

Cathodic Voltammetric Behavior of Pillar[5]quinone in Nonaqueous Media. Symmetry Effects on the Electron Uptake Sequence

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S Supporting Information

ABSTRACT: The cathodic voltammetric behavior of pillar[5]quinone was investigated in dichloromethane solution. Our data show that the symmetry of the macrocycle has a pronounced effect on the electron uptake sequence. The uptake of the first five electrons follows a 2-1-2 pattern, and only a total of eight electrons could be injected into the macrocycle under our experimental conditions.

The pillar[*n*]arenes constitute an interesting family of synthetic supramolecular receptors, which have attracted considerable attention in the past decade.^{1–3} Their ease of functionalization⁴ makes them particularly attractive compared to other supramolecular host families. We are specifically interested in the preparation and electrochemical properties of pillar[*n*]quinones.⁵ Currently, pillar[5]quinone^{6,7} (P5Q, see structure in Figure 1) is the only known member of this series

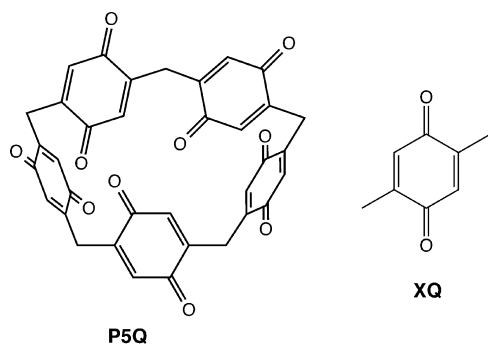


Figure 1. Structures of pillar[5]quinone (P5Q) and the model quinone compound, *p*-xyloquinone (XQ).

of multi-quinone macrocyclic hosts, although various pillar[*n*]arenes have also been reported in which just one or two aromatic rings are oxidized to quinones.^{8,9} A number of structurally related calix[*n*]quinones are known and their electrochemical properties have been investigated in nonaqueous solution.^{10,11} However, calix[*n*]arenes are conformationally more complicated than pillar[*n*]arenes, and, as a result, the electrochemical behavior of calix[*n*]quinones is typically rather complex, reflecting the equilibration among multiple conformers. Our expectation was that P5Q might exhibit simpler voltammetric behavior that could be understood in terms of straightforward pentagonal symmetry considerations.

P5Q was recently reported as an active constituent of the cathode in all-solid-state lithium organic batteries with composite polymer electrolytes.¹² In this work, we focus on the nonaqueous electrochemical behavior of P5Q, which reflects in a unique way the symmetry of this macrocyclic compound.

P5Q was prepared by oxidation of the readily available 1,4-dimethoxypillar[5]arene with Oxone/iodobenzene according to the method reported by Shivakumar and Sanjayan,⁷ which is easily scalable and does not require chromatographic purification. The isolated P5Q was characterized by its published ¹H and ¹³C NMR spectroscopic and mass spectrometric data.

The voltammetric behavior of simple quinones in nonaqueous solvents is very well established. Under aprotic conditions, quinones undergo two consecutive, reversible one-electron reductions. The first reduction (eq 1) leads to the formation of the corresponding radical anion, which, in turn, can be further reduced to a dianion (eq 2) at more negative potentials.



Since P5Q contains five identical quinones in its macrocyclic structure, we selected *p*-xyloquinone (XQ, see Figure 1) as the most suitable model compound. Using square wave voltammetry (SWV), its cathodic electrochemical behavior in dichloromethane solution shows the two anticipated cathodic waves (Figure 2A) at half-wave potentials of -0.67 and -1.19 V vs Ag/AgCl. It must be noted that the second cathodic wave is broader than the first. This is not particularly surprising, as Evans has reported on the differences between the two consecutive reduction waves observed with simple quinones.¹³ The second reduction wave is typically less developed or broader than the first wave, partially due to the larger sensitivity of the dianion to residual protic species or to the slower rates of heterogeneous electron transfer for the second one-electron reduction process. However, in normal pulse voltammetry (NPV) conditions, the two consecutive waves exhibit similar heights (Figure 2B), as expected for consecutive one-electron reductions.

The voltammetric behavior of P5Q is depicted in Figure 3. Assuming a poor level of communication between adjacent

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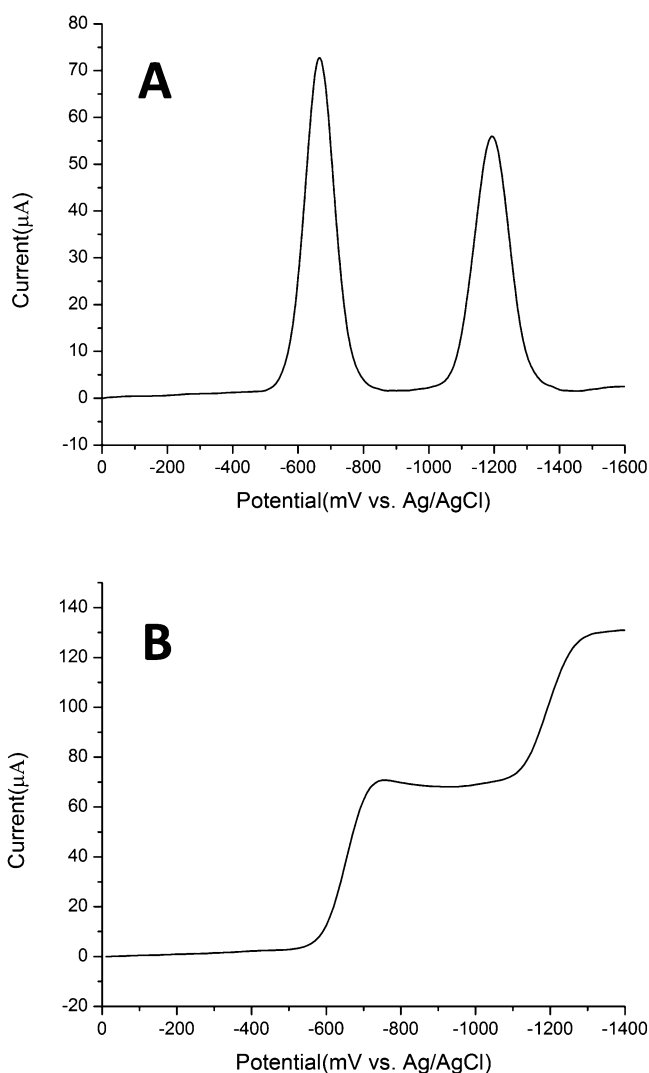


Figure 2. Cathodic voltammetric behavior on glassy carbon (0.07 cm^2) of 1.0 mM XQ in CH_2Cl_2 solution also containing 0.1 M TBAPF_6 as the supporting electrolyte. (A) Square wave voltammetry. (B) Normal pulse voltammetry.

quinone groups in the macrocycle, we would anticipate the observation of two five-electron waves; the first one corresponding to the uptake of one electron by each of the quinone units ($\text{P5Q} + 5\text{e}^- \rightleftharpoons \text{P5Q}^{5-}$), and the second one corresponding to the uptake of a second electron per quinone to yield a macrocyclic compound with 10 negative charges ($\text{P5Q}^{5-} + 5\text{e}^- \rightleftharpoons \text{P5Q}^{10-}$). However, the experimental data clearly differ from these expectations, as shown in [Figure 3](#). Four peaks with variable intensities are observed in the square wave voltammogram; similarly, four different waves are observed in the normal pulse voltammogram. In order to assign each of these voltammetric features to reduction events associated with the uptake of well-defined numbers of electrons, we turned to a methodology that combines voltammetric data with diffusion coefficient measurements obtained with NMR spectroscopic techniques. We have previously reported on the combined use of these techniques to determine the number of electrons involved in the oxidation of dendrimer-like species containing multiple ferrocene centers.¹⁴

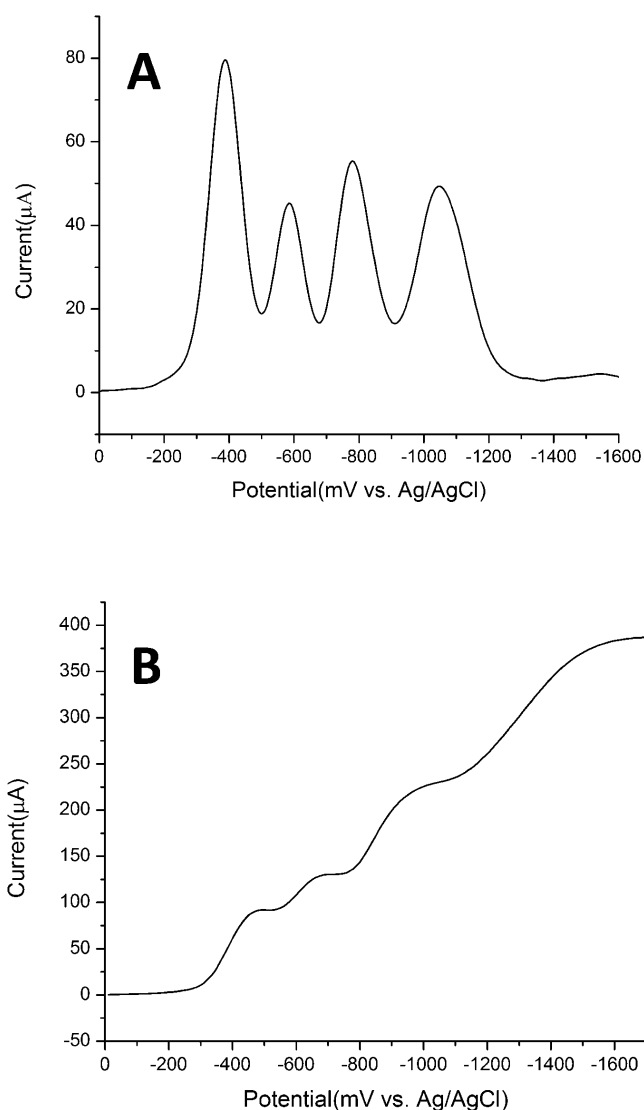


Figure 3. Cathodic voltammetric behavior on glassy carbon (0.07 cm^2) of 1.0 mM P5Q in CH_2Cl_2 solution also containing 0.1 M TBAPF_6 as the supporting electrolyte. (A) Square wave voltammetry. (B) Normal pulse voltammetry.

In NPV the limiting current (i_d) reached after each wave under conditions of diffusion control is given by

$$i_d = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}(\tau - \tau')^{1/2}} \quad (3)$$

where n is the number of electrons involved, F is Faraday's constant, A is the projected area of the electrode, D_0 represents the diffusion coefficient, C_0^* is the bulk concentration of electroactive species, and τ and τ' are the times associated with current measurements in the NPV experiment. If we use the same electrode, concentration of electroactive species and NPV time parameters for two different reducible compounds, such as XQ and P5Q, it is clear that

$$\frac{(i_d)_{\text{P5Q}}}{n_{\text{P5Q}}\sqrt{D_{\text{P5Q}}}} = \frac{(i_d)_{\text{XQ}}}{n_{\text{XQ}}\sqrt{D_{\text{XQ}}}} \quad (4)$$

Therefore, if we independently measure the diffusion coefficients of P5Q and XQ (D_{P5Q} and D_{XQ}) using NMR spectroscopic techniques, the NPV limiting current for the first

reduction of XQ, which is known to involve the uptake of a single electron ($n_{\text{XQ}} = 1$), and the NPV limiting current for any reduction wave of P5Q, we can determine the number of electrons (n_{P5Q}) involved in the latter reduction process using eq 4.

The diffusion coefficient values were measured using the pulse gradient stimulated echo (PGSE) NMR spectroscopic method, which we have used often in previous work.¹⁴ We obtained values of 4.01×10^{-5} and 7.98×10^{-5} cm²/s for P5Q and XQ, respectively, in CD₂Cl₂ solution at 25 °C. Since the medium composition in the NMR spectroscopic and voltammetric experiments is different (CD₂Cl₂ for NMR and 0.1 M TBAPF₆-CH₂Cl₂ for electrochemistry), it is necessary to correct for the viscosities of both solutions in order to obtain the diffusion coefficient values of P5Q and XQ under voltammetric conditions. We used an Ostwald viscometer to measure the viscosities of both solvent systems and found that the D_0 values under voltammetric conditions are related to those measured under NMR conditions by the simple equation,

$$D_0 = 0.959(D_0)_{\text{NMR}} \quad (5)$$

Therefore, the D_0 values for P5Q and XQ, corrected for voltammetric conditions, are 3.85×10^{-5} and 7.65×10^{-5} cm²/s, respectively. Table 1 gives the half-wave potential ($E_{1/2}$)

Table 1. Electrochemical Data for the Voltammetric Reduction of P5Q in CH₂Cl₂ also Containing 0.1 M TBAPF₆

wave	$E_{1/2}$, V vs Ag/AgCl ^a	i_d , μA ^b	n_{cum} ^c	n ^d
1	-0.388	92.4 ± 1.6	1.9	1.9
2	-0.596	132.3 ± 4.6	2.7	0.8
3	-0.800	224.9 ± 5.1	4.6	1.9
4	-1.080	374.7 ± 22	7.7	3.1

^aObtained directly from the peak potential values measured in SWV experiments. Error margin, ± 0.005 V. ^bLimiting current values measured from the initial baseline, giving rise to cumulative numbers of electrons (n_{cum}), which, in turn, were used to obtain the number of electrons (n) associated with each wave. ^cCumulative number of electrons ($\pm 10\%$) taken from the beginning of the reduction process. ^dNumber of electrons ($\pm 10\%$) corresponding to the particular wave.

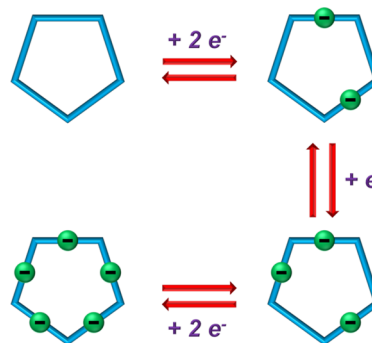
values and limiting currents for each of the four waves observed in the voltammetric reduction of P5Q. The limiting current for the first one-electron reduction wave of XQ under NPV conditions (Figure 2B) was determined to be 69.3 ± 2.3 μA . Therefore, the limiting currents and the diffusion coefficients can be used to determine the number of electrons involved in the reduction event corresponding to each one of the waves.

The experimental and calculated data shown in Table 1 indicate that the four successive waves observed in the voltammetric reduction of P5Q correspond to 2, 1, 2, and 3 electrons, respectively. In order to rationalize this finding we must take into account the structure and geometry of the P5Q macrocycle and accept that there is some level of electronic communication between adjacent quinone units in P5Q, perhaps just the result of electrostatic repulsions.

As mentioned before, if the quinone groups were completely independent from each other, the cathodic voltammetric behavior of P5Q would consist of two consecutive five-electron waves. Accepting that adjacent quinone groups maintain a level of electronic communication is necessary to rationalize the observed voltammetric behavior. If we consider the uptake of electrons by the five connected quinone units, it is clear that the

pentagonal symmetry plays a significant role. Uptake of the first electron is followed at a very similar potential by the uptake of a second electron, as both negative charges can be primarily located in quinone units that are not directly adjacent (see Scheme 1). This leaves a neutral quinone group in between two

Scheme 1. Steps in the Five-Electron Reduction Process of the P5Q Macrocycle



charged quinones and two adjacent, uncharged quinones completing the P5Q²⁻ macrocycle. Therefore, uptake of the third electron must proceed in one of the two adjacent, uncharged quinones, in order to minimize the repulsive interactions among the three charged quinone units at this stage. After uptake of the third electron, the macrocycle only contains two uncharged quinones, and both are equivalent, as each is directly connected to two anion radicals. Therefore, the P5Q⁵⁻ species is formed by the uptake of the last two electrons at very similar potentials (Scheme 1). These simple arguments, based on the minimization of repulsive interactions on the reduced macrocycle, explain the sequence of the first three voltammetric waves and their associated numbers of electrons (2-1-2). The set of half-wave potentials for the uptake of the first five electrons starts at -0.388 V, while the first reduction of monomeric XQ takes place at -0.67 V. These values can be rationalized by the electron withdrawing effects that the neighboring quinones have on one another, leading to a less negative potential in P5Q for the first two one-electron reductions. On the other hand the repulsive forces among the added electrons result in a substantially more negative potential (-0.800 V) for the fourth and fifth one-electron processes, while the third electron is taken at an intermediate potential of -0.596 V. Therefore, the observed $E_{1/2}$ values are also consistent with the proposed 2-1-2 scheme for electron uptake.

The last wave observed in the voltammograms, however, clearly corresponds to three electrons, thus leading to the octa-anion, P5Q⁸⁻. Within the investigated potential range, the fully reduced deca-anion (P5Q¹⁰⁻) is not observed in dichloromethane solution. This highly charged anionic species would correspond to the uptake of two electrons per quinone group, which could be expected on the basis of the electrochemical behavior of XQ and many other quinones.¹³ However, the spatial proximity of the quinone groups in the P5Q macrocycle may hinder the accumulation of ten negative charges in such a small molecular volume and prevent the formation of the deca-anion in the low polarity medium (CH₂Cl₂ solution) in which we conducted our voltammetric experiments.

Overall, our experimental data provide support for a four-step mechanism in the reduction of P5Q, which reflects the pentagonal symmetry of this macrocycle and the effects of the

accumulation of negative charge in a relatively small molecular framework. We are currently continuing the investigation of the reduced forms of PSQ using EPR spectroscopic techniques and working on the synthesis of pillar[6]quinone to carry out similar experiments on a related compound with hexagonal symmetry.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05546.

Experimental details on the electrochemical and NMR diffusion coefficient measurements, and derivation of eqs 4 and 5 (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Xue, M.; Yang, Y.; Chi, X. D.; Zhang, Z. B.; Huang, F. H. *Acc. Chem. Res.* **2012**, *45*, 1294.
- (2) Ogoshi, T. *J. Inclusion Phenom. Mol. Recognit. Chem.* **2012**, *72*, 247.
- (3) Cragg, P. J.; Sharma, K. *Chem. Soc. Rev.* **2012**, *41*, 597.
- (4) Strutt, N. L.; Zhang, H.; Schneebeli, S. T.; Stoddart, J. F. *Acc. Chem. Res.* **2014**, *47*, 2631.
- (5) Lao, K.-U.; Yu, C.-H. *J. Comput. Chem.* **2011**, *32*, 2716.
- (6) Cao, D.; Kou, Y.; Liang, J.; Chen, Z.; Wang, L.; Meier, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 9721.
- (7) Shivakumar, K. I.; Sanjayan, G. J. *Synthesis* **2013**, *45*, 896.
- (8) Han, C.; Zhang, Z.; Yu, G.; Huang, F. *Chem. Commun.* **2012**, *48*, 9876.
- (9) Pan, M.; Xue, M. *Eur. J. Org. Chem.* **2013**, *2013*, 4787.
- (10) Gómez-Kaifer, M.; Reddy, P. A.; Gutsche, C. D.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 3580.
- (11) Webber, P. R. A.; Beer, P. D.; Chen, G. Z.; Felix, V.; Drew, M. G. B. *J. Am. Chem. Soc.* **2003**, *125*, 5774.
- (12) Zhu, Z.; Hong, M.; Guo, D.; Shi, J.; Tao, Z.; Chen, J. *J. Am. Chem. Soc.* **2014**, *136*, 16461.
- (13) Lehmann, M. W.; Evans, D. H. *J. Electroanal. Chem.* **2001**, *500*, 12.
- (14) Sun, H.; Chen, W. Z.; Kaifer, A. E. *Organometallics* **2006**, *25*, 1828–1830.