

Syntheses, Structures, and Properties of Quinone-Bridged Calix[6]arenes

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The quinone-bridged calix[6]arenes **1** and **2**, carrying a 1,4-benzoquinone moiety in the cavity of a calixarene macrocycle, were synthesized from the corresponding *p*-methoxyphenol derivatives. X-ray crystallography revealed the structures of **1** and **2**, in which the quinone moiety is located inside the cone-shaped calix[6]arene framework and surrounded by the lower-rim substituents. Their ^{1}H NMR spectra showed upfield shifts of the protons on the bridging unit in comparison with reference compounds without the calixarene framework, in accordance with their crystal structures. The cyclic voltammograms of **1** and **2** showed two waves, the second ones being considerably broadened. Their reduction potentials were found to be negatively shifted in comparison with those of the reference compounds. These shifts were explained in terms of the nonbonded interaction between the ether oxygen atoms of the calixarene moiety and the quinone moiety, as well as the sterically restricted access of the counter cation to the semiquinone anion radical. Reactions of **1** with hydroxylamine and phenylhydrazine afforded the corresponding hydroquinone along with the quinone monoimine derivatives, indicating that electron transfer from the amines proceeds quickly, although the negatively shifted reduction potentials of **1** are apparently unfavorable for the electron transfer process.

Macrocyclic molecules constitute a major class of complexing agents for metal ions and small organic molecules, and their inner phase provides a unique microenvironment to the included guest species.[1–4] Recently, redox reactions of chemical species captured in the cavity of macrocyclic host molecules such as cyclophanes, calixarenes, and carcerands have been attracting increasing attention.[5–10] In these complexes based on noncovalent interaction, however, only the averaged properties of the complexed and dissociated guest species are observable. Furthermore, the geometry of the guest molecule in the cavity of the macrocycle is often ambiguous. If the guest molecule is covalently anchored in the cavity with well-defined geometry, one can expect that the effects of the surrounding macrocycle on the properties of the intracavity species may be elucidated much more definitely.

We have been investigating the synthesis and applications of calix[6]arenes bridged by a functionalized *m*-xylene-α,α'-diyl unit.[11–18] Stabilization of highly reactive species such as a sulfenic acid[19,20] and selenenic acids[21,22] has been achieved and their reactivities were investigated. This framework has also been utilized for concave reagents by Lüning et al.[23–27] The large cavity of this framework is also expected to serve as a reaction field for redox-active species covalently anchored in it. Although a large number of macrocyclic quinones such as calixquinones have been reported so far,[28–31] there has been no example of a compound bearing a quinone moiety covalently fixed in the cavity. In this paper, we describe the synthesis and structures of the quinone-bridged calix[6]arenes **1** and **2**. The relationships between the electrochemical properties and the structural features of **1** and **2** as well as their chemical reactivities are also delineated. Parts of this work have been communicated.[32]

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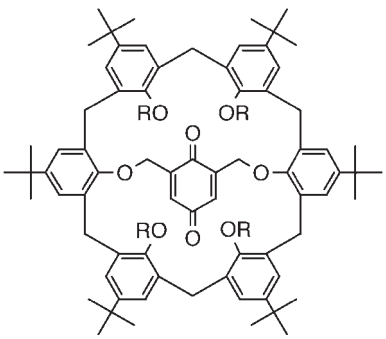

1 (R = Bn)
2 (R = Et)

Chart 1.

Results and Discussion

Synthesis. We previously reported that capping the lower rim of the *m*-xylene-α,α'-diyl-bridged calix[6]arenes with arylmethyl groups can freeze the conformation of the calixarene macrocycle.[13,14] For construction of a rigid framework, we introduced benzyl groups into the lower rim of the calixarene moiety of **1**. Synthesis of **1** was effected by the route shown in Scheme 1, where a *p*-methoxyphenol unit was used as a precursor to the quinone moiety. Bridged compound **5** was prepared by the reaction of *p*-*t*-butylcalix[6]arene (**3**)[33] with tribromide **4**[34] in 73% yield by using the previously reported method.[17] Benzylation of the four hydroxy groups of **5** in the presence of cesium carbonate afforded almost exclusively the cone isomer **6** of the tetrasubstituted product in 93% yield. The spectral features of **6** are essentially the same as those of other bridged calix[6]arenes fixed in a cone conformation that we have reported so far.[13–16,21,22] The bromine atom of **6** was

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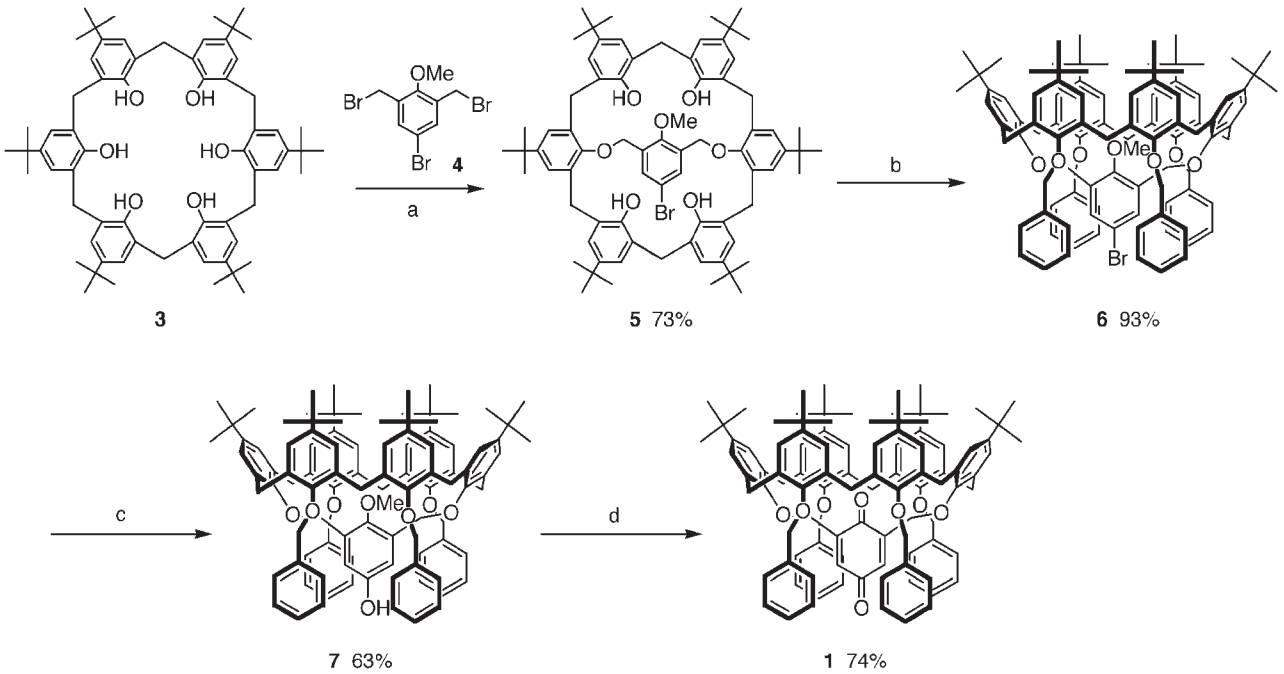
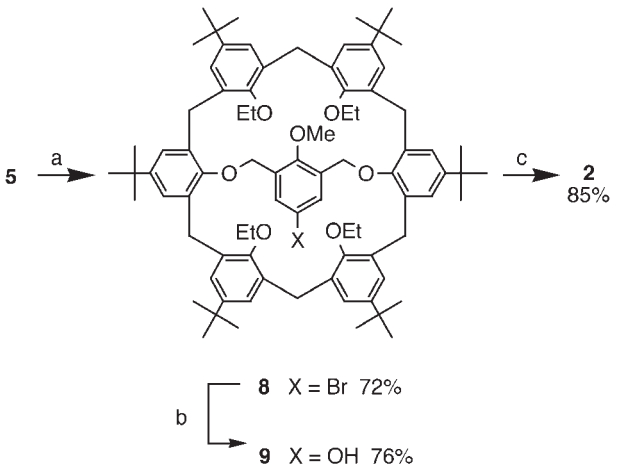


Scheme 1. Synthesis of the quinone-bridged calix[6]arene **1**. Reagents and conditions: (a) KOH, THF/DMF (10:1), rt; (b) $PhCH_2Br$, Cs_2CO_3, DMF, 70 °C; (c) (i) *t*-BuLi, THF, −78 °C, (ii) $B(OMe)_3$, (iii) H_2O_2, aq. NaOH; (d) $FeCl_3$, AcOH, C_6H_6/CH_3CN (1:2), rt.

replaced by a hydroxy group via lithiation followed by reaction with trimethyl borate and subsequent treatment with an alkaline solution of hydrogen peroxide. *p*-Methoxyphenols are known to be oxidized to the corresponding quinones under mild conditions.[35] Oxidation of **7** with iron(III) chloride afforded the target compound **1** as pale yellow crystals. Compound **1** was also found to adopt a cone conformation like the intermediates **6** and **7**, indicating that no conformational change occurred during the chemical modification of the bridging unit.

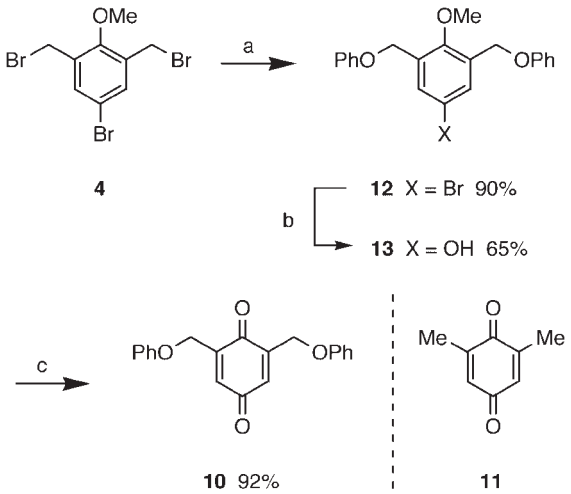
In order to investigate the effects of the lower-rim aromatic rings on the properties of the quinone moiety of **1**, the tetraethylated derivative **2** was also prepared according to a similar synthetic procedure (Scheme 2). Recently, we reported that the conformational mobility of the *m*-xylene-α,α'-diyl-bridged calix[6]arene can be modulated by the lower-rim capping groups.[36] In contrast with the tetrabenzylated compounds, the corresponding tetraethylated compounds were found to exist as equilibrium mixtures of the conformational isomers in solution, although they can be observed independently on the NMR time-scale. We also reported that the ratios of the conformational isomers depend on the functionality on the bridging unit.[36] In the ^1H NMR spectra ($CDCl_3$) of the ethyl derivatives **2**, **8**, and **9**, which are expected to exist as equilibrium mixtures of the conformational isomers, only the cone isomers were observed. These results indicate that the cone isomers of **2**, **8**, and **9** are thermodynamically much more stable than other isomers. In the cone isomers of **8** and **9**, the methoxy group in the folded shape shows a good fit to the cavity of the cone-shaped calix[6]arene framework, as described previously.[36] In the case of quinone **2**, the preference for the cone isomer can be reasonably explained in terms of the interaction between ether oxygen atoms and olefinic carbon atoms of the quinone moiety, as supported by its crystal structure.



Scheme 2. Synthesis of the quinone-bridged calix[6]arene **2**. Reagents and conditions: (a) EtI, Cs_2CO_3, DMF, 70 °C; (b) (i) *t*-BuLi, THF, −78 °C, (ii) $B(OMe)_3$, (iii) H_2O_2, aq. NaOH; (c) $FeCl_3$, AcOH, C_6H_6/CH_3CN (1:2), rt.

The reference compounds **10** and **11** without the calixarene framework were also prepared. 2,6-Bis(phenoxymethyl)-1,4-benzoquinone (**10**) was synthesized from the corresponding *p*-bromoanisole derivative **12** in two steps (Scheme 3). 2,6-Dimethyl-1,4-benzoquinone (**11**) was prepared according to the literature.[37]

Spectroscopic Properties. In the infrared spectra of both **1** and **2**, the C=O absorption was observed at 1653 cm^{-1}. This value is almost the same as those of the reference compounds **10** (1657 cm^{-1}) and **11** (1653 cm^{-1}) without the calixarene framework. On the other hand, in the ^1H and ^{13}C NMR spectra, large upfield shifts for H2, C1, and C3 were observed for both **1** and **2** in comparison with the phenoxymethyl derivative **10**

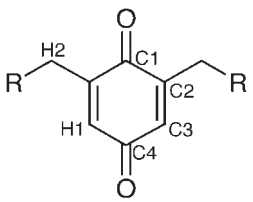


Scheme 3. Synthesis of the reference compounds. Reagents and conditions: (a) PhOH, K_2CO_3, DMF, rt; (b) (i) *t*-BuLi, THF, −78 °C, (ii) $B(OMe)_3$, (iii) H_2O_2, aq. NaOH; (c) $FeCl_3$, AcOH, C_6H_6/CH_3CN (1:2), rt.

Table 1. ^1H and ^{13}C NMR Chemical Shifts (δ)[a] of Quinones **1**, **2**, **10**, and **11**[a]

Compound	H1	H2	C1	C2	C3	C4	C5
1	6.36	2.47	182.99	143.58	127.44	187.28	67.38
2	6.62	2.34	183.16	144.78	126.80	189.06	67.45
10	6.96	4.96	186.29	144.03	132.09	186.86	63.11
11	6.56	2.06	187.59	145.76	133.26	188.16	15.93

a) Measured in $CDCl_3$. Atom labeling is shown in Scheme 4.



Scheme 4. Atom labeling for Table 1.

(Table 1). These results indicate that the quinone moiety of **1** and **2** is magnetically shielded by the surrounding aromatic rings of the calixarene framework. The upfield shift of H1, which was observed only for the benzyl derivative **1**, is probably due to the shielding effect of the four benzyl groups at the lower rim.

The electronic absorption spectra of the quinone-bridged calix[6]arenes **1** and **2** are shown in Fig. 1. The broad absorption feature of the benzyl derivative **1** was observed as a shoulder at around 340 nm. However, it was difficult to determine the exact wavelength of maximum absorption and the absorption coefficient of the quinone moiety of **1** due to the strong absorption of the ten benzene rings of the bridged calix[6]arene framework. On the other hand, the ethyl derivative **2** showed an absorption peak at 334 nm. The molar extinction coefficients of **1** and **2** are larger than those of the reference compounds **10** and **11**. This is probably due to weak charge transfer from the electron-rich aromatic rings of the calixarene framework to the quinone moiety.[38,39]

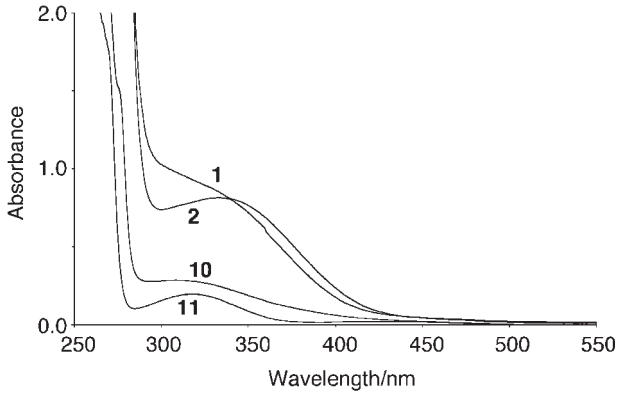


Fig. 1. Electronic absorption spectra of **1**, **2**, **10**, and **11** (5×10^{-4} M) in chloroform.

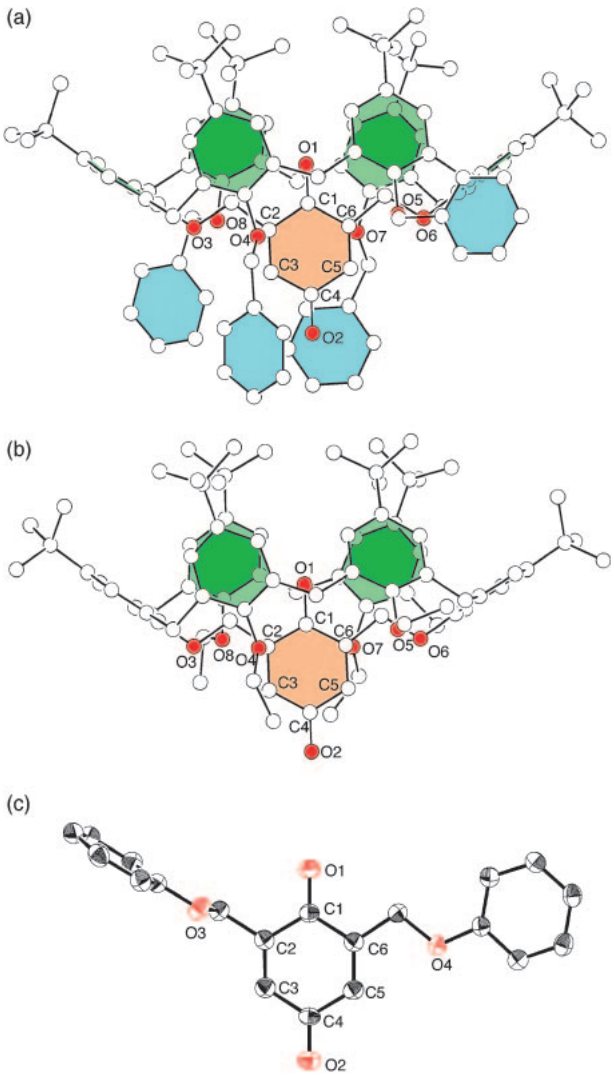
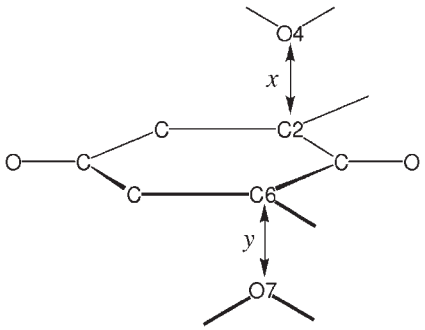


Fig. 2. X-ray structures of the quinone-bridged calix[6]-arenes (a) **1** and (b) **2**. (c) ORTEP drawing of reference compound **10**. Solvent molecules and hydrogen atoms are omitted for clarity.

Crystal Structures. The crystal structures of the quinone-bridged calix[6]arenes **1** and **2** were determined by X-ray crystallography (Fig. 2). The quinone moiety of **1** and **2** is accom-

Table 2. Selected Bond Lengths (Å) of Quinones **1**, **2**, and **10**

	1	**2**	**10**
C1–C2	1.492(4)	1.430(12)	1.497(3)
C2–C3	1.327(4)	1.377(15)	1.335(3)
C3–C4	1.475(4)	1.501(14)	1.479(3)
C4–C5	1.486(4)	1.465(11)	1.481(3)
C5–C6	1.330(4)	1.350(15)	1.335(3)
C6–C1	1.481(4)	1.458(15)	1.494(3)
C1–O1	1.227(3)	1.269(13)	1.223(3)
C4–O2	1.227(4)	1.252(12)	1.223(3)



Scheme 5. Schematic drawing of the interaction between quinone and calix[6]arene moieties. Compound **1**: $x = 3.172(3)$, $y = 3.219(3)$ Å; compound **2**: $x = 3.092(10)$, $y = 3.224(10)$ Å.

modated inside the cone-shaped calixarene framework and is surrounded by the lower rim substituents. It was found that there is a strong resemblance between the conformations of **1** and **2** in the crystalline state. In both cases, the two carbonyl groups of the quinone moiety are not particularly close to either the six aromatic rings of the calixarene macrocycle or to the benzyl and ethyl groups at the lower rim. The structural parameters of the quinone moieties of **1** and **2** are almost the same as those of the reference compound **10** (Table 2), and no unusual geometrical features were observed. However, significant nonbonded contacts were observed between the olefinic carbon atoms of the quinone moiety and the oxygen atoms of the calixarene lower-rim in **1** and **2** (Scheme 5). Similar contacts were reported for the [2.2]- and [3.3]cyclophanes containing both 1,4-benzoquinone and hydroquinone moieties, which were reported to show strong charge-transfer bands in the electronic spectra.[38,39]

Electrochemistry. The cyclic voltammograms of quinones **1**, **2**, and **10** are shown in Fig. 3. Two waves were observed for both of the quinone-bridged calix[6]arenes **1** and **2**. These two waves can be attributed to the formation of a monoanion radical and a dianion of the quinone moiety, which is similar to other benzoquinone derivatives, including **10** and **11**.[40] The second waves of **1** and **2** were found to be considerably broadened. This can be explained either by a slower rate of electron transfer through the calixarene macrocycle or by conformational changes during the redox processes.

The reduction/oxidation potentials of **1**, **2**, **10**, and **11** are summarized in Table 3. The first reduction potentials of **1** and **2** (indicated as E_1) are shifted to a more negative region than those of the reference compounds **10** and **11**, indicating

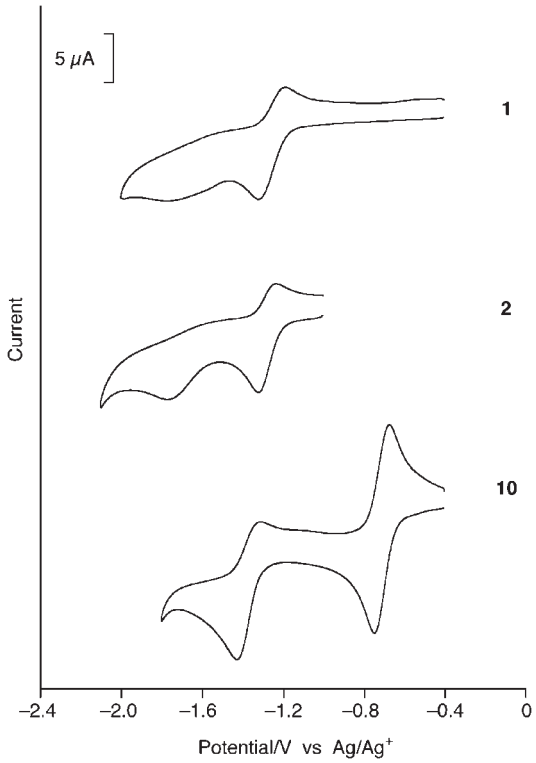


Fig. 3. Cyclic voltammograms of **1**, **2**, and **10** (5×10^{-4} M) in dichloromethane containing 0.1 M tetrabutylammonium perchlorate on a glassy carbon electrode. Reference electrode, Ag/Ag^+, scan rate, 100 $mV \cdot s^{-1}$.

Table 3. Reduction Potentials (V) of Quinones **1**, **2**, **10**, and **11**[a)]

	1	**2**	**10**	**11**
E_1 (0/−1)	−1.25	−1.27	−0.71	−0.91
E_2 (−1/−2)	−1.6 (br)	−1.6 (br)	−1.37	−1.44

a) Measured in 5×10^{-4} M dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate on a glassy carbon electrode. Reference electrode, Ag/Ag^+, scan rate, 100 $mV \cdot s^{-1}$.

that **1** and **2** are more difficult to reduce. A similar negative shift was reported for the oxidation potential of ferrocene incorporated in a water-soluble calix[6]arene.[5,6]

There are several conceivable reasons for the observed negative shifts of the reduction potentials of **1** and **2**. Since the potential of the phenoxymethyl-substituted quinone **10** is more positive than that of the methyl derivative **11**, the two CH_2OAr substituents at the 2,6-positions of the quinone moiety of **1** do not seem to be responsible for the observed negative shift. Electrons are known to be particles for which tunneling is very important. It is unlikely, therefore, that the steric hindrance around the quinone moiety of **1** and **2** caused by the calixarene framework restricts the access of electrons to the central quinone moiety. In fact, sterically hindered quinones such as 2,5- and 2,6-di-*t*-butyl-1,4-benzoquinone are reported to have reduction potentials not so different from those of the corresponding dimethyl derivatives.[35]

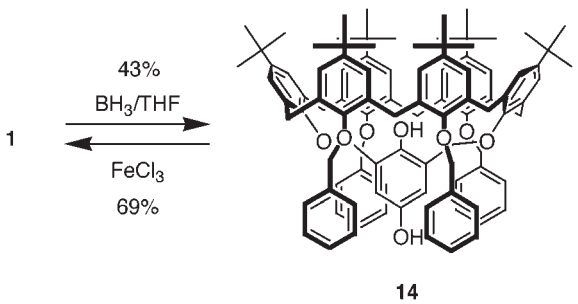
The calixarene frameworks of compounds **1** and **2** are con-

sidered to affect the redox properties of their quinone moieties in the following two ways. One is the effect of the counter cation in electrochemical measurements. Usually, ionic species generated in the redox processes of cyclic voltammetry are stabilized by forming a tightly bound ion pair in organic solvents. The calixarene frameworks of **1** and **2**, however, interfere with the access of the counter cations to the semiquinone anion moiety, causing destabilization of the reduced form of the quinone and resulting in negatively shifted potentials. The other factor is the through-space interaction between the quinone moiety and the calixarene framework. X-ray crystallographic analysis of **1** and **2** indicates the interaction between the olefinic carbon atoms of the quinone moiety and the ether oxygen atoms of the lower rim. Such nonbonded interactions are considered to raise the LUMO of the quinone, which result in the more negative reduction potentials of **1** and **2**. A similar observation was described in the literature, where the reduction potentials of some cyclic monoquinones bearing ether oxygens are more negative than their carbon analogues.[41]

The second waves (indicated as E_2) of **1** and **2** were also observed at more negative regions than those for **10** and **11**, similar to the first reduction potentials (E_1). However, these shifts of E_2 are smaller than those of E_1. This can be explained by the change of the electron density of the bridging unit. After the one-electron reduction, the increased electron density of the bridging unit causes a conformational change in such a way that it minimizes the electronic repulsion between the ether oxygen and the semiquinone anion radical. As a result, smaller shifts are expected for the second reduction potentials because the effect of the ether oxygen becomes weaker in the semiquinone anion radical intermediate.

Chemical Reduction. Reduction of **1** with borane/THF afforded the hydroquinone derivative **14** in 43% yield; it could be oxidized to **1** again with iron(III) chloride (Scheme 6). It is noteworthy that the reversible chemical redox reactions of the quinone-bridged calix[6]arene **1** are possible, in spite of the incomplete reversibility of its cyclic voltammogram.

The structure of the hydroquinone derivative **14** was established by X-ray crystallographic analysis, which shows its dimeric structure with a cyclic hydrogen bonding network including three molecules of methanol (Fig. 4). In the crystal structure of **14**, there is no nonbonded contact between the ether oxygen and the bridging unit, such as was observed in quinones **1** and **2**. It was also revealed that the conformation of the central bridging unit of **14** is different from those of **1** and **2** (Scheme 7). There is intramolecular hydrogen bonding



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Scheme 6. Chemical redox reactions of the quinone-bridged calix[6]arene **1**.

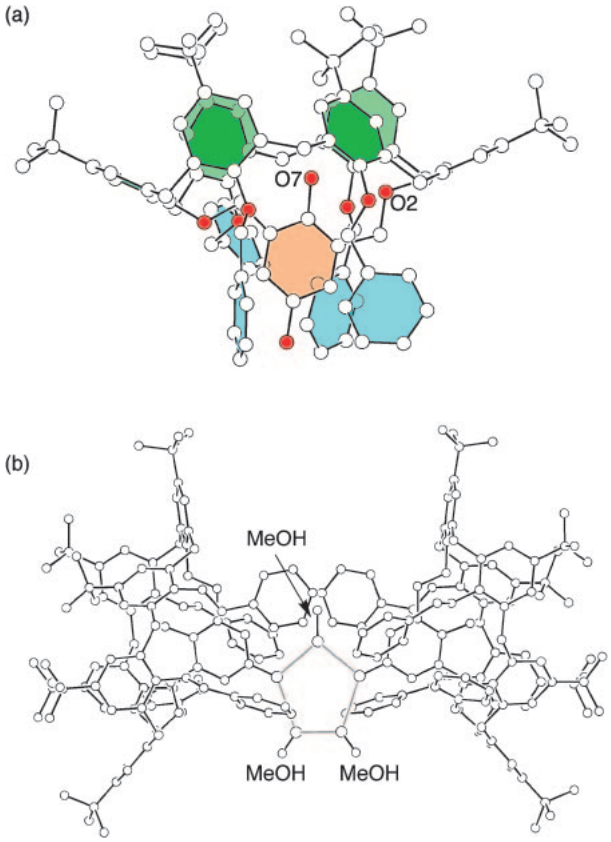
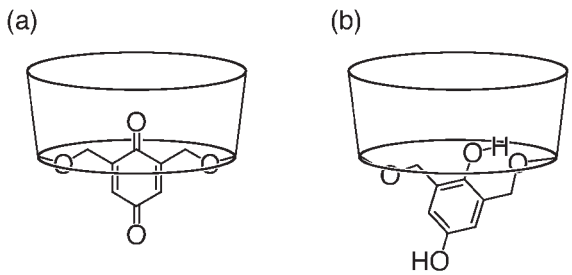


Fig. 4. (a) X-ray structure of hydroquinone **14**. (b) Plot showing the formation of a dimeric form. Hydrogen atoms, disordered atoms, and a chloroform molecule are omitted for clarity.



Scheme 7. Schematic drawings of the conformations of the bridging units of (a) **1** and (b) **14**.

between the central hydroxy group (O7–H) and the ether oxygen atom of the bridging unit (O2) with an O2···O7 distance of 2.621(4) Å, which stabilizes the unsymmetrical conformation schematically depicted in Scheme 7(b). The bridging unit of **14** hangs down below the cavity of calix[6]arene in comparison with those of **1** and **2** bearing the symmetrical conformation shown in Scheme 7(a).

This structural change was also observed in solution. In the ^{1}H NMR spectra of **1**, the signal of the methylene protons connected to the quinone moiety appeared at δ 2.47, whereas those of the corresponding methylene protons of **14** were observed at δ 4.14 (Fig. 5). These results clearly indicate that the shielding effect of the surrounding calix[6]arene moiety of **14** on the methylene protons is very small. This is probably because

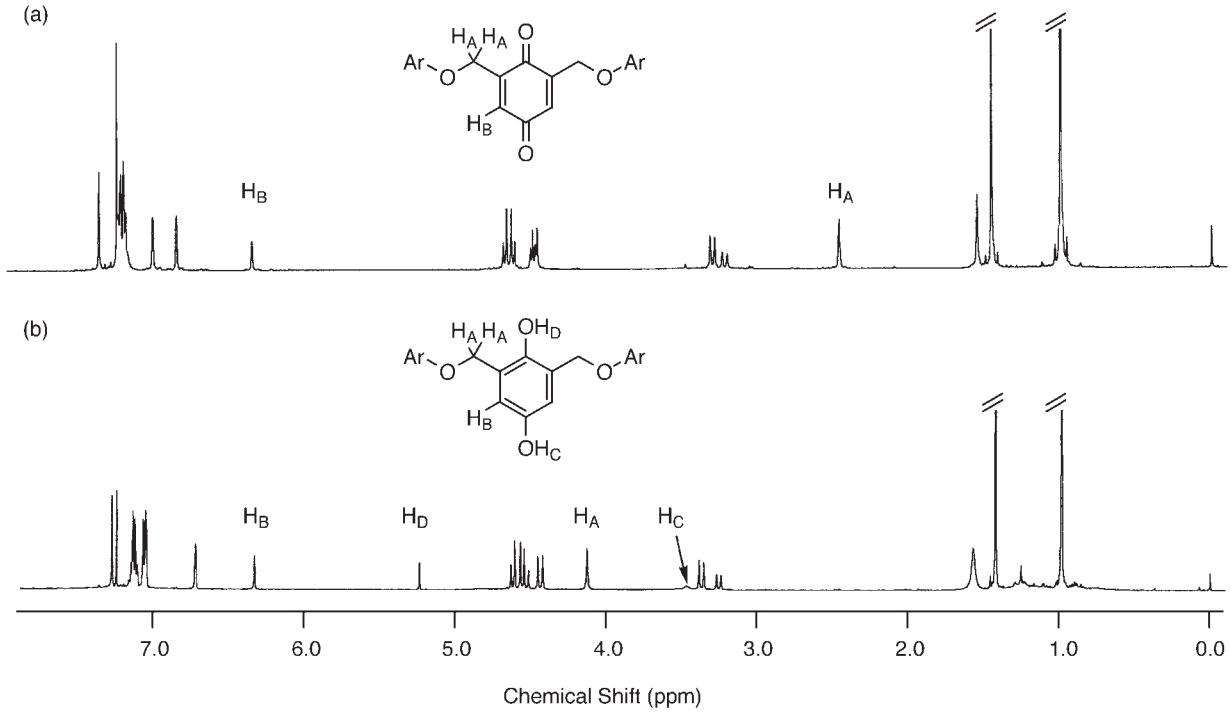


Fig. 5. ^{1}H NMR spectra of (a) quinone **1** and (b) hydroquinone **14** in $CDCl_3$.

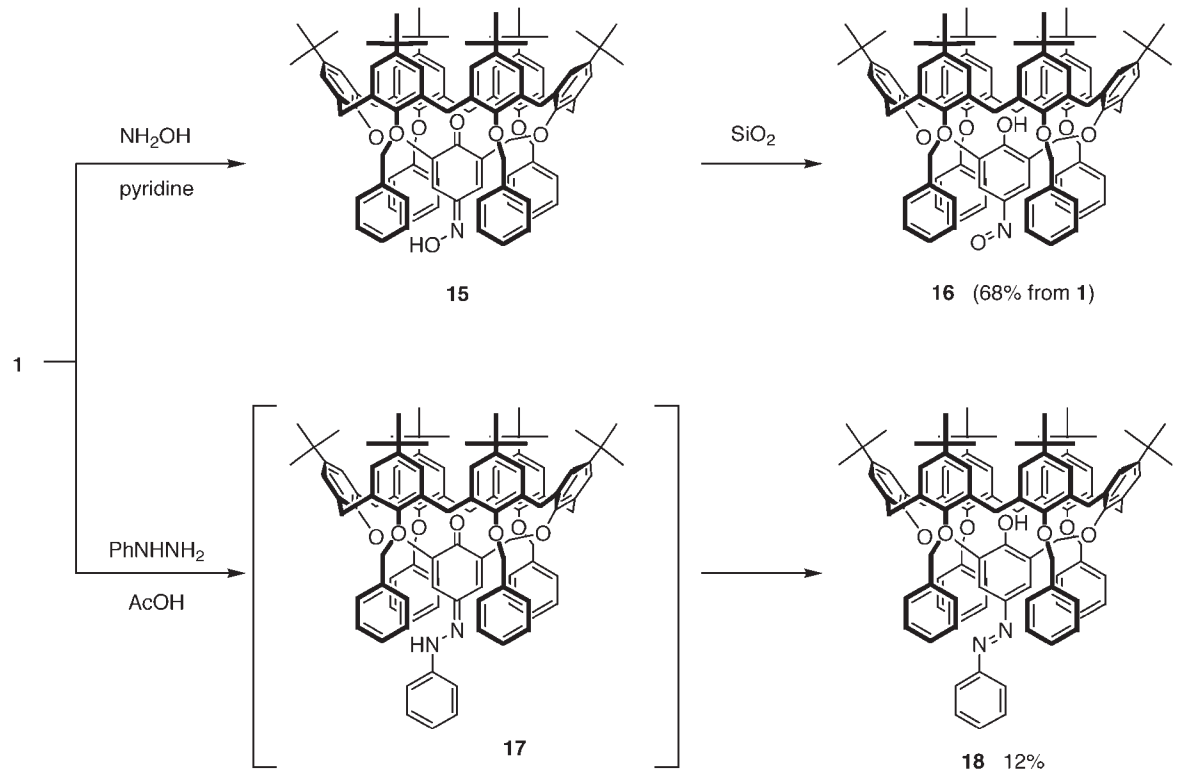
the bridging unit of hydroquinone **14** lies much lower than that of quinone **1**, as shown in Scheme 7, which is consistent with the conformations of **1** and **14** in the crystalline state. In addition, a downfield shift of the ^{1}H NMR signal (δ 5.25) of the hydroxy group directing towards the cavity of **14** was observed, while the signal of the outer one was observed at δ 3.48. This also supports the presence of an intramolecular hydrogen bond between the inner hydroxy group and the ether oxygen atom.

Reaction with Hydroxylamine or Phenylhydrazine. The reactivities of the quinone-bridged calix[6]arenes are expected to be different from those of the parent quinones because their reduction potentials are negatively shifted. The reaction of the quinone-bridged calix[6]arene **1** with an excess amount of hydroxylamine afforded a crude mixture containing the quinone monooxime derivative **15** as a major product (Scheme 8), which was confirmed by its ^{1}H NMR spectrum (Fig. 6). This mixture was found to contain no quinone dioxime,[42] indicating that the reaction toward the intracavity carbonyl group of **1** was hampered by the calix[6]arene macrocycle. Interestingly, chromatographic separation of this mixture on silica gel gave the *p*-nitrosophenol derivative **16** (68%) and hydroquinone **14** (26%); no quinone monooxime **15** was observed. These results indicate that quinone monooxime **15** readily isomerizes on silica gel to afford *p*-nitrosophenol **16**, even though the inner carbonyl group of **15** is surrounded by the calix[6]arene macrocycle.

Similarly, the reaction of quinone **1** with an excess of phenylhydrazine gave a crude mixture containing the phenylazophenol derivative **18** and hydroquinone **14** (Scheme 8). It is considered that addition of the hydrazine to one of the carbonyl groups of the quinone moiety led to the formation of the hydrazone derivative **17**, which underwent isomerization to **18** under the reaction conditions. It should be noted that hydroquinone **14** was predominantly formed in this reaction. Compound **14** is considered to be formed by reduction involving an electron transfer from the amine. However, the process is not considered to be favorable in view of the negatively shifted reduction potentials of **1**, which imply reduced ability as an electron acceptor. The formation of **14** can be explained in terms of the steric hindrance around the quinone moiety of **1**. It is obvious that the addition of nucleophiles to the carbonyl group in the cavity is severely hampered by the calix[6]arene framework. Moreover, the four lower-rim benzyl groups of **1** hinder the access of amines to the carbonyl group on the lower-rim side, which results in the suppression of the addition reaction also on this side. Thus the electron transfer from the amine proceeds faster than the addition reaction, although the negatively shifted reduction potentials are apparently unfavorable for this process. This is one of the reactions that reflect the structural features of the quinone-bridged calix[6]arene **1**.

Conclusion

The quinone-bridged calix[6]arenes **1** and **2** containing a 1,4-benzoquinone moiety in the cavity were synthesized. X-ray crystallographic analysis of **1** and **2** revealed that the quinone moiety is located inside the cone-shaped calix[6]arene framework and is surrounded by the lower-rim substituents. Their structures can be viewed as an image of a 1,4-benzoquinone included in the cavity of calix[6]arene and covalently anchored through the CH_2O linkages. The spectroscopic properties of the quinone-bridged calix[6]arenes were investigated, showing that the quinone moiety is located in a magnetically shielded region. The reduction potentials of **1** and **2** were found to be negatively shifted from those of the reference compounds without the calix[6]arene framework. These shifts can



Scheme 8. Reaction of quinone-bridged calix[6]arene **1** with hydroxylamine or phenylhydrazine.

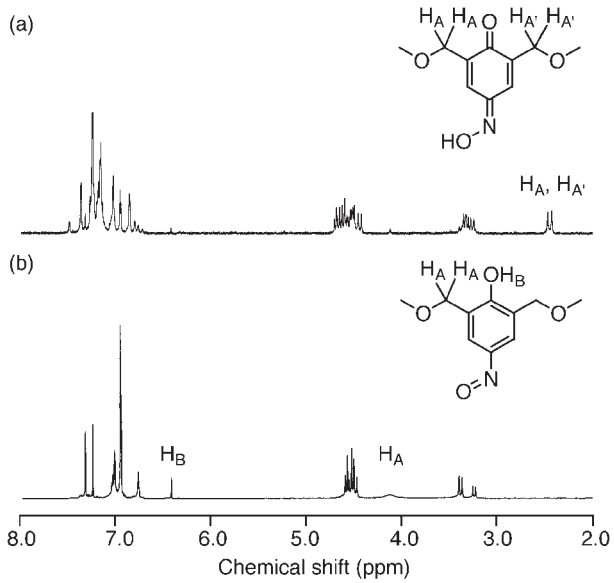


Fig. 6. Part of the ^{1}H NMR spectra of (a) monooxime **15** and (b) nitrosophenol **16** in $CDCl_3$.

be explained in terms of the nonbonded interaction between the calixarene moiety and the quinone moiety, as well as the restricted interaction between the anion radical and the counter cation. Reactions of the quinone-bridged calix[6]arene **1** with hydroxylamine and phenylhydrazine afforded the corresponding hydroquinone in addition to the quinone monoimine derivatives, indicating that electron transfer from the amine proceeds quickly despite the negatively-shifted reduction potentials of **1**.

Experimental

Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. THF was purified by distillation from sodium diphenylketyl under argon atmosphere before use. Benzene was distilled from lithium tetrahydridoaluminate. DMF and acetonitrile (special grade) were purchased from Wako Pure Chemical Industries Ltd. and used without purification. Tetrabutylammonium perchlorate was supplied from Tomiyama Chemicals as lithium battery grade. Dichloromethane for electrochemical measurements was purchased from Kanto Chemicals as an HPLC grade and used without purification. Column chromatography and preparative TLC were carried out with Wakogel C-200 and Merck Kieselgel 60PF254 Art. 7747, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500, a JEOL JNM-A500, and a JEOL EX-AL270 spectrometers. Assignments of NMR signals were based on 2D-COSY, HMQC, and HMBC spectra. IR spectra were recorded on a JASCO FT/IR-300E spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, the University of Tokyo.

Materials. *p-t*-Butylcalix[6]arene (**3**),[33] 5-bromo-1,3-bis(bromomethyl)-2-methoxybenzene (**4**),[34] and 2,6-dimethyl-1,4-benzoquinone (**11**)[37] were prepared by the procedures described in the literature.

37,40-[5-Bromo-2-methoxy-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-38,39,41,42-tetrol (5). To a suspension of potassium hydroxide (85%, 830 mg, 12.6 mmol) and *p-t*-butylcalix[6]arene (**3**) (900 mg, 0.92 mmol) in THF (350 mL) and DMF (35 mL), which was stirred at room temperature for 1 h, was added tribromide **4** (328 mg, 0.88 mmol) and this mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was treated with aq. NH_4Cl, ex-

tracted with chloroform, dried over $MgSO_4$, and evaporated to dryness. The residue was recrystallized from chloroform/methanol to afford bridged compound **5** (802 mg, 73%) as colorless crystals: mp 222–224 °C; ^{1}H NMR (270 MHz, $CDCl_3$, −50 °C) δ 1.20 (s, 18H), 1.23 (s, 18H), 1.29 (s, 18H), 3.22 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.3 Hz, 1H), 3.52 (d, J = 13.2 Hz, 2H), 3.63 (d, J = 12.8 Hz, 2H), 4.02 (s, 3H), 4.04 (d, J = 13.8 Hz, 1H), 4.06 (d, J = 13.2 Hz, 1H), 4.22 (d, J = 13.3 Hz, 2H), 4.59 (d, J = 10.4 Hz, 2H), 4.61 (d, J = 12.8 Hz, 2H), 5.81 (d, J = 10.4 Hz, 2H), 7.04 (brd, 2H), 7.09 (brd, 2H), 7.13 (brd, 2H), 7.15 (brd × 2, 4H), 7.20 (brd, 2H), 7.53 (s, 2H), 8.93 (s, 2H), 9.00 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −50 °C) δ 31.15 (CH_3), 31.49 (CH_3 × 2), 32.69 (CH_2), 32.75 (CH_2), 32.98 (CH_2), 33.15 (CH_2), 33.71 (C), 33.84 (C), 34.17 (C), 60.12 (CH_3), 74.70 (CH_2), 116.23 (C), 125.12 (CH), 125.27 (CH), 125.62 (CH), 125.74 (CH × 2), 126.26 (CH), 126.53 (C), 126.67 (C), 126.98 (C), 127.39 (C), 131.80 (C), 132.67 (C), 132.71 (C), 134.59 (CH), 141.75 (C), 142.07 (C), 147.38 (C), 149.53 (C), 149.71 (C), 150.03 (C), 158.l9 (C). Found: C, 74.93; H, 7.77; Br, 7.26%. Calcd for $C_{75}H_{91}BrO_7$: C, 74.92; H, 7.80; Br, 6.65%.

38,39,41,42-Tetrabenzyloxy-37,40-[5-bromo-2-methoxy-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene (6). To a suspension of tetrol **5** (475 mg, 0.40 mmol) and cesium carbonate (1.57 g, 4.8 mmol) in DMF (40 mL) was added benzyl bromide (290 µL, 2.4 mmol) and the reaction mixture was stirred at 70 °C for 1 d. After the addition of aq. NH_4Cl, the mixture was extracted with chloroform, dried over $MgSO_4$, and the solvent was evaporated to dryness. The crude product was purified by recrystallization (chloroform/methanol) to give **6** (576 mg, 93%) as colorless crystals: mp 291–300 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 3H), 1.00 (s, 36H), 1.43 (s, 18H), 3.12 (d, J = 14.5 Hz, 2H), 3.25 (d, J = 15.3 Hz, 4H), 4.10 (s, 4H), 4.47 (d, J = 15.3 Hz, 4H), 4.50 (d, J = 14.5 Hz, 2H), 4.64 (d, J = 12.1 Hz, 4H), 4.67 (d, J = 12.1 Hz, 4H), 7.01 (d, J = 1.5 Hz, 4H), 7.08–7.19 (m, 24H), 7.26 (s, 4H), 7.40 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.78 (CH_2), 30.84 (CH_2), 31.49 (CH_3), 31.69 (CH_3), 34.04 (C), 34.22 (C), 60.54 (CH_3), 68.55 (CH_2), 74.84 (CH_2), 115.07 (C), 123.88 (CH), 125.22 (CH), 127.11 (CH × 2), 127.93 (CH), 128.13 (CH), 128.87 (CH), 132.19 (C), 133.39 (C), 133.70 (C), 134.45 (C), 137.78 (C), 144.85 (C), 145.25 (CH), 152.26 (C), 152.77 (C), 155.67 (C). Found: C, 79.15; H, 7.40; Br, 5.31%. Calcd for $C_{103}H_{115}BrO_7 \cdot H_2O$: C, 79.15; H, 7.54; Br, 5.11%.

4-Methoxy-3,5-{(38,39,41,42-tetrabenzyloxy-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-37,40-diyl)bis(oxymethylene)}-phenol (7). To a solution of bromide **6** (228 mg, 0.15 mmol) in THF (25 mL) was added *t*-butyllithium (1.68 M in pentane, 280 µL, 0.47 mmol) and the mixture was stirred for 20 min at −78 °C. After the addition of trimethyl borate (100 µL, 0.9 mmol), the mixture was stirred for 1 h at −78 °C and then at room temperature for 14 h. To the solution was added a solution of NaOH (600 mg) and 30% hydrogen peroxide (3 mL) in water (10 mL) and the mixture was stirred for 5 h at room temperature. After the addition of water and aq. NH_4Cl, the mixture was extracted by chloroform, dried over $MgSO_4$, and evaporated to dryness. The residue was subjected to preparative TLC (silica gel, chloroform/hexane, 2:1) to give phenol **7** (138 mg, 63%) as colorless crystals: mp 222–225 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (s, 3H), 1.01 (s, 36H), 1.43 (s, 18H), 3.25 (d, J = 14.4 Hz, 2H), 3.34 (d, J = 15.2 Hz, 4H), 3.38 (s, 1H), 4.15 (s, 4H), 4.53 (d, J = 15.2 Hz, 4H), 4.60 (d, J = 11.8 Hz, 4H), 4.60 (d, J = 14.4 Hz, 2H), 4.64 (d, J = 11.8 Hz, 4H), 6.55 (s, 2H), 6.70 (d, J = 1.9 Hz, 4H), 7.09–7.20 (m, 20H), 7.23 (d, J = 1.9 Hz, 4H), 7.28 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.55 (CH_2), 31.00 (CH_2), 31.54 (CH_3), 31.71 (CH_3), 34.07 (C), 34.22 (C), 60.37 (CH_3), 68.94 (CH_2), 74.95 (CH_2), 113.86 (CH), 123.99 (CH), 125.33 (CH), 127.11 (CH), 127.37 (CH), 128.09 (CH), 128.14 (CH), 132.34 (C), 132.76 (C), 133.13 (C), 133.75 (C), 138.01 (C), 144.94 (C), 145.10 (C), 149.96 (C), 150.03 (C), 152.39 (C), 153.01 (C). Found: C, 83.21; H, 7.93%. Calcd for $C_{103}H_{116}O_8$: C, 83.47; H, 7.93%.

37,40-[5-Bromo-2-methoxy-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butyl-38,39,41,42-tetraethoxycalix[6]arene (8). Compound **8** was prepared in 72% yield from tetrol **5** (475 mg, 0.40 mmol) in a manner similar to that of **6**. **8**: colorless crystals, mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (s, 3H), 0.98 (s, 36H), 1.24 (t, J = 6.9 Hz, 12H), 1.45 (s, 18H), 3.21 (d, J = 14.3 Hz, 2H), 3.39 (d, J = 15.0 Hz, 4H), 3.64–3.74 (m, 8H), 4.15 (s, 4H), 4.42 (d, J = 14.3 Hz, 2H), 4.49 (d, J = 15.0 Hz, 4H), 6.70 (d, J = 1.7 Hz, 4H), 7.08 (d, J = 1.7 Hz, 4H), 7.33 (s, 4H), 7.38 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.51 (CH_3), 27.19 (CH_2), 30.73 (CH_2), 31.47 (CH_3), 31.71 (CH_3), 34.00 (C), 34.24 (C), 60.31 (CH_3), 68.45 (CH_2), 68.66 (CH_2), 114.28 (C), 123.81 (CH), 125.17 (CH), 128.11 (CH), 128.65 (CH), 132.27 (C), 133.19 (C), 133.67 (C), 134.76 (C), 144.60 (C), 145.12 (C), 152.39 (C), 152.76 (C), 155.83 (C). Found: C, 76.20; H, 8.19; Br, 6.16%. Calcd for $C_{83}H_{107}BrO_7 \cdot 0.5H_2O$: C, 76.35; H, 8.34; Br, 6.12%.

3,5-{(5,11,17,23,29,35-Hexa-*t*-butyl-38,39,41,42-tetraethoxycalix[6]arene-37,40-diyl)bis(oxymethylene)}-4-methoxyphenol (9). Compound **9** was prepared in 76% yield from bromide **8** (323 mg, 0.25 mmol) in a manner similar to that of **7**. **9**: colorless crystals, mp 248–252 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (s, 3H), 0.98 (s, 36H), 1.24 (t, J = 7.0 Hz, 12H), 1.45 (s, 18H), 3.23 (d, J = 14.0 Hz, 2H), 3.40 (d, J = 15.3 Hz, 4H), 3.60 (dq, J = 9.4, 7.0 Hz, 4H), 3.71 (dq, J = 9.4, 7.0 Hz, 4H), 4.19 (s, 4H), 4.43 (d, J = 14.0 Hz, 2H), 4.51 (d, J = 15.3 Hz, 4H), 4.88 (br, 1H), 6.68 (d, J = 1.8 Hz, 4H), 6.75 (s, 2H), 7.12 (d, J = 1.8 Hz, 4H), 7.32 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.53 (CH_3), 27.05 (CH_2), 30.79 (CH_2), 31.48 (CH_3), 31.71 (CH_3), 33.97 (C), 34.19 (C), 60.04 (CH_3), 68.62 (CH_2), 68.74 (CH_2), 112.81 (CH), 123.77 (CH), 125.21 (CH), 128.21 (CH), 132.34 (C), 132.92 (C), 133.18 (C), 133.64 (C), 144.53 (C), 144.81 (C), 149.87 (C), 150.20 (C), 152.34 (C), 152.75 (C). Found: C, 79.31; H, 8.62%. Calcd for $C_{83}H_{108}O_8 \cdot H_2O$: C, 79.64; H, 8.86%.

2,6-{(38,39,41,42-Tetrabenzyloxy-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-37,40-diyl)bis(oxymethylene)}-1,4-benzoquinone (1). To a solution of **7** (100 mg, 0.68 mmol) in benzene (5 mL) was added dropwise a solution of iron(III) chloride (250 mg, 1.5 mmol) in acetic acid (0.5 mL) and acetonitrile (10 mL). After 10 min, yellow precipitates were collected and dried to afford **1** (73.6 mg, 74%) as pale yellow crystals: mp 187–198 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 36H), 1.46 (s, 18H), 2.47 (s, 4H), 3.23 (d, J = 16.5 Hz, 2H), 3.31 (d, J = 14.7 Hz, 4H), 4.48 (d, J = 14.7 Hz, 4H), 4.50 (d, J = 16.5 Hz, 2H), 4.63 (d, J = 11.4 Hz, 4H), 4.68 (d, J = 11.4 Hz, 4H), 6.36 (s, 2H), 6.86 (s, 4H), 7.02 (s, 4H), 7.17–7.25 (m, 20H), 7.38 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.78 (CH_2), 29.80 (CH_2), 31.41 (CH_3), 31.75 (CH_3), 34.19 (C), 34.39 (C), 67.38 (CH_2), 75.35 (CH_2), 125.19 (CH), 125.43 (CH), 127.44 (CH), 127.72 (CH), 127.76 (CH), 127.79 (CH), 128.38 (CH), 130.99 (C), 133.90 (C), 134.45 (C), 137.31 (C), 143.58 (C), 145.41 (C), 146.16 (C), 152.71 (C), 153.54 (C), 182.99 (C), 187.28 (C); IR

(KBr) ν 1653 cm^{-1} (C=O). HRMS (FAB+) m/z found 1465.8427, calcd for $C_{102}H_{113}O_8$, 1465.8435 $[M + H]^+$. Found: C, 82.92; H, 7.71%. Calcd for $C_{102}H_{112}O_8 \cdot 0.5H_2O$: C, 83.06; H, 7.71%.

2,6-{(5,11,17,23,29,35-Hexa-*t*-butyl-38,39,41,42-tetraethoxycalix[6]arene-37,40-diyl)bis(oxymethylene)}-1,4-benzoquinone (2). Compound **2** was prepared in 85% yield from **9** (20 mg, 0.017 mmol) in a manner similar to that of **1**. **2**: pale yellow crystals, mp 224 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (s, 36H), 1.32 (t, $J = 6.9$ Hz, 12H), 1.47 (s, 18H), 2.34 (s, 4H), 3.32 (d, $J = 16.6$ Hz, 2H), 3.39 (d, $J = 14.8$ Hz, 4H), 3.79 (dq, $J = 9.8$, 6.9 Hz, 4H), 3.82 (dq, $J = 9.8$, 6.9 Hz, 4H), 4.34 (d, $J = 16.6$ Hz, 2H), 4.47 (d, $J = 14.8$ Hz, 4H), 6.62 (s, 2H), 6.87 (s, 4H), 6.96 (s, 4H), 7.42 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.68 (CH_3), 26.92 (CH_2), 29.61 (CH_2), 31.37 (CH_3), 31.76 (CH_3), 34.14 (C), 34.42 (C), 67.45 (CH_2), 69.27 (CH_2), 125.12 (CH), 125.45 (CH), 126.80 (CH), 127.76 (CH), 130.93 (C), 133.92 (C), 134.72 (C), 144.78 (C), 145.15 (C), 146.26 (C), 153.12 (C), 153.48 (C), 183.16 (C), 189.06 (C); IR (KBr) ν 1653 cm^{-1} (C=O). Found: C, 79.70; H, 8.42%. Calcd for $C_{82}H_{104}O_8 \cdot H_2O$: C, 79.70; H, 8.65%.

5-Bromo-2-methoxy-1,3-bis(phenoxymethyl)benzene (12). A suspension of tribromide **4** (358 mg, 1.0 mmol), phenol (243 mg, 2.6 mmol), and potassium carbonate (691 mg, 5 mmol) in DMF (80 mL) was stirred for 24 h at room temperature. After the addition of water and aq. NH_4Cl, the mixture was extracted with chloroform, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by chromatography (silica gel, chloroform/hexane, 1:2) to give **12** (359 mg, 90%) as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.08 (s, 4H), 7.00–7.03 (m, 6H), 7.36 (t, $J = 7.9$ Hz, 4H), 7.72 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.68 (CH_3), 64.28 (CH_2), 114.70 (CH), 117.41 (C), 121.21 (CH), 129.52 (CH), 132.36 (CH), 132.55 (C), 155.20 (C), 158.54 (C).

4-Methoxy-3,5-bis(phenoxymethyl)phenol (13). To a solution of bromide **12** (360 mg, 0.90 mmol) in THF (20 mL) was added *t*-butyllithium (1.58 M, 1.7 mL, 2.7 mmol) and the mixture was stirred for 20 min at −78 °C. After the addition of trimethyl borate (600 μL, 5.4 mmol), the mixture was stirred for 1 h at −78 °C and then at room temperature for 14 h. To the solution was added a solution of NaOH (3.6 g) and 30% hydrogen peroxide (9 mL) in water (30 mL) and the mixture was stirred for 8 h at room temperature. After the addition of water and aq. NH_4Cl, the mixture was extracted by chloroform, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on silica gel (chloroform) to afford phenol **13** (198 mg, 65%) as colorless crystals: mp 107–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 3H), 5.05 (s, 4H), 5.50 (brs, 1H), 6.90 (s, 2H), 6.94–6.98 (m, 6H), 7.26–7.30 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.81 (CH_3), 64.78 (CH_2), 114.79 (CH), 116.08 (CH), 121.09 (CH), 129.52 (CH), 131.44 (C), 149.58 (C), 152.18 (C), 158.51 (C). Found: C, 73.94; H, 6.13%. Calcd for $C_{21}H_{20}O_4 \cdot 0.25H_2O$: C, 73.99; H, 6.06%.

2,6-Bis(phenoxymethyl)-1,4-benzoquinone (10). To a solution of **13** (17 mg, 0.05 mmol) in benzene (5 mL) was added dropwise a solution of iron(III) chloride (250 mg, 1.5 mmol) and acetic acid (0.5 mL) in acetonitrile (10 mL). After 10 min, the solvent was removed and chromatographic separation on silica gel (benzene) afforded yellow solids, which were recrystallized from acetone/hexane to give **10** (14.6 mg, 92%) as yellow crystals: mp 140–142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (s, 4H), 6.96 (s, 2H), 6.97 (d, $J = 7.4$ Hz, 4H), 7.01 (t, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.11 (CH_2), 114.71 (CH), 121.81 (CH), 129.71 (CH), 132.09 (CH), 144.03 (C), 157.74 (C), 186.29 (C), 186.86 (C); IR (KBr) ν 1657 cm^{-1} (C=O); UV ($CHCl_3$) λ_{max} (ε) 309.5 nm (5.6×10^2). Found: C, 74.72; H, 5.11%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

Reduction of Quinone 1. To a solution of freshly prepared quinone **1** (25.8 mg, 0.018 mmol) in THF (4 mL) was added a solution of borane/THF (1.0 M, 60 μL) and the mixture was stirred at room temperature for 2 d. After the addition of water, the mixture was extracted with chloroform, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by preparative TLC (silica gel, chloroform/hexane, 1:1) to afford hydroquinone **14** (11.2 mg, 43%) as well as starting material **1** (5.6 mg, 21%). **14**: colorless crystals, mp 242–246 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (s, 36H), 1.42 (s, 18H), 3.26 (d, $J = 14.3$ Hz, 2H), 3.37 (d, $J = 15.3$ Hz, 4H), 3.48 (br, 1H), 4.14 (s, 4H), 4.45 (d, $J = 15.3$ Hz, 4H), 4.54 (d, $J = 14.3$ Hz, 2H), 4.57 (d, $J = 11.9$ Hz, 4H), 4.63 (d, $J = 11.9$ Hz, 4H), 5.25 (s, 1H), 6.34 (s, 2H), 6.75 (d, $J = 1.8$ Hz, 4H), 7.05–7.08 (m, 12H), 7.11–7.16 (m, 12H), 7.29 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 27.75 (CH_2), 30.72 (CH_2), 31.41 (CH_3), 31.64 (CH_3), 34.10 (C), 34.28 (C), 70.71 (CH_2), 74.77 (CH_2), 111.87 (CH), 123.94 (C), 124.14 (CH), 125.28 (CH), 127.04 (CH), 127.26 (CH), 127.85 (CH), 128.04 (CH), 132.10 (C), 133.08 (C), 133.63 (C), 137.94 (C), 145.26 (C), 146.06 (C), 146.27 (C), 146.83 (C), 152.03 (C), 152.52 (C). Found: C, 82.69; H, 7.79%. Calcd for $C_{102}H_{114}O_8 \cdot H_2O$: C, 82.44; H, 7.87%.

Reaction of 1 with Hydroxylamine. To a solution of freshly prepared quinone **1** (15 mg, 0.01 mmol) in pyridine-d_5 (0.6 mL) was added hydroxylamine hydrochloride (7.2 mg, 0.10 mmol) and the mixture was heated at 60 °C for 4 h. After the addition of aqueous methanol, the precipitates were collected to give a crude product of quinone monooxime **15**. The precipitates were subjected to preparative TLC (silica gel, chloroform/hexane 2:1) to give *p*-nitrosophenol **16** (9.3 mg, 68%) and hydroquinone **14** (3.9 mg, 26%). **16**: pale green crystals, mp 237–241 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 36H), 1.46 (s, 18H), 3.24 (d, $J = 14.5$ Hz, 2H), 3.39 (d, $J = 15.4$ Hz, 4H), 4.13 (brs, 4H), 4.49 (d, $J = 15.4$ Hz, 4H), 4.53 (d, $J = 11.5$ Hz, 4H), 4.54 (d, $J = 14.5$ Hz, 2H), 4.58 (d, $J = 11.5$ Hz, 4H), 6.44 (s, 1H), 6.78 (d, $J = 2.1$ Hz, 4H), 6.95–6.97 (m, 14H), 7.02 (d, $J = 2.1$ Hz, 4H), 7.02–7.06 (m, 8H), 7.34 (s, 4H). Found: C, 81.56; H, 7.57; N, 1.15%. Calcd for $C_{102}H_{113}NO_8 \cdot H_2O$: C, 81.73; H, 7.73; N, 0.93%.

Reaction of 1 with Phenylhydrazine. To a solution of freshly prepared quinone **1** (15 mg, 0.01 mmol) in benzene-d_6 (0.6 mL) was added phenylhydrazine (10 μL) and acetic acid (10 μL). After heating at 60 °C for 2 h, the mixture was evaporated and the residue was subjected to preparative TLC (silica gel, chloroform/hexane, 2:1) to give phenylazophenol **18** (2.1 mg, 12%) and hydroquinone **14** (7.0 mg, 45%). **18**: yellow solids; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 36H), 1.44 (s, 18H), 3.26 (d, $J = 14.7$ Hz, 2H), 3.35 (d, $J = 15.4$ Hz, 4H), 4.21 (brs, 4H), 4.49 (d, $J = 15.4$ Hz, 4H), 4.54 (d, $J = 14.7$ Hz, 2H), 4.57 (d, $J = 12.2$ Hz, 4H), 4.64 (d, $J = 12.2$ Hz, 4H), 6.03 (s, 1H), 6.77 (d, $J = 1.8$ Hz, 4H), 6.95–7.04 (m, 20H), 7.16 (d, $J = 1.8$ Hz, 4H), 7.31 (s, 4H), 7.46 (t, $J = 7.7$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.62 (brs, 2H), 7.91 (d, $J = 7.7$ Hz, 2H).

Electrochemical Measurements: A glassy carbon rod (outside diameter 3 mm, Tokai Carbon GC-20) was embedded in Pyrex glass, and a cross-section was used as a working electrode. Cy-

Table 4. Crystallographic Data for **1**·0.5C_6H_6, **2**·THF, **10**, and **14**·1.5MeOH·$CHCl_3$

	1·0.5C_6H_6	**2**·THF	**10**	**14**·1.5MeOH·$CHCl_3$
Formula	$C_{105}H_{115}O_8$	$C_{86}H_{112}O_9$	$C_{20}H_{16}O_4$	$C_{104.5}H_{121}Cl_3O_{9.5}$
Temperature/K	120	120	120	150
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	$C2/c$
a/Å	47.782(2)	23.250(2)	7.030(3)	51.115(3)
b/Å	11.969(1)	12.036(1)	17.042(4)	20.274(1)
c/Å	30.850(1)	27.297(1)	13.050(4)	18.132(1)
β/deg	99.895(1)	102.811(1)	95.219(17)	95.732(3)
V/Å^3	17381(2)	7448.6(8)	1557.0(9)	18696(2)
Z	8	4	4	8
D_{calcd}/g cm^{-3}	1.150	1.150	1.367	1.162
Reflections collected	47445	19867	4017	53963
Unique reflections	16036	9765	2243	16045
R_{int}	0.050	0.065	0.030	0.047
F_{000}	6472	2800	672	7000
$\mu_{MoK\alpha}$/mm^{-1}	0.071	0.073	0.095	0.155
Limiting indices	$0 < h < 57$	$0 < h < 27$	$0 < h < 8$	$0 < h < 62$
	$0 < k < 14$	$0 < k < 14$	$0 < k < 20$	$0 < k < 24$
	$-37 < l < 36$	$-32 < l < 31$	$-15 < l < 15$	$-21 < l < 21$
Restraints/parameters	0/1036	12/906	0/281	6/1153
Goodness of fit (F^2)	1.057	1.018	1.068	1.041
R indices ($I > 2\sigma(I)$)	$R1 = 0.0713$	$R1 = 0.1088$	$R1 = 0.631$	$R1 = 0.0868$
	$wR2 = 0.1823$	$wR2 = 0.2098$	$wR2 = 0.1602$	$wR2 = 0.2175$
R indices (all data)	$R1 = 0.0869$	$R1 = 0.2900$	$R1 = 0.0757$	$R1 = 0.1272$
	$wR2 = 0.1951$	$wR2 = 0.2506$	$wR2 = 0.1769$	$wR2 = 0.2464$

clic voltammetry was carried out in a standard one-compartment cell under an argon atmosphere equipped with a platinum-wire counter electrode and a Ag/Ag^+ reference electrode (10 mM $AgClO_4$ in 0.1 M (n-Bu)$_4NClO_4$–MeCN, $E^{\circ\prime}$ (ferrocene/ferrocenium in 0.1 M (n-Bu)$_4NClO_4/CH_2Cl_2$) = 0.214 V vs Ag/Ag^+) with a BAS CV-50W voltammetric analyzer. All runs were performed in 0.5 mM solutions in dry dichloromethane in the presence of 0.1 M (n-Bu)$_4NClO_4$ under argon.

X-ray Crystallographic Study: Single crystals of **1**·0.5C_6H_6, **2**·THF, **10**, and **14**·1.5MeOH·$CHCl_3$ were grown in benzene/acetonitrile, THF/dichloromethane, acetone/hexane, and chloroform/methanol solutions, respectively. The intensity data were collected on a MAC Science DIP-2030 imaging plate area detector with Mo Kα radiation ($\lambda = 0.71069$ Å). The data were corrected for Lorentz and polarization factors, and for absorption using the multi-scan method. Crystallographic and experimental data were listed in Table 4. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97.[43] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized using the riding model. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-253446–253449. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retreiving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336066; or deposit@ccdc.cam.ac.uk).

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