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LETTERS

Crown-annelated *p*-phenylenediamine derivatives as electrochemical and fluorescence-responsive chemosensors: cyclic voltammetry studies

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Abstract—Cyclic voltammetry studies on crown-annelated tetraalkyl-*p*-phenylenediamine derivatives, in the presence of metal mono- and dications, reveal high selectivity toward dications, of potential value for the development of electrochemical sensors.

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1. Introduction

Previous work in our laboratory has resulted in transition metal-based methodology for the synthesis of functionalized tetraalkyl-*p*-phenylenediamine (TAPD) derivatives.[1] These compounds are related to the well-known tetramethyl-*p*-phenylenediamine, which undergoes facile one-electron oxidation to generate a stable radical cation, Wurster's blue.[2] We have already reported on the redox behavior of several functionally substituted TAPDs, from which it was shown that electron withdrawing substituents on the alkylamine group cause a positive shift of the redox potential in proportion to the degree of electron withdrawal.[3] Logically, one could parlay this behavior into an electrochemical sensing device by using one or both alkylamine substituents as a receptor for an appropriate analyte that would cause similar changes. The ease with which our methodology can provide substituted TAPD systems suggests that a very high level of analyte specificity can be built into the molecule by choosing a functionalized amine that can behave as a highly selective receptor. Electrochemical chemosensors have utilized tetrathiofulvalenes,[4] nitrobenzenes,[5] quinones,[5] and ferrocene[6] as the redox active moiety. The ease with which the redox potential of our TAPD systems can be adjusted,[3] coupled with our recent introduction of TAPDs having thioalkyl side chains to permit attachment to, e.g. electrode surfaces,[1c] suggests that these molecules may have considerable potential as electrochemical sensors. We describe in this letter our preliminary experiments that were designed to test this capability.

2. Results and discussion

Crown-annelated tetraalkyl-*p*-phenylenediamines **1** and **2** were prepared as described in the preceding paper, in order to test the effect of metal cation complexation by the crown ether on the redox behavior of the TAPD. Thus, one would expect that the radical cations **3** and **4**, that result from one-electron oxidation of **1** and **2**, respectively, would be destabilized when a metal cation (M in structures) is bound within the crown ether (the radical cation is delocalized;[2g] two extreme resonance structures are shown here for convenience). This would result in a positive shift of the redox potential, depending on the degree of interaction between cation and the aza-crown nitrogen atom, which is in turn proportional to the cation/crown binding constant, as well as the charge density on the cation. As a result, significantly different responses to dications versus monocations should ensue, since the increased positive charge within the cation/crown complex will have a substantial effect on the redox behavior of the TAPD.

We have studied the cyclic voltammetry behavior[7] of **1** and **2** in acetonitrile in the presence of the metal perchlorates over a range of metal ion concentrations ($LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$ and $Ba(ClO_4)_2$; owing to the poor solubility of $KClO_4$ in acetonitrile, KPF_6 was used instead). Prior to making these measurements, we also determined the binding constants for these systems, from their UV absorption

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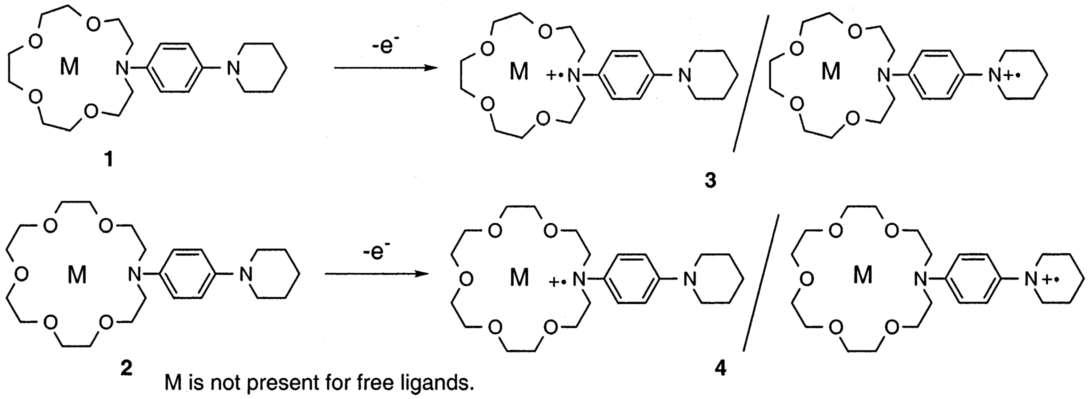
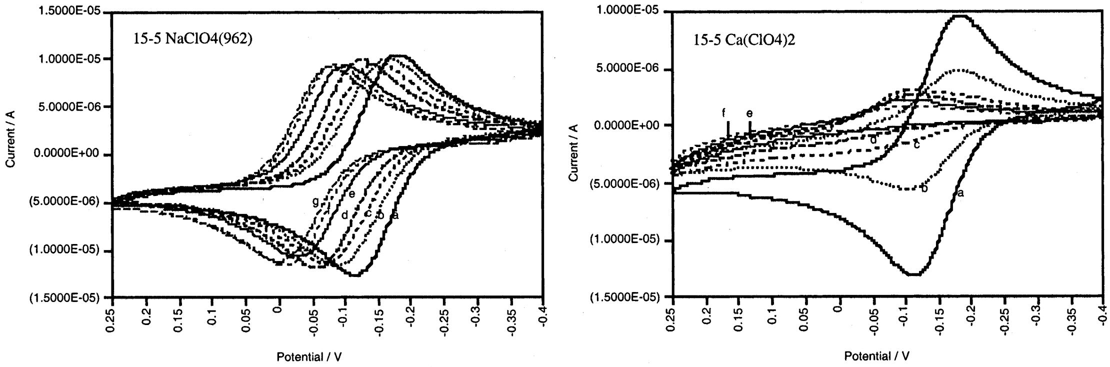


M is not present for free ligands.
For 1:1 complexes, M = Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}

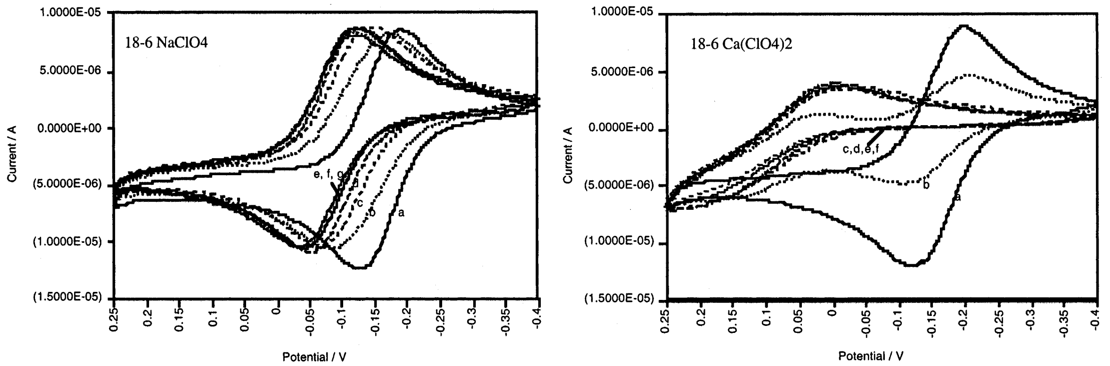
spectra, and these are reported in the preceding paper. We also ran a control experiment to show that tetramethyl-*p*-phenylenediamine remains unaffected by the metal cations studied.

We illustrate here the contrasting effects of dications versus monocations on the redox behavior of TAPD derivatives **1** and **2**. Typical cyclic voltammograms in the presence of increasing concentrations of sodium and calcium perchlorates are presented in Fig. 1. All monocations show effects very similar to sodium, but with slight variation in the shift of the CV curve, consistent with the changes in binding constant recorded in the accompanying paper. Thus, **1**+Li^+ at its maximum concentration (15 equiv.) leads to a positive shift of 0.14 V in the oxidation wave (versus Na^+, +0.12 V), compared with **1** in the absence of metal cation, while K^+ gives a positive shift of only 0.06 V. Similar effects are observed for compound **2** (+0.06 V shift for Li^+, +0.10 for Na^+, +0.20 for K^+). The most noteworthy feature of the voltammograms is that oxidation of the TAPD is completely suppressed in the presence of 1 equiv. of



CV of **1** (1 mM) in acetonitrile with increasing amounts of $NaClO_4$: a) 0, b) 0.5, c) 1, d) 2, e) 5, f) 10, g) 15 equiv

CV of **1** (1 mM) in acetonitrile with increasing amounts of $Ca(ClO_4)_2$: a) 0, b) 0.5, c) 0.8, d) 1, e) 1.5, f) 2 equiv.



CV of **2** (1 mM) in acetonitrile with increasing amounts of $NaClO_4$: a) 0, b) 0.5, c) 1, d) 2, e) 5, f) 10, g) 15 equiv

CV of **2** (1 mM) in acetonitrile with increasing amounts of $Ca(ClO_4)_2$: a) 0, b) 0.5, c) 1, d) 1.5, e) 2, f) 5 equiv.

Figure 1. Effect of Na^+ and Ca^{2+} on cyclic voltammograms of **1** and **2**. Supporting electrolyte was 0.1 M Bu_4NPF_6; glassy carbon working electrode; Pt wire counter electrode; non-aqueous Ag/Ag^+ reference electrode.

Ca^{2+}; identical suppression was observed for Mg^{2+} and Ba^{2+}. This is consistent with the high binding constants noted for these cations, together with the fact that there is now a much greater charge density close to the TAPD crown nitrogen, which results in very considerable destabilization of the radical cations **3** and **4**.

A more meaningful comparison of mono- versus dications is the voltammogram for each TAPD run in the presence of 2 equiv. of the cation. For example, **1** shows small shifts in its oxidation wave for Li^+ (+0.1 V), Na^+ (+0.03 V) and K^+ (+0.01 V, estimated), while there is no oxidation in the presence of any of the dications at this concentration. Similarly, **2** gives shifts for Li^+ (+0.03 V), Na^+ (+0.08 V), and K^+ (+0.15 V), that parallel the binding constant data, while 2 equiv. of all dications completely suppresses oxidation.

3. Conclusions

Crown-annelated TAPDs appear to be capable of electrochemical sensing of metal dications, which give responses that are considerably different from those of monocations. Future studies in our laboratory will explore the scope of this phenomenon, as well as the development of more selective amine receptors that will ultimately allow greater specificity for selected metal cations.

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7. Cyclic voltammetry was carried out using a CH Instruments electrochemical analyzer. The supporting electrolyte (0.1 M n-Bu_4NPF_6) was prepared using CH_3CN (HPLC grade) and degassed for 30 min before use. n-Bu_4NPF_6 (electrochemical grade) was purchased from Fluka Co. and used as received. Glassy carbon (GC, ∅ 3 mm) was used as a working electrode, and the counter electrode was a platinum wire. A non-aqueous (in CH_3CN) Ag/Ag^+ electrode (filled with 0.01 M $AgNO_3$ and 0.1 M n-Bu_4NPF_6 in CH_3CN) served as the reference electrode. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. Titrations were performed using 5 mL of a 1 mM solution of redox-active compounds to which the metal cation solutions (0.1 or 0.5 M) were added using a microsyringe, and the final concentration changes were less than 5%. The scan rate was 50 mV/s. The potential of the regular ferrocene/ferricinium couple was 90 mV under our experimental conditions.