Anal. Chem. **2000,** *72,* 1860−1865

Development of Chemical Sensors Based on Redox-Dependent Receptors. Preparation and Characterization of Phenanthrenequinone-Modified Electrodes

Yu Ge and Diane K. Smith*

Department of Chemistry, San Diego State University, San Diego, California 92182-1030

The study of phenanthrenequinone(PQ)-modified electrodes, prepared by electropolymerization of a phenanthrenequinone-pyrrole derivative, is described. The surface-confined PQ is shown to behave similarly to PQ in solution, acting as a redox-dependent receptor toward aromatic ureas in aprotic solvents. Large, positive shifts in the $E_{1/2}$ of the $PQ^{0/-}$ redox couple are observed in the presence of these ureas, due to a strong hydrogen bonding interaction between the PQ radical anion and urea. The effect is fully reversible. Of the substrates examined, only aromatic ureas produce a significant shift. Nonaromatic ureas or other HN and HO containing compounds have little effect on the $E_{1/2}$. The magnitude of the shift is also independent of electrode coverage, allowing reproducible measurements to be made despite significant loss in material from the surface.

The design and characterization of new electrochemical sensors continues to be an extremely active area of research in analytical chemistry.[1] As with all types of sensors, a key component is the recognition element, which must show some degree of selective interaction with the analyte. However, with electrochemical sensors, this interaction usually does not directly produce the analytical signal. Instead, recognition is coupled to separate transduction components and these create an electrochemically detectable signal. For example, the recognition element in a polymer membrane ISE is the selective ion-exchange agent or neutral ionopher, but the signal is a change in potential across the membrane. With amperometric enzyme electrodes, the enzyme is the recognition element, but, in many cases, the enzyme redox chemistry is not directly electrode-accessible and the signal is actually reduction or oxidation of the enzyme cofactor through a mediator.

The fact that multiple chemical components are required to couple recognition to signal production in most electrochemical sensors means that the chemical side of the sensor is, by necessity, complex. In contrast, with optical sensors, the signal is often a change in the optical properties of the recognition element itself. This means that recognition and transduction are combined in a single molecule, greatly simplifying the chemical side of the sensor. However, this ability to combine recognition and transduction is not unique to optical recognition. It is also possible to design molecules whose electrochemical properties change in a detectable fashion upon interaction with an analyte. Our group has focused its research efforts on one way to do this, through the use of redox-dependent receptors.[2,3]

A receptor can be defined as a compound that selectively binds another compound (substrate) through a variety of noncovalent interactions. A *redox-dependent* receptor is one in which the binding strength to a particular substrate changes upon reduction or oxidation of the receptor. If this occurs and the redox process is reversible, then the redox potential of the receptor will change in the presence of the substrate. That change in redox potential can then be used to detect and measure the concentration of substrate by electrochemical means, even though the substrate itself may not be electroactive.

The equilibria involved in redox-dependent receptor−substrate binding is given in eq 1, where R stands for the receptor and S the substrate that binds to the receptor. K_{ox} and K_{red} are the binding constants between the substrate and the oxidized and reduced forms of the receptor, respectively. Assuming excess substrate concentration, application of the Nernst equation and

$$\begin{array}{ccc} R + e^- & \leftrightarrow & R^- \\ +S \updownarrow K_{ox} & & +S \updownarrow K_{red} \\ RS + e^- & \leftrightarrow & RS^- \end{array} \qquad (1)$$

the equilibrium constant expressions to this scheme leads to eq 2 at 25 °C

$$\Delta E' = \frac{0.0592V}{n} \log \left(\frac{1 + K_{red}[S]}{1 + K_{ox}[S]} \right) \qquad (2)$$

where $\Delta E'$ is the change in the formal redox potential of the receptor after adding substrate. This equation predicts an ISE-like response, that is, a $60/n$ mV change in observed E' per decade change in substrate concentration over a concentration range between approximately $1/K_{ox}$ and $1/K_{red}$. For example, if the weak

(1) Janata, J.; Josowicz, M.; Vanysek, P.; DeVaney, D. M. *Anal. Chem.* **1998**, *70*, 179R.

(2) (a) Smith, E. A.; Lilienthal, R. R.; Fonseca, R. J.; Smith, D. K. *Anal. Chem.* **1994**, *66*, 3013. (b) Lilienthal, R. R.; Smith, D. K. *Anal. Chem.* **1995**, *67*, 3733. (c) Lilienthal, N. A.; Enlow, M. A.; Othman, L.; Smith, E. A.; Smith, D. K. *J. Electroanal. Chem.* **1996**, *414*, 107.

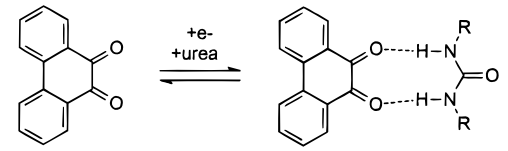
(3) (a) Ge, Y.; Lilienthal, R. R.; Smith D. K. *J. Am. Chem. Soc.* **1996**, *118*, 3976. (b) Ge, Y.; Smith, D. K., submitted to *J. Org. Chem.*

10.1021/ac991120w CCC: $19.00
Published on Web 03/18/2000

binding constant was 1 M^{-1} and the strong binding constant was 1000 M^{-1} then ΔE is expected to be linear with respect to log[S] between approximately 1 mM and 1 M. At lower concentrations, no significant binding occurs in either oxidation state, and at higher concentrations the receptors are saturated in both oxidation states.

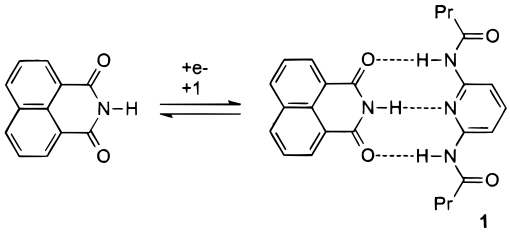
Most of the work with redox-dependent receptors has focused on the development of such receptors for ionic compounds.[4] In contrast, we have focused our efforts on the design of redox-dependent receptors for neutral organic compounds.[2,3] Most recently, we have been exploring the concept of redox-dependent hydrogen bonding as a particularly potent means to design such receptors.[3] The concept, which is also being actively explored by Rotello[5] and Tucker,[6] is straightforward. Hydrogen bonds are known to have substantial electrostatic character. Therefore, a reduction or oxidation process that leads to a change in partial charge on one of the components in a hydrogen bond will have a significant effect on the strength of that hydrogen bond. In particular, if the negative charge on the hydrogen acceptor or the positive charge on the hydrogen donor is increased, the strength of the hydrogen bond will be increased. Alternatively, if the negative charge on the hydrogen acceptor or the positive charge on the hydrogen donor is decreased, the strength of the hydrogen bond will be decreased.

In our earlier work,[3] we showed that substantial effects can be produced even in very simple systems. Specifically we looked at the behavior of 9,10-phenanthrenequinone, **PQ**, and 1,8-naphthalimide, **NI**. Both **PQ** and **NI** undergo reversible one-electron reductions in aprotic media to form radical anions, eq 3 and 4. Although the radical is delocalized, most of the negative



(3)

PQ



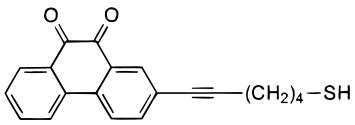
(4)

1

charge resides on the oxygens due to their greater electronegativity. For this reason, substrates with appropriately positioned N−H groups hydrogen bond with the carbonyl oxygens much more strongly in the reduced states. Examples of good substrates are urea derivatives with **PQ** and the diamidopyridine derivative **1** with **NI**. The increase in binding strength is detected by large positive shifts in the redox potential of **PQ** and **NI** in the presence of these substrates. In effect, the substrates stabilize the radical anions through hydrogen bonding, making it easier to reduce the quinone or diimide in their presence.

The initial studies with redox-dependent hydrogen-bonding receptors were conducted with both receptor and substrate in solution. However, to use redox-dependent receptors as sensors, as well as in most other applications, they will need to be attached to surfaces. In working toward the goal of creating practical electrochemical sensors based on redox-dependent receptors, we have chosen to utilize phenanthrenequinone as a prototypical example of a redox-dependent hydrogen-bonding receptor and explore its electrochemical and redox-dependent binding behavior when attached to electrode surfaces.

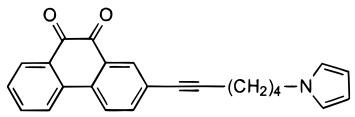
Recently, one of the most popular methods for attaching molecular species to electrode surfaces is to take advantage of the strong chemisorption between a thiol or disulfide and a Au surface.[7] In initial studies we explored this method by preparing the phenanthrenequinone thiol derivative, **2**. Although we were successful in attaching **2** to gold electrodes, the electrochemistry



2

of the phenanthrenequinone was considerably different than in solution and, even more problematic, the electrodes were not very stable in nonaqueous solution.[8]

In this paper we employ electropolymerization of a phenanthrenequinone pyrrole derivative, **PQP**, as an alternate method to attach phenanthrenequinone to electrode surfaces. Like thiols,



PQP

electropolymerization of functionalized pyrroles has been widely used to prepare modified electrodes,[9] including those containing anthraquinone[10] and benzoquinone[11] groups. Another type of redox-dependent receptor, a ferrocene-containing crown ether, has also been attached to electrodes using this method.[12]

(4) Beer, P. D.; Gale, P. A.; Chen, Z. *Adv. Phys. Org. Chem.* **1998**, *31*, 1.

(5) (a) Deans, R.; Niemz, E.; Breinlinger, E.; Rotello, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 10863−10864. (b) Niemz, A.; Rotello, V. M. *Acc. Chem. Res.* **1999**, *32*, 44.

(6) Carr, J. D.; Lambert, L.; Hursthouse, M. B.; Malik, K. M. A.; Tucker, J. H. R. *Chem. Commun.* **1997**, 1649.

(7) Finklea, H. O. In *Electroanalytical Chemistry. A Series of Advances*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, p 109.

(8) Smith, D. K.; Ge, Y.; Lilienthal, R. R. In *New Directions in Electroanalytical Chemistry*; Leddy, J., Wightman, R. M., Eds.; Electrochemical Society: Philadelphia, 1996; p 305.

(9) (a) Deronzier, A.; Moutet, J.-C. *Coord. Chem. Rev.* **1996**, *147*, 339. (b) Curran, D.; Grimshaw, J.; Perera, S. D. *Chem. Soc. Rev.* **1991**, *20*, 391. (c) Deronzier, A.; Moutet, J.-C. *Acc. Chem. Res.* **1989**, *22*, 249.

(10) (a) Moteki, S.; Sykes, A. G. *J. Electroanal. Chem.* **1998**, *447*, 91. (b) Allietta, N.; Pansu, R.; Bied-Charreton, C.; Albin, V.; Bedioui, F.; Devynck, J. *Synth. Met.* **1996**, *81*, 205. (c) Andrieux, C. P.; Audebert, P. *J. Electroanal. Chem.* **1990**, *285*, 163. (d) Audebert, P.; Bidan, G.; Lapkowski, M. *J. Electroanal. Chem.* **1987**, *219*, 165.

(11) (a) Aquino-Binag, C. N.; Kumar, N.; Lamb, R. N. *Chem. Mater.* **1996**, *8*, 2579. (b) Schuhmann, W.; Huber, J.; Wohlschlaeger, H.; Strehlitz, B.; Gruendig, B. *J. Biotechnol.* **1993**, *27*, 129.

(12) (a) Ion, A. C.; Popescu, A.; Ungureanu, M.; Moutet, J.-C.; Saint-Aman, E. *Adv. Mater. (Weinheim, Ger.)* **1997**, *9*, 711. (b) Ion, A. C.; Moutet, J.-C.; Pailleret, A.; Popescu, A.; Saint-Aman, E.; Siebert, E.; Ungureanu, M. *J. Electroanal. Chem.* **1999**, *464*, 24.

With functionalized pyrroles, the electroactive group is typically attached to the pyrrole nitrogen via an alkyl chain. Oxidation of the pyrrole creates a radical cation which couples with another radical cation or with a neutral pyrrole followed by further charge transfer. A neutral dimer is formed after two protons are eliminated. The dimer is then oxidized immediately to the radical cation at the applied potential. The oligomers and/or polymers of pyrrole formed in this manner contain pyrrole units connected mainly by 2,5-linkages. Since they are considerably less soluble than the monomer, they remain on the electrode surface. Electrode derivatization is usually accomplished by cycling the electrode potential through the polypyrrole and pyrrole oxidation waves. These increase in size with each cycle as more material is deposited on the electrode. The coverage can be controlled by monitoring the current and stopping when it reaches a desired value.

As detailed in the Results and Discussion section, preparation of phenanthrenequinone-modified electrodes via electropolymerization of the pyrrole derivative, **PQP**, proved much more successful than the thiol method. At low coverages the electrochemistry of the quinone is well-behaved and shows sensitivity to aromatic ureas similar to that seen in solution. The electrodes are also much more stable in aprotic solvent than those prepared from the phenanthrenequinone thiol derivative, **2**.

EXPERIMENTAL SECTION

Synthetic Procedures. ^{1}H NMR spectra were recorded on a Varian Unity^{plus} 400 MHz spectrometer. Unless specified, $CDCl_3$ was used as the solvent for ^{1}H NMR. All chemical shifts are reported in ppm and are relative to TMS. *J* values refer to H−H coupling constants. Mass spectra were recorded on a MS-9 AEI spectrometer. Reaction solvents were either freshly distilled from a drying reagent or obtained as the anhydrous grade from the manufacturer and stored under N_2. Other chemicals were of reagent grade and used as supplied from the manufacturer.

Toluene-4-sulfonic Acid Hex-5-ynyl Ester, 3. Triethylamine (7.0 mL, 50.0 mmol) was added dropwise to a solution of 5-hexyn-1-ol (1.96 g, 20.0 mmol) and *p*-toluenesulfonyl chloride (4.56 g, 24.0 mmol) in CH_2Cl_2 (15 mL) at room temperature. The solution was then stirred until the starting material disappeared (∼1 h). Afterward, the solvent was removed in vacuo and the residue taken into CH_2Cl_2 (100 mL). The solution was washed with water (1 × 25 mL), 0.5 N HCl (3 × 25 mL), saturated sodium bicarbonate (3 × 25 mL), and brine (1 × 25 mL) and dried over $MgSO_4$. A yellow oil was obtained (5.44 g) after removing the solvent. The crude product was chromatographed (silica gel column, 0−10% EtOAc/Hexane) to afford a colorless oil (4.75 g, 18.8 mmol). ^{1}H NMR ($CDCl_3$) δ 1.57 (m, 2H), 1.79 (m, 2H), 1.94 (t, J = 2.4 Hz, 1H), 2.18 (td, J = 11, 2.8 Hz, 2H), 2.47 (s, 3H), 4.08 (t, J = 6.4 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H); MS m/z 252 (M^+).

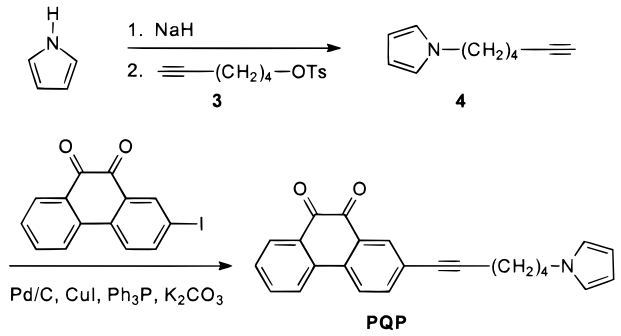
1-(Pyrrol-1-yl)-5-hexyne, 4. To a solution of pyrrole (1.34 g, 20.0 mmol) in DMF (30 mL) cooled to 0 °C was added NaH (60% dispersion in mineral oil, 0.88 g, 22.0 mol) under N_2. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was then cooled to 0 °C again and a white solid precipitated. Next, a solution of toluene-4-sulfonic acid hex-5-ynyl ester (**3**, 2.52 g, 10.0 mmol) in DMF (10 mL) was added, and the resulting mixture was stirred for 2 h at room temperature. The reaction was quenched with MeOH (10 mL) followed by water (400 mL). The aqueous solution was extracted with ethyl ether (4 × 100 mL), and the combined organic extracts were washed with water (3 × 100 mL) and brine (1 × 100 mL) and then dried over $MgSO_4$. A yellow oil (1.3 g) was obtained after the solvent was evaporated in vacuo. The crude oil was chromatographed (silica gel, 10% CH_2Cl_2/hexane) to yield a colorless oil (1.1 g, 7.47 mmol). ^{1}HNMR (CD_3OD) 1.46 (m, 2H), 1.87 (m, 2H), 2.18 (m, 3H), 3.92 (t, J = 7.2 Hz, 2H), 6.03 (t, J = 2.0 Hz, 2H), 6.66 (d, J = 2.0 Hz, 2H); MS m/z 148($M^+ + 1$).

2-Iodophenanthrenequinone. A mixture of nitric acid (2 mL) and sulfuric acid (5 mL) was added to a solution of phenanthrenequinone (2.08 g, 10.0 mmol) and I_2 (2.56 g, 5.0 mmol) in acetic acid (100 mL). The solution was then heated to reflux for 4 h, and a small amount of orange solid formed. The mixture was allowed to cool to room temperature and sit for 10 h without stirring. It was then cooled to 10 °C and filtered. The solid was washed with CH_2Cl_2 (3 × 5 mL) and dried under vacuum for 2 h to afford a bright orange crystalline solid (2.43 g, 7.23 mmol, 72% yield). ^{1}H NMR ($CDCl_3$) δ 7.55 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 15 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 8.4, 2.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.50 (d, J = 2.0 Hz, 1H); MS m/z 336 (M^+).

2-(6-(Pyrrol-1-yl-5-hexynyl))phenanthrenequinone, **PQP.** 2-Iodophenanthrenequinone (159 mg, 0.476 mmol), 10% Pd/C (101 mg, 0.0949 mmol), CuI (36.3 mg, 0.191 mmol), Ph_3P (99.9 mg, 0.381 mmol), and K_2CO_3 (164 mg, 1.19 mmol) were mixed in a 1:1 solution of water and dimethoxyethane (10 mL) at room temperature. The mixture was degassed with N_2 for 5 min and stirred for 30 min under N_2. 1-(Pyrrol-1-yl)-5-hexyne (**4**, 100 mg, 0.679 mmol) was then added, and the mixture was heated to 80 °C for 2 h. After cooling, the reaction mixture was extracted with CH_2Cl_2 (5 × 20 mL). The extracts were combined, dried over $MgSO_4$ and filtered through Celite. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (silica gel, 10−20% CH_2Cl_2/hexane) to produce an orange solid (121 mg, 0.342 mmol). ^{1}H NMR ($CDCl_3$) 1.58−1.68 (m, 2H), 1.92−2.02 (m, 2H), 2.47 (t, J = 7.0 Hz, 2H), 3.97 (t, J = 7.0 Hz, 2H), 6.04 (t, J = 2.9 Hz, 2H), 6.70 (t, J = 2.9 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.69 (dd, J = 8.4, 1.8 Hz, 1H), 7.73 (t, J = 7.3 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.99 (d, J = 8.0 Hz, 1H), 8.19 (s, 1H), 8.20 (t, J = 7.0 Hz, 1H); MS m/z 354 ($M + H^+$).

Electrochemical Procedures. Voltammetry experiments were performed with a PAR model 263 digital potentiostat with the model 270 electrochemistry software package. The acquisition mode was set to "ramp" in order to simulate an analogue experiment. The CH_3CN used as solvent was freshly distilled from CaH_2 and filtered through an activated alumina column right before use. A glassy carbon disk (5-mm diameter) was used as the working electrode in all experiments. It was first polished with 0.25 μM diamond polishing paste, rinsed thoroughly with water, then polished with 0.05 μM alumina paste and rinsed thoroughly with water and acetone. All measurements were conducted under N_2 in a one-compartment cell with a Pt-wire counter electrode. A Ag wire was used as a pseudoreference electrode in the solution-phase experiments with ferrocene as an internal reference. A Ag wire in a solution of 0.1 M Bu_4NPF_6/CH_3CN was placed in a separate compartment and used as a reference for the derivatized electrode testing.

Scheme 1



Electrode Derivatization. A freshly polished glassy carbon electrode was placed in a cell containing a solution of 1.0 mM **PQP** in 0.1 M NBu_4PF_6/CH_2Cl_2. A Ag wire was used as the reference electrode and Pt wire as the counter electrode. The glassy carbon electrode was cycled between −0.9 and 1.7 V three times at 100 mV/s starting in the negative direction. The electrode was then rinsed with CH_2Cl_2 and then acetone and dried under N_2. Once the acetone evaporated, the electrode was used immediately.

Voltammetry Procedures. Solvents and electrolytes were added to a cell containing working, reference, and counter electrodes and protected under N_2. The solution was degassed with N_2 for 2 min. After taking the background scan, the quinone and internal reference, if needed, were added for solution-phase experiments and the CV was taken. Then the guest was added and the CV taken again. With the derivatized electrodes, two cells, one with guest and the other without, were used. The difference in half-wave potentials before and after adding the guest or between the cells was then calculated.

RESULTS AND DISCUSSION

Synthesis. The synthesis of the pyrrole-terminated phenanthrenequinone, **PQP**, is outlined in Scheme 1. Tosylate **3** was prepared from tosyl chloride and the commercially available alcohol using triethylamine as a base. Deprotonation of pyrrole with NaH followed by reaction with **3** gave the alkyne-terminated pyrrole, **4**. This was then coupled with 2-iodophenanthrenequinone, which was prepared from phenanthrenequinone using a modified version of a literature procedure.[13]

A number of different reaction conditions, including the standard Heck coupling procedure, have been tried in our lab to couple 2-iodophenanthrenequinone with alkynes. Most of them give the desired product but the yields are poor. The best results have been obtained using the conditions reported here, which are similar to those described by Beicher and Cosford.[14]

Electrode Derivatization. Glassy carbon disk electrodes were chosen for derivatization with **PQP** because preliminary studies indicated that the pyrrole polymer adheres to the carbon surface longer than Pt or Au, giving a more stable electrode. The electrodes were derivatized with **PQP** by scanning from 0 V to −0.9 V then up to +1.6 V and back to 0 V vs Ag wire several times in a cell containing a 1 mM solution of **PQP** in 0.1 M Bu_4NPF_6/CH_2Cl_2. CH_2Cl_2 was used instead of the more commonly used CH_3CN because of the limited solubility of the monomer in the latter. The process was monitored by checking the redox current of phenanthrenequinone.

(13) Slyusarchuk, V. T.; Novikov, A. N. *J. Org. Chem. USSR* **1967**, *3*, 1283.
(14) Beicher, L.; Cosford, N. D. P. *Synlett* **1995**, 1115.

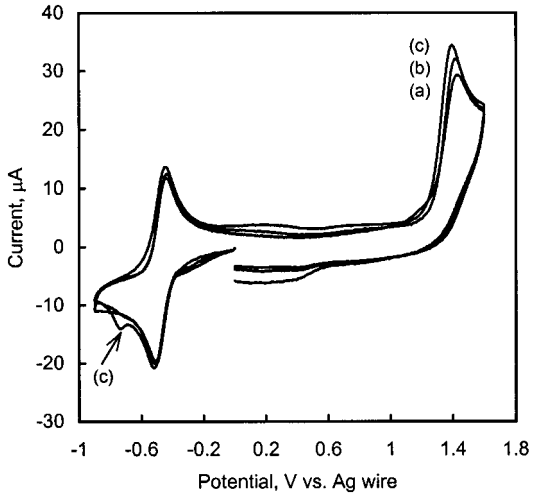


Figure 1. Derivatization of a C electrode with PQP. Scans (a), (b), and (c) are the first, second, and third CV scans of a glassy C electrode in a 1 mM solution of PQP in 0.1 M Bu_4NPF_6/CH_2Cl_2. Scan rate = 100 mV/s.

Figure 1 shows cyclic voltammograms (CVs) of the derivatization process. Voltammograms a, b, and c are the first, second and third scans, respectively. The anodic peak at about 1.5 V is the oxidation peak of pyrrole, the broad waves between 0 and 0.5 V are due to polypyrrole, and the redox couple at about −0.5 V is phenanthrenequinone. The current of all waves increases as more scans are conducted, a result of more material present on the electrode surface after polymerization. The redox potential of the phenanthrenequinone appears to shift toward more negative potentials as the film grows, but this may be an artifact of the Ag-wire reference electrode. The peak-to-peak separation does increase, probably because of slower kinetics resulting from the multiple layers. Also note that an extra reduction wave grows in at potentials negative of the original quinone reduction. This is probably due to the existence of a number of different environments within the film, which will change the redox potential of quinone. Thicker films result if more cycles are conducted, but this leads to very complicated quinone electrochemistry with multiple overlapping voltammetric waves. To simplify interpretation, the cycles were limited so as to give very low coverage of phenanthrenequinone on the electrode.

After the derivatization process was over, the electrodes were rinsed with solvent, dried under N_2, then placed in a CH_3CN solution containing no pyrrole. Even when the derivatization cycles were kept to a minimum the initial CVs of the derivatized electrodes often exhibited multiple overlapping peaks in the quinone region as shown in Figure 2a. However, upon cycling in fresh electrolyte, the quinone wave decreased in size and simplified, eventually reaching a stable voltammogram with the very small peak-to-peak separation characteristic of a very thin layer of electroactive material, Figure 2b. In other cases the shoulder on the negative side of the reduction peak persisted even after a stable voltammogram was obtained as shown in Figure 3a.

Behavior of C/PQP Electrodes. Figure 3 shows the CVs of a C/PQP electrode in the presence of different amounts of 1-phenyl-3-propylurea. Scan a is the electrode by itself. Scans b,

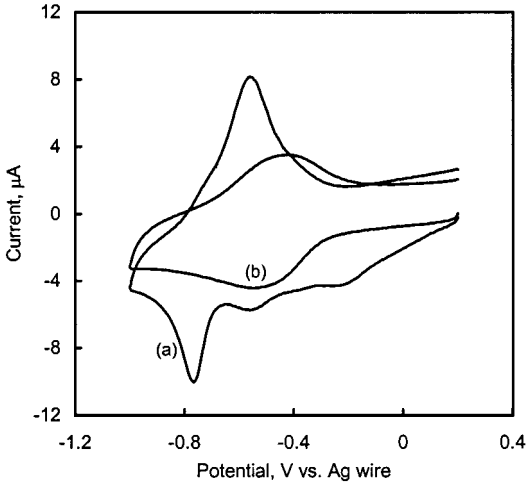


Figure 2. CVs of a C/PQP electrode in 0.1 M Bu_4NPF_6/CH_3CN: (a) first scan after derivatization, (b) 16th scan after derivatization. Scan rate = 100 mV/s.

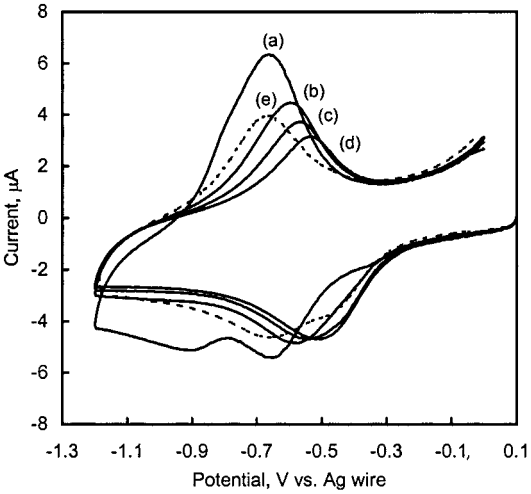


Figure 3. CVs of a C/PQP electrode in the presence of different amounts of 1-phenyl-3-propylurea in 0.1 M Bu_4NPF_6/CH_3CN: (a) 0 mM urea, (b) 5 mM urea, (c) 10 mM urea, (d) 20 mM urea, (e) fresh cell, 0 mM urea. Scan rate = 100 mV/s.

c, and d are the CVs of the derivitized electrode taken in the presence of 5, 10 and 20 mM 1-phenyl-3-propylurea, respectively. As observed in the solution phase, the redox potential of the phenanthrenequinone shifts toward more positive values in the presence of urea, indicating a strong interaction between the surface-confined quinone radical anion and the urea. Most importantly, the process is reversible. Scan e is a CV taken with the same electrode in a blank cell after taking the CVs in the urea solutions. The redox potential of the primary quinone wave has returned to close to its original value. (Interestingly, the shoulder that was originally on the negative side of the primary reduction peak has disappeared and a shoulder now appears on the positive side. On electrodes with no shoulder to begin with there is still no shoulder after returning the electrode to the blank solution.)

To confirm that the shift in redox potential of the derivitized electrode is the result of binding between the urea and phenanthrenequinone and not a change in a property of the solution or the polymer film due to nonspecific interactions, the same electrode was also examined in the presence of 1,1-dibutyl-3-phenylurea. This urea has only one N−H and does not give a

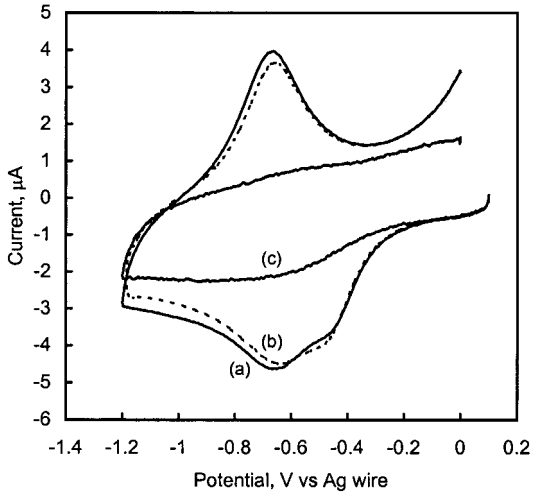


Figure 4. CVs of a C/PQP electrode in the presence of 1,1-dibutyl-3-phenylurea in 0.1 M Bu_4NPF_6/CH_3CN: (a) 0 mM urea, (b) 5 mM urea, (c) polished electrode. Scan rate = 100 mV/s.

Table 1. Shifts in Half-Wave Potential, $\Delta E_{1/2}$, of Phenanthrenequinone, PQ, and Derived Electrode, C/PQP, in CH_3CN upon Addition of Substrates[a]

	$\Delta E_{1/2}PQ^{0/1-}$ (mV)	
substrate (10.0 mM)	PQ in soln	C/PQP
1,3-di-(4-trifluoromethyl)phenyl urea	173 ± 10	65 ± 5
1,3-diphenyl urea	119 ± 10	107 ± 17
1-phenyl-3-propyl urea	66 ± 12	63 ± 8
butyl urea	17 ± 6	1 ± 7
1,3-dipropyl urea	14 ± 9	2 ± 6
1,1-dibutyl-3-phenyl urea	2 ± 2	3 ± 13
ethylene glycol	2 ± 3	0 ± 15
water	1 ± 2	7 ± 15
ethanol	3 ± 8	1 ± 2
propylamine	0 ± 11	0 ± 7

[a] The reported $\Delta E_{1/2}$ values are the average of at least 3 measurements. The error values correspond to the 95% confidence limits.

significant shift in the redox potential of phenanthrenequinone in solution. Figure 4 shows the CV of (a) the derivitized electrode by itself, (b) the electrode upon addition of 1,1-dibutyl-3-phenylurea, and (c) the electrode after polishing. Just as in solution, 1,1-dibutyl-3-phenylurea causes no significant shift in the potential of the surface-confined quinone wave. This supports the conclusion that the shift seen with 1-phenyl-3-propyl urea is due to the specific interaction between this urea and the phenanthrenequinone radical anion on the electrode surface.

Table 1 lists the shifts in half-wave potential, $\Delta E_{1/2}$, observed for a C/PQP electrode in the presence of 10 mM of various guests in CH_3CN and $\Delta E_{1/2}$s observed for phenanthrenequinone in solution under the same conditions. The results show that the surface-confined phenanthrenequinone is even more selective than that in solution. Only the aromatic ureas, the guests which cause a large shift in $E_{1/2}$ of phenanthrenequinone in solution, cause a significant shift with the derivitized electrodes. With 1,3-diphenylurea and 1-phenyl-3-propylurea, the magnitude of the shift is similar to that observed in solution. Surprisingly,1,3-di-(4-trifluoromethylphenyl)urea, the guest which causes the largest shift in solution, gives a smaller shift than the other aromatic ureas with the surface-confined phenanthrenequinone. The reason for this is not obvious. It may be a steric effect.

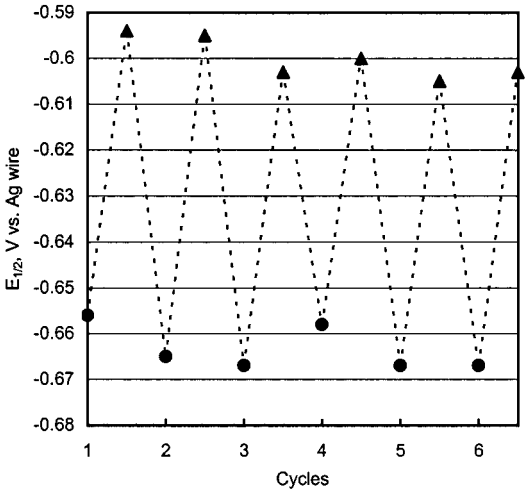


Figure 5. $E_{1/2}$ values for a C/PQP electrode transferred back and forth between a blank cell (●) and a cell containing 10 mM diphenylurea (▲) in 0.1 M Bu_4NPF_6/CH_3CN.

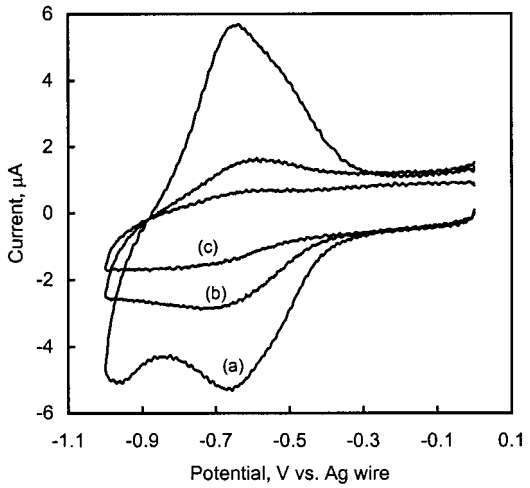


Figure 6. CVs of a C/PQP electrode in 0.1 M Bu_4NPF_6/CH_3CN: (a) first scan after conditioning, (b) last scan after 93 CVs in 31 different cells, about 9 h after first scan, (c) after polishing the electrode. Scan rate = 100 mV/s.

The reproducibility in potential of the derivatized electrodes is also good. Figure 5 shows the variation in $E_{1/2}$ for the surface-confined quinone as the electrode is taken back and forth between a blank solution and a solution containing 10 mM phenylpropylurea. The $E_{1/2}$ values in the blank solution are within 11 mV of each other, as are those in the urea solution.

A gradual loss in coverage does occur as the C/PQP electrodes are used. The loss is more rapid in the presence of aromatic ureas, probably because binding helps solubilize the pyrrole oligomers. However, despite the loss in coverage, the potential of the pyrrole remains constant making it possible to use some of the electrodes for a remarkable length of time. Figure 6 shows CV's of one electrode (a) immediately after equilibration and (b) after 9 h of experiments, including 93 CVs in 31 cells. Despite the significant loss in coverage that occurred, the redox potential of the electrode only changed from -656 ± 0 to -650 ± 4 mV between CV a and CV b, and the electrode was still usable at the end. Although not all C/PQP electrodes lasted as long as this one, the behavior of this electrode indicates it is possible to produce electrodes with the stability required for chemical sensors using this methodology.

CONCLUSIONS

In this project, we successfully demonstrated that redox-dependent receptors such as phenanthrenequinone can be confined on the electrode surface by polymerizing pyrrole derivatives of the receptors. The electrodes derivitized with phenanthrenequinone-pyrrole polymer are reasonably stable in organic media such as methylene chloride and acetonitrile. Although loss in coverage occurs, the redox potential of the surface-confined phenanthrenequinone is stable under different conditions over a several-hour-long testing period. Significantly, the behavior of the phenanthrenequinone on the electrode surface is very similar to that in solution. The redox potential of the phenanthrenequinone in the derivatized electrodes shifts positive in the presence of aromatic ureas, and the relative sizes of the shifts are largely in accordance with those observed in solution. Such electrodes can be considered as aromatic urea sensors and could be used to detect and measure the concentration of such ureas in the millimolar range in organic media.

The lower detection limit for diphenylurea with the C/PQP electrodes is approximately 1 mM. As discussed in the Introduction, this is consistent with a binding constant of approximately 10^3 between the PQP radical anion and the urea. This seems reasonable, given that the binding constant between phenanthrenequinone and diphenylurea is 900 M^{-1} in DMF solution.[3b] The binding constant to neutral phenanthrenequinone cannot be determined with a great deal of accuracy, but appears to be between 0.1 and 0.01 M^{-1}, which would correspond to an upper detection limit of >10 M. However, we are unable to verify this with the C/PQP electrodes because rapid loss of coverage occurs above 50 mM of urea, presumably due to solubilization of the PQP oligomers after bonding to urea.

Since loss of coverage is always an issue with modified electrodes, this project also points out an inherent advantage that modified-electrode sensors, in which the signal is a change in potential, have over those in which the signal is a change in current. With the latter, the magnitude of the signal will be proportional to both the concentration of analyte and the amount of electroactive material on the electrode, so a decrease in coverage will decrease the sensitivity and alter the calibration of the sensor. However, with sensors such as those described here, the magnitude of the signal will depend only on the concentration of analyte. As long as enough material remains on the electrode that ΔE can be reliably measured, the calibration will stay the same.

ACKNOWLEDGMENT

The authors wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation for partial support of this work.

Received for review September 29, 1999. Accepted January 24, 2000.

AC991120W