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Electrochemical Switching of Lariat Ethers: Enhanced Cation Binding by One- and Two-electron Reduction of an Anthraquinone Sidearm†

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The first example of cation binding enhancement by electrochemical switching in a lariat ether, accomplished by one- or two-electron reduction of a quinone sidearm, is presented.

The concept of altering macrocyclic polyether binding properties by various switching mechanisms is now well-established. Macrocycles whose binding properties can be switched by photochemical processes,[1] changes in pH,[2] thermally controlled permeability,[3] and redox chemistry[4] have all been reported. Our work has focused primarily on lariat ethers having nitroaromatic sidearms[5] although quinone sidearms in lariat ethers or as an integral part of the ring system have both been reported.[6,7] We report here the first example of binding enhancement by electrochemical switching in a lariat ether which is accomplished by one- or two-electron reduction of a quinone sidearm.

Electrochemical reduction on a glassy carbon electrode at 25 °C in purified acetonitrile containing 0.1 M tetrabutylammonium perchlorate results in the observation of two quasi-reversible redox waves for both (**1**) and (**2**).‡ Voltammograms were recorded using a BAS-100 analyser equipped with 100% i.r. drop compensation. Under these conditions, the first and second redox potentials for (**1**) ($E^{\circ\prime}$ taken as the average of anodic and cathodic peak potentials) are observed at −0.88 V and −1.44 V [*vs.* standard calomel electrode (SCE) see Table 1]. The corresponding couples for (**2**) were observed at −0.88 V and −1.37 V. The similarity in these values demonstrates

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† For the previous parts in this series, see reference 5.

‡ Compound (**1**): M.p. 170—171 °C, lit.[8] m.p. 169 °C, obtained by methylation ($K^{+-}O$–Bu^t, 1-hydroxyanthraquinone, MeI, 1 equiv. 18-crown-6). Compound (**2**) ($K^{+-}O$–Bu^t, 1-hydroxyanthraquinone, 15-crown-5-CH_2-$OSO_2C_6H_4Me$-*p*, MeCN, 1 equiv. 18-crown-6) was obtained as a yellow solid, m.p. 90—92 °C, and gave satisfactory analytical (C,H) data. ^1H N.m.r. ($CDCl_3$): δ 3.70—4.20 (m, 21 H), 7.25—8.25 (m, 7 H).

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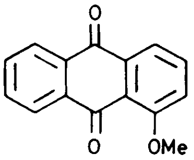
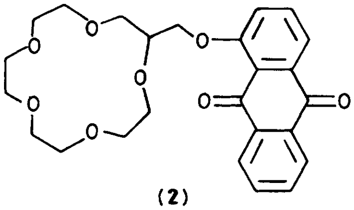
Table 1. Cation dependence of quinone electrochemistry.[a]

	Cation	Equiv.	E_p^{c1}	E_p^{a1}	$E^{\circ\prime 1}$	E_p^{c2}	E_p^{a2}	$E^{\circ\prime 2}$	E_p^{c3}	E_p^{a3}	$E^{\circ\prime 3}$	E_p^{c4}	E_p^{a4}	$E^{\circ\prime 4}$	ΔE^{1-2}	Enhancement[c]	ΔE^{3-4}	Enhancement
(1)	—	—	−1.48	−1.41	−1.44	—	—	—	−0.90	−0.85	−0.88	—	—	—	—	—	—	—
	Li^+	0.5	−1.47	−1.38	−1.42	−1.18[b]	—	—	−0.91	−0.84	−0.88	−0.68	−0.62	−0.65	—	—	0.23	7.7 × 10^3
	Li^+	1.0	−1.46	−1.37	−1.42	−1.18	—	—	−0.92	−0.83	−0.88	−0.69	−0.60	−0.64	—	—	—	—
	Na^+	Adsorption only observed																
	K^+	0.5	−1.46	−1.39	−1.42	−1.30	−1.20	−1.25	−0.91	−0.86	−0.88	—	—	—	0.17	7.5 × 10^2	—	—
	K^+	1.0	−1.45	−1.39	−1.42	−1.28	−1.18	−1.23	−0.91	−0.86	−0.88	—	—	—	—	—	—	—
(2)	—	—	−1.44	−1.30	−1.37	—	—	—	−0.91	−0.86	−0.88	—	—	—	—	—	—	
	Li^+	0.5	−1.49	−1.29	−1.39	−1.20	−1.11	−1.16	−0.91	−0.84	−0.88	−0.71	−0.65	−0.68	0.23	7.7 × 10^3	0.20	2.4 × 10^3
	Li^+	1.0	—	—	—	−1.18	—	—	−0.91	−0.83	−0.87	−0.71	−0.62	−0.66	—	—	—	—
	Na^+	0.5	−1.40	−1.30	−1.35	—	—	—	−0.91	−0.83	−0.87	−0.74	−0.72	−0.73	—	—	0.14	2.3 × 10^2
	Na^+	1.0	−1.39	−1.31	−1.35	—	—	—	−0.90	−0.83	−0.86	−0.74	−0.71	−0.72	—	—	—	—
	K^+	0.5	−1.42	−1.29	−1.36	—	—	—	−0.90	−0.83	−0.86	—	—	—	—	—	—	—
	K^+	1.0	−1.39	−1.25	−1.32	—	—	—	−0.87	−0.81	−0.84	—	—	—	—	—	—	—

[a] The redox potentials ($E^{\circ\prime}$) were taken as the average of anodic and cathodic peak potentials (E_p^a, E_p^c). [b] Adsorption peak. [c] Enhancements were calculated for 0.5 equiv. of cation.



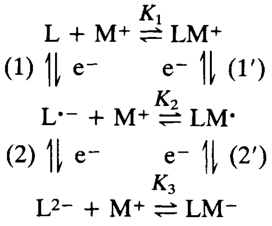
(1)



(2)

the negligible influence of the lariat ether macroring when cations are absent. Addition of $LiClO_4$ to a millimolar solution of (**1**) in MeCN results in the observation of a new quasi-reversible redox couple at −0.65 V [step (1′) in Scheme 1] and a peak at −1.18 V apparently owing to adsorption. Based on our previous studies,[5] the difference in redox potentials corresponds to a cation binding enhancement of 7.7 × 10^3. The expected redox couple corresponding to step (2′) in Scheme 1, if present, could not be discerned owing to the previously noted adsorption.

Addition of $NaClO_4$ to (**1**) gave no voltammetric information owing to adsorption. When $KClO_4$ was added to a solution of (**1**) (as above) a new redox couple was observed at −1.25 V which is believed to result from redox of the reduced species $LM^{\cdot}$ [pathway (2′) in Scheme 1]. To our knowledge, this is the first example of cation binding enhancement by a dianionic ether.



$$\begin{array}{ccc}
L + M^+ & \overset{K_1}{\rightleftharpoons} & LM^+ \\
(1)\ \updownarrow e^- & & e^-\ \updownarrow\ (1') \\
L^{\cdot -} + M^+ & \overset{K_2}{\rightleftharpoons} & LM^{\cdot} \\
(2)\ \updownarrow e^- & & e^-\ \updownarrow\ (2') \\
L^{2-} + M^+ & \overset{K_3}{\rightleftharpoons} & LM^-
\end{array}$$

Scheme 1

Extension of our previous analyses of electrochemical cycles such as the one shown above in Scheme 1, permit us to determine the binding enhancement (K_3/K_2) for a doubly-reduced system compared with the radical anion. Based on $\Delta E^{\circ\prime}$ between couples (2) and (2′) (0.17 V), this value, K_3/K_2, is 7.5 × 10^2. We cannot determine K_2/K_1 directly since no redox couple was observed for process (1′). This unexpected result can be rationalized as follows. The neutral quinone has

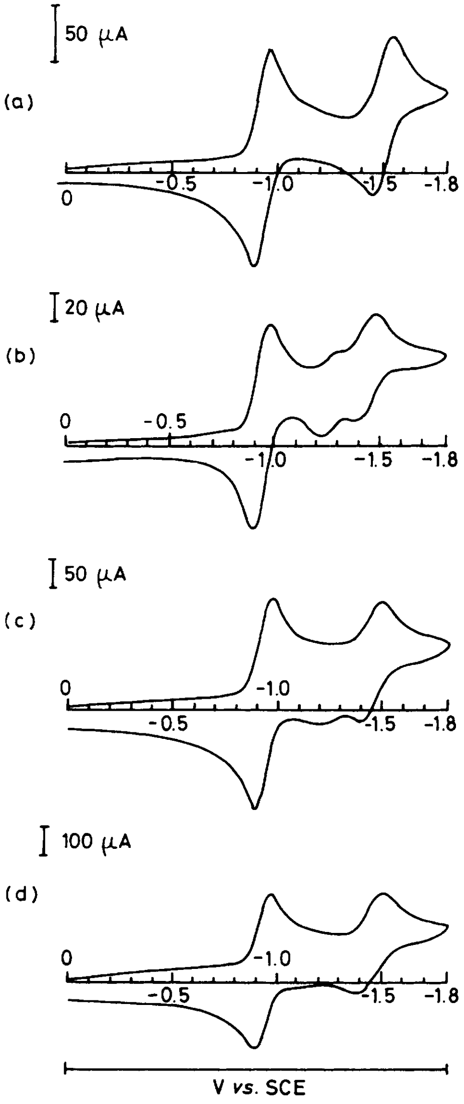


Figure 1. Cyclic voltammograms for compound (**1**) (a) alone, and in the presence of 0.5 equiv. of $KClO_4$ using scanning rates of (b) 100 mV s^{-1}; (c) 500 mV s^{-1}; and (d) 1000 mV s^{-1}.

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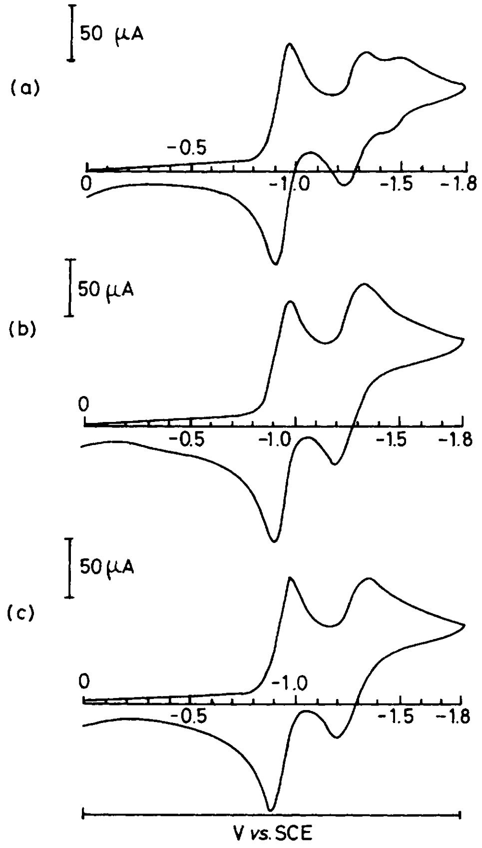

Figure 2. Cyclic voltammograms for compound (**1**) scanned at 100 mV s^{-1} in the presence of (a) 1.0 equiv. K^+; (b) 1.5 equiv. K^+; and (c) 2.0 equiv. K^+.

only a small affinity for K^+ *i.e.*, K_1 is small. Thus, the concentration of LM^+ is small and little reduction occurs over pathway (1′). The reaction sequence: pathway (1), K_2, pathway (2′) leads to LM^- despite the lack of reaction along pathway (1′). A competition exists, on the voltammetric timescale, between pathway (2) and K_2 so that couples (2) and (2′) show nearly the same current (see Figure 1). The voltammograms (b)—(d) shown in Figure 1 were all obtained in the presence of 0.5 equiv. K^+ at 100, 500, and 1000 mV s^{-1}, respectively. At the lower scan rates, there is sufficient time between successive reductions (1), (2) for equilibrium K_2 to compete effectively with pathway (2). Thus redox couple (2′) is clearly observed. As the scan rate increases, (2) dominates, until, at 1000 mV $^{-1}$ [Figure 1(d)], redox couple (2′) is totally inhibited.

In an effort to increase the concentration of LM^+ so that pathway (1′) could be observed, we sequentially increased the K^+ concentration while scanning at 100 mV s^{-1}, Figure 2. Even at 2.0 equiv. of K^+, no redox couple could be observed which could be attributed to reaction along pathway (1′). In addition, no reaction along pathway (2) was observed.

We presume cation interactions with (**1**) involve solvation of the cation by the two adjacent oxygens. When the crown macroring is present as in (**2**), five more oxygen atoms can provide additional solvation thus reducing interaction of the ion with the aromatic ring oxygens. In the presence of Li^+, two additional redox couples {−0.68 V [pathway (1′)], −1.16 V [pathway (2′)]} are observed for (**2**), see Figure 3. The reduction-induced binding enhancements for Li^+, K_2/K_1 is 2.4 $\times 10^3$, which corresponds to a $\Delta E^{\circ\prime}$ of 0.20 V. The enhancement is less than that observed for (**1**) which lacks the competing macroring. The binding enhancement based upon $\Delta E^{\circ\prime}$ of 0.23 V owing to two-electron transfer (K_3/K_2) is 7.7 $\times 10^3$.

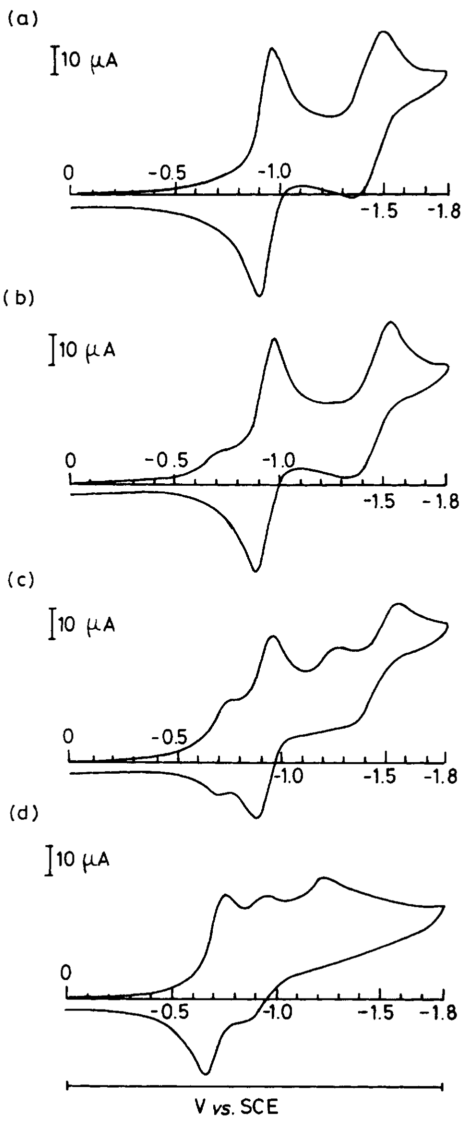

Figure 3. Cyclic voltammograms for compound (**2**) scanned at 100 mV s^{-1} (a) alone and in the presence of (b) 0.25 equiv. Li^+; (c) 0.5 equiv. Li^+; (d) 1.0 equiv. Li^+.

The interaction of (**2**) with Na^+ produces a cyclic voltammogram having three quasi-reversible redox couples. The new couple appears at −0.73 V. When [2.2.1]cryptand is added to this solution, the original voltammogram is obtained, indicating that ion pair formation is reversible. From the $\Delta E^{\circ\prime}$ value of 0.14 V, we calculate the cation binding enhancement K_2/K_1 to be 2.3×10^2. This is lower than the corresponding value for Li^+ since the ring competes more successfully to solvate Na^+ than Li^+.

When K^+ is added to (**2**) we failed to observe a new redox couple suggesting that the value of $\Delta E^{\circ\prime}$ is zero within experimental error, in agreement with the trend shown for Li^+ and Na^+. The only enigmatic result remaining is our failure to observe a redox couple for pathway (2′) in the Na^+–(**2**) case.

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