Chemistry of 1,8-Naphthalenesultone: Synthesis of a Water-Soluble Tetrasulfonated C_{2v} Calixnaphthalene

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Introduction

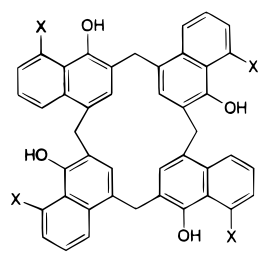
The syntheses of calix[4]naphthalenes, which are a new class of cyclic 1-naphtholformaldehyde tetramers, have been reported previously.[1,2] These compounds and their simple ester and ether derivatives show interesting conformational behavior;[2,3] however, their solubilities are rather limited and thus far have precluded a thorough examination of their potential host−guest properties,[4] aside from a preliminary examination of some of their ionophoric properties using alkali metal picrates.[5]

Most calixarenes[6] are insoluble in water, but Arduni et al.[7] reported the first water-soluble calix[4]arene by functionalization of the lower rim, and Shinkai [8] synthesized upper-rim para-substituted sulfonatocalixarenes, e.g., **5**, which are more water soluble and form aqueous solution-state complexes with metal cations, organic cations, and neutral molecules. Since direct sulfonation of calix[4]naphthalenes **1**−**3** produced intractable products, the *peri*-tetrasulfonatocalix[4]naphthalene, **6** was therefore synthesized by condensation of formaldehyde and the readily available 1,8-naphthalenesultone (**7**). This paper describes the synthesis and characterization of **6** and some chemical reactions of the precursor sultone **7**.

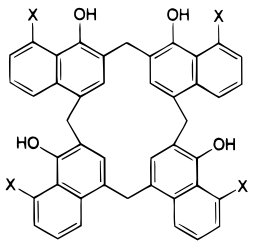
Results and Discussion

Shinkai produced the *para*-substituted sulfonatocalix[6]arene, **5** by first removing the *tert*-butyl groups of *p-tert*-butylcalix[6]arene by a *retro* Friedel−Crafts reaction using $AlCl_3$ and then sulfonating with an excess of concentrated sulfuric acid. Atwood[9] synthesized the pentasodium salt of calix[4]arene sulfonate **8** in 80% yield by reacting *p-tert*-butylcalix[4]arene directly with concentrated sulfuric acid for 3 h followed by addition of a large excess of Na_2CO_3. However, when either of these, or similar sulfonating conditions, were employed with calix[4]naphthalenes **1**−**3**, only intractable dark tars were obtained from which no desired product could be detected or isolated. That this approach failed to yield the desired results with these calix[4]naphthalenes could be due to their being more easily oxidizable than the calix[4]arenes. For example, the dihydroxy naphthalenone compound **9** was isolated from a $DMSOd_6$ solution of **1** that had been left standing for several weeks in an NMR tube. Its structure was established by single-crystal X-ray analysis and presumably was formed from **1** by aerial oxidation.

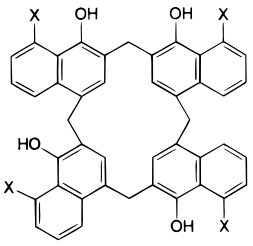
Commercially available 1,8-naphthalenesultone (**7**) was therefore used as a precursor compound for cyclooligomerization with formaldehyde. It contains a masked sulfonic acid group as it is an internal ester of the corresponding hydroxynaphthalenesulfonic acid, which in principle, can be easily regenerated to make it water-soluble. Since the five-membered ring is fused at the peri positions of the naphthalene ring, it is strained and, as



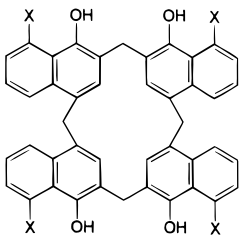
1 X = H
10 X = SO_3H



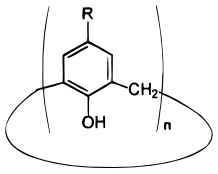
2 X = H
11 X = SO_3H



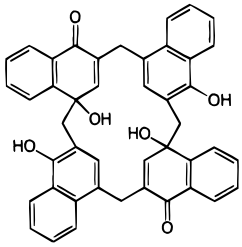
3 X = H
12 X = SO_3H



4 X = H
6 X = SO_3H



5 n = 6 ; R = SO_3H
8 n = 4 ; R = $SO_3^{\ominus}$, $Na^{\oplus}$



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‡ Mu'Tah University.

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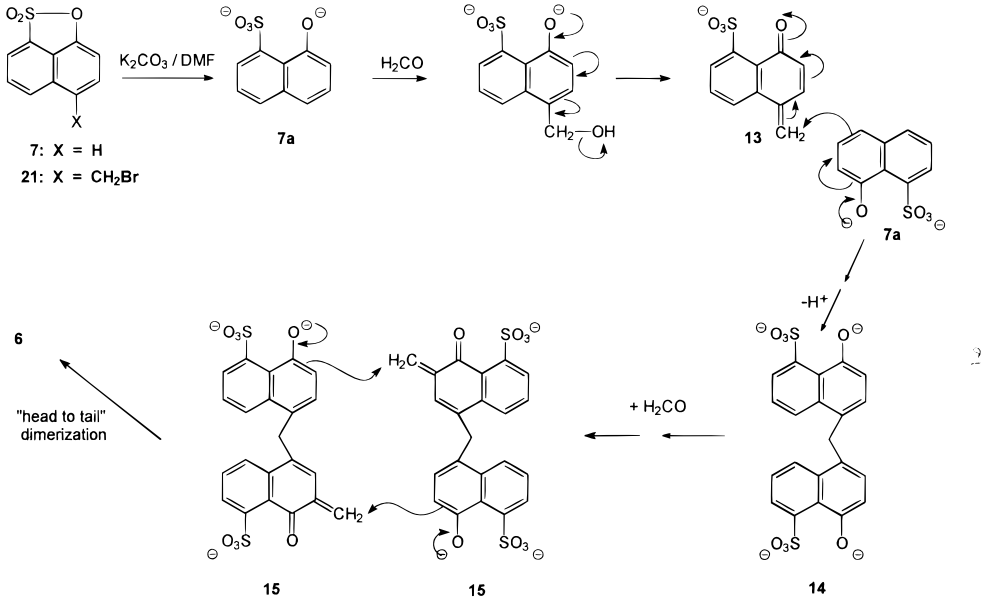
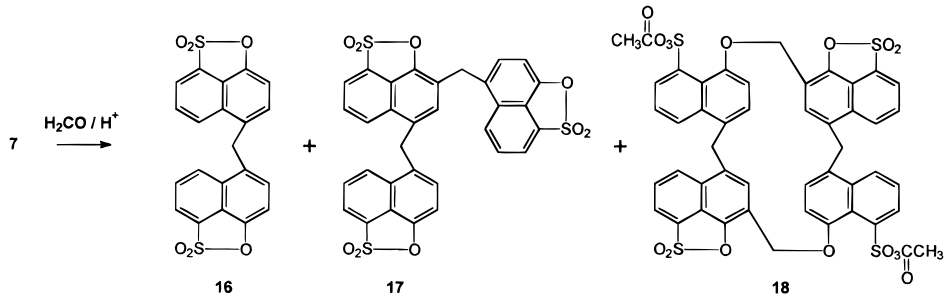
Scheme 1



Scheme 2



a result, has some unique chemical properties.[10] Thus, electrophilic substitution readily occurs, usually at the 4-position, but nucleophiles attack the sulfur atom resulting in sulfur−oxygen bond fission.

When **7** was refluxed with Cs_2CO_3 and formalin in DMF solution, followed by acidification and crystallization, the cyclic tetramer **6** was formed in 15% yield. Characterization of this product was initially conducted by ^{1}H and ^{13}C NMR analysis. Its ^{13}C NMR spectrum reveals 12 ^{13}C signals, which is in accord with structure **6** but is not consistent with any of the other three structural isomers **10**−**12** that are theoretically possible. Assignment of the ^{13}C signals was based upon connectivity established by long-range HETCOR experiments.[11] The ^{1}H NMR shows two sharp singlets at δ 4.44 and 4.00, which correspond to the two methylene bridges. That these signals are singlets and that all the other signals in the ambient-temperature ^{1}H NMR spectrum are sharp is indicative of conformational flexibility. The IR spectrum is also consistent with **6**, but a mass spectrum could only be obtained by electrospray mass spectrometry (ESMS)[12,13] in the negative-ion mode, using an aqueous solution of **6**. Suitable crystals for single-crystal X-ray analysis or elemental analysis have not yet been obtained.

A proposed mechanism to rationalize the preferential formation of **6** via a "*hemi*calixarene"-type pathway[6] is depicted in Scheme 1. The sulfonate dianion **7a** presumed to form under the basic conditions employed reacts with a *p*-naphthoquinone-type intermediate,[2] **13**, itself formed by condensation of formaldehyde with **7a**, to form the para-para product, **14**. Condensation of **14** with formaldehyde resulting in the formation of the *o*-naphthoquinone **15**, followed by a "head-to-tail" dimerization of **15**, could thus lead to the formation of **6**.

Under acidic conditions (3% sulfuric acid in glacial acetic acid, 2 h), **7** reacted with formaldehyde to afford a dimer **16** and a trimer **17**. When the reaction time was extended for up to 6 days, none of the anticipated cyclic tetramer was obtained. Instead, dimer **16**, trimer **17**, and a new cyclic condensation product, oxacalix[4]naphthalene sultone (**18**), were obtained (Scheme 2).

The ^{1}H NMR spectrum of **18** reveals two singlets at 3.90 and 5.24 ppm, due to the methylene protons on C-11 and C-27 (confirmed by HETCOR to be correlated with the ^{13}C signal at 30.46 ppm) and to the oxymethylene protons on C-3 and C-19 (confirmed by HETCOR to be correlated with the ^{13}C signal at 57.19 ppm). The doublets at 7.05 and 7.21 ppm and the singlet at 7.32 ppm are due to the interannular aromatic protons. The singlet at 2.00 ppm is due to the methyls of the acetoxy groups, which are confirmed by the presence of a carbonyl absorption at 1743 cm^{-1} in the infrared spectrum. NOED determinations confirmed the structural assignment made and that the compound appears to be in rapid dynamic equilibrium between two 1,3 alternate-type

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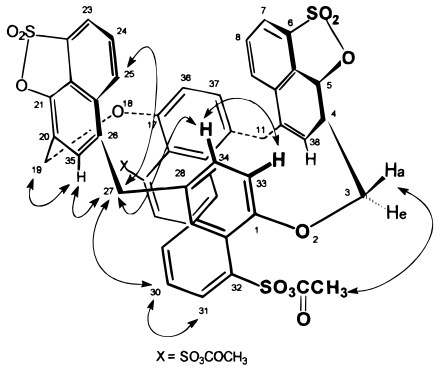
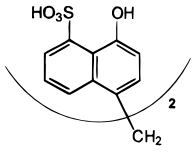


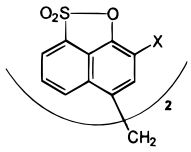
Figure 1. Structure and selected NOE correlations for **18**.

conformations (Figure 1). Mass spectrometric data are in agreement with the structural assignment made.

Two stepwise convergent approaches similar to those previously used[2] to synthesize the four calixnaphthalenes **1**−**4**, but utilizing the easily obtainable dimer **16**, were investigated. In principle, functionalization at the 2- and 2′-positions of **16** could be potentially effected by bromomethylation or formylation to form **19** or **20**, respectively, and a coupling reaction of **19** with **16** could then afford the target cyclic tetramer **6**. However, when either



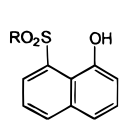
16b



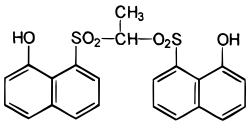
19 X = CH_2Br
20 X = CHO

sultone **7**, dimer **16**, or trimer **17** was treated with paraformaldehyde in the presence of HBr, in each case only 4-(bromomethyl)-1,8-naphthalene sultone (**21**) was obtained. Thus, in the case of **7**, only substitution at the 4-position of the naphthalene ring by a bromomethyl cation occurred, but in the cases of **16** and **17**, retro-Friedel−Crafts reactions appeared to have also occurred. Attempts to functionalize the 2- and 2′-positions of **16** by treatment with α,α-dichloromethyl methyl ether in the presence of $TiCl_4$ only afforded unreacted starting materials. When **16** was first hydrolyzed to its corresponding hydroxysulfonic acid **16b** and then treated with paraformaldehyde in the presence of HBr and $ZnBr_2$ in acetic acid, however, only an intractable dark brown crude product was obtained. Its ^{1}H NMR spectrum showed it to consist of a mixture of oligomers or polymers.

To evaluate the possibility of forming a calixnaphthalene product containing a sulfone group, phenyl (1-hydroxy-8-naphthyl)sulfone (**22**) was easily obtained[14] when **7** was treated with phenylmagnesium bromide. However, when **7** was treated with ethylmagnesium bromide instead, an unexpected product, **23**, was obtained. The fact that this product forms suggests that the methylene group attached to the sulfonyl group is sufficiently acidic enough to form a carbanion that can couple with another molecule of **7**. Nonetheless, when the condensation of either **22** or **23** with formaldehyde under basic conditions was attempted, no clearly defined product could be discerned in the crude products, their NMR spectra suggesting the formation of only resinous products.



22: R = Ph



23

Water-soluble calixarene hosts are known to form complexes with neutral aromatic guests in aqueous solution. Shinkai,[15] for example, has investigated the complexation properties of the *p*-sulfonatocalix[6]arene with a variety of guest molecules. Formation of complexes was evidenced by the enhancement of the solubilities of aromatic guests in water. The effect of **6** on the solubility of naphthalene in water was determined by measuring the fluorescence[16] emission intensities of aqueous naphthalene solutions, naphthalene being chosen as a potential indicator guest on the basis of its size relative to that of **6**. The results showed that **6** did not enhance the solubility of naphthalene guests in water.

To form a complex with neutral guests, a macromolecular host should be conformationally rigid and have defined hydrophilic and hydrophobic parts. It is possible that the failure of **6** to act as a host can be ascribed to it being too conformationally flexible and/or that its hydroxy and sulfonic acid groups are not situated in an upper and lower rim of the molecular basket as is typically found with the sulfonatocalixarenes. We are currently working to evaluate this hypothesis by designing conformationally more rigid calixnaphthalene molecules in which hydrophilic and hydrophobic components are more definitely separated.

In conclusion, it has been shown that a water-soluble calixnaphthalene-type product is formed from the DMF−base-mediated condensation of 1,8-naphthalenesultone with formaldehyde. Spectroscopic methods established that this product, **6**, is cyclic and has C_{2v} symmetry. Under these conditions, none of the other three potential isomers could theoretically be formed were obtained. In acidic media, a linear dimer and trimer were formed, but the only cyclic tetramer that was obtained was the novel oxysulfonato compound **18**. A limited complexation study using **6** as a potential water-soluble host with naphthalene as guest failed to indicate any host−guest complex formation.

Experimental Section

For general experimental conditions and instrumentation employed, see ref 2. Electrospray mass spectra (ESMS) in the negative mode were recorded on a Fisons VG-Quattro triple quadrupole mass spectrometer, equipped with an electrospray ionization source, capable of analyzing ions up to *m*/*z* 4000. A 486, 66 MHz personal computer equipped with Fisons MASSLYNX mass spectrometry data system software was used for data acquisition and processing. The temperature of the ES ionization source was maintained at 70 °C. The operating voltage of the ES capillary was 3.00 kV, and the HV lens was at 0.50 kV throughout the operation. ESMS were obtained by scanning in the multichannel analysis mode (MCA) with a scan dwell time of 1 s. Spectra were an average of three to four scans.

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The mass scale was calibrated in the negative-ion mode using a horse heart myoglobin solution. MS/MS experiments were conducted on the same instrument. Fragment ion spectra of mass-selected ions were produced by collision with argon in the second (RF only) hexapole. Argon collision gas was added in the enclosed chamber of the hexapole to give a pressure of 2×10^{-5} mBar for collisional activation of the sample ions. The resulting fragments were analyzed by the third quadrupole. Collision energies of 50 eV were used in MS−MS experiments. Precursor ion scans were obtained by scanning the first quadrupole while selecting a given *m*/*z* value with the third quadrupole.

***peri*-Sulfonatocalix[4]naphthalene (6).** To a solution of freshly sublimed 1,8-naphthalene sultone (**7**) (2.06 g, 10 mmol) in DMF (10 mL) under N_2 were added formalin (aqueous 37% formaldehyde solution, 0.70 mL, 8.6 mmol) and Cs_2CO_3 (2.0 g, 6.13 mmol) in water (3 mL). The reaction mixture was refluxed for 52 h and then cooled to room temperature. After being poured into 5% hydrochloric acid (30 mL), the reaction mixture was left in a refrigerator for 1 day. A white precipitate formed that was filtered and washed with deionized water until the washings were neutral to pH paper and then dried under vacuum. The crude product was crystallized from 95% ethanol to afford **6** as a white powder (0.42 g, 15%): mp 256−275 °C (with dec); ^{1}H NMR (DMSO-d_6) δ 4.00 (s, 4H), 4.44 (s, 4H) 6.63 (s, 4H), 7.27 (m, 4H), 7.94 (d, J = 9 Hz, 4H), 8.06 (d, J = 9 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 29.2, 35.5, 121.4, 124.2, 124.8, 126.2, 127.0, 127.8, 130.8, 133.6, 142.6, 150.4; MS (ESMS) (*m*/*z*, rel int) 537.3 ([M + 6Na − 8H]$^{2-}$, 15), 471.5 ([M − 4H]$^{4-}$ 15), 358.0 ([M + 6Na − 9H]$^{3-}$, 63), 321.0 ([M + Na − 4H]$^{3-}$, 13), 313.7 ([M − 4H],$^{4-}$ 65), 287.4 ([M − 3H − SO_3H]$^{3-}$, 51), 235.3 ([M − 4H],$^{4-}$ 100), 229.7 ([M − 4H − H_2O],$^{4-}$ 72). The MS/MS spectrum of the parent ion at *m*/*z* 313.7 also shows fragments at *m*/*z* 235.3 and 229.7. The former fragment corresponds to the [M − 4H]$^{4-}$ ion, which is formed from the *m*/*z* 313.86 ion by loss of a proton. The fragment at *m*/*z* 229.7 corresponds to the [M − 4H − H_2O]$^{4-}$ ion.

X-ray Data for 9. Crystal data for **9**: $C_{44}H_{32}O_6$, monoclinic, space group P2/*n* (#13), a = 17.112(6) Å, b = 11.285(4) Å, c = 22.461(3) Å, β = 107.67 (2)°, Z = 4, D_{calc} = 1.00 g/cm^3, crystal size = 0.40 × 0.35 × 0.20 mm. Intensity data were measured at 299 K on a Rigaku AFC6S diffractometer with Mo Kα (λ = 0.710 69 Å) to $2\theta_{max}$(deg) = 45.1°; 5777 unique reflections converged to a final R = 0.042, for 2256 reflections with $I > 2.00\sigma(I)$; R_w = 0.107. These data are not suitable for crystallographic purposes other than as supporting evidence for the structure proposed. Cavities in the cell contained severely distorted solvent, modeled here as oxygen atoms only. The refinement was correspondingly poor. The dataset was weak, and there was insufficient data to justify full anisotropic refinement.

Bis(1,8-sultonyl-4-naphthyl)methane (16) and 2,4-Bis-[(1′,8′-sultonyl-4′-naphthyl)methyl]-1,8-naphthalenesultone (17). To a solution of **7** (206 mg, 1.30 mmol) and paraformaldehyde (120 mg, 4.0 mmol) in glacial acetic acid (10 mL) was carefully added concentrated sulfuric acid (0.3 mL). The clear solution was refluxed for 2.5 h. After being cooled to room temperature, the reaction solution was poured onto crushed ice (10 g). A white precipitate formed that was filtered, washed with water until the washings were neutral to pH paper, and dried under vacuum. A crude product was obtained (202 mg), which was purified by preparative thin-layer chromatography (PLC) using 50% dichloromethane/petroleum ether (30−60 °C) as eluent. The dimer **16** (148 mg, 54%) and the trimer **17** (21 mg, 8%) were obtained as white powders. Dimer **16**: mp 296−298 °C; ^{1}H NMR (DMSO-d_6/$CDCl_3$ (4:1)) δ 4.95 (s, 2H, 7.26 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.96 (m, 2H), 8.41 (d, J = 8.6 Hz, 2H), 8.49 (d, J = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6/$CDCl_3$) 32.4, 106.5, 121.0, 121.7, 127.9, 129.5 (x2), 129.8, 130.5, 131.2, 145.0; MS (*m*/*z*, rel int 425 (M$^+$ + 1, 25), 424 (M$^+$, 100), 360 (M$^+$ − SO_2, 16), 296 (M$^+$ − 2SO_2, 24), 268 (26), 267 (12), 240 (24), 239 (81), 238 (12), 237 (20), 120 (66), 118 (14); HRMS M$^+$ 424.0030, calcd for $C_{21}H_{12}S_2O_6$ 424.0075. Trimer **17**: mp >300 °C (with dec); ^{1}H NMR (DMSO-d_6) δ 4.58, 4.87 (s, 4H), 7.07 (s, 1H), 7.24 (d, J = 9 Hz), 7.26 (d, J = 6 Hz), 7.36 (d, J = 6 Hz), 7.48 (d, J = 9 Hz, 4H), 7.73, 7.82, 7.97 (m × 3, 3H), 8.24 (d, J = 9 Hz, 1H), 8.35 (d, J = 9 Hz, 1H), 8.39 (d, J = 9 Hz, 1H), 8.41 (d, J = 9 Hz, 1H), 8.49 (d, J = 9 Hz, 1H), 8.52 (d, J = 9 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 29.9, 32.3, 106.5, 106.6, 106.7, 106.8, 121.9, 122.0, 122.4, 129.3, 129.5, 129.8, 129.9, 130.1, 130.8, 131.0, 118.9, 120.7, 120.8, 121.1, 127.7 (×2), 128.7, 129.4, 129.7, 130.5, 131.2, 131.7, 132.1, 142.2, 144.8, 144.9; MS (*m*/*z*, rel int) δ 642 (M$^+$, 18), 424 (11), 363 (8), 239 (34), 237 (15), 226 (7), 213 (8), 203 (7), 187 (4), 182 (5), 155 (9), 127 (15), 119 (11); HRMS M$^+$ 642.0085, calcd for $C_{32}H_{18}S_3O_9$ 642.0113.

Oxacalix[4]naphthalenesultone (18). To a solution of **7** (3.9 g, 25 mmol) and paraformaldehyde (2.4 g, 80 mmol) in glacial acetic acid (100 mL) was carefully added concentrated sulfuric acid (3.0 mL). The clear solution was refluxed for 6 days. After being cooled to room temperature, the reaction solution was poured onto crushed ice (200 g). The gray precipitate was filtered, washed with water until the washing were neutral to pH paper, and dried under vacuum. A 200 mg sample of the crude product was purified by PLC using CH_2Cl_2 as solvent. Three major products were isolated in the following order of increasing polarity: dimer **16** (30 mg), trimer **17** (18 mg), and oxacalixnaphthalene **18** (15 mg). Compound **18** was obtained as a white solid: mp 265−270 °C (with dec); ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 6H), 4.85 (s, 4H), 5.24 (s, 4H), 7.06 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.33 (s, 2H), 7.80−7.90 (m, 4H), 8.05 (m, 4H), 8.16 (d, J = 8.1 Hz, 2H), 8.24 (d, J = 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 18.5, 30.5, 57.2, 104.6, 104.7, 120.1, 120.5, 127.2, 127.3, 127.6, 127.7, 127.9, 113.3, 118.9, 119.0, 125.7, 125.8, 125.9, 128.2, 129.4, 129.7, 140.7, 143.0; MS (FAB$^+$, NOBA as a matrix) (*m*/*z*, rel int) 516 (M^{2+}, $C_{44}H_{32}O_{16}S_4$ Na_4, 1), 494 (2.2), 436 (4), 395 (7), 367 (6).

Attempted Functionalization of the 2-Position of Bis(1,8-sultonyl-4-naphthyl)methane (16). A. Bromomethylation of 16. To a solution of the sultone dimer **16** (800 mg, 1.88 mmol) and paraformaldehyde (400 mg, 13.3 mmol) in glacial acetic acid (50 mL) were added 30% HBr in glacial acetic acid (50 mL) and anhydrous $ZnBr_2$ (700 mg, 3.14 mmol). The reaction mixture was heated to 90−100 °C and maintained at that temperature for 1 week. After being cooled to room temperature, the reaction solution was poured onto crushed ice (20 g). The white precipitate was filtered, washed with water until the washings were neutral to pH paper, and dried under vacuum. TLC revealed at least five spots. The crude product was separated by column chromatography with dichloromethane as eluent. The major fraction was rechromatographed with 30% ethyl acetate/hexanes as eluent. A cream-colored crystalline product was obtained (103 mg, 9%), whose structure was assigned to be 4-(bromomethyl)-1,8-naphthalene sultone (**21**): mp 143−145 °C (lit.[17] mp 145−146 °C); ^{1}H NMR ($CDCl_3$) δ 4.92 (s, 2H), 7.10 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.95 (q, J = 7.2, 8.1 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) 29.1, 106.2, 121.2, 128.8, 129.2, 130.5, 122.1, 128.6, 129.4, 144.8, 147.4; MS (*m*/*z* rel int)300 (M$^+$, 4), 298 (M$^+$, 4), 219 (100), 155 (35).

B. Formylation of 16. To a solution of the sultone dimer **16** (100 mg, 0.24 mmol) in dry dichloromethane (5 mL) cooled to 0−5 °C in a salt−ice bath were added $TiCl_4$ (0.10 mL, 0.90 mmol) and α,α-dichloromethyl methyl ether (0.10 mL, 1.10 mmol). After the ice bath was removed, the reaction mixture was warmed to room temperature and stirred for 3 h. When the crude reaction mixture was checked by TLC, the starting material remained unchanged with no evidence of product formation.

Phenyl(1-hydroxy-8-naphthyl)sulfone (22). To dry diethyl ether (25 mL) were added magnesium turnings (2.4 g, 100 mmol) and bromobenzene (23.4 mL, 100 mmol) in diethyl ether (25 mL). After being stirred for 5 min, the solution became cloudy and exothermic with resulting reflux of the solvent. The rest of the bromobenzene was added dropwise. The solution was maintained at gentle boiling for an additional hour after the addition of the bromobenzene was completed. A benzene solution (50 mL) of **7** (2.50 g, 12.1 mmol) was added to the Grignard reagent solution. The reaction mixture was refluxed for 4 h, and after the mixture was cooled to room temperature, 5% hydrochloric acid (50 mL) was added to the solution. After being stirred for 15 min, the aqueous and organic layers were

(17) Schetly, G. *Helv. Chim. Acta* **1948**, *31*, 1229.

separated. The aqueous layer was extracted with benzene. The benzene extracts (20 mL × 2) were combined and dried over anhydrous magnesium sulfate. After the solvent was filtered and evaporated the residue obtained was crystallized from benzene. Sulfone **22** was obtained as colorless needles (2.05 g, 59%): mp 134.5−135.0 °C (lit.[14] mp 140 °C); ^{1}H NMR ($CDCl_3$) δ 7.19 (d, J = 7.3 Hz, 1H), 7.51 (m, 6H), 7.81 (m, 1H), 7.84 (m, 1H), 8.13 (q, J = 8.4, 1.2 Hz, 1H), 8.58 (q, J = 7.5, 1.2 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 112.2, 119.4, 120.0, 124.6, 125.4, 127.9, 130.7, 131.7, 135.2, 136.2, 144.7, 152.4; MS (*m*/*z*, rel int) 285 ($M^+ + 1$, 18), 284 (M^+, 100), 219 (18), 218 (14), 206 (27), 189 (6), 142 (38).

1′,1′-Bis(1-hydroxy-8-naphthyl)sulfonato]ethane (23). To a solution of **7** (2.0 g, 10 mmol) in dry benzene (50 mL) was added ethylmagnesium bromide (3.0 M ether solution, 8 mL) over 30 min. The reaction mixture was refluxed for 4 h. After the mixture was cooled to room temperature, 5% hydrochloric acid (50 mL) was added. After the solution was stirred for 15 min, the aqueous and organic layers were separated. The aqueous layer was extracted with benzene (20 mL × 2). The benzene extracts were combined and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent gave a residue, which was crystallized from benzene. The product **23** was obtained as colorless needles (0.95 g, 44%): mp 197−198 °C; IR (KBr, cm^{-1}) 3300 (s, br, OH), 1510 (m), 1496 (s), 1400 (s), 1353 (s) 1250, 1120; ^{1}H NMR ($CDCl_3$) δ 2.11 (d, J = 7.2 Hz, 3H), 6.54 (m, 1H), 6.89 (m, 2H), 7.31 (m, 6H), 7.81 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 8.3, 78.4, 118.4, 122.8, 123.4, 127.9, 128.3, 131.0, 133.0, 135.8, 136.9, 149.5; MS (*m*/*z*, rel int) 443 ($M^+ + 1$, 15), 442 (M^+, 55), 236 (7), 234 (6), 191 (22), 190 (100), 174 (21), 171 (12), 162 (20), 144 (36); HRMS M^+ 442.0491 calcd for $C_{22}H_{18}S_2O_6$ 442.0545.

Complexation Studies. A series of aqueous *peri*-sulfonatocalixarene (**6**) solutions of different concentrations were prepared. Naphthalene (215.0 mg) was suspended in each solution of **6** (10.00 mL) in capped test tubes and sonicated for 1 h at room temperature. Residual undissolved naphthalene solid was removed by centrifugation followed by filtration. The intensities of fluorescence emissions of the saturated aqueous naphthalene solutions were measured on a Varian SF-330 spectrofluorometer at 340 nm with excitation at 285 nm.

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Supporting Information Available: High resolution ^{1}H and ^{13}C NMR spectra and mass spectra of compounds **6, 16**−**18**, and **23** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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