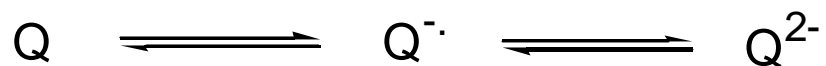
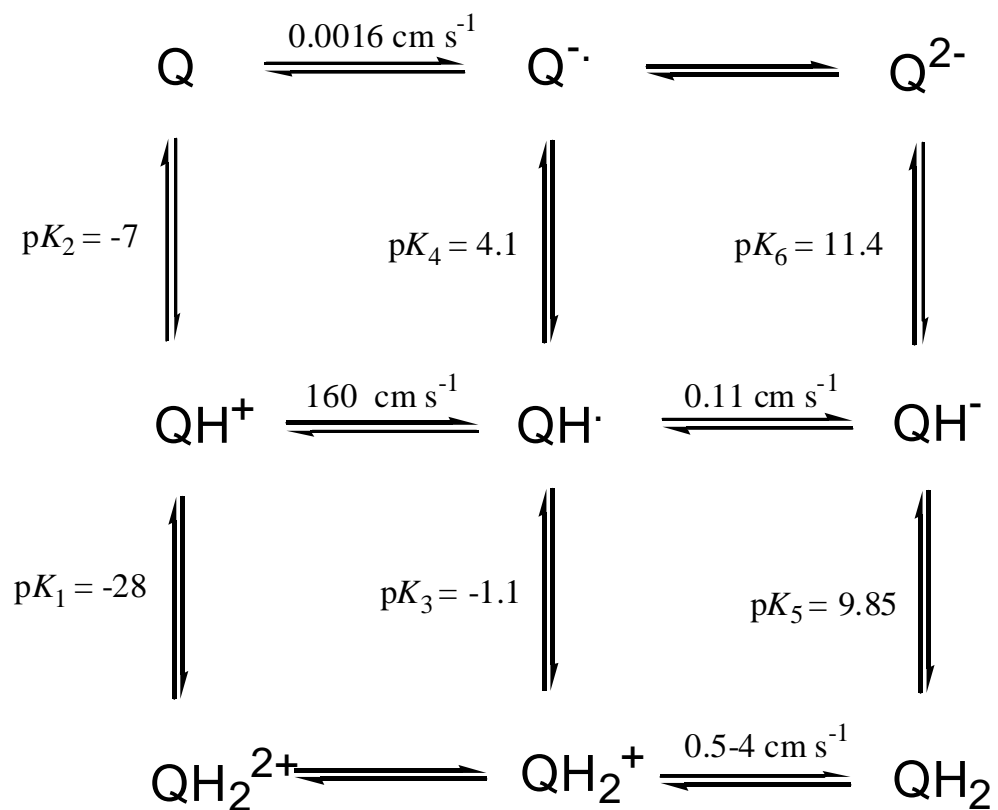


The scheme for electrochemical reduction of quinone

In aprotic media



In protic media

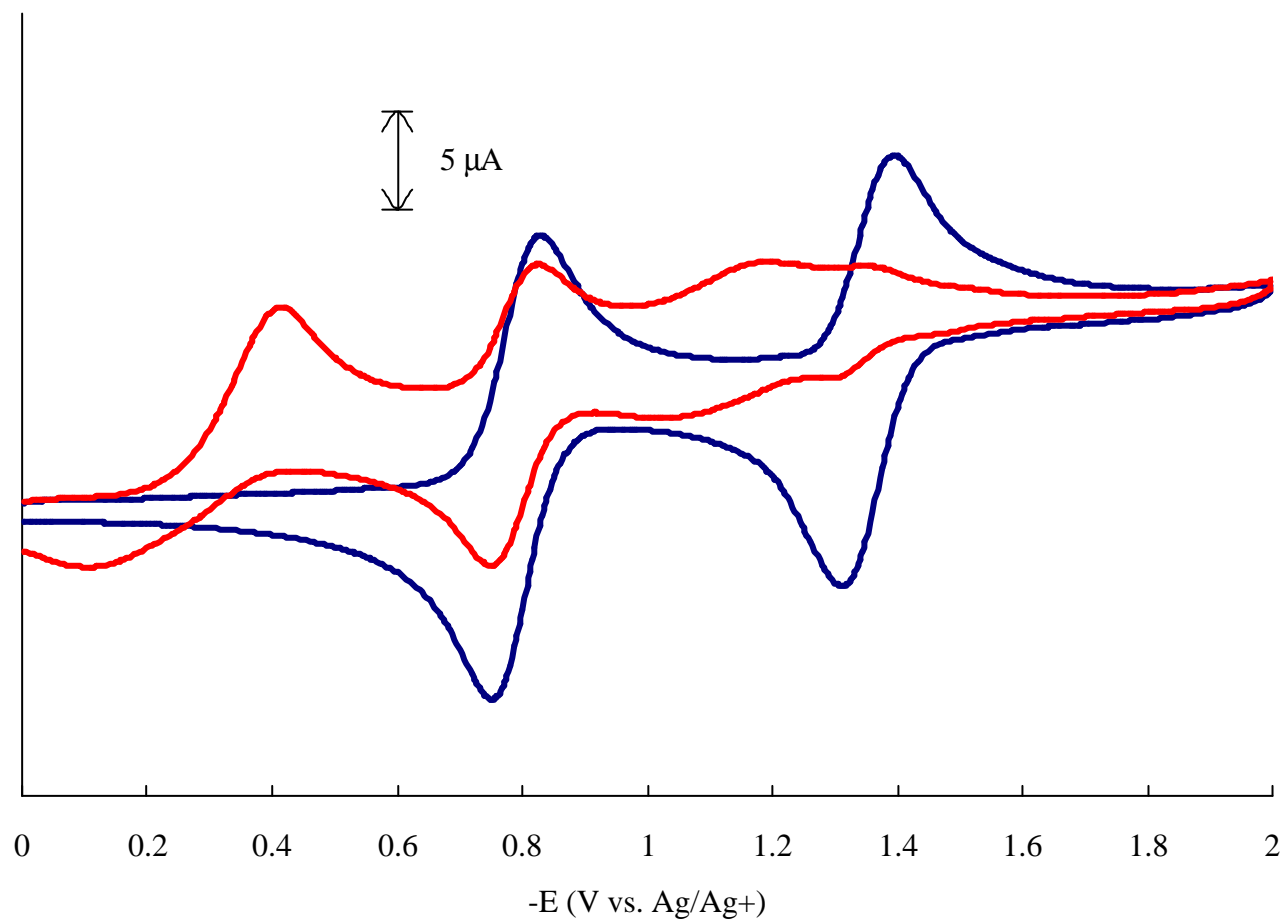


Our research area and tools.

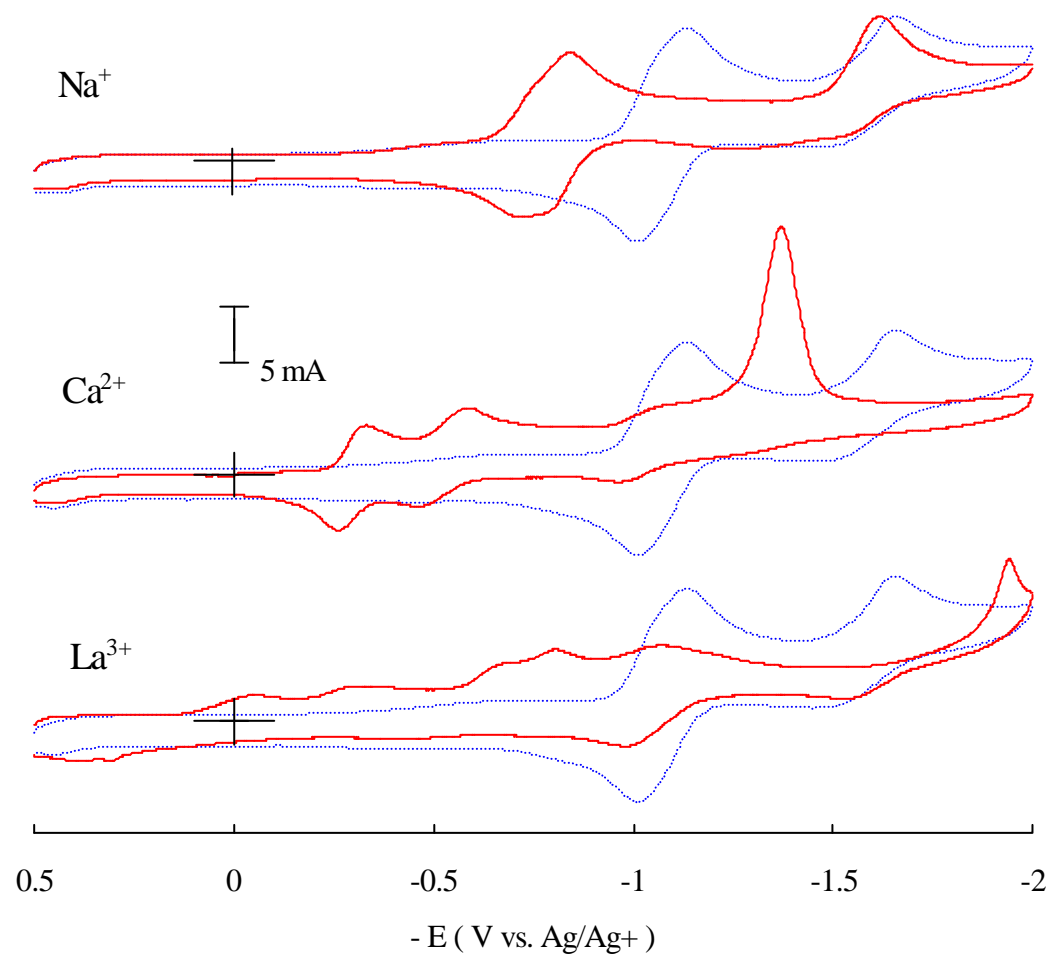
1. Host-guest chemistry (Calixarene)
2. Electrochemistry of quinone (bulk, surface)
3. Electrochemical sensors
4. Nanobiochip
5. Potentiometry.
6. QCM
7. SPM
8. Impedance

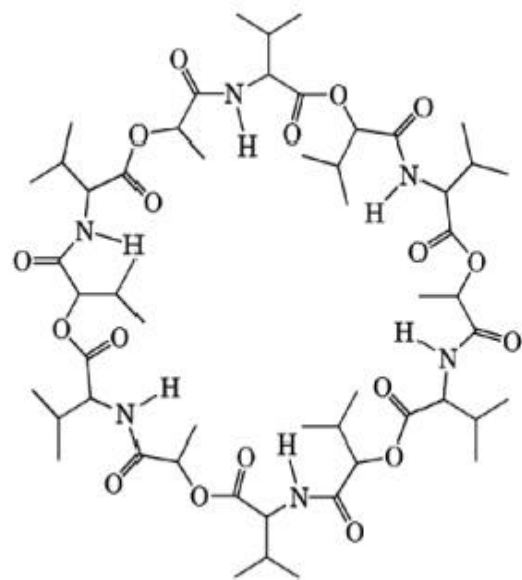
Cyclic voltammograms of 1,4-benzoquinone

in the presence of NH_4^+ 1 equivalent

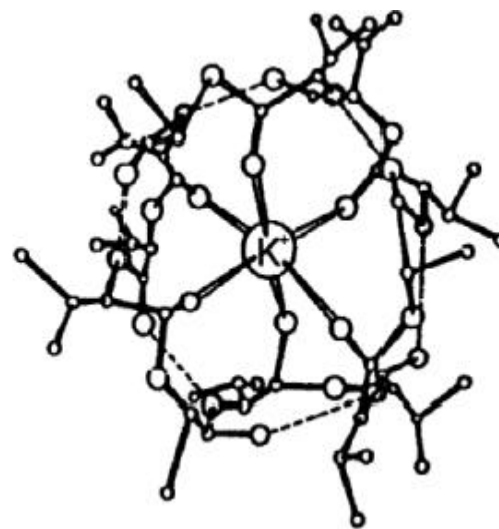


0.5 mM MeO-CDQ and 1 equivalent of metal ions





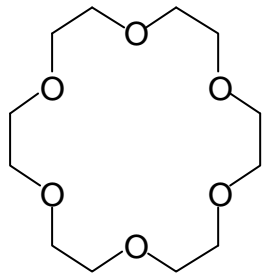
(a)



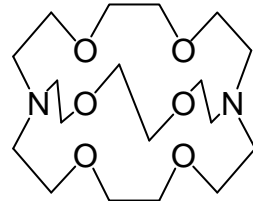
(b)

Structure of (a) valinomycin and of (b) its potassium complex

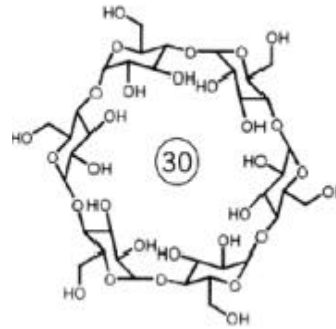
Artificial Receptors



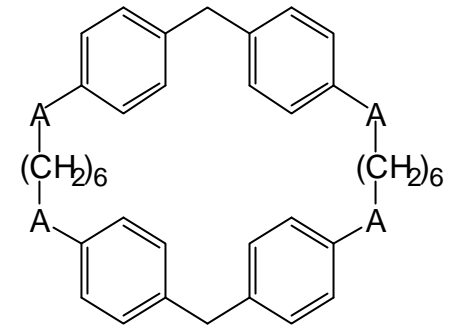
Crown Ether



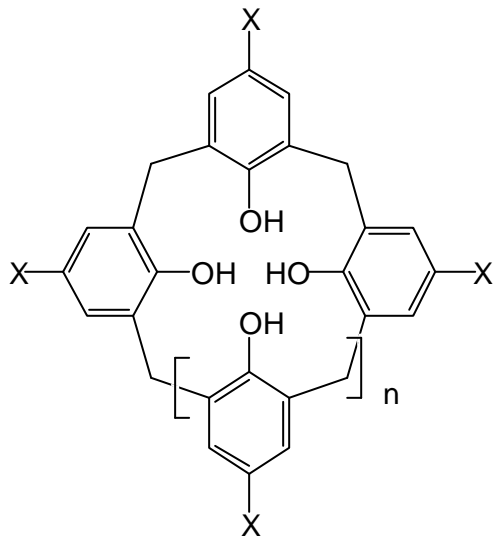
Cryptand



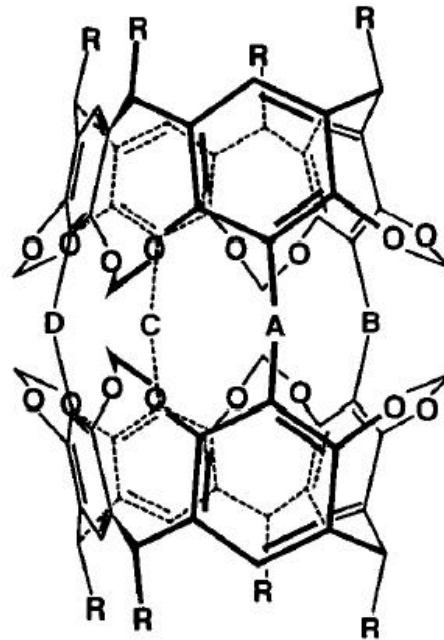
Cyclodextrin



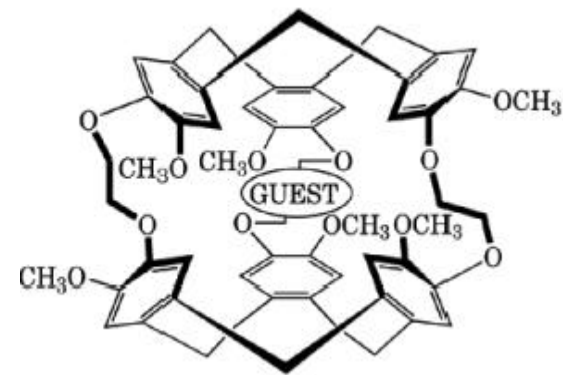
Cyclophane



Calixarene



Carcerand



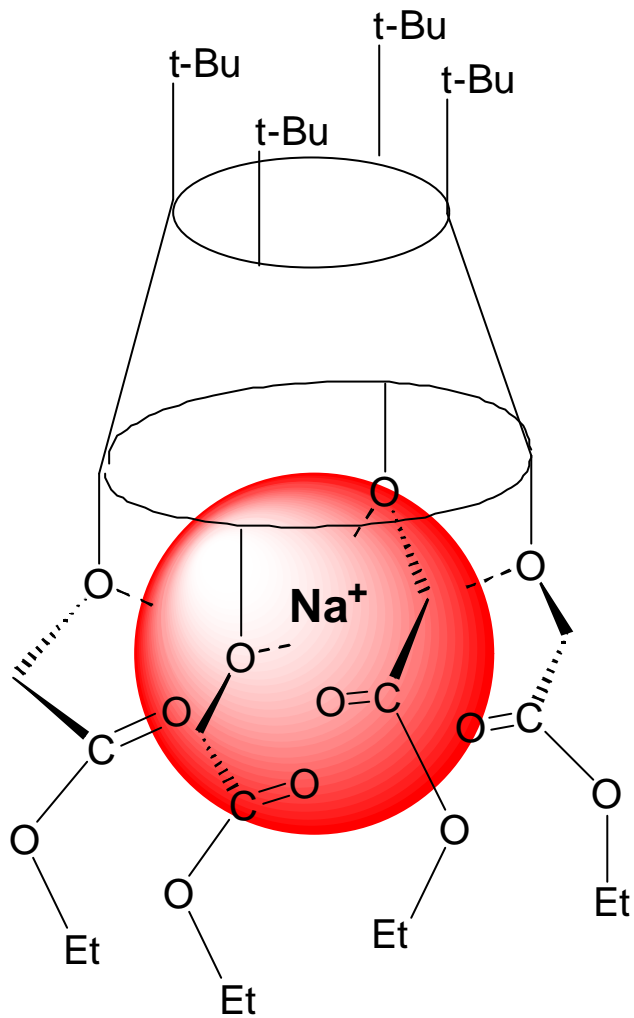
Cryptophane

The origin of the term, 'Calix'

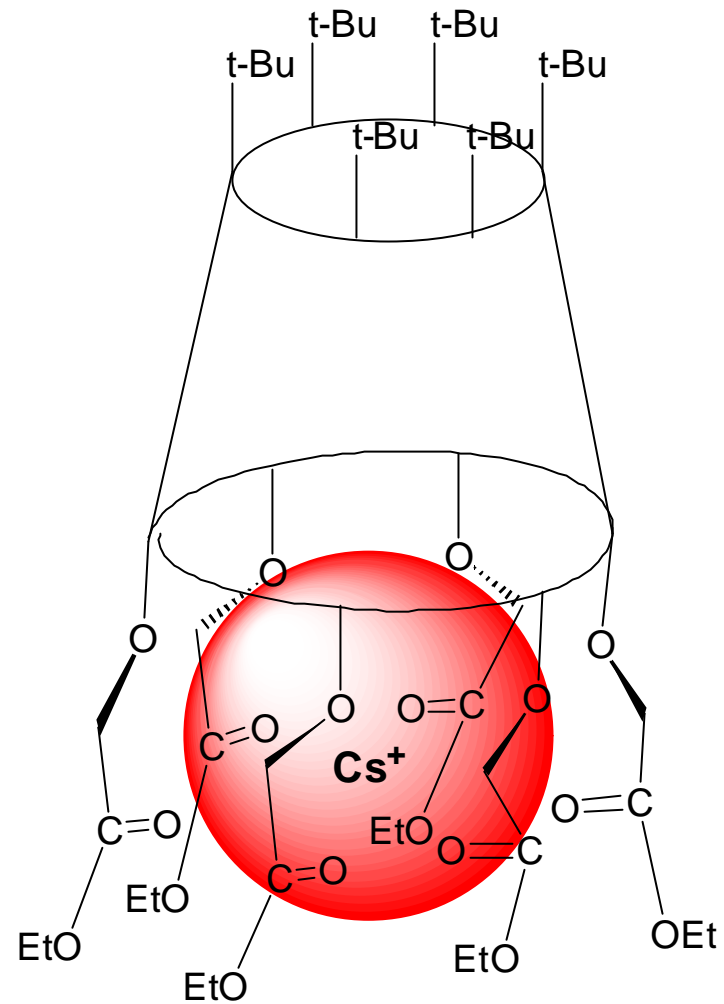


**Space-filling molecular
model of a cyclic tetramer**

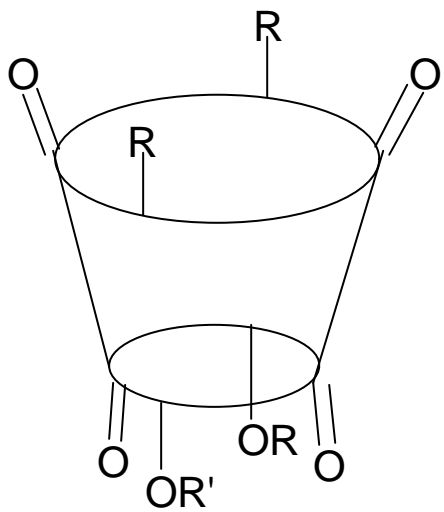
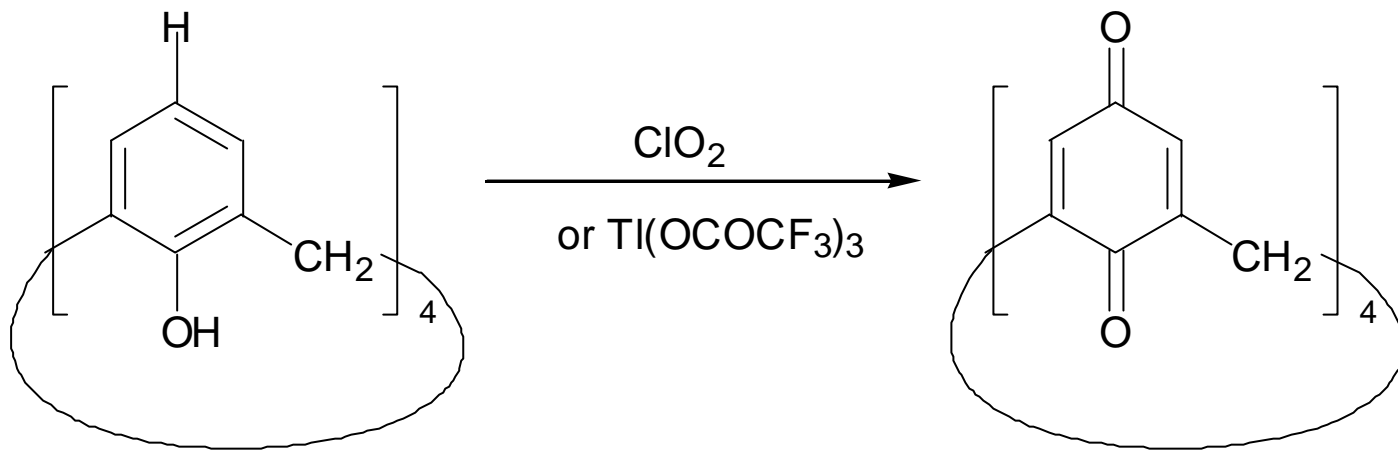
Calix crater



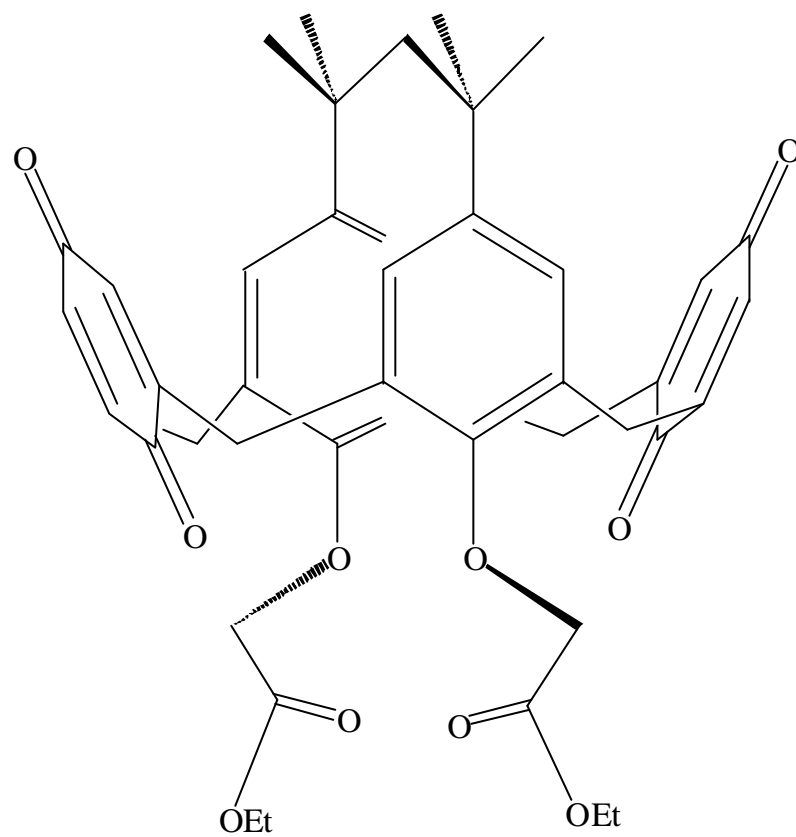
Sodium - selective Calix[4]arene

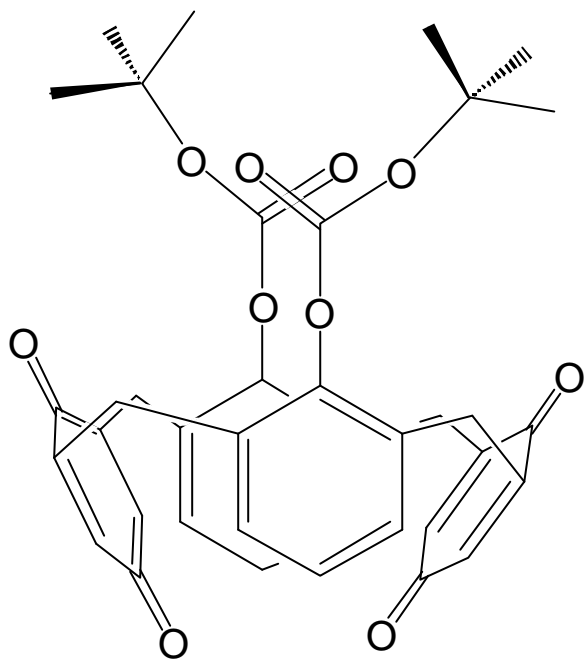


Cesium - selective Calix[6]arene

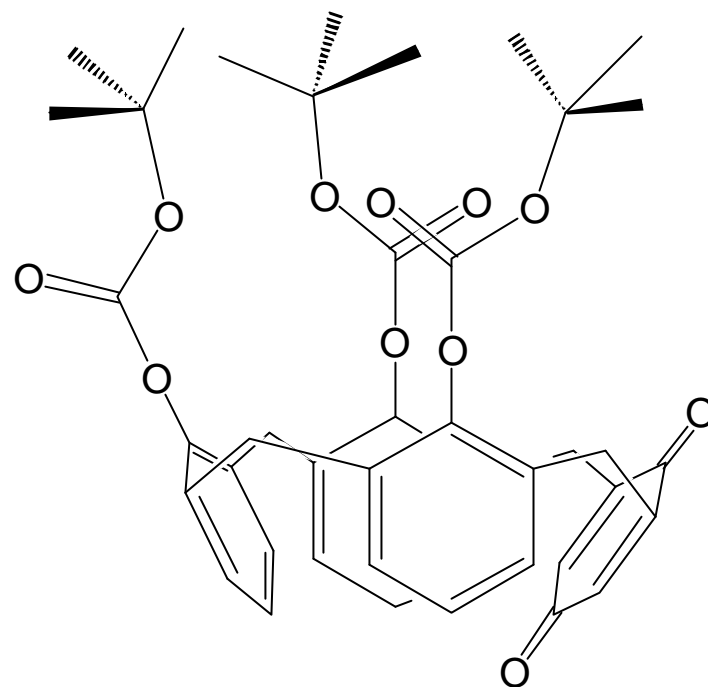


Calix[4]arenediquinone



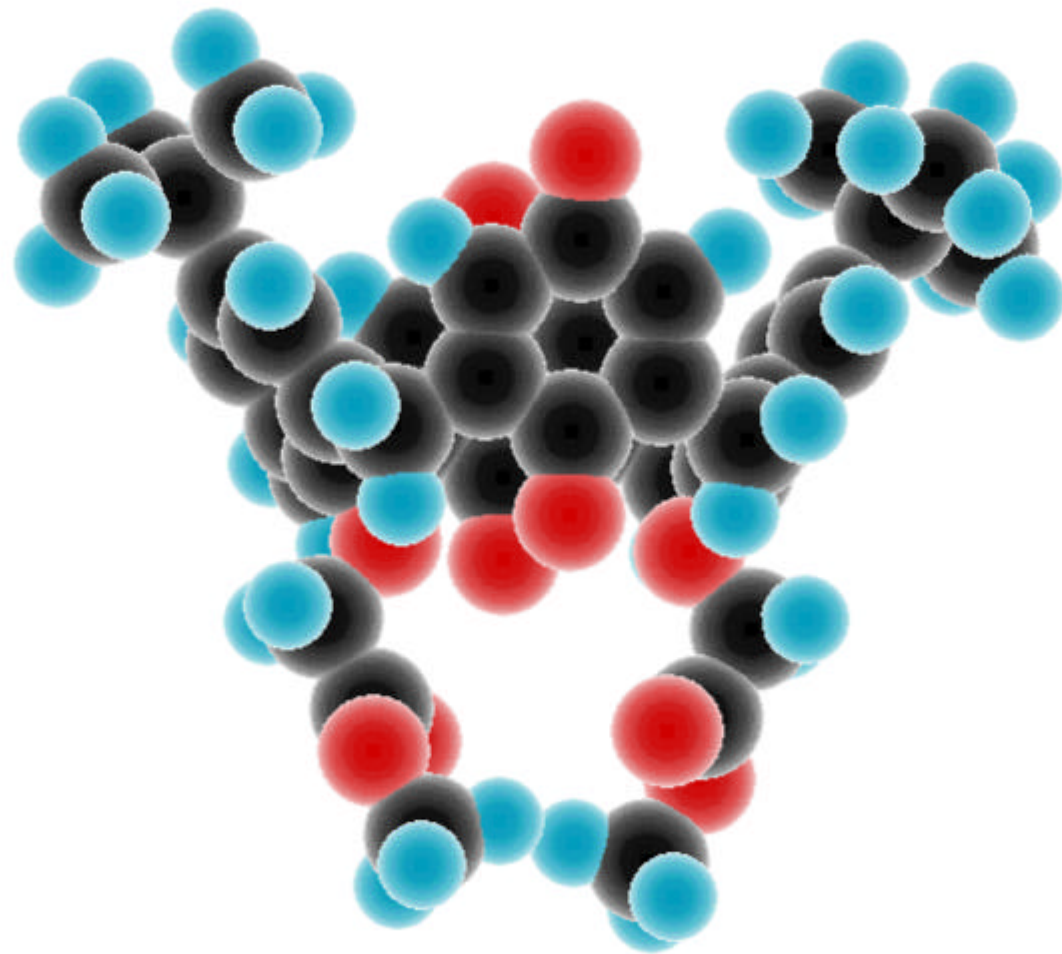


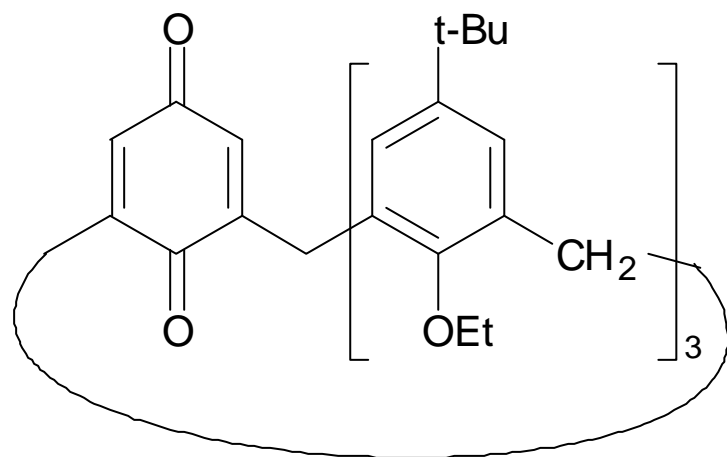
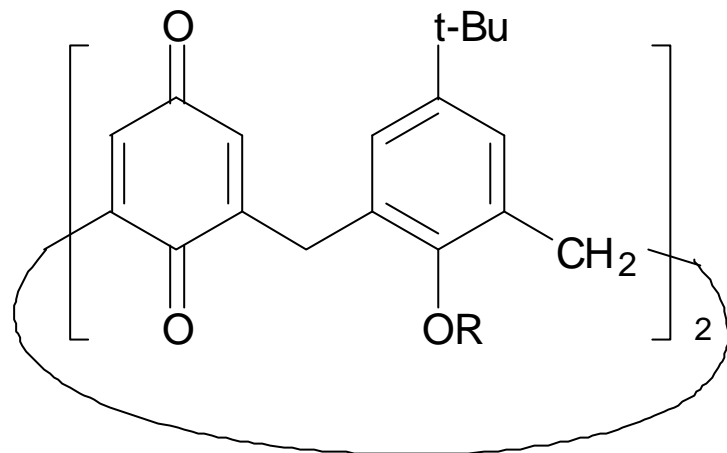
Calix[4]arene - diquinone
(CDQ)

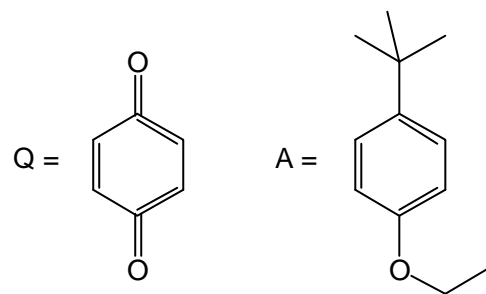
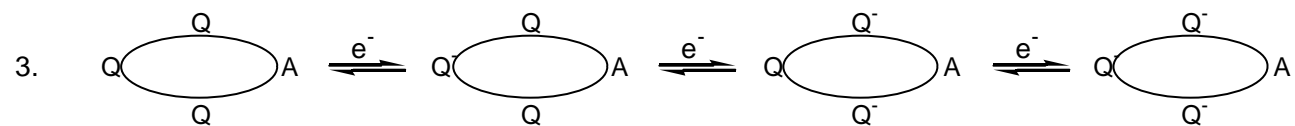
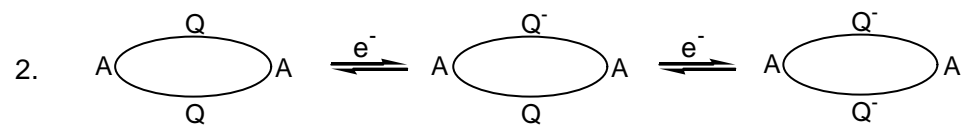
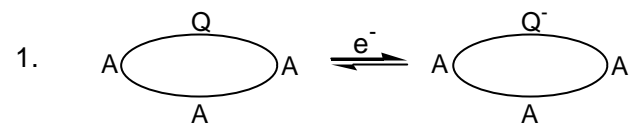


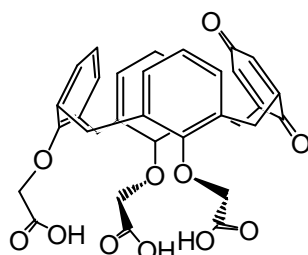
Calix[4]arene - monoquinone
(CMQ)

Calix[4]arenediquinone

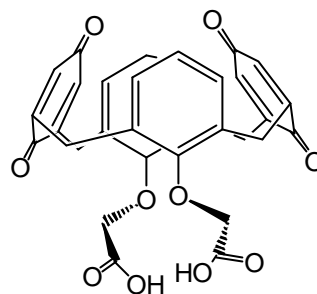




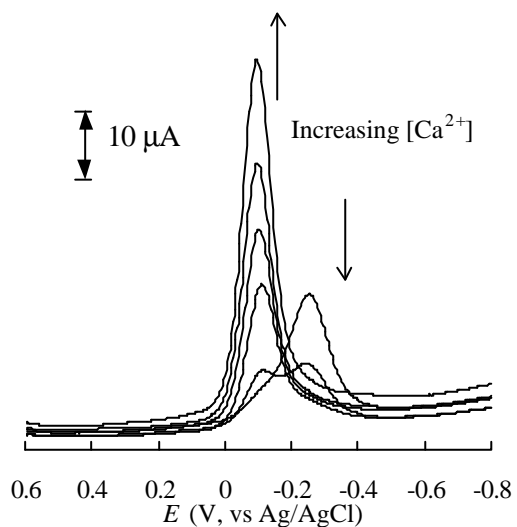




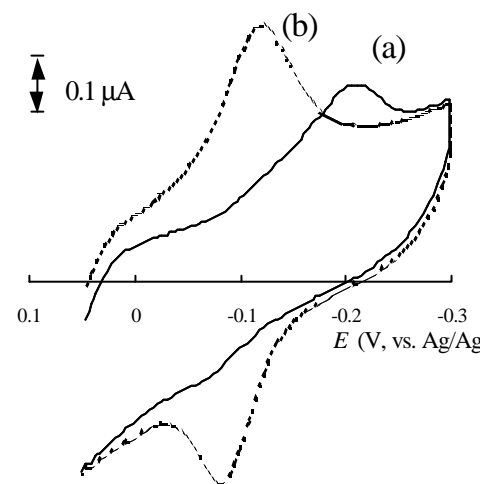
L1



L2

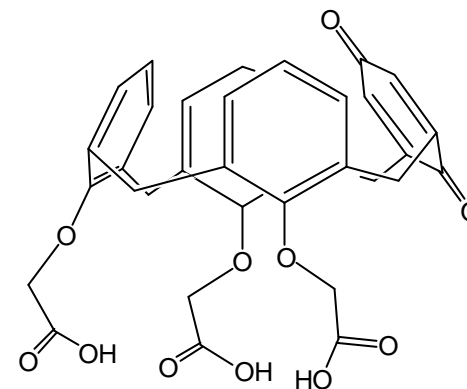
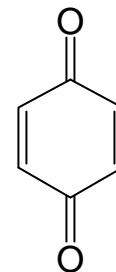
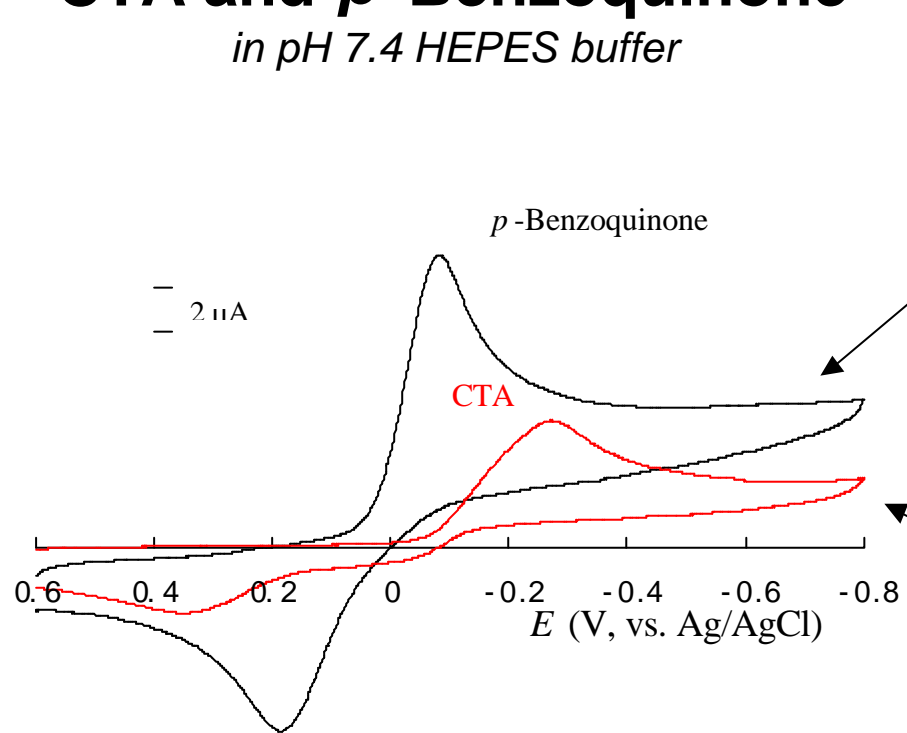


Square-wave voltammograms of 0.5 mM L1 where the concentration of Ca^{2+} is 0, 0.05, 0.25, 0.50, 1.00 and 2.50 mM, respectively in the presence of 0.15 M Na^+ in 0.05 M HEPES buffer of pH 7.4.



Cyclic voltammograms of L2 film on silver electrode in the absence (a) and presence (b) of Ca^{2+} in HEPES buffer of pH 7.4. The scan rate is 10 mV/s.

Cyclic Voltammograms of CTA and *p*-Benzoquinone *in pH 7.4 HEPES buffer*

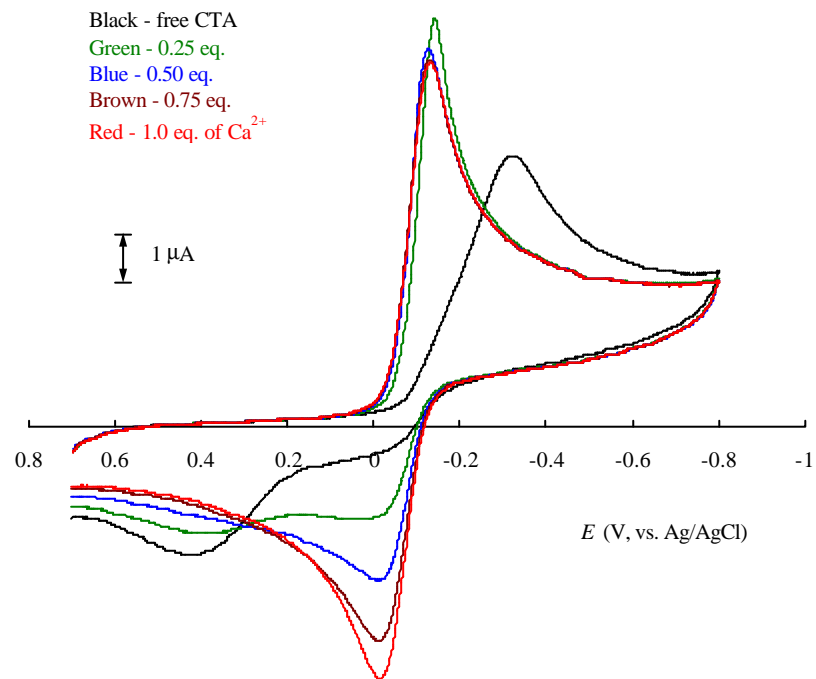


Calix[4]arenemonoquinone triacid (CTA)

Cyclic Voltammograms of CTA

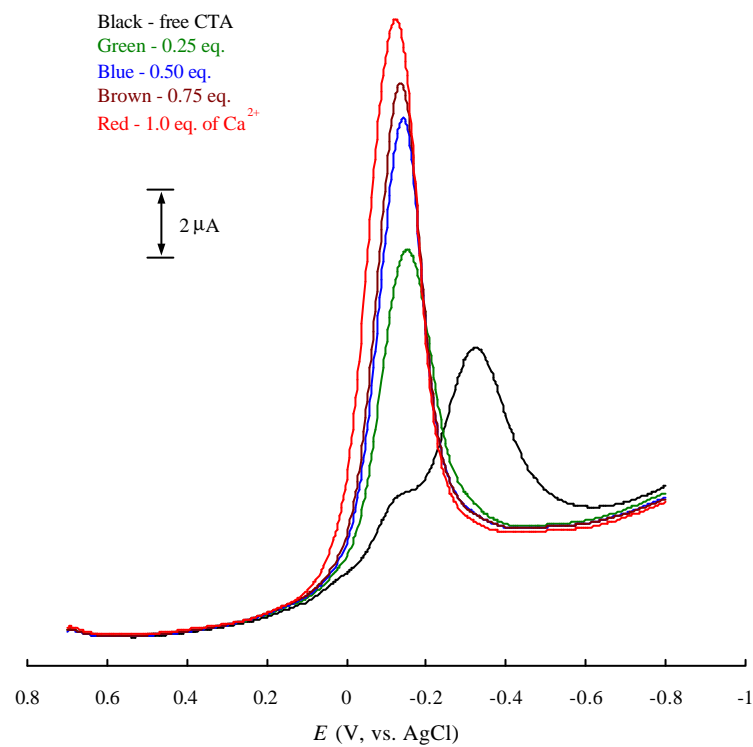
upon the addition of Ca^{2+} 0, 0.25, 0.50, 0.75, 1.0 equivalent to 0.5 mM CTA

0.05 M HEPES buffer which pH was controlled to be 7.4 by Et_4NOH



Square-Wave Voltammograms of CTA

in the presence of Ca^{2+} 0, 0.25, 0.50, 0.75, and 1.0 equivalent to 0.5 mM CTA



Square-Wave Voltammograms of CTA

in the absence and the presence of Ca^{2+}

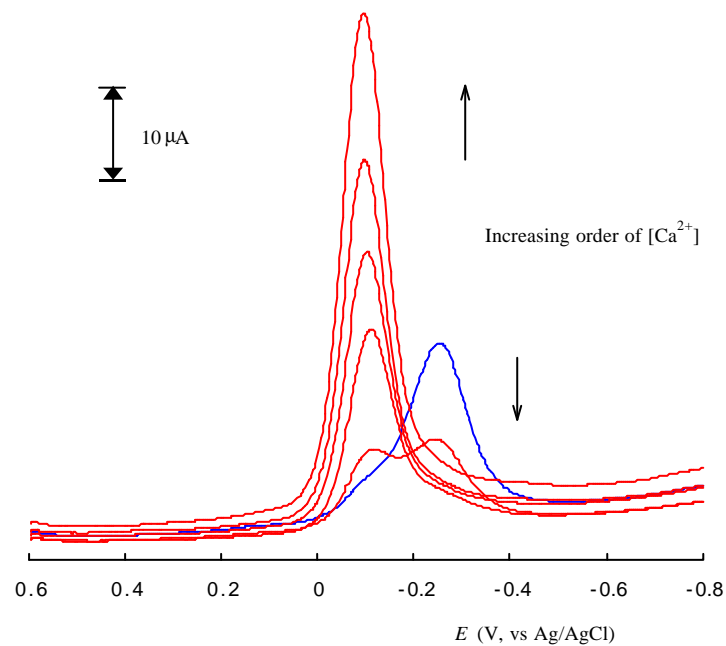
0.05, 0.25, 0.50, 1.00 and 2.50 mM

in pH 7.4 HEPES buffer, 0.5 mM CTA and 0.15 M Na^+

Step potential; 4 mV, amplitude; 25 mV, frequency; 100 Hz

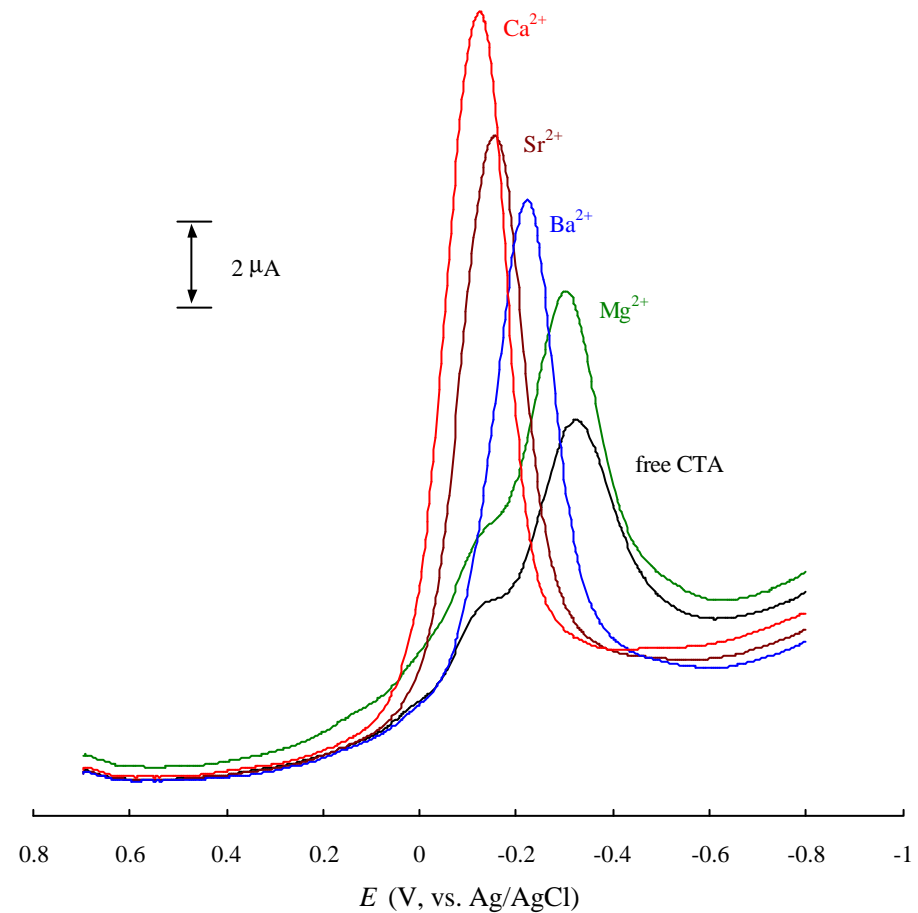
Blue - 0.5 mM CTA + 0.15 M Na^+

Red - 0.05, 0.25, 0.50, 1.00, and 2.50 eq. of Ca^{2+}



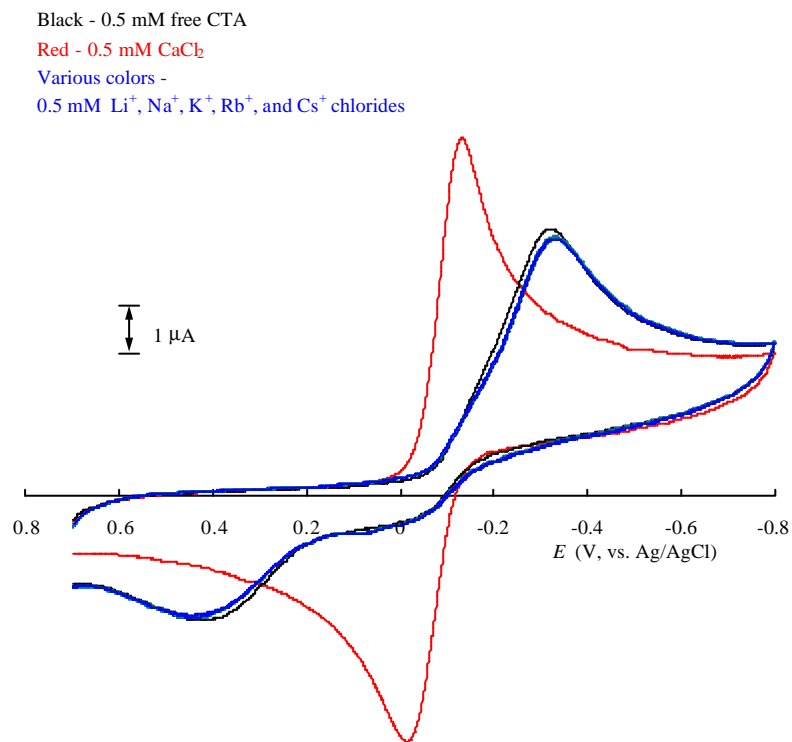
Square-Wave Voltammograms of CTA

in the absence and presence of alkaline earth metal ions
Step potential; 4 mV, amplitude; 25 mV, frequency; 100 Hz



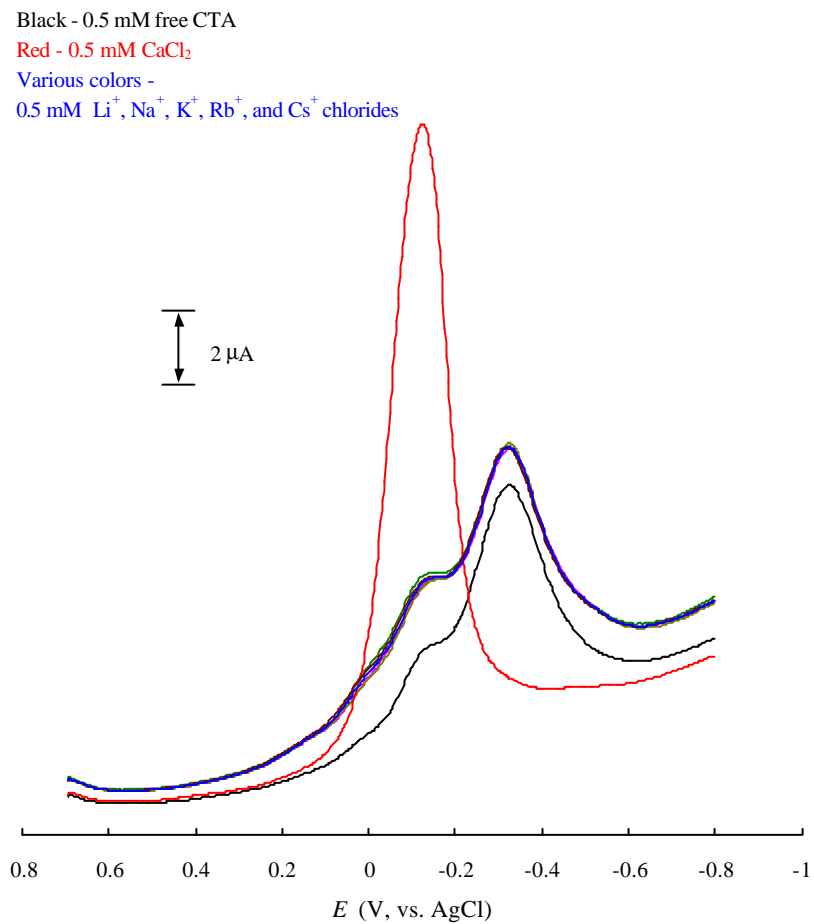
Cyclic Voltammograms of CTA

in the absence and presence of various alkali metal ions

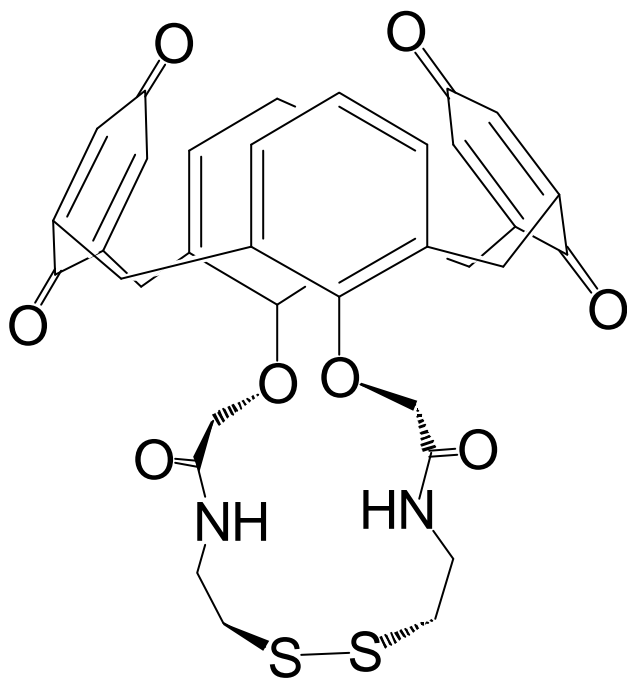


Square-Wave Voltammograms of CTA

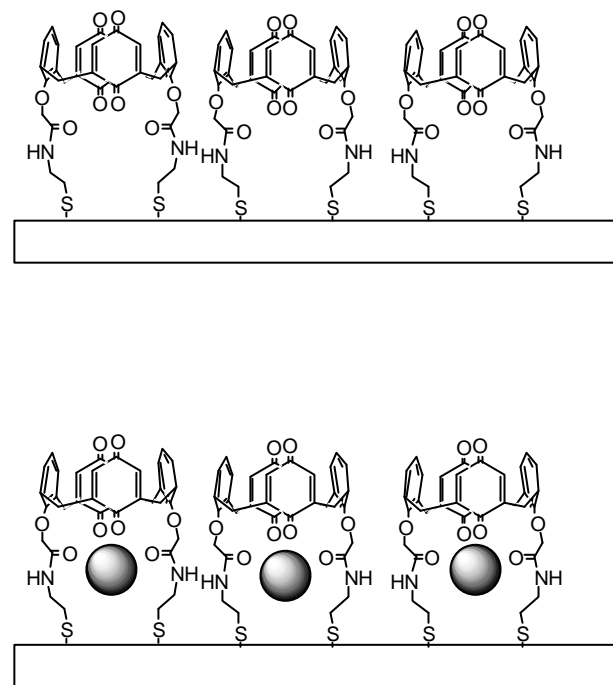
*in the absence and presence of various alkali metal ions
step potential; 4 mV, amplitude; 25 mV, frequency; 100 Hz*



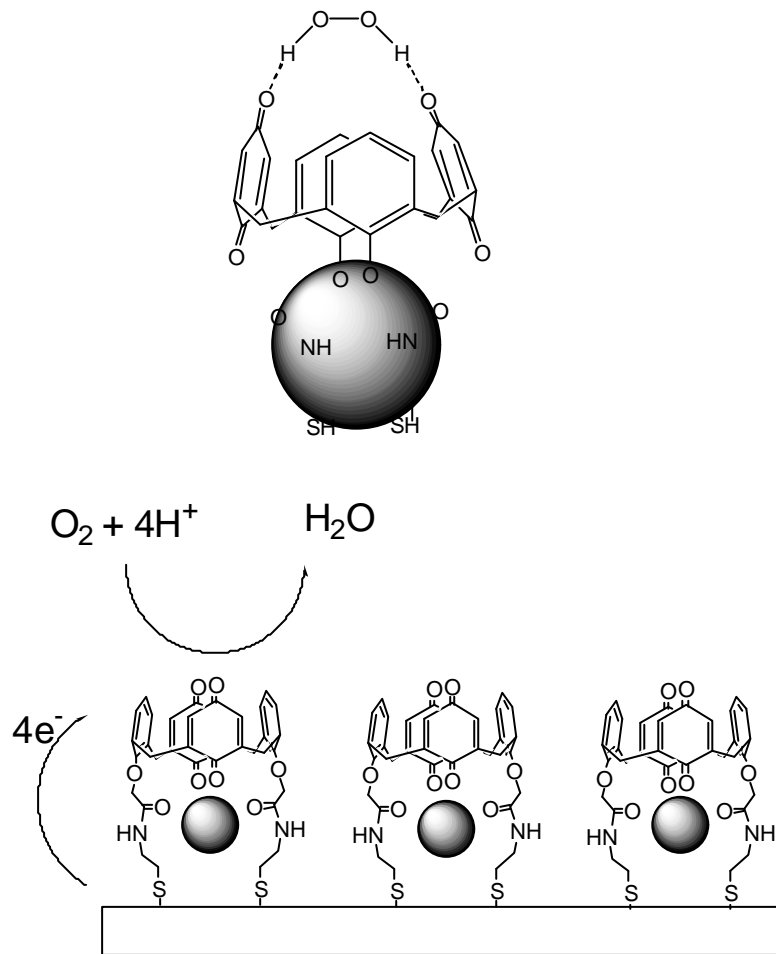
Calix[4]arenequinone disulfide (CDS)



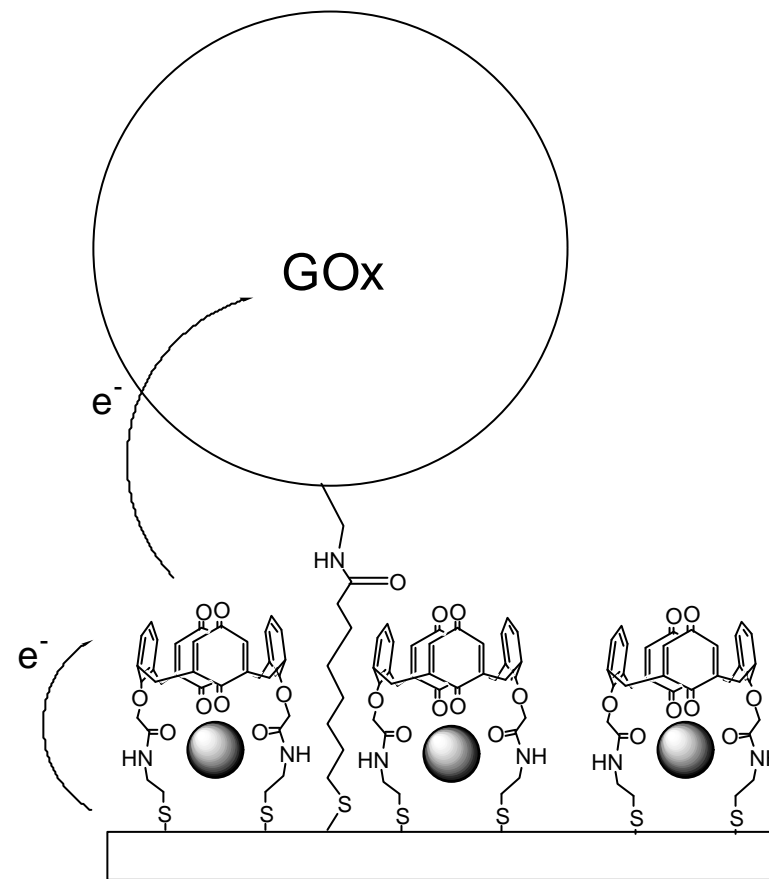
Calix[4]arenequinone disulfide (CDS)



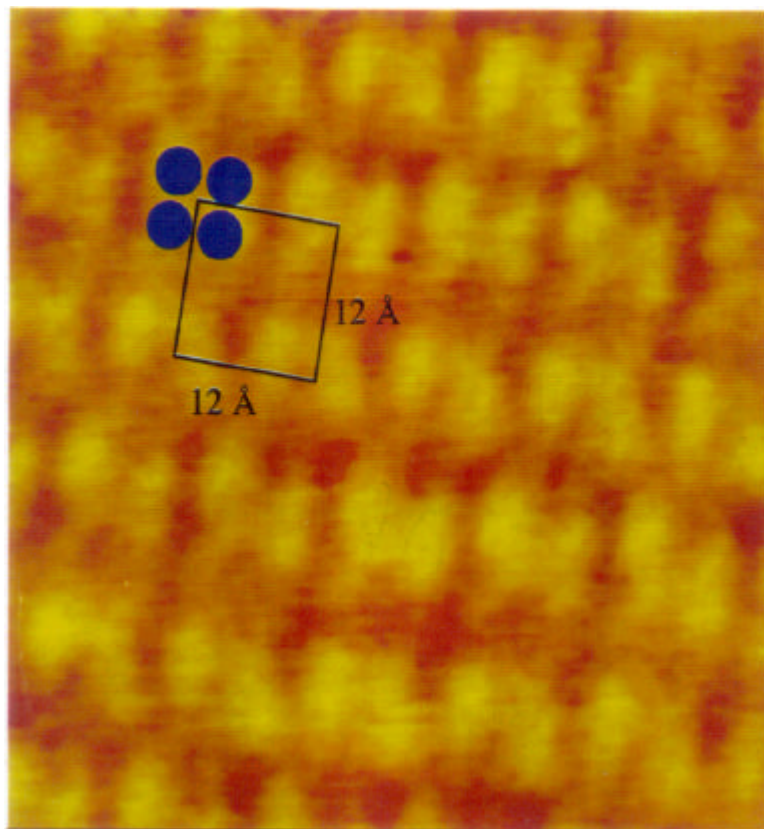
Electrocatalytic Redox Scheme of Glucose Oxidase



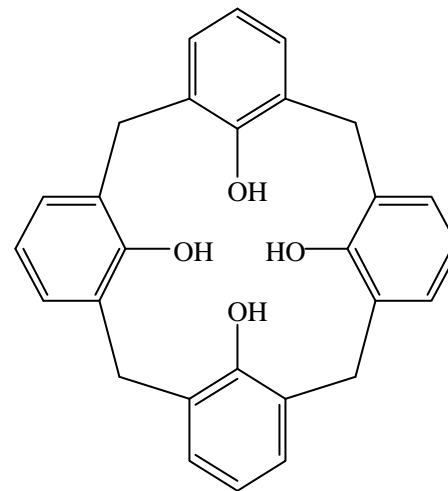
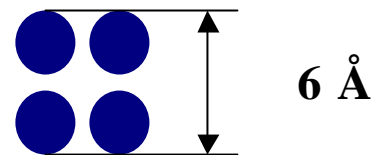
Electrocatalytic Redox Scheme of Glucose Oxidase



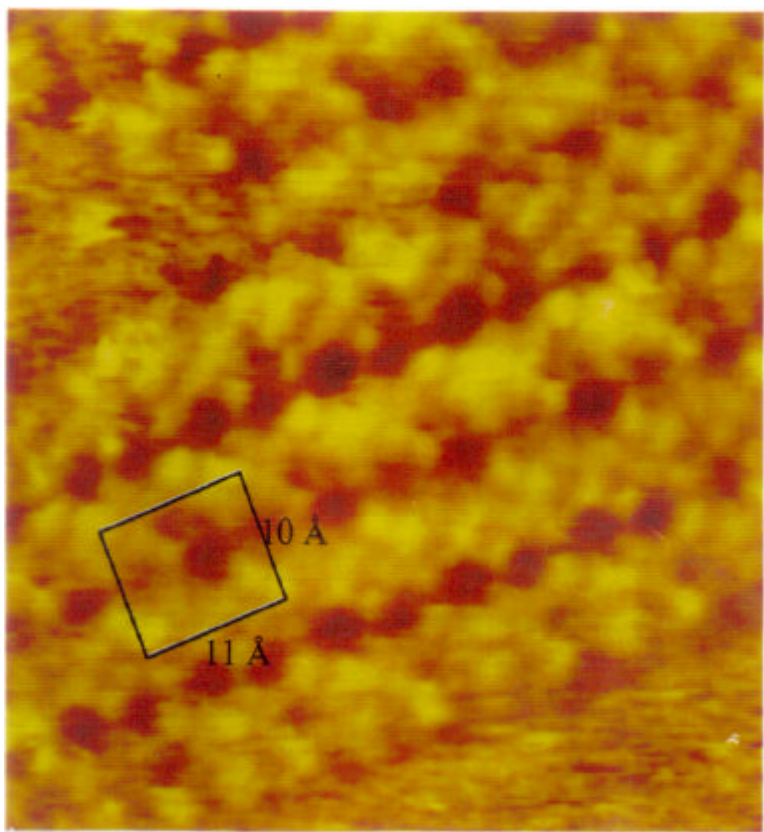
STM Image of Calix(4)arene on Au(111) in 0.1 M HClO₄



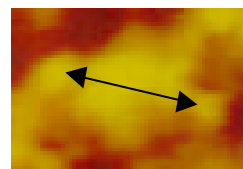
6.0 nm × 6.0 nm



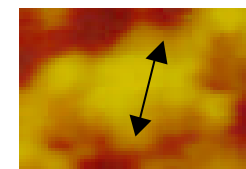
STM Image of Calix(4)arenequinone Disulfide on Au(111) in 0.1 M HClO₄



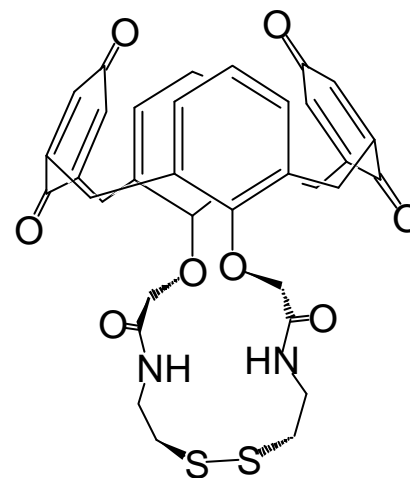
6.0 nm × 6.0 nm



9 Å



7.8 Å



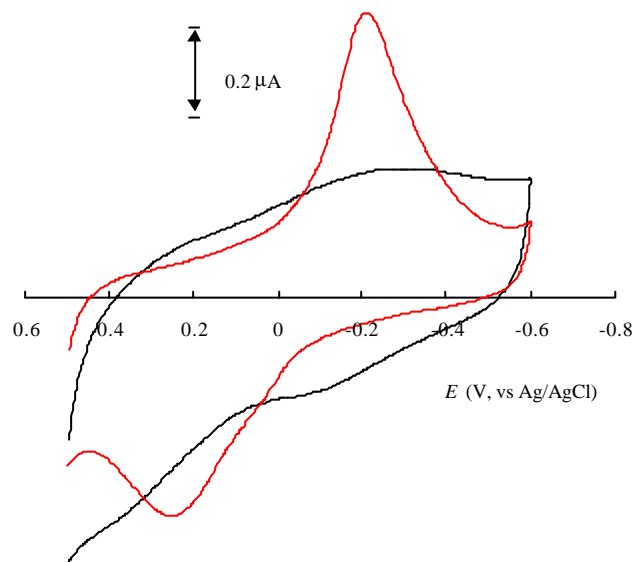


Fig. Cyclic voltammograms of CDS-modified (solid line) and bare gold disk electrode (dotted line). 0.1 M HEPES buffer (pH=7.4). Ref.=Ag/AgCl(in 3 M KCl), counter=Pt wire. Scan rate=50 mV/s.

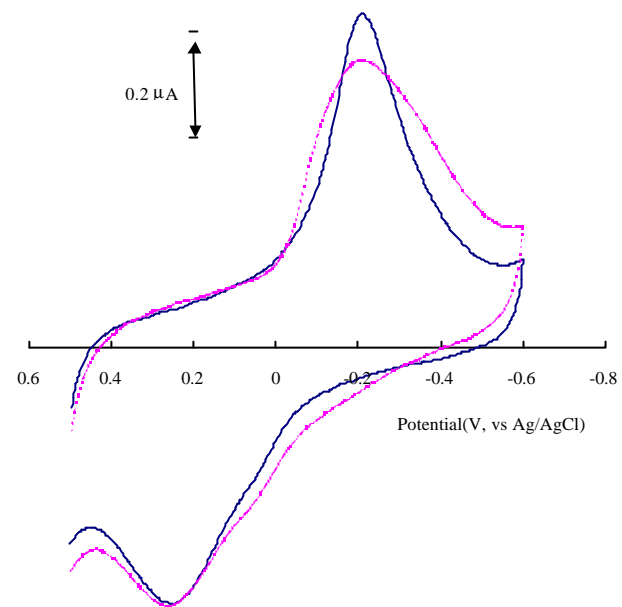
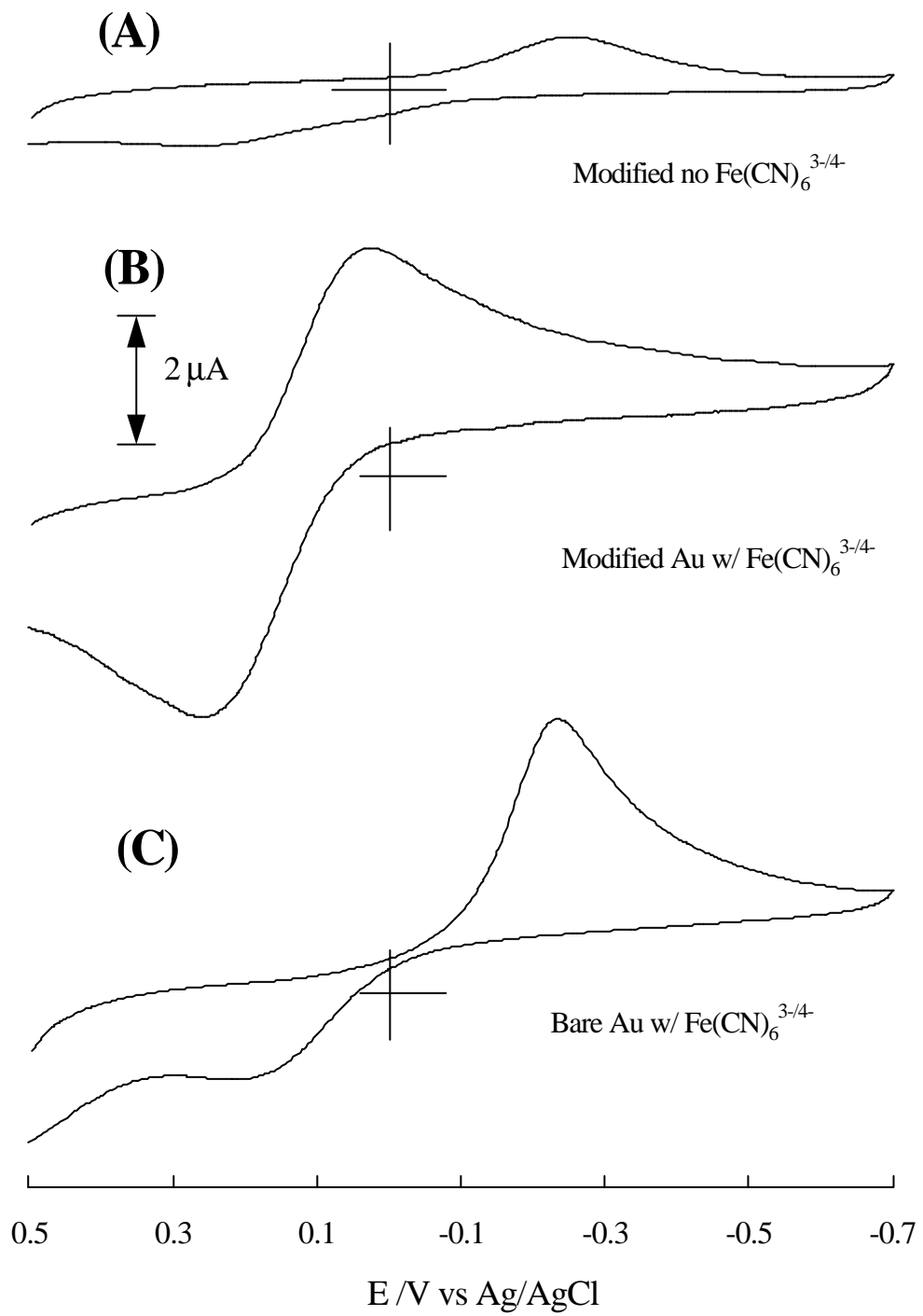


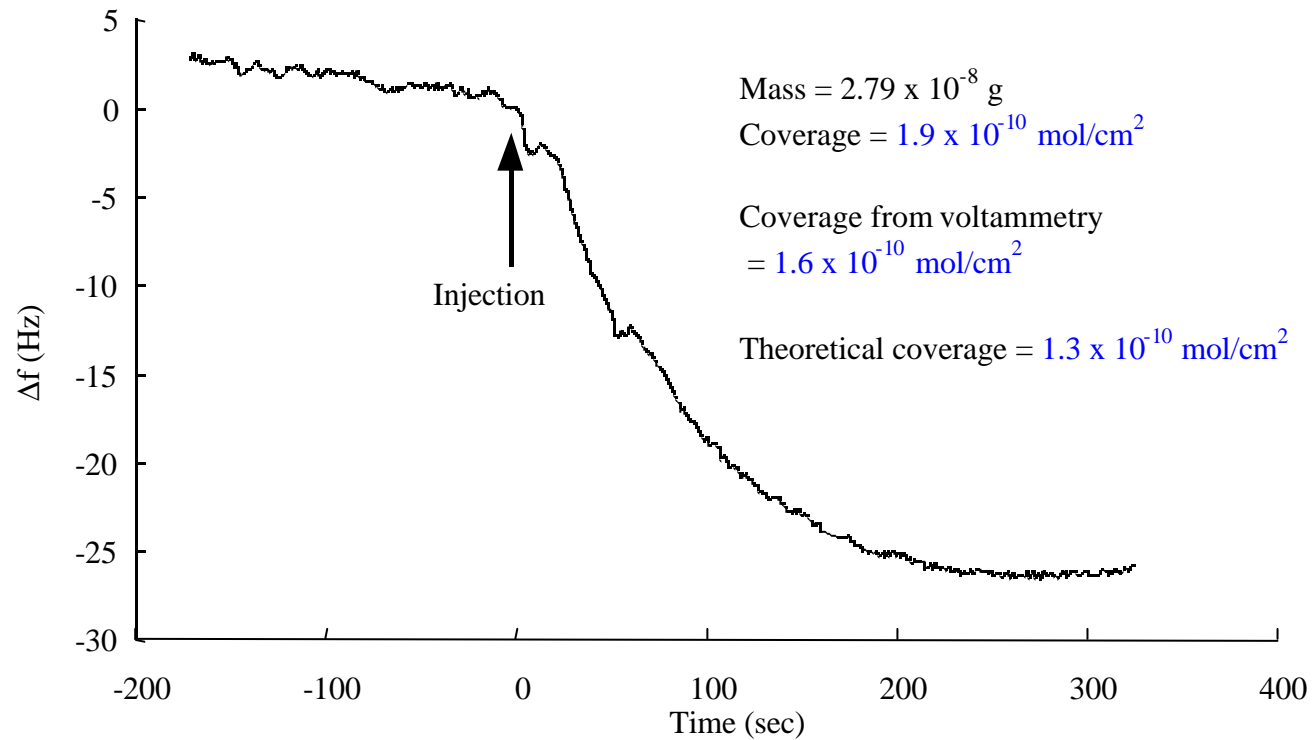
Fig. Effect of Ca²⁺ addition on the behavior of CDS-modified Au electrode. Solid line without Ca²⁺ and dotted line with 10 mM Ca²⁺. 0.1 M HEPES buffer. Ref.=Ag/AgCl (in 3 M KCl), counter =Pt wire. Scan rate=50 mV/s.



Frequency change due to the formation of CDS SAM

The substrate is gold-deposited QCM electrode whose area is 0.22 cm^2 .

The concentration of CDS after injection is 0.5 mM in CH_2Cl_2 .

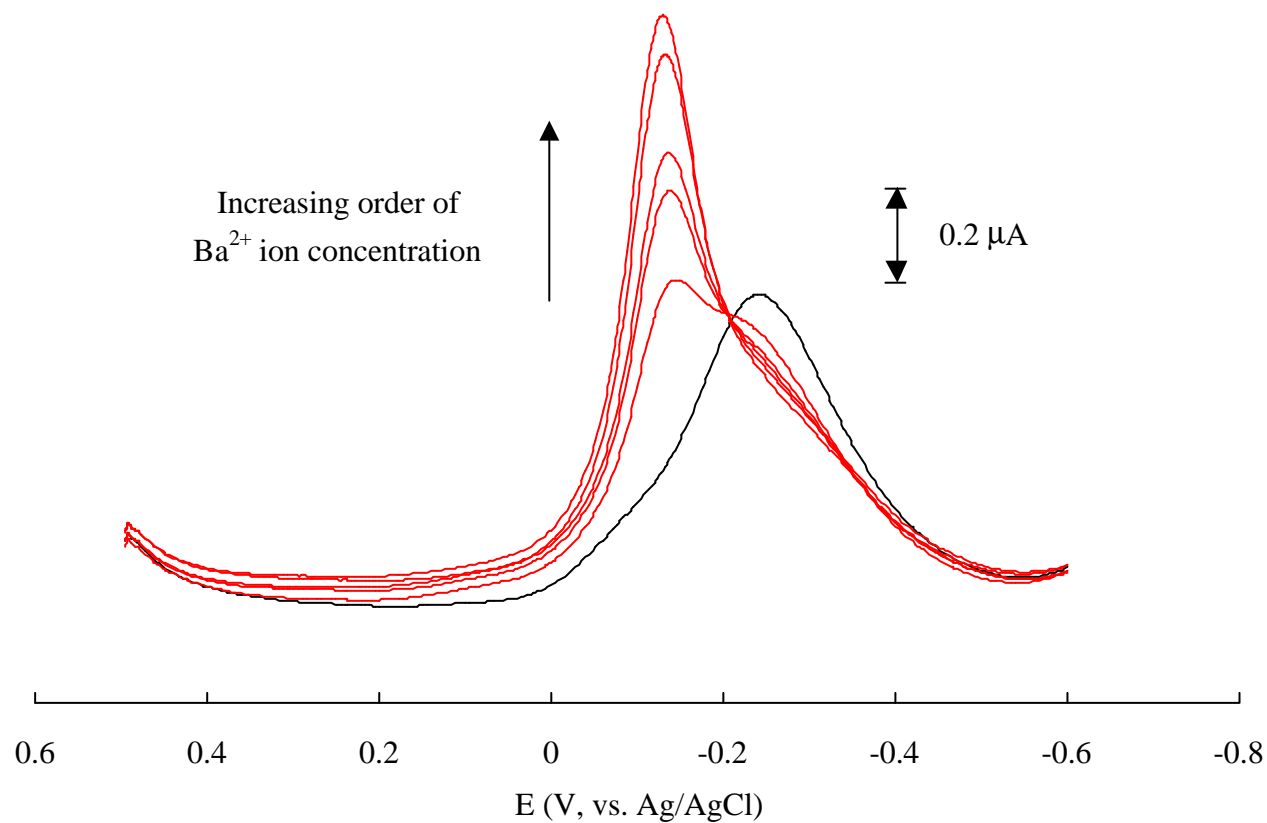


Square wave voltammograms of CDS-modified gold disk electrode in the absence(black) and presence(red) of Ba²⁺ ion

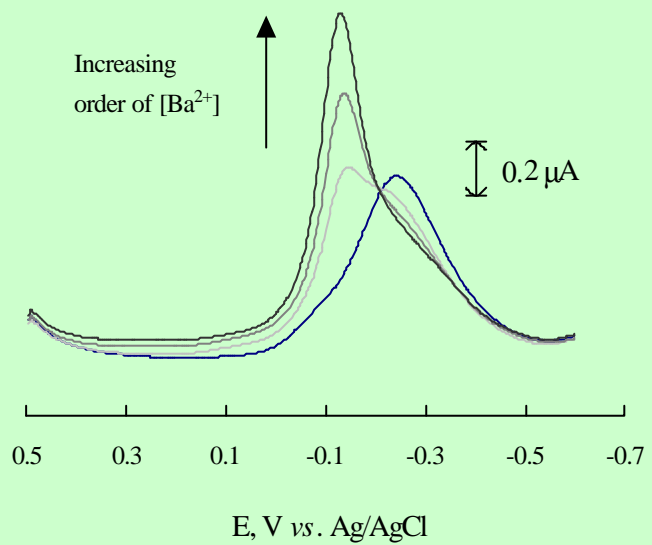
[Ba²⁺]=0, 0.1, 0.5, 1, 5, 10 mM. 0.1 M HEPES buffer(pH 7.4).

Amplitude; 25 mV, step potential; 4 mV, frequency; 15 Hz.

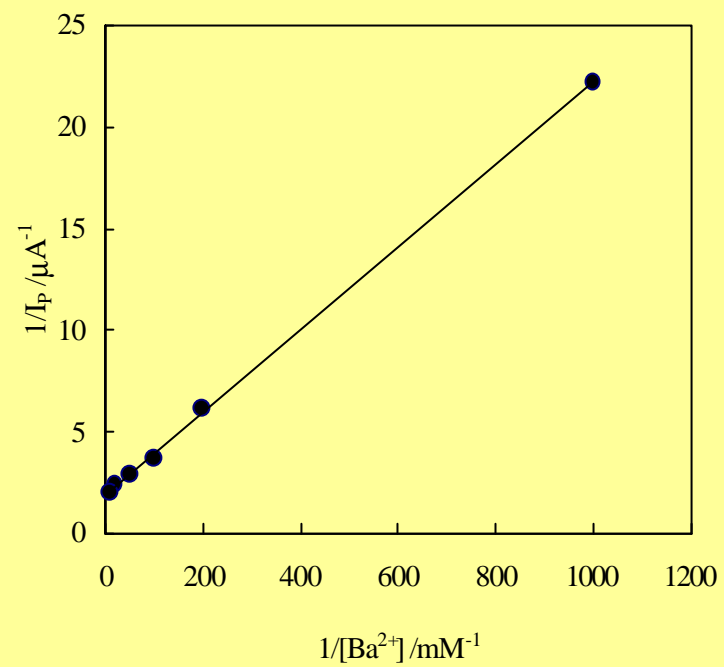
Reference electrode; Ag/AgCl(in 3 M KCl), counter electrode; Pt wire.

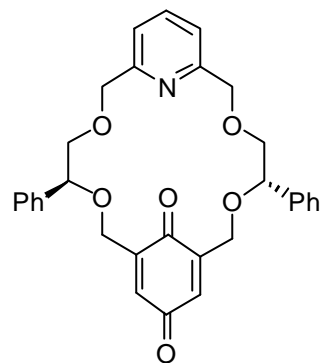


(A)

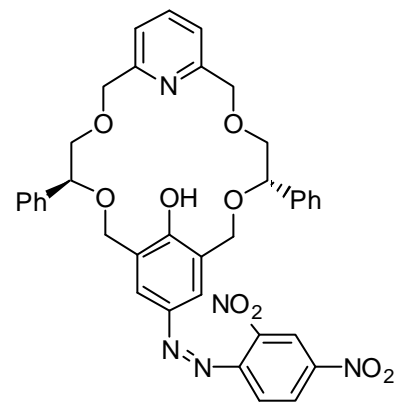


(B)



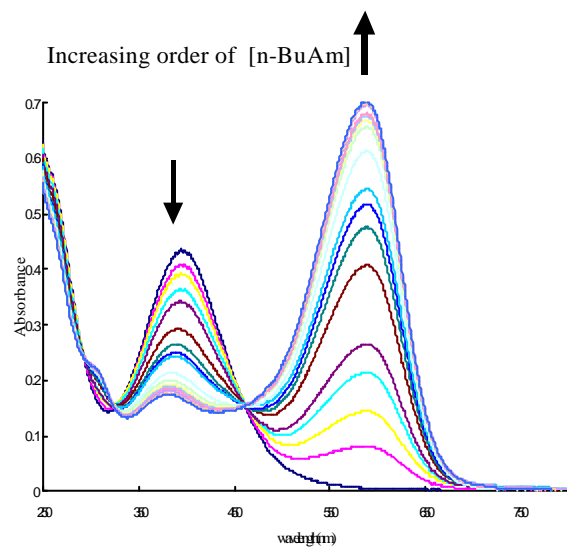


(a) HS-1555

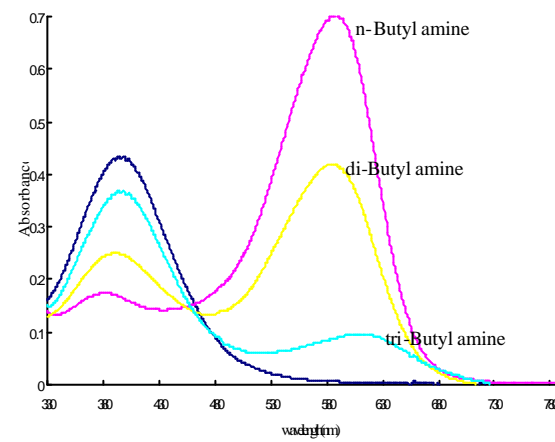


(b) HS-1555

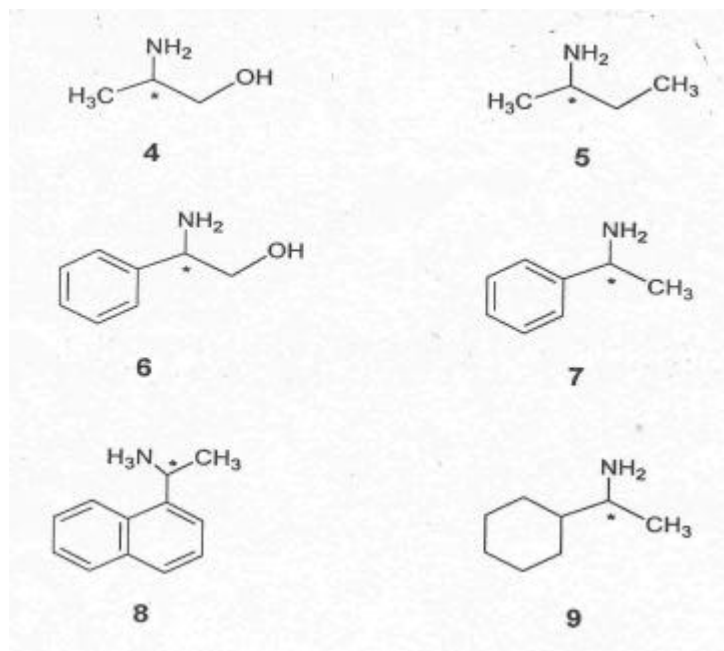
Host Compounds; Pyridino Crowns with Quinone (a) and Nitroazophenol (b)



(a) UV -vis spectra of HS 1556 in the presence of n-butylamine



(b) UV -vis spectra of HS 1556 in the presence of various alkylamines



Structure of chiral alkylamines; alaninol (4), *sec*-butylamine (5), phenylglycinol (6), methylbenzylamine (7), naphthylethylamine (8), cyclohexylethylamine (9)

1. Absorption maxima and association constants of HS 1556 with various Chiral amines

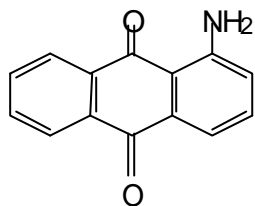
| Amine | I_{\max} of complex ^a (nm) | | ΔI_{\max} (nm) | K^c ($10^3 / M^{-1}$) | | K_R / K_S |
|-------|---|--------------|------------------------|---------------------------|----------------|-------------|
| | (R) - isomer | (S) - isomer | | (R) - isomer | (S) - isomer | |
| 4 | 563 | 568 | -5 | 12.6 (± 0.7) | 11.7 (± 0.3) | 1.07 |
| 5 | 588 | 588 | 0 | 104 (± 6) | 67.4 (± 5) | 1.55 |
| 6 | 563 | 563 | 0 | 7.19 (± 0.5) | 7.05 (± 0.07) | 1.02 |
| 7 | 583 | 578 | 5 | 11.3 (± 0.6) | 13.3 (± 0.03) | 0.85 |
| 8 | 578 | 578 | 0 | 6.72 (± 0.1) | 7.94 (± 0.06) | 0.85 |
| 9 | 584 | 584 | 0 | 89.8 (± 0.3) | 87.9 (± 0.4) | 1.02 |

^aConcentrations of **3** and **4-9** are 20 mM and 4000 mM, respectively.

$$^b \Delta I_{\max} = I_{\max,(R)} - I_{\max,(S)}$$

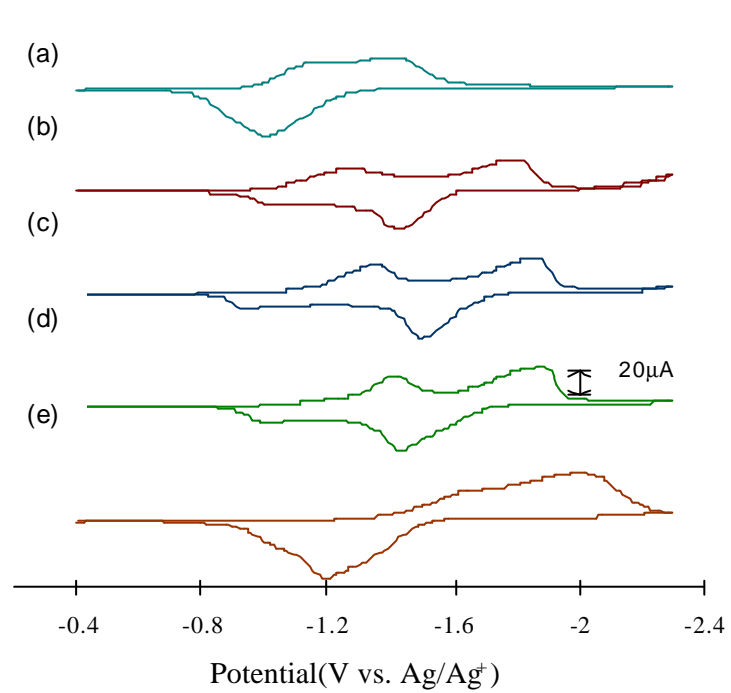
^cAverages and standard deviations (in parentheses) of three independent measurements.

Polymerization of 1-amino-9,10-anthraquinone

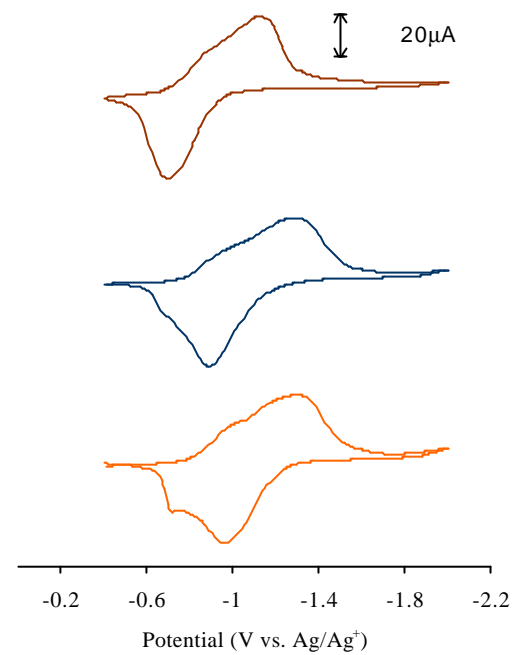


1-amino-9,10-anthraquinone (AAQ)

- In general quinone-induced molecules are difficult to polymerize, for quinone groups play terminators during polymerization.
- But, 1-amino-5,8-naphthoquinone and 1-amino-9,10-anthraquinone can be polymerized following same mechanism as aniline.
- Optimal conditions for polymerization of AAQ were studied with electrochemistry and QCM.



CVs of redox wave of quinone groups in the presence of (a) 0.01M Li⁺, (b) 0.01M Na⁺, (c) 0.01M K⁺, (d) 0.01M Rb⁺ and (e) 0.01M Cs⁺.

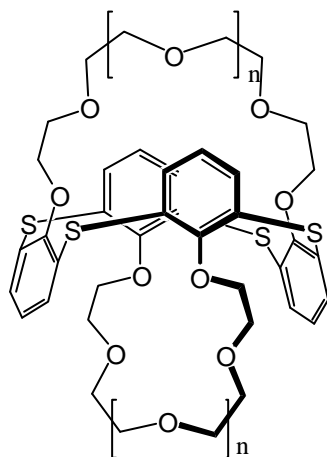


CVs of redox waves of quinone group in the presence of (a) Ca²⁺, (b) Sr²⁺ and (c) Ba²⁺.

Potentiometric study of thiacalixarenes



Response towards transition metal ions?



thiacalix[4]biscrown ether

Selectivity coefficients of Thiacalix[4]biscrown-6 towards alkali and alkali-earth metal ions; FIM (interference ion : 0.01M NO₃⁻)

| Ionophore | Calix[4]arene-crown-6 | Calix[4]biscrown-6 | Thiacalix[4]biscrown-6 |
|------------------|-----------------------|--------------------|------------------------|
| Rb ⁺ | -0.89 | -0.7 | -1.68 |
| K ⁺ | -2.18 | -2.5 | -3.0 |
| Na ⁺ | -4.46 | -4.9 | -3.56 |
| Li ⁺ | -4.81 | -5.2 | -4.26 |
| Ba ²⁺ | -5.2 | -6.1 | -5.44 |
| Sr ²⁺ | -5.3 | - | -5.2 |
| Ca ²⁺ | -5.4 | -5.95 | -5.5 |
| Mg ²⁺ | -5.5 | - | -5.88 |

Biomolecular and molecular layer techniques for nanobiochip.

Development of electrochemical detection techniques for biomolecular layers

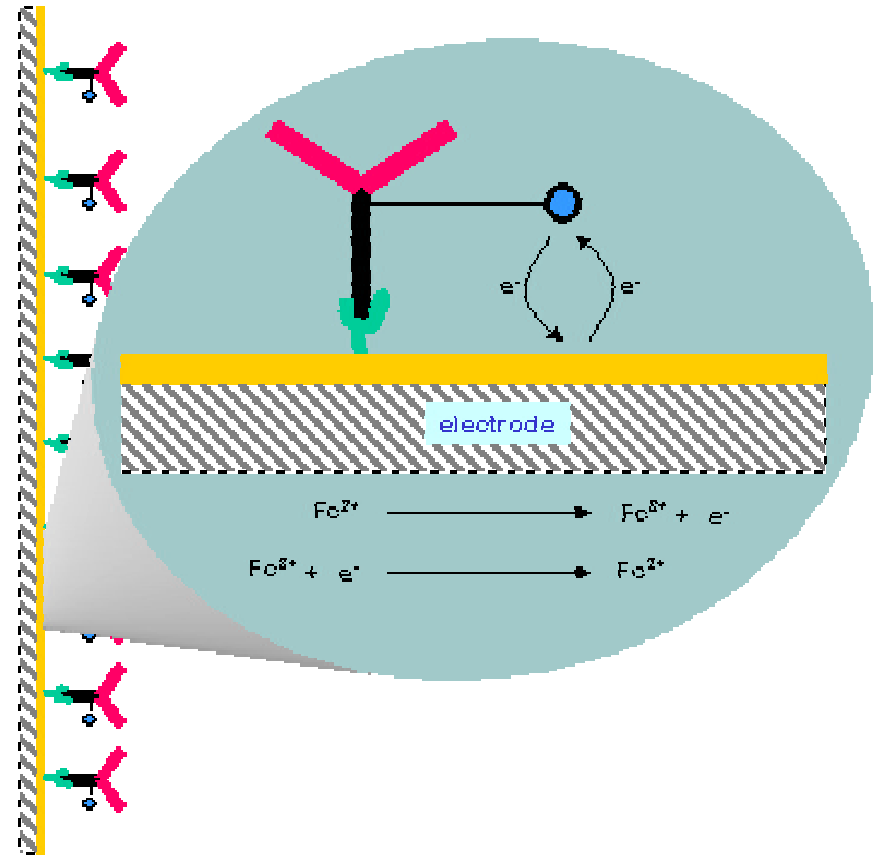
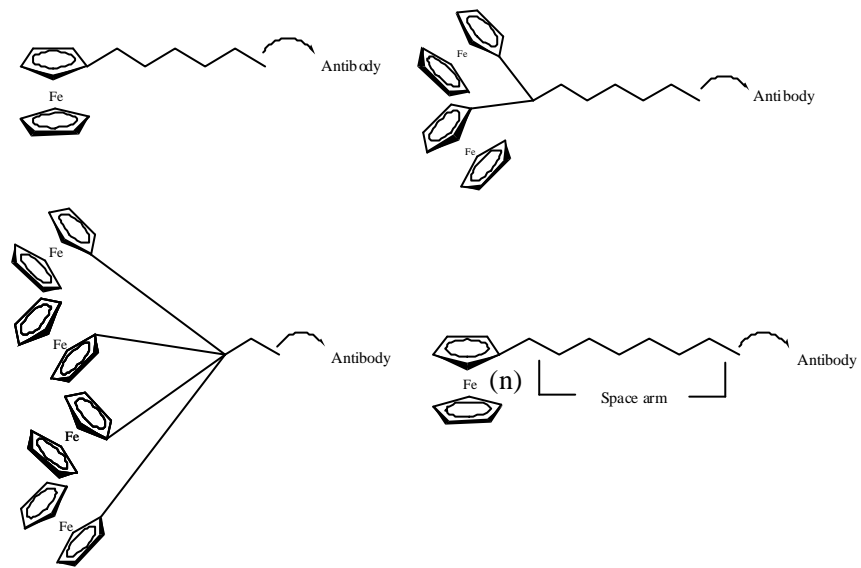
2002.12.01 ~ 2005.11.30

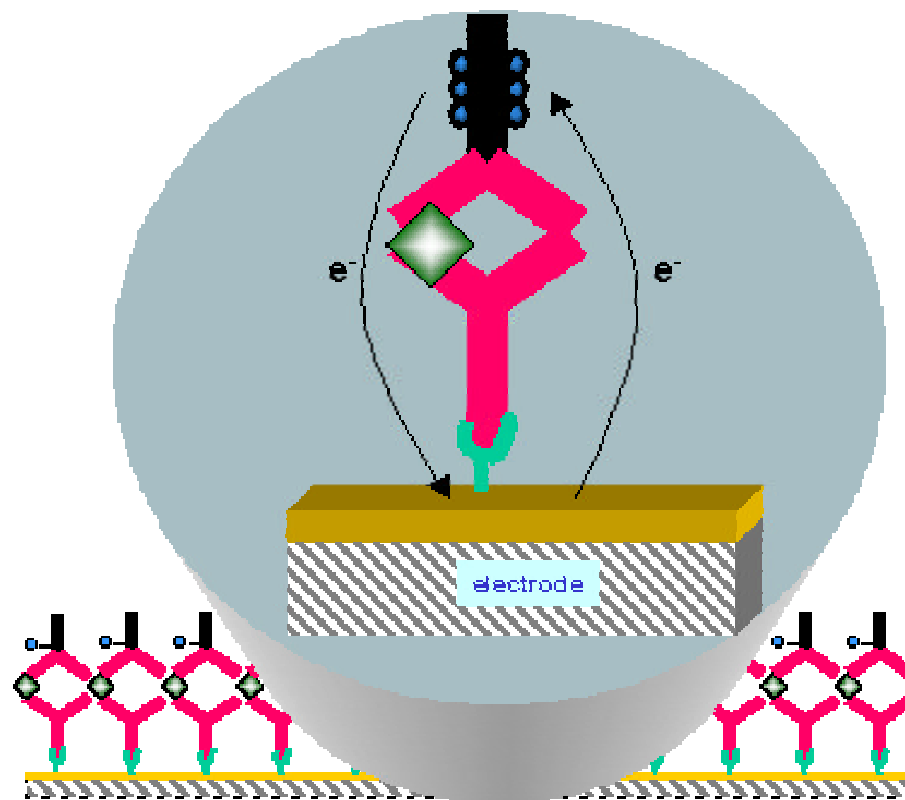
Strategy

- Highly sensitive electrochemical detection of bio-reaction (antigen-antibody interaction, complementary reaction between DNAs)
- Monitoring bioreactions on nanobiochip using scanning electrochemical microscopy(SECM)

Approach

- Antigen modified with redox-active group
- Characterization of antigen and redox species.
- Chemical signal amplification (NADH₂)
- Development of nano-level SECM-SPM technique





Oxidation of ferrocene ion by FADH₂