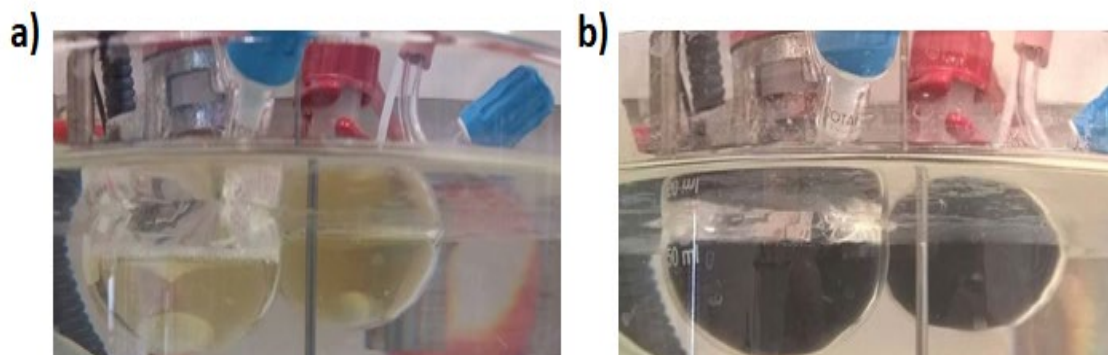


**S7:** <sup>1</sup>H-RMN Spectrum (d<sub>6</sub>-DMSO, 400 MHz) of a copolymer between STFSI (wt.% = 85) and monomer (2) (wt.% = 15).

*Conductive ion sensitive aqueous PEDOT dispersions:* Solutions of iron chloride (III) (0.036 mg, 0.22 mmol), ammonium persulfate (0.161 g, 0.71 mmol) and the styrene-based copolymer (0.210 g) were prepared in individual aqueous solutions and stirred during 5h previous to their use. Afterwards, the polyelectrolyte solution was transferred to the reactor and EDOT monomer was added (0.038 mL, 0.36 mmol) keeping under nitrogen flow at 10°C for 30 min. Addition of the oxidant solutions composed of iron chloride and ammonium persulfate starts the polymerization. The reaction is kept running under static inert atmosphere during 64h. Purification has been done by ultrafiltration, washing firstly with 1M hydrochloric acid (150mL). After stirring for two more hours with a 50% content of the previous used acid solution, a last washing with water was performed. Concentrations were adjusted to about 1 weight % of content after filtration, in correlation with a calibration curve obtained by UV-Vis

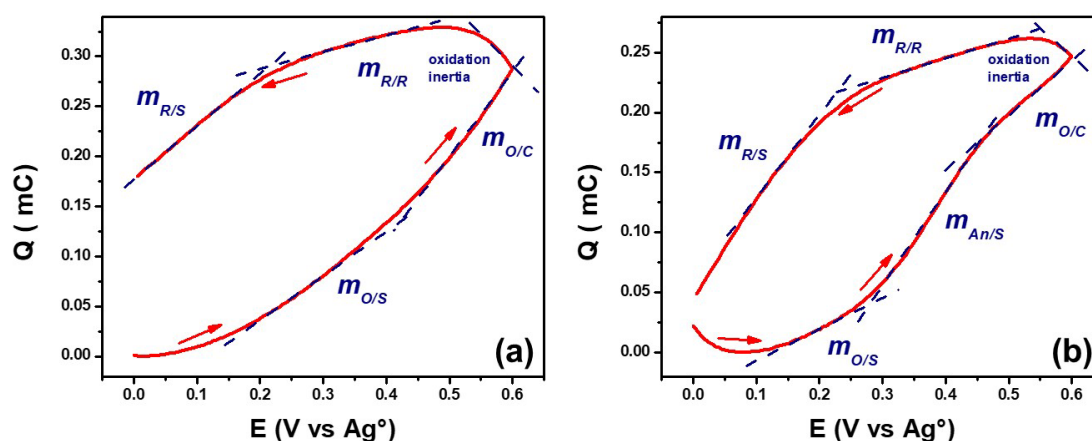


absorption spectroscopy analysis. Inks were stored protected from light at constant temperature and under stirring.



**S8:** Aqueous dispersion formation of the ion-sensitive PEDOT based ink: a) Before the addition of the oxidants, brownish polyelectrolyte solution; b) After addition of the oxidants, formation of the PEDOT based ink.

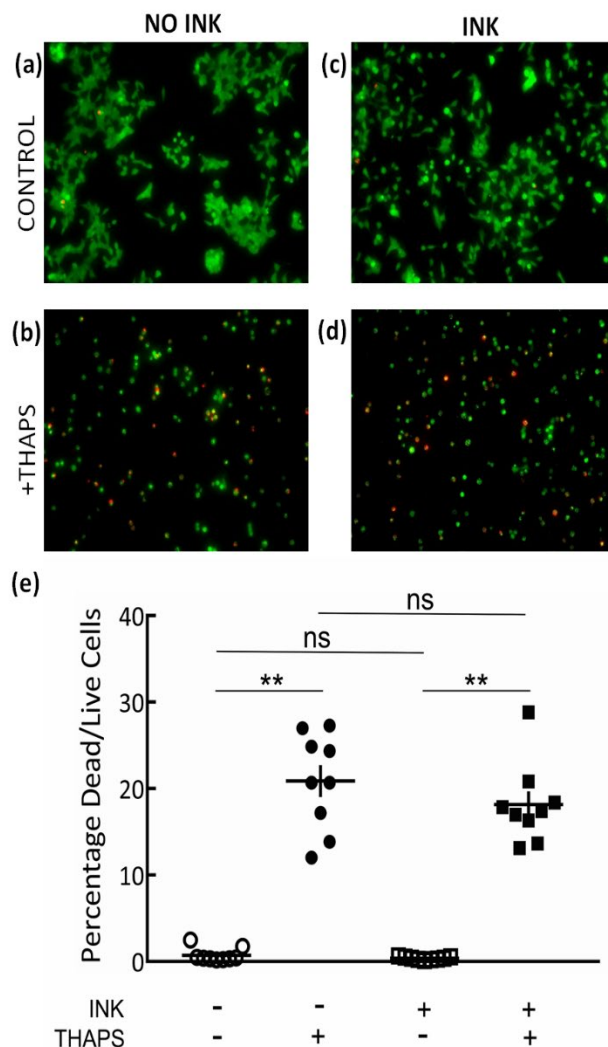
*In-situ electrochemical-conductance measurements:* *In-situ* electrochemical-conductance measurements were carried out using a two potentiostat system, specially built for this application. As working electrodes, DropSens interdigital microarrange electrodes (IDMAE), featuring separated Pt bands (10  $\mu\text{m}$ ) deposited on it, were used. A three-electrode electrochemical cell fitted with a Pt foil counter electrode separated approximately 0.5 cm from the working electrode (parallel and of the same size as the working electrode), a pseudo-reference electrode (Ag wire) and the IDMAE were used for the studies. A constant potential difference of 10 mV provided by one potentiostat was applied between the IDMAE branches to generate the drain current that circulates through the polymer during conductance determinations. The conductance of the dropcasted films was measured in real time during the cyclic voltammetry experiment in an aqueous 0.1 M tetramethyl ammonium chloride (TMAC) solution at 25 °C. Conductance was calculated according to Ohm's Law, which is directly related with specific conductivity. More details about this technique and examples of the use of conductance measurements in conducting polymers can be found elsewhere in the literature<sup>[2]</sup>



**S9:** Charge-potential plots of a drop-casted film in a 0.1 M TMAC aqueous solution obtained from the integration of the (a) 1st and (b) 10th potentiodynamic scan.

*Cytotoxicity evaluation: direct evaluation and apoptosis test:* Determination of the rate of programmed cell death was performed by the use of a LIVE/DEAD Kit (ThermoFisher Scientific, USA). This sensitive two-colour fluorescence cell viability assay allows discrimination between alive and dead cells with two probes that measure established parameters of cytotoxicity and cell viability, i.e. intracellular esterase activity and plasma membrane integrity. Polymer films were deposited on coverslips (18 mm diameter). Prior to use, they were washed (by sonication in acetone, ethanol and isopropanol baths), air dried and activated (surface plasma cleaning, 15min). Films were formed by spin-coating of the ink (previously formulated) at the optimal speed to obtain maximal film coverage (generally for 30 s at 500-800 rpm, followed by a cycle at 1200-1800 rpm). Coated coverslips were cured at 50°C for 10 min followed by heating to 120°C for one hour. After cooling, films were placed in a 12 well multiwell that had been sterilized by UV treatment ( $\lambda=254$  nm, 30 min) prior to cell culture. Before adding cells in the medium, coverslips were rinsed with 1.5 ml/well of PBS+/+ buffer (composition in mM: KCl 2.67;  $\text{KH}_2\text{PO}_4$  1.67; NaCl 138,  $\text{Na}_2\text{PO}_4$  8,  $\text{CaCl}_2$  1.8,  $\text{MgCl}_2$  1.0) and dried overnight. 50,000 INS-1 clonal  $\beta$ -cells were added per well and cultured as described for

3 days.<sup>[3]</sup> Coverslips were either visualized and documented by phase contrast microscopy or further processed for apoptosis measurements. In the latter case, cell media were replaced by fresh media with or without thapsigargin (0.1  $\mu$ M, as positive control) for 6h prior to analysis. Imaging was used after de-freeze. The Live/Dead cell kit was used according to the manufacturer and 150  $\mu$ L of final solution were added per coverslip for 15 min at 37°C followed by imaging. For each data point three coverslips were examined, experiments were repeated independently nine times and areas of fluorescence calculated by ImageJ.<sup>[4]</sup> Statistical analysis was performed using GraphPad Prism7.



**Figure S10.** Cytotoxicity study of the ion sensitive inks: Clonal  $\beta$  cells (INS832-13) cultured for 72 h on (a, c) control coverslips or coverslips covered with the ink studied (PEDOT: PSTFSI-85-co-P(2)-15 with 18-crown-6 moieties). (b, d) Apoptosis induced by thapsigargin

(6h, 10  $\mu$ M) on control coverslips or coverslips covered with the same ink. All micrographs present merged images (green: FYTC filter, live cells; red: YFP filter, dead cells). (e): quantitative assessment of apoptosis. Given are individual data points, means and SEM; N= 9. \*\*,  $p < 0.001$ ; ns, not significant (Kruskal Wallis and Dunne post-hoc test)

## References

- [1] Data fitting was performed with the AFFINImeter server (<http://www.affinimeter.com>). Unless stated otherwise the experimental data were fitted using a simple 1:1 binding model.
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