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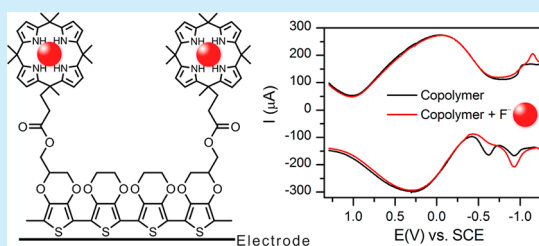
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## EDOT-Functionalized Calix[4]pyrrole for the Electrochemical Sensing of Fluoride in Water

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## S Supporting Information

**ABSTRACT:** A new calix[4]pyrrole compound bearing an electropolymerizable EDOT substituent (**1**) was synthesized, and its electrochemical behavior was investigated. The anion sensor ability of **1** was also studied in solution and in the solid state. Compound **1** interacts with halide ions selectively in solution, which illustrates its possible application as an anion sensor. To test possible practical applications, **1** and EDOT were electropolymerized on an ITO electrode, and this electrode was used as an effective fluoride anion sensor in the solid state.



High concentrations of fluoride that occur naturally in some ground waters can cause bone and teeth degradation disorders, such as fluorosis. At lower concentrations, fluoride can inhibit tooth decay.<sup>1</sup> For the prevention of dental caries, a fluoride concentration between 0.5 and 1.0 ppm in drinking water is considered beneficial. On the other hand, concentrations above 1.0 ppm increase the risk of dental fluorosis and can lead to skeletal fluorosis. In rare instances, fluoride concentrations in naturally occurring groundwater sources may be up to 10 ppm, and these waters must be defluoridated before use as drinking water.<sup>2</sup> Therefore, the determination of fluoride anion concentrations has emerged as an important goal. This need is driven not just by the need to control water supply fluoride anion concentrations but also by the recognition that certain chemical warfare agents produce fluoride anion upon hydrolysis.<sup>3</sup> Among the methods suggested for the determination of fluoride in water, ion-selective electrodes, and colorimetric methods are the most widespread.<sup>2</sup> Both methods require special instrumentation and relatively high cost. Therefore, a need remains for methods that permit the simple, cost-effective sensing and determination of fluoride in aqueous environments. Here we present a new calix[4]pyrrole system bearing electropolymerizable EDOT substituent (**1**) and show it may be used for fluoride anion sensing.

Calix[4]pyrroles (CPs) are an important class of neutral anion receptors<sup>4</sup> that contain four pyrrole units connected to each other via *sp*<sup>3</sup>-hybridized carbon atoms.<sup>5</sup> These macrocycles, alone or in combination with other electro- and photoactive moieties, have been exploited as building blocks for the construction of molecular materials with anion recognition properties.<sup>6</sup> Recent studies wherein this macrocycle is covalently attached to solid supports or polymeric materials<sup>7</sup> have served to

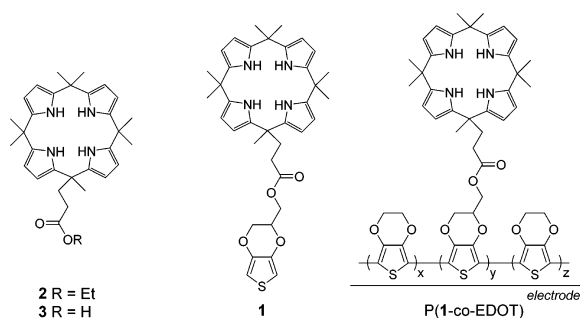
show that CPs can be highly effective anion receptors under mixed organic–aqueous interfacial conditions.

Recently, conductive polymers have been shown to yield sensor materials for anions, cations, biomacromolecules, and neutral analytes.<sup>8</sup> Poly(3,4-ethylenedioxythiophene) (PEDOT) has received tremendous attention in the past decade and has become one of the most investigated conducting polymers. The interest in PEDOT reflects its remarkable conducting properties, as well as high chemical stability, good film-forming ability, low band gap, and outstanding environmental stability.<sup>8,9</sup> To obtain polymers combining PEDOT with improved properties, synthetic efforts have been devoted toward the preparation of substituted 3,4-(ethylenedioxy)thiophene (EDOT)-based monomers. To maintain the integrity of PEDOT and its polyconjugated backbone, substitution of the monomer is typically carried out on the ethylenedioxy bridge.<sup>9,10</sup> To the best of our knowledge there is only one study of EDOT-based hydrogen-bonding polymers for anion recognition. This work, carried out by Anzenbacher and co-workers, involved the use of anion-binding dipyrrolylquinoxaline moieties incorporated into PEDOT giving rise to systems suitable for the sensing of aqueous phosphates.<sup>11</sup>

We conceived that immobilization of CP macrocycles onto an electrode surface would allow fast and cost-effective determination of fluoride anion in water. One way of doing this would involve the production of an electropolymerized matrix consisting of a CP bound to the macromolecular moiety. As detailed below, we have prepared such a system. It was prepared from the carboxylic acid-functionalized CP (**3**) that was, in turn

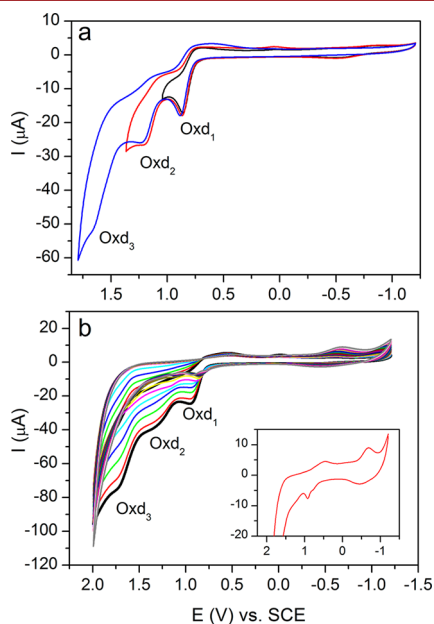
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obtained from its corresponding ester derivative (**2**); esterification then produced the EDOT-functionalized CP (**1**). Electropolymerization of **1** with EDOT gave P(**1-co-EDOT**), a material that permits fluoride anion sensing both in solution and in the solid state.

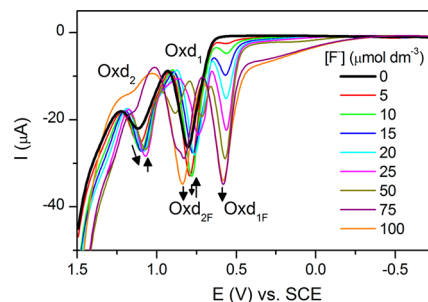
The redox properties of **1** were examined on a Pt working electrode in an acetonitrile/tetrabutylammonium perchlorate (AN/TBAP) electrolyte system (Figure 1). Monomer **1**



**Figure 1.** CVs of **1** recorded with (a) different vertex potentials and (b) repetitive CV cycles at 0.100 V s<sup>-1</sup> scan rate in acetonitrile/tetrabutylammonium perchlorate (AN/TBAP) on a Pt working electrode.

illustrates three oxidation processes, Oxd<sub>1</sub> ( $E_{1/2}$  = 0.82 V,  $\Delta E_p$  = 120 mV,  $I_{pc}/I_{pa}$  = 0.42), Oxd<sub>2</sub> ( $E_{1/2}$  = 1.15 V,  $\Delta E_p$  = 98 mV,  $I_{pc}/I_{pa}$  = 0.35), and Oxd<sub>3</sub> ( $E_{pa}$  = 1.66 V). The first two oxidation reactions are quasi-reversible with respect to changes in  $E_{1/2}$ ,  $\Delta E_p$ , and  $I_{pc}/I_{pa}$  with the scan rates. It is well documented that EDOT species generally give an oxidation process at more positive potentials.<sup>12</sup> Similarly, **1** illustrates an EDOT-based oxidation process at 1.66 V, in addition to the CP based oxidation processes as shown in Figure 1a. The voltammetric responses of **1** are in agreement with the similar compounds reported in the literature.<sup>13</sup> For instance, Solak and co-workers reported two irreversible oxidation peaks at 0.70 and 1.10 V for CP-based films.<sup>14</sup> Gale and co-workers also reported a CP derivative bearing a polymerizable pyrrole unit. This compound gave two oxidation processes at 0.45 and 0.60 V.<sup>8a</sup>

We also tested the redox response of **1** in the presence of various anions (as their Bu<sub>4</sub>N<sup>+</sup> salts). Figure 2 illustrates the



**Figure 2.** Square wave voltammetry (SWV) of **1** as recorded at a scan rate of 0.100 V s<sup>-1</sup> with increasing concentrations of F<sup>-</sup> in an AN/TBAP electrolyte system using a Pt working electrode.

square wave voltammetry (SWV) response of **1** ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) during titration with F<sup>-</sup> ions using an AN/TBAP electrolyte. Compound **1** gives two oxidation peaks, Oxd<sub>1</sub> at 0.80 V and Oxd<sub>2</sub> at 1.11 V, without F<sup>-</sup> ions during the anodic SWV scan. When F<sup>-</sup> ions were added gradually, first both of the oxidation peaks increase in current intensity with a negative potential shift, while a new peak Oxd<sub>1F</sub> starts to grow in at 0.54 V. The oxidation peaks Oxd<sub>1</sub> decrease in intensity, while Oxd<sub>2</sub> stays constant and the Oxd<sub>1F</sub> peak continues to increase in current intensity until the F<sup>-</sup> concentration reaches 25 μmol dm<sup>-3</sup>. After this point, a new peak at 0.91 V, Oxd<sub>2F</sub>, starts to increase in intensity. The value of this peaks shifts to 0.80 V as the concentration of F<sup>-</sup> ions increases. Finally, both the Oxd<sub>1</sub> and Oxd<sub>2</sub> signals disappear, while two new peaks, Oxd<sub>1F</sub> and Oxd<sub>2F</sub>, are observed. These different voltammetric responses observed during the incremental addition of F<sup>-</sup> ions are taken as evidence of strong fluoride anion complexation.<sup>15</sup>

To investigate the selectivity of **1**, its interaction with various halide anions (e.g., Br<sup>-</sup>, Cl<sup>-</sup>, and F<sup>-</sup>) was measured. Addition of these anions to a solutions of **1** gave different electrochemical responses (cf. Figure S13, Supporting Information). When 100 μmol dm<sup>-3</sup> of Br<sup>-</sup> was tested with **1** ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) using the AN/TBAP electrolyte, the Oxd<sub>1</sub> and Oxd<sub>2</sub> peaks (at 0.80 and 1.11 V) of **1** were seen to shift to 0.76 and 0.89 V, respectively. When Cl<sup>-</sup> ions (100 μmol dm<sup>-3</sup>) were added into this solution (i.e., the solution pretreated with Br<sup>-</sup>), the oxidation peaks shift to 0.66 and 0.94 V, respectively. These new peak shifts are thought to reflect the relatively stronger interaction of the Cl<sup>-</sup> anion with the CP core of **1** as compared to Br<sup>-</sup>. When F<sup>-</sup> ions (100 μmol dm<sup>-3</sup>) were added to this anion-containing solution, **1** the oxidation peaks shift to 0.54 and 0.80 V, respectively. On this basis, we conclude that **1** allows for the selective sensing of fluoride anion, even in the presence of potentially competitive anions, namely bromide and chloride.

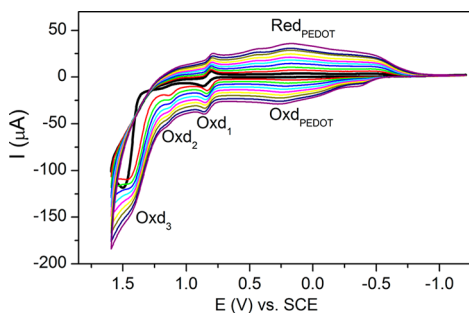
For practical applications, an immobilized sensing material is preferred. Therefore, we decided to coat receptor **1** on an electrode via electropolymerization and to test the electrochemical anion sensing ability of the resulting material. Figure 1b shows initial attempts to electropolymerize monomer **1**, specifically repetitive CVs reflecting consecutive potential cycling of an AN/TBAP electrolyte containing **1** ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>). Within the potential window of the electrolyte system, both quasi-reversible and irreversible redox waves (Oxd<sub>1</sub>, Oxd<sub>2</sub>, and Oxd<sub>3</sub>) were observed that were found to decrease in current intensity with small potential shifts being seen during

consecutive CV cycles. Moreover, a small oxidation wave at 0.90 V and a quasi-reversible cathodic couple at  $-0.60$  V were observed. This voltammetric behavior is consistent with electropolymerization of **1** occurring on the Pt working electrode and formation of Pt/P(**1**) composite electrode.

The observed decrease in the peak currents is most probably due to a decrease in electrode conductivity after modification with the electropolymerized film. This proposition was supported by conductivity measurements. For this purpose, CVs of bare Pt and Pt/P(**1**) electrodes were compared in the presence of a redox probe, potassium ferricyanide. Because of the blocking of the electron-transfer reaction on the Pt/P(**1**) electrode, the normally reversible redox couple of ferricyanide became irreversible with a positive potential shift and a decrease in the peak current. These results are consistent with the presence of a film on the electrode that blocks electron transfer reactions involving ferricyanide.

The Pt/P(**1**) electrode was tested as an anion sensor in water. Unfortunately, this electrode was not found to give a characteristic redox response in aqueous solution. This finding is thought to reflect the fact that the conductivity of the electropolymerized film of **1** is insufficient.

To increase the conductivity and redox activity of the modified electrode based on **1**, we prepared a copolymer using a 1:1 mixture of **1** and EDOT. It is well documented in the literature that EDOT gives conductive and redox-active films on various electrodes.<sup>16</sup> Thus, we aimed to increase the conductivity of the electrode by incorporating EDOT units while keeping the CP subunits as the anion recognition sites within the copolymer structure. Figure 3 shows the repetitive CV response of a 1:1



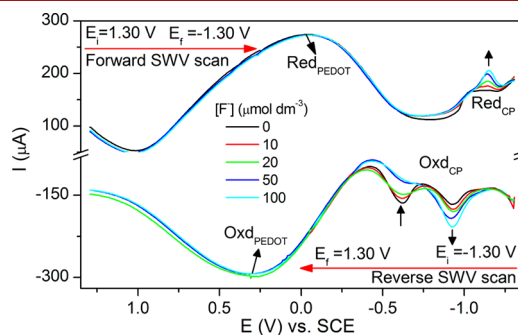
**Figure 3.** Repetitive CV scans of **1** and an EDOT mixture (1:1) recorded at a  $0.100 \text{ V s}^{-1}$  scan rate in AN/TBAP on a Pt working electrode.

mixture of EDOT and **1**, with the changes being fully consistent with the formation of a copolymer P(**1-co**-EDOT). An inspection of Figure 3 reveals that the anodic wave at  $0.24 \text{ V}$  and its couple at  $0.17 \text{ V}$  increase in current intensity as a function of repetitive CV scans. These redox responses are characteristic of an electropolymerized PEDOT material (cf. Figure S14, Supporting Information, for repetitive CV scans of PEDOT). The main differences between PEDOT and P(**1-co**-EDOT) are the reversible redox couples Oxd<sub>1</sub> and quasi-reversible Oxd<sub>2</sub>, which are the characteristic oxidation peaks of **1**. Further, the observed enhancements in the current peaks of Oxd<sub>1</sub> and Oxd<sub>2</sub> support the conclusion that a copolymer is being formed.

Spectroelectrochemical analysis of the films formed on ITO electrodes with different concentration ratios of EDOT and **1** provide support for the proposed copolymerization process and the presence of **1** in the polymer backbone (cf., Figure S15, Supporting Information). Since PEDOT and P(**1-co**-EDOT) are

colorless films in their oxidized forms, they do not give an absorption band in their UV–vis spectra. As a result, both of the absorption bands at  $613 \text{ nm}$  (assigned to the presence of EDOT) and a shoulder at  $477 \text{ nm}$  (assigned to the presence of **1**) decrease in intensity, and the blue films become colorless when a  $1.20 \text{ V}$  potential was applied. The relative ratio of the absorption bands changes considerably in the spectra as the ratio of **1** and EDOT (see Figure S15, Supporting Information) is varied. When the ratio of **1** in the copolymer composition is increased, the band at  $477 \text{ nm}$  becomes more distinctive. Moreover, the film on the ITO becomes less uniform and its color changes from bright to pale blue as the ratio of **1** increases. While the band at  $613 \text{ nm}$  is obviously an absorption corresponding to the EDOT unit, it is reasonable to attribute the other absorption band at  $477 \text{ nm}$  to the CP-functionalized EDOT **1**.

Finally, a copolymer, P(**1-co**-EDOT) was coated on an ITO electrode via a set of successive 5 CV cycles using a 1:1 mixture of **1** and EDOT. The modified electrode obtained in this way was then used as a fluoride sensor in water. Figure 4 illustrates the

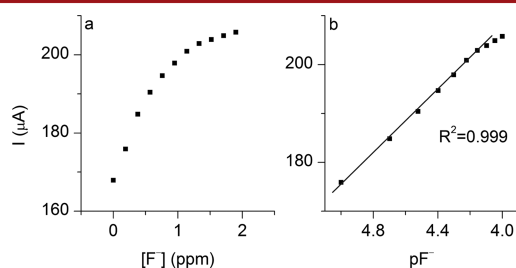


**Figure 4.** SWV of an ITO/P(**1-co**-EDOT) electrode recorded at a scan rate of  $0.100 \text{ V s}^{-1}$  during titration with increasing amounts of  $\text{F}^-$  in an  $\text{H}_2\text{O}/\text{LiClO}_4$  electrolyte system.

SWV responses of the ITO/P(**1-co**-EDOT) electrode in aqueous solution during titration with  $\text{F}^-$  anion. SWVs of ITO/P(**1-co**-EDOT) and ITO/PEDOT (see Figure S16, Supporting Information, for SWV of ITO/PEDOT) are different from one another. This supports the contention that a copolymer is present in the ITO/P(**1-co**-EDOT) composite electrode. While the ITO/PEDOT electrode gave only Oxd<sub>PEDOT</sub>/Red<sub>PEDOT</sub> redox responses, the ITO/P(**1-co**-EDOT) composite electrode gives Oxd<sub>CP</sub>/Red<sub>CP</sub> waves in addition to Oxd<sub>PEDOT</sub>/Red<sub>PEDOT</sub> waves. Moreover, when the CP-free ITO/PEDOT electrode was exposed to  $\text{F}^-$  anions, no discernible change in the Oxd<sub>PEDOT</sub>/Red<sub>PEDOT</sub> redox features was observed. This result shows that PEDOT on its own does not interact with  $\text{F}^-$ . On the other hand, an inspection of Figure 4 shows that while the Oxd<sub>PEDOT</sub>/Red<sub>PEDOT</sub> redox waves at  $0.30$  and  $0.06 \text{ V}$  for the ITO/P(**1-co**-EDOT) composite electrode do not change upon exposure to  $\text{F}^-$ , the Oxd<sub>CP</sub>/Red<sub>CP</sub> waves undergo considerable concentration-dependent changes upon exposure to  $\text{F}^-$ . For instance, during the forward SWV scan, a new wave grows in at  $-1.15 \text{ V}$ , while the wave at  $-1.02 \text{ V}$  disappears. At the same time, the wave recorded at  $-0.61 \text{ V}$  decreases and the wave at  $-0.93 \text{ V}$  increases in current intensity during the reverse SWV scans. All of these voltammetric responses are taken as an indication that the CP units of P(**1-co**-EDOT) interact with the fluoride anions. In a plot of  $[\text{F}^-]$  vs current intensity, an enhancement in the current for the redox feature at  $-1.15 \text{ V}$  was seen. This increase was found to be in a logarithmic fashion over the  $0$  and  $2 \text{ ppm F}^-$



concentration regime (Figure 5a). When pF was plotted vs current intensity, a linear correlation was obtained up to 1.33



**Figure 5.** Estimates of the detection limit of the ITO/P(1-co-EDOT) electrode for the sensing of aqueous  $F^-$  using the current intensities at  $-1.15$  V: (a) current changes observed as the  $F^-$  concentration was increased and (b) corresponding semilogarithmic plot.

ppm  $F^-$  (Figure 5b). Moreover, the detection limit for the ITO/P(1-co-EDOT) electrode was found to be as low as 0.19 ppm in water.

In conclusion, we have synthesized an EDOT-functionalized calixpyrrole derivative **1** that permits the selective, electrochemical-based sensing of various halide anions in AN. A conductive polymer was produced from this monomer via electropolymerization in the presence of EDOT. Electrodes supported on both Pt and ITO surfaces, respectively, were prepared in this way. The P(1-co-EDOT) electrode was found to sense the fluoride anion in water, with a limit of detection of 0.19 ppm. The ease of synthesis and relatively inexpensive nature of the present polymerized electrode leads us to suggest that calixpyrrole-containing EDOT polymers could find practical application in the electrochemical sensing of low concentration fluoride anions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures along with characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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