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# An electroactive polymeric material and its voltammetric response towards alkali metal cations in neat water

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Dedicated to Professor Metin Balci on the occasion of his 60th birthday

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## Abstract

The syntheses and characterization of a unique system based on thiophene, pyrrole and benzo-15-crown-5 (SNS-Crown) and its corresponding polymer (PSNS-Crown) are reported. Furthermore, selective, clear and reversible voltammetric responses of the conjugated polymer (PSNS-Crown) film towards the alkali series $Li^+$, $Na^+$ and $K^+$ in both neat water and organic media (ethanol) are described.

*Keywords:* Chemosensor; Ion sensing; Crown ethers; Polythiophene; Polypyrrole

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Redox-switched binding is well established and enables the strength of a binding interaction to be controlled by oxidation or reduction.[1–4] In particular, the binding of guest molecules at conducting polymers bearing suitable recognizing groups allows modulating and switching the transport behaviour of the conjugated chains if the recognition process is reversible. This principle may be exploited in iono-electronics devices in which the complexation/decomplexation process results in an externally induced ON/OFF switching. Considerable effort has been devoted to that end where polythiophenes are substituted with crown ethers and/or polyether chains to design modified electrodes for electrochemical and bioelectrochemical sensors.[5–10] However, polypyrroles functionalized with crown ethers for molecular recognition have been much less exploited due to the difficulties in their synthesis.[11,12] Furthermore, most of the polymers with crown ether appendages have solubility problems and water incompatibility. Herein, we report the synthesis of an electroactive polymeric material and its voltammetric response towards alkali metal cations ($Li^+$, $Na^+$ and $K^+$) in both neat (with no organic solvent and/or additive) water and ethanol. Our inspiration came not only from previous reports,[11,12] but also from the fact that SNS-based polymers[13,14] can be amplified to create viable materials.

The synthesis of monomer, SNS-Crown, was carried out via a two-step reaction sequence: acylation of thiophene with succinyl dichloride to give 1,4-di(thien-2-yl)butane-1,4-dione[15] followed by Paal–Knorr reaction of the dione with 4-amino-benzo-15-crown-5 (see Supplementary data). Anodic oxidation of SNS-Crown in 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$)/ethanol solution gave a single irreversible peak at 0.68 V (vs Ag/AgCl). During the second scan, a reversible redox couple ($E_{pa} = 0.56$ V, $E_{pc} = 0.39$ V) was observed and the current intensity of this peak increased after each successive cycle (Fig. 1a) which clearly indicated the formation of an electroactive polymer (PSNS-Crown) on the working electrode surface (Scheme 1). PSNS-Crown was soluble in acetone, DMSO, DMF, propylene chloride and *N*-methyl-2-pyrolidone.

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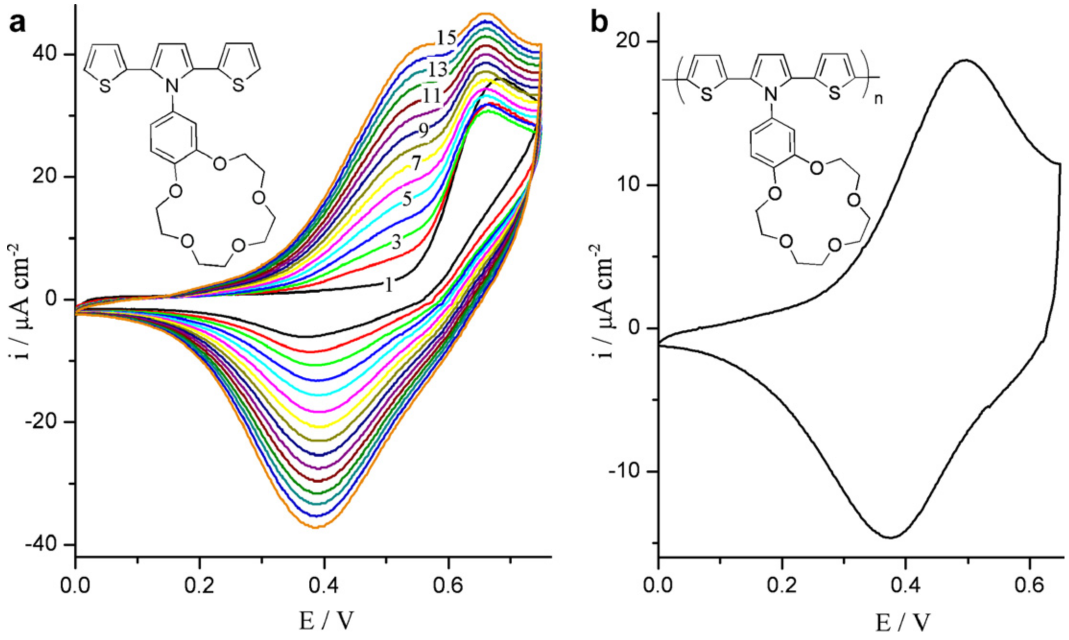
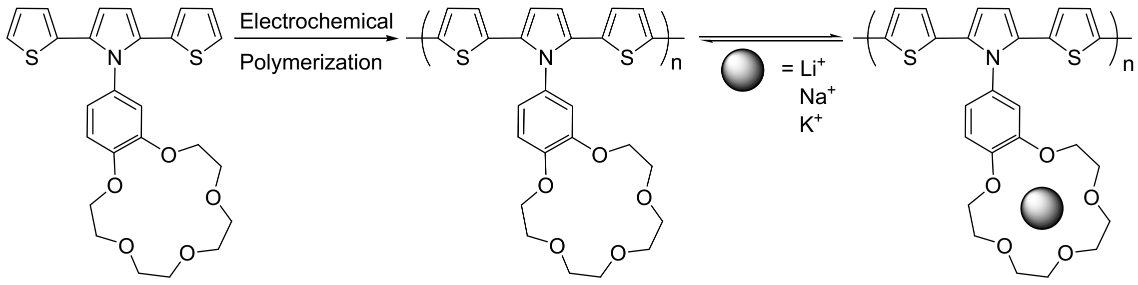


Fig. 1. (a) Repeated scan electropolymerization of $1.0 \times 10^{-3}$ M SNS-Crown and (b) cyclic voltammogram of PSNS-Crown film using an ITO electrode at 100 mV/s in 0.1 M $TBAClO_4$/ethanol solution.



**SNS-Crown** **PSNS-Crown** **PSNS-Crown-M**

Scheme 1. Electrochemical polymerization of SNS-Crown and ion recognition by the PSNS-Crown film to give PSNS-Crown-M.

We first examined the redox behaviour of the polymer film by cyclic voltammetry. The polymer film exhibited a single and well-defined reversible redox couple ($E_{pa} = 0.50$ V, $E_{pc} = 0.38$ V vs Ag/AgCl) when the potential was scanned between 0.0 V and 0.7 V (Fig. 1b).

Next we investigated the changes in the redox behaviour of the PSNS-Crown film in the presence of alkali cations: $Li^+$, $Na^+$ and $K^+$ in neat water. The PSNS-Crown film was cycled in the presence of alkali cations: $Li^+$, $Na^+$ and $K^+$ as perchlorate salts in neat water. We were delighted to note that the anodic peak due to polymer oxidation was shifted negatively, and reversibly in water, and stabilized after two scans (Fig. 2).

Similar results were obtained when ethanol was used as the solvent instead of water. Table 1 summarizes the shifts of the anodic peak of PSNS-Crown when replacing $TBA^+$ by $Li^+$, $Na^+$ and $K^+$. The observed negative shifts in the case of PSNS-Crown can be attributed to the formation of PSNS-Crown-M after interaction of the ions with the macrocyclic appendage of the conjugated polymer. It was also evident that the observed shifts were in agreement with the well-established size-fit concept in terms of cavity size of benzo-15-crown-5 (1.7–2.2 Å). Since the diffusion and the mobility of $K^+$ into the polymer would be more difficult when compared to $Li^+$ or $Na^+$ due to ionic radius, a smaller shift in the oxidation potential was observed (Table 1). However, the presence of $Na^+$ the size of which matched well with the size of the crown ether caused the largest shift. On the other hand, the observed shifts might also be attributed to a conformational change in the polymeric structure after complexation with the cations to give PSNS-Crown-M.

The voltammetric responses are quite good when compared to known polypyrroles containing crown ether appendages[11,12] which either showed no recognition or only minor responses to alkali cations in water. Conse-

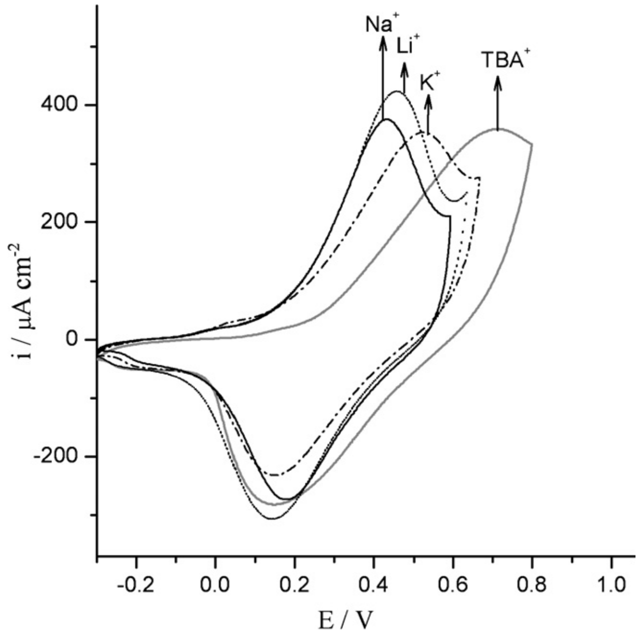


Fig. 2. Cyclic voltammograms of PSNS-Crown film (13 mC/cm$^2$) using an ITO electrode in 0.1 M $TBAClO_4$/ethanol and successive voltammograms of the same film in separate solutions of 0.1 M $LiClO_4$, $NaClO_4$ and $KClO_4$/water at a scan rate of 100 mV/s for the second run.

quently, it can be stated that PSNS-Crown is an efficient sensor for these cations since it gives significant reversible shifts in neat water as well as in organic media.

As an aside, we also examined changes in the oxidation potential of PSNS-Crown versus ion concentration ($Li^+$ and $Na^+$) by cyclic voltammetry. Addition of ions (as $LiClO_4$ and $NaClO_4$) to PSNS-Crown film in $TBAClO_4$/ethanol solution resulted in a decrease in the current intensity of the polymer film (Fig. 3a). It was evident that the plot of concentration versus anodic peak current could be used to determine the ion concentration in solution (Fig. 3b).

Table 1
Alkali cation diameters[16] and the shifts of the anodic peaks of PSNS-Crown film with respect to $TBA^+$ after addition of alkali cations in water and ethanol

| M | Diameter (Å) | In water | | In ethanol | |
|---|---|---|---|---|---|
| | | $\Delta E_{pa}$ (mV) | $\Delta E_{pc}$ (mV) | $\Delta E_{pa}$ (mV) | $\Delta E_{pc}$ (mV) |
| $Li^+$ | 1.36 | −252 | −3 | −87 | −25 |
| $Na^+$ | 1.94 | −279 | 36 | −112 | 18 |
| $K^+$ | 2.66 | −186 | 3 | >300 | 5 |

It is noteworthy that the selective voltammetric response of PSNS-Crown film in neat water towards alkali cations; $Li^+$, $Na^+$ and $K^+$, reveals the transduction of chemical information into an electrical response which now paves the way for voltammetric determination of the above ions in water. The polymeric sensor keeps working even after prolonged standing under ambient conditions.

To conclude, the synthesis of an electroactive polymeric material and its clear and reversible voltammetric response towards alkali metal cations ($Li^+$, $Na^+$ and $K^+$) in both neat water and ethanol were described. The present study circumvents the aforementioned problems through a rational design of a processable hybrid material where the stability of polythiophene, conductivity of polypyrrole and selectivity of benzo-15-crown-5 towards alkali cations are combined. Work to design and synthesize of other polymeric sensors is currently underway in our laboratories.

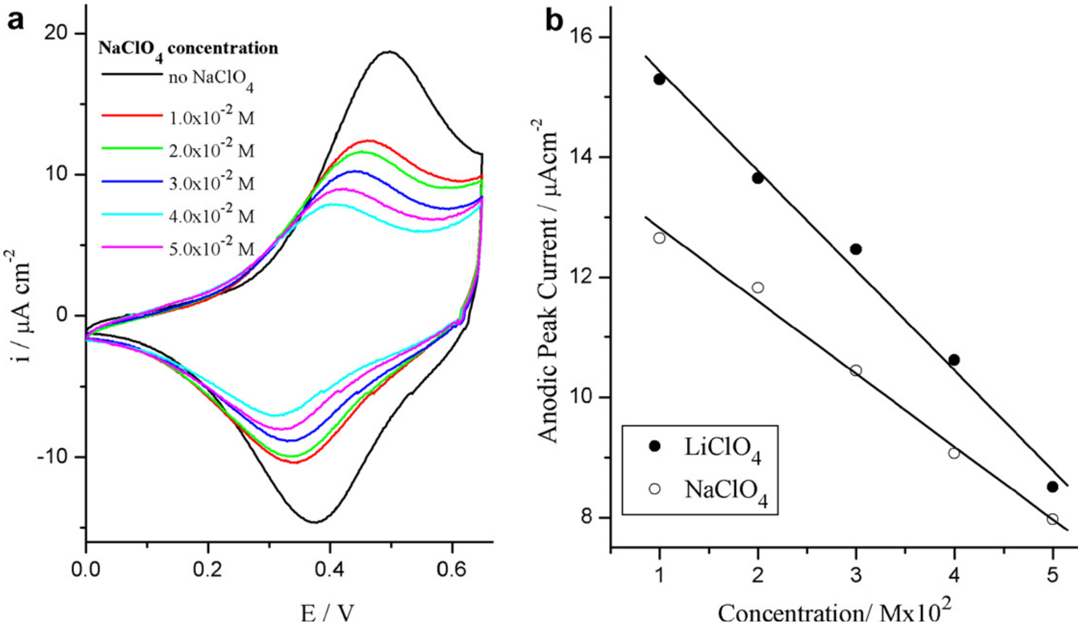


Fig. 3. (a) Cyclic voltammograms of PSNS-Crown on ITO in ethanol solution containing 0.1 M $TBAClO_4$ on the addition of alkali metal salts at a scan rate of 50 mV/s and (b) anodic peak currents of PSNS-Crown as a function of concentration.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.139.

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