

High-Spin Polyarylmethyl Polyradical: Fragment of a Macrocyclic 2-Strand Based upon Calix[4]arene Rings

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Abstract: Annelated triple-calix[4]arene-based tetradecaether **1-(OMe)₁₄** is synthesized. Its three isomers, **1X-(OMe)₁₄**, **1Y-(OMe)₁₄**, **1Z-(OMe)₁₄**, are isolated and characterized. The corresponding triarylmethyl carbopolyanion is prepared and oxidized to polyradical **1**. SQUID magnetometry for **1** in THF-*d*₈/2-MeTHF gives $S = 6.2$, below the theoretical value of 7 expected for strong ferromagnetic coupling between 14 “unpaired” electrons. Chemical quenching studies suggest that approximately one deuterium from the deuterated solvent is incorporated in **1**, thus accounting in part for $S < 7$. Study of the temperature dependence of magnetization indicates that ferromagnetic coupling between “unpaired” electrons is not very strong in **1**; i.e., the thermal population of low-spin excited states is detected in the cryogenic temperature range. Upon exposure of **1** in THF-*d*₈/2-MeTHF to ambient temperature for 30 min, a narrow distribution of spin systems with an “average” $S = 2.5$ is obtained; upon a longer exposure time of 24 h, an “average” $S = 1$ is produced.

Introduction

Two- and three-dimensional networks are prerequisites for numerous interesting magnetic phenomena.¹ Networks of organic π -conjugated polyradicals, in which strong through-bond ferromagnetic couplings are achieved, may provide a route to an organic ferromagnet with a high Curie temperature.^{2,3} From the synthetic point of view, polyradical networks, which are highly annelated polymacrocyclic systems, are difficult targets.^{4,5} Oligomeric fragments of 2-strand are more straightforward synthetic goals (Figure 1).^{3d} Trimeric fragments of 2-strand, with three linearly annelated macrocyclic rings, are especially attractive targets, accessible by convergent synthetic routes. Representative examples of such molecules are provided by annelated calix[4]arenes, annelated macrocyclic DNA strands, or annelated tetra-*o*-phenylenes.^{6,7}

Calix[4]arene-based polyradicals have been shown to have adequate properties as high-spin building blocks.^{4,8,9} Synthesis

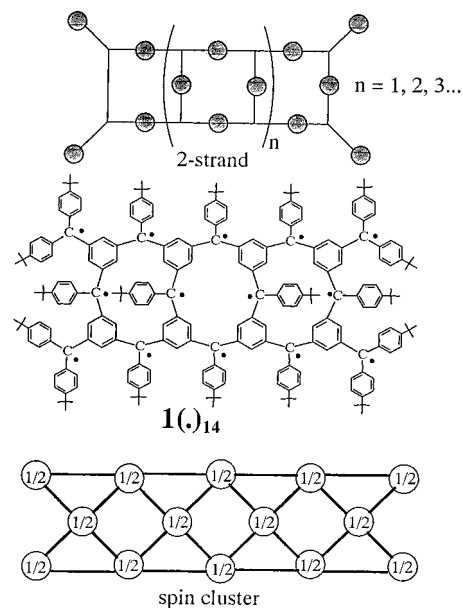


Figure 1. 2-Strand, tetradecaradical **1(•)₁₄** and spin cluster corresponding to **1(•)₁₄**. Full circles in the 2-strand indicate sites for “unpaired” electrons (e.g., triarylmethyl sites). Circles and lines in the spin cluster representation correspond to sites with “unpaired” electrons and spin coupling pathways through 1,3-phenylene moieties, respectively.

and studies of an annelated calix[4]arene, such as the trimacrocyclic tetradecaradical **1(•)₁₄**, is an initial step toward the synthesis of highly annelated polymacrocyclic polyradicals (Figure 1).^{3d}

For a polyradical with high-spin ground state, ferromagnetic coupling between “unpaired” electrons is a prerequisite.¹⁰ For **1(•)₁₄**, this condition is satisfied through linking triarylmethyl sites with 1,3,5-phenylene moieties.^{10,11} However, some “unpaired” electrons will not be generated, due to side (or incomplete) chemical reactions; we refer to such triarylmethyl sites as defects.^{8,12} The high degree of connectivity, associated

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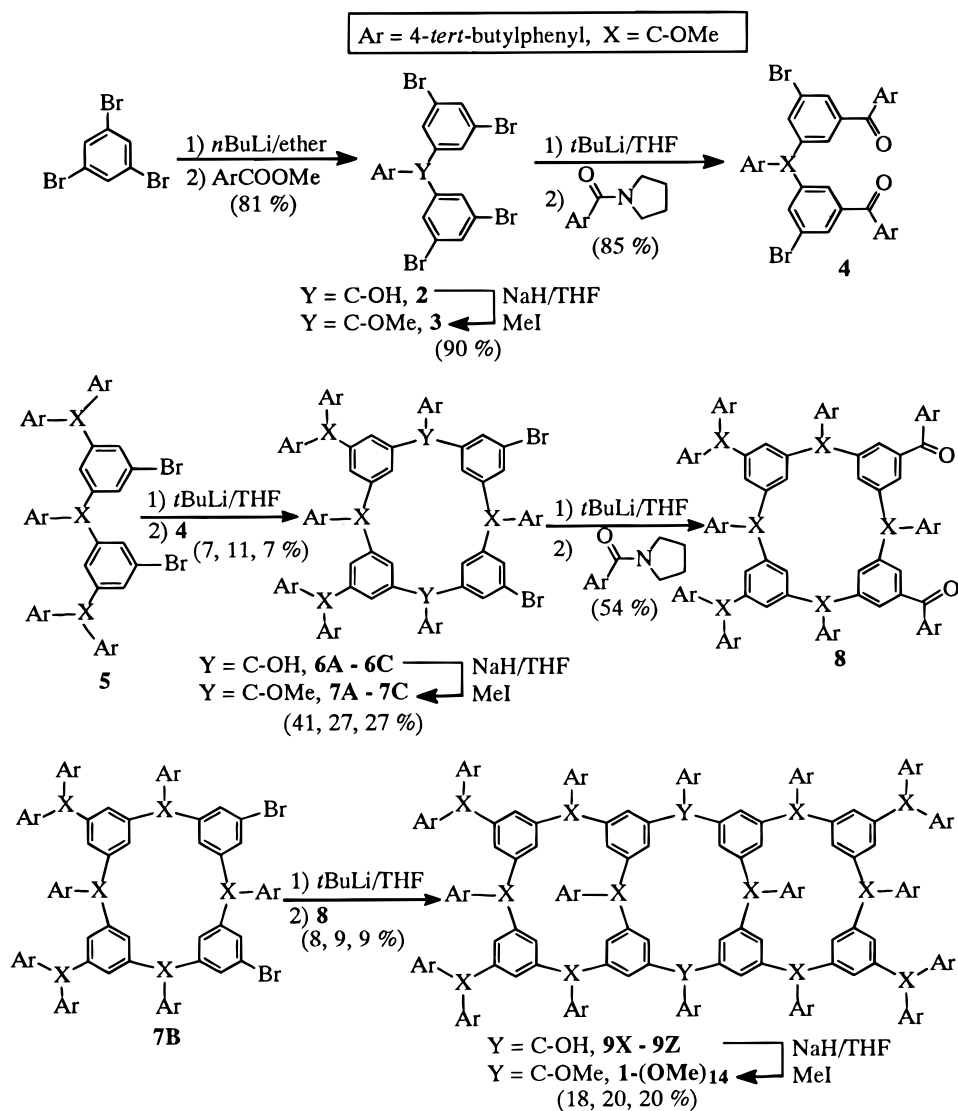
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Scheme 1. Synthesis of Triple-Calix[4]arene Tetradecaethers **1-(OMe)₁₄** (The Three Isolated Isomers Are Labeled **1X-(OMe)₁₄**, **1Y-(OMe)₁₄**, and **1Z-(OMe)₁₄**)

with a 2-strand, as illustrated by a cluster representation for **1(•)₁₄**, may help to maintain π -conjugation and ferromagnetic coupling between all remaining electrons (Figure 1). In order to quantitatively evaluate the impact of defects on ferromagnetic coupling in a high-spin polyradical, it is convenient to define a parameter (Q), the percentage of polyradicals, in which all remaining "unpaired" electrons are contained in a single spin system with uninterrupted coupling.¹³ For example, if a yield for generation of site with "unpaired" electron is 95%, the following values of Q are obtained: 98, 97, and 96% for 2-strands with 14, 26, and 38 sites (Figure 1, $n = 1, 3$, and 5),¹³ 99 and 94% for monomacrocycles with 8 and 14 sites.^{8,13}

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~ 70 and $\sim 50\%$ for dendrimers with 15 and 31 sites,¹⁴ and $\sim 25\%$ for a linear chain with 30 sites.¹⁵ Therefore, high-spin polyradicals, based on 2-strands, should possess ferromagnetic coupling even in the presence of moderate density of defects.

This paper describes synthesis and magnetic studies of 2-strand trimacrocyclic high-spin polyradical.

Results and Discussion

1. Synthesis of Annelated Trimacrocyclic Tetradecaether 1-(OMe)₁₄. The synthesis is based upon a convergent route, i.e., the construction of the two outer calix[4]arene rings precedes the assembly of the center ring. Because of large number of possible cis/trans isomers for **1-(OMe)₁₄**, only one of the most abundant isomers of the outer calix[4]arene ring is used in the synthesis.

Addition of methyl 4-*tert*-butylbenzoate to 2 equiv of monolithiated 1,3,5-tribromobenzene¹⁶ in ether produces alcohol **2**; subsequent etherification of **2** with sodium hydride/iodomethane gives ether **3** (Scheme 1). Double Li/Br exchange of

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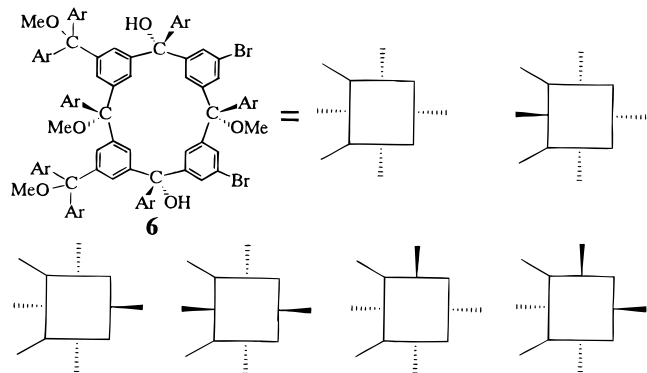


Figure 2. Cis/trans isomers of calix[4]arene diols **6**. “Ar” corresponds to 4-*tert*-butylphenyl.

3 with *t*-BuLi in THF followed by addition of 1-(4-*tert*-butylbenzoyl)pyrrolidine and hydrolysis provides diketone **4**. In the macrocyclization step to form the outer calix[4]arene ring, **5** (0.010 M in THF) is subjected to double Li/Br exchange with *t*-BuLi (1.7 or 1.5 M in pentane); subsequently, diketone **4** (0.025 M in THF) is rapidly cannulated to a precooled (-78°C) solution of the dilithium compound.^{8,17} Four cis/trans isomers for calix[4]arene diol **6** are isolated [**6A** (7%), **6B** (11%), **6C** (7%), and **6D** (variable, very small yields)] in the order of increasing polarity on silica gel. Compounds **6A** and **6B** have no elements of symmetry; **6C** and **6D** have a symmetry plane on the NMR time scale. Among six possible cis/trans isomers for diol **6**, two of them have no elements of symmetry and the other four have a symmetry plane (Figure 2). The two possible nonsymmetrical isomers correspond to **6A** and **6B**.

Etherifications of **6A–C** provide the corresponding isomers **7A–C**. The isomer **7B** is selected for further synthetic transformations. Following conversion of **7B** to diketone **8**, the macrocyclization step to form the center calix[4]arene ring mimics the procedure outlined above, except **7B** and **8** (0.013 M in THF) are used in the place of **5** and **4**.^{8,17} Three isomers are isolated for triple-calix[4]arene diol: **9X** (~8%), **9Y** (~9%), and **9Z** (~9%); the first two isomers have no element of symmetry, and the third one has a 2-fold element of symmetry on the NMR time scale. Etherifications of **9X–Z** give the corresponding tetradecaethers **1X-(OMe)₁₄**, **1Y-(OMe)₁₄**, and **1Z-(OMe)₁₄**.¹⁸

IR spectra show the presence of the OH groups in the products of both macrocyclization steps, calix[4]arene diols **6A–D** and triple-calix[4]arene diols **9X** and **9Y**.

In FAB MS, all 14 macrocyclic intermediates give the expected $(M - \text{OCH}_3)^+$ cluster ions as the most intense signals in the high mass range; the diols show additional, moderately intense $(M - \text{OH})^+$ cluster ions. Measured and calculated isotopic distributions for $(M - \text{OCH}_3)^+$ cluster ions show satisfactory agreement. FAB MS for triple-calix[4]arene **1Y-(OMe)₁₄** is shown in Figure 3.

Most NMR spectra are obtained in CDCl_3 . However, for some polyethers with large number of Ar_3COX ($X = \text{H}, \text{CH}_3$) moieties, benzene-*d*₆ and cyclohexane-*d*₁₂ are used as solvents. For selected diols, **6C**, **6D**, **9Y**, **9Z**, ¹H NMR spectra are also recorded in the presence of small amounts of D₂O in order to identify resonances corresponding to the OH groups.

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(18) Detailed analysis of the possible isomers for the annelated triple-calix[4]arenes is complicated because **7B**, used in the synthesis, corresponds to one of the two nonsymmetrical isomers of **7**. Another problem is the possibility of the noninterconverting (rigid) conformations for the center calix[4]arene ring (ref 6). We thank the reviewer for pointing out rigidity of the center ring in the annelated triple-calix[4]arenes.

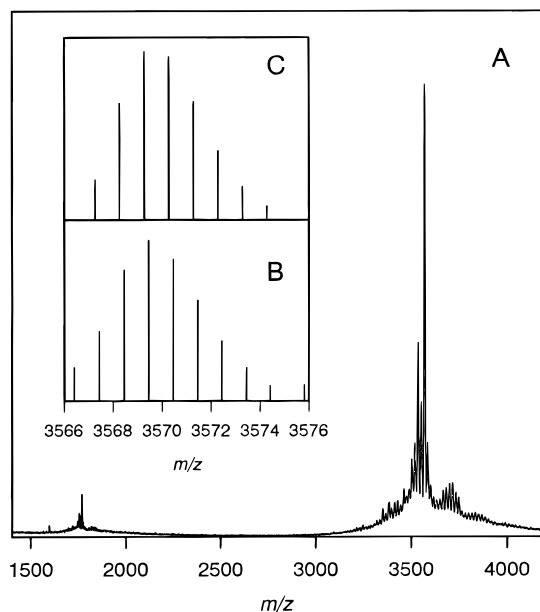


Figure 3. FAB MS for **1Y-(OMe)₁₄**. (A) Partial low-resolution spectrum. (B) Stick plot for the $(M - \text{OCH}_3)^+$ ion cluster from the high-resolution spectrum. (C) Calculated stick plot for the $(M - \text{OCH}_3)^+$ ion cluster with formula $\text{C}_{255}\text{H}_{297}\text{O}_{13}$ at natural isotopic abundance.

¹³C DEPT/NMR spectra are obtained for most synthetic intermediates in Scheme 1, except for all triple-calix[4]arene derivatives, which are available only in small amounts. The spectra are analyzed by comparing numbers of the expected and measured resonances in distinct spectral regions (e.g., quaternary aromatic). Several spectral overlaps are encountered for each calix[4]arene derivative, containing between 47 and 98 nonequivalent carbon atoms. Among the least resolved spectral regions are methyl carbons of the *t*-Bu groups and nonquaternary carbons in the aromatic region.

All compounds with only one calix[4]arene ring have sharp ¹H NMR spectra at ambient temperature. For triple-calix[4]arene derivatives, ¹H NMR spectra at ambient temperature are broadened. However, at elevated temperatures (348 K), sharp spectra are obtained, suggesting fast exchange between conformations on the NMR time scale (Figures 4 and 5).

All synthetic intermediates in Scheme 1 possess ¹H resonances in three regions: aromatic (8.8–6.3 ppm), C-OCH₃/C-OH moieties (3.2–2.1 ppm), and *tert*-butyl groups (1.4–1.1 ppm) (Figures 4 and 5). For selected macrocyclic polyethers, aromatic regions are analyzed with the help of ¹H–¹H COSY correlations. The following discussion of the ¹H NMR spectra for two isomers of triple-calix[4]arene tetradecaether, **1Y-(OMe)₁₄** and **1Z-(OMe)₁₄**, highlights the spectral patterns encountered in all other macrocyclic derivatives described in this work.

The isomer **1Y-(OMe)₁₄**, which lacks elements of symmetry on the NMR time scale, gives the most complex ¹H NMR spectrum in the aromatic region. In the COSY spectrum, there are 48 “singlet” off-diagonal peaks, 32 “quadruplet” off-diagonal peaks, and two singlets without off-diagonal peaks. The 48 “singlet” off-diagonal peaks correlate 24 1-proton triplet ($J \approx 2$ Hz) resonances (eight 3-proton AMX/ABC spin systems), corresponding to the eight inner benzene rings. The 32 “quadruplet” off-diagonal peaks correlate 32 2-proton doublet ($J \approx 9$ Hz) resonances (16 4-proton AX/AB spin systems), corresponding to 16 outer benzene rings (4-*tert*-butylphenyls). The two prominent singlets (at 7.214 and 7.181 ppm) are two

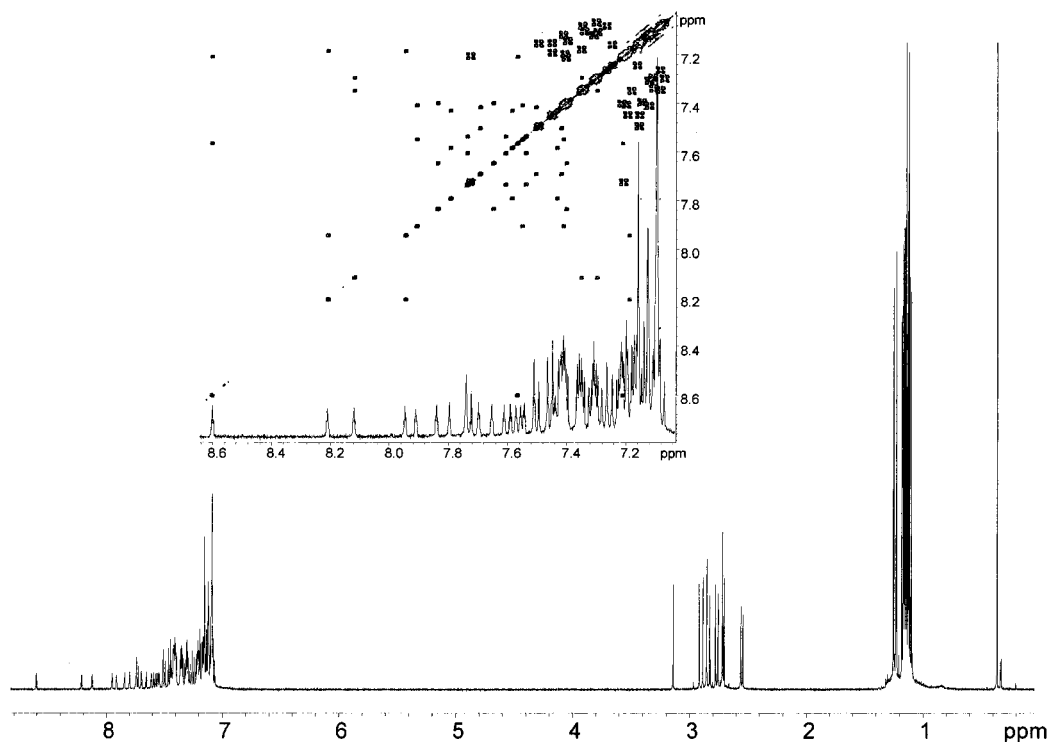


Figure 4. ^1H NMR (500 MHz, C_6D_6) spectrum for $1\text{Y}-(\text{OMe})_{14}$ at 348 K. Main plot: full spectrum, EM = -1.85 , GB = 1.20 . Insert plot: ^1H - ^1H COSY correlation in the aromatic region.

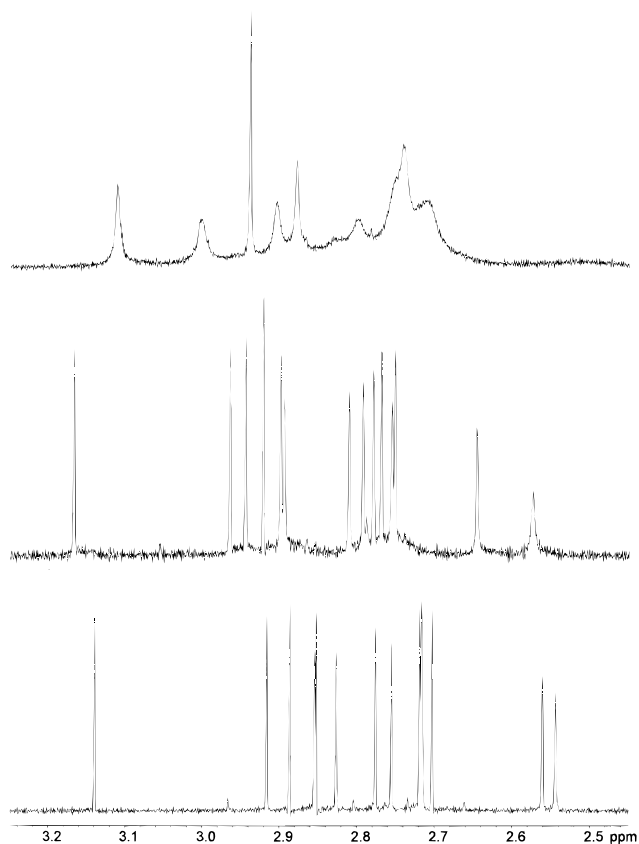


Figure 5. Partial ^1H NMR (500 MHz, C_6D_6) spectra for $1\text{Y}-(\text{OMe})_{14}$ in the C-OCH₃ region. Top: 298 K, EM = 0.10 . Middle: 328 K, EM = -1.85 , GB = 1.20 . Bottom: 348 K, EM = -1.85 , GB = 1.20 .

collapsed 4-proton AB systems, corresponding to the remaining two outer benzene rings (4-*tert*-butylphenyls) (Figure 4).

The symmetrical isomer, $1\text{Z}-(\text{OMe})_{14}$, provides much simpler picture. In the COSY45 spectrum, there are 24 “singlet” and 20 “quadruplet” off-diagonal” peaks. The 24 “singlet” off-

diagonal peaks correlate 12 2-proton triplets ($J \approx 2$ Hz), corresponding to four pairs of the inner benzene rings. The 20 “quadruplet” off-diagonal” peaks correlate 4 2-proton and 16 4-proton doublets ($J \approx 9$ Hz), corresponding to two single and eight pairs of the outer benzene rings.

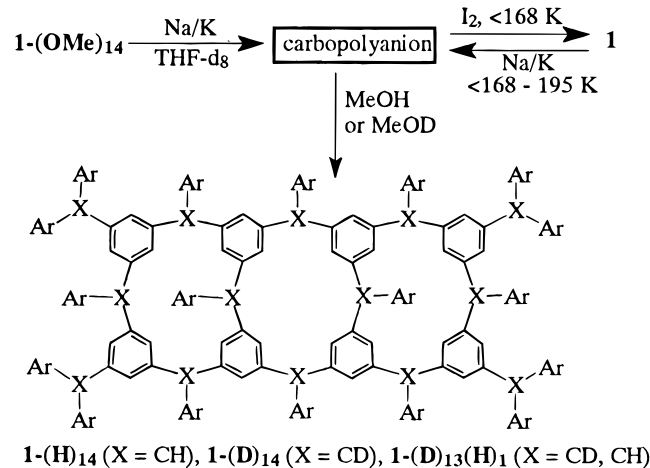
For all 14 macrocyclic intermediates, most peaks are resolved for the C-OCH₃/C-OH moieties, with the exception of accidental spectral overlaps. This spectral region is the best insight into purity of triple-calix[4]arene derivatives. The ^1H NMR spectrum for $1\text{Y}-(\text{OMe})_{14}$ at 348 K shows 12 3-proton and 1 6-proton resonances, in addition to several small peaks. The latter may correspond to another isomer of tetradecaether or an unknown impurity. However, 14 3-proton singlets can be resolved at 328 K (Figure 5). For the symmetrical isomer, $1\text{Z}-(\text{OMe})_{14}$, 6 sharp and 1 broadened 6-proton resonances are found at 348 K.

In the *t*-Bu group region, the number of singlet resonances equals to the number of the AX/AB spin systems with $J \approx 9$ Hz for the aromatic protons, except for accidental spectral overlaps. For $1\text{Y}-(\text{OMe})_{14}$, 14 9-proton and 2 18-proton resonances are resolved. For the symmetrical isomer, $1\text{Z}-(\text{OMe})_{14}$, at 348 K, 5 18-proton and 1 54-proton resonances are resolved, in addition to 1 18-proton resonance overlapped with the signal from the solvent.

The analysis of the ^1H NMR spectra for $1\text{Y}-(\text{OMe})_{14}$ (and, analogously, for $1\text{X}-(\text{OMe})_{14}$) indicates lack of elements of symmetry on the NMR scale for this isomer. However, for $1\text{Z}-(\text{OMe})_{14}$ 2-fold element of symmetry, which divides the center calix[4]arene ring, is found. Eight 4-*tert*-butylphenyls, associated with the exocyclic triarylmethyl centers, appear as four diastereotopic pairs.

2. Preparation and Quenching Studies of Annelated Trimacrocyclic Polyradical 1. In these studies, isomers, $1\text{X}-(\text{OMe})_{14}$, $1\text{Y}-(\text{OMe})_{14}$, and $1\text{Z}-(\text{OMe})_{14}$ are typically used as a mixture, designated as $1-(\text{OMe})_{14}$. Polyradicals are generated by the sequential procedure, similar to that described previ-

Scheme 2. Generation of Polyradical **1** and Quenching Studies Where "Ar" Corresponds to 4-*tert*-Butylphenyl



ously,^{19,20} but with modifications to accommodate micromolar scale (Scheme 2).

Treatment of tetradecaether **1-(OMe)₁₄** with an excess of Na/K alloy in tetrahydrofuran (THF) or tetrahydrofuran-*d*₈ (THF-*d*₈) gives red solutions of the corresponding carbopolyanion. A quenching experiment is carried out in order to verify structure of carbopolyanion. When the carbopolyanion is prepared in THF and treated with MeOH, hydrocarbon **1-(H)₁₄** is isolated. The ¹H NMR spectra of **1-(H)₁₄** consist of broad resonances suggesting a complex mixture of isomers possessing aromatic, triarylmethane (Ar₃CH), and *tert*-butyl hydrogens and devoid of CH₃O groups. FAB MS shows (M - H)⁺ ion cluster, with the most intense isotopic component at *m/z* 3179.1.²¹

Oxidation of the carbopolyanion in THF-*d*₈ with I₂, at the temperatures close to the freezing point of the reaction mixture, gives the annelated trimacrocylic polyradical **1**. [The addition of I₂ in small portions is accompanied by transfers of small amounts of THF-*d*₈ or 2-methyltetrahydrofuran (2-MeTHF).] Part of the reaction mixture is transferred at low temperature to a quartz tube, flame sealed, and stored in liquid nitrogen for magnetic studies; the remaining reaction mixture in the oxidation vessel is stirred with Na/K alloy at low temperature and, subsequently, treated with MeOH or MeOD.

The hydrocarbon product isolated from the MeOH-quench of polyradical **1** in THF-*d*₈ gives a ¹H NMR spectrum similar to that for **1-(H)₁₄**. However, FAB MS shows an ion cluster with identical isotopic peak height pattern, which is shifted by +1 amu, compared to that for **1-(H)₁₄**.^{22,23} This discrepancy may result from errors in integrations in the ¹H NMR spectrum. Because of large numbers of protons and broadness of peaks, such errors may be on the order of |1H|. These results are compatible with **1-(H)₁₃(D)₁** (D₁ isotopomer of **1-(H)₁₄**), for which (M - H)⁺ cluster is observed in FAB MS.

The hydrocarbon product isolated from MeOD quench of polyradical **1** in 2-MeTHF/THF-*d*₈ gives a ¹H NMR spectrum with integration suggesting presence of approximately two triarylmethane hydrogens. Also, a broad singlet at the chemical

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(21) Isotopic intensities in FAB MS for low molecular weight calix[4]-arene-based polyarylmethanes are compatible with M⁺ and (M + H)⁺ clusters (ref 8).

(22) The +1 amu mass shift of the (M - H)⁺ clusters between **1-(H)₁₄** and **1-(H)₁₃(D)₁** was confirmed by repeating FAB MS analysis for both compounds, using a narrow mass range, high-resolution scan with identical mass calibration.

(23) The amount of **1-(H)₁₃(D)₁** was insufficient to permit observation of its ²H NMR spectrum in a reasonable acquisition time.

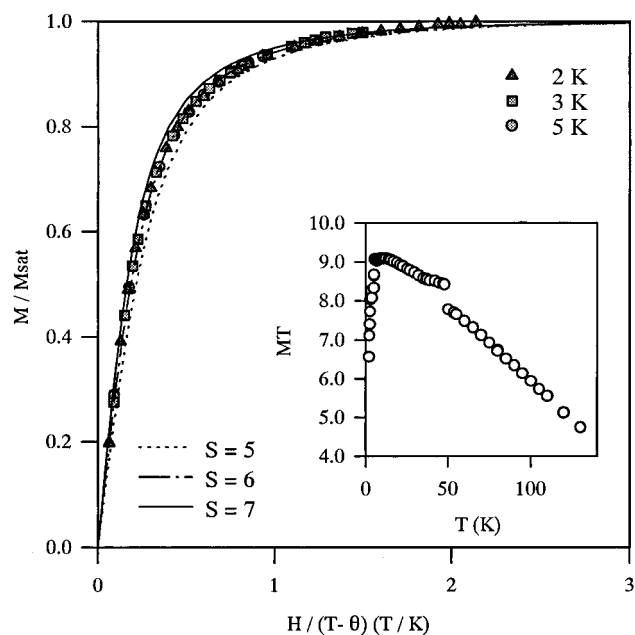


Figure 6. SQUID magnetometry ($H = 0\text{--}5.0$ T) for polyradical **1** in THF-*d*₈/2-MeTHF. Main plot: M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.34$ K; the experimental points are obtained at $T = 2, 3,$ and 5 K. The lines correspond to the $S = 5, 6,$ and 7 Brillouin functions. The fitting parameters at $T = 2, 3,$ and 5 K are $S = 6.20, 6.22,$ and 6.20 and $M_{\text{sat}} \times 10^3 = 6.03, 6.03,$ and 5.98 emu; the parameter dependence is $0.33, 0.44,$ and 0.60 . Inset: plot of MT vs T at $H = 0.5$ T.

shift corresponding to triarylmethane deuteria is observed in the ²H NMR spectrum. FAB MS shows an ion cluster with significantly wider isotopic distribution, shifted by +12/13 amu, compared to that for **1-(H)₁₄**. Because of the possible isotope effects, the contributions of (M - D)⁺, (M - H)⁺, and other plausible clusters to the overall intensity is not known; consequently, the relative amounts of D₁₄-D₁₁ isotopomers are difficult to estimate. This product, labeled **1-(D)₁₄**, corresponds to a distribution of highly deuterated isotopomers of **1-(H)₁₄**.

Magnetization (M) is measured as a function of magnetic field ($H = 0\text{--}5.0$ T) and temperature ($T = 1.8\text{--}130$ K) for 0.001 M **1** in THF-*d*₈/2-MeTHF or **1** in THF-*d*₈, using a SQUID magnetometer.

For **1** in THF-*d*₈/2-MeTHF, the M vs H data at $T = 2, 3,$ and 5 K are initially fit to a Brillouin function, M vs H/T , with two variable parameters, spin, S , and magnetization at saturation, M_{sat} . However, temperature-dependent values of S are obtained, suggesting presence of small antiferromagnetic interactions. Introduction of a mean-field parameter, $\theta = -0.34$, i.e., replacing H/T with $H/(T - \theta)$, gives an adequate fit with $S = 6.2$ (Figure 6).²⁴ When the sample is melted at 130 K and, then, slowly refrozen in the magnetometer, S does not change but $|\theta|$ decreases from 0.34 to 0.23. Analogous analysis for **1** in THF-*d*₈ gives $S = 5.8$ and a very small $|\theta| < 0.05$ K ($\theta < 0$) but the fit to Brillouin function is not as good as for the sample with $S = 6.2$ (Figure 7). Increasing temperature of the sample to 170 K, followed by slow cooling in the magnetometer, also decreases $|\theta|$.

The M vs T data at constant $H = 0.5$ T are plotted as MT vs T (Figures 6 and 7, insert plots). A downward turn of the plot at low T is consistent with both negative mean-field parameter ($\theta < 0$) and partial saturation of M at low T . More important is the downward slope at high T , suggesting thermal population of low-spin excited states; that is, the intramolecular ferromagnetic coupling is not strong.

(24) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. Also, see: note 28.

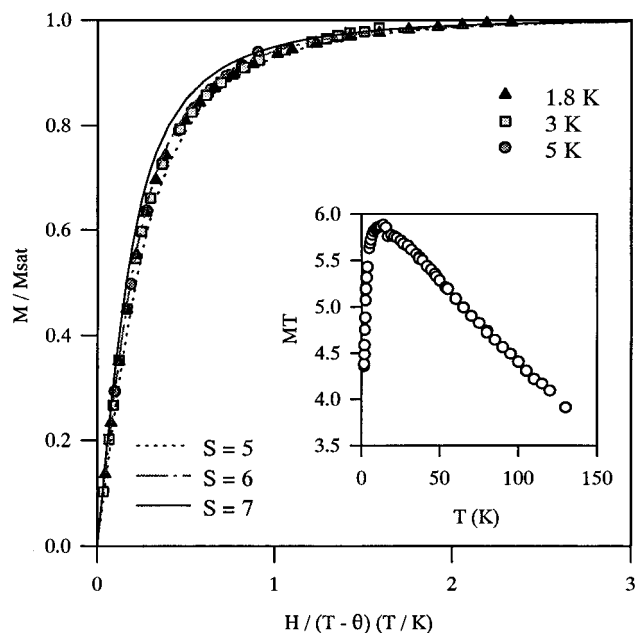


Figure 7. SQUID magnetometry ($H = 0\text{--}4.8$ T) for polyradical **1** in THF- d_8 . Main plot: M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.025$ K; the experimental points are obtained at $T = 1.8, 3,$ and 5 K. The lines correspond to the $S = 5, 6,$ and 7 Brillouin functions. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 5.77, 5.78,$ and 5.76 and $M_{\text{sat}} \times 10^3 = 3.85$ emu at all temperatures; the parameter dependence is $0.29, 0.42,$ and 0.63 . Inset: plot of MT vs T at $H = 0.5$ T.

The lower value of S , compared to the theoretical $S = 7$ for a perfect high-spin tetradecaradical, may be explained by the presence of defects. Quenching experiments suggest that in the reaction sequence in Scheme 2, one deuteron (or deuterium) is abstracted from the solvent, at the stage of carbopolyanion (or tetradecaradical); this would lead to a polyradical with $S = 6.5$. Furthermore, inadvertent moisture, excess of I_2 , dimerization, etc., could further lower the average S to the observed value of $S = 6.2$ for **1** in THF- d_8 /2-MeTHF and $S = 5.8$ for **1** in THF- d_8 . Differences in values of S between the two types of samples may arise from different temperatures at which their oxidations are carried out; that is, the melting points (or softening range) of the two reaction mixtures are significantly different. The sites of the defects, corresponding to lowering value of S from 7 to 6.2 and 5.8, could not rigorously be determined.

For isolated polyradicals, in which intramolecular ferromagnetic coupling between all its "unpaired" electrons is associated with energy exceeding RT (strong coupling), the data M vs H/T should follow one Brillouin function and the plot MT vs T should be flat throughout the T range; i.e., the polyradical would behave as a perfect paramagnet. The drop off in the MT vs T plot at high T suggests the presence of low-lying low-spin excited state(s). One of the possible structures is shown in Figure 8. Our speculation is that strain in the center calix[4]arene ring may increase basicity of its arylmethyl carbanion sites and, therefore, facilitate formation of the defect. Furthermore, severe twisting of arylmethyl bonds around the remaining site with "unpaired" electron in the center calix[4]-arene ring could weaken the spin coupling. Therefore, the resultant structure could be approximated as a trimer of $S_1 = 1/2, S_2 = S_3 = 3$. For such symmetric trimer, the Heisenberg hamiltonian, $-2J(S_1S_2 + S_1S_3)$, is analytically solvable;^{25,26} elucidation of eigenvalues reveals that the energy difference between the $S = 13/2$ ground state and $S = 11/2$ lowest excited

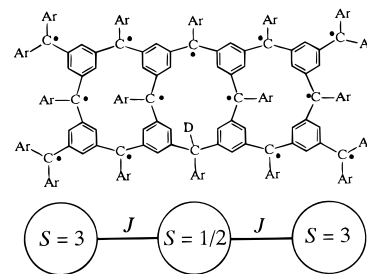


Figure 8. Tentative structure for polyradical **1** and the corresponding symmetric trimer model. "Ar" corresponds to 4-*tert*-butylphenyl.

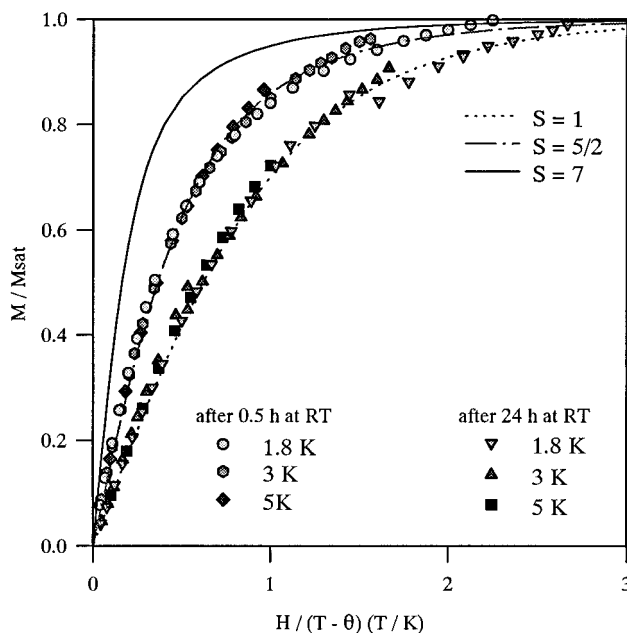


Figure 9. SQUID magnetometry ($H = 0\text{--}5.0$ T) for polyradical **1** in THF- d_8 /2-MeTHF, following exposure to ambient temperature. (The initial value of S is 6.2, see Figure 6.) The lines correspond to the Brillouin functions with $S = 7, 5/2,$ and 1 . After 0.5 h at ambient temperature, the M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.20$ K, plot corresponds to the experimental points at $T = 1.8, 3,$ and 5 K. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 2.56, 2.54,$ and 2.59 and $M_{\text{sat}} \times 10^3 = 2.62, 2.62,$ and 2.61 emu; the parameter dependence is $0.41, 0.62,$ and 0.84 . After 24 h at ambient temperature, the M/M_{sat} vs $H/(T - \theta)$, $\theta = 0$ K, plot corresponds to the experimental points at $T = 1.8, 3,$ and 5 K. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 1.04, 1.14,$ and 1.13 and $M_{\text{sat}} \times 10^3 = 1.13, 1.11,$ and 1.12 emu; the parameter dependence is $0.52, 0.80,$ and 0.96 .

state is only J . For **1** in THF- d_8 , the MT vs T data are fit to the trimer model with $J/k \approx 70$ K.^{27,28} This J/k should be scaled by a factor of 2 to obtain J'/k across "twisted" 1,3-phenylene moieties in the center calix[4]arene ring, i.e., $J'/k \approx 140$ K.²⁹

The small but significant value $|\theta|$, ($\theta < 0$) of the mean-field correction, especially for more concentrated **1** in THF- d_8 /2-MeTHF, suggests small antiferromagnetic interactions for

(27) Adequate fit to the trimer model requires introduction of a third variable parameter, M_{dia} (J and number of moles, N , are the other two parameters) to account for a small error (ca. 1%) of point-by-point correction for diamagnetism. Standard errors and parameter dependencies for variable parameters are as follows: 3% and 0.97 (J), 0.1% and 0.51 (N), 5% and 0.97 (M_{dia}).

(28) Consideration of simple Boltzmann factors shows that population of the excited states in the 1.8–5 K range is negligible for the model trimer with $J/k = 70$ K. More rigorously, when $M(H, T)$ is calculated for the model trimer, excellent fits to Brillouin function at $T = 1.8, 3,$ and 5 K, with two variable S and M_{sat} , are obtained; i.e., $S = 6.500$ in the 1.8–5 K range, as expected for the ground trimer.

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polyradicals in frozen solution. Determination of whether these antiferromagnetic interactions are intra- or intermolecular by dilution studies is hampered by the lack of sufficient amount of tetradecaether precursors for polyradical.

Interestingly, when 0.001 M **1** in THF-*d*₈/2-MeTHF is measured after exposures to ambient temperature for 30 min and 24 h, the *M* vs *H* data approximately follow Brillouin functions and indicate decrease of *S* from the original value of 6.2 to ~2.5 and ~1, respectively (Figure 9). Also, $M_{\text{sat}} \times 10^3$, which is linearly related to the number of "unpaired" electrons in the sample, decreases from 6.0 to 2.6 and 1.1 emu, respectively. However, M_{sat}/S , which is linearly related to number of moles of spin systems with an "average" *S*, is approximately constant for the samples with *S* = 6.2, ~2.5, and ~1. Surprisingly, thermal decomposition of **1** does not interrupt ferromagnetic coupling between the remaining "unpaired" electrons; i.e., the "unpaired" electrons belong to a single ferromagnetically coupled spin system.

Conclusion

A trimeric fragment of 2-strand, based on calix[4]arene macrocycles, provides polyradical with high-spin ground state. The measured value of spin, *S* = 6.2, is below the theoretical value of 7. Quenching studies suggest presence of defects; i.e., not all 14 but only 12 or 13 "unpaired" electrons are generated in polyradical **1**. Furthermore, ferromagnetic coupling between these "unpaired" electrons is relatively weak, compared to that of typical 1,3-phenylene-based polyarylmethyls, presumably, because of out-of-plane distortion of the π -conjugated system.

Two- or three-dimensional net will require careful design to accommodate π -conjugation, connectivity compatible with ferromagnetic coupling, adequate steric hindrance to stabilize radical sites, and efficient synthetic methodology.

Experimental Section

Materials and Special Procedures. Ether and tetrahydrofuran (THF) for use on vacuum line were distilled from sodium/benzophenone in a nitrogen atmosphere. Iodine (99.999%, resublimed crystals, ultradry) was obtained from Johnson-Mathey. THF-*d*₈ (99.95% D), which was obtained from Cambridge Isotope Labs, was doubly vacuum transferred from sodium/benzophenone prior to the use. *t*-BuLi was obtained from either Aldrich (1.7 M in pentane) or Across (1.5 M in pentane). Other major chemicals, including MeOD (99.5+% D), were obtained from Aldrich. Synthesis of dibromotriether **5** was previously described.⁸ Vacuum lines (10^{-3} Torr) were used for all air-sensitive synthetic procedures.²⁰

NMR Spectroscopy and Other Analyses. NMR spectra were obtained with Omega spectrometers (¹H, 300 and 500 MHz) in CDCl₃, benzene-*d*₆, and acetone-*d*₆; the chemical shift references were ¹H (TMS, 0.0 ppm; benzene-*d*₆, 7.15 ppm; acetone-*d*₆, 2.04 ppm) and ¹³C (CDCl₃, 77.0 ppm). Coupling constants (*J*) are given in hertz. Unless indicated otherwise, exponential multiplications (EM) of 0.1 and 1.0 Hz, prior to Fourier transform, were used for ¹H and ¹³C NMR spectra, respectively. For those selected ¹H and ¹³C NMR spectra, where spectral resolution was enhanced by combination of exponential multiplication and Gaussian broadening (GB), prior to Fourier transform, parameters EM and GB are shown with the spectral data. ²H NMR spectrum for **1-(D)**₁₄ (and attempted spectrum for **1-(H)**₁₃(**D**)₁) in acetone was obtained without lock (40 000 scans, 0.13 s acquisition time). IR spectra were obtained as previously described.¹⁴

Elemental analyses were completed by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85060.

Alcohol 2. *n*-BuLi (24.0 mL of a 2.5 M solution in hexanes, 60.0 mmol) was added dropwise to 1,3,5-tribromobenzene (18.89 g, 60.0 mmol) in ether (500 mL) at -78 °C. After 2 h, methyl 4-*tert*-butylbenzoate (5.174 g, 26.92 mmol) in ether (20 mL) was added to the above reaction mixture. The reaction mixture was allowed to warm to ambient temperature overnight. After the reaction was quenched

with water and the solution was extracted with ether, the ether layer was washed with water and brine and then dried over MgSO₄. Concentration in vacuo gave a brown solid (19.43 g). Recrystallization from hexane gave 13.86 g (81%) of light yellow crystals. From three reactions on the 18 g scale, 41.15 g (81%) of alcohol **2** was obtained from 15.52 g of methyl 4-*tert*-butylbenzoate; mp 146 °C; ¹H NMR (CDCl₃) 7.615 (t, *J* = 2, 2 H), 7.431 (d, *J* = 2, 4 H), 7.382 (d, *J* = 8.5, 2 H), 7.069 (d, *J* = 8.5, 2 H), 2.678 (s, 1 H), 1.332 (s, 9 H); ¹³C{¹H}-DEPT(135°) NMR (CDCl₃) 151.7, 149.5, 141.5, 133.4, 129.5, 127.4, 125.7, 122.9, 80.5, 34.6, 31.2; CH, CH₃ 133.4, 129.5, 127.4, 125.7, 31.2.

Ether 3. Sodium hydride (4.16 g of 60% dispersion in mineral oil, 0.104 mol) was washed with pentane under nitrogen flow followed by addition of THF (215 mL). The resultant suspension was cooled to 0 °C. A solution of alcohol **2** (13.14 g, 20.79 mmol) in THF was added to the suspension, followed, after 1 h, by iodomethane (20.8 mL, 0.333 mol). The reaction mixture was allowed to warm to ambient temperature and followed with TLC until the starting material was not detectable. After extraction with ether, the combined organic layer was washed with water and brine and then dried over MgSO₄. Concentration in vacuo gave a light yellow solid, which was recrystallized from MeOH/ether to give two crops of colorless crystals (12.41 g, 92%) of ether **3**. From three reactions on the 13 g scale, 37.67 g (90%) of ether **3** was obtained from 40.90 g of alcohol **2**: mp 180 °C; ¹H NMR (CDCl₃) 7.565 (t, *J* = 2, 2 H), 7.516 (d, *J* = 2, 4 H), 7.378 (d, *J* = 8.5, 2 H), 7.177 (d, *J* = 8.5, 2 H), 3.007 (s, 3 H), 1.337 (s, 9 H); ¹³C{¹H}DEPT(135°) NMR (CDCl₃) 151.3, 147.9, 136.6, 133.1, 129.9, 129.1, 125.3, 122.7, 85.5, 52.2, 34.6, 31.3; CH, CH₃ 133.1, 129.8, 129.1, 125.3, 52.2, 31.3. Anal. Calcd for C₂₄H₂₂OBr₄: C, 44.62; H, 3.43. Found: C, 44.54; H, 3.77.

Diketone 4. *t*-BuLi (26.3 mL of a 1.5 M solution in pentane, 39.5 mmol) was added to ether **3** (6.380 g, 9.876 mmol) in THF (200 mL) at -78 °C over a period of 20 min. After 3 h, 1-(4-*tert*-butylbenzoyl)-pyrrolidine (5.018 g, 21.72 mmol) in THF (100 mL) was quickly added to the reaction mixture. The reaction mixture was allowed to warm to ambient temperature overnight. After the reaction was quenched with water and the solution was extracted with ether, the combined organic layer was washed with water and brine and then dried over MgSO₄. Concentration in vacuo gave a light yellow solid (9.085 g). Column chromatography (silica gel, 230–400 mesh, 5% ether in hexane) produced 7.290 g (91%) of colorless solid of diketone **4**, which was of sufficient purity for the next step in the synthesis. From four reactions on the 3, 4, and 6 g scales, 21.71 g (85%) of diketone **4** was obtained from 20.42 g of ether **3**. A sample for elemental analysis was obtained by additional treatment with MeOH (to remove residual hexanes): mp 128–130 °C; FAB MS (ONPOE), *m/z* (% RA for *m/z* 300–810) at (*M* + *H*)⁺ 807.1 (50), 808.1 (30), 809.1 (100), 810.1 (50), 811.1 (60), 812.1 (20) at (*M* - OCH₃)⁺ 775.1 (25), 776.1 (15), 777.1 (50), 778.1 (30), 779.1 (30), 780.1 (15); calcd. for C₄₆H₄₉O₃Br₂ at (*M* + *H*)⁺ 807.2 (50), 808.2 (30), 809.2 (100), 810.2 (50), 811.2 (60), 812.2 (30); ¹H NMR (CDCl₃) 7.904 (t, *J* = 2, 2 H), 7.826 (t, *J* = 2, 2 H), 7.715 (t, *J* = 2, 2 H), 7.666 (d, *J* = 8.5, 4 H), 7.456 (d, *J* = 8.9, 4 H), 7.367 (d, *J* = 8.5, 4 H), 7.248 (d, *J* = 8.5, 4 H), 3.046 (s, 3 H), 1.333 (s, 18 H), 1.332 (s, 9 H); ¹³C{¹H}DEPT(135°) NMR (CDCl₃) 194.3, 156.9, 151.2, 146.6, 139.5, 137.2, 134.1, 133.8, 131.5, 130.2, 129.0, 128.4, 125.5, 125.3, 122.6, 86.0, 52.2, 35.1, 34.5, 31.3, 31.1. CH, CH₃: 134.1, 131.6, 130.2, 129.0, 128.3, 125.5, 125.3, 52.2, 31.3, 31.0. Anal. Calcd for C₄₆H₄₈O₃Br₂: C, 68.32; H, 5.98. Found: C, 68.29; H, 6.17.

Calix[4]arene Diols 6. *t*-BuLi (5.90 mL of 1.7 M solution in pentane, 10.0 mmol) was added to a solution of dibromo triether **5** (2.764 g in 250 mL of THF, 2.50 mmol) at -78 °C. After 1 h, a solution of diketone **4** (2.022 g in 100 mL of THF, 2.50 mmol) was cannulated to the reaction mixture. The reaction mixture was allowed to warm to ambient temperature overnight. After the reaction was quenched with water (25 mL) and the solution was extracted with ether, the combined organic layer was washed with water and brine and then dried over MgSO₄; concentration in vacuo gave a yellow solid. Column chromatography (TLC grade silica gel, hexane/ether, 6 to 9%) produced three isomers (in the order of increasing polarity on silica gel) **6A**, **6B**, and **6C**, which were of sufficient purity for the next step in the synthesis. For example, from eight reactions on the 1 and 2 g scales, 1.941 g of **6A** (7%), 3.250 g of **6B** (11%), and 2.021 g of **6C** (7%) were obtained

from 17.956 g of dibromo triether **5**. In selected runs, a small amount of the fourth isomer **6D** was isolated.

For 6A: FAB MS (ONPOE), m/z (% RA for m/z 400–2000) at $(M - OCH_3)^+$ 1721.8 (50), 1722.8 (60), 1723.8 (100), 1724.8 (95), 1725.8 (85), 1726.8 (65), 1727.8 (35) at $(M - OH)^+$ 1735.7 (20), 1736.7 (25), 1737.7 (45), 1738.7 (45), 1739.7 (40), 1740.7 (30), 1741.7 (15); calcd for $C_{113}H_{127}O_5Br_2$ at $(M - OCH_3)^+$ 1721.8 (35), 1722.8 (45), 1723.8 (100), 1724.8 (100), 1725.8 (95), 1726.8 (70), 1727.8 (35), 1728.8 (15); 1H NMR (500 MHz, EM = -1.9, GB = +0.9, $CDCl_3$) 7.534 (t, J = 2, 1 H), 7.492 (t, J = 2, 1 H), 7.439–7.421 (m, 4 H), 7.360 (t, J = 2, 1 H), 7.273 (t, J = 2, 1 H), 7.258–7.256 (m, 4 H), 7.240–7.054 (m, 22 H), 7.015 (d, J = 9, 2 H), 6.912–6.895 (m, 3 H), 6.805 (d, J = 9, 2 H), 6.769 (t, J = 2, 1 H), 6.635 (t, J = 2, 1 H), 6.337 (t, J = 2, 1 H), 2.859 (s, 3 H), 2.722 (s, 3 H), 2.764 (s, 3 H), 2.745 (s, 2 H), 2.721 (s, 3 H), 1.311 (s, 9 H), 1.301 (s, 9 H), 1.290 (s, 9 H), 1.271 (s, 9 H), 1.263 (s, 27 H), 1.238 (s, 9 H); $^{13}C\{^1H\}$ DEPT(135°) NMR (125 MHz, EM = -1.1, GB = +0.9, $CDCl_3$) aromatic quaternary region expected 28 resonances, found 27 resonances at 150.5 (q), 150.2 (q), 150.1 (q), 149.7 (q), 149.40 (q), 149.36 (q), 149.32 (q), 149.0 (q), 148.7 (q), 146.1 (q), 145.6 (q), 145.3 (q), 144.8 (q), 144.4 (q), 143.8 (q), 143.31 (q), 143.27 (q), 143.24 (q), 142.9 (q), 141.10 (q), 141.04 (q), 140.98 (q), 140.87 (q), 139.0 (q), 138.3 (q), 122.0 (q), 121.8 (q); aromatic nonquaternary region expected 28 resonances, found 28 resonances at 129.7, 129.4, 129.3, 129.0, 128.8, 128.7, 128.41, 128.40, 128.34, 128.25, 127.9, 127.8, 127.60, 127.55, 127.44, 127.37, 127.1, 126.0, 125.8, 125.6, 124.8, 124.7, 124.6, 124.5, 124.41, 124.36, 124.34, 124.32; aliphatic region 87.1 (q), 86.9 (q), 86.7 (q), 86.2 (q), 81.8 (q), 81.4 (q), 52.1, 52.0, 51.96, 51.9, 34.46 (q), 34.43 (q), 34.41 (q), 34.37 (q), 34.35 (q), 31.38, 31.37, 31.34, 31.32; IR (cm^{-1}) 3500 (O–H), 1596 (Ar).

For 6B: FAB MS (ONPOE), m/z (% RA for m/z 400–1800) at $(M - OCH_3)^+$ 1720.9 (10), 1721.9 (45), 1723.0 (55), 1724.0 (100), 1725.0 (90), 1726.0 (85), 1727.0 (60), 1728.0 (30); at $(M - OH)^+$ 1736.0 (20), 1737.0 (25), 1737.9 (40), 1738.9 (40), 1739.9 (35), 1741.0 (25), 1742.0 (10); 1H NMR (500 MHz, EM = -1.9, GB = +0.9, $CDCl_3$) 7.482–7.472 (m, 2 H), 7.461 (t, J = 2, 1 H), 7.442 (t, J = 2, 1 H), 7.420 (t, J = 2, 1 H), 7.300 (t, J = 2, 1 H), 7.246–6.968 (m, 33 H), 6.868 (t, J = 2, 2 H), 6.829 (t, J = 2, 1 H), 6.635 (t, J = 2, 1 H), 2.849 (s, 3 H), 2.823 (s, 3 H), 2.770 (s, 3 H), 2.684 (s, 3 H), 2.608 (s, 1 H), 2.585 (s, 1 H), 1.288 (s, 9 H), 1.282 (s, 9 H), 1.280 (s, 9 H), 1.272 (s, 18 H), 1.270 (s, 9 H), 1.266 (s, 9 H), 1.260 (s, 9 H); $^{13}C\{^1H\}$ -DEPT(135°) NMR (125 MHz, EM = -1.2, GB = +2.0, $CDCl_3$) aromatic quaternary region expected 28 resonances, found 27 resonances at 150.3 (q), 150.2 (q), 150.0 (q), 149.52 (q), 149.46 (q), 149.43 (q), 149.34 (q), 149.30 (q), 148.81 (q), 148.78 (q), 145.32 (q), 145.21 (q), 145.16 (q), 145.10 (q), 143.7 (q), 143.6 (q), 143.24 (q), 143.21 (q), 142.9 (q), 142.7 (q), 141.4 (q), 141.3 (q), 140.6 (q), 140.1 (q), 138.9 (q), 122.0 (q), 121.8 (q); aromatic nonquaternary region expected 28 resonances, found 24 resonances at 130.0, 129.6, 129.2, 128.9, 128.64, 128.59, 128.48, 128.14, 128.11, 128.06, 127.9, 127.8, 127.48, 127.44, 127.39, 126.72, 126.66, 125.0, 124.73, 124.64, 124.56, 124.47, 124.39, 124.36; aliphatic region 87.0 (q), 86.8 (q), 86.7 (q), 86.2 (q), 81.63 (q), 81.60 (q), 52.2, 52.1, 52.0, 34.4 (q), 34.47 (q), 34.34 (q), 31.42, 31.37; IR (cm^{-1}) 3500 (O–H), 1598 (Ar).

For 6C: FAB MS (3-NBA) m/z (% RA for m/z 400–2000) at $(M - OCH_3)^+$ 1721.8 (50), 1722.8 (60), 1723.8 (100), 1724.8 (95), 1725.8 (85), 1726.8 (60), 1727.8 (30), 1728.8 (10); at $(M - OH)^+$ 1735.8 (20), 1736.8 (25), 1737.8 (40), 1738.8 (40), 1739.8 (35), 1740.8 (25), 1741.8 (15). 1H NMR (500 MHz, EM = -1.9, GB = +0.9, $CDCl_3$) 7.473 (t, J = 2, 2 H), 7.465 (t, J = 2, 2 H), 7.421 (t, J = 2, 2 H), 7.318 (d, J = 9, 4 H), 7.272 (t, J = 2, 2 H), 7.230–7.212 (m, 8 H), 7.088 (d, J = 9, 2 H), 7.001 (d, J = 9, 4 H), 6.944 (d, J = 9, 4 H), 6.867 (d, J = 9, 2 H), 6.732 (t, J = 2, 2 H), 6.456 (t, J = 2, 2 H), 2.819 (s, 6 H), 2.797 (s, 2 H, exch. D_2O), 2.751 (s, 3 H), 2.589 (s, 3 H), 1.328 (s, 18 H), 1.300 (s, 9 H), 1.287 (s, 18 H), 1.274 (s, 9 H), 1.270 (s, 18 H); $^{13}C\{^1H\}$ DEPT(135°) NMR (125 MHz, EM = -1.1, GB = +0.9, $CDCl_3$) aromatic quaternary region expected 16 resonances, found 15 resonances at 150.4 (q), 149.8 (q), 149.5 (q), 149.4 (q), 148.7 (q), 145.1 (q), 145.0 (q), 143.9 (q), 143.4 (q), 142.6 (q), 141.2 (q), 140.8 (q), 140.5 (q), 139.7 (q), 122.0 (q); aromatic nonquaternary region expected 16 resonance, found 14 resonances at 130.1, 129.8, 128.5, 128.4, 128.3, 127.9, 127.7, 127.5, 127.46, 127.4, 126.2, 124.8, 124.5, 124.4; aliphatic region 87.1 (q), 86.7 (q), 86.2 (q), 81.9 (q), 52.05, 51.97, 51.94, 34.49

(q), 34.40 (q), 34.38 (q), 34.36 (q), 31.40, 31.37, 31.33; IR (cm^{-1}) 3500 (O–H), 1599 (Ar).

For 6D: FAB MS (3-NBA) m/z (% RA for m/z 400–2300) at $(M - OCH_3)^+$ 1721.9 (45), 1722.9 (55), 1723.9 (100), 1724.9 (95), 1725.9 (85), 1726.9 (60), 1727.9 (30), 1728.9 (10); at $(M - OH)^+$ 1736.0 (15), 1737.0 (20), 1738.0 (40), 1739.0 (35), 1740.0 (35), 1741.0 (20), 1742.0 (10); 1H NMR (500 MHz, EM = -1.1, GB = +0.5, $CDCl_3$) 7.467 (t, J = 2, 2 H), 7.447 (t, J = 2, 2 H), 7.372 (t, J = 2, 2 H), 7.355 (t, J = 2, 2 H), 7.318 (d, J = 9, 4 H), 7.24–7.07 (m, 20 H), 7.016 (d, J = 9, 2 H), 6.872 (d, J = 9, 2 H), 6.858 (d, J = 9, 4 H), 6.705 (t, J = 2, 2 H), 6.477 (t, J = 2, 2 H), 6.706 (bs, 2 H), 6.477 (bs, 2 H), 2.898 (s, 3 H), 2.808 (s, 6 H), 2.746 (s, 2 H, exchangeable D_2O), 2.712 (s, 3 H), 1.370 (s, 18 H), 1.310 (s, 9 H), 1.275 (s, 18 H), 1.270 (s, 18 H), 1.267 (s, 9 H); IR (cm^{-1}) 3500 (O–H), 1567 (Ar).

Calix[4]arene Hexaethers 7. Sodium hydride (0.42 g of 60% dispersion in mineral oil, 10.6 mmol) was washed with pentane under nitrogen flow followed by addition of THF (40 mL). The resultant suspension was cooled to 0 °C. A solution of **6A** (1.857 g in 30 mL of THF, 1.060 mmol) was added to the suspension. After 15 min, iodomethane (4.51 g, 3.29 mmol) was added to the reaction mixture. The reaction mixture was allowed to warm to ambient temperature slowly. After the mixture was extracted with ether, the combined organic layer was washed with water and brine and then dried over $MgSO_4$; concentration in vacuo gave a yellow solid. An analogous procedure was used to convert isomers **6B** and **6C** to the corresponding hexaethers **7B** and **7C**.

7A. From **6A** (1.857 g), 1.652 g of crude **7A** was obtained. Column chromatography (TLC grade silica gel, hexane/ether, 96:4) gave a pale yellow solid, 1.200 g. Crystallization/precipitation from methanol/ether gave a white powder, 0.782 g (41%), with mp = 196–197 °C. For **7A:** FAB MS (3-NBA) m/z (% RA for m/z 400–1900) at $(M - OCH_3)^+$ 1748.8 (15), 1749.8 (50), 1750.8 (60), 1751.8 (100), 1752.8 (100), 1753.8 (85), 1754.8 (65), 1755.8 (30), 1756.8 (15); calcd for $C_{113}H_{131}O_5Br_2$ at $(M - OCH_3)^+$ 1749.8 (35), 1750.8 (45), 1751.8 (95), 1752.8 (100), 1753.8 (95), 1754.8 (70), 1755.8 (40), 1756.8 (15); 1H NMR (500 MHz, EM = -1.2, GB = +0.7, $CDCl_3$, 1H - 1H COSY cross-peak) 7.582 (t, J = 2, 1 H, 7.276, 6.776), 7.513 (t, J = 2, 1 H, 7.344, 7.049), 7.389 (t, J = 2, 1 H, 7.357, 7.115), 7.357 (t, J = 2, 1 H, 7.389, 7.115), 7.344 (t, J = 2, 1 H, 7.513, 7.049), 7.292 (t, J = 2, 1 H, 7.152, 7.108), 7.284 (d, J = 9, 2 H, 7.158), 7.269 (t, J = 2, 1 H, 7.582, 6.776), 7.220 (d, J = 9, 4 H, 7.161), 7.220 (d, J = 9, 2 H, 7.124), 7.213 (d, J = 9, 2 H, 7.017), 7.200 (d, J = 9, 2 H, 7.051), 7.191 (d, J = 9, 2 H, 7.120), 7.161 (d, J = 9, 4 H, 7.220), 7.161 (d, J = 9, 2 H, 6.944), 7.158 (d, J = 9, 2 H, 7.284), 7.152 (t, J = 2, 1 H, 7.292 (overlapped), 7.108), 7.124 (d, J = 9, 2 H, 7.220), 7.120 (d, J = 9, 2 H, 7.191), 7.115 (t, J = 2, 1 H, 7.389, 7.357), 7.051 (d, J = 9, 2 H, 7.200), 7.049 (t, J = 2, 1 H, 7.513, 7.344), 7.017 (d, J = 9, 2 H, 7.213), 7.018 (t, J = 2, 1 H, 7.152, 7.292), 6.944 (d, J = 9, 2 H, 7.161), 6.776 (t, J = 2, 1 H, 7.582, 7.276), 2.910 (s, 3 H), 2.849 (s, 3 H), 2.844 (s, 3 H), 2.788 (s, 3 H), 2.648 (s, 3 H), 2.619 (s, 3 H), 1.311 (s, 9 H), 1.284 (s, 18 H), 1.282 (s, 9 H), 1.278 (s, 9 H), 1.269 (s, 9 H), 1.267 (s, 18 H); $^{13}C\{^1H\}$ -DEPT(135°) NMR (125 MHz, EM = -1.0, GB = +2.0, $CDCl_3$) aromatic quaternary region expected 28 resonances, found 26 resonances at 150.12 (q), 149.96 (q), 149.91 (q), 149.40 (q), 149.35 (q), 149.28 (q), 148.3 (q), 147.8 (q), 146.0 (q), 145.0 (q), 143.4 (q), 143.3 (q), 142.8 (q), 142.0 (q), 141.5 (q), 141.4 (q), 141.3 (q), 141.2 (q), 141.1 (q), 140.8 (q), 140.6 (q), 139.3 (q), 139.0 (q), 138.8 (q), 121.5 (q), 121.4 (q); aromatic nonquaternary region expected 28 resonances, found 23 resonances at 130.0, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.47, 128.44, 128.35, 128.32, 128.26, 128.1, 127.6, 127.5, 127.3, 126.4, 124.8, 124.6, 124.5, 124.4, 124.3; aliphatic region 87.3 (q), 86.9 (q), 86.8 (q), 86.62 (q), 86.59 (q), 86.47 (q), 52.4, 52.3, 51.99, 51.95, 51.91, 34.46 (q), 34.37 (q), 34.34 (q), 31.39, 31.34; IR (cm^{-1}) 1598 (Ar). Anal. Calcd for $C_{116}H_{134}O_6Br_2$: C, 78.09; H, 7.57. Found: C, 78.13; H, 7.65.

7B. From **6B** (2.969 g), 2.679 g of crude **7B** was obtained. Column chromatography (TLC grade silica gel, hexane/ether, 96.5:3.5) gave a colorless solid, 1.602 g. A sample of 1.35 g was repurified by column chromatography and precipitation from methanol/ether to give a white powder, 0.8028 g (27%), with mp = 192–194 °C; FAB MS (3-NBA) m/z (% RA for m/z 400–2000) at $(M - OCH_3)^+$ 1748.2 (10), 1749.2 (15), 1750.2 (50), 1751.2 (55), 1752.2 (100), 1753.2 (90), 1754.2 (85),

1755.2 (60), 1756.2 (30), 1757.2 (15); ¹H NMR (500 MHz, EM = -0.6, GB = +0.5, CDCl₃, ¹H-¹H COSY cross-peak) 7.556 (t, *J* = 2, 1 H, 7.294, 6.815), 7.474 (t, *J* = 2, 1 H, 7.341, 7.118), 7.414 (t, *J* = 2, 1 H, 7.354, 7.170), 7.354 (t, *J* = 2, 1 H, 7.414, 7.170), 7.341 (t, *J* = 2, 1 H, 7.474, 7.118), 7.294 (t, *J* = 2, 1 H, 7.556, 6.815), 7.269 (d, *J* = 9, 2 H, 7.198), 7.238 (t, *J* = 2, 1 H, 7.134, 7.091), 7.231 (s, collapsed AB system, 4 H), 7.229 (d, *J* = 9, 2 H, 7.182), 7.209 (d, *J* = 9, 2 H, 7.012), 7.202 (d, *J* = 9, 2 H, 7.101), 7.202 (d, *J* = 9, 2 H, 7.091), 7.198 (d, *J* = 9, 2 H, 7.269), 7.198 (d, *J* = 9, 2 H, 7.016), 7.189 (d, *J* = 9, 2 H, 7.094), 7.182 (d, *J* = 9, 2 H, 7.091), 7.170 (t, *J* = 2, 1 H, 7.414, 7.354), 7.134 (t, *J* = 2, 1 H, 7.238, 7.091), 7.118 (t, *J* = 2, 1 H, 7.474, 7.341), 7.101 (d, *J* = 9, 2 H, 7.202), 7.094 (d, *J* = 9, 2 H, 7.189), 7.091 (d, *J* = 9, 2 H, 7.202), 7.091 (t, *J* = 2, 1 H, 7.238, 7.134), 7.016 (d, *J* = 9, 2 H, 7.198), 7.012 (d, *J* = 9, 2 H, 7.209), 6.815 (t, *J* = 2, 1 H, 7.556, 7.294), 2.905 (s, 3 H), 2.855 (s, 3 H), 2.821 (s, 3 H), 2.756 (s, 3 H), 2.729 (s, 3 H), 2.667 (s, 3 H), 1.286 (s, 18 H), 1.284 (s, 9 H), 1.282 (s, 9 H), 1.276 (s, 9 H), 1.275 (s, 9 H), 1.270 (s, 18 H); ¹³C{¹H}DEPT(135°) NMR (125 MHz, EM = -1.1, GB = +0.5, CDCl₃) aromatic quaternary region expected 28 resonances, found 25 resonances at 150.0 (q), 149.9 (q), 149.8 (q), 149.44 (q), 149.37 (q), 149.26 (q), 149.23 (q), 148.3 (q), 148.2 (q), 145.9 (q), 144.5 (q), 143.7 (q), 142.7 (q), 142.6 (q), 141.9 (q), 141.37 (q), 141.33 (q), 141.2 (q), 140.94 (q), 140.90 (q), 140.6 (q), 139.25 (q), 139.20 (q), 139.15 (q), 121.4 (q); aromatic nonquaternary region expected 28 resonances found 25 resonances at 130.4, 129.8, 129.5, 129.2, 129.1, 128.80, 128.76, 128.50, 128.46, 128.30, 128.22, 128.10, 128.05, 127.9, 127.7, 127.3, 125.7, 124.9, 124.6, 124.5, 124.43, 124.41, 124.38, 124.36, 124.33; aliphatic region 87.1 (q), 86.9 (q), 86.8 (q), 86.6 (q), 86.3 (q), 52.3, 52.2, 52.0, 51.97, 51.96, 51.94, 34.43 (q), 34.39 (q), 34.37 (q), 34.35 (q), 34.34 (q), 31.37, 31.34, 31.32; IR (cm⁻¹) 1598 (Ar). Anal. Calcd for C₁₁₆H₁₃₄O₆Br₂: C, 78.09; H, 7.57. Found: C, 78.12; H, 7.64.

7C. From **6C** (1.920 g), 1.824 g of crude **7C** was obtained. Column chromatography (TLC grade silica gel, hexane/ether, 98:2) followed by crystallization/precipitation from methanol/ether gave a light yellow powder, 0.520 g (27%). A sample of analytical purity was obtained from another small scale reaction (from 0.105 g of **6C**); column chromatography (TLC grade silica gel, hexane/ether, 95:5) gave a colorless solid, 0.035 g (33%), with mp = 188–189 °C: FAB MS (3-NBA) *m/z* (% RA for *m/z* 400–2100) at (M-OCH₃)⁺ 1749.9 (55), 1750.9 (65), 1751.9 (100), 1752.9 (100), 1753.9 (90), 1754.9 (70), 1755.9 (40); ¹H NMR (500 MHz, EM = -1.85, GB = +1.20, CDCl₃, ¹H-¹H COSY cross-peak) 7.428 (t, *J* = 2, 2 H, 7.252, 6.974), 7.390 (t, *J* = 2, 2 H, 7.298, 7.111), 7.298 (t, *J* = 2, 2 H, 7.390, 7.111), 7.290 (d, *J* = 9, 2 H, 7.149), 7.252 (t, *J* = 2, 2 H, 7.428, 6.974), 7.223 (d, *J* = 9, 4 H, 7.192), 7.205 (d, *J* = 9, 2 H, 7.069), 7.193 (d, *J* = 9, 4 H, 7.145), 7.192 (d, *J* = 9, 4 H, 7.223), 7.187 (d, *J* = 9, 4 H, 7.013), 7.149 (d, *J* = 9, 2 H, 7.290), 7.145 (d, *J* = 9, 4 H, 7.193), 7.111 (t, *J* = 2, 2 H, 7.390, 7.298), 7.069 (d, *J* = 9, 2 H, 7.205), 7.013 (d, *J* = 9, 4 H, 7.187), 6.974 (t, *J* = 2, 2 H, 7.428, 7.252), 2.927 (s, 3 H), 2.817 (s, 6 H), 2.787 (s, 6 H), 2.774 (s, 3 H), 1.327 (s, 9 H), 1.293 (s, 9 H), 1.284 (s, 36 H), 1.269 (s, 18 H); ¹³C{¹H}DEPT(135°) NMR (125 MHz, EM = -1.0, GB = +2.0, CDCl₃) aromatic quaternary region expected 16 resonances, found 16 resonances at 150.0 (q), 149.8 (q), 149.5 (q), 149.3 (q), 149.2 (q), 147.4 (q), 145.5 (q), 143.0 (q), 142.5 (q), 141.42 (q), 141.33 (q), 141.26 (q), 140.4 (q), 139.6 (q), 138.4 (q), 121.5 (q); aromatic nonquaternary region expected 16 resonances, found 16 resonances at 130.2, 130.0, 128.9, 128.54, 128.5, 128.21, 128.17, 128.13, 128.11, 127.8, 127.3, 124.9, 124.6, 124.43, 124.39, 124.33; aliphatic region 87.2 (q), 86.9 (q), 86.6 (q), 86.4 (q), 52.4, 52.3, 52.1, 34.46 (q), 34.42 (q), 34.38 (q), 34.36 (q), 31.4; IR (cm⁻¹) 1597 (Ar). Anal. Calcd for C₁₁₆H₁₃₄O₆Br₂: C, 78.09; H, 7.57. Found: C, 78.35; H, 7.73.

Calix[4]arene Diketone 8. *t*-BuLi (0.27 mL of a 1.7 M solution in pentane, 0.46 mmol) was added to a solution of hexaether **7B** (0.200 g in 2.5 mL of THF, 0.11 mmol) at -78 °C. After 1 h, the reaction mixture was allowed to warm to -50 °C for 10 min by replacing the dry ice/acetone bath with an EtOH/liquid N₂ bath. After a solution of 1-(4-*tert*-butylbenzoyl)pyrrolidine (57.2 mg in 0.7 mL of THF, 0.25 mmol) was added to the reaction mixture at -78 °C, the reaction temperature was raised to room temperature overnight. The reaction was quenched with water (1 mL) followed by aqueous workup of the resulting solution. Column chromatography (TLC grade silica gel,

hexane/ether, 90:10) gave a light yellow solid, which was of sufficient purity for the next step in the synthesis. From two reactions on the 0.2 and 0.3 g scales, 0.295 g (54%) of calix[4]arene diketone **8** was obtained from 0.500 g of **7B**. For **8**: FAB MS (3-NBA) *m/z* (% RA for *m/z* 400–2300) at (M-OCH₃)⁺ 1912.6 (15), 1913.6 (20), 1914.6 (75), 1915.6 (100), 1916.6 (75), 1917.6 (40), 1918.6 (15); ¹H NMR (500 MHz, EM = -1.85, GB = 1.20, C₆D₆, ¹H-¹H COSY cross-peak) 8.519 (t, *J* = 2, 1 H, 8.028, 7.986), 8.393 (t, *J* = 2, 1 H, 8.188, 8.154), 8.188 (t, *J* = 2, 1 H, 8.393, 8.154), 8.154 (t, *J* = 2, 1 H, 8.393, 8.188), 8.121 (t, *J* = 2, 1 H, 8.711, 7.502), 8.028 (bs, 1 H, 8.519, 7.986), 7.986 (t, *J* = 2, 1 H, 8.519, 8.028), 7.871 (t, *J* = 2, 1 H, 8.121, 7.502), 7.799 (t, *J* = 2, 1 H, 7.792, 7.702), 7.792 (t, *J* = 2, 1 H, 7.799, 7.702), 7.747 (d, *J* = 9, 2 H, 7.182), 7.702 (t, *J* = 2, 1 H, 7.799, 7.792), 7.694 (d, *J* = 9, 2 H, 7.135), 7.540 (d, *J* = 9, 2 H, 7.204), 7.507 (d, *J* = 9, 2 H, 7.248), 7.502 (t, *J* = 2, 1 H, 8.121, 7.871), 7.496 (d, *J* = 9, 2 H, 7.233), 7.475 (d, *J* = 9, 2 H, 7.281), 7.461 (d, *J* = 9, 2 H, 7.152), 7.438 (d, *J* = 9, 2 H, 7.146), 7.433 (d, *J* = 9, 2 H, 7.233), 7.384 (d, *J* = 9, 2 H, 7.186), 7.281 (d, *J* = 9, 2 H, 7.475), 7.248 (d, *J* = 9, 2 H, 7.507), 7.233 (d, *J* = 9, 2 H, 7.433), 7.224 (d, *J* = 9, 2 H, 7.496), 7.204 (d, *J* = 9, 2 H, 7.540), 7.186 (d, *J* = 9, 2 H, 7.384), 7.182 (d, *J* = 9, 2 H, 7.747), 7.152 (d, *J* = 9, 2 H, 7.475), 7.146 (d, *J* = 9, 2 H, 7.438), 7.135 (d, *J* = 9, 2 H, 7.694), 3.019 (s, 3 H), 3.000 (s, 3 H), 2.958 (s, 3 H), 2.931 (s, 3 H), 2.908 (s, 3 H), 2.849 (s, 3 H), 1.210 (s, 9 H), 1.203 (s, 9 H), 1.190 (s, 9 H), 1.183 (s, 9 H), 1.177 (s, 9 H), 1.174 (s, 9 H), 1.160 (s, 9 H), 1.142 (s, 9 H), 1.129 (s, 9 H), 1.118 (s, 9 H); ¹³C{¹H}DEPT(135°) NMR (125 MHz, EM = -1.10, GB = 0.90, CDCl₃) carbonyl group region expected 2 resonances, found 2 resonances at 195.70 (q), 195.66 (q); aromatic quaternary region expected 32 resonances found 31 resonances at 156.09 (q), 156.07 (q), 149.87 (q), 149.84 (q), 149.7 (q), 149.4 (q), 149.3 (q), 149.22 (q), 149.18 (q), 146.36 (q), 146.32 (q), 143.9 (q), 143.6 (q), 143.5 (q), 143.1 (q), 142.6 (q), 141.8 (q), 141.6 (q), 141.41 (q), 141.37 (q), 141.29 (q), 141.24 (q), 140.9 (q), 140.5 (q), 139.6 (q), 139.42 (q), 139.37 (q), 137.1 (q), 136.8 (q), 134.58 (q), 134.50 (q); aromatic nonquaternary region expected 32 resonances, found 25 resonances at 132.3, 130.6, 130.4, 130.3, 129.7, 129.25, 129.19, 128.8, 128.6, 128.53, 128.46, 128.42, 128.35, 128.2, 128.1, 125.15, 125.09, 124.8, 124.57, 124.55, 124.39, 124.36, 124.35, 124.33, 124.28; aliphatic region 87.2 (q), 86.93 (q), 86.91 (q), 86.80 (q), 86.77 (q), 52.5, 52.22, 52.11, 52.09, 52.00, 51.91, 35.02 (q), 35.00 (q), 34.39 (q), 34.34 (q), 34.32 (q), 34.30 (q), 34.27 (q), 34.23 (q), 31.36, 31.34, 31.29, 31.27, 31.10, 31.09; IR (cm⁻¹) 1662 (C=O), 1599 (Ar).

Triple-calix[4]arene Diols 9. *t*-BuLi (0.28 mL of 1.7 M solution in pentane, 0.48 mmol) was added to a solution of **7B** (0.209 g in 9 mL of THF, 0.12 mmol) at -78 °C. After 1 h, the reaction mixture was warmed to -50 °C for 10 min. A solution of calix[4]arene diketone **8** (0.229 g in 9 mL of THF, 0.12 mmol) was fast cannulated to the above reaction mixture at -78 °C. The reaction mixture was allowed to warm to ambient temperature. After 48 h, the reaction was quenched with water (2 mL), and aqueous workup gave a yellow solid, 0.500 g. Column chromatography (TLC grade silica gel, hexane/ether, ~10:1) gave three isomers **9X** (following further purification by PTLC, 34.2 mg, 8%), **9Y** (38.1 mg, 9%), and **9Z** (38.9 mg, 9%), which were of sufficient purity for the next step in the synthesis.

For 9X: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 3400–4100) 3510 (35), 3525 (30), 3541 (100), 3555 (35); narrow-range scan, *m/z* (% RA for *m/z* 3490–3560) at (M-OCH₃)⁺ 3537.1 (15), 3538.1 (25), 3539.1 (50), 3540.1 (85), 3541.1 (100), 3542.1 (90), 3542.1 (60), 3544.1 (35), 3545.1 (20); calcd for C₂₅₃H₂₉₃O₁₃ at (M-OCH₃)⁺ 3539.2 (25), 3540.2 (70), 3541.2 (100), 3542.2 (95), 3543.2 (70), 3544.2 (40), 3545.2 (20), 3546.3 (10); ¹H NMR (CDCl₃) 8.200–6.570 (m, ArH), 2.799–1.838 (OCH₃, OH), 1.331–1.139 (C(CH₃)₃); IR (cm⁻¹) 3500 (O-H), 1598 (Ar).

For 9Y: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 3400–4100) 3510 (35), 3525 (35), 3541 (100), 3555 (40); narrow-range scan, *m/z* (% RA for *m/z* 3490–3575) at (M-OCH₃)⁺ 3537.2 (20), 3538.2 (30), 3539.2 (55), 3540.2 (85), 3541.2 (100), 3542.2 (85), 3543.2 (65), 3544.2 (35), 3545.2 (25); ¹H NMR (500 MHz, EM = -2.10, GB = 1.10, C₆D₆) 8.572–6.987 (m, Ar-H), 2.963 (s, 3H), 2.938 (s, 3 H), 2.910 (s, 3 H), 2.898 (s, 3 H), 2.864 (s, 3 H), 2.846 (s, 6 H), 2.779 (s, 3 H), 2.762 (s, 3 H), 2.725 (s, 3 H), 2.704 (s, 2 H, exchangeable D₂O), 2.683 (s, 3 H), 2.661 (s, 3 H), 1.314 (s, 9 H),

1.301 (s, 9 H), 1.290 (s, 9 H), 1.269 (s, 9 H), 1.235 (s, 9 H), 1.220 (s, 9 H), 1.209 (s, 18 H), 1.202 (s, 9 H), 1.198 (s, 9 H), 1.194 (s, 9 H), 1.183 (s, 9 H), 1.178 (s, 9 H), 1.175 (s, 36 H), 1.158 (s, 9 H); IR (cm⁻¹) 3500 (O-H), 1596 (Ar).

For 9Z: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 3400–4100) 3510 (40), 3525 (40), 3541 (100), 3555 (40); narrow-range scan, *m/z* (% RA for *m/z* 3475–3580) at (M - OCH₃)⁺ 3537.3 (20), 3538.3 (30), 3539.3 (55), 3540.3 (85), 3541.3 (100), 3542.3 (90), 3543.3 (65), 3544.3 (35), 3545.3 (30); ¹H NMR (CDCl₃) 7.857–6.684 (m, Ar-H), 2.719 (s, 6 H), 2.687 (s, 6 H), 2.645 (s, 6 H), 2.613 (s, 6 H), 2.581 (s, 1 H, exchangeable D₂O), 2.542 (s, 6 H), 2.198 (s, 1 H, exchangeable D₂O), 2.146 (s, 6 H), 1.341–1.180 (C(CH₃)₃).

Triple-calix[4]arene Tetradecaethers 1-(OMe)₁₄. Sodium hydride (0.30 g of 60% dispersion in mineral oil) was washed with pentane under nitrogen flow followed by addition of THF (3 mL). One-half (1.5 mL) of the resultant suspension was transferred to a solution of diol **9Y** (31.2 mg in 1 mL of THF) at 0 °C; the other half (1.5 mL) was transferred to a solution of diol **9Z** (24.1 mg in 1 mL of THF) at 0 °C. After 10 min, iodomethane (0.1 mL) was added to each reaction mixture. The reactions were quenched with a few drops of methanol followed by aqueous workup. PTLC (hexane/ether, 10:1) followed by treatment with methanol gave tetradecaethers **1Y-(OMe)₁₄** (5.8 mg, 18%) and **1Z-(OMe)₁₄** (4.9 mg, 20%). Tetradecaether **1X-(OMe)₁₄** (7.0 mg, 20%) was obtained by the same method from 34.2 mg of diol **9X**.

For 1X-(OMe)₁₄: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 700–4800) 3538 (40), 3570 (100); narrow-range scan, *m/z* (% RA for *m/z* 3520–3585) at (M - OCH₃)⁺ 3565.5 (15), 3566.5 (20), 3567.5 (50), 3568.5 (80), 3569.5 (100), 3570.5 (90), 3571.5 (65), 3572.5 (35), 3573.4 (15); Calcd for C₂₅₅H₂₉₇O₁₃ at (M - OCH₃)⁺ 3567.3 (25), 3568.3 (70), 3569.3 (100), 3570.3 (100), 3571.3 (70), 3572.3 (40), 3573.3 (20), 3574.3 (10); ¹H NMR (500 MHz, C₆D₆, 298 K) 8.756–6.990 (m, ArH), 3.099 (s, 3 H), 2.982 (s, 3 H), 2.946 (s, 3 H), 2.897 (s, 3 H), 2.871 (s, 3 H), 2.853 (s, 3 H), 2.788 (s, 3 H), 2.771 (s, 3 H), 2.727 (s, 3 H), 2.685 (s, 3 H), 2.666 (s, 9 H), 2.312 (s, 3 H), 1.331 (s, 9 H), 1.321 (s, 9 H), 1.290 (s, 9 H), 1.276 (s, 9 H), 1.270 (s, 9 H), 1.249 (s, 9 H), 1.233 (s, 9 H), 1.209 (s, 9 H), 1.202 (s, 18 H), 1.199 (s, 9 H), 1.190 (s, 9 H), 1.174 (s, 9 H), 1.160 (s, 9 H), 1.156 (s, 18 H), 1.120 (s, 9 H), 1.072 (s, 9 H); ¹H NMR (500 MHz, EM = -1.85, GB = 1.20, C₆D₆, 348 K) 8.652 (t, *J* = 2, 1 H), 8.153 (t, *J* = 2, 1 H), 8.085 (t, *J* = 2, 1 H), 8.072 (t, *J* = 2, 1 H), 7.890 (t, *J* = 2, 1 H), 7.846 (t, *J* = 2, 1 H), 7.820 (t, *J* = 2, 1 H), 7.804 (d, *J* = 9, 1 H), 7.788 (t, *J* = 2, 1 H), 7.734 (t, *J* = 2, 1 H), 7.724 (t, *J* = 2, 1 H), 7.692 (t, *J* = 2, 1 H), 7.669 (t, *J* = 2, 1 H), 7.654 (t, *J* = 2, 1 H), 7.627 (t, *J* = 2, 1 H), 7.593 (d, *J* = 9, 1 H), 7.530 (t, *J* = 2, 1 H), 7.511–7.150 (m, ArH), 7.127 (d, *J* = 9, 1 H), 7.104 (d, *J* = 9, 1 H), 7.076 (d, *J* = 9, 1 H), 7.033 (d, *J* = 9, 1 H), 6.991 (t, *J* = 2, 1 H), 3.210 (s, 3 H), 2.975 (s, 3 H), 2.917 (s, 6 H), 2.892 (s, 3 H), 2.851 (s, 3 H), 2.847 (s, 3 H), 2.820 (s, 3 H), 2.815 (s, 3 H), 2.803 (s, 3 H), 2.758 (s, 3 H), 2.750 (s, 3 H), 2.724 (s, 3 H), 2.430 (s, 3 H), 1.329 (s, 9 H), 1.317 (s, 9 H), 1.308 (s, 9 H), 1.263 (s, 9 H), 1.243 (s, 9 H), 1.240 (s, 9 H), 1.233 (s, 9 H), 1.222 (s, 9 H), 1.221 (s, 9 H), 1.214 (s, 9 H), 1.205 (s, 9 H), 1.198 (s, 18 H), 1.186 (s, 9 H), 1.181 (s, 9 H), 1.165 (s, 9 H), 1.151 (s, 9 H), 1.129 (s, 9 H).

For 1Y-(OMe)₁₄: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 700–4800) 3538 (45), 3570 (100); narrow-range scan, *m/z* (% RA for *m/z* 3515–3590) at (M - OCH₃)⁺ 3565.5 (15), 3566.5 (20), 3567.5 (45), 3568.5 (80), 3569.5 (100), 3570.5 (85), 3571.5 (65), 3572.5 (35), 3573.5 (20), 3574.4 (10); ¹H NMR (500 MHz, C₆D₆, 298 K) 8.752–6.989 (m, ArH), 3.111 (s, 3 H), 3.001 (s, 3 H), 2.938 (s, 3 H), 2.903 (s, 3 H), 2.879 (s, 3 H), 2.798–2.709 (27 H), 1.299 (s, 9 H), 1.283 (s, 9 H), 1.273 (s, 9 H), 1.253 (s, 9 H), 1.220 (s, 9 H), 1.211 (bs, 18 H), 1.194 (s, 27 H), 1.190 (s, 9 H), 1.182 (s, 9 H), 1.161 (bs, 27 H), 1.136 (s, 9 H); ¹H NMR (500 MHz, EM = -1.85, GB = 1.20, C₆D₆, 348 K, ¹H–¹H COSY cross-peak) 8.665 (t, *J* = 2, 1 H, 7.629, 7.271), 8.272 (t, *J* = 2, 1 H, 8.008, 7.254), 8.182 (t, *J* = 2, 1 H, 7.413, 7.364), 8.008 (t, *J* = 2, 1 H, 8.272, 7.254), 7.971 (t, *J* = 2, 1 H, 7.614, 7.475), 7.900 (t, *J* = 2, 1 H, 7.712, 7.468), 7.857 (t, *J* = 2, 1 H, 7.649, 7.496), 7.799 (t, *J* = 2, 1 H, 7.670, 7.601), 7.791 (d, *J* = 9, 2 H, 7.271), 7.757 (t, *J* = 2, 1 H, 7.568, 7.481), 7.712 (t, *J* = 2, 1 H, 7.900, 7.486), 7.670 (t, *J* = 2, 1 H, 7.799, 7.601), 7.649 (t, *J* = 2, 1 H, 7.857, 7.496), 7.629 (t, *J* = 2, 1 H, 8.665, 7.271), 7.614 (t, *J* = 2, 1 H, 7.971, 7.475), 7.601

(t, *J* = 2, 1 H, 7.799, 7.670), 7.568 (t, *J* = 2, 1 H, 7.757, 7.481), 7.560 (d, *J* = 9, 2 H, 7.219), 7.514 (d, *J* = 9, 2 H, 7.258), 7.514 (d, *J* = 9, 2 H, 7.219), 7.496 (t, *J* = 2, 1 H, 7.857, 7.649), 7.481 (t, *J* = 2, 7.670, 7.568), 7.477 (d, *J* = 9, 2 H, 7.186), 7.475 (t, *J* = 2, 1 H, 7.971, 7.568), 7.472 (d, *J* = 9, 2 H, 7.258), 7.468 (t, *J* = 2, 1 H, 7.900, 7.712), 7.467 (d, *J* = 9, 2 H, 7.279), 7.461 (d, *J* = 9, 2 H, 7.210), 7.415 (d, *J* = 9, 2 H, 7.245), 7.413 (t, *J* = 2, 1 H, 8.182, 7.364), 7.412 (d, *J* = 9, 2 H, 7.147), 7.405 (d, *J* = 9, 2 H, 7.169), 7.373 (d, *J* = 9, 2 H, 7.186), 7.365 (d, *J* = 9, 2 H, 7.133), 7.364 (t, *J* = 2, 1 H, 8.182, 7.413), 7.360 (d, *J* = 9, 2 H, 7.173), 7.329 (d, *J* = 9, 2 H, 7.147), 7.311 (d, *J* = 9, 2 H, 7.227), 7.279 (d, *J* = 9, 2 H, 7.467), 7.271 (t, *J* = 2, 1 H, 8.665, 7.629), 7.271 (d, *J* = 9, 2 H, 7.791), 7.258 (d, *J* = 9, 2 H, 7.514), 7.258 (d, *J* = 9, 2 H, 7.472), 7.254 (t, *J* = 2, 1 H, 8.272, 8.008), 7.245 (d, *J* = 9, 2 H, 7.415), 7.227 (d, *J* = 9, 2 H, 7.311), 7.219 (d, *J* = 9, 2 H, 7.560), 7.219 (d, *J* = 9, 7.514), 7.214 (s, 4 H), 7.210 (d, *J* = 9, 2 H, 7.461), 7.186 (d, *J* = 9, 2 H, 7.477), 7.186 (d, *J* = 9, 2 H, 7.373), 7.181 (bs, 4 H), 7.173 (d, *J* = 9, 2 H, 7.360), 7.169 (d, *J* = 9, 2 H, 7.405), 7.147 (d, *J* = 9, 2 H, 7.412), 7.147 (d, *J* = 9, 2 H, 7.329), 7.133 (d, *J* = 9, 2 H, 7.365), 3.199 (s, 3 H), 2.976 (s, 3 H), 2.946 (s, 3 H), 2.914 (s, 3 H), 2.912 (s, 3 H), 2.887 (s, 3 H), 2.836 (s, 3 H), 2.815 (s, 3 H), 2.779 (s, 3 H), 2.776 (s, 6 H), 2.762 (s, 3 H), 2.621 (s, 3 H), 2.604 (s, 3 H), 1.316 (s, 9 H), 1.312 (s, 9 H), 1.291 (s, 9 H), 1.288 (s, 9 H), 1.242 (s, 9 H), 1.231 (s, 9 H), 1.227 (s, 9 H), 1.221 (s, 9 H), 1.217 (s, 9 H), 1.210 (s, 9 H), 1.204 (s, 18 H), 1.192 (s, 9 H), 1.189 (s, 9 H), 1.183 (s, 18 H), 1.174 (s, 9 H), 1.161 (s, 9 H); partial (methoxy and *tert*-butyl groups) ¹H NMR (500 MHz, EM = -1.85, GB = 1.20, C₆D₆, 328 K) 3.168 (s, 3 H), 2.966 (s, 3 H), 2.945 (s, 3 H), 2.923 (s, 3 H), 2.901 (s, 3 H), 2.896 (s, 3 H), 2.812 (s, 3 H), 2.794 (s, 3 H), 2.780 (s, 3 H), 2.769 (s, 3 H), 2.756 (s, 3 H), 2.753 (s, 3 H), 2.648 (s, 3 H), 2.575 (bs, 3 H), 1.315 (s, 9 H), 1.306 (s, 9 H), 1.298 (s, 9 H), 1.283 (s, 9 H), 1.247 (s, 9 H), 1.239 (s, 9 H), 1.227 (s, 9 H), 1.222 (s, 9 H), 1.215 (s, 9 H), 1.206 (s, 9 H), 1.201 (s, 9 H), 1.197 (s, 9 H), 1.194 (s, 9 H), 1.191 (s, 9 H), 1.184 (s, 9 H), 1.178 (s, 9 H), 1.170 (s, 9 H), 1.153 (s, 9 H).

For 1Z-(OMe)₁₄: FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 700–4800) 3538 (40), 3570 (100); narrow-range scan, *m/z* (% RA for *m/z* 3510–3595) at (M - OCH₃)⁺ 3566.5 (20), 3567.5 (50), 3568.5 (85), 3569.5 (100), 3570.5 (95), 3571.5 (65), 3572.5 (40), 3573.5 (20); ¹H NMR (500 MHz, cyclohexane-*d*₁₂, 298 K) 8.297 (bs, ArH), 7.447 (s, ArH), 7.288–6.939 (m, ArH), 7.795 (s, ArH), 7.697 (s, ArH), 2.779 (bs, OCH₃), 2.693 (s, OCH₃), 2.619 (s, OCH₃), 2.423–1.810 (2 bs, OCH₃), 1.381–1.217 (overlapped, C(CH₃)₃); ¹H NMR (500 MHz, EM = -1.85, GB = 1.20, cyclohexane-*d*₁₂, 348 K, ¹H–¹H COSY45 cross-peak) 8.087 (t, *J* = 2, 2 H, 6.948, 6.682), 7.547 (t, *J* = 2, 2 H, 7.079, 6.936, after 2-Hz Gaussian broadening in both dimensions), 7.344 (t, *J* = 2, 2 H, 7.251, 6.878), 7.271 (d, *J* = 9, 4 H, 7.167), 7.251 (t, *J* = 2, 2 H, 7.344, 6.878), 7.211 (t, *J* = 2, 2 H, 7.190, 7.001), 7.190 (t, *J* = 2, 2 H, 7.211, 7.001), 7.177 (d, *J* = 9, 4 H, 7.103), 7.167 (d, *J* = 9, 4 H, 7.271), 7.160 (d, *J* = 9, 4 H, 7.075), 7.140 (d, *J* = 9, 4 H, 7.066), 7.131 (d, *J* = 9, 2 H, 7.016), 7.103 (d, *J* = 9, 4 H, 7.177), 7.079 (d, *J* = 9, 4 H, 6.836), 7.075 (d, *J* = 9, 4 H, 7.160), 7.079 (t, *J* = 2, 2 H, 7.547, 6.936), 7.071 (d, *J* = 9, 4 H, 7.031), 7.066 (d, *J* = 9, 4 H, 7.140), 7.050 (d, *J* = 9, 2 H, 7.014), 7.050 (d, *J* = 9, 4 H, 7.031), 7.031 (d, *J* = 9, 4 H, 7.050), 7.031 (d, *J* = 9, 4 H, 7.071), 7.016 (d, *J* = 9, 2 H, 7.131), 7.014 (d, *J* = 9, 2 H, 7.050), 7.010 (d, *J* = 9, 4 H, 6.845), 7.001 (t, *J* = 2, 2 H, 7.211, 7.190), 6.948 (t, *J* = 2, 2 H, 8.087, 6.682), 6.936 (t, *J* = 2, 2 H, 7.547, 7.079), 6.878 (t, *J* = 2, 2 H, 7.251, 7.344), 6.845 (d, *J* = 9, 4 H, 7.010), 6.836 (d, *J* = 9, 4 H, 7.079), 6.682 (t, *J* = 2, 2 H, 8.087, 6.948), 2.841 (s, 3 H), 2.707 (s, 6 H), 2.680 (s, 6 H), 2.637 (s, 6 H), 2.607 (s, 6 H), 2.486 (s, 6 H), 2.156 (bs, 6 H), 1.380 (bs, cyclohexane-*d*₁₂ possibly overlapping some resonances for *t*-Bu groups), 1.293 (s, 18 H), 1.252 (s, 54 H), 1.245 (s, 18 H), 1.239 (s, 18 H), 1.232 (s, 18 H), 1.214 (s, 18 H).

Reaction of Tetradecaethers 1-(OMe)₁₄ with Na/K and MeOH Quenching Product 1-(H)₁₄. A drop of Na/K alloy was added to a stirred tetradecaether (~1 mg) in THF (~0.5 mL) in a Schlenk vessel. After 4 days of stirring, MeOH (few drops) was added. The usual aqueous workup with ether gave crude product. Preparative TLC (2% ether in hexane) gave **1-(H)₁₄** (~1 mg), most likely, as a mixture of isomers: ¹H NMR (500 MHz, acetone-*d*₆) 7.7–6.2 (bm, 96 H), 5.6–4.8 (bm, ~14 H), 1.5–1.0 (bm, ~200 H); FAB MS (3-NBA) wide-range scan, *m/z* (% RA for *m/z* 1150–4900) 1399 (90), 3180 (100);

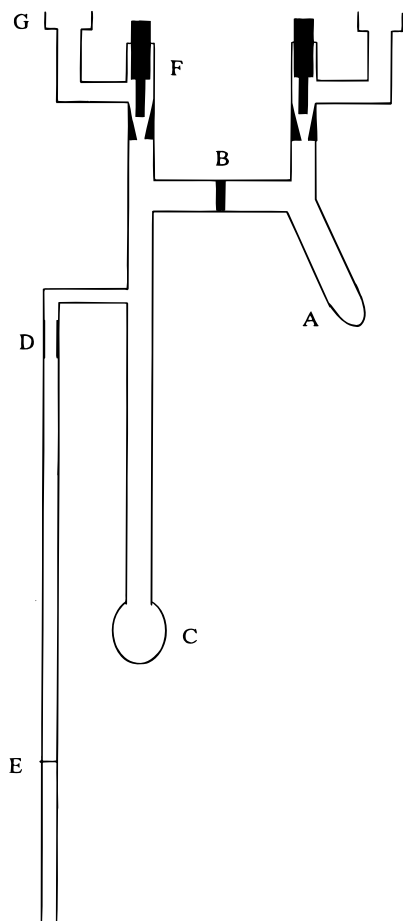


Figure 10. Vessel for preparation of polyradical 1. "A" is a compartment for generation of carbopolyanion, "B" is a coarse glass frit, "C" is a compartment for generation of polyradical, "D" is a glass-to-quartz seal, "E" is a 5 mm o.d. quartz tube with a thin flat bottom, ca. 65 mm from the end of the tube, "F" is a 4-mm high-vacuum Kontes stopcock, and "G" is a 9 mm solv-seal joint.

narrow-range scan, m/z (% RA for m/z 3110–3230) at $(M - H)^+$ 3177.1 (40), 3178.1 (75), 3179.1 (100), 3180.1 (95), 3181.1 (85), 3182.1 (60); calcd for $C_{242}H_{271}$ 3177.1 (27), 3178.1 (73), 3179.1 (100), 3180.1 (90), 3181.1 (61), 3182.1 (33).

Tetradecaradical 1: Quenching Studies and SQUID Magnetometry. Tetradecaether (~2 mg) was placed in the compartment A of the oxidation vessel (Figure 10). Following the heating of the vessel under vacuum overnight (compartment A to ~60 °C and the rest of the vessel to 200 °C), the vessel was moved to an argon-filled glovebox and a drop of Na/K alloy was attached to the wall in the compartment A. The vessel was connected to the vacuum line, THF- d_8 (~0.3 mL) was transferred under high vacuum from purple sodium/benzophenone, and the Na/K alloy was allowed to contact the solution. After ~4 days of stirring, the reaction mixture (deep red color) was filtered and cooled to the temperature just above the freezing point of THF- d_8 (approximately -105 °C) with an acetone/EtOH/liquid nitrogen bath. A small amount of iodine was transferred over the vacuum line to the reaction mixture, followed by small amount of solvent, either 2-MeTHF or THF- d_8 . While the temperature was maintained as low as possible to permit stirring of the reaction mixture (-115 °C, for 2-MeTHF, as

follow up solvent), this process was repeated 10–15 times until the reaction mixture attained pale yellow-green color. While maintaining the reaction mixture at near freezing point, a small portion of the reaction mixture was transferred to the quartz tube to form a band of the ~4 mm height, 65 mm from the end of the tube. The tube was flame sealed and stored in liquid nitrogen for insertion to SQUID magnetometer.

The remainder of the polyradical was stirred with Na/K at near freezing point of the reaction mixture for several hours and, then, at -78 °C a few days. At -78 °C, either MeOH or MeOD (few drops) was added. The usual aqueous workup with ether gave crude product. Preparative TLC (2% ether in hexane) gave **1-(X)₁₄** (X = H, D, ~1 mg), most likely, as a mixture of isomers.

Tetradecaradical 1 in THF- d_8 /2-MeTHF after MeOD quench, 1-(D)₁₄: 1H NMR (500 MHz, acetone- d_6) 7.7–6.2 (bm, 96 H), 5.6–4.8 (bm, ~2 H), 1.5–1.0 (bm, ~200 H); 2H NMR (76.8 MHz, acetone- d_6) ~5.4 (bs); FAB MS (3-NBA) wide-range scan, m/z (% RA for m/z 1500–3280) 3193 (100); narrow-range scan, m/z (% RA for m/z 3000–3260) at $(M - D)^+/(M - H)^+$ 3188.1 (50), 3189.1 (70), 3190.1 (85), 3191.1 (100), 3192.1 (100), 3193.1 (93), 3194.2 (70), 3195.2 (55).

Tetradecaradical 1 in THF- d_8 after MeOH quench, 1-(H)₁₃(D)₁: 1H NMR (500 MHz, acetone- d_6) 7.7–6.2 (bm, 96 H), 5.6–4.8 (bm, ~14 H), 1.5–1.0 (bm, ~200 H); FAB MS (3-NBA) wide-range scan, m/z (% RA for m/z 1500–3280) 3181 (100); narrow-range scan, m/z (% RA for m/z 3000–3260) at $(M - H)^+$ 3178.2 (65), 3179.2 (80), 3180.2 (100), 3181.2 (95), 3182.2 (85), 3183.2 (70); calcd for $C_{242}H_{270}D_1$ 3178.1 (27), 3179.1 (73), 3180.1 (100), 3181.1 (90), 3182.1 (61), 3183.1 (33).

SQUID Magnetometry. A Quantum Design (San Diego, CA) MPMS55 was used. The sample tubes were inserted to the magnetometer at low temperature under helium atmosphere as described previously.³⁰ Following the insertion to the sample chamber at 10 K, the sample was immediately cooled to 30–40 K for a few minutes. Subsequently, temperature in the sample chamber was increased to 90 K for 15–20 min and several sequences of helium purging and pumping were applied to remove residual oxygen.

Following the measurement, the sample tube was allowed to attain ambient temperature. After 6 weeks, the magnetic moment was negligible (~1% of the original value) and the sample was carefully inserted to the magnetometer and subjected to the identical sequence of measurements as the original sample. Such data were used for point-by-point correction for diamagnetism.

Numerical Curve Fitting. SigmaPlot for Windows software package was used for numerical curve fitting. The reliability of a fit is measured by the parameter dependence, which is defined as dependence = $1 - ((\text{variance of the parameter, other parameter constant})/(\text{variance of the parameter, other parameters changing}))$. Values close to 1 indicate overparametrized fit.

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