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Electrochemical and Quantum Chemical Investigation of Tetranitrocalix[4]arenes: Molecules with Multiple Redox Centers

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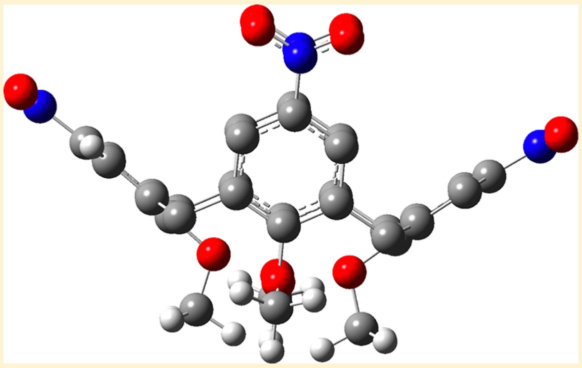
S Supporting Information



ABSTRACT: The calix[4]arene skeleton is electrochemically inactive, but it is a useful stable frame for building "smart" molecules and supramolecular assemblies. Suitable substitution on the upper (and/or lower) rim leads to unusual and surprising properties in this system. Polynitrocalix[4]arenes with reducible nitro groups located at the upper rim represent molecules with multiple redox centers where the potential for interactions between them is the focus of interest. The title compounds are promising precursors, e.g., for design and synthesis of sensors. In this work, the stepwise reduction of two tetranitrocalixarenes was investigated electrochemically, and the results were correlated with quantum chemical calculations. The order of individual electron transfers was described as a consequence of molecular geometry. Two independent pairs of equivalent nitro groups were identified whose reduction potential depends upon their respective locations in the molecule. All nitro groups are electronically isolated and thus are reduced independently yielding poly radical ions. The increasing charge has negligible impact on the geometry of the calixarene, which maintains its pinched shape even when carrying an overall molecular charge of −4.

INTRODUCTION

Due to their capability for host−guest interaction and complex formation, molecules based on a calix[4]arene nucleus have been and continue to be broadly investigated, and many new derivatives have been synthesized and characterized.[1−3] They can be used, e.g., as model systems for studies of molecular recognition, in analytical chemistry as sensors and receptors, for selective trapping of cations, anions, and neutral substances,[4−8] in medicine as ligands for luminescent complexes,[9] for magnetic resonance imaging, and other applications.[10] The chemical functionalization of the calix[4]arene nucleus, both at the upper and lower rim, has been reviewed.[11]

The title nitrocalix[4]arenes[12−14] have attracted considerable attention for their ability to form films that exhibit second-order optical properties[12,13] and are also promising precursors enabling an alternative synthetic strategy: introduction of functional groups, prolongation of the pendant chains, and thus the preparation of a specific cavity where electrochemistry can be carried out. This approach is based on the fact that in aprotic media aromatic nitro groups are easily reducible in a reversible one-electron wave at a cathode, giving rise to a stable radical anion. At more negative potentials, hydroxylamine derivatives are produced in a process involving successive formation of the nitro group dianion which is then protonated and ejects hydroxide to afford nitrosobenzene, followed by two successive electron transfers, for an overall three-electron step.[15,16] Upon addition of suitable reactants, the electrosynthesis could continue in the customary fashion, modified by inclusion of substrates in the calixarene cavity, yielding more complicated structures. The limited number of previous publications dealing with electrochemical studies of calixarenes involves calixarenes bearing electroactive substituents like ferrocene, quinone, or $Ru(bipy)_3$ groups,[17,18] or calixarenes as sensors for host−guest interaction.[19] Several contributions have been devoted to electrochemical oxidation of nonsymmetric sulfonated or hydroxylated calixarenes under formation of quinone derivatives.[20]

Nitrocalix[4]arenes represent not only reducible precursors for electrosynthesis, but they also represent a system in which one, two, three, or four electroactive groups can exist in a single molecule, opening possibilities for complex intramolecular electron interactions. In addition to this, the nitro groups could serve simultaneously as redox probes by providing information on the effects of the otherwise electrochemically inactive calixarene core. The presence of four nitro groups in one calixarene molecule raises many questions, among them: Are they reduced simultaneously or stepwise? Which part of the molecule is reduced first? Do the nitro groups influence each other? Is the molecular geometry of the reduced forms different from the original one?

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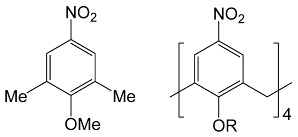
In the present work, the voltammetric behavior of the model compound 4-methoxy-3,5-dimethylnitrobenzene (**1**) and two tetranitrocalixarenes **2a** and **2b** (Scheme 1), with different substitution on the lower rim, was investigated in a nonaqueous solvent (DMF). (The computations to be described later were carried out on the hypothetical molecule **2c** for reasons of computational efficiency.) Although calixarenes can exist in different conformations,[21] only those derivatives with a well-defined and fixed *cone* conformation were used for the present experiments. The *cone* conformation is defined as one in which all four nitro groups are at the upper rim of the pseudo bowl of the calixarene. In addition to the experimental electrochemical approach, the problem of the order of reduction of the four nitro groups as well as the geometry of the resulting anion radicals was also treated theoretically since for reliable interpretation of the experimental results a correlation with quantum chemical calculations was found to be necessary.

Scheme 1. Nitroarenes Studied Electrochemically



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2a, R = *n*-Pr
b, R = CH_2CO_2Et
c, R = Me

RESULTS AND DISCUSSION

The values of all reduction potentials are summarized in Table 1, and polarograms of **1** and a typical tetranitrocalixarene are presented in Figure 1. The first electron transfer in the model compound **1** occurs at the same potential as those of the other two calixarenes, demonstrating that because of the relatively rigid and electronically nonconjugated backbone of calix[4]-arenes, the nitro groups on the upper rim of the neutral form do not interact electronically with their neighbors. The derivative with ester groups at the lower rim (**2b**) is reduced slightly less negatively than the propoxy derivative (**2a**), reflecting the electron-withdrawing effect of the ester substituent. Otherwise, the reduction behavior of **2a** and **2b** is identical.

Table 1. Reduction Potentials of Nitroarenes in *N,N*-Dimethylformamide

compd	E_1[a] (V)	E_2[a] (V)	E_3[a] (V)
1	−1.21		−2.23[b]
2a	−1.22	−1.48	−2.6[b]
2b	−1.20	−1.41	−2.55[b]

[a]Half-wave potentials measured in relative to SCE_{aq}. [b]Broad wave.

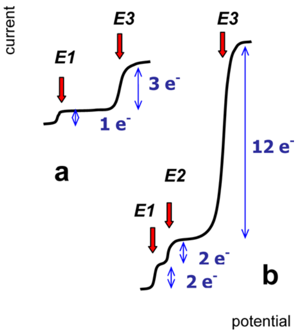

Figure 1. (a) Polarogram of **1** in dimethylformamide containing 0.1 M electrolyte. (b) Polarogram of **2a** under the same conditions as (a). Potentials are presented in the Table 1.

Monomer 1. Prior to the investigation of the authentic tetranitrocalix[4]arenes, the electroreduction of model compound **1** was examined. Two waves were observed, a one-electron reversible wave and an irreversible wave at more negative potentials corresponding to uptake of three electrons. This behavior has been observed for many other nitroarenes in aprotic media.[15,16] As mentioned earlier, this is generally accepted to correspond to a mechanism in which a one-electron reversible process at potential E_1 produces a radical anion; The anion radicals produced in this step are stable in aprotic media and even in aqueous alkali. This step is followed by an irreversible complex composite step (E_3) in which the anion radical anion is reduced to a dianion; this is followed quickly by protonation by traces of a proton donor (probably water) in the medium and subsequent ejection of hydroxide ion to form nitrosobenzene, and finally, two-electron reduction of the latter, producing phenylhydroxylamine.

As an adjunct to our computational work, we felt it would be useful to be able to compute the reduction potentials of groups located at different points on the calixarene nucleus. Traditionally, electrode potentials have been reported relative to an external reference electrode. Recent advances in understanding the thermodynamic parameters involved in electron transfer at electrodes have, however, led to the concept of *absolute electrode potential*, which represents the intrinsic ease of oxidation or reduction of any given substance.[22a,b] The absolute electrode potential of a given redox system is a *computed* value and may be defined as the difference between the computed energies of the reduced and oxidized forms of the couple in solution. The IUPAC-recommended value of the absolute potential of the normal hydrogen electrode (NHE) in acetonitrile at 25 °C is 4.60 ± 0.010 V.[22b] Using a method for computing absolute potentials of redox potentials developed by one of us,[22c] we estimate that E_1 of nitrosobenzene (reversible potential) should be 0.18 V positive of that of nitrobenzene (see the Supporting Information); the experimental difference is 0.19 V.[23] Our computations predict that the reversible one-electron potential for reduction of nitrosobenzene anion radical to the corresponding dianion should be about 0.1 V negative of that of nitrobenzene, though the several overlapping voltammetric waves observed in this potential region result in a broad wave around E_3, which prevents us from confirming this prediction.

Using a method for ab initio estimation of redox potentials developed by one of us,[22] we compute that E_1 of nitrosobenzene (reversible potential) should be 0.18 V positive of that of nitrobenzene (see the Supporting Information); the experimental difference is 0.19 V.[23] Our computations predict that the reversible one-electron potential of nitrosobenzene anion radical should be about 0.1 V negative of that of nitrobenzene; however the several coupled chemical processes taking place in this potential region result in a broad wave around E_3, thus preventing making this comparison.

Tetranitrocalix[4]arenes 2a−c. The voltammograms of tetranitrocalix[4]arenes **2a** and **2b** exhibit two two-electron waves at almost identical potentials E_1 and E_2, and the reversibility of both waves was again established by cyclic

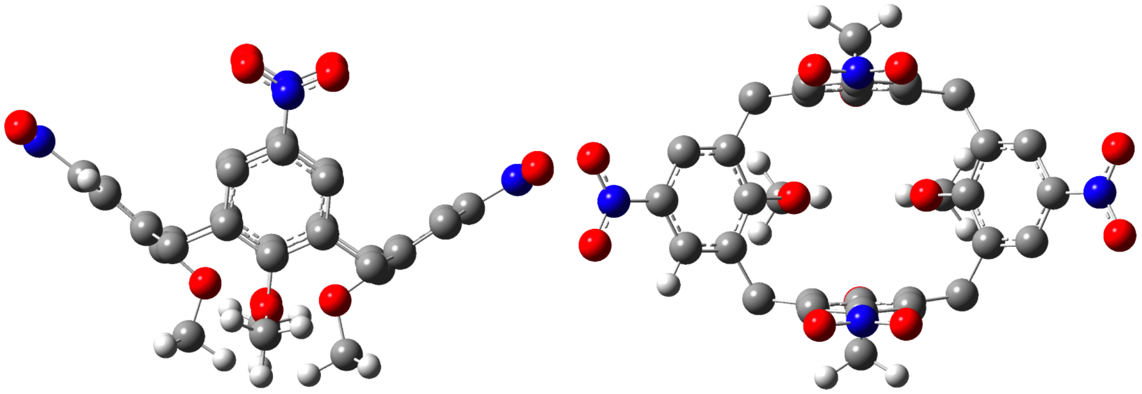

Figure 2. Computed molecular model of tetra-*p*-nitrocalix[4]arene **2c**. Left: side view, in which the rear pinched arene ring is eclipsed by the front. Right: top view, showing the much shorter distance between the pinched nitro groups compared to the distant groups.

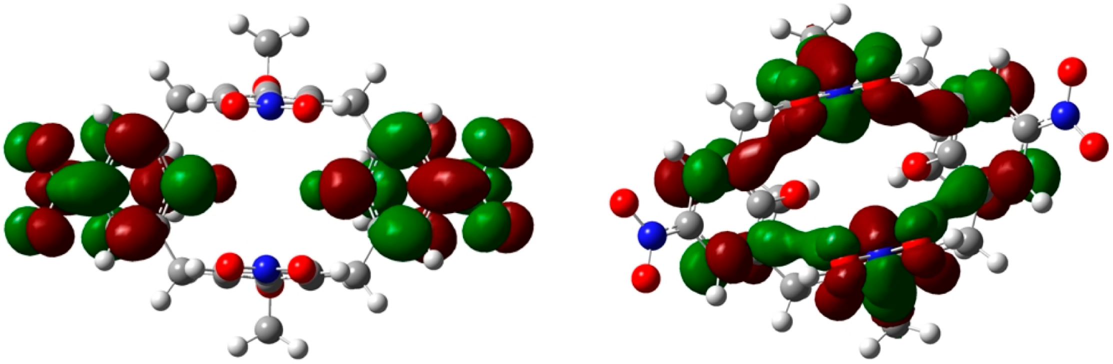

Figure 3. Left: Localization of the HOMO (left) of the dianion diradical of **2c** on the distant nitrobenzene groups. Right: Localization of the LUMO of the same species on the pinched nitrobenzenes.

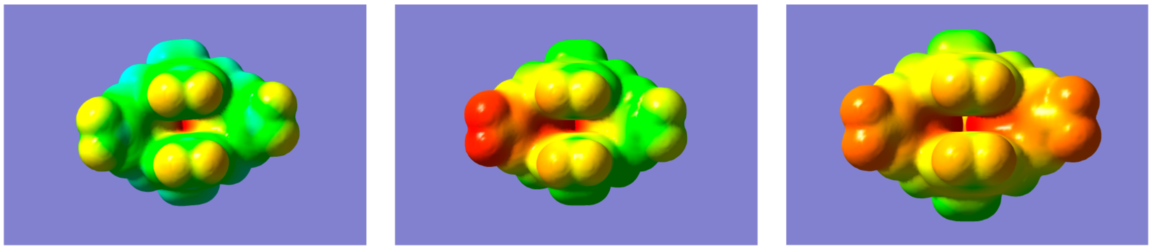

Figure 4. Electrostatic potential maps of **2c**. Left: neutral form. Center: monoanion radical. Right: dianion diradical. Color coding: red, highly negative; yellow, slightly negative; green, slightly positive; blue, highly positive.

voltammetry at a scan rate of 50 mV/s; the $i_{p,a}$ to $i_{p,c}$ ratio is close to unity and the ΔE_p is 75−85 mV.[24] The current at each wave (peak) corresponds to two electrons; this follows unambiguously from comparison of their wave heights with that of the one-electron reversible wave of the model **1**. From the reversibility and from the number of involved electrons it is evident that there are four reversible electron transfer reactions representing one-electron reduction of each nitro group to the corresponding stable anion radical. Since two nitro groups are reduced more easily than the other two, the four nitro groups on the upper rim of tetranitrocalix[4]arenes are not equivalent but form two energetically different types and, incidentally, demonstrating that **2a,b** do not exist in a symmetrical bowl conformation in solution. The X-ray crystal structure analysis[14] of **2a** as well as all computed models (Figures 2−5) are in full agreement with this electrochemical result, showing that in the molecules ot the calix[4]arene two nitrobenzene rings on opposite sides of the calixarene are close to each other in which the benzenoid rings lie in nearly parallel planes with an interplanar angle of only a few degrees, whereas the other two are distant and directed away from each other with an interplanar angle of >90° (Figure 2). We refer to these as the "pinched" and "distant" nitro groups, respectively.

Observation of reversible two-electron waves at E_1 and E_2 indicates that the two nitro groups within each couple do not interact, i.e., they act equivalently and independently. Each of the two waves is simply a superposition of two one-electron waves at the same potential. Several lines of evidence permit the conclusion that the distant nitro groups of **2** are reduced at the more positive potential E_1, whereas the pinched groups are reduced at E_2:

(1) The HOMO of the dianion includes the distant nitro groups, but not the pinched nitro groups (Figure 3a). There is no electron density or orbital localization on the pinched nitro groups. Conversely, the calculated LUMO of the dianion resulting from reduction at E_1 includes the

pinched nitro groups but not the distant groups (Figure 3b). Hence, the first two electrons go into the distant nitro groups and the third and fourth electrons go into the pinched groups.

(2) Electrostatic potential maps of **2c** and its monoanion radical and dianion diradical clearly demonstrate that the first electron is added to one of the distant nitrobenzenes followed by addition of the second electron to the other distant nitrobenzene (Figure 4).

(3) Computation of the reduction potentials of the two possible isomeric mononitrocalixarenes (Figure 5) shows that reduction of a distant nitro group is easier than a pinched nitro group. (It was not possible to optimize the structures of these mononitro derivatives, so single-point computations were made. Attempts at optimization of these resulted in isomerization to a symmetrical open bowl conformation.) It is known that the unpaired electron in nitrobenzene anion radical is almost completely localized on the nitro group.[25] The fact that the first reduction potentials E_1 of **2a** and **2b** are due to reduction of the distant nitro groups might therefore be explained as due to the fact that this places the negatively charged nitro groups as far as possible from each other in the resulting dianions. However, it appears that more is involved; computations indicate that distant nitro groups are intrinsically easier to reduce than pinched groups: the energies were computed of the two hypothetical mononitrocalixarenes (5-nitro and 11-nitro) and their corresponding anion radicals, one with the nitro group on a distant ring and the other on a pinched ring (see Supporting Information).[24] From these computations, the reduction potential of the distant nitrobenzene is predicted to be 0.32 V positive of that of the pinched nitrobenzene, in good agreement with the experimental difference of 0.26 V (Table 1). Furthermore, the electrostatic potential map of the anion radical formed by addition of an electron to the hypothetical unsymmetrical 5,11-dinitrocalixarene containing one distant and one pinched nitro group shows clearly an overwhelming preponderance of negative charge at the distant position (Figure 6).

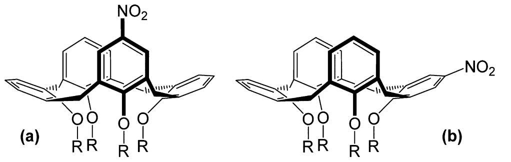

Figure 5. Two possible isomeric mononitrocalixarenes (a) "pinched"; (b) "distant".

The first two reduction waves (E_1 and E_2) involve overall transfer of a total of four electrons. These waves are followed by a single, broad irreversible wave (E_3) at about −2.5 V with a total limiting current corresponding to approximately 12 electrons. This indicates that the four nitro radical anions are further simultaneously reduced according to the expected three-electron composite step (see above). The broadness of this wave is evidently caused by several processes at potentials very close to each other. Because of this fact and the proximity to the cathodic potential limit, it is, however, impossible to distinguish individual steps.

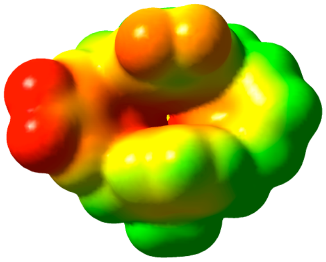

Figure 6. Electrostatic potential map of the anion radical of the unsymmetrical dinitrocalixarene. Color coding: red, highly negative; yellow, slightly negative; green, slightly positive; blue, highly positive.

Quantum Chemical Calculations. Density functional computations were carried out for five redox forms of the tetranitro calixarene **2c**: neutral molecule, monoanion, dianion, trianion, and tetraanion at the B3LYP/6-31G+d level, which has been the most widely used general purpose computational level for intermediate-sized organic molecules in recent years.[26b,c] All results confirmed the pinched shape of the molecule and in general reproduced the pinched structure of the neutral tetranitro compound.[14] After computation of all five reduction states (ranging from the neutral to the tetraanion), in all cases similar flat conformational minima were found. Therefore, it is possible to assume that they are all about the same geometry. Using the distance between the two nitrogen atoms of the pinched groups as a measure of the relative geometries, we conclude that this distance is between 5 and 6 Å in all five species; the distance between the distant nitrogen atoms is around 12−12.5 Å. The data show a tendency for the "pinched" N−N distance to increase with increasing charge: all of the species show minima around 5.5 and 6.0 Å. It is difficult to say whether these correspond to a single conformation of about 5.5−6.0 Å, or two closely spaced conformations. In any case neutral **2c** and its monoanion appear to prefer the 5.5 Å geometry, while the tetraanion prefers 6.0 Å and higher. It was found that the dianion is a triplet, i.e., that it has two unpaired electrons in different orbitals; computations on both the singlet and triplet at different N−N distances were carried out, from which it became clear that the triplet is more stable than the singlet by at least 5 kcal/mol at any inter-ring distance. This is consistent with our conclusion that the groups are reduced independently.

■ CONCLUSIONS

Two tetranitrocalix[4]arenes **1a,b** were investigated electrochemically and by quantum chemical calculations. The presence of four electrochemically active centers (four nitro groups) in one calixarene skeleton is responsible for several remarkable results. The nitro groups are formally electronically equivalent, but in fact there are two types of them due to the pinched shape of the calix. Their reduction starts with two 2-electron reversible waves. That means that the four nitro groups are divided into two different couples of identical and noninteracting nitro groups. As a result, they are reduced in stepwise fashion and reversibly in successive two-electron steps. Orbital and electrostatic potential maps of the dianion of **2c** and studies on the hypothetical unsymmetrical 5,11-dinitro and 5-nitro and 11-nitro derivatives clearly demonstrate that the "distant" nitro groups are reduced more readily than the "pinched" isomers. The first two electrons go individually to the distant nitro groups with formation of the stable dianion diradical, and the reduction of the other two (pinched) nitro groups then proceeds at higher (more negative) potential. This is likely due to the fact that reduction of a nitrobenzene in the pinched position is affected by the through-space π-interaction of the pinched phenyl rings. All four transferred electrons are strictly localized at the four nitro groups without any delocalization or intramolecular communication. The stepwise reduction up to four electrons has negligible influence on the geometry of the molecule; all species have a pinched shape (even in solution) in which the distance between the two closest nitrogen atoms is about 5−6 Å, whereas the distance of the other two nitrogens ranges to 12−12.5 Angstroms. The different oxo substituents at the lower rim have only a small influence on the redox potential. The total reduction pathway follows the usual four-electron mechanism of reduction of aromatic nitro compounds in aprotic media.

■ EXPERIMENTAL SECTION

The tetranitrocalix[4]arenes were prepared according to published procedures,[14] and their purity and identity was checked by elemental analysis and NMR.

Dimethylformamide (DMF) was purified by double distillation: First, very slow azeotropic distillation at atmospheric pressure on a 1 m long column was performed: 100 mL of benzene p.a. and 100 mL of distilled water were added to 1.5 L of DMF (p.a., Lachner, Czech Republic), and the mixture was distilled, removing the aqueous phase as the benzene−water azeotrope at around 78 °C, after which the benzene phase was then distilled. When the temperature increased to over 100 °C, the distillation was interrupted and fractionation was continued slowly under reduced pressure at about 50−60 °C. The first 100−200 mL of DMF was removed for recycling, and the next fraction of pure, dry DMF exhibited a cathodic potential limit at -3 V vs SCE). Tetrabutylammonium tetrafluoroborate (TBATFB, 0.1 M) and tetrabutylammonium hexafluorophosphate (TBAHFP) recrystallized from ethanol were used as electrolytes.

For all experiments, a three-electrode system was used. A dropping mercury electrode (DME) with controlled drop time (2 s) was utilized in DC polarography, and a hanging mercury drop electrode (HMDE, Metrohm) was used for cyclic voltammetry. A platinum wire or platinum foil served as an auxiliary electrode and the potentials were measured relative to saturated calomel reference electrode (SCE) separated from the nonaqueous solution by a salt bridge containing identical DMF solution.

Polarographic and voltammetric experiments were carried out using an analog potentiostat (either of models PA3 or PA4 from Laboratorni přistroje Praha) using an XY recorder to record the data or a digital potentiostat PGSTAT101 (Autolab-Metrohm). Scan rates of 5−10 mV/s for polarography and 50−500 mV/s for cyclic voltammetry were employed. The solution was deaerated by argon prior each electrochemical experiment.

Computations. Quantum chemical calculations on **2c** and the hypothetical 5-mononitro-, 11-mononitro-, and *unsym*-5,11-dinitrocalix[4]arenes were carried out using the Gaussian '09 suite of computational programs.[26] As noted earlier, energies were computed by density functional theory (DFT)[26a,b] using the B3LYP functional[26c] together with the 6-31G basis set, i.e., with the addition of both diffuse orbitals and *d*-orbitals to the first row elements (C, N, and O). Solvation energies in acetonitrile (dielectric constant $\varepsilon = 37.5$, chosen as a representative polar electrochemical solvent) were computed by the polarizable continuum method (PCM) of Tomasi.[27] The computed free energies of all species (in hartrees; 1 hartree =627.5 kcal/mol) are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computed energies in hartrees and optimized coordinates of all species. Computations of the energies and geometries of the first and second reduction potentials of **2c** and the distant and pinched mononitrocalixarene isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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