# Responsive Supramolecular Polythiophene Assemblies

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**Abstract:** The simple preparation of a novel family of smart polymers based on acid−base complexes between an acidic conjugated polymer (poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid)) and various amine-containing molecules is described. The neutralization of the acid form of the polymer can be monitored optically in real time through the decrease of the 800 nm absorption band, characteristic of a self-acid-doped state. Moreover, by electrostatically binding adequate responsive substituents, thermochromic, ionochromic, photochromic, and biochromic materials have been easily developed. These optical features seem related to a conformational change of the conjugated main chain driven by side-chain disordering. Furthermore, aminosilane-treated substrates can undergo further modification through electrostatic interactions with partially pre-neutralized polymers, yielding very efficient electrochemical solid-state sensors. It is believed that such a simple methodology, based on electroactive and photoactive supramolecular polymeric assemblies, may open the way to the design of integrated chemical systems incorporating both a trigger and a transducer and can find applications in the areas of biosensors, drug screening, and diagnostics.

## Introduction

The search for smart polymers is an exploding research field due to the high demand for materials capable of carrying out increasingly complex tasks and performing various functions. In this respect, functionalized regioregular $\pi$-conjugated polythiophenes are a very promising class of materials exhibiting impressive chromic responses upon exposure to specific stimuli,[1] opening the way to the design of a variety of sensory devices. For instance, these polymers, bearing adequately designed side chains, can undergo striking conformational changes when exposed to heat, light, or various chemical and biochemical moieties giving rise to thermochromism, photochromism, ionochromism, or even biochromism. These optical transitions, from deep violet (maximum of absorption around 550 nm) to bright yellow (maximum of absorption near 400 nm), are believed to be related to a planar-to-nonplanar (from highly conjugated to less conjugated) conformational transition of the backbone. Indeed, in conjugated polymers, there is a strong correlation between the electronic structure and the backbone conformation, any change in the main chain conformation leading to a modification of the effective conjugation length associated with a shift of the absorption in the UV−visible range. However, studies on different polythiophene derivatives have suggested that this conformational modification of the main chain could be driven by order−disorder transitions of the side chains, side-chain disordering disrupting planar polythiophene assemblies.[1] A similar approach was also developed with functionalized $\pi$-conjugated polydiacetylenes[2,3] and $\sigma$-conjugated polysilanes.[4] However, in all cases, the detection or recognition event is mainly a function of the nature and characteristics of the side chains, requiring the cumbersome design, synthesis, and purification of numerous monomeric and polymeric derivatives. In this paper, we report a novel and simple method to introduce the required side chains through the use of acid−base interactions. Indeed, it is shown here that poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid)[5] can react with various basic molecules to yield tunable, functionalized (through electrostatic interactions), and chromic polymers. New responsive, both in solution and in the solid state, polymers can then be easily prepared and utilized to detect a large number of different and targeted external stimuli. Moreover, the electroactivity of these polymers also allows the development of versatile and tunable electrochemical devices.

## Results and Discussion

As recently reported,[5] self-acid-doped (presumably, an acid-catalyzed oxidation by oxygen of the polythiophene) poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) (PMTOES) exhibits a large absorption band around 800 nm, characteristic of an oxidized and conducting (5 S/cm) form. Stepwise addition of sodium hydroxide aliquots resulted in a progressive neutralization of the polymer, with the neutral and insulating ($<10^{-6}$ S/cm) polymeric salt showing a very different absorption spectrum (maximum of absorption at 540 nm instead of 800 nm), from pale gray to deep violet. Similarly, PMTOES treated with *n*-butylamine (or various other amine derivatives) shows a marked pale gray-to-violet color transition with the decrease of the initial absorption band at 800 nm and the increase of a new band centered around 540 nm, indicating a progressive neutralization of the acidic and oxidized form with the concurrent formation of a neutral and amine-bearing polymeric material (Figure 1). Simple acid−base chemistry has thus been used to introduce a variety of substituents which otherwise would require many synthetic and purification steps.

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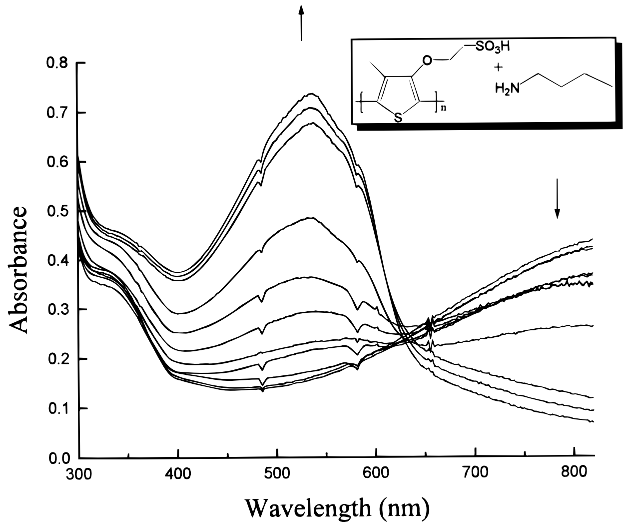

**Figure 1.** UV−visible absorption spectra of an aqueous solution of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) ($\sim 10^{-4}$ M) upon addition of *n*-butylamine, at room temperature.

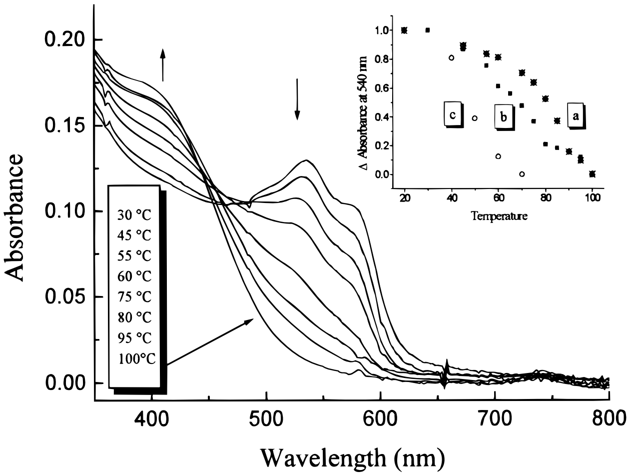

**Figure 2.** Temperature-dependent UV−visible absorption spectra of the 1:1 complex between *n*-butylamine and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) in water. Evolution of the relative absorbance at 540 nm as a function of the temperature for (a) sodium poly(2-(4-methyl-3-thienyloxy)ethane sulfonate), (b) butylammonium poly(2-(4-methyl-3-thienyloxy)ethane sulfonate), and (c) tetrabutylammonium poly(2-(4-methyl-3-thienyloxy)ethane sulfonate).

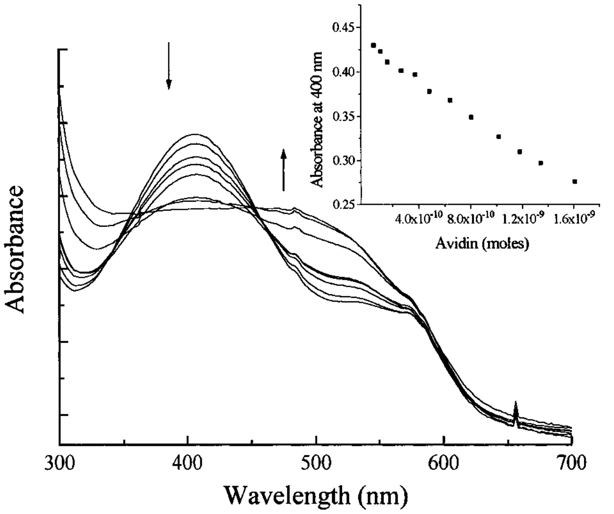

**Figure 3.** UV−visible absorption spectra of the 1:1 complex between biocytin hydrazide and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) ($\sim 5 \times 10^{-7}$ mol) as a function of the addition of avidin, in water/methanol (98:2, v/v).

Interestingly, these polymers bearing electrostatically bound substituents, in addition to being facile and straightforward to obtain, have been found to possess similar characteristics to those having covalently bound substituents. For instance, aqueous solutions of sodium poly(2-(4-methyl-3-thienyloxy)-ethanesulfonate) undergo a thermally induced violet-to-yellow color (a shift of the absorption maximum from 540 to 400 nm) transition, which is believed to be related to a rod-to-coil (planar to nonplanar) conformational transition of the conjugated backbone.[5] Upon electrostatic neutralization of PMTOES with different amine-bearing moieties, the thermochromic behavior observed upon heating of the neutral solutions (Figure 2) revealed a decrease of the 540 nm absorption band and the apparition of a new band around 400 nm with the accompanying color changes from violet to yellow. This thermochromic feature is similar to that observed for the polymeric sodium salt,[5] but the temperature range of the chromic transition was found to be strongly dependent on the nature of the substituents. Indeed, the increase of the bulkiness of the electrostatically bound substituents seems to disrupt more easily the planar polythiophene assemblies (Figure 2, inset). The highly conjugated (violet) form is believed to be associated with intermolecular and intramolecular (through chain folding) aggregates, while upon heating, side-chain disordering disrupts these assemblies to yield nonplanar (less conjugated) polymer chains.[6] A similar cation size-dependent chromaticity has been recently reported with salts involving regioregular poly(thiophene-3-propionic acid) and could be explained by a similar sterically induced disruption of the aggregated phase.[7]

In addition to the modulation of the thermochromic characteristics of polythiophenes through the tuning of the electrostatically attached substituents, various functional substituents can be easily attached to the polythiophene backbone combining the inherent chromic properties of the latter species with the affinity and/or recognition properties of adequately selected substituents, opening the way to the fabrication of integrated chemical systems which incorporate both a trigger and a transducer. For example, the synthesis of a water-soluble biochromic polythiophene derivative has been previously obtained through the covalent attachment of biotin to a thiophene copolymer, containing randomly distributed sodium sulfonate and biotin terminal groups.[8] The addition of avidin, well-known for its very strong interaction with biotin, resulted in a sharp color change of the polymer solution. The tedious multistep synthesis of the biotinylated polythiophene derivative can be advantageously replaced by the electrostatic binding of an adequately functionalized biotin derivative (i.e. biocytin hydrazide, an amine-functionalized biotin derivative) to PMTOES. The solution composition is then adjusted (by adding to water a few percent of a cosolvent, methanol, ethanol, tetrahydrofuran, etc.) in such a way that the main absorption is around 400 nm, indicating that the polythiophene backbone is predominantly in the coiled form (a similar effect can be obtained in pure water by increasing the temperature). A progressive decrease of the 400 nm absorption band is then observed upon the addition of aliquots of avidin, while the absorption around 500−550 nm increases (Figure 3). The addition of avidin seems to induce a

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rigidification of the polymeric chains that could be related to the fact that four binding sites are present on each avidin molecule, each being able to interact with a nearby biotin that could possibly result in cooperative bindings. In contrast, in the case of random copolythiophene with covalently bound avidin,[8] avidin binding induced a disordering of the polythiophene backbone (formation of the coil conformation). The difference between these two systems may be due to the different density and distribution of the binding moieties, multiple bindings to avidin creating a rigidification of the polythiophene backbone and a single binding leading to a coil conformation. Indeed, a violet precipitate was previously observed with random copolymers and was attributed to possible intermolecular cross-linkings.[8] A violet precipitate was also observed in the present study but after 2 or 3 days. Moreover, the fact that an isosbestic point is also present in this conformational transition of the conjugated backbone indicates also a cooperative mechanism where the twisting of a first unit seems to induce the twisting of a series of neighboring units. This phenomenon has always been found with regioregular chromic polythiophenes[1] and involves therefore an amplification (at least a factor of 100, here) of the detection. The absorption characteristics vary linearly with increasing avidin amounts (Figure 3, inset), opening the way to the design of simple biochromic sensory devices, with $10^{-9}-10^{-11}$ mol detection ranges. In the present study, above $10^{-8}$ mol of avidin, the optical response is saturated.

Similarly, it has been shown that regioregular polythiophene derivatives bearing covalently attached oxyethylene oligomers can detect optically the presence of several alkali metal ions.[9] This characteristic can be duplicated with the electrostatic complexation of amino-oligo(oxyethylene) to the sulfonic acid polythiophene derivative. Upon the addition of increasing aliquots of potassium thiocyanate (KSCN), the main absorption band (540 nm) of the aqueous polymer solution decreases while a new band, around 400 nm, is appearing. Photochromic polythiophenes also can be obtained through acid−base complexation with 4-phenylazoaniline. Upon irradiation, the predominantly *trans*-azobenzene side chains undergo an isomerization forcing the main polymeric chains to a rod-to-coil transition, in a manner similar to what has been observed with regioregular polythiophenes covalently modified with azobenzene moieties.[10]

The generality of the acid−base complexation reactions between poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) and amine-bearing molecules also opens the way to a novel area of surface modification through the use of electrostatic interactions. Self-assembled monolayers of alkanesilanes on glass or alkanethiols on gold are now well-known[11−13] and have been the subject of intensive research activities during recent years. Moreover, such monolayers have attracted a lot of attention as potential building blocks for supramolecular assemblies with use of layer-by-layer deposition methods.[14−16] For instance, by using a similar approach to that developed by Decher et al.,[14,15] a silanized glass microscope slide bearing amino-terminal groups (using 3-aminopropyltrimethoxysilane) was dipped into an aqueous solution of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid). Presumably, a monolayer of the oxidized self-acid-doped polymer was then transferred onto the substrate. An absorption band appears in the range of 500−550 nm, indicating an acid−base interaction (neutralization) between the amine-bearing substrate and the acidic polymer. It has to be noticed that the absorbance at 550 nm (0.002 per monolayer) of the resulting ultrathin polythiophene film is in the same range as that observed for a monolayer of a similar polymer (but in a nonplanar form, with a maximum of absorption near 400 nm) prepared with the Langmuir−Blodgett technique,[17] indicating that both techniques can be useful to obtain ultrathin (monolayer) polythiophene films with, obviously, different morphologies. Moreover, when a partially pre-neutralized polymer is used, a functionalized polythiophene monolayer can be easily electrostatically bound to the amine-bearing substrate (Figure 4).

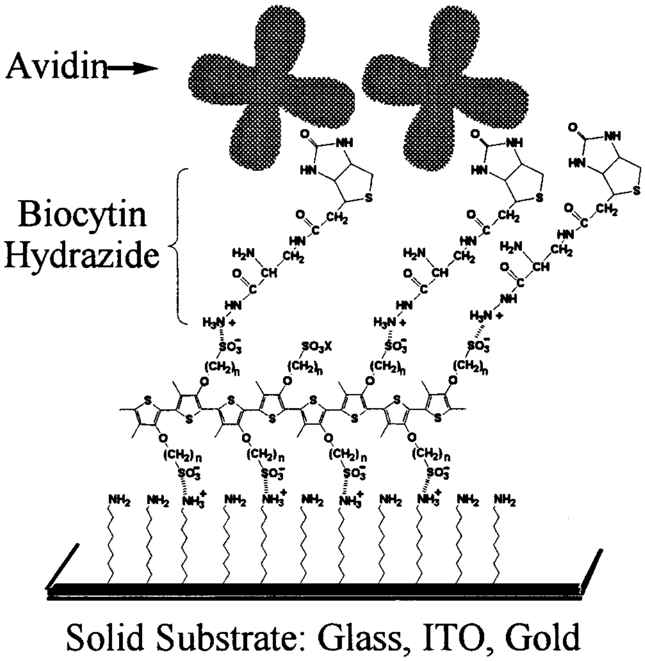

**Figure 4.** Schematic description of the modified electrode.

This easy process of attaching substituents and polymeric monolayers onto various substrates through the use of electrostatic interactions allows the preparation of a large number of solid-state recognition/affinity sensors. The deposition of monolayers is particularly critical for these solid-state sensors since it is believed that the interaction between large biochemical species and binding sites will mainly occur at the interface, and therefore, it is important to maximize the surface/volume ratio for such applications. Moreover, due to the fact that these polythiophene derivatives are also electroactive, any perturbation in the conformation of the main chain may result in a huge difference in the electronic structure of these materials and hence in their electrochemical properties. For instance, a monolayer of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) has been deposited on a silanized ITO-coated glass. Its cyclic voltammogram has been recorded and revealed an oxidation process at +0.88 V vs Ag/AgCl (Figure 5a). Upon deposition of a monolayer bearing biocytin hydrazide moieties, the oxidation peak remains around +0.90 V (Figure 5b), while the treatment of this modified electrode with avidin results in a 200 mV positive shift of the oxidation peak at +1.08 (Figure 5c). These results can be explained by a planar-to-nonplanar conformational transition of the polymeric backbone induced by the incorpora-

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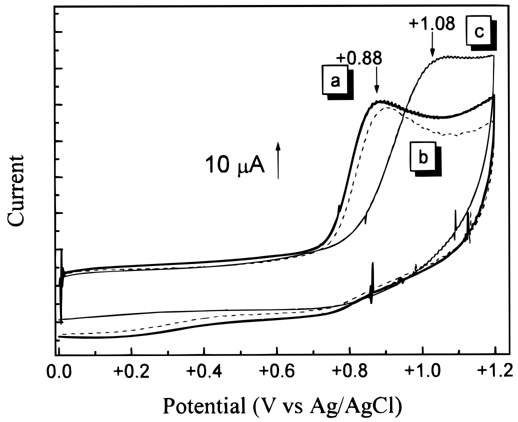

**Figure 5.** Cyclic voltammogram of a monolayer deposited on an aminosilane-treated ITO electrode of (a) poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid), (b) a 0.5:1 complex between biocytin hydrazide and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid), and (c) a 0.5:1 complex between biocytin hydrazide and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) dipped into an aqueous avidin solution. All cyclovoltammograms have been recorded in acetonitrile with 0.1 M of tetrabutylammonium tetrafluoroborate at a scan rate of 100 mV/s vs Ag/AgCl.

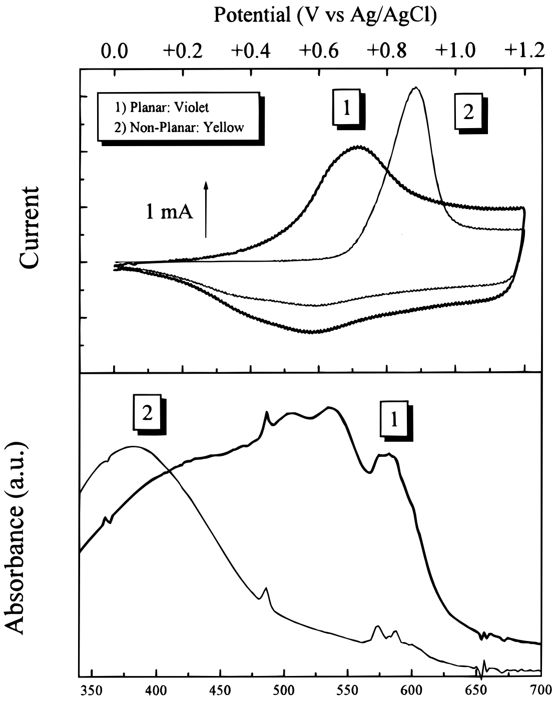

**Figure 6.** Cyclic voltammogram and UV−visible absorption spectrum of cast films of poly(3-(2-methyl-1-butoxy)-4-methylthiophene in (1) a highly conjugated form and (2) a less conjugated form. All cyclovoltammograms have been recorded in acetonitrile with 0.1 M of tetrabutylammonium tetrafluoroborate at a scan rate of 100 mV/s vs Ag/AgCl.

tion of the huge avidin, which is in agreement with the blue shift observed for the UV−visible absorption maximum. Moreover, these electrochemical results with polythiophene monolayers are consistent with those obtained with cast films of poly(3-(2-methyl-1-butoxy)-4-methylthiophene)[18] on platinum electrodes which can be obtained either in the yellow or violet form depending upon film preparation. The difference in the effective conjugation lengths also induces a 200 mV shift in the oxidation potential (Figure 6).

## Conclusion

From all these results, it is clear that the electrostatic attachment of various functional groups to water-soluble poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) profoundly affects the optical and electrochemical properties of the resulting new materials. Through the adequate choice of substituents, a variety of optical features can be easily obtained, such as thermochromism, ionochromism, photochromism and biochromism. For solid-state devices, the deposition of monolayers of polythiophenes can be obtained through the use of amine-bearing self-assembled monolayers (SAMs), a strong complex being formed between the remaining sulfonic acid groups of the polymer and the amine groups of the SAMs. By pre-neutralizing some of the sulfonic acid groups with adequately chosen substituents, functionalized electroactive polymeric substrates can be easily obtained which can be used to carry out a variety of subsequent reactions and can display interesting recognition or field-responsive features. For instance, it is believed that this new and simple methodology based on supramolecular polymeric assemblies can find many applications in the areas of diagnostics, therapeutics and drug screening.[1,2,19]

## Experimental Section.

**Materials.** Sodium 2-(4-methyl-3-thienyloxy)ethanesulfonate and the corresponding polymer have been synthesized as described previously.[5] The sulfonic acid form of the polymer has been obtained by passing an aqueous solution of the sodium salt polymer through a strong cation ($H^+$) exchange resin (Dowex HCR-W2) column. Amino-poly(ethylene glycol) (amino-PEG) (Sherwater), *n*-butylamine, 4-phenylazoaniline, tetrabutylammonium tetrafluoroborate, tetrabutylammonium bromide, 3-aminopropyltrimethoxysilane (Aldrich), and biocytin hydrazide and avidin (Pierce) were used as received. Neutralization of the sulfonic acid polymeric solution was usually carried out by the stepwise addition of aliquots of the various amine-bearing molecules. Amino-functionalized silanized ITO-coated glass has been prepared following well-established procedures.[14−16] For instance, an ITO-coated glass (Applied Glass) plate was dipped in a 70−30 $H_2SO_4$−$H_2O_2$ solution for 10 s in such a way as to enhance the hydrophilic nature of the surface to ensure the proper anchoring of the siloxane groups without destroying the conductive oxide layer. The glass plates are silanized by dipping them in a 5% solution of aminopropyl trimethoxysilane in toluene for various periods of time. For such a short silane derivative, an immersion time of 30 mn was found to be optimum in order to avoid the occurrence of multilayer deposition while obtaining an acceptable surface coverage. After several cycles of sonication and rinsing with fresh toluene, the glass plates were heated to 105 °C for 1 h to allow the condensation reaction of the siloxane to proceed. The ITO electrodes were stored in dry argon prior to use. The electrostatic transfer of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) onto the ITO-coated glass slides was carried out by dipping the slides in a 0.01 M aqueous solution of the polymer. A 50% pre-neutralization of the sulfonic acid polymer with biocytin hydrazide allows the transfer of biotinylated polythiophene onto amine-bearing silanized ITO-coated glass.

**Physical Methods.** UV−visible absorption spectra were obtained with a Hewlett-Packard diode array spectrophotometer (Model 8452A). Cyclic voltammetry measurements were obtained with an EG&G potentiostat/galvanostat (Model 273). Ag/AgCl reference electrode and platinum electrodes were used. Electrochemical measurements were performed at 100 mV/s with use of an electrolyte made of 0.1 M tetrabutylammonium tetrafluoroborate dissolved in acetonitrile. The

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silanized ITO-coated glass electrodes are dipped for various periods of time in different polymeric solutions. After copious rinsing to remove unbound polymeric chains and drying with dry argon, it was found that an immersion time of 1 min is sufficient to obtain reproducible cyclic voltammograms. The biocytin-coated electrodes were then immersed in an aqueous avidin solution at room temperature. Reproducible cyclic voltammograms have been obtained after a dipping time of about 10 min.

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