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The first calixarenequinhydrone: syntheses, self-organized films and solvatochromism

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ABSTRACT: Di(methoxy-*p*-*tert*-butyl)calix[4]arenediquinone (**2**) was prepared from di(methoxy-*p*-*tert*-butyl)calix[4]arene. Reduction of **2** led to its calix[4]arenedihydroquinone analog **3**. Partial reduction of **2** by 0.5 equiv. of a reducing agent led to the calix[4]arenequinhydrone charge-transfer complex **4**, which exhibits an intense solvatochromic absorption band in the visible region. Thus, λ_{max} varies from 627 nm in $CHCl_3$ to 677 nm in Et_2O. The association between two moieties of calix[4]arenequinonehydroquinone disodium salt was evidenced by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. The optical absorptions of **4** and a quinhydrone-containing polymer were compared. A calix[4]arenequinonecyclohexadienone derivative was also obtained and characterized by X-ray diffraction. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: calixarene; quinone; quinhydrone; self-organization; charge-transfer complex; solvatochromism

INTRODUCTION

The control of self-organization of supramolecular networks is currently of much interest in chemistry and materials science.[1,2] Intermolecular hydrogen bonding and π–π stacking stabilize numerous molecular networks of organic, organometallic or biological nature.[3–8] A very simple and interesting example is the well-known quinhydrone that is a molecular complex between *p*-benzoquinone (BQ) and hydroquinone (H_2Q) (Fig. 1). Its crystal structure reveals the formation of regular alternate donor/acceptor stacks,[9,10] while infinite molecular chains form through hydrogen bonds between the hydroxyl and the carbonyl groups. Recently, the quinhydrone role was evidenced in biological systems: the quinone reductase activity of the inner-membrane protein DsbB, which is present in *Escherichia coli*, involves a quinhydrone-type charge-transfer complex.[11] The family of calixarenes occupies an important place in host–guest chemistry,[12–14] but only a few examples of calixarenes are known to accommodate neutral entities.[15–20]

In order to obtain calixarene self-organized solids, we planned to synthesize calixarenequinhydrone-type charge-transfer complexes. By tuning the size and the number of arenes constituting the calixarene and also the number of acceptor (and donor) groups, various kinds of architecture would be expected. Following this concept, it appears that a calix[4]arene possessing both one acceptor group and one donor group would lead to linear arrangements or cyclic structures (Fig. 2). An equimolar mixture of calix[4]arenediquinone and calix[4]arenedihydroquinone would behave in the same way. Furthermore, a two-dimensional honeycomb structure could be reached starting from calix[6]arenes bearing three acceptor or donor groups.

In addition to its glue role, the formation of quinhydrone-type complexes induces particular optical properties. The presence of a charge-transfer band, of strong intensity and sensitive to the environment, would make it possible to carry out optical detection of the molecules that would interact with calixarenes. This could be applied to build up new molecular material-based sensors.[21]

The first example of molecular sensors using calixarenes was reported at the end of the 1980s.[22] Even though most of the studies on calixarene-based sensors concern ions,[23,24] some neutral species sensors have been also prepared.[25,26] These are based on the partial inclusion of

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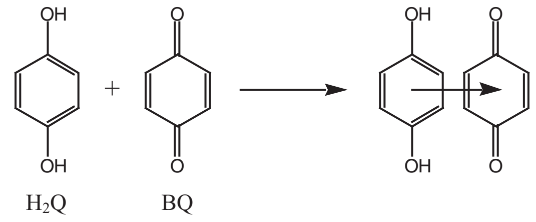


Figure 1. Schematic view of quinhydrone charge-transfer complex from dihydroquinone and *p*-benzoquinone

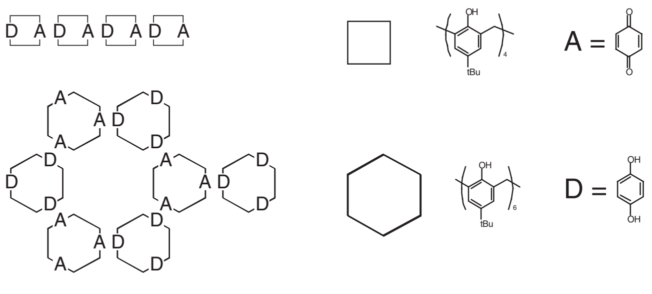


Figure 2. Examples of one- and two-dimensional arrangements possibly obtained with calix[4]arenes and calix[6]arenes bearing donor (D) and acceptor (A) groups

the molecules within the cavity associated with weak intermolecular interactions. The size of the cavity and its hydrophilic or hydrophobic character allow discrimination between molecules. Classical transducers are used, namely quartz-coated nanobalance[26,27] and surface acoustic wave (SAW) based sensors.[28,29]

The choice of intermolecular charge-transfer complexes allows one simultaneously to organize materials in a particular way and also to provide a simple tool of detection. Indeed, it is well known that charge-transfer complexes are solvatochromic materials.[30] Hence the complexation of a particular guest molecule into such calixarenes should be easily detected by the shift of the charge-transfer band observed in the visible region of the absorption spectrum. Different types of chromogenic calixarenes have been synthesized, which are based on donor–acceptor moieties, namely azophenol,[31–33] pyridylphenol[34] and indoaniline.[35] However, to our knowledge, all reported compounds give rise to intramolecular charge-transfer interactions. Our target molecules are the 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-25,27- diquinone **2** ($X_4Me_2Q_2$) and the 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-25,27-dihydroquinone **3** [$X_4Me_2(H_2Q)_2$] (Fig. 3).

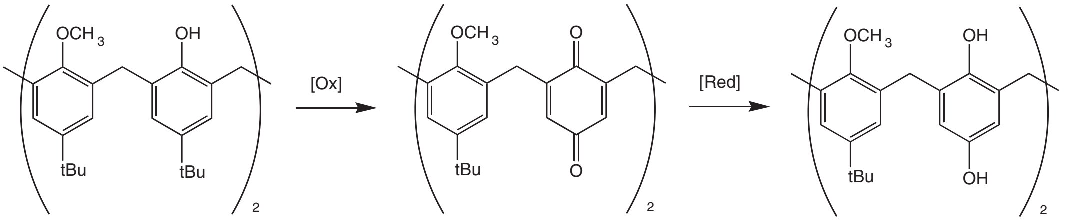
Classically, *p*-benzoquinone is prepared by oxidation of hydroquinone.[36] Calixquinones have been known for about 15 years, with the synthesis of calix[4]quinone, which is a tetraquinone molecule. Three different pathways were described to reach this molecule from calix[4]arene.[37,38] One of them starts from an azo compound, which is reduced to its tetraamino analog, the last step consisting in its oxidation by $FeCl_3$ and K_2CrO_4 in acetic acid. An alternative to that oxidation step is the use of ClO_2 in aqueous acetone.[39] In addition, the preparation of two calix[4]arenediquinones by oxidation of phenol rings by $Tl(NO_3)_3$ has also been reported.[40] In that case, two out of the four arenes have to be previously *O*-alkylated. The same procedure was extended to trimethoxytri-*p*-*tert*-butylcalix[6]arene, leading to trimethoxytri-*p*-*tert*-butylcalix[6]arenetriquinone.[41] Gutsche and co-workers preferred thallium(III) trifluoroacetate to prepare $X_4Me_2Q_2$.[39,42] We applied this method, the advantage of which is that it can be used directly on the *p*-*tert*-butylcalixarenes. It is worth noting that a few dialkylcalix[4]arenequinones have also been obtained by electrochemical oxidation of the corresponding *p*-*tert*-butylphenols.[43,44]

Calixarenehydroquinone analogs can be obtained by reduction of calixarenequinones with sodium borohydride in ethanol[45] or $Na_2S_2O_4$.[37] Thus, the synthesis of $X_4Me_2(H_2Q)_2$ (**3**) has been reported.[39] In this paper, we describe the preparation of calixarenequinhydrone **4** with NaH as reducing agent in various solvents and the solvent effects on its absorption properties, in solution and thin films.

RESULTS AND DISCUSSION

Synthesis

Using the methodology developed by McKillop *et al.*[46] and applied to various calixarenes,[47] we synthesized **2** as described by Gutsche's group.[39] Crystals of **2** were obtained by slow evaporation of a CH_2Cl_2 solution.



$X_4Me_2H_2$ **1** $X_4Me_2Q_2$ **2** $X_4Me_2(H_2Q)_2$ **3**

Figure 3. Schematic pathway from dimethoxycalix[4]arene $X_4Me_2H_2$ to the dimethoxycalix[4]arenediquinone $X_4Me_2Q_2$ **2** and dimethoxycalix[4]arene-dihydroquinone $X_4Me_2(H_2Q)_2$ **3**

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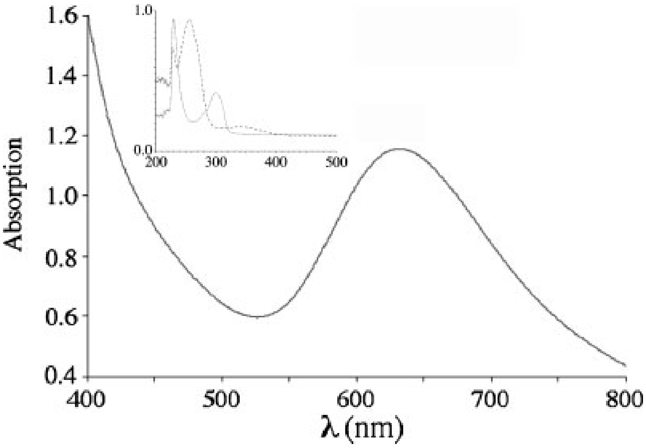

Figure 4. Absorption spectrum of calix[4]arenequinhydrone **4** in CH_2Cl_2 and those of calix[4]arenediquinone **2** (dashed line) and calix[4]arenedihydroquinone **3** (solid line) (inset)

During its purification by chromatography on silica, a product was eluted before **2** and isolated as 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]-27-quinone-23-[(1′-methyl-1′-trifluoroacetate)ethyl]-23-ol-25-cyclohexadienone (**5**) (Fig. 6). Cyclohexadienones had been proposed as intermediates in the oxidation of *p*-*tert*-butylphenol into *p*-quinone.[46] However, surprisingly, in our case, the trifluoroacetate moiety is not connected to the ring on the carbon bearing the *tert*-butyl group, but at the site of one of the methyl groups. This compound was characterized by ^{1}H NMR spectroscopy. Crystals of **5** were obtained by slow evaporation from a CH_2Cl_2–ethanol solution. On reduction of diquinone **2** by $NaBH_4$ we synthesized the corresponding dihydroquinone **3** as reported for a calix[4]arene monoquinone.[45] Infrared spectra showed the disappearance of vibrations characteristic of C=O in quinone **2** at 1653 (strong), 1629 and 1612 cm^{-1}.

Quinhydrone is classically prepared as purple needles from aqueous solutions (0.1 M) of *p*-benzoquinone and 1,4-dihydroquinone. It was not possible to prepare calixarenequinhydrone by simply mixing calixarenequinone **2** and calixarenedihydroquinone **3** owing to the lack of solubility of **3**. We tried unsuccessfully to generate calixarenequinhydrone from equimolar mixtures of **2** and **3** in sealed tubes heated to 150 °C, both in water and ethanol. We choose to prepare calixarenequinhydrone **4** directly from **2** upon reduction by 0.5 equiv. of reducing agent, leading to the sodium salt of **4** as shown by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry. The blue precipitate exhibits a sharp C=O vibration at 1658 cm^{-1}, shifted by 5 cm^{-1} compared with the starting quinone. For this step, reduction by NaH was preferred to ensure better control of the stoichiometry and to avoid the presence of boron species derived from $NaBH_4$ in the final product. It is worth noting that the disodium salt of quinhydrone (BQ-Na_2Q) has been known for a long time as a deep blue precipitate.[48]

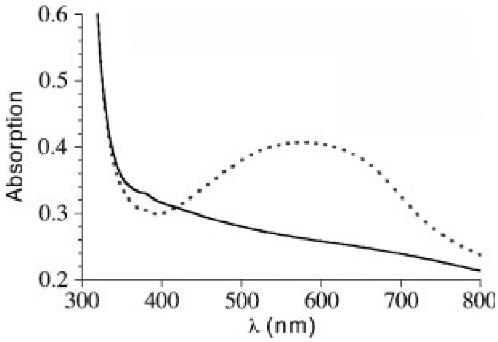

Figure 5. Absorption spectrum of a film of hydroquinone dispersed in PMMA (25%, w/w) prepared from acetonitrile solution with (dashed line) and without (solid line) benzoquinone

NMR analysis

The ^{1}H NMR spectrum of **3** recorded in DMSO-d_6 showed two singlets at δ7.72 and 8.46 ppm, assigned to hydroxyl protons of hydroquinone. Indeed, on addition of

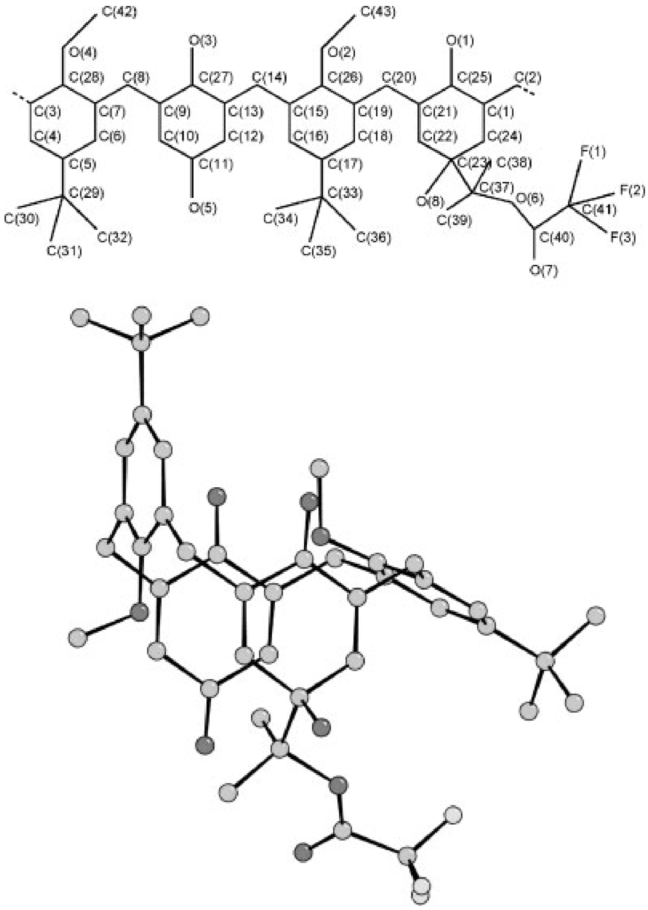

Figure 6. X-ray crystal structure of **5** (hydrogen atoms have been omitted for clarity) and the corresponding numbering scheme

D_2O to the NMR sample tube of **3**, disappearance of the signals was observed. At this point in our studies we were not able to distinguish between the hydroxyl groups involved in intramolecular hydrogen bonding with methoxy groups. It is worth noting that the NMR signals are as sharp for **3** as for **1**. In contrast, signals are broader for **2**, indicating that the disappearance of intramolecular hydrogen bonds allows faster interconversion between cone and partial cone isomers as seen for other calixquinones.[47] At 380 K, in deuterated 1,1,2,2-tetrachloroethane, signals become thinner, except for the inter-ring CH_2 protons. This temperature corresponds to the coalescence between the axial and equatorial protons. In **3**, methylene protons appear as two doublets, one of which is masked by the water signal at 3.31 ppm, but appears at 3.26 ppm when a drop of D_2O is intentionally added. The ^1H NMR spectrum of **5** recorded in $CDCl_3$ showed eight singlets in the aromatic region, which indicate the absence of symmetry elements. Two singlets (nine H each) can be attributed to *tert*-butyl groups, which are very close of each other (δ1.33 and 1.35 ppm). A third singlet at 1.01 ppm integrates for only six H. This was attributed to a dimethyl moiety on the cyclohexadienone ring, as confirmed by X-ray analysis. One singlet (four H) at 2.68 ppm and four doublets (one H each) were attributed to the methylene resonances. The ^{19}F NMR spectrum of **5** confirms the presence of a trifluoroacetate moiety.

X-ray analysis

Compound **2** crystallized in a monoclinic system (space group *C2/m*), $a = 15.703$, $b = 14.764$, $c = 16.257$ Å, $\alpha = \gamma = 90°$, $\beta = 117.40°$, $Z = 4$. These parameters are very close to those reported by Beer *et al.*[47] (space group *C2/m*): $a = 15.619$, $b = 14.652$, $c = 16.206$ Å, $\alpha = \gamma = 90°$, $\beta = 117.65°$.

Compound **5** crystallized as yellow crystals ($0.07 \times 0.09 \times 0.11$ mm) in a monoclinic system (space group $P2_1/c$), $a = 13.12405(9)$, $b = 18.9229(12)$, $c = 16.9078(11)$ Å, $\alpha = \gamma = 90°$, $\beta = 97.634(5)°$, $V = 4161.7(5)$ Å,^{3} $Z = 4$. Of the 30 730 reflections collected at 250 K, 3468 were used; 458 parameters were refined on F to give the final R indices ($R_1 = 0.111$ and $wR_2 = 0.123$). The compound exists in a partial cone conformation in the solid state (Fig. 6). Compound **5** is composed of two *p*-*tert*-butylanisole moieties and one quinone ring. The fourth ring is a cyclohexadienone ring, with two short C—C distances, namely C(1)—C(24) = 1.343(10) Å and C(21)—C(22) = 1.342(10) Å. One hydroxyl group and one trifluoroacetate isopropyl moiety are connected to the tetrahedral carbon of the ring. This means that one methyl fragment of the *tert*-butyl group was substituted by a trifluoroacetate moiety. The distance between the hydroxyl group and the cyclohexadienone ring is given by C(23)—O(8) = 1.573(11) Å. The distance O(8)—O(6) = 2.901 Å is compatible with the existence of a hydrogen bond between the hydroxyl group and the singly bound oxygen atom of the trifluoroacetate moiety. The cyclohexadienone ring is almost parallel to the quinone ring and perpendicular to the mean plane of the two benzene rings.

Mass spectrometric analysis

$X_4Me_2(H_2Q)_2$ (**3**) is characterized by the pseudomolecular ion signal MNa^+ at *m/z* 619.19 in the MALDI-TOF mass spectrum, with no signal corresponding to the initial quinone $X_4Me_2Q_2$. The MALDI-TOF mass spectrum of calixquinhydrone **4** obtained from a suspension in Et_2O–pentane shows two series of signals, starting from *m/z* 615.31 and 1277.73, respectively. The signal at *m/z* 1277.73 was assigned to the association of two moieties of calixarenequinonehydroquinone disodium salt, $[X_4Me_2Q(Na_2Q)]_2H^+$. Theoretically, it could correspond also to one calixarenediquinone $X_4Me_2Q_2$ associated with the tetrasodium salt of the calixarenedihydroquinone, $X_4Me_2(Na_2Q)_2$. A signal at *m/z* 1299.64 corresponds to the association of the non-protonated dimer with one sodium ion $[X_4Me_2Q(Na_2Q)]_2Na^+$. It is worth noting that these signals assigned to dimers are absent on the spectra of $X_4Me_2Q_2$ and $X_4Me_2(H_2Q)_2$. This indicates that the signal at *m/z* 1277.73 does not correspond to a non-specific dimer but clearly to the calixarenequinhydrone complex. A second series of signals appears in the spectrum of **4** in the *m/z* range 600–700. The signal at *m/z* 639.25 was assigned to $[X_4Me_2Q(Na_2Q)]H^+$, which is the protonated disodium salt of calix[4]arenequinonehydroquinone. The signal at *m/z* 617.31 was assigned to $[X_4Me_2Q(H_2Q)]Na^+$ and the signal at *m/z* 615.31 to $[X_4Me_2Q_2]Na^+$, whereas $[X_4Me_2(H_2Q)_2]Na^+$ was also present (*m/z* 619.31).

The conclusion of these mass spectrometric studies is that the main product of the partial reduction of the calix[4]arenediquinone **2** is the calix[4]arenequinonehydroquinone disodium salt and that a specific dimer of this compound is visible in the MALDI-TOF mass spectrum. The calix[4]arenequinonehydroquinone disodium salt $X_4Me_2Q(Na_2Q)$ contains both acceptor and donor moieties, which allow the formation of self-assemblies as shown in Fig. 2.

Film preparation

A few drops of a suspension of **4** were deposited on a glass substrate and covered with a second glass slide. Then films were characterized by visible absorption. In order to compare the optical properties of calixarenequinhydrone with those of quinhydrone, we also prepared films of quinhydrone. This was not possible directly from solutions since needles formed, leading to nonhomogeneous films. We chose to prepare quinhydrone dispersed in a polymer, namely poly(methyl methacrylate)

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(PMMA, $M_w = 84\,000\,g\,mol^{-1}$; polydispersity = 2.0 as determined by GPC). To a solution of PMMA (1.7 mg) in acetonitrile (10 ml), 5 mg of H_2Q were added. H_2Q–PMMA (75:25, w/w) films were obtained on glass slides from one drop of the solution, by spin coating or by spontaneous evaporation. Then a drop of BQ solution (5 mg in 10 ml of CH_3CN) was added, leading after spontaneous drying to a colored film. At lower PMMA percentages in the film crystallites appeared, which led to darker films associated with stronger absorption in the visible region.

Ultraviolet–visible spectroscopic investigations

The absorption spectrum of **4** prepared in CH_2Cl_2 shows a strong absorption band at 632 nm, absent in the spectrum of calix[4]arenediquinone **2** and calix[4]arene dihydroquinone **3** (Fig. 4). The existence of the calix[4]arenequinonehydroquinone disodium salt $X_4Me_2Q(Na_2Q)$ that contains both acceptor and donor moieties, as deduced from MALDI-TOF mass spectrometric analyses, explains the existence of that charge-transfer band. Films prepared from that solution exhibit a strong blue coloration associated with the existence of a charge-transfer complex. By way of comparison, films of quinhydrone in PMMA prepared from acetonitrile solutions show a maximum wavelength at 580 nm (Fig. 5).

When the synthesis of **4** was carried out in different solvents, the λ_{max} of the charge-transfer band was greatly shifted, up to 677 nm in diethyl ether and down to 580 nm in CH_3CN (Table 1). The absorption spectra of films also depend on the solvent used to prepare **4**, as indicated in Table 1. The solvatochromism of that absorption band confirms its charge-transfer nature. Indeed, it is well known that a transition between two states with different charge distributions depends on the polarity of the solvent in which it is determined; increasing the polarity of a solvent increases the stability of the most polar state.[30]

Table 1. UV–visible absorption of calix[4]arene derivatives **2**, **3** and **4** compared with that of quinone, hydroquinone and quinhydrone in solutions and films

Molecule (solvent)	λ_{max} (nm) in solution (λ_{max} for film)
BQ (CH_3CN)	243 ($\log \varepsilon = 4.4$) 291 ($\log \varepsilon = 2.6$)
H_2Q (CH_3CN)	225 ($\log \varepsilon = 3.7$) 293 ($\log \varepsilon = 3.6$)
$X_4Me_2Q_2$ **2** (CH_3CN)	228 ($\log \varepsilon = 4.3$) 256 ($\log \varepsilon = 4.4$) 339 ($\log \varepsilon = 3.3$)
$X_4Me_2(H_2Q)_2$ **3** (CH_3CN)	229 ($\log \varepsilon = 4.4$) 299 ($\log \varepsilon = 4.0$)
Quinhydrone (H_2O)	440 ($\log \varepsilon = 2.9$) (in 0.05 M HCl)[46] 530 shoulder (0.1 M in water)[a] (580 in PMMA)
Calix[4]arenequinhydrone **4** (CH_2Cl_2)	632 (630)
4 ($CHCl_3$)	627
4 (CH_3CN)	(580)
4 (Et_2O)	677

[a] Most of the quinhydrone crystallized as needles.

CONCLUSION

This paper illustrates the possibility of generating quinhydrone-type charge-transfer complexes from calix[4]arenediquinone. These complexes exhibit a strong solvatochromic behavior. The preparation of other calixarenequinhydrone derivatives is in progress. This work represents a first step towards new self-organized calix[4]arenes but also to molecular material-based sensors.

EXPERIMENTAL

All experimental manipulations were carried out under argon using Schlenk tube techniques. Acetonitrile and dichloromethane were distilled from over CaH_2 under argon. Diethyl ether was distilled from over sodium–benzophenone under argon. Trifluoroacetic acid and thallium(III) trifluoroacetate were purchase from Strem Chemicals and Alfa-Aesar, respectively, and used as received. $NaBH_4$ (Acros) and NaH were used as received.

Compound **1** was prepared according to the literature.[40] Chromatographic separations were performed on silica gel 60 (SiO_2, Merck, particle size 40–63 μm). Gel permeation chromatography of PMMA was carried out with an Ultrastyragel column with THF as solvent, at 40 °C and 1 ml min^{-1}. The detectors used were an R410 refractometer and an experimental differential viscosimeter. MALDI-TOF mass analysis was performed on a PerSeptive Biosystems (Framingham, MA, USA)Voyager Elite TOF mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). It was operated at 20 kV in the reflectron delayed extraction mode. The best spectra were recorded in the absence of matrix. ^1H and ^{19}F NMR spectra were recorded on a Bruker AC-300 spectrometer and UV–visible spectra on a Shimadzu UV-2101PC spectrometer.

Synthesis of 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]-arene-25,27-diquinone (**2**) and 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]-27-quinone-23-[(1′-methyl-1′-trifluoroacetate)ethyl]-23-ol-25-cyclohexadienone (**5**). To a solution of $Tl(OCOCF_3)_3$ (4.84 g; 8.9 mmol) in trifluoroacetic acid (8 ml), 1.00 g (1.48 mmol) of **1** was added and stirred for 2 h in the dark and under argon. The trifluoroacetic acid was then removed in vacuum and the residue poured into ice–water (30 mL). The product was extracted with chloroform. The organic layer was then

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washed with water, dried over $MgSO_4$, filtered and evaporated. The residue was purified by chromatography on silica gel plates with CH_2Cl_2–acetone (95:5) as eluent and the product **2** isolated as a yellow powder (0.59 g, 67%).

Compound **2**: MALDI-TOF MS: *m/z* 615.24 ($M+Na^+$) IR (KBr): 1653(s) (C═O), 1629, 1612, 1468, 1297, 1205, 1115, 1008, 925, 884 cm^{-1} UV–visible: λ_{max} (CH_3CN) 228 nm (log $\varepsilon = 4.3$), 256 nm (log $\varepsilon = 4.4$), 339 nm (log $\varepsilon = 3.3$) ^1H NMR (300 MHz, 380 K, $C_2D_2Cl_4$): δ(ppm) 1.33 [s, 18H, $C(CH_3)_3$, 3.12 (s, 6H, OCH_3), 3.53 (br s, 8H, $ArCH_2Ar$), 6.26 (s, 4H, QuH), 7.18 (s, 4H, ArH). Anal. Calcd for $X_4Me_2Q_2{\cdot}H_2O$: C, 74.73; H, 6.93. Found: C, 74.70; H, 6.86%.

During its purification by chromatography on silica, another product (**5**) was eluted before **2** and isolated as a yellow powder (0.10 g, 10%).

Compound **5**: ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 1.01 [s, 6H, $C(CH_3)_2$, 1.33 [s, 9H, $C(CH_3)_3$, 1.35 [s, 9H, $C(CH_3)_3$, 2.68 (s, 4H, $ArCH_2Ar$), 3.22 (d, $J = 13$ Hz, 1H, $ArCH_2Ar$), 3.42 (d, $J = 13$ Hz, 1H, $ArCH_2Ar$), 3.74 (s, 6H, OCH_3), 3.92 (d, $J = 13$ Hz, 1H, $ArCH_2Ar$), 4.15 (d, $J = 13$ Hz, 1H, $ArCH_2Ar$), 5.89, 6.38, 6.42, 6.98, 7.05, 7.15, 7.25, 7.35 (8 s, 8H, ArH, QuH and cyclohexadienone). ^{19}F NMR (282 MHz, $C_2D_2Cl_4$): $\delta - 76.50$ (s, CF_3CO_2).

Synthesis of 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]-arene-25,27-dihydroquinone (**3**). To a solution of **2** (230 mg; 0.388 mmol) in 10 ml of ethanol were added 67 mg (1.78 mmol) $NaBH_4$. The reaction mixture was stirred, at room temperature, until the yellow solution turned colorless. After addition of 0.2 M HCl (7 ml), the product was extracted with CH_2Cl_2 (50 ml). The organic phase was washed with 10% aqueous $NaHCO_3$ solution, dried over Na_2SO_4, filtered and evaporated to dryness to give **3** as a white powder (178 mg, 77%).

Compound **3**: MALDI-TOF MS: *m/z* 619.19 ($M+Na^+$) IR (KBr) 1484, 1462, 1238, 1208, 988, 854 cm^{-1} UV–visible: λ_{max} (CH_3CN) 229 nm (log $\varepsilon = 4.4$), 299 nm (log $\varepsilon = 4.0$) ^1H NMR (300 MHz, DMSO-d_6): δ(ppm) 1.16 [s, 18H, $C(CH_3)_3$], 3.26 (d, $J = 12$ Hz, 4H, $ArCH_2Ar$, visible only on addition of one drop of D_2O), 3.91 (s, 6H, OCH_3), 4.18 (d, $J = 12$ Hz, 4H, $ArCH_2Ar$), 6.47 (s, 4H, ArH), 7.09 (s, 4H, ArH), 7.72 (s, 2H, OH), 8.46 (s, 2H, OH). Anal. Calcd for $C_{38}H_{44}O_6{\cdot}3H_2O$: C, 70.13; H, 7.74. Found: C, 69.66; H, 7.45%.

Synthesis of 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]-arenequinhydrone (**4**). To a solution of **2** (25 mg; 42 μmol) in 4 ml of dried CH_2Cl_2 were added 2.5 mg (100 μmol) of NaH. The reaction mixture was stirred, at room temperature and in the dark for 3 h. The solution, initially yellow, turned to light bluish green after 30 min, parrot green after 1 h and finally to a deep blue suspension.

Compound **4**: IR (KBr): 1658(s) cm^{-1} (C═O). UV–visible: λ_{max} (CH_2Cl_2) 632 nm. MALDI-TOF MS: *m/z* 1277.73 $[X_4Me_2Q(Na_2Q)]_2H^+$.

Supplementary material

Tables listing detailed crystallographic data, atomic positions, parameters and bond lengths and angles for compound **5** are available free of charge from the Cambridge Data Center via the Internet at http://www.ccdc.cam.ac.uk/data_request/cif (CCDC 265637).

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