

New Colorimetric and Fluorometric Chemosensor Based on a Cationic Polythiophene Derivative for Iodide-Specific Detection

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Considerable research has been recently focused on the specific detection of inorganic anions because of their important roles in biological, industrial, and environmental processes. Recent reviews^{1,2} reported the different ways to specifically detect a given anion in the presence of the other anionic analytes. Many systems capable of recognizing, sensing, and transporting negatively charged species are based on supramolecular chemistry,³ which allows one to design anion-sensing receptors with new selectivities. The detection of anions is observed by spectroscopic or electrochemical means upon anion binding to the receptor. Some examples of selective chemosensors made with small molecules were described for fluoride,^{4,5} nitrate,⁶ and cyanide⁷ anions. Moreover, the use of polymeric membranes doped with various metalloporphyrins exhibits a highly selective and reversible response to chloride ion.⁸ Some conjugated polypyrroles were also reported for iodochromic⁹ property. However, there is still a challenge to find new anion-selective optical sensing. Among the range of biologically important anions, iodide is of particular interest due to its essential role for thyroid gland function. In addition, elemental iodine is used in synthesizing some organic chemicals, in manufacturing dyes, in medicine (its radioactive isotope), in analytical chemistry, and in other applications. We report here new water-soluble cationic polythiophene derivatives which can easily optically detect the presence of iodide over a wide range of other anions (F^- , Cl^- , Br^- , CO_3^{2-} , HCO_3^- , $H_2PO_4^-$, HPO_4^{2-} , CH_3COO^- , $EDTA^{4-}$, SO_4^{2-} , $(C_6H_5)_4B^-$). This simple, rapid, and versatile methodology is based on the different electrostatic interactions (self-assembly of two opposite charges) and the conformational change of the cationic poly(3-alkoxy-4-methylthiophene).

The new monomers were prepared according to our previously published procedure for the specific detection of nucleic acids.¹⁰ The corresponding polymers **1** and **2** were obtained from the oxidative polymerization in chloroform by using $FeCl_3$ as the oxidizing agent (Scheme 1).¹¹ As expected, all polymers are soluble in aqueous solutions. All tests described in this paper were carried out at room temperature, in deionized water. The aqueous solution of the cationic polymer **1** is yellow with a maximum absorption wavelength (λ_{max}) at 406 nm (Figure 1A,a and C,a). This absorption maximum at a short wavelength should be related to a random-coil conformation of the polythiophene derivative, as any twisting of the conjugated backbone leads to a decrease of the effective conjugation length.¹² The same UV-vis spectrum was observed upon addition of 5×10^{-8} mol of NaF to the solution of polymer **1** (Figure 1A,b and C,b). The presence of NaCl (Figure 1A,c and C,c) or NaBr (Figure 1A,d and C,d) induced a slight red shift ($\lambda_{max} = 412$ nm for NaCl and 423 nm for NaBr). This displacement toward lower energy values ($\lambda_{max} = 543$ nm) becomes more important when NaI was added to the cationic polymer solution which instantaneously changed color from yellow to red-violet (Figure 1A,e and C,e). The violet form shows an absorption

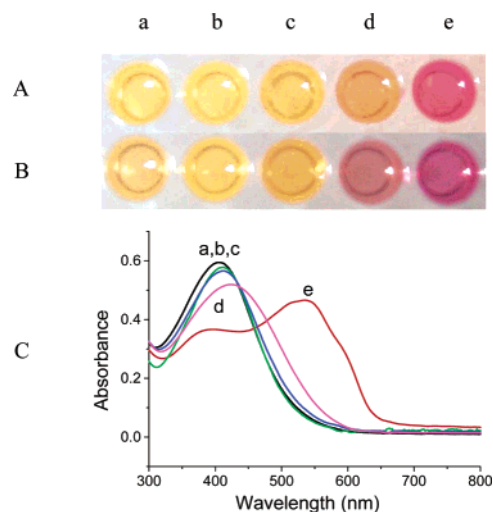
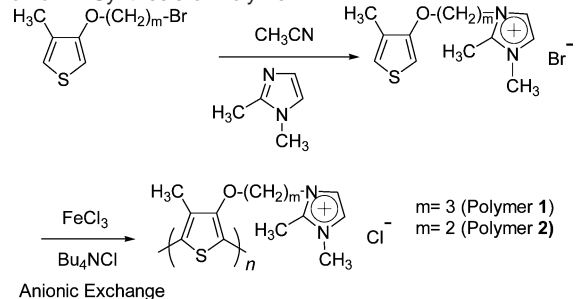


Figure 1. (A) Photographs of solutions of (a) polymer **1** ($110 \mu\text{L}$ of 1.66×10^{-4} M on a monomer unit basis), (b) **1** + NaF, (c) **1** + NaCl, (d) **1** + NaBr, (e) **1** + NaI. (B) Assays of photographs A, 4 days after. The quantity of all salts used here is 5×10^{-8} mol. (C) UV-Vis absorption spectra corresponding to the different assays in photograph A.

Scheme 1. Synthesis of Polymer 1



spectrum like that obtained in the solid state. These results show the important influence of iodide anions which promote the aggregation and planarization of polymer **1**. After 4 days, only the bromide solution changes color (Figure 1B,d).

To verify the anionic specificity, some assays were performed with other sodium salts, such as Na_2SO_4 , Na_2CO_3 , $NaHCO_3$, NaH_2PO_4 , Na_2HPO_4 , CH_3COONa , etc. Under identical conditions [see Supporting Information (SI)], the color of all mixture solutions stays yellow with $\lambda_{max} < 440$ nm. In addition, similar results were observed when the sodium cation was replaced by a potassium (SI). Figure 2 shows the ratio of absorbance measured at 540 and 400 nm (A_{540}/A_{400}) versus the increasing amount of different anions added. These optical results confirmed that the positively charged polymer **1** is selectively sensitive to iodide ions and independent of the nature of cation. However, some anionic (mainly hydro-

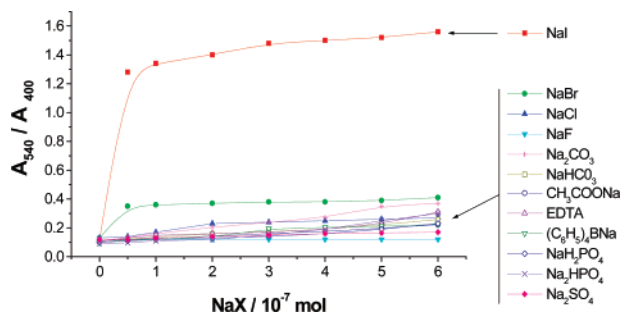


Figure 2. UV-Vis titration curves (A_{540}/A_{400}) of polymer **1** (110 μL of 1.66×10^{-4} M based on monomeric units) with increasing quantity of different anions (from 0 to 6×10^{-7} mol or 0 to 33 equiv in charge).

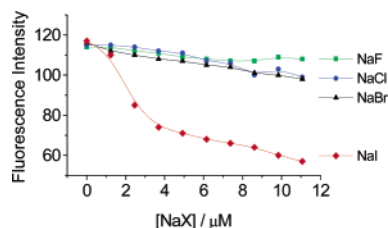


Figure 3. Fluorescence intensity of polymer **1** as a function of the concentration of different sodium salts.

phobic) interferences such as PF_6^- , BF_4^- , SCN^- , ClO_4^- were observed (SI).

Interestingly, a fluorometric detection of anion binding is also possible because the fluorescence of poly(3-alkoxy-4-methylthiophene)s is quenched in the planar or aggregated form.¹² The yellow or random-coil form of polymer **1** is fluorescent with a emission maximum at 550 nm when it is excited at 420 nm, but upon addition of an increasing amount of KI, the fluorescence intensity decreases, and the maximum of emission is slightly red shifted (SI). The fluorescence quenching experiments shown in Figure 3 were carried out in the following manner: Solutions of polymer **1** in water were added at room temperature, with increasing quantities of concentrated solutions of the desired anion (in the form of NaX salts). The concentration of polymer **1** in all experiments was 7.3×10^{-6} M (based on monomeric units). The excitation used is at 420 nm, and the fluorescence emission intensity was measured at 550 nm (without recording the entire emission spectrum). These curves demonstrate that the fluorescence quenching effect is much more important in the case of the iodide anion, as compared to the use of any other ions. To demonstrate that iodide is not responsible for such a quenching effect, we synthesized the water-soluble polymer **2**. The iodide or another halogen salts did not affect the maximum of absorption (Figure 4), and the fluorescence titration of polymer **2** with the iodide anion was much less sensitive than the use of polymer **1** (SI). The iodide-induced optical properties are strongly dependent on the nature and the length of the side chain.

These optical results represented here are in good agreement with previously published work^{13,14} concerning conjugated polymers bearing crown ethers and their ionochromic behaviors toward alkali

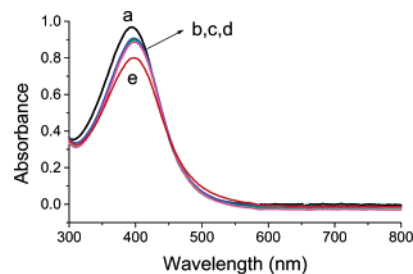


Figure 4. UV-Vis absorption spectra of (a) polymer **2** (110 μL of 1.66×10^{-4} M, on a monomer unit basis), (b) **2** + NaF, (c) **2** + NaCl, (d) **2** + NaBr, (e) **2** + NaI (the quantity of all salts used here is 5×10^{-8} mol).

metal cations. Molecular modeling and X-ray diffraction measurements on oligomers and polymers will be carried out to design new polymers for selective detection of other anions and to understand these phenomena because the similar imidazolium salt does not show appreciable affinity for iodide.¹⁵

In conclusion, an interesting methodology that allows a simple optical (colorimetric or fluorometric) detection of iodide has been developed. This rapid, selective, and versatile method is based on conformational modifications of the conjugated backbone of cationic poly(3-alkoxy-4-methylthiophene) upon binding of iodide anions.

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Supporting Information Available: Experimental preparations for the monomer and polymer and UV-vis and fluorescence spectra with different anions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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