ᴵMENTATION PAGE			Form Approved OMB No. 0704-0188

AD-A245 798 ‖‖‖‖‖‖‖‖‖‖‖‖	1b RESTRICTIVE MARKINGS		
	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report # 46		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION Massachusetts Inst. of Tech.	6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Office of Sponsored Programs M.I.T., Room E19-702, Cambridge, MA 02139		7b ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	

8c. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 1113ES 800 N. Quincy Arlington, VA 22217-5000	10 SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO 84-K-0553	PROJECT NO	TASK NO 051-597	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Chemically Sensitive Microelectrochemical Devices: New Approaches to Sensors

12 PERSONAL AUTHOR(S)
C.A. Mirkin, J.R. Valentine, D. Ofer, J.J. Hickman, M.S. Wrighton

13a TYPE OF REPORT technical	13b TIME COVERED FROM 90 TO 91	14 DATE OF REPORT (Year, Month, Day) 92/2/4	15 PAGE COUNT 32

16 SUPPLEMENTARY NOTATION
submitted for publication/published in: American Chemical Society Symposium Series Volume on Biosensors

17	COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) microelectrochemical devices, microelectrodes
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

see attached document

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92-03265
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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak	22b TELEPHONE (Include Area Code) 202-696-3945	22c OFFICE SYMBOL

Office of Naval Research

Contract N00014-84-K-0553

Task No. 051-597

Technical Report #46

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Prepared for Publication

in

American Chemical Society Symposium Series
Volume on Biosensors

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

CHEMICALLY SENSITIVE MICROELECTROCHEMICAL DEVICES: NEW APPROACHES TO SENSORS

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Abstract

New kinds of microelectrochemical sensors are described involving two redox active molecules immobilized onto a microelectrode. One redox species is chemically insensitive with respect to variation in $E_{1/2}$, e.g. a ferrocene derivative, and serves as an internal reference in a linear sweep voltammogram. The second species is chemically sensitive, e.g. a pH sensitive quinone or a CO sensitive ferraazetine derivative, which has an $E_{1/2}$ that varies with the changes in the chemical environment. A linear sweep voltammogram thus shows two waves, one for the reference molecule and one for the indicator molecule. The shift for the indicator wave along the potential or current axis provides a method for analyte detection. Surface derivitization, proof-of-structure, and proof-of-concept sensor functions are demonstrated.

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Introduction

Described herein are the proof-of-concept results demonstrating a new approach to electrochemical sensors based upon chemically sensitive microelectrochemical devices (*1-2*). A typical device consists of at least two individually addressable electrodes. The working electrode is a microelectrode and is derivatized with at least one molecule that has a chemically sensitive formal potential and serves as the indicator, and one molecule that has a chemically insensitive formal potential and serves as a reference. The indicator and reference molecules are confined to the electrodes either by monolayer self assembly techniques (*3-10*) or by dissolving in a thin film of solid electrolyte. Detection in these systems is accomplished by measuring either the potential difference, ΔE, associated with current peaks for oxidation (or reduction) of microelectrode-confined redox reagents, where the magnitude of ΔE can be related to the concentration of analyte, **Scheme 1a**; or in some systems, by measuring the change in current ΔI associated with the shifted peak, where ΔI can be related to the reaction of the indicator molecule with the of analyte, **Scheme Ib**.

In the case of a two-terminal device, current peaks for oxidation (or reduction) of the reference and indicator molecules are determined from two-terminal, linear sweep voltammograms using a counter electrode having an area much larger than the sensor electrode, **Scheme I**. A relatively large surface area counter electrode is needed so that the linear sweep of applied voltage produces only a change in the potential of the sensor electrode. For example, if the counter electrode is 10^3 times larger than the sensor electrode, the counter electrode potential will change ~1 mV upon application of a one volt potential difference. A key advantage of this device configuration is that it does not require a third reference electrode. A second advantage is that the footprint of the sensor can be quite small. And third, the system is self-assessing in that the linear sweep voltammetry yields an assessment of the surface coverage of the indicator and reference molecules. The sensor is viable as long as current peaks are measurable.

Realization of two-terminal microsensors like that represented in **Scheme I** depends on the discovery of viable reference and indicator molecules that can be confined to electrode surfaces. Described herein are three different microelectrochemical sensing sytems. The first is a three-terminal microelectrochemical sensing system for CO based upon an indicator molecule,
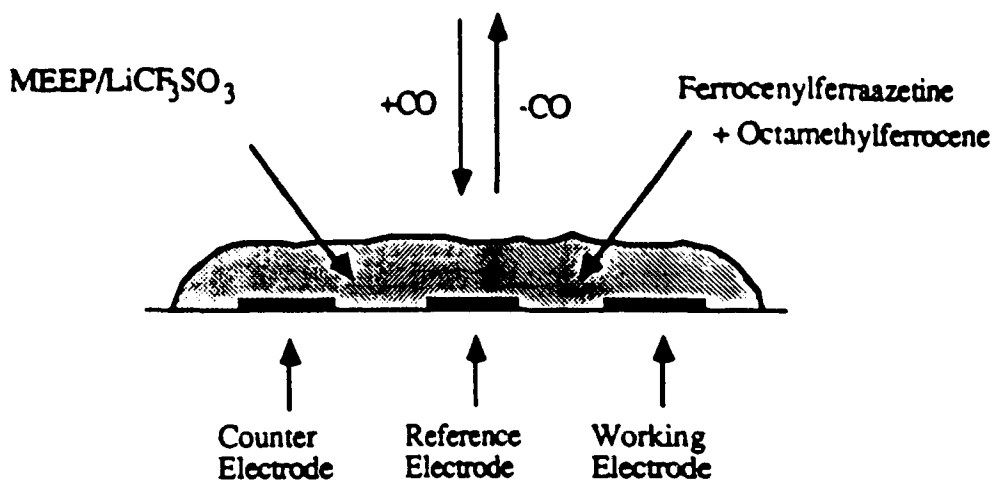
ferrocenyl ferraazetine, that selectively reacts with CO (2). The second microelectrochemical

system is bas.-1 upon a disulfide functionalized ferrocenyl ferraazetine that can be adsorbed onto Au

or Pt via monolayer self-assembly techniques. Efforts to make a two-terminal CO sensor based upon

the self-assembled ferraazetine will be discussed. Finally, a two-terminal system based upon the

self-assembly of a pH sensitive hydroquinone and a pH insensitive ferrocene will be described (1).

A Solid State Molecule-based Sensor for CO: The Solid-state Electrochemistry of Ferrocenyl Ferraazetine in MEEP/LiCF$_3$SO$_3$.

It has been reported that ferraazetine complexes **1a,b** show facile, reversible CO insertion to

form ferrapyrrolinone complexes **2a,b**, equation 1 (5-6). We synthesized ferrocenyl ferraazetine **1c**

$$\text{(1)}$$

1a, R= Bu^t
1b, R=Ph
1c, R=ferrocene
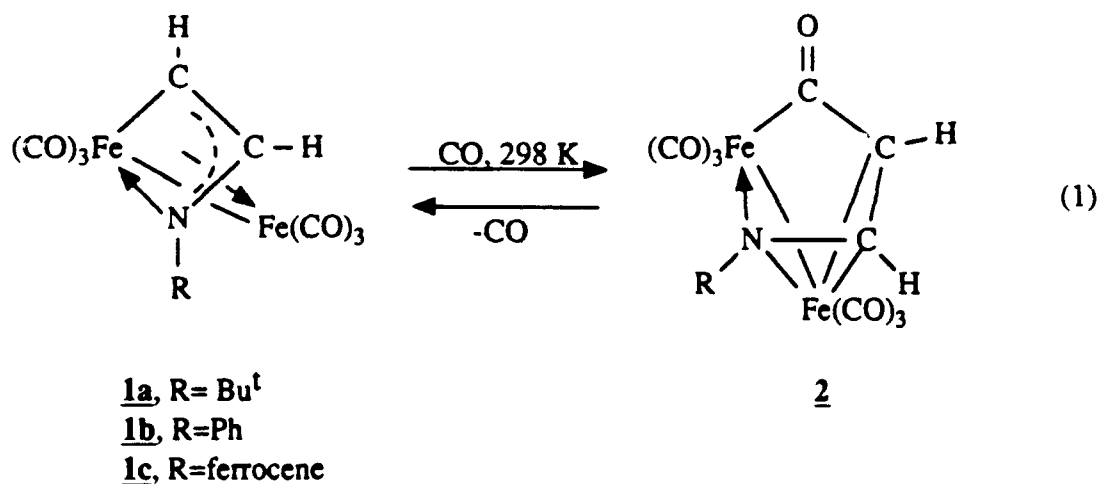
with the aim of demonstrating a reversible redox active molecule which undergoes CO insertion to

give a product with a different redox potential. Like **1a** and **1b**, **1c** reacts with CO to form a

ferrapyrrolinone complex **2c**, in the dark. Significantly, while **1c** is photosensitive, **1c** at 298 K is

chemically inert to 1 atm of the following gases: air (not containing CO), pure H$_2$, O$_2$, or CO$_2$.

Using a solid state system similar to the ones pioneered by Murray (13-15), we have investigated the

solid state electrochemistry of **1c** and **2c**. Our electrochemical system, diagrammed in **Scheme II**, is

comprised of a microelectrode array (16-18), the solid electrolyte MEEP

(poly[(2-(2'-methoxyethoxy)ethoxy phosphazene]) (19-22), and CO sensitive **1c**.

MEEP/LiCF₃SO₃   +CO | -CO   Ferrocenylferraazetine + Octamethylferrocene

Counter Electrode   Reference Electrode   Working Electrode

MEEP ▬ Poly [bis(2-(2-methoxyethoxy)ethoxy) phosphazene]

Scheme II. Solid-state microelectrochemical system for detecting CO.

Complex **1c** was isolated as a microcrystalline solid from the reaction of ferrocenyl phosphinimine, $FcN=PPh_3$ and $Fe_2(\mu\text{-}CH_2)(CO)_8$, (23) and has spectral features similar to **1a** and **1b**, eq. 2. (11-12) FTIR shows that ~1 mM **1c** is converted rapidly ($t_{1/2}<$ 1 min) and quantitatively to **2c** upon exposure to 1 atm of CO in THF solution, and it also confirms that the same chemistry occurs in a thin film of MEEP/Li[CF₃SO₃] at 298 K, Figures 1a and 1b respectively.

The solid-state electrochemistry of **1c** and **2c** was investigated at Pt microelectrodes (144 μm long x 2 μm wide x 0.1 μm thick), **Scheme II**, and compared to the electrochemical behavior in THF/[n-Bu₄N]PF₆, Figure 2. Octamethylferrocene (24) has been used as an internal reference in the solid electrolyte medium because the formal potential of octamethylferrocene is ~400 mV negative of the formal potential of sensor molecule **1c**. To functionalize the electrodes, 6 mg (0.012 mmol) of **1c** and 3 mg (0.010 mmol) of octamethylferrocene were dissolved in a 50% solution of 4:1 MEEP/Li[CF₃SO₃] in THF and a film was cast on the microelectrode array. A cyclic voltammogram of a 1:1 mixture of octamethylferrocene and **1c** in a THF-saturated Ar atmosphere is shown in Figure 2a. When the atmosphere is changed to a THF-saturated CO atm, a ~100 mV shift in $E_{1/2}$ relative to the octamethylferrocene is observed in less than 1 min. A similar effect is observed for the electrochemistry of compound **1a** in the liquid electrolyte, Figure 2b. At intermediate conversion of **1c** to **2c**, the cyclic voltammogram shows signals for each complex.

Therefore, in this system sensing is accomplished by monitoring the growth of the electrochemical response for **2c**.

In the THF/[n-Bu$_4$N]PF$_6$ medium, the conversion of **2c** back to **1c** can be effected by purging the system of CO using an Ar stream with $t_{1/2} < 1$h at 25 °C. In the solid state-state system, reversion was atempted by pulling a vacuum for 20 min on the MEEP/Li[CF$_3$SO$_3$]/**2c** mixture. E$_{1/2}$ of the ferrocenyl unit remained constant, indicating that loss of CO does not occur. In addition, FTIR of a similarly prepared sample showed that **2c** remained in the mixture with no apparent reformation of **1c** after vacuum treatment for 20 min or upon standing for 8 h in air at 25 °C. Li$^+$ coordination to the O atom of **2c** to give **3c** may be responsible for the irreversibilty observed in the solid-state experiment, equation (2). ^{1}H NMR supports this conclusion where 7.5 (C(O)CHC$\underline{H}$) and 27.5 Hz
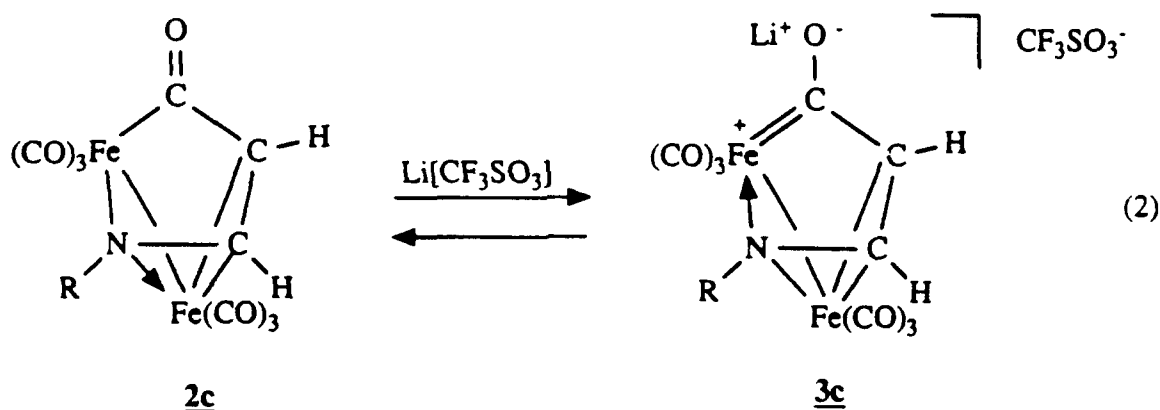

$$ \text{2c} \quad \xrightarrow[\longleftarrow]{\text{Li[CF}_3\text{SO}_3]} \quad \text{3c} \qquad (2) $$

(C(O)C$\underline{H}$CH) shifts in the resonances for the matallacyclic ring H resonances can be observed upon the addition of 0.1 M Li[CF$_3$SO$_3$] to a THF-d$_8$ solution of **2c**. Similarly, alkyl cations and H$^+$ are known to attack the O atom of the metallacyclic ring carbonyl of **2b** and **2c**, and the product formed from the methylation of **2b** has been crystallographically characterized (12). Furthermore, alkali cations, through a interaction similar to that proposed in equation (2), are known to inhibit the decarbonylation of transition metal acyl complexes (25).

Because of the irreversible reaction between **1c** and CO to form **2c** and the concomitant irreversible 100 mV shift in E$_{1/2}$ in the solid-state, accumulation of CO may be monitored by measuring the growth of the electrochemical response for **2c**. Such a device could be used to measure an accumulated exposure to CO, or simply as a disposable detector that measures a change

in CO concentration in a given environment by monitoring the ratio of the currents associated with **2c** and **1c**. One of the device limitations is that because of slow diffusion in the solid electrolyte, slow scan rates must be used and if the indicator and reference molecules of interest are unstable in one redox form, the system may not be durable. An advantage of a molecule based approach to sensing systems is that the selectivity of the system can be designed by choice of indicator molecule. In fact **1c** does not react with the usual atmospheric gases or H_2 demonstrating that the solid-state microelectrochemical system in **Scheme II** is selective for CO.

Towards a Two-terminal Solid-state Sensor for CO: The CO Dependent Solid-state Electrochemistry of Self-assembled Ferrocenyl Ferraazetine and 11-Ferrocenylundecyl Thiol. Having demonstrated the CO dependent solid-state electrochemistry of ferrocenyl ferraazetine, we synthesized a ferrocenyl ferraazetine molecule with disulfide functionality (**1d**), Scheme III. The specific aim was to design a CO sensitive molecule that could be confined to the working electrode of a two-terminal device via monolayer self assembly techniques. Disulfides have been shown to irreversibly adsorb to Au and Pt surfaces (*3-10*). ^{1}H NMR and mass spectrometry are consistent with the proposed structure for compound **1d**. The FTIR spectrum of **1d** in THF exhibits metal carbonyl bands at 2067, 2024, 1989, 1985 cm^{-1} similar to the spectra for other ferraazetine derivatives **1a-c** (*2, 5-6*). Like derivatives **1a-c**, **1d** reacts with CO (1 atm) at 298 K in CH_2Cl_2 to form a ferrapyrrolinone complex **2d**, equation (3).


1d   **2d**
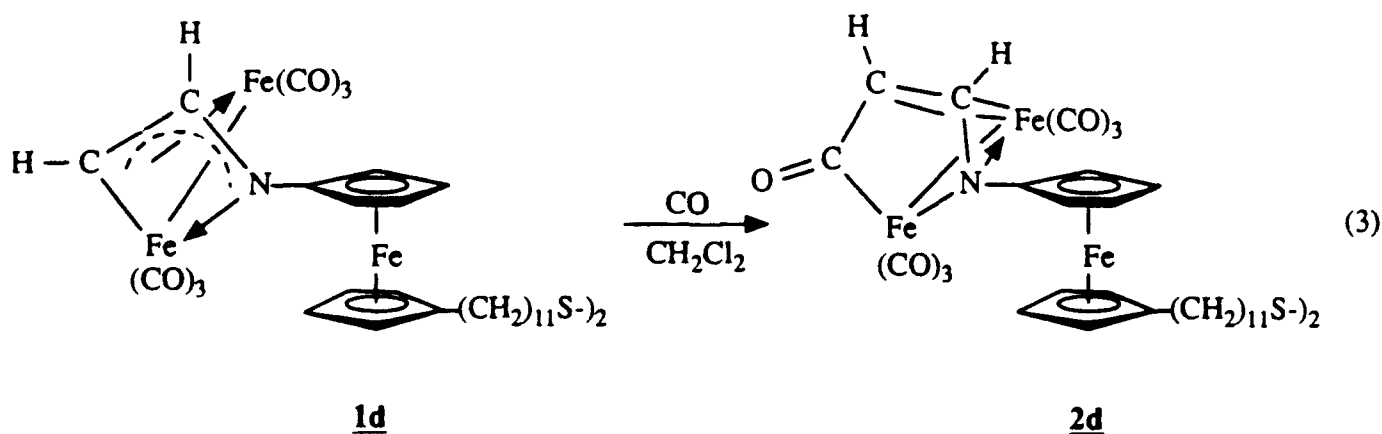
Au or Pt macroelectrodes (~0.02 cm^2) may be modified with **1d** by soaking them in a 0.1 mM hexane solution of **1d** at 298 K for 24 h. The electrochemical response is consistent with about one

monolayer of molecules, $\sim 2 \times 10^{-10}$ mol/cm^2. An internal reference molecule, bis(1, 1',

11-undecylthiol)ferrocene **4a**, may be incorporated into the film by soaking the **1d** modified

electrode for 30 min in a ~ 1 mM hexane solution of **4a**, equation (4). The electrochemical response
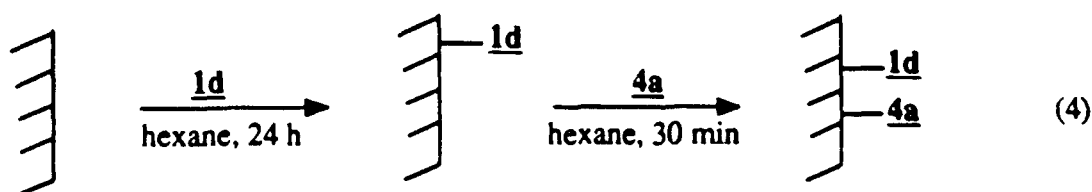

Au or Pt electrode
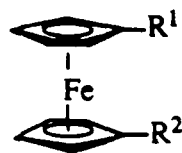
4a, R^1= (CH$_2$)$_{11}$SH, R^2= (CH$_2$)$_{11}$SH
4b, R^1=H, R^2= (CH$_2$)$_{11}$SH

$$\underline{\mathbf{4c}}, R^1=H, R^2= \overset{\overset{O}{\|}}{C}(CH_2)_{10}SH$$

is almost ideal ($\Delta E_p \cong 0$ and $i_p \propto$ scan rate) and shows two waves consistent with binding **4a** onto the

Au. Total coverages determined from integration of the current-voltage curves are 8-9 x 10^{-10}

mol/cm^2. Figure 3 shows the cyclic voltammetry of a similarly treated 0.02 cm^2 electrode before

and after exposure to CO. The wave at the more negative potential is assigned to the internal

reference molecule and does not shift upon exposure to CO. The wave at more positive potential is

assigned to sensor molecule **1d** and it shifts 120 mV upon exposure to CO indicating formation of

2d, equation (3). The conversion of **1d** to **2d** on Au or Pt surfaces may also be monitored by

specular reflectance IR. Shown in Figure 1c, is the FTIR spectrum of a **1d** treated Pt electrode (~ 1

cm^2) before and after exposure to CO. The terminal CO region (2200-1800 cm^{-1}) is displayed in

Figure 1c. Note the shift to higher energy for the metal carbonyl bands after the electrode is exposed

to CO, and note the similarity of the spectra to those obtained for **1c** in THF solution and a

MEEP/LiCF$_3$SO$_3$ film, Figures 1a and 1b, respectively. Similar results are obtained with Au

microelectrodes (200 μm^2). The solid state electrochemistry of **1d** adsorbed onto Au and Pt

microelectrodes is currently being investigated.

Two-terminal, Voltammetric Microsensor with an Internal Reference For Measuring H⁺ Activity in Highly Acidic Media.

This system is prepared by the self-assembly of a hydroquinone alkane thiol **5**, which has a pH dependent redox center (26), and the chemically insensitive ferrocenyl alkane thiol **4b** or acyl

Electrode with
Relatively High
Surface Area

$$5 = $$
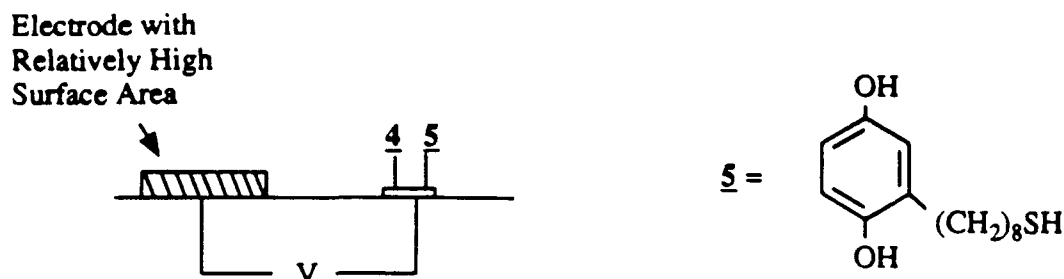
Scheme IV. Cross-sectional view of a two-terminal voltammetric microsensor based on the self-assembly of a hydroquinone thiol **5** and a ferrocenyl thiol **4** serving as reference and indicator respectively.

alkane thiol, **4c** (27-28), **Scheme IV**. **4b**, **4c**, and **5** have been previously attached separately to Au electrodes (29-32). Au microelectrodes ($\sim 10^3$ μm^2) or macroelectrodes (~ 1 cm^2) can be modified with **5** and **4c** by dipping the Au into solutions containing one or both of the thiol reagents. Figure 4 shows cyclic voltammograms for Au macroelectrodes modified with pure **4c**, pure **5**, and a combination of the two. The electrochemical response is persistent and consistent with about one monolayer of redox active molecules. Coverages determined from integration of the current-voltage curves are 3-5 x 10^{-10} mol/cm². The cyclic voltammetry for a Au microelectrode derivatized with **4c** and **5** at two values of pH, Figure 5, indicates that the redox potential for the Fc⁺/Fc system, equation (5), is pH insensitive, whereas the redox response for the Q/QH₂ system, equation (6), depends on pH. The microelectrodes may be run vs. a macroscopic Pt counter electrode in a two-terminal configuration, and the cyclic voltammograms are superimposable on the curves shown in Figure 5 where a saturated calomel reference electrode (SCE) was used. Figure 6 shows, for pH 0-10, the lack of an effect of pH on $E_{1/2}$ of the surface confined Fc⁺/Fc system and also shows the pH dependence of the potential difference between the cathodic current peaks, ΔE_{pc}, for the processes

shown in equations (5) and (6). The linear response to the solution pH comprises the basis for a pH sensor system where the Fc$^+$/Fc serves as the reference and the Q/QH$_2$ serves as the indicator, **Scheme I.**

(5)

(6)
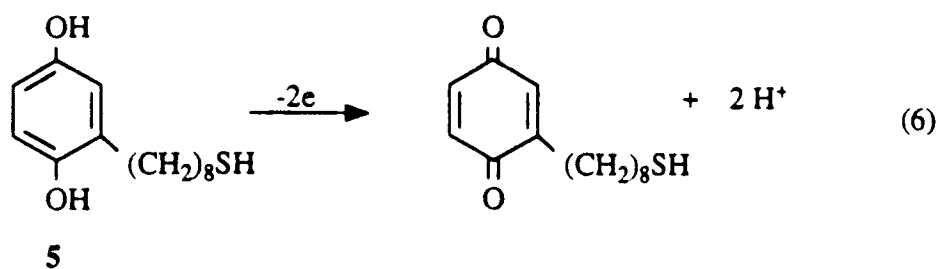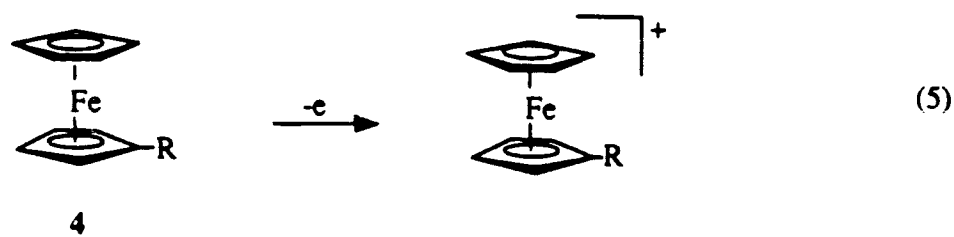
The surface-confined Fc$^+$/Fc system behaves ideally (33) at all values of pH investigated (0-10). The surface-confined Q/QH$_2$ is not ideal, in that there is a large difference in the potential for the anodic and cathodic current peaks. Such behavior is well documented for other quinones (34-35). Despite the non-ideality, the effect of pH on the electrochemical response of Q/QH$_2$ is reproducible. Both the anodic and cathodic current peaks for the quinone system shift to more positive potentials at lower pH.

Study of electrodes modified with **4b** and **5**, and subsequently examined in highly acidic media establishes a possible application of this device. Figure 7 illustrates the electrochemical response in aqueous media containing different concentrations of HClO$_4$. Amazingly, the electrochemical response of the redox molecules persists even in 10 M HClO$_4$. Note that the response for the Q/QH$_2$ system moves from ~0.5 V negative (pH = 11) of **5** to ~0.5 V positive (10 M HClO$_4$) of **5** for the

media used. Measuring H^{+} activity in highly acidic media is thus possible with a **4b/5**-modified electrode. Earlier work has established the constancy of the redox potential of a surface-confined ferrocene at very high H^{+} activity (35), justifying our use of ferrocene as an internal reference in such media.

Summary

The proof-of-concept microsensor systems described herein can be easily extended by use of other specific indicator molecules. It should be clear that monolayer redox reagents and microelectrodes are not required, but their use has the advantage that very small amounts of charge are involved in detection. The self-assembly of thiol and disulfide reagents provides a reproducible method, applicable to many chemical functionalities (3-10, 29-32), for assembly of device-active materials, but there are a large number of other electrode modification techniques that can be useful (33). Au electrodes derivitized with thiol reagents are quite robust, but obviously long term durability is an issue in many sensor applications. The pH sensing system can be used intermittently over a period of several weeks with reproducible response to variation in pH. The two CO sensing systems are not nearly as durable as the pH sensing system and the signal is lost after prolonged cycling. Nevertheless the systems illustrate some of the important requirements necessary to make useful two-terminal microelectrochemical sensors. Experiment are in progress to demonstrate multiple-response, two-terminal microsensors by incorporating more than one indicator molecule.

EXPERIMENTAL

Instruments and equipment: IR spectra were recorded using either a Nicolet 60SX or 170SX Fourier transform infrared spectrometer. ^{1}H NMR were recorded using a Bruker WM250 or AC250 Fourier transform spectrometer and mass spectra were recorded using a Finnegan MAT System 8200 mass spectrometer.

Materials: All solvents were dried by stirring over Na/benzophenone (pentane, tetrahydrofuran, toluene) or CaH_2 (CH_2Cl_2) and were freshly distilled prior to use. All chemicals were commercially available and used as received unless otherwise specified. All reactions and procedures were

performed under Ar atmosphere unless otherwise specified. Bu_4NPF_6 was recrystallized from CH_3CH_2OH prior to use. MEEP was donated by Professor Harry Allcock at the Pennsylvania State University. Octamethylferrocene and compounds **1c** (2), **4b**, **4c**, and **5** (2) were prepared by literature methods. $[N_3CpFeCp-(CH_2)_{11}S]_2$ was prepared by a modification of the Nesmayonov method for the preparation of triazoferrocene from bromoferrocene. Experiments involving **1c** and **5** have been previously described (1-2).

Synthesis of $[(PPh)_3P=N-CpFeCp-(CH_2)_{11}S]_2$. To a CH_2Cl_2 solution of $[N_3CpFeCp-(CH_2)_{11}S]_2$ (100 mg, 0.082 mmol) was added 25 mg (0.092 mmol) of PPh_3. The color changed from orange to red and after 2 h, the solvent was evaporated. Chromatography on alumina with 1:1 CH_2Cl_2/penatne as the eluent gave unreacted $[N_3CpFeCp-(CH_2)_{11}S]_2$. When the eluent was changed to 1% diethyl ether in CH_2Cl_2, a dark orange band of $[(PPh)_3P=N-CpFeCp-(CH_2)_{11}S]_2$ came off the column. The solvent was removed via rotary evaporation yielding 95 mg (0.073 mmol) of an oily yellow product, $[(PPh)_3P=N-CpFeCp-(CH_2)_{11}S]_2$.

$[(PPh)_3P=N(Fc)(CH_2)_{11}S]_2$: Yield = 90% MS (FAB+, High Res.) Cald: 1293.4798; Found: 1293.4793. ^1H NMR: δ 7.81 (m, 6H), 7.02 (m, 9H), 4.09 (m, 2H), 3.92 (m, 2H), 3.89 (m, 4H), 2.62 (t, 2H, J_{HH}= 7.5 Hz), 2.56 (t, 2H, J_{HH}= 7.6 Hz), 1.66 (m, 2H), 1.37-1.18 (m, 16H).

Synthesis of CO sensor molecule **1d**. 95 mg (0.073 mmol) of $[(PPh)_3P=N(Fc)(CH_2)_{11}S]_2$ was dissolved in CH_2Cl_2 and added to a flask containing 28 mg (0.08 mmol) of $Fe_2(\mu-CH_2)(CO)_8$ dissolved in 20 mL of CH_2Cl_2. The mixture was stirred for 24 h, and the color changed from yellow to dark red. The solvent was removed via rotary evaporation and the residue was chromatographed on silica gel. 1:3 CH_2Cl_2:pentane as an eluent gave a light yellow band of unreacted PPh_3. 1:1 CH_2Cl_2:pentane as eluent brought down a red band of **1d**. Solvent was removed via rotary evaporation yielding 69 mg (0.05 mmol) of a microcrystalline solid, **1d**.

1d: Yield = 68 % MS (FAB+, High Res.) Cald: 1381.0075; Found: 1381.0080. IR (CH_2Cl_2) 2066 (m), 2026 (vs), 1989 (s), 1995 (s) cm^{-1}. ^{1}H NMR (C_6D_6) δ 6.04 (d, J_{HH}= 1.9 Hz), 5.53 (d, J_{HH}= 1.9 Hz), 3.97 (m), 3.93 (m), 3.74 (m), 3.59 (m), 3.74 (m), 3.59 (m), 2.57 (t, 2H, J_{HH}= 7.25 Hz), 2.19 (t, 2H, J_{HH}= 8.0 Hz), 1.66 (m, 2H), 1.31 (m, 16 H).

Electrode surface derivitization with **1d** and **4a**. In a typical experiment, Au or Pt electrodes of the appropriate size were soaked in a 0.1 mM hexane solution of **1d** for 24 h. Cyclic voltammetry in CH_2Cl_2/Bu_4NPF_6 solution indicated monolayer coverage (4-8 x 10^{-10}) of **1d** as did specular reflectance FTIR spectroscopy. The **1d** treated electrodes were then soaked in a 0.1 M hexane solution of **4a** for 15 min. Cyclic voltammetry in CH_2Cl_2/Bu_4NPF_6 indicated that the monolayer formed in this manner consisted of approximately 1:1 **1d**:**4a**.

Exposure of a **1d** and a **4a** treated electrode to CO. An electrode treated with **1d** and **4a** in the aforementioned manner was placed in a 50 mL 3-neck flask containing 30 mL of 0.1 M CH_2Cl_2 solution of Bu_4NPF_6. CO was then bubbled into the solution for 10 min and a cyclic voltammogram was subsequently recorded. The wave assigned to **1d** had shifted +120 mV relative to the **4a** wave. Similarly, when a 1x1 cm^2 Au electrode treated with **1d** and **4a** was placed in a vial and purged with CO for 10 min, specular reflectance IR indicated surface conversion of **1d** to **2d**.

Acknowledgement

References

1. Preliminary results have been reported in Hickman, J.J.; Ofer, D.; Laibinis, P.E.; Whitesides, G. M.; Wrighton, M. S. *Science* **1991**, *252*, 688.

2. Preliminary results have been reported in Mirkin, C. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 8596.

3. Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.

4. Brown, A. P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem.* **1976**, *72*, 379.

5. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897.

6. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1986**, *108*, 3559

7. Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

8. Bain, C. D.; Whitesides, G. M. *Science* **1988**, *240*, 62.

9. Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.

10. Bain, C. D., Whitesides, G. M. *Angew. Chem.* **1989**, *101*, 522.

11. Mirkin, C. A.; Lu, K-L; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 7279.

12. Mirkin, C. A.; Lu, K-L; Snead, T. E.; Young, B.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 3800.

13. Pinkerton, M. J.; Mest, L. E.; Zhang, H.; Watanabe, M.; Murray, R. W. *J. Am. Chem. Soc.* **1990**, *112*, 3730.

14. Geng, L.; Longmire, M. L.; Reed, R. A.; Parker, J. F.; Barbour, C. J.; Murray, R. W. *Chem. MAter.* **1989**, *1*, 58.

15. Geng, L.; Longmire, M. L.; Reed, R. A.; Kim, M-. H.; Wooster, T. T.; Oliver, B. N.; Egekeze, J.; Kennedy, J. W.; Jorgenson, J. W.; Parker, J. F.; Murray, R. W. *J. Am. Chem. Soc.* **1989**, *111*, 1614

16. White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.

17. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.

18. Talham, D. R.; Crooks, R. M.; Cammarata, V.; Leventis, N.; Schloh, M. O.; Wrighton, M. S. Proceedings of NATO ASI "Lower-Dimensional Systems and Molecular Electronics" Spetses, Greece, 1989, R. M. Metzger, P. Day, G. Papavassiliou, eds., Plenum Press.

19. Allcock, H. R. Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

20. Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

21. Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

22. Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *Solid State Ionics*, **1986**, *18*, 258.

23. Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

24. Schmit, V. G.; Ozman, S. *Chem. Zeit.* **1976**, *100*, 143.

25. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 355-399 and references therein.

26. "Introduction to Organic Chemistry", A. Streitwiser and C. Heathcock, 2nd Ed., Macmillan, New York (1981), pg 1014-1020

27. Peerce, P.J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *108*, 121.

28. Modro, T. A.; Yates, K.; Janata, J. *J. Am. Chem. Soc.* **1975**, *97*, 1492.

29. Stern, D. A.; Wellner, E.; Salaita, G. N.; Laguren-Davidson, L.; Lu, F.; Batina, N.; Frank, D. G.; Zapien, D. C.; Walton, N.; Hubbard, A. T. *J. Am. Chem. Soc.* **1988**, *110*, 4885.

30. Hubbard, A. T. *Chem. Rev.* **1988**, *88*, 633.

31. Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.

32. Hickman, J.J., Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 1128.

33. Murray, R. W. in *Electroanaltical Chemistry*, A. J. Bard, Ed. (Dekke, New York, 1984), Vol 13, p 191 and references therein.

34. Laviron, E.; *J. Electroanal. Chem.* **1983**, *146*, 15.

35. Laviron, E.; *J. Electroanal. Chem.* **1984**, *164*, 213.

36. Nesmayanov, A. N.; Drozd, V. N.; Sazonova, V. A. *DAN SSSR*, **1963**, *150*, 321.

Figure Captions

Figure 1. A) FTIR of ferraazetine, **1c**, in THF before (——) and after (-----)exposure to CO. B) FTIR of ferraazetine, **1c**, in 4:1 MEEP/[LiCF$_3$SO$_3$] before (——) and after (-----) exposure to CO. C) Specular reflectance FTIR of ferraazetine, **1d**, adsorbed onto a Pt electrode before (——) and after (-----) exposure to CO.

Figure 2. A.) Solid-state cyclic voltammetry at a Pt microelectrode of a 1:1 mixture of octamethylferrocene (wave at more negative potential) and ferrocenyl ferraazetine (waves at more positive potentials) dissolved in a 4:1 mixture of MEEP/Li[CF$_3$SO$_3$] before and after exposure to CO. B.) Cyclic voltammetry (vs AgNO$_3$/Ag) at a Pt disk (1-mm diameter) of 0.2 mM **1a** in THF/0.1 M [n-Bu$_4$N]PF$_6$ before and after the addition of CO.

Figure 3. Cyclic voltammetry at a 0.02 cm^2 Au electrode treated with ferraazetine, **1d**, and bis(1,1', 11-undecylthiol)ferrocene, **4a**, in CH$_2$Cl$_2$/0.1 M [n-Bu$_4$N]PF$_6$ before (top) and after (bottom) exposure to CO.

Figure 4. Cyclic voltammetry at three scan rates for Au macroelectrodes in 1.0 M NaClO$_4$ at pH 1.5 buffer (phosphate) derivatized with only acyl ferrocene thiol, **4c**, (5.2 x 10^{-10} mol/cm^2) (top); only quinone thiol, **5**, (5.6 x 10^{-10} mol/cm^2) (middle); and a mixture of **4c** and **5** at 2.8 x 10^{-10} mol/cm^2 and 2.8 x 10^{-10} mol/cm^2, respectively (bottom).
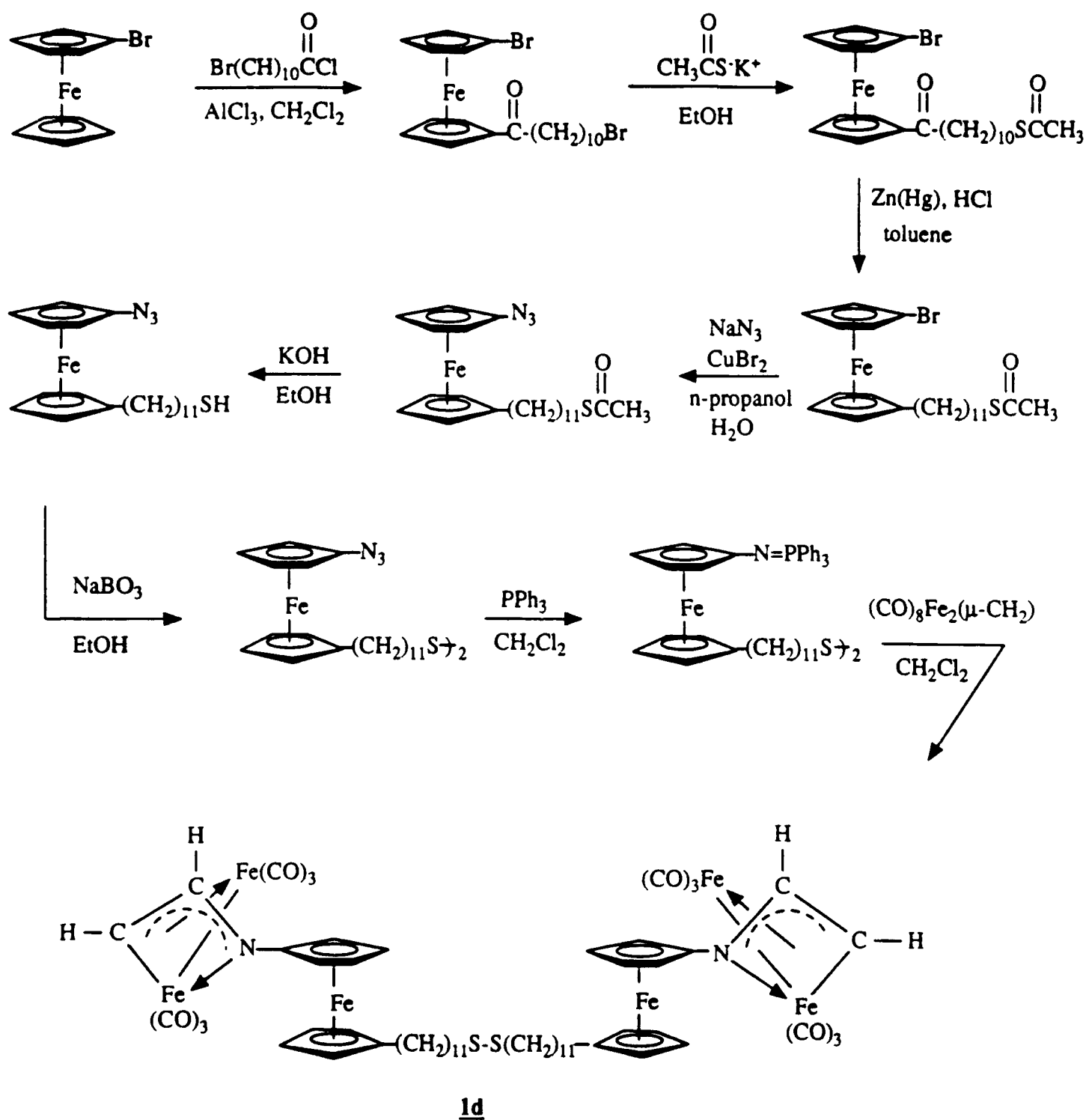
Figure 5. Cyclic voltammetry (500 mV/s) of Au microelectrodes derivatized with a mixture of **4c** and **5** at pH 1.4 and pH 6.0. The solutions used were phosphate buffers in 1.0 M NaClO$_4$ base electrolyte; an SCE reference electrode was used.

Figure 6. Plot of $E_{1/2}$ vs. SCE for the surface-confined acyl ferrocene thiol vs. pH (top) and plot of difference in cathodic current peak for surface-confined acyl ferrocenium and quinone vs. pH from two-terminal, voltammetric scans. All data are from voltammograms recorded at 500 mV/s in 1.0 M $NaClO_4$ in buffered solution.
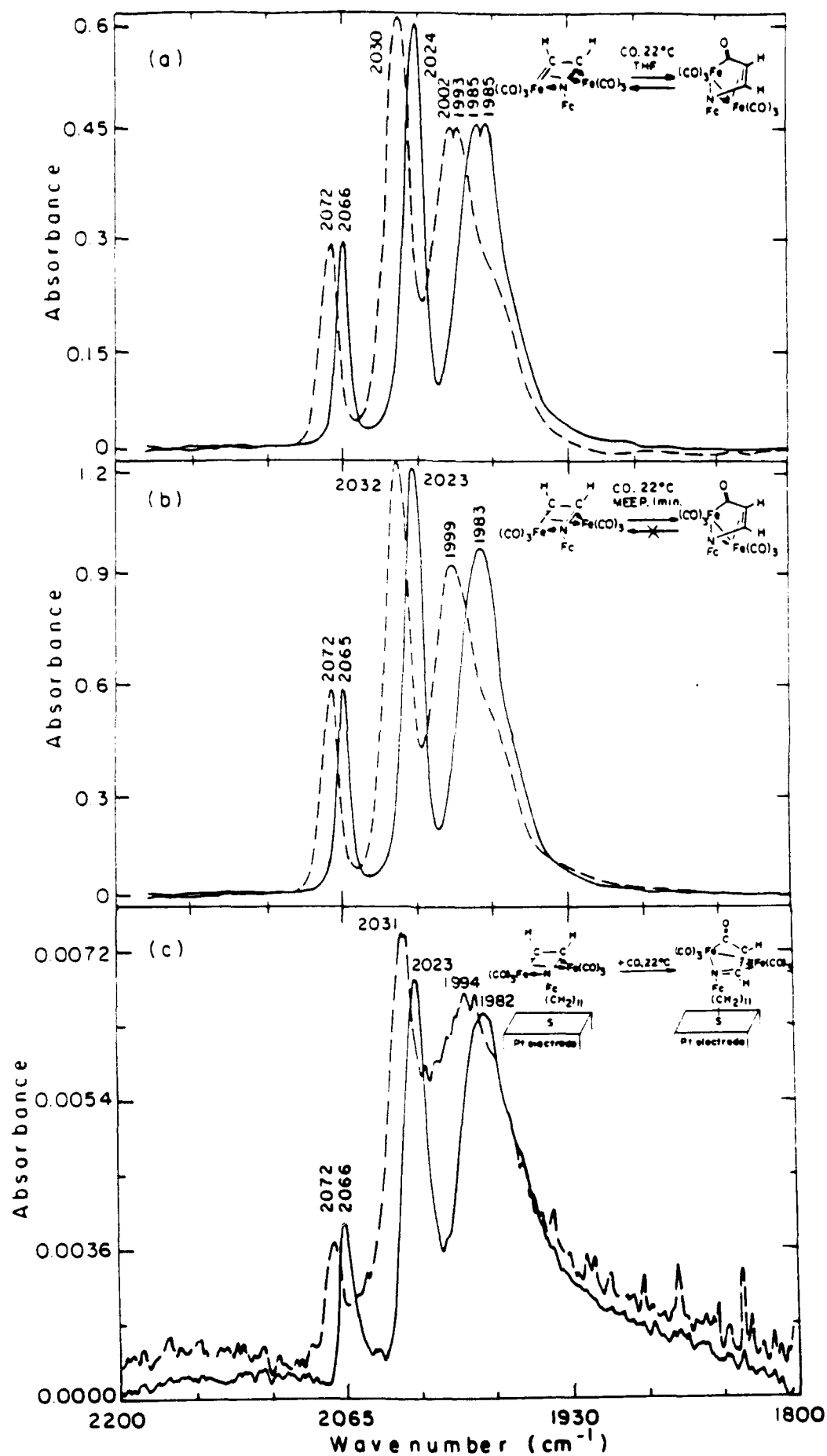
Figure 7. Cyclic voltammetry (500 mV/s) for a Au macroelectrode derivatized with alkyl ferrocene thiol, **4b**, and quinone thiol, **5**, in (from top to bottom): 1.0 M $NaClO_4$ buffered to pH 11 with phophate; 0.1 M $HClO_4$; 1.0 M $HClO_4$; 10 M $HClO_4$. Note that the reference is taken to be the average position of the oxidation and reduction waves for the ferrocene system.
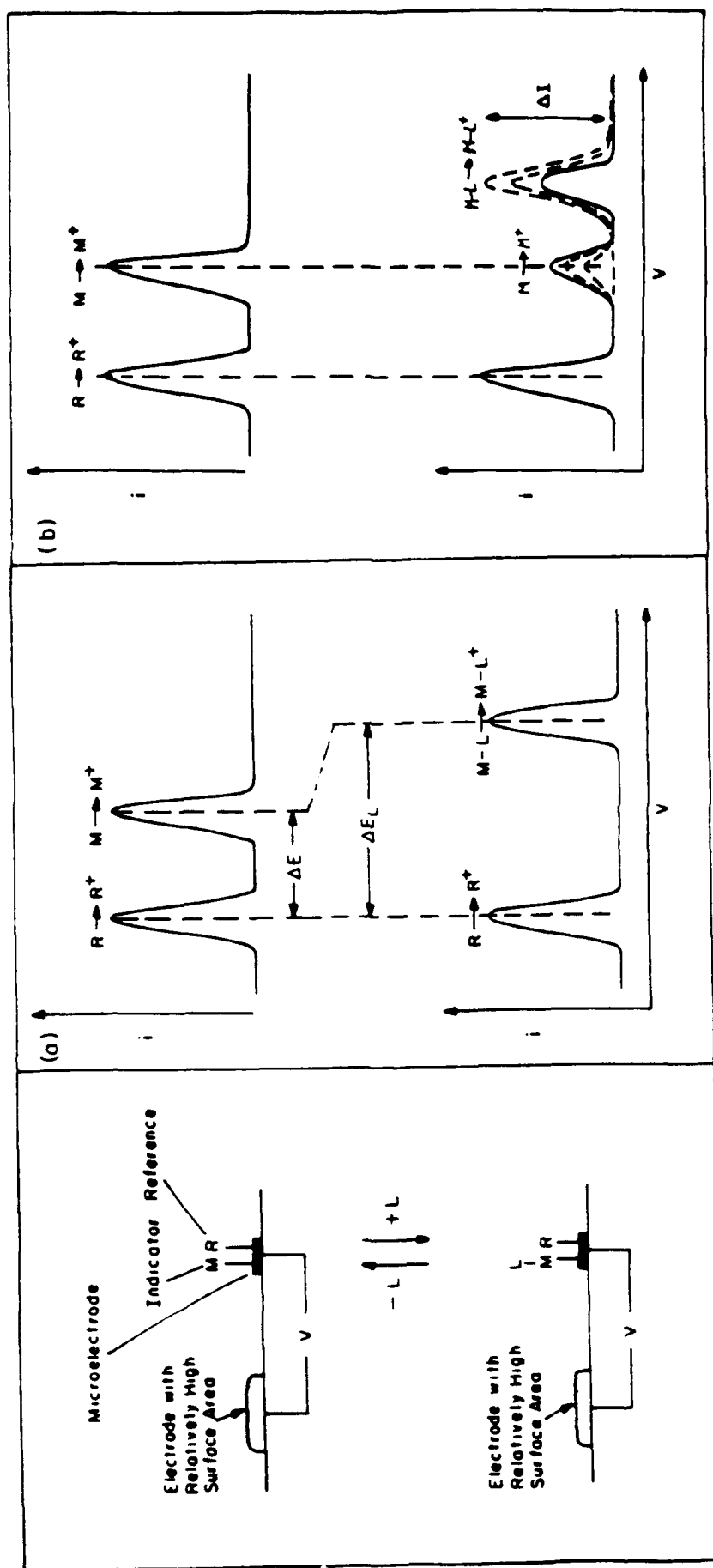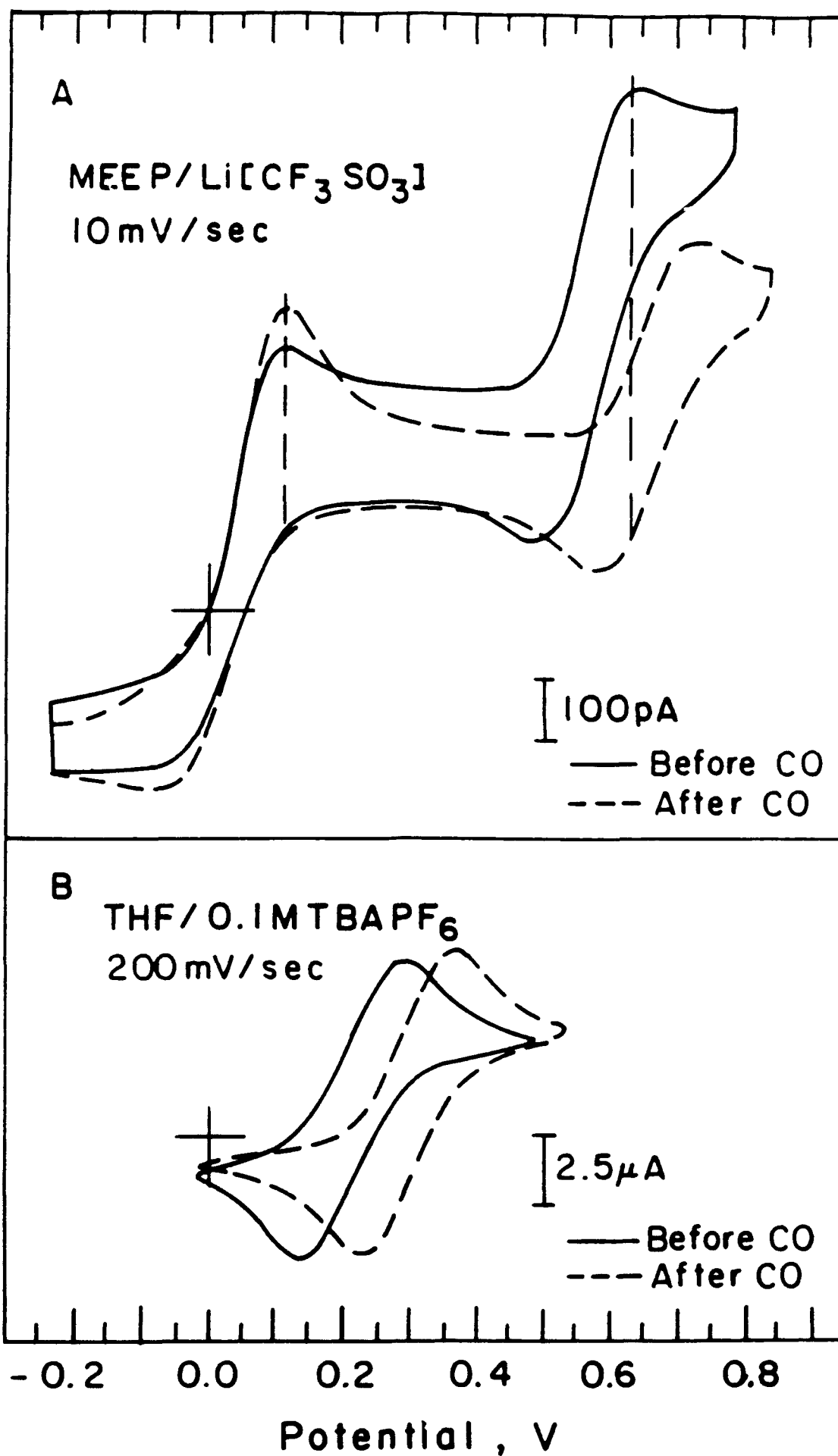
Scheme I. Concept of a two-terminal microsensor showing two possible idealized responses to a species L which binds to the indicator molecule M. A) The linear sweep voltammograms reveal a difference between the current peaks for oxidizing the reference molecule, R, and M or M-L. The position of the current peak along the potential axis, V, is variable and depends on the concentration of L. B) The linear sweep voltammograms reveal a decrease in amplitude for the current peak assigned to M and proportional growth of a new current peak assigned to M-L.
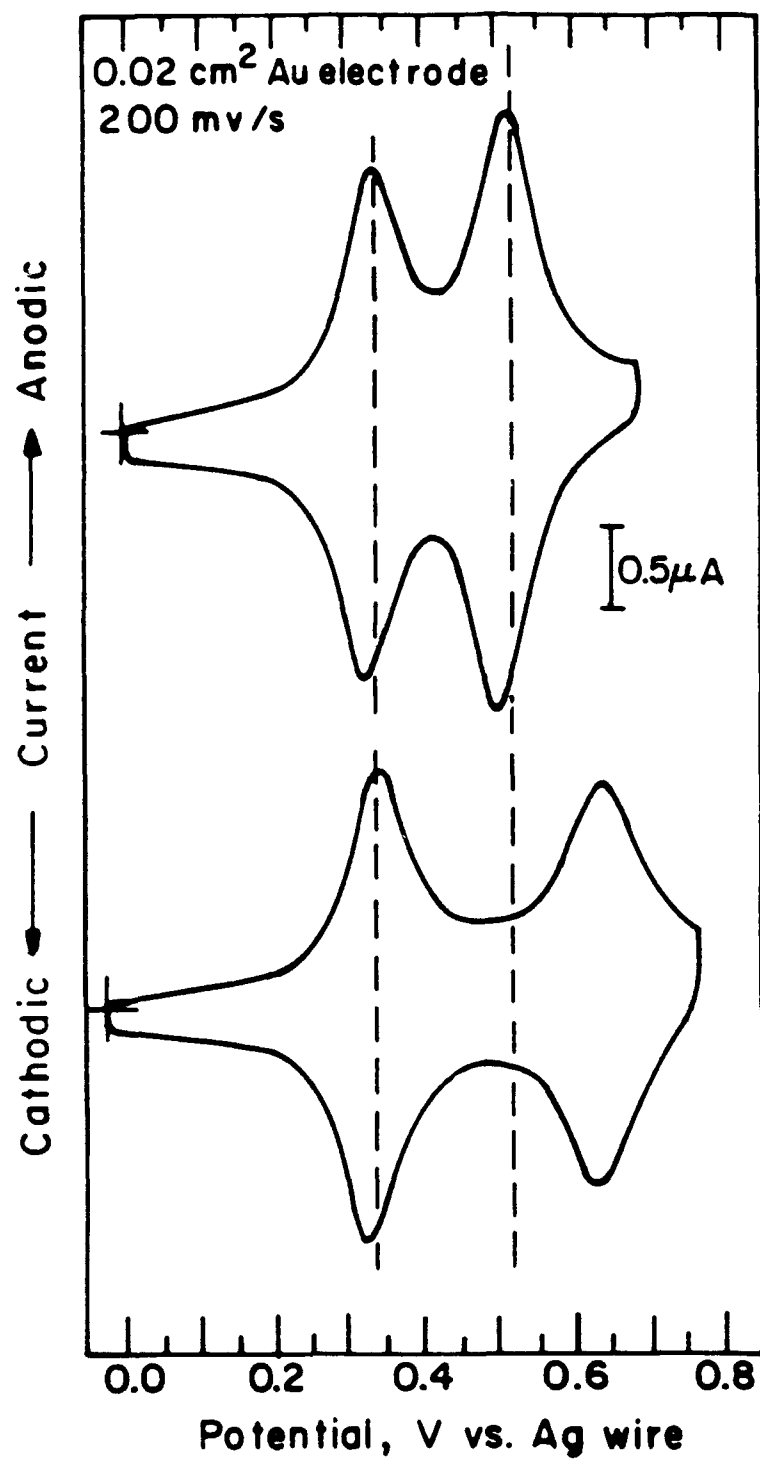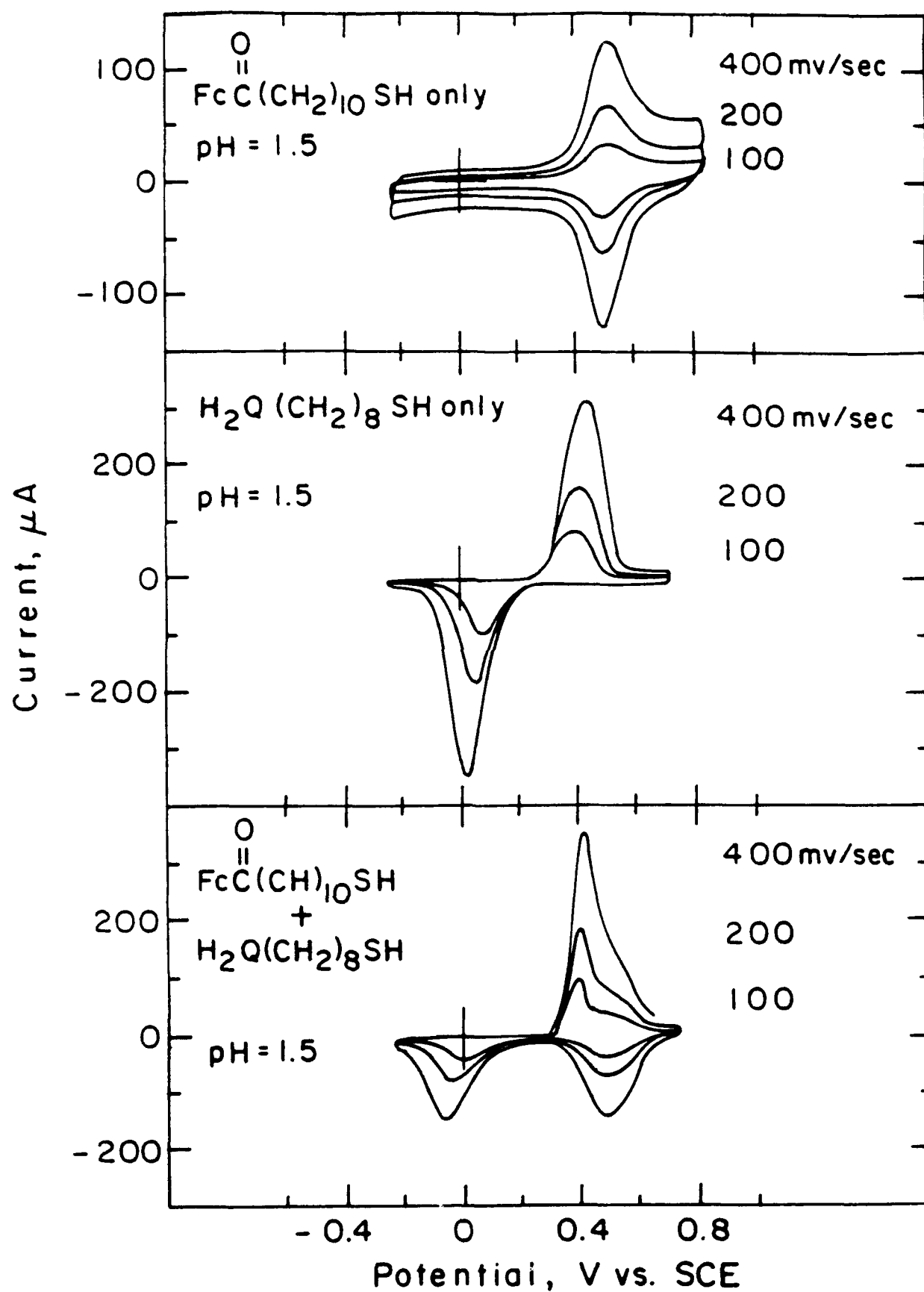
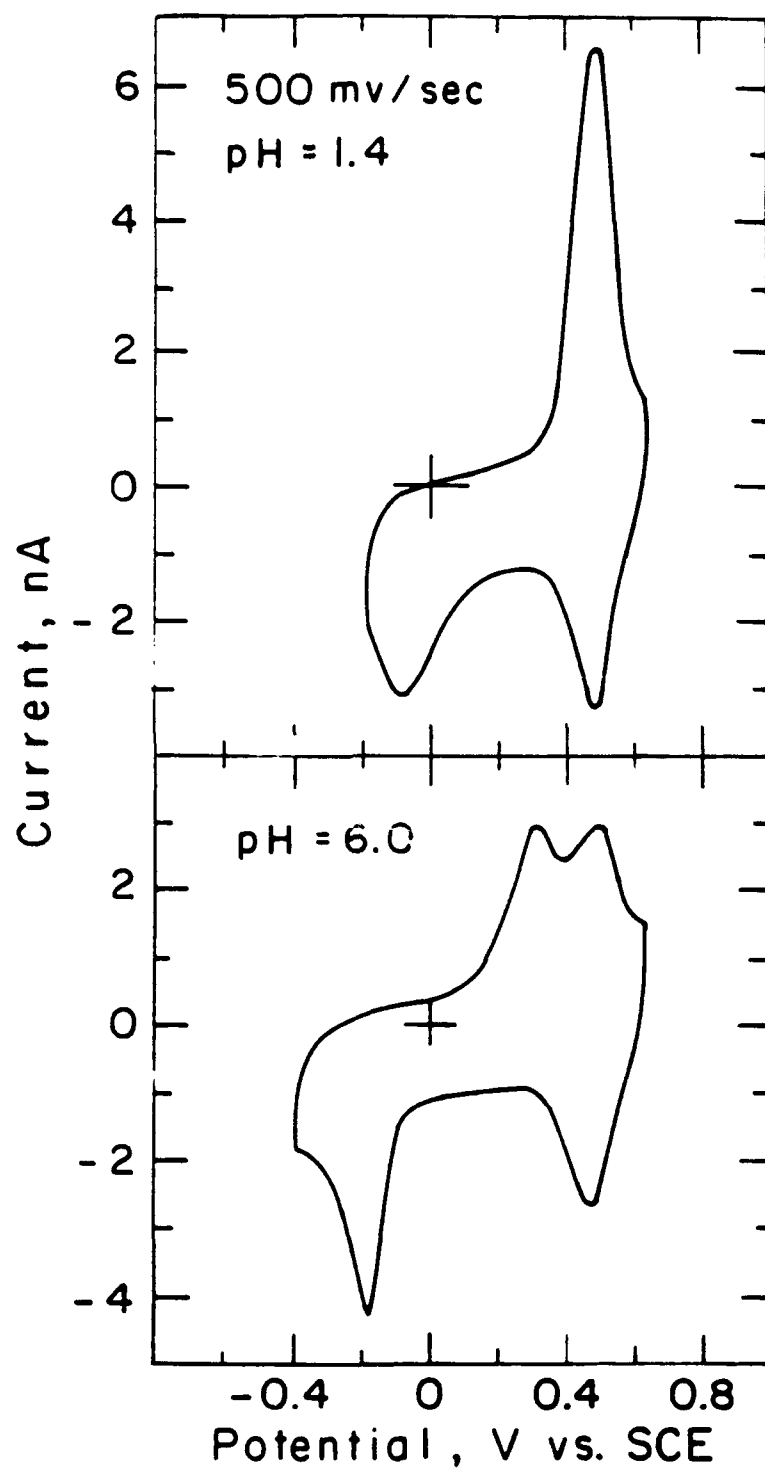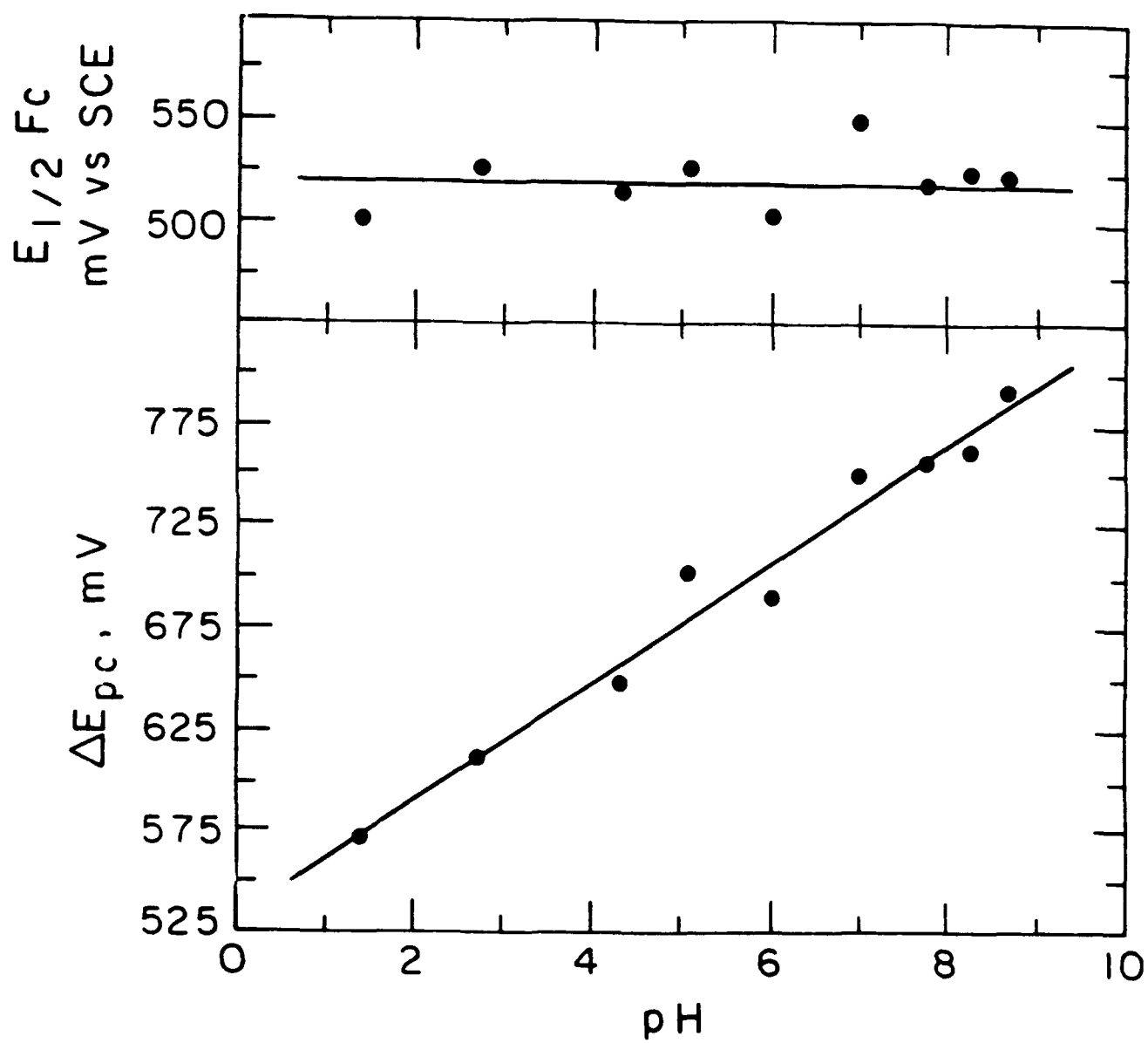**Scheme III.** The synthetic scheme for surface-confined CO sensor molecule **1d**.

A

MEEP/Li[CF₃SO₃]
10mV/sec

$$I\,100pA$$

—— Before CO
--- After CO

B

THF/0.1MTBAPF₆
200mV/sec

$$I\,2.5\mu A$$

—— Before CO
--- After CO

Anodic ← Current → Cathodic

Potential, V
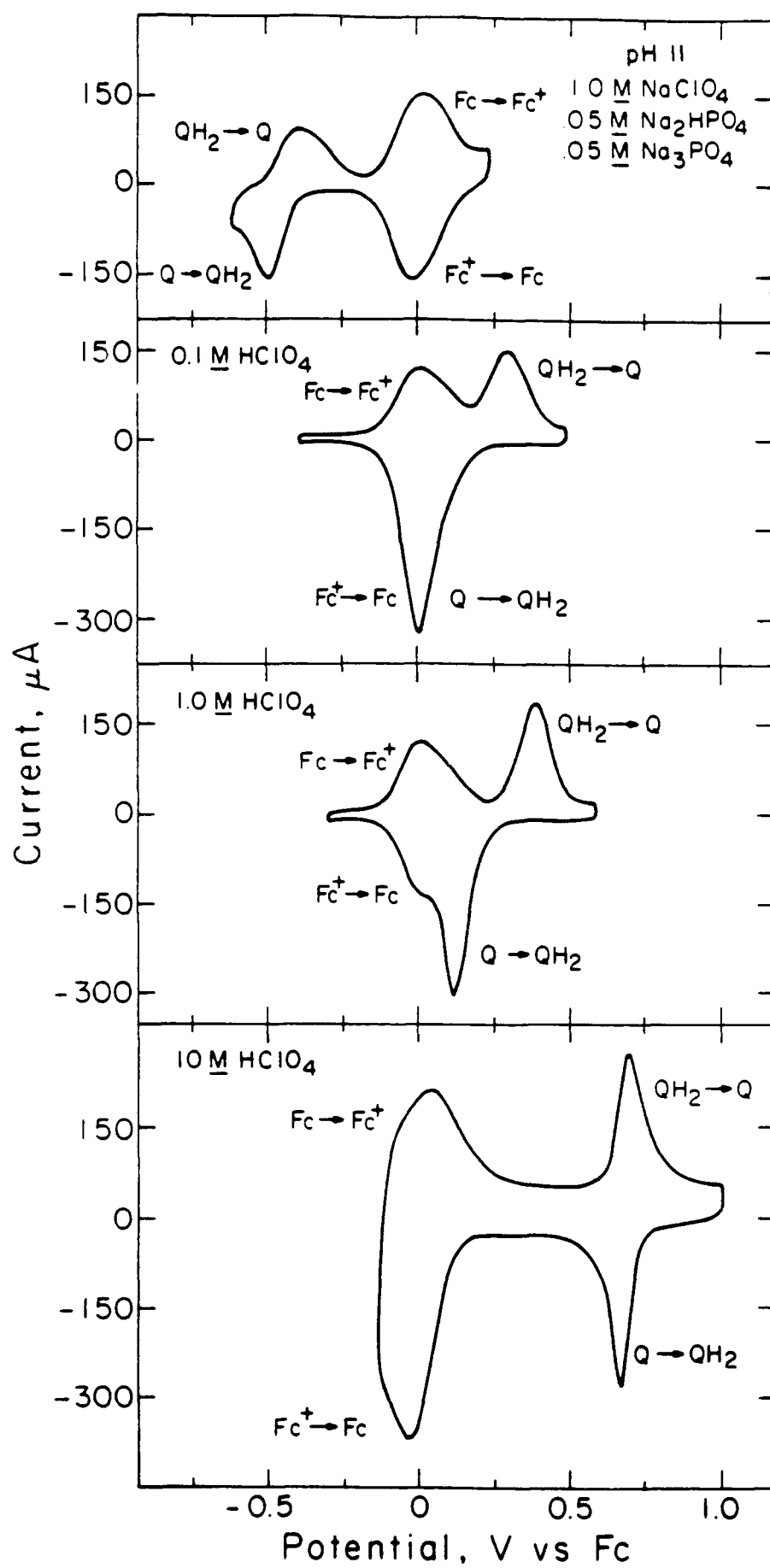
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