

4-oxocyclohexadienylidene Porphyrinogen as an Electrochemical Anion Receptor

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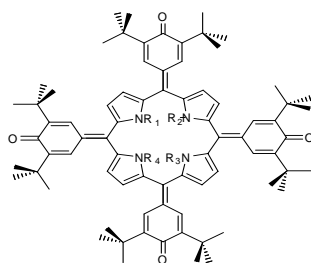
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Abstract. Sensitive and selective detection of biologically and environmentally important anions has been a vast growing field in supramolecular chemistry [1,2]. Much research has been devoted to designing sensors that can selectively recognize anions. Recently, we have reported an anionic and solvatochromatic sensor [5]. (**Scheme 1**) In this investigation, the effect of various anions on the redox states of the porphyrinogen and its N-substituted analogues were studied. Cyclic voltammetry (CV) was employed to probe the changes in the redox potentials of the receptors upon complexation with anions. Upon addition of F⁻ to porphyrinogen, a cathodic shift of ~520 mV corresponding to 1F⁻ complex was observed. The F⁻ ion had the greatest effect on the porphyrinogen redox potentials while other anions gave modest shifts. DFT computational studies on the anion binding correlated well with the electrochemical results.

1. Introduction

Electrochemical molecular recognition is a burgeoning area of supramolecular chemistry [1,2]. An aim in this area is to develop hosts for charged or neutral species. Anions play a grand role in biology and chemistry. Anions are involved in 70% of enzymatic binding and reactions, while DNA, our genetic carrier, is a polyanion [1,2]. The leaching of phosphates and nitrates used in fertilizers in to rivers is detrimental to the environment. Excess fluoride in the body can lead to fluorosis, a type of fluoride toxicity [3].

A sensor, in general, must be able to respond and report the guest binding event. In the case of an electrochemical sensor, a change in the host materials redox potential upon guest complexation will be observed. Other electrochemical anion binding sensors have employed the use of redox active moieties attached to an anion binding group [1,2]. The compound used in this study, 4-oxocyclohexadienylidene Porphyrinogen, is a redox active unit and anion binding unit in one entity.



1: R₁=R₂=R₃=R₄=H
2: R₁=R₃=H; R₂=R₄=CH₂C₆H₅
Scheme 1: Figure of Receptors

2. Experimental

Cyclic Voltammetry Studies

Compounds **1** and **2**, shown in Scheme 1, used in the study were prepared by formerly reported methods [4,5]. Cyclic voltammetry (CV) was used to probe the changes in the redox states of the porphyrinogen upon complexation of anions. Cyclic voltammograms were recorded for receptor **1** and **2** in *o*-dichlorobenzene (ODB) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. This supporting electrolyte was chosen due to the weak binding of the hexafluorophosphate to the receptor as shown in previous work [4]. After addition of anions, the response of the first oxidation of the porphyrinogen was monitored. Electrochemical sensors should have a cathodic shift upon complexation with anions. In other terms, it should be easier to seize an electron from the

compound. Upon addition of 3 equivalents F⁻ to compound **1** (Figure 1), the first oxidation shifted 519 mV in the cathodic direction, making it easier to oxidize. This new peak corresponds to the **1**F⁻ complex. On the other hand, 3 equivalents of the perchlorate (ClO₄⁻) ion to **1** (Figure 2), only shifted the first oxidation 32 mV. Cathodic perturbations the first oxidation of receptors **1** and **2** in the presence of 3 equivalents of F⁻, Cl⁻, C₂H₃O₂⁻, NO₃⁻, ClO₄⁻ and H₂PO₄⁻ are summarized in Table 1. Similar electrochemical results were seen with receptor **2** as the various anions were added.

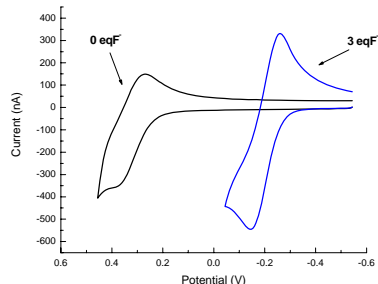


Figure 1 CV of **1** with 3 eq of F⁻. Scan Rate: 100 mV/s Pt working Electrode; (Referenced to Fc/Fc⁺)

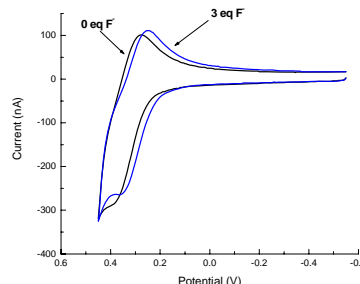


Figure 2 CV of **1** with 3 eq of ClO₄⁻. Scan Rate: 100 mV/s Pt working electrode; (Referenced to Fc/Fc⁺)

Ab initio B3LYP/3-21G() Modeling of Anion Binding of the Porphyrinogens*

To gain a better insight on the molecular and electronic structure, computational studies were performed using density functional methods at the B3LYP/3-21G(*) level. The computational studies correlated with the electrochemical results with the shift of the oxidation upon the anion binding to the porphyrinogen.

Table 1- Cathodic shift of first oxidation for porphyrinogen receptor **1** and **2** in presence of 3eq. anions

Anion	1	2
F ⁻	519	600
Cl ⁻	-	-
C ₂ H ₃ O ₂ ⁻	444	539
NO ₃ ⁻	61	32
ClO ₄ ⁻	32	48
H ₂ PO ₄ ⁻	455	521

3. Conclusions

In conclusion, a new set of electrochemical receptors for anions were studied as potential electrochemical sensors. Compounds **1** and **2** in the presence of various anions had shifts in both reduction and oxidation potentials. The magnitude of the shift depended on the anion that was added.

4. Acknowledgements

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