

Cation Recognition Properties of Polypyrrole 3-Substituted by Azacrown Ethers

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The synthesis of new functionalized conducting polypyrroles bearing azacrown ethers at C-3 is described; these show selective cation binding on voltammetric cycling in organic media.

The functionalization of polypyrrole has been studied for many years through the covalent bonding of various active groups on the nitrogen atom of the pyrrole nucleus, owing to the easy chemical access to such a modified monomer. Thus, the N-substitution of pyrrole with organometallic complexes derived from porphyrins,¹ cyclam² or polypyridine³ has led to

polypyrroles with promising modified electrode behaviour. However, it has been also largely observed that poly(N-substituted pyrroles) possess extremely low conductivity, of the order of 10^{-4} S cm⁻¹ or less, indicating an important loss of conjugation, which strongly limits the potential interest of these polymers. On the other hand, it has been clearly shown

by us and others that the equivalent 3-substituted pyrroles give rise to highly conducting polymer films, with highly reversible electrochemical behaviour.^{4,5} Although the synthesis of 3-substituted polypyrroles is not as straightforward as that of *N*-substituted ones, it falls readily into the scope of synthetic chemistry and furthermore remains a real challenge. In this regard, the amidification of the carboxylic group of pyrrole-3-acetic acid with optically active amino acids has proved very fruitful for the synthesis of new conducting polypyrrole films exhibiting circular dichroism^{5d} as well as adjustable hydrophilic properties.^{5f} As recently reviewed,⁶ the electrochemical recognition of ions by macrocyclic receptors that contain an electrochemical responsive signalling function in close proximity to a host binding site is also an active research field. To this end, azacrown ethers, which are known for their selective complexing properties towards alkaline cations,⁷ can be grafted onto polypyrrole following the same synthetic scheme. We present here new functionalized polypyrroles substituted at the 3-position of the aromatic nucleus by such crown ethers, which are designed for molecular recognition toward cations.

The monomer synthesis involves the condensation of pyrrole-3-acetic acid⁸ and azacrown ether,⁹ following a known procedure.^{5f} After cooling the reactants in dichloromethane to 5 °C, *N,N'*-dicyclohexylcarbodiimide (DCC) was added and the obtained mixture allowed to warm-up and maintained under stirring for 15 h at room temp. Acetic acid was then added to destroy the DCC excess. The combined organic extracts were washed with water, dried (MgSO₄) and concentrated to obtain a crude product which, eluted on a silica gel column, to afford pure crystals after solvent evaporation: *N*-pyrrol-3-ylacetyl monoaza 12-crown-4 **1**; chemical yield, 66%; m.p. 97–98 °C; NMR (CDCl₃) δ 8.38 (s, 1 H); 6.62 (m, 2H), 6.1 (m, 1 H), 3.2–3.55 (m, 16 H) and 2.65 (s, 2 H); and *N*-pyrrol-3-ylacetyl monoaza 18-crown-6 **2**; chemical yield 70%; m.p. 104–106 °C; NMR (CDCl₃) δ 8.68 (s, 1 H), 6.62 (m, 2 H), 6.1 (m, 1 H), 3.4–3.6 (m, 24 H) and 2.75 (s, 2 H).

Electrochemical experiments have been performed in a one-compartment cell with a platinum disk (0.07 cm²) working electrode, the solutions being degassed by argon bubbling. Molecules **1** and **2** electropolymerize under the same conditions as pyrrole itself, in a 0.1 mol dm⁻³ monomer and 0.5 mol dm⁻³ LiClO₄ acetonitrile solution at 0.9 V (vs. SCE), leading to a black film on the anode. The electrochemical characterization of these films in acetonitrile 0.1 mol dm⁻³ LiClO₄ shows voltammetric behaviour very similar to that of unsubstituted polypyrrole in organic electrolyte: *E*₀ = 0.03 and 0.10 V (vs SCE) for, respectively, poly(**1**) and poly(**2**). The coulombic charge exchanged in the as-obtained redox systems corresponds to one positive charge for four pyrrole units in the polymer chains, assuming 100% polymerization yield (Fig. 1). It must be pointed out that fairly thick films, of some tenths of μm, can be obtained, which agrees with the relatively high conductivity determined on doped films, of ca. 1 S cm⁻¹. These results confirm the potential interest of 3-substitution on polypyrrole, which preserves its conductivity and electroactivity. In water electrolyte however the electroactivity of the polymer bearing the larger azacrown ethers,

poly(**2**), becomes weaker, less reversible and shifted to higher potential (Fig. 1). Limitations of the ionic conductivity inside the polymer film can be invoked here, originating from the increased hydrophobic character of the material for larger azacrown ether substituents, as already observed in a previous work on polypyrroles 3-substituted with linear polyether chains.^{5b}

The electrochemical selectivity of these electropolymerized polymers toward cation has been studied in water and organic electrolytes, by analysing the alkaline series Li⁺, Na⁺ and K⁺. In the case of poly(**1**), no difference is observed in the cyclic voltammogram regarding the electrolyte cation (lithium, sodium or potassium), whether in water or in organic medium. Inversely, if poly(**2**) does not exhibit cation recognition for this alkaline series in water, a clear-cut change in its voltammetric behaviour appears in organic electrolyte when sodium or potassium are used instead of lithium. As shown in Fig. 2(b), when a film of poly(**2**), electrochemically prepared in an electrolytic medium containing Li⁺, is analysed using Na⁺ or K⁺ electrolyte, the anodic wave shifts from 0.10 V (vs. SCE) towards higher potential upon successive cycling (scans 1 to 4) and stabilizes at 0.48 (scan 5) and 0.52 V (vs. SCE) respectively for Na⁺ and K⁺, thus corresponding to a large potential shift of ca. 400 mV. Interestingly, when poly(**2**) is prepared in an electrolytic medium containing Na⁺ or K⁺ instead of Li⁺, and electrochemically characterized using these same electrolytes Na⁺ or K⁺, the positively-shifted voltammograms are obtained directly, with anodic peaks at, respectively, 0.48 and 0.52 V (vs. SCE). Furthermore, results also show that the replacement of Li⁺ by Na⁺ or K⁺ is irreversible.

These results bring the first clear evidence of a functionalized conducting polymer showing selective voltammetric response toward alkaline electrolyte cation, sodium or potassium vs. lithium. Both the size of the substituted azacrown ethers and the solvation of the cation have to be considered for discussing this effect. The cage size of aza-18-crown-6 is comparable to that of the well documented polyether 18-

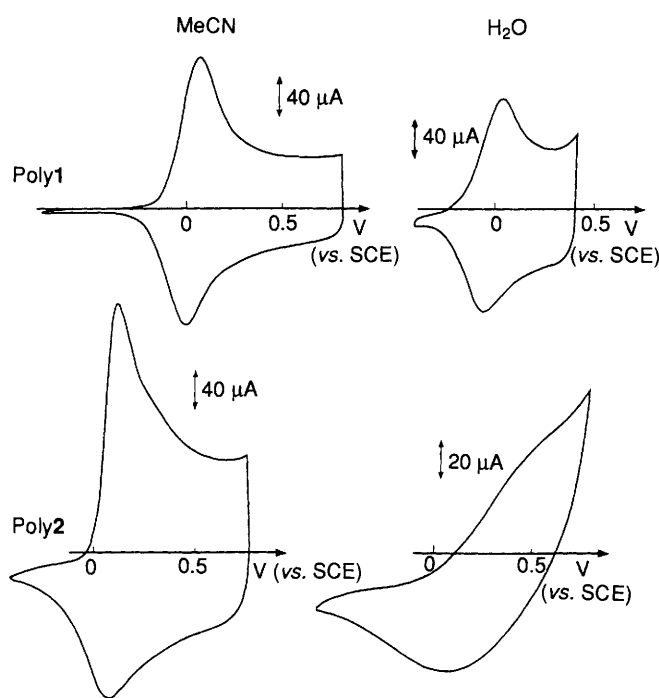
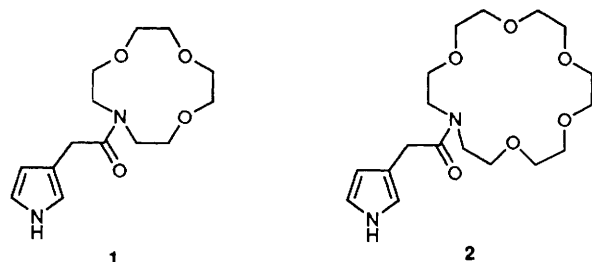


Fig. 1 Voltammograms of deposited films of poly(**1**), and poly(**2**), on Pt electrode, $Q_{\text{polym.}} = 0.1 \text{ C cm}^{-2}$ for poly(**1**) and 0.5 C cm^{-2} for poly(**2**), in MeCN and water electrolytes ($0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in both cases); potential sweep rate, 20 mV s^{-1}

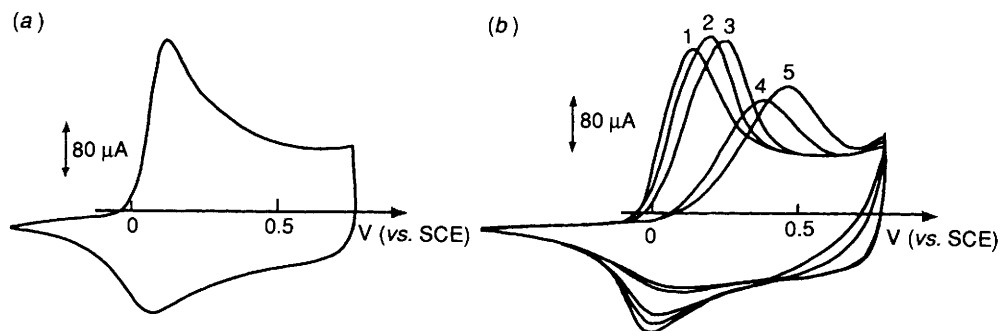


Fig. 2 Voltammograms of films of poly(2), electropolymerized on platinum electrode ($Q_{\text{polym}} = 0.1 \text{ C cm}^{-2}$) in MeCN 0.1 mol dm^{-3} LiClO_4 , and analysed in MeCN containing either 0.1 mol dm^{-3} LiClO_4 (a), or 0.1 mol dm^{-3} NaClO_4 (b) (successive scans 1 to 5); potential sweep rate; 50 mV s^{-1}

crown-6, with a diameter of *ca.* 2.6 to 3.2 Å. It appears well shaped for the complexation of sodium or potassium, with ionic diameters of 1.94 and 2.66 Å respectively, as evidenced by the stability constants of corresponding complexes in organic media.⁷ Poly(2) is thus well designed for the selective recognition of Na^+ or K^+ . On the other hand, the much smaller size of the aza-12-crown-4 cage, of the order of 1 Å, is not at all suited for these alkaline cations, even for Li^+ which has an ionic diameter of 1.36 Å, explaining thus the absence of any recognition from poly(1).

Solvent effects on the complexing properties of crown ethers towards alkaline cations have also been analysed in the literature, much weaker stability constants being observed in water as compared with organic media.⁷ This effect, which can be explained by a strong competition of H_2O for cation solvation, argues for the fact that no cation effect is observed for poly(2) in aqueous media. Finally, the absence of lithium recognition by poly(2) in acetonitrile can be explained both by the large difference between cation and cage sizes, and also by the fact that the small hard lithium cation can be more tightly solvated in this solvent than Na^+ or K^+ .

The striking result evidenced in this work concerns the observed transfer of the cation binding information to the conducting polymer chain, expressing the transduction of chemical information into an electrical signal. Achievement of molecular recognition with specifically functionalized conducting polymer has already been described. Differentiation of the enantiomeric form of chiral electrolyte anions has been demonstrated during the electrochemically driven doping process of polythiophene¹⁰ or polypyrrole¹¹ substituted with optically active groups. A cationic dependence of the voltammetric waves has also been shown for polythiophenes substituted by linear polyether chains, however without clear discrimination between alkaline cations.¹² Here, for the first time, a functionalized conducting polymer is proposed, which shows clear selective recognition in the alkaline series, and this result allows us to point out the determining role played by the position used in the heterocycle for the covalent binding of the substituent. As a matter of fact, similar crown ethers have been recently substituted at the N position of polypyrrole, but these polymers did not show any recognition property toward these alkaline cations.¹³ In this latter case, the redox potentials lie near 0.7 V (vs. SCE) whatever the cation, a very high value signifying weak conjugation of the π -electrons along the conducting chains. This result can be interpreted by a large deviation from coplanarity of the polypyrrole chain, induced by the N-substitution.¹⁴ Flexibility of the functionalized conjugated polymer backbone can be put forward in order to explain this cation recognition effect. 3-Substituted polypyrroles exhibit a much larger configurational flexibility than N-substituted ones, the easy access to coplanarity being expressed by high conductivity and low redox potential of the

former. Chain segment mobility in poly(1) and poly(2) allows the azacrown ethers' substituent to adapt to the electrolytic cations and ensure an efficient complexation. The bulkiness of the metal complexed cage may be thought to induce a stiffening of the polymer chain environment and hence a decrease of its flexibility, leading to deviation from coplanarity inside the polyaromatic chain and thus to an increase of the potential of the redox system. Configurational entropy or free volume properties of 3-substituted polyheterocycles thus appear very promising for realizing new functionalized materials with molecular recognition and electrical transducing properties.¹⁵

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