

Organic Spin Clusters: Ferromagnetic Spin Coupling through a Biphenyl Unit in Polyarylmethyl Tri-, Penta-, Hepta-, and Hexadecaradicals

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Abstract: Polyarylmethyl high-spin polyradicals are designed to possess a structure corresponding to simple spin clusters, where component spins (S') arise from strong ferromagnetic coupling through 1,3-phenylene units and weak ferromagnetic spin coupling between the component spins is mediated via 3,4'-biphenylene (or 3,5,4'-biphenylene) units. This rational design permits not only modular and highly convergent synthesis of very high-spin molecules but also detailed analysis of their magnetic data. A series of polyether precursors for the corresponding polyarylmethyl tri-, penta-, hepta-, and hexadecaradicals are prepared. The polyradicals are generated and characterized in frozen tetrahydrofuran (or tetrahydrofuran- d_8) solutions, using bulk magnetization studies. The measured values of S , from fits of magnetization vs magnetic field data to Brillouin functions at low temperatures, indicate high-spin ground states; e.g., $S = 7.2$ vs theoretical $S = 8$ for hexadecaradical. Estimated yields per site for generation of "unpaired" electrons are as high as 98% for the best samples of penta-, hepta-, and hexadecaradicals. The magnetization vs temperature data are fit to the Boltzmann distribution of energy levels, obtained from Heisenberg Hamiltonian; the fits produced ferromagnetic coupling constants (J/k) through 3,4'-biphenylene units. For tri- and pentaradical, for which exact analytical solutions to the Heisenberg Hamiltonian can be obtained by the vector model, values of $J/k \approx 90$ K are obtained. Hepta- and hexadecaradical, which could not be exactly solved by the vector model, are approximated as a dimer of the $S' = 5/2$ and 1 component spins and a trimer of the $S' = 5/2$, 3 and $5/2$ component spins, respectively; the corresponding values of J/k , 13 and 4 K, are found to be scaled by the fraction of component spin directly connected through the weak spin coupler (3,4'-biphenylene unit).

Introduction

Very-high-spin organic molecules provide intellectual challenge and contribute to the understanding of organic magnetism.¹ They pose fascinating problems involving synthesis of functionalized mesoscopic-size molecules, attaining ferromagnetic coupling between large number of "unpaired" electrons (i.e., very-high-spin) and informative magnetic characterization. High-spin dendritic and macrocyclic polyradicals are two main classes of such molecules.^{2–5} Dendritic and macrocyclic polyarylmethyl polyradicals with up to 31 and 8 sites for "unpaired" electrons, respectively, have been prepared.^{2,3} The S values for

dendrimers are drastically lower than expected (e.g., $5/2$ rather than $31/2$); in contrast, those for macrocycles are close to the expected values (e.g., 3.8 rather than $8/2$).^{2a–c,3} Because the yield for generation of "unpaired" electrons is finite in a multisite polyradical, there will be sites with "unpaired" electrons missing. We refer to such sites as defects. The most detrimental defects are those that interrupt ferromagnetic coupling (π -conjugation) between the remaining "unpaired" electrons in the polyradical, leading to mixtures of spin systems with low values of S . The key difference between dendrimers and macrocycles is revealed by considering polyradicals with one defect. In dendrimers, there are approximately 50% of the inner sites; a defect at one of these sites would interrupt spin coupling. In macrocycles, there is no such sites; i.e., a defect would lower the overall S by only $1/2$.^{1d,3,6} However, the increased number of sites in monomacrocyclic system is associated with greater probability of encountering two or more defects, which may interrupt spin coupling. Annelation of macrocycles significantly alleviates this problem.^{1d,7} Recently, an annelated triple-calix[4]arene macrocyclic polyarylmethyl polyradical with 14 sites for "unpaired" electrons and $S = 6.2$ has been prepared.⁸ Such a polyradical not only requires an elaborate synthesis but also imposes additional constraints on its stability and strength of ferromagnetic coupling.⁸

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(2) For high-spin polyarylmethyls, see: (dendritic) (a) Rajca, S.; Rajca, A. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; pp 1830–1834. (b) Rajca, A. *Adv. Mater.* **1994**, *6*, 605. (c) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688. (star-branched) (d) Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *114*, 1884.

(3) For macrocyclic polyarylmethyls, see: (a) Rajca, A.; Rajca, S.; Padmakumar, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2091. (b) Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806.

(4) For high-spin polycarbenes, see: Nakamura, K.; Inoue, K.; Iwamura, H. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 872. Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 5550. Matsuda, K.; Nakamura, N.; Inoue, K.; Koga, N.; Iwamura, H. *Chem. Eur. J.* **1996**, *2*, 259. Matsuda, K.; Nakamura, N.; Inoue, K.; Koga, N.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1483.

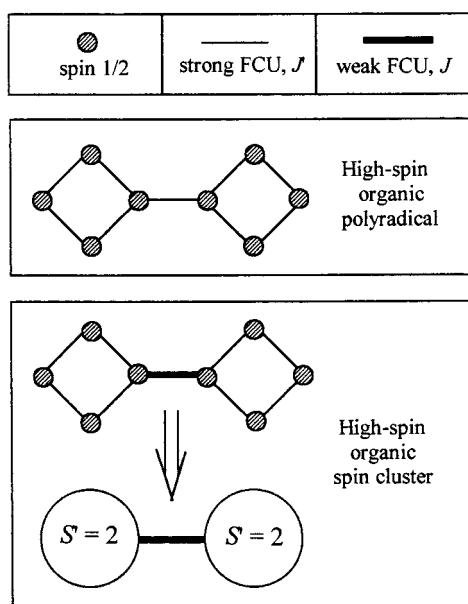
(5) For a linear polymer with $S \approx 4$, see: Murray, M. A.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.-H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152.

(6) In principle, attaching sites with "unpaired" electrons to a chain as pendants, should provide a polyradical with some resistance to defects. However, only relatively low values of S could be attained with such systems so far: Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Lahti, P. M. *J. Am. Chem. Soc.* **1996**, *118*, 9695.

(7) Rajca, A. In *Modular Chemistry*; Michl, J., Ed.; Kluwer Academic Publications: Dordrecht, The Netherlands, in press.

(8) Rajca, A.; Lu, K.; Rajca, S. *J. Am. Chem. Soc.* In press.

All of the very-high-spin polyradicals, mentioned above, may be viewed as ensembles of alternating sites for "unpaired" electrons with 1,3-phenylenes (1,3,5-phenylynes), which function as strong ferromagnetic coupling units (strong FCUs).^{1b} In an alternative design, high-spin modules (component spins, S') are linked with weak FCUs to form simple spin clusters. In such polyradicals, ferromagnetic coupling in high-spin modules (intramodular ferromagnetic coupling, J') is very strong, compared to the interaction between the modules (intermodular ferromagnetic coupling, J) and the thermal energy (kT) in the applicable temperature range, i.e., $J' \gg J \approx kT$. An analogy can be drawn to a high-spin transition metal cluster, with metal ions corresponding to the modules.⁹



The spin cluster design is implemented with polyarylmethyl polyradicals.^{1d} Strong ferromagnetic coupling (J') within the modules is achieved by alternating triarylmethyl sites with 1,3-phenylenes (or 1,3,5-phenylynes) as ferromagnetic coupling units (FCUs). Weak ferromagnetic coupling (J) between the modules is mediated with 3,4'-biphenylenes (or 3,5,4'-biphenylynes) as FCUs.^{10,11} It is estimated that $J/J' \approx 1/6$, based upon the available electron-proton spin couplings in triphenylmethyl and 4-biphenyldiphenylmethyl monoradicals.¹² Polyradicals 1–4 are designed as simple spin clusters (Figure 1).

The present design offers important advantages in approach to very-high-spin organic polyradicals.

Exchange interactions, primarily responsible for ferromagnetic coupling (J), should be adequately described by Heisenberg Hamiltonian, $H = -2\sum_{i>j} J_{ij}S_iS_j$, in organic polyradicals.^{1c,d} Because exact energy eigenvalues of Heisenberg Hamiltonian for spin dimers and symmetrical trimers are readily available,

(9) For a preliminary outline of the concept of organic spin clusters, see: Rajca, A. In *Proceedings from the 5th International Conference on Molecule-Based Magnets*; Osaka, Japan, 1996; *Liq. Cryst. Mol. Cryst.* In press.

(10) For a 3,4'-biphenylene-based diarylmethyl, see: Rajca, A.; Rajca, S. *J. Am. Chem. Soc.* **1996**, *118*, 8121.

(11) For 3,4'-biphenylene-linked dicarbene and dinitrene, see: Teki, Y.; Fujita, I.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 11499. Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532.

(12) Selected electron-proton spin coupling constants (in gauss, from ENDOR experiments) are for triphenylmethyl, 1.143 (H3), 2.857 (H4), and, for diphenyldiphenylmethyl, 0.193 (H3'), 0.487 (H4'): Maki, A. H.; Allendoerfer, R. D.; Danner, J. C.; Keys, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 4225.

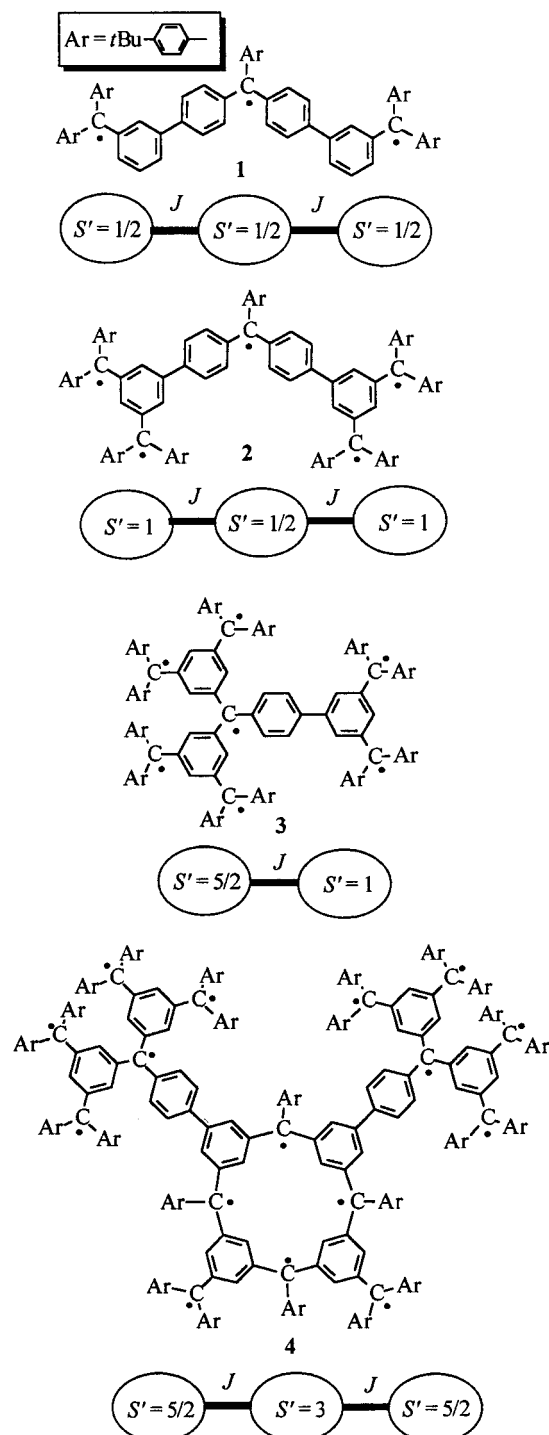
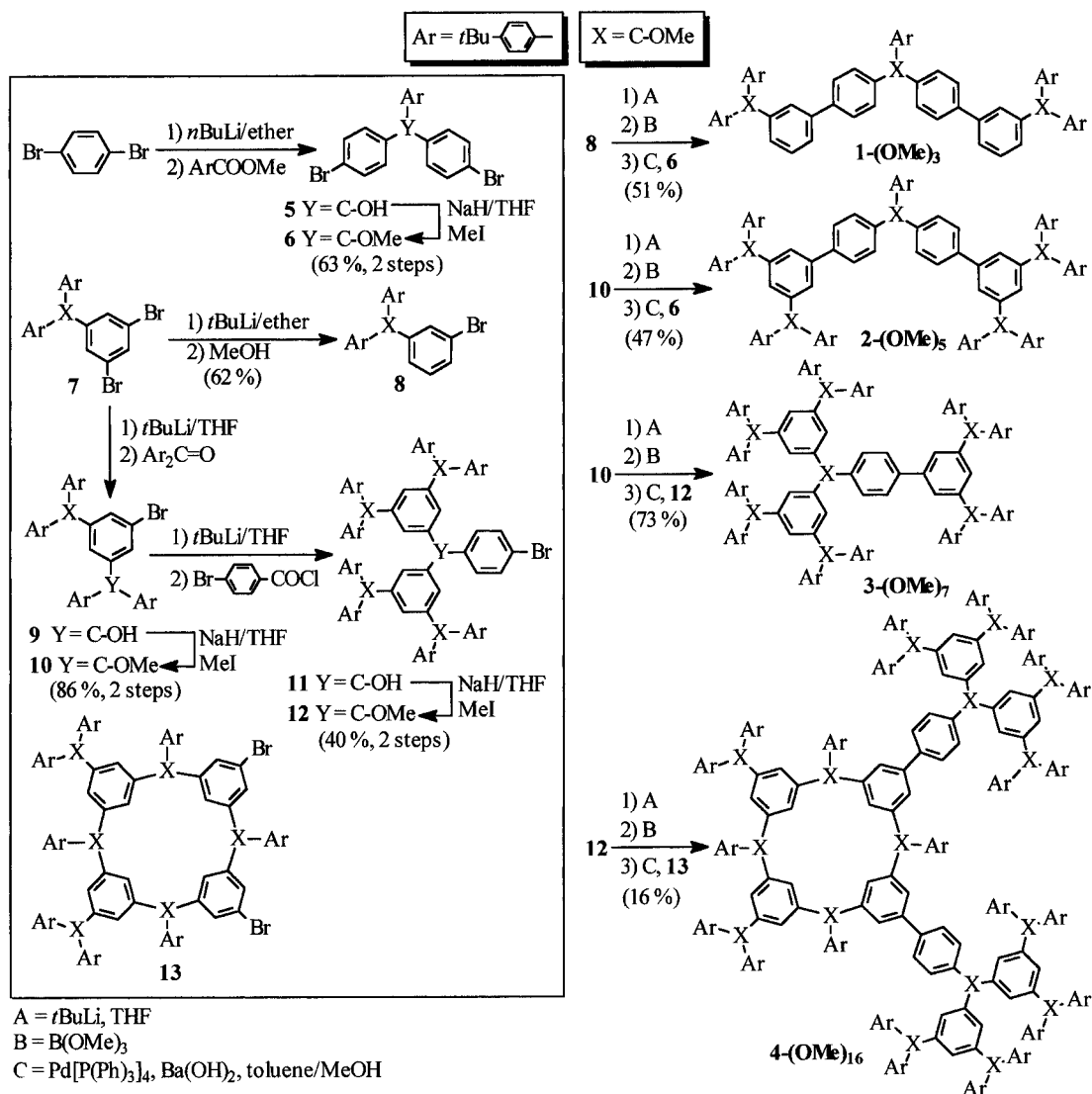


Figure 1. Triradical 1, pentaradical 2, heptaradical 3, hexadecaradical 4, and their representations as spin clusters.

more informative description of magnetic data is possible, including temperature dependence for $J \approx kT$.

Dendritic modules are designed to minimize the number of the inner sites for "unpaired" electrons. Consequently, polyradicals 1–3 possess only one site, where one defect may interrupt spin coupling; hexadecaradical 4 has two such sites. Moreover, 4-biphenyl substituents at these sensitive sites should make the radicals more stable.¹³ In particular, 3,4'-biphenyl-based triplet diradical has been isolated as a solid, stable at ambient temperature.¹⁰

(13) Tris(4-biphenyl)methyl does not dimerize in solution at ambient temperature: Dünnebacke, D.; Neumann, W. P.; Penenory, A.; Stewen, U. *Chem. Ber.* **1989**, *122*, 533.

Scheme 1. Synthesis of Modules and Their Assembly To Give Polyethers **1-(OMe)₃**, **2-(OMe)₅**, **3-(OMe)₇**, and **4-(OMe)₁₆**

Modular and highly convergent routes can be applied to the synthesis of the polyarylmethyl polyether precursors to such spin cluster polyradicals. 1,3-Phenylene-connected macrocyclic and/or dendritic modules can be connected via C(aryl)-C(aryl) bond-forming reactions to produce 3,4'-biphenylene-linked (or 3,5,4'-biphenylene-linked) ensembles of modules; no subsequent functionalizations of the triarylmethyl sites are needed.¹⁰

Results and Discussion

1. Synthesis of Polyethers. Modular and highly convergent synthesis is employed to prepare polyethers **1-(OMe)₃**, **2-(OMe)₅**, **3-(OMe)₇**, and **4-(OMe)₁₆**. The synthesis is carried out in two stages: (1) preparation of 1,3-phenylene-connected triarylmethyl modules with 3- and 4-bromoaryl functional groups and (2) linking the modules with 3,4'-biphenylene (or 3,5,4'-biphenylene) moieties (Scheme 1).

4-Bromophenyllithium, prepared by Li/Br exchange from 1,4-dibromobenzene, is added to methyl 4-*tert*-butylbenzoate to give triarylmethanol **5**; etherification with MeI gives ether **6** in 63% yield.¹⁴

Aryllithium, which is obtained via Li/Br exchange on dibromoaryl compound **7**,^{3a} is either quenched with MeOH or treated with 4,4'-*tert*-butylbenzophenone to give compound

8 (62%) or **9**, respectively;¹⁵ etherification of triarylmethanol **9** with MeI gives ether **10** (86%).

Li/Br exchange of **10**, followed by addition of 4-bromobenzoyl chloride, provides triarylmethanol **11**; etherification with MeI gives pentaether **12** (40%).

Modules **6**, **8**, **10**, **12**, and the previously prepared macrocyclic module **13** are used in the following synthetic steps.⁸ Dibromocalix[4]arene hexaether **13** is a single *cis/trans* isomer, with no elements of symmetry on the NMR time scale.⁸

Suzuki coupling, without isolation of boronic acid derivatives, is employed to connect the modules.¹⁶ For a pair of modules, one of the modules is subjected to Li/Br exchange, followed by addition of B(OMe)₃, removal of the solvent under nitrogen flow and vacuum, and heating with the other module in the presence of Pd(Ph₃P)₄ and barium hydroxide in toluene/MeOH.

(14) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon, Oxford, 1974; Chapter 4. For 4-bromophenyllithium, see: Gilman, H.; Langham, W.; Moore, F. W. *J. Am. Chem. Soc.* **1940**, *62*, 2327. For a derivative of module **6**, without the *tert*-butyl substituent, see: Hellwinkel, D.; Stahl, H.; Gaa, H. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 794.

(15) For an ethyl ether derivative of module **8**, see: Rajca, A. *J. Org. Chem.* **1991**, *56*, 3557.

(16) For a recent review on Suzuki coupling, see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. For the use of barium hydroxide and an *in situ* procedure, see: Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. Maddaford, S. P.; Keay, B. A. *J. Org. Chem.* **1994**, *59*, 6501.

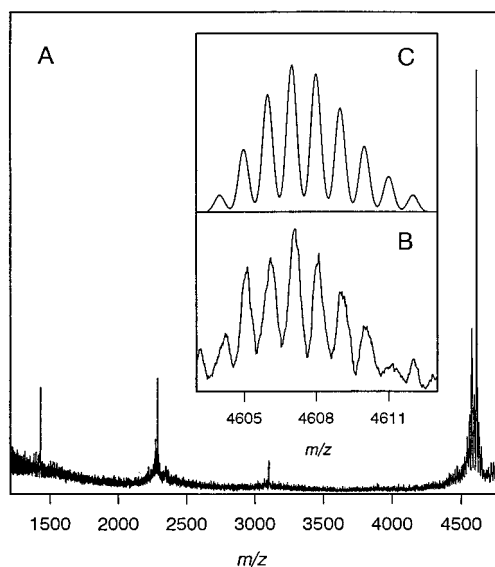


Figure 2. FAB MS for **4-(OMe)₁₆**. (A) Partial low-resolution spectrum. The most intense peak is at m/z 4607. (B) Spectrum for the $(M - OCH_3)^+$ ion cluster from the high-resolution spectrum. (C) Calculated spectrum for the $(M - OCH_3)^+$ ion cluster with formula $C_{331}H_{389}O_{15}$ at natural isotopic abundance.

Isolated yields for 3,4'-biphenylene-linked polyethers are 51% (**1-(OMe)₃**), 47% (**2-(OMe)₅**), 73% (**3-(OMe)₇**), and 16% (**4-(OMe)₁₆**).

Polyethers **1-(OMe)₃**, **2-(OMe)₅**, **3-(OMe)₇**, and **4-(OMe)₁₆** are characterized by FAB MS, IR, and NMR spectroscopies and C/H elemental analyses.

All polyethers show expected $(M - OCH_3)^+$ cluster ions as the most intense signals in the high mass range of FAB MS. For the largest molecules studied, heptaether **3-(OMe)₇** and hexadecaether **4-(OMe)₁₆**, isotopic distributions for $(M - OCH_3)^+$ were calculated and found in satisfactory agreement with the experimental values. For **4-(OMe)₁₆**, the three most intense isotopic peaks of $(M - OCH_3)^+$ possess the following experimental m/z values and relative amplitudes (% RA): 4606.1 (84), 4607.1 (100), 4608.1 (86), vs calculated for $C_{331}H_{389}O_{15}$, 4606.0 (80), 4607.0 (100), 4608.0 (94) (Figure 2).

IR spectra for all polyethers show strong bands at ~ 1600 and ~ 1080 cm^{-1} corresponding to vibrational modes involving benzene rings and ethereal linkages (C–O–C), respectively. Synthetic intermediates, which possess hydroxyl group, have broad bands at ~ 3600 cm^{-1} .

NMR spectra for triether **1-(OMe)₃** and pentaether **2-(OMe)₅** are straightforward. NMR spectra for more sterically hindered heptaether **3-(OMe)₇** are best interpreted in terms of three nonequivalent sets of four 4-*tert*-butylphenyl groups; similarly, synthetic precursors **11** and **12**, possess two nonequivalent sets of four 4-*tert*-butylphenyl groups.¹⁷

¹H NMR spectra for hexadecaether **4-(OMe)₁₆** in C_6D_6 are obtained at 293, 328, and 348 K. Resonances in the aromatic, MeO group, and 4-*tert*-butyl group regions are found (Figures 3 and 4).

Aromatic region of the spectrum is best resolved at 348 K. COSY correlation shows 32 "singlet" off-diagonal peaks, 12 "quadruplet" off-diagonal peaks, and 2 groups of overlapped off-diagonal peaks. The 32 "singlet" peaks are correlated within 4 sets of 6 and 4 sets of 2. The 4 sets of 6 are associated with 12 1-proton triplet ($J = 2$ Hz) resonances, corresponding to the four benzene rings of the calix[4]arene macrocycle. The 4 sets

of 2 are associated with four 2-proton doublet and four 1-proton triplet ($J = 2$ Hz) resonances, corresponding to the four 1,3,5-trisubstituted benzene rings of the dendritic branches. (Spectral overlap in the 1D NMR spectrum does not permit unequivocal assignment of one doublet/triplet pair.) The 12 "quadruplet" peaks correlate 12 2-proton doublet ($J = 9$ Hz) resonances, corresponding to the 12 1,4-disubstituted benzene rings. The 2 groups of overlapped diagonal peaks (7.43–7.51, 7.18–7.26 ppm) must account for the remaining 1,4-disubstituted benzene rings.

In the MeO group region, 9–11 singlets are resolved in the 293–348 K range (Table 1). The requirement for an even number of resonances for the MeO groups in **4-(OMe)₁₆** suggests at least one accidental isochrony in the best resolved spectrum (at 328 K). Thus, the MeO groups should appear as at least 12 singlets; i.e., eight 3 H and four 6 H resonances.

In the *tert*-butyl group region, 11–13 singlets are resolved in the 293–348 K range (Table 1). In the best resolved spectrum (at 293 K), isochronies involving two ¹H singlet resonances integrating to three and six *tert*-butyl groups must be accidental. In conjunction with the requirement for an even number of ¹H resonances for the *tert*-butyl groups, the spectrum at 293 K should contain at least 16 singlets; i.e., eight 9 H and eight 18 H resonances.

¹H NMR spectra for hexadecaether **4-(OMe)₁₆** in C_6D_6 are compatible with a single *cis/trans* isomer of calix[4]arene ring, lacking any elements of symmetry on the NMR time scale. The two dendritic pentaether branches and their four diether sub-branches are asynchronous. Each of the four diether sub-branches contains two nonequivalent pairs of 4-*tert*-butylphenyl groups; the other eight 4-*tert*-butylphenyl groups are nonequivalent.

2. Generation of Polyradicals and Quenching Studies.

Treatment of a polyether with an excess of Na/K alloy in tetrahydrofuran (THF) or tetrahydrofuran-*d*₈ (THF-*d*₈) gives purple-red solutions of the corresponding carbopolyanions (Scheme 2).¹⁰ For tri- and pentaethers, the purple-red solution is preceded by an incipient formation of blue-purple solution of an intermediate carbanion; analogously, blue color is initially observed for hepta- and hexadecaethers.

Oxidation of the carbopolyanions with I_2 at low temperatures (168–178 K) gives the corresponding polyradicals in THF (or THF-*d*₈).^{10,18,19} The best results, as indicated by the magnitude of S from magnetization studies, are achieved by addition of I_2 in small portions (titrations). A sequence of color changes, which is associated with oxidation of each carbopolyanion, serves as an indicator, e.g., in oxidation leading to hexadecaradical **4**, initial purple-red color of carbopolyanion turns to blue color, followed by green color, and, finally, yellow-brown color of polyradical. The intermediate blue color appears when most of I_2 (80–90%) is added to the reaction mixture; probably, at this stage of oxidation, the only carbanion sites left intact are those two sites substituted with 4-biphenyl moiety. [It is noted that triarylmethyl and 4-biphenyldiarylmethyl (aryl = alkylphenyl) carbanions in THF are red ($\lambda_{max} \approx 490$ nm) and blue ($\lambda_{max} \approx 590$ nm), respectively; the corresponding radicals are yellow ($\lambda_{max} \approx 350$ nm) and orange-red ($\lambda_{max} \approx 380$ nm).]¹⁹ The green color appears when almost all I_2 (95+%) is added to the reaction mixture; at this stage of oxidation, only very small amount 4-biphenyl-substituted carbanion is left. This sequence of colors is exactly reversed when a polyradical is stirred with alkali metal at low temperature (Scheme 2).

(17) (a) For stereochemistry of propellers, see: Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (b) For sterically hindered polyarylmethyl derivatives, see: Rajca, A.; Janicki, S. *J. Org. Chem.* **1994**, *59*, 7099.

(18) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890.

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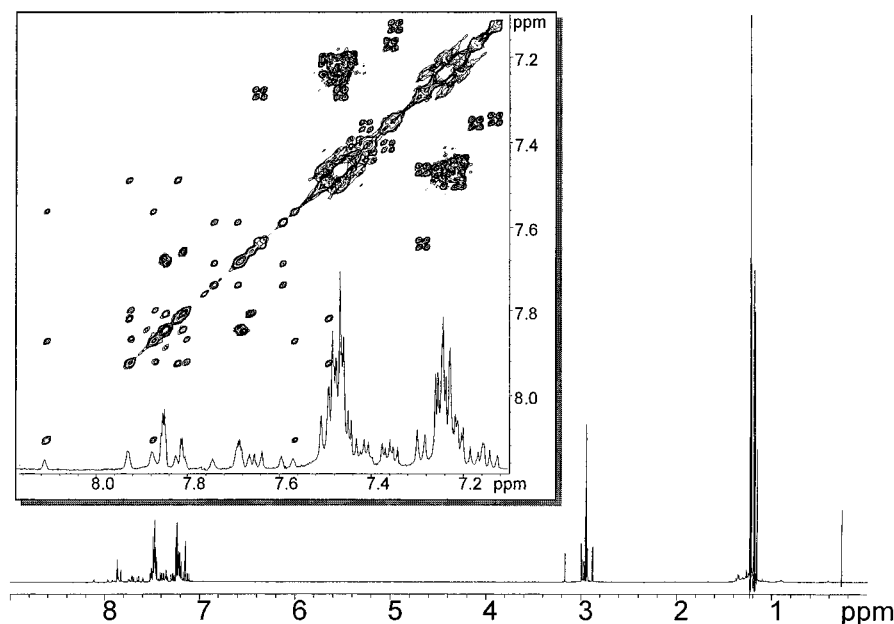


Figure 3. ^1H NMR (500 MHz, C_6D_6) spectrum for 4-(OMe)_{16} at 348 K. Main plot: full spectrum, EM = -1.5 Hz, GB = 0.9 Hz. Peaks at 7.15 and 0.26 ppm correspond to residual less-than-fully deuterated benzene and water, respectively. Insert: ^1H - ^1H COSY correlation in the aromatic region. Two pairs of peaks, located near the diagonal, at (7.89, 7.84 ppm), (7.84, 7.89 ppm), (7.84, 7.80 ppm), (7.80, 7.84 ppm), and diagonal peak at 7.75 ppm correspond to unknown impurities or instrumental artifacts.

A small portion of polyradical in THF (or THF- d_8) is transferred at low temperature to the quartz tube for magnetization studies. Similarly prepared samples of **1** and **2**, with additional dilution with 2-methyltetrahydrofuran (2-MeTHF), are employed for ESR spectroscopy. The remaining reaction mixture is treated with Na/K alloy or Li at low temperature, and, MeOH or MeOD is then added to produce hydrocarbons **1-(H)**₃, **2-(H)**₅, and **4-(H)**₁₆ and deuterated products **1-(D)**₃, **2-(D)**₅, **3-(D)**₇, and **4-(D)**₁₆, respectively (Scheme 2). [Hydrocarbon **3-(H)**₇ is obtained by the MeOH quench of carbopolyanion, which is directly generated from **3-(OMe)**₇.]

In the FAB MS of hydrocarbons **1-(H)**₃, **2-(H)**₅, and **3-(H)**₇, cluster ions corresponding to $\text{M}^+ / (\text{M} - \text{H})^+$ are observed; for hydrocarbon **4-(H)**₁₆, isotopic peaks are not resolved and only an average mass peak is found at m/z 4158. For deuterated products **1-(D)**₃, **2-(D)**₅, **3-(D)**₇, and **4-(D)**₁₆, the peaks of maximum amplitude in the isotopic cluster ions or average mass peaks are shifted by 3, 5, 7, and 15 amu, relative to the corresponding hydrocarbons.²⁰

The ^1H and ^{13}C NMR spectra of the aromatic and *tert*-butyl groups regions for hydrocarbons **1-(H)**₃, **2-(H)**₅, and **3-(H)**₇ and their deuterated isotopomers are analogous to those for the corresponding polyethers **1-(OMe)**₃, **2-(OMe)**₅, and **3-(OMe)**₇. The ^1H resonances of the triarylmethane protons appear as singlets in the 5.52–5.20 ppm range. Their integration ratios are 1:2 (**1-(H)**₃), 1:4 (**2-(H)**₅), and 2:4:1 (**3-(H)**₇); the resonances with integration of 1 H are assigned to the 4-biphenyl-substituted sites. For deuterated isotopomers (**1-(D)**₃, **2-(D)**₅, **3-(D)**₇), ^1H integrations suggest that overall deuterations at the triarylmethane sites are in the range of 96–97%; however, degree of deuteration per site is typically less at the 4-biphenyl-substituted sites (~95%) compared to that of the other sites (~97%).

The ^1H NMR spectra for **4-(H)**₁₆ and **4-(D)**₁₆ consist of broad, unresolved peaks at the chemical shifts corresponding to aromatic, triarylmethane, and *tert*-butyl regions. Probably, these two compounds are complex mixtures of *cis/trans* isomers. (For

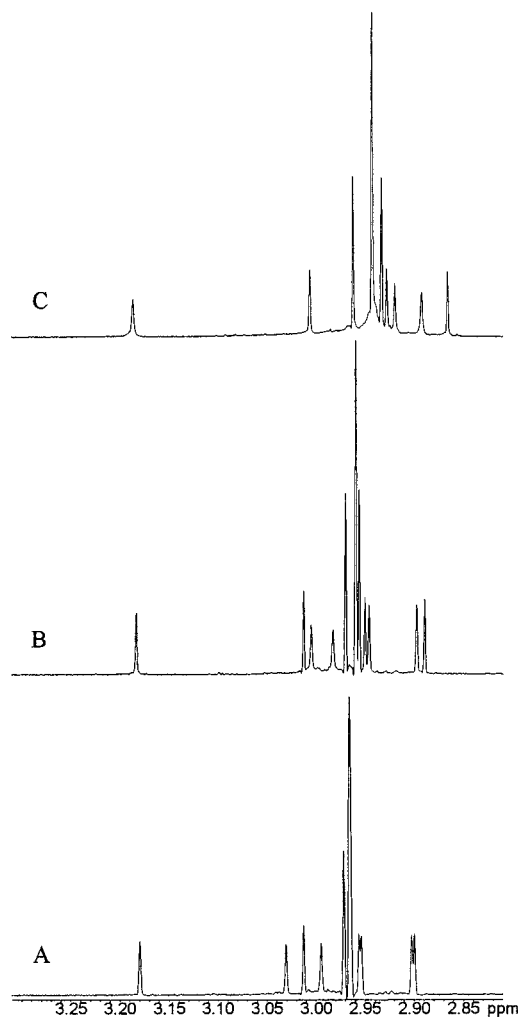
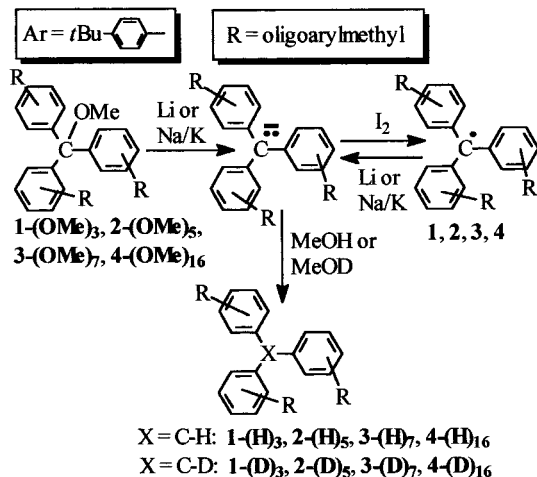


Figure 4. Partial ^1H NMR (500 MHz, C_6D_6) spectra for 4-(OMe)_{16} in the C-OCH₃ region. (A) 348 K, EM = -1.5 Hz, GB = 0.9 Hz. (B) 328 K, EM = -1.5 Hz, GB = 0.9 Hz. (C) 293 K, EM = -1.6 Hz, GB = 0.9 Hz.

(20) Uncertainty about the relative contribution of the $\text{M}^+ / (\text{M} - \text{H})^+$ and $\text{M}^+ / (\text{M} - \text{H})^+ / (\text{M} - \text{D})^+$ ions to the isotopic clusters in **4-(H)**₁₆ and the deuterated compounds complicates interpretation of the observed isotopic shifts.

Table 1. Relative Peak Integrations for the Partial ^1H NMR in the MeO- and *t*-Bu Group Regions for Hexadecaether **4**-(OMe)₁₆

T [K]	MeO groups	<i>t</i> -Bu groups
293	9 peaks; 1:1:2:6:2:1:1:1:1	13 peaks; 1:6:2:2:2:1:2:3:1:1:1:1:1
328	11 peaks; 1:1:1:1:2:4:2:1:1:1:1	12 peaks; 1:8:2:2:1:2:1:1:2:1:2:1
348	10 peaks; 1:1:1:1:2:6:1:1:1:1	11 peaks; 1:8:2:2:1:1:3:3:1:1:1

Scheme 2. Generation of Polyradicals **1–4** and Quenching Studies

the previously studied, more symmetrically substituted, macrocyclic calix[4]arene hydrocarbons, *cis/trans* isomers could be isolated or detected in comparable amounts.)^{3b} Integration of the triarylmethyl region in **4**-(D)₁₆ gives ~1 H (vs 16 H in **4**-(H)₁₆), which is within the error of integration for such molecules with such large numbers of protons, appearing as broad resonances. Therefore, the degree of deuteration for **4**-(D)₁₆, based on both ^1H NMR spectroscopy and FAB MS,²⁰ is estimated only approximately in the D₁₄–D₁₆ range.

Incomplete deuterium incorporation may originate in protonation of the initially formed carbanion by trace amounts of proton sources (moisture, residual MeOH, etc.) in the reactants and surface of the reaction vessel (with possible H/D KIE). Slightly lesser degree of deuteration at the 4-biphenyl-substituted sites compared to other sites correlates with initial formation of 4-biphenyl-substituted carbanions, as deduced from color changes at the early stages of reactions of *both* polyethers and polyradicals with alkali metal (preceding text).

Isolation of both protonated and deuterated quenching products confirms that the connectivity of the hydrocarbon framework in polyradicals and the precursor polyethers is identical. The high overall deuteration at the triarylmethyl sites only alludes to the possibility of high yield for generation of “unpaired” electrons. In addition to incorporation of hydrogens at triarylmethyl sites, other types of defects may affect the yield for “unpaired” electrons such as formation of dimers, addition of iodine to triarylmethyl sites (Ar₃C–I), or incomplete oxidation of carbopolyanion. All of the above defects will affect the overall spin values for polyradicals and introduce impurities with potentially different spin coupling properties. However, only the defects involving incorporation of hydrogens are detectable by the MeOH/MeOD quenching experiments.

3. Spin Cluster Model. Magnetic interactions in isolated organic polyradicals (e.g., as dilute solutions in diamagnetic solvents) are expected to be dominated by isotropic exchange interactions between “unpaired” electrons.^{1c,d} In polyarylmethyl high-spin polyradicals, “unpaired” electrons are localized at triarylmethyl sites, with the comparable magnitude of spin

density at the trityl carbon and the three adjacent benzene rings.^{1d,12,21} Therefore, Heisenberg Hamiltonian, $H = -2\sum_{i>j} J_{ij}S_iS_j$, with ferromagnetic couplings ($J_{ij} > 0$) between the nearest-neighbor sites should be appropriate as starting point for describing magnetism in such polyradicals.^{1c,d,22,23} When **1–4** are considered as oligomers of spins $1/2$, without any assumptions about spin couplings, **1** (trimer) and **2** (pentamer) are exactly solvable while **3** (heptamer) and **4** (hexadecamer) are not solvable by the vector decoupling (Figure 5).^{9,24,25} When J' (1,3-phenylene) $\gg J$ (3,4'-biphenylene) $\approx kT$ for **2** (pentamer), inspection of the Heisenberg Hamiltonian eigenvalues implies that the five highest in energy spin states are negligibly populated (Figure 5). Therefore, pentaradical **2** is adequately described by considering population of the five lowest in energy spin states, which correspond to a trimer of the $S' = 1, 1/2$, and 1 component spins (Figure 1).⁹ When $J' \gg J$ for **3** and **4**, exactly solvable spin dimer and trimer should provide useful approximations (Figure 1). High-spin ground states are predicted for polyradicals **1–4** with ferromagnetic couplings J' , $J > 0$.

For both **1** and **2**, considered as spin trimers, each pairwise J -coupling between the component spins (S') involves all triarylmethyl spin sites associated with S' . However, for **3** and **4**, only a fraction of the spin sites may be involved; i.e., only 1 out of 5 and 2 out of 6 spin sites participate in the pairwise J -coupling of the terminal $S' = 5/2$ and the center $S' = 3$ spins. Similarly to the case of dimer of $S' = 1$ spins for $S = 2$ tetradical, studied by Dougherty and co-workers, values for pairwise J -coupling between S' spins in the dimer (**3**) and trimer (**4**) should be scaled by $1/5$ and $(1/5)(2/6) = 1/15$, respectively.^{9,26} Therefore, the relative values of J for spin dimers and trimers corresponding to polyradicals **1–4** should be $J, J, J/5, J/15$.

In a diradical, where two triarylmethyl sites are connected through a 3,4'-biphenylene unit, a small thermal population of the lowest excited state in the 1.8–160 K temperature range was observed but it was insufficient for a reliable measurement of J in frozen THF.^{10,27} Decreasing the energy gap between the high-spin ground state and the lowest excited state, which is $2J$ in the diradical, should increase thermal population of the excited states.^{1d} In polyradicals **1–4**, the energy gaps are $J, J, (7/5)J, (6/15)J$, with scaling factors for **3** and **4** included, i.e., significantly less than in the diradical.⁹

4. ESR Spectroscopy of Triradical **1 and Pentaradical **2**.** X-Band (9.3 GHz) ESR spectra for 10^{-4} M **1** and **2** in 2-MeTHF/THF are obtained at 80 K. Line shape and intensity distortions are found, especially for **2**, even at the lowest attainable microwave power settings at these experimental conditions.

For **1**, the $\Delta m_s = 1$ region of the spectrum consists of five equally spaced lines, of which the center line is relatively intense. The spectral width is ~70 G. The line spacing, relative

(21) For electron localization in 1,3-connected polyarylmethyls, see: Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242. Reference 19.

(22) Heisenberg, W. *Z. Phys.* **1926**, *38*, 441. Dirac, P. A. M. *Proc. R. Soc.* **1926**, *112A*, 661. Heisenberg, W. *Z. Phys.* **1928**, *49*, 619.

(23) For valence bond calculations on polycarbenes, see: Teki, Y.; Takui, T.; Kitano, M.; Itoh, K. *Chem. Phys. Lett.* **1987**, *142*, 181. Alexander, A. A.; Klein, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 3401.

(24) Belorizky, E.; Fries, P. H. *J. Chim. Phys. (Paris)* **1993**, *90*, 1077.

(25) For reviews on magnetism of polynuclear metal complexes, see: Cairns, C. J.; Bush, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1. Gatteschi, D.; Caneschi, A.; Sessoli, R.; Cornia, A. *Chem. Soc. Rev.* **1996**, 101.

(26) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. Jacobs, S. J.; Schultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

(27) Unpublished data from this laboratory.

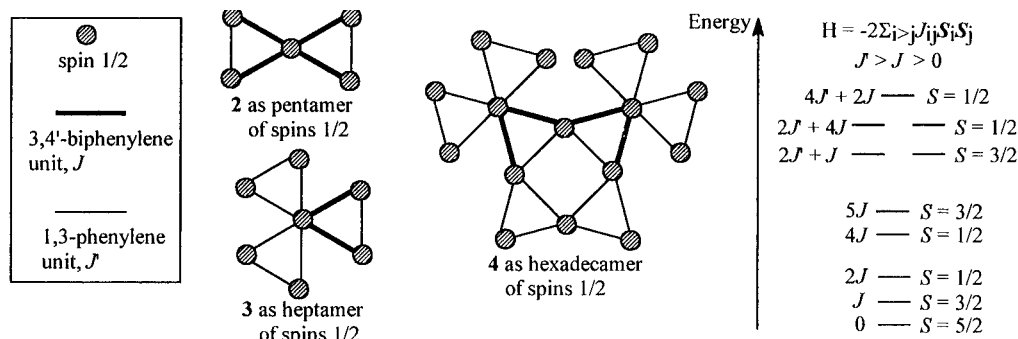


Figure 5. Pentamer, heptamer, and hexadecamer of spins $1/2$, corresponding to pentaradical **2**, heptaradical **3**, and hexadecaradical **4**. Energy eigenvalues from the Heisenberg Hamiltonian for pentaradical **2** are shown for $J, J' > 0$ (both couplings ferromagnetic). J and J' are spin coupling through 3,4'-biphenylene and 1,3-phenylene units, respectively.

intensities, and approximate line shapes are compatible with an $S = 3/2$ state with the following zero field splitting (zfs) parameters: $|E/hc| \approx 0 \text{ cm}^{-1}$ and $|D/hc| \approx 0.0016 \text{ cm}^{-1}$. Analogous 1,3-phenylene-based $S = 3/2$ triradical has $|D/hc| \approx 0.004\text{--}0.006 \text{ cm}^{-1}$, depending on conformation.²⁸

For **2**, the $\Delta m_s = 1$ region of the spectrum consists of seven lines, with the 2:1:1:1:1:2 spacings and the relatively intense center line. The spectral width is $\sim 140 \text{ G}$. The line spacing, relative intensities, and approximate line shapes are compatible with an $S = 5/2$ state with $|E/hc| \approx 0 \text{ cm}^{-1}$ and $|D/hc| \approx 0.0016 \text{ cm}^{-1}$. The analogous 1,3-phenylene-based $S = 5/2$ pentaradical has $|D/hc| = 0.0027 \text{ cm}^{-1}$.^{3b}

Similar to the analogous 1,3-phenylene-based half-integral spin tri- and pentaradicals, no resonances are detected in the $\Delta m_s = 2$ regions for **1** and **2** at 80 K.^{3a,28} The experimental difficulties are further compounded by relatively small values of $|D/hc|$ for **1** and **2**.²⁹

ESR spectra provide support for high-spin states of **1** and **2**. Their $|D/hc|$ values are significantly decreased compared to those of their 1,3-phenylene-based counterparts, as expected for increased distances between triarylmethyl sites with "unpaired" electrons.³⁰ The decreased spectral resolution for 3,4'-biphenylene-based polyradicals would severely limit any information content of the ESR spectra for $S > 3$.³¹ Quantitative studies of the ESR signal intensity (I) vs temperature (T), which could in principle be used to determine J , are obstructed by the relatively low softening point of 2-MeTHF matrix at $< 90 \text{ K}$, difficulties in detecting $\Delta m_s = 2$ signals, and microwave saturation in **1** and **2**. In the relatively more favorable case of integral spin 3,4'-biphenylene-based diradical with $|D/hc| \approx 0.0025 \text{ cm}^{-1}$, similar experimental limitations has provided only partial I vs T determination.¹⁰ Bulk magnetization studies provide alternative technique for characterization and avoiding restrictions of the ESR spectroscopy for spin-dilute polyradicals **1–4**.

5. Magnetic Studies of Polyradicals 1–4. Magnetization (M) is measured as a function of magnetic field ($H = 0\text{--}5.0 \text{ T}$) and temperature ($T = 1.8\text{--}160 \text{ K}$) for frozen solutions of polyradicals **1–3** in THF and **4** in THF- d_8 (or THF) using a SQUID magnetometer. Concentrations of polyradicals are in the $10^{-3}\text{--}10^{-5} \text{ M}$ range, which translates to a typical "unpaired" electron concentration in the 10^{-3} to 10^{-4} M range.

(28) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 2396.

(29) For smaller $|D/hc|$, intensity of the $\Delta m_s = 2$ resonance, relative to the $\Delta m_s = 1$ region, is expected to decrease: Weissman, S. I.; Kothé, G. *J. Am. Chem. Soc.* **1975**, *97*, 2537.

(30) In the simplest model for interpreting relative values of triplet $|D/hc| \propto 1/r^3$ (r = distance between "unpaired" electrons), only dipolar contributions to $|D/hc|$ and localized "unpaired" electrons are assumed. Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

(31) The problem of rapidly declining ESR spectral resolution for homologous polyradicals with larger values of S is discussed in ref 3b.

M vs T data at $H = 0.5$ or 2.0 T for polyradicals are fit as MT vs T to Heisenberg Hamiltonian-based spin cluster models (eqs 1–4, Experimental Section). An initial fit may involve as many as four variable parameters: J/k (spin coupling constant in Kelvin), N (number of moles of polyradical), θ (mean field parameter for small intermolecular magnetic interactions), and M_{dia} (correction for diamagnetism). However, for samples with satisfactory point-by-point correction for diamagnetism and negligible intermolecular magnetic interactions, such as hexadecaradical **4**, only two variable parameters, J/k and N , are needed.

M vs H data at $T = 1.8, 3,$ and 5 K for tri- and pentaradicals **1** and **2** are fit to a Brillouin function with mean field parameter, M vs $H/(T - \theta)$;^{32,33} θ is adjusted until the two variable parameters, spin, S , and magnetization at saturation, M_{sat} , are identical for each T . Values of θ are similar but not identical to those obtained from MT vs T fits. For hepta- and hexadecaradicals **3** and **4**, adequate fits to simple Brillouin functions, M vs H/T , with two variable parameters, S and M_{sat} , are obtained.³²

The use of Brillouin functions to describe magnetization at low temperatures ($1.8\text{--}5 \text{ K}$) is appropriate because of relatively large values of ferromagnetic J/k for **1–4**; that is, in this temperature range, almost all spin systems are expected to be in their high-spin ground states. For example, when M vs H data are generated for hexadecaradical **4**, using eq 4 (Experimental Section) for M with $J/k = 4.2 \text{ K}$ (see the following text), excellent fits to simple Brillouin functions (M vs H/T) are obtained with the following values of S : 8.00 (1.8 K), 8.00 (3 K), and 7.99 (5 K).

For triradical **1**, $J/k = 90 \pm 20 \text{ K}$, corresponding to a ferromagnetic coupling through 3,4'-biphenylene moiety, is obtained from a fit to a symmetrical trimer of the three $S' = 1/2$ component spins (Figure 6). The values of J/k and quality of the fits are significantly sample-dependent, presumably, due to presence of conformations, which possess different values of J/k .²⁸ Typical sample has $S \approx 1.3$. Relatively large and negative values for $\theta = -0.60\text{--}(-0.18) \text{ K}$, with $|\theta|$ decreasing upon dilution with THF, suggest significant intermolecular antiferromagnetic interactions for the triradical. Also, quality of the M vs $H/(T - \theta)$ fits significantly improves for $|\theta| < 0.4$.³⁴

For pentaradical **2**, fit to a pentamer of the five $S' = 1/2$ component spins gives $J/k = 90 \pm 5 \text{ K}$ and $J'/k > 200 \text{ K}$,

(32) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.

(33) Bino, A.; Johnston, D. C.; Goshorn, D. P.; Halbert, T. R.; Stiefel, E. I. *Science* **1988**, *241*, 1479.

(34) For relatively large $|\theta|$ (compared to T), a self-consistent version of the mean field approximation should be used for fitting M vs H data; for a recent discussion, see: Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57 and references therein.

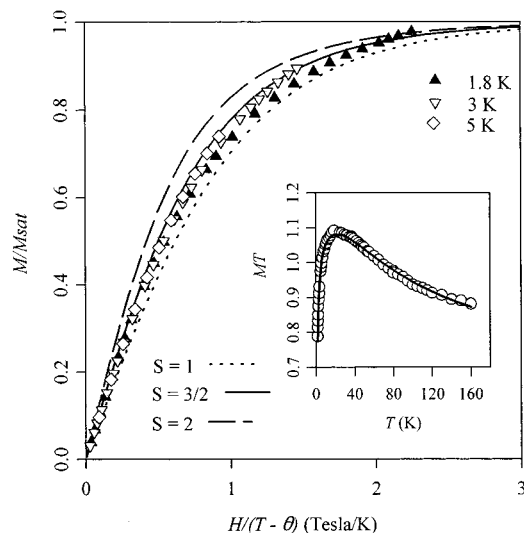


Figure 6. SQUID magnetometry ($H = 0\text{--}5.0$ T) for triradical **1** in THF. Main plot: M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.42$ K. Experimental points at $T = 1.8, 3,$ and 5 K and Brillouin functions with $S = 1, 3/2, 2$ are shown, as symbols and lines, respectively. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 1.26$ and $M_{\text{sat}}10^2 = 1.02, 1.04, 1.06$ emu; the parameter dependence is $0.59, 0.83,$ and 0.96 . Insert: MT vs T at $H = 1.0$ T. Open circles are the experimental points. The solid line is the numerical fit to the $S' = 1/2, 1/2, 1/2$ symmetrical trimer model (eq 1). The fitting parameters and their parameter dependencies are $J/k = 92$ K (0.94), $N = 6.0 \times 10^{-7}$ mol (0.86), $\theta = -0.60$ K (0.71), and $M_{\text{dia}} = 1.4 \times 10^{-5}$ emu (0.91). All experimental data are plotted after both the point-by-point and the numerical corrections ($M_{\text{dia}} = 1.4 \times 10^{-5}$ emu) for diamagnetism.

corresponding to ferromagnetic couplings through 3,4'-biphenylene and 1,3-phenylene moieties. Because the fits are relatively insensitive to values of $J/k > 200$ K and overparametrized, $J/k = 500$ K $\gg J/k \approx T$ is set constant, eliminating J/k as variable parameter. Typical values of S are in the 2.3–2.4 range. Values for $|\theta|$, which are an order of magnitude less than those for the triradical and decrease upon dilution with THF, suggest only small intermolecular antiferromagnetic interactions ($\theta < 0$) for the pentaradical (Figure 7).

For heptaradical **3**, fit to a dimer of the $S' = 5/2, 1$ component spins give $J/k = 13 \pm 2$ K. Typical sample has $S = 3.3$. Intermolecular antiferromagnetic interactions are negligible ($q = 0$ K) for the heptaradical (Figure 8).

For hexadecaradical **4**, fit to a symmetrical trimer of the $S' = 5/2, 3, 5/2$ component spins gives $J/k = 4 \pm 1$ K. Values of S are in the 6.6–7.2 range; the lowest value of 6.6 is for the most dilute sample; $\theta = 0$ K suggests negligible intermolecular antiferromagnetic interactions for hexadecaradical (Figure 9).

6. Defects and Interpretation of Magnetic Data. Less than perfect 100% yield for generation of “unpaired” electrons implies presence of defects in polyradicals, as mentioned in the preceding text.

Interpretation of the M vs H data at low T in polyradicals **1–4** can be reduced to consideration of spin systems arising from defects. (Thermal population effects, relevant to spin coupling J , are negligible in these conditions.) Two types of spin sites (triarylmethyl sites in **1–4**) can be discerned, depending on their impact on spin of polyradical. The first type, which we refer to as “defect sensitive sites”, are those where one defect interrupting π -conjugation will lead to a mixture of spin systems, drastically lowering the overall value of S . The second type, which we refer to as “defect insensitive sites”, are those where one defect retains a single spin system, lowering its value of S by $1/2$. In **1–4**, these two types correspond to

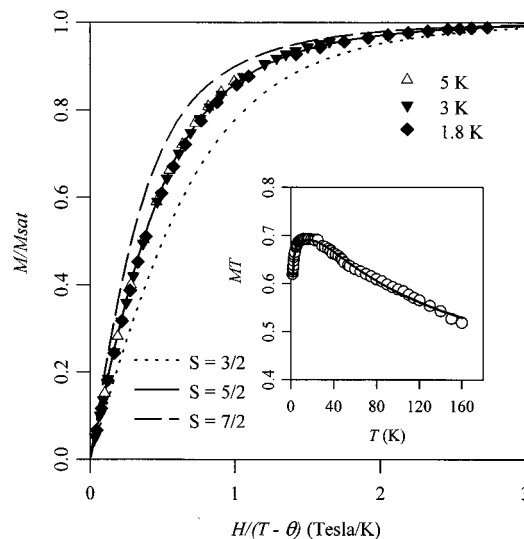


Figure 7. SQUID magnetometry ($H = 0\text{--}5.0$ T) for pentaradical **2** in THF. Main plot: M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.025$ K. Experimental points at $T = 1.8, 3,$ and 5 K and Brillouin functions with $S = 3/2, 5/2, 7/2$ are shown as symbols and lines, respectively. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 2.40$ and $M_{\text{sat}}10^3 = 8.90, 8.98,$ and 9.05 emu; the parameter dependence is $0.37, 0.59,$ and 0.86 . Insert: MT vs T at $H = 0.5$ T. Open circles are the experimental points. The solid line is the numerical fit to the $S' = 1/2$ pentamer trimer model (eq 2), with $J/k = 500$ K. The fitting parameters and their parameter dependencies are $J/k = 89$ K (0.94), $N = 3.2 \times 10^{-7}$ mol (0.81), $\theta = -0.093$ K (0.66), and $M_{\text{dia}} = 4.0 \times 10^{-5}$ emu (0.92). All experimental data are plotted after both the point-by-point and the numerical corrections ($M_{\text{dia}} = 4.0 \times 10^{-5}$ emu) for diamagnetism.

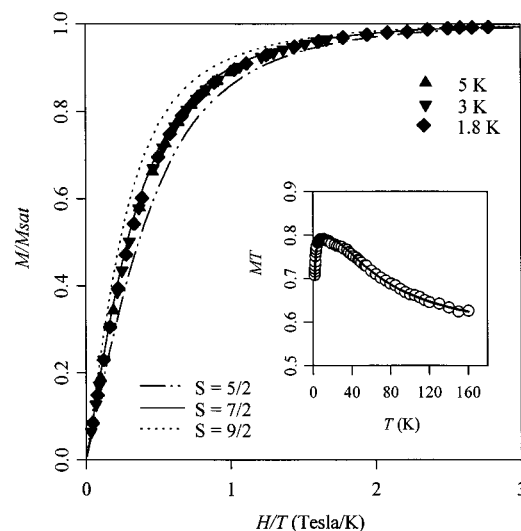


Figure 8. SQUID magnetometry ($H = 0\text{--}5.0$ T) for heptaradical **3** in THF. Main plot: M/M_{sat} vs H/T . Experimental points at $T = 1.8, 3,$ and 5 K and Brillouin functions with $S = 5/2, 7/2, 9/2$ are shown as symbols and lines, respectively. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 3.28$ and $M_{\text{sat}}10^3 = 8.34, 8.33,$ and 9.31 emu; the parameter dependence is $0.33, 0.50,$ and 0.78 . Insert: MT vs T at $H = 0.5$ T. Open circles are the experimental points. The solid line is the numerical fit to the $S' = 5/2, 1$ dimer model (eq 3). The fitting parameters and their parameter dependencies are $J/k = 12$ K (0.83), $N = 2.0 \times 10^{-7}$ mol (0.54), and $M_{\text{dia}} = 4.1 \times 10^{-6}$ emu (0.80). All experimental data are plotted after both the point-by-point and the numerical corrections ($M_{\text{dia}} = 4.1 \times 10^{-6}$ emu) for diamagnetism.

the 4-biphenyl-substituted sites and the other triarylmethyl sites, respectively. A simple model is proposed for evaluation of impact of defects on spin of polyradical. Parameter p is defined as probability of finding an “unpaired” electron at spin site, for

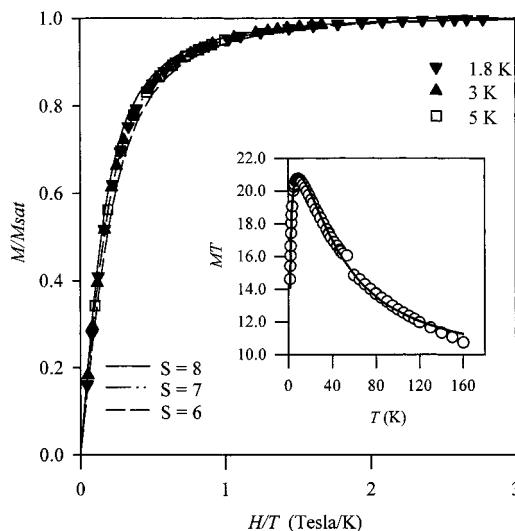


Figure 9. SQUID magnetometry ($H = 0\text{--}5.0$ T) for hexadecaradical **4** in THF- d_8 . Main plot: M/M_{sat} vs H/T . Experimental points at $T = 1.8, 3,$ and 5 K and Brillouin functions with $S = 6, 7, 8$ are shown as symbols and lines, respectively. The fitting parameters at $T = 1.8, 3,$ and 5 K are $S = 7.16, 7.19, 7.14$ and $M_{\text{sat}}10^2 = 1.165, 1.164,$ and 1.161 emu; the parameter dependence is $0.27, 0.37,$ and 0.53 . Inset: MT vs T at $H = 0.5$ T. Open circles are the experimental points. The solid line is the numerical fit to the $S' = 5/2, 3, 5/2$ symmetrical trimer model (eq 4). The fitting parameters are $J/k = 4.3$ K and $N = 1.2 \times 10^{-7}$ mol, with parameter dependence of 0.57 . Point-by-point correction was used for all data to account for diamagnetism.

simplicity, it is assumed that p is identical for all sites.^{2c,35} The parameter p may be related to yield per site for generation of “unpaired” electrons, 100% p %. Spin systems, caused by defects at the defect sensitive sites, are explicitly enumerated. Defects at the defect insensitive sites are accounted for approximately, by scaling their contribution to spin with a factor of p . In **4**, the following spin systems, arising from defects at the two 4-biphenyl-substituted sites, should be taken into account: for no defects, one system with spin $1 + 7p$; for one defect, three systems with spin $(1/2 + 5p), p, p$; for two defects, five systems with spin $3p, p, p, p, p$. (Figure 10 shows spin systems arising from one defect.) Equations for M , derived from this model, are used for numerical fit of the M vs H/T data (eq 5 in the Experimental Section). The resultant values of p allow for calculation of average spin $\langle S \rangle$ for a polyradical (Table 2, eq 6 in the Experimental Section). For p 's near one in polyradicals with connectivity of **1–4**, $S \approx \langle S \rangle$ within experimental errors. Consequently, values of S from fits to the variable spin Brillouin function (results section) may be used to estimate p . Values of p , for polyradicals **2–4** range from 0.95 to 0.98, with the best samples for each polyradical attaining 0.98 (Table 2).³⁵ Incidentally, sample of **4** with an excellent yield per site, 100% p = 98%, has $S = 7.2$, which is 10% lower than the theoretical value of $S = 8$, and contains 100% p ^{16%} = 72% of hexadecaradical with all 16 “unpaired” electrons intact. This clearly illustrates the importance of the problem of defects in very-high-spin polyradicals.

As far as the M vs T data for wide range of T are concerned, the presence of defects implies that polyradicals **1–4** may possess admixtures of uncoupled spins and spin clusters with different energy levels and, in some cases, J/k , compared to the spin clusters of the defect-free polyradicals. The question

(35) Assumptions of identical probability p for each site are common to the simplest versions of percolation theories: Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.

(36) Estimate of p for triradical **1** is not reported because its relatively large negative values of θ introduce significant error in values of S .³⁴

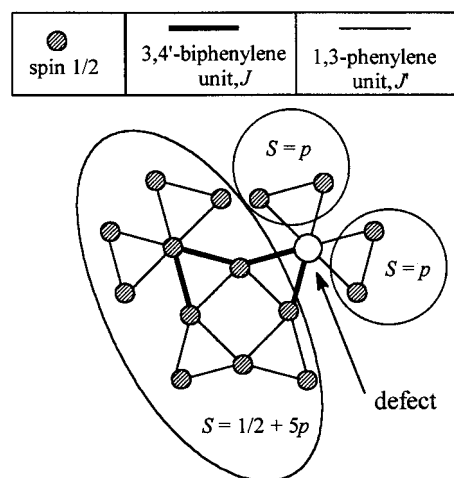


Figure 10. Enumeration of spin systems for hexadecaradical **4** with one defect at the 4-biphenyl-substituted site. Yield per site for generation of “unpaired” electrons (100% p) is assumed identical for each site.

Table 2. Equations for Average Spin ($\langle S \rangle$) As a Function of Parameter p , Where 100% p Is Yield Per Site for Generation of “Unpaired” Electrons in Polyradicals **1–4**^a

polyradical	$\langle S \rangle$	S	p
1	$1.5p/(2 - p)$		
2	$2.5p/(2 - p)$	2.40	0.98
3	$3.5p/(3 - 2p)$	3.28	0.98
4	$8p/(5 - 4p)$	7.2	0.98

^a Estimated parameters p are from experimental values of S for the best samples of **2–4** (Figures 7–9).

arises about the effect of such admixtures on the fitted values of J/k . However, inclusion of variable parameter p would overparametrize and/or severely complicate the MT vs T fits. Thus, the impact of the fixed amounts of the spin impurities are tested in the simplest polyradical, **1**. For example, admixture of 20% of an $S = 1/2$ monoradical or 10% $S = 1$ diradical (with identical J/k) lowers value of J/k by only $\sim 3\%$.

Conclusions

Spin cluster approach to very-high-spin polyradicals provides a series of adequately characterized polyradicals, including the $S = 8$ ground state hexadecaradical. Discriminating use of 3,4'-biphenylene and 3,5,4'-biphenylene ferromagnetic coupling units in polyarylmethyl polyradicals allows for simplified modular synthesis of their precursors, for attainment high yields for generation of “unpaired” electrons, and for improved magnetic characterization.

The next steps in design of very-high-spin polyradicals are (1) use of larger number of modules, (2) increase in the number of sites for “unpaired” electrons per module, and (3) use of only macrocyclic modules.¹⁰ Such organic mesomolecules and polymers hold a promise of greatly exceeding the present values of S .

Experimental Section

Materials and Special Procedures. Ether, tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF) for use on the 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 use. *t*-BuLi was obtained from either Aldrich (1.7 M in pentane) or Across (1.5 M in pentane). Other major

commercially available chemicals, including MeOD (99.5+% D), were obtained from Aldrich. Preparations of **7** and dibromocalix[4]arene hexaether (**13**) have been described.^{3,8}

For preparation of polyradicals, solutions of carbopolyanions in THF (or THF-*d*₈) were prepared in argon-filled Vacuum Atmospheres or M. Braun gloveboxes or a 10⁻³ Torr vacuum line. In selected preparations, starting from polyethers **1-(OMe)**₃, **2-(OMe)**₅, and **3-(OMe)**₇, all glassware and metalware were heated in the Braun glovebox antechamber to 180 °C under 10⁻³ Torr vacuum overnight. In all preparations, starting from hexadecaether **4-(OMe)**₁₆, vacuum line was used; the vessel and the procedures are described elsewhere.⁸ All polyethers were heated under 10⁻³ Torr vacuum in the 50–70 °C mineral oil bath overnight, prior to their use in preparation of carbopolyanions.

NMR Spectroscopy and Other Analyses. NMR spectra were obtained using Omega spectrometer (¹H, 500 MHz) in CDCl₃, benzene-*d*₆, THF-*d*₈; the chemical shift references were ¹H, TMS, 0.0 ppm, benzene-*d*₆, 7.15 ppm, acetone-*d*₆, 2.04 ppm, THF-*d*₇, 3.48 ppm, and ¹³C, CDCl₃, 77.0 ppm, THF-*d*₈, 67.45 ppm. Coupling constants (*J*) are reported in hertz. Typical 1D FID was subjected to exponential multiplication with an exponent of 0.1 Hz (for ¹H) and 1.0–2.0 Hz (for ¹³C); for selected spectra, both exponential and gaussian multiplications (EM and GB, respectively) were used, with exponents indicated as EM and GB for each applicable spectrum. IR spectra were obtained as described previously.^{2c} ESR spectra are acquired, using a liquid nitrogen dewar, as described elsewhere.^{3b} GC MS analyses were carried out using Hewlett-Packard 5890/5972 instrument equipped with a 30 m × 0.25 mm DB-5 capillary column. Typical oven temperatures were stepped up from 100 to 280 °C at a rate of 20 °C/min. FAB MS analyses were carried out at the Nebraska Center for Mass Spectrometry.

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

Etherification of Triarylmethanols.^{17b} **General Procedure.** A round bottom flask with sidearm was charged with NaH (60% dispersion in mineral oil, 3–20 equiv based on triarylmethanol). After mineral oil was removed with pentane under nitrogen flow, THF was added, and during cooling with an ice bath, triarylmethanol (1 equiv) in THF was then added. (The concentration of triarylmethanol in the reaction mixture was 0.01–0.05 M). The resultant suspension was stirred for 1–4 h during which time the temperature of cooling bath was allowed to reach ambient temperature. After the bath was recooled to 0 °C, MeI (1.5–3 equiv based on NaH) was added. Following 4–19 h of stirring at ambient temperature, aqueous workup was carried out. The ether extract was dried over MgSO₄ and, then, concentrated in vacuo to give crude modules **6**, **10**, and **12**.

Module 6. *n*-BuLi (34.0 mL of 2.5 M solution in hexane, 85 mmol) was added to a solution of 1,4-dibromobenzene (20.0 g, 84.8 mmol) in ether (300 mL) at –78 °C. After 2.5 h, methyl 4-*tert*-butylbenzoate (7.36 g, 38.3 mmol) was added as liquid by syringe under nitrogen flow at –78 °C. The reaction mixture was allowed to warm to ambient temperature for 1 day, and the reaction mixture was quenched with water (300 mL). After extraction with ether (2 × 150 mL), the combined organic layer was dried over MgSO₄. Concentration in vacuo gave 17.99 g of light yellow viscous liquid, which is triarylmethanol **5**, suitable for use in the next step in the synthesis. ¹H NMR (500 MHz, CDCl₃): δ 7.434, 7.167 (AB, *J* = 8, 8 H), 7.327, 7.110 (AB, *J* = 9, 4 H), 2.713 (s, 1 H), 1.309 (s, 9 H).

Etherification of **5** (0.921 g, 1.942 mmol), according to the general procedure, gave 1.04 g of light yellow viscous liquid. Separation by column chromatography with (TLC grade silica gel, hexane to 1% ether/hexane) gave 0.594 g of white solid (63%), mp 110–112 °C. ¹H NMR (500 MHz, EM = –1.2, GB = 0.9, CDCl₃): δ 7.416, 7.298 (AB, *J* = 9, 8 H), 7.307, 7.245 (AB, *J* = 9, 4 H), 3.024 (s, 3 H), 1.302 (s, 9 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 4 resonances; found, 4 resonances at 150.4 (q), 143.3 (q), 139.1 (q), 121.2 (q); aromatic nonquaternary region, expected, 4 resonances; found, 4 resonances at 131.0, 130.2, 128.6, 124.9; aliphatic region, 82.4 (q), 52.1, 34.5 (q), 31.3. CI GC-MS: *m/z* (%RA for *m/z* = 50–500) at (M – OCH₃)⁺ 455 (15), 457 (30), 459 (15) and at (M – C₁₀H₁₃)⁺ 331 (100), 333 (97).

Module 8. *t*-BuLi (4.40 mL of 1.7 M solution in pentane, 7.48 mmol) was added to a solution of **7** (2.00 g, 3.68 mmol) in ether (65 mL) at –78 °C. After 3.5 h, the reaction was quenched with MeOH (1 mL) at –78 °C and warmed to ambient temperature for 30 min. The reaction mixture was washed with 100 mL of water and extracted with ether (3 × 50 mL); the combined organic layer was washed with brine (25 mL) and dried over MgSO₄. Concentration in vacuo gave 1.625 g of clear viscous liquid. Separation by column chromatography (230–400 mesh silica gel, 10% benzene in hexane) gave 1.056 g of white solid (62%). Recrystallization of 150 mg of this white solid with MeOH/ether gave 100 mg of white crystals, mp 124–126 °C. ¹H NMR (500 MHz, EM = –1.6, GB = 0.9, CDCl₃): δ 7.685 (t, *J* ≈ 2, 1 H), 7.351 (dt, *J* = 8, *J* ≈ 2, 1 H), 7.326 (dt, *J* = 8, *J* ≈ 2, 1 H), 7.306, 7.293 (AB, *J* = 9, 8 H), 3.026 (s, 3 H), 1.307 (s, 18 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 4 resonances; found, 4 resonances at 150.0 (q), 148.0 (q), 139.9 (q), 122.0 (q); aromatic nonquaternary region, expected, 6 resonances; found, 6 resonances at 131.0, 129.7, 129.2, 128.7, 127.1, 124.7; aliphatic region, resonances at 86.4 (q), 52.0, 34.4 (q), 31.3. CI GC-MS: *m/z* (%RA for *m/z* = 50–500) at (M – OCH₃)⁺ 433 (47), 435 (47) and at (M – C₁₀H₁₃)⁺ 331 (100), 333 (93).

Module 10. *t*-BuLi (27.0 mL of 1.5 M solution in pentane, 40.5 mmol) was added to a solution of **7** (10.91 g, 20.05 mmol) in THF (180 mL) at –78 °C over the period of 10 min. After 1 h, 4,4'-*di-tert*-butylbenzophenone (5.89 g, 20.05 mmol) was added under nitrogen flow at –78 °C. The reaction mixture was allowed to warm to ambient temperature for 1 day; the reaction mixture was quenched with water (300 mL). After extraction with ether (2 × 200 mL), the combined organic layer was dried over MgSO₄. Concentration in vacuo gave 16.04 g of light yellow viscous liquid, which is triarylmethanol **9**, suitable for use in the next step in the synthesis. ¹H NMR (500 MHz, CDCl₃): δ 7.590 (t, *J* ≈ 2, 1 H), 7.429 (t, *J* ≈ 2, 1 H), 7.265, 7.084 (AB, *J* = 9, 4 H), 7.221 (t, *J* ≈ 2, 1 H), 7.243, 7.186 (AB, *J* = 9, 4 H), 2.931 (s, 3 H), 2.576 (s, 1 H), 1.305 (s, 18 H), 1.302 (s, 18 H).

Etherification of **9** (16.04 g, 21.13 mmol), according to the general procedure, followed by recrystallization from MeOH/ether afforded 14.09 g (86%) of white solid, mp 206–208 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.580 (d, *J* ≈ 2, 2 H), 7.301 (t, *J* ≈ 2, 1 H), 7.245, 7.179 (AB, *J* = 9, 16 H), 2.943 (s, 3 H), 1.305 (s, 36 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 4 resonances; found, 4 resonances at 149.8 (q), 146.5 (q), 140.2 (q), 121.9 (q); aromatic nonquaternary region, expected, 4 resonances; found, 4 resonances at 128.6, 128.5, 128.4, 124.5; aliphatic region, resonances at 86.5 (q), 52.0, 34.4 (q), 31.4.

Module 12. *t*-BuLi (9.50 mL of 1.5 M solution in pentane, 14.3 mmol) was added to a solution of **10** (5.248 g, 6.79 mmol) in THF (60 mL) at –78 °C. After 2.5 h, the temperature in the cooling bath was allowed to warm to –20 °C over a period of 20 min; subsequently, 4-bromobenzoyl chloride (0.675 g, 3.08 mmol) was added under nitrogen flow at –20 °C. After 2 h at –20 °C, the reaction mixture was allowed to warm to ambient temperature overnight. The reaction mixture was quenched with water (200 mL). After extraction with ether (2 × 200 mL), the combined organic layer was dried over MgSO₄. Concentration in vacuo gave 5.55 g of light yellow viscous liquid. Column chromatography (TLC grade silica gel, 10% ether in hexane) afforded triarylmethanol **11** (1.70 g, 35%), which is suitable for use in the next step in the synthesis. ¹H NMR (500 MHz, EM = –1.2, GB = 0.85, CDCl₃): δ 7.28–7.24 (m, 8 H), 7.163, 7.108 (AB, *J* = 9, 16 H), 7.160, 7.106 (AB, *J* = 9, 16 H), 6.930 (d, *J* = 8, 2 H), 2.778 (s, 1 H, exch. D₂O), 2.731 (s, 12 H), 1.265 (s, 72 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): aromatic quaternary region, expected, 8 resonances; found, 8 resonances at 149.38 (q), 149.35 (q), 146.3 (q), 145.5 (q), 143.2 (q), 141.13 (q), 141.09 (q), 120.8 (q); aromatic nonquaternary region, expected, 8 resonances; found, 7 resonances at 130.5, 130.0, 129.4, 128.47, 128.41, 125.5, 124.3; aliphatic region, 86.8 (q), 82.2 (q), 51.9, 34.3 (q), 31.4. FABMS (3-NBA) cluster: *m/z* (%RA for *m/z* = 340–1800) at (M – OCH₃)⁺ 1539.9 (80), 1540.9 (87), 1541.9 (100), 1542.9 (84), 1543.9 (49). IR (cm⁻¹): 3600 (O–H), 1593 (Ar), 1081 (C–O–C).

Etherification of **11** (1.59 g, 1.01 mmol), according to the general procedure, gave 1.63 g of light yellow viscous liquid. Filtration through flash silica with 5% ether in hexane and recrystallization from MeOH/ether afforded 1.40 g (87%) of white solid, mp 134–136 °C. ¹H NMR (500 MHz, EM = -0.90, GB = 0.80, CDCl₃): δ 7.300 (d, *J* = 2, 4 H), 7.245 (t, *J* = 2, 2 H), 7.234, 7.042 (AB, *J* = 8, 4 H), 7.161, 7.115 (AB, *J* = 8, 16 H), 7.161, 7.111 (AB, *J* = 8, 16 H), 2.779 (s, 12 H), 2.748 (s, 3 H), 1.522 (s, 72 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 8 resonances; found, 7 resonances at 149.3 (q), 143.6(q), 142.6 (q), 142.2 (q), 141.28 (q), 141.25 (q), 120.5 (q); aromatic nonquaternary region, expected, 8 resonances; found, 6 resonances at 130.48, 130.45, 129.3, 128.3, 127.1, 124.3; aliphatic region, 87.2 (q), 86.8 (q), 52.04, 51.97, 34.3 (q), 31.4. FABMS (3-NBA) cluster: *m/z* (% RA for *m/z* = 340–1800) at (M - OCH₃)⁺ 1153.9 (85), 1154.9 (82), 1155.9 (100), 1156.9 (81), 1157.9 (50). IR (cm⁻¹): 1593 (Ar), 1082 (C-O-C). Anal. Calcd for C₁₀₈H₁₂₉O₅Br: C, 81.58; H, 8.37. Found: C, 81.18; H, 7.95.

General Procedure for Polyethers 1-(OMe)₃, 2-(OMe)₅, 3-(OMe)₇, and 4-(OMe)₁₆ (Suzuki Coupling).¹⁶ *t*-BuLi (1.5 or 1.7 M solution in pentane, 2.1 equiv) was added to the first module (1 equiv) 0.02–0.06 M in THF at -78 °C. After 2–3 h, the reaction mixture was allowed to warm to -20 to -30 °C for 10–15 min and, then, B(OMe)₃ (1.1–1.25 equiv) was added to the reaction mixture. After warming to ambient temperature overnight, the reaction mixture was dried under N₂ flow and, then, evacuated. Subsequently, the following components were added to the reaction mixture: the second module (neat, under N₂ flow), Ba(OH)₂·8H₂O (0.6–1.0 equiv, neat, under N₂ flow), Pd(PPh₃)₄ (0.03–0.05 equiv per C bond, either neat in an N₂ glovebag or 0.01–0.02 M in degassed toluene), and toluene/MeOH (1:1, degassed by N₂ bubbling). The reaction mixture was allowed to reflux under N₂ atmosphere for 1–3 days. After extraction with ether, the ether layer was dried over MgSO₄, filtered, and concentrated in vacuo to give a crude product.

1-(OMe)₃. Following the general procedure for Suzuki coupling, starting from **8** (0.302 g, 0.648 mmol) and **6** (0.143 g, 0.293 mmol), reflux for 3 days in toluene/MeOH (30 mL) gave the crude product as a clear oil. Separation by column chromatography with (TLC grade silica gel, 5% ether in hexane), followed by recrystallization from MeOH gave 0.130 g of white solid (51%), mp 164–166 °C. ¹H NMR (500 MHz, EM = -1.2, GB = 0.6, CDCl₃): δ 7.733 (t, *J* = 2, 2 H), 7.491 (s, 8 H), 7.438 (dt, *J* = 8, *J* = 2, 2H), 7.400 (dt, *J* = 8, *J* = 2, 2 H), 7.37–7.28 (m, 22 H), 3.090 (s, 3 H), 3.057 (s, 6 H), 1.304 (s, 9 H), 1.298 (s, 36 H). ¹H NMR (500 MHz, EM = -1.2, GB = 0.85, C₆D₆, ¹H-¹H COSY cross-peaks in the aromatic region): δ 8.190 (t, *J* = 2, 2 H, 7.598, 7.375), 7.623 (d, *J* = 9, 8 H, 7.242), 7.598 (dt, *J*₁ = 8, *J*₂ = 2, 2 H, 8.190, 7.180), 7.544 (d, *J* = 9, 4 H, 7.482), 7.544 (d, *J* = 8, 2 H, 7.289), 7.482 (d, *J* = 9, 4 H, 7.544), 7.375 (dt, *J*₁ = 8, *J*₂ = 2, 2 H, 8.190, 7.180), 7.289 (d, *J* = 8, 2 H, 7.544), 7.242 (d, *J* = 9, 8 H, 7.623), 7.180 (t, *J* = 8, 2 H, 7.598, 7.375), 3.112 (s, 6 H), 3.045 (s, 3 H), 1.219 (s, 9 H), 1.166 (s, 36 H). [Note: ¹H-¹H COSY cross-peak a between resonances at 7.598 and 7.375 ppm was not detected.] ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 8 resonances; found, 8 resonances at 149.8 (q), 149.6 (q), 145.5 (q), 143.3 (q), 140.7 (q), 140.4 (q), 140.0 (q), 139.7 (q); aromatic nonquaternary region, expected, 10 resonances; found, 10 resonances at 129.0, 128.7, 128.6, 128.1, 127.5, 127.1, 126.5, 125.3, 124.7, 124.6; aliphatic region, 86.8 (q), 86.7 (q), 52.1, 52.0, 34.4 (q), 31.4. FABMS (3-NBA) cluster: *m/z* (% RA for *m/z* = 350–1240) at (M - OCH₃)⁺, 1065.8 (16), 1066.8 (15), 1067.8 (100), 1068.8 (84), 1069.8 (37), 1070.8 (12). IR (cm⁻¹): 1602 (Ar), 1079 (C-O-C). Anal. Calcd for C₈₀H₉₀O₃: C, 87.39; H, 8.25. Found: C, 87.61; H, 8.08.

2-(OMe)₅. Following the general procedure for Suzuki coupling, starting from **10** (0.503 g, 0.650 mmol) and **6** (0.143 g, 0.293 mmol), reflux for 2 days in toluene/MeOH (30 mL) gave the crude product as a clear oil. Column chromatography with (TLC grade silica gel, benzene/hexane, 2:1) and recrystallization from MeOH gave 0.235 g of white solid (47%), mp 184–186 °C. ¹H NMR (500 MHz, EM = -1.2, GB = 1.2, CDCl₃): δ 7.647 (d, *J* = 2, 4 H), 7.481, 7.458 (AB, *J* = 9, 8 H), 7.363 (t, *J* = 2, 2 H), 7.336, 7.295 (AB, *J* = 8, 2 H), 7.239 (s, 32 H), 3.074 (s, 3 H), 2.979 (s, 12 H), 1.298 (s, 72 H), 1.294 (s, 9 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 8 resonances; found, 8 resonances at 149.7

(q), 149.5 (q), 144.2 (q), 143.1 (q), 141.0 (q), 140.6 (q), 139.9 (q), 139.5 (q); aromatic nonquaternary region, expected, 8 resonances; found 7 resonances at 129.0, 128.6, 128.5, 126.5, 124.67, 124.63, 124.4; aliphatic region, 86.9 (q), 86.7 (q), 52.08, 52.02, 34.4 (q), 31.4, 31.3. FABMS (3-NBA) cluster: *m/z* (% RA for *m/z* = 400–2000) at (M - OCH₃)⁺ 1682.0 (18), 1683.0 (23), 1684.0 (83), 1685.0 (100), 1686.0 (68), 1687.0 (32), 1688.0 (14). IR (cm⁻¹): 1595 (Ar), 1081 (C-O-C). Anal. Calcd for C₁₂₄H₁₄₆O₃₅: C, 87.77; H, 8.57. Found: C, 86.70, H, 8.44.

3-(OMe)₇. Following the general procedure for Suzuki coupling, starting from **10** (0.146 g, 0.189 mmol) and **12** (0.202 g, 0.127 mmol), reflux for 1 day in toluene/MeOH (8 mL) gave a the crude product as a light yellow viscous solid. Column chromatography (TLC grade silica gel, 5% ether in hexane) and recrystallization from MeOH gave 0.204 g of white solid (73%), mp 168–172 °C. ¹H NMR (500 MHz, EM = -1.40, GB = 0.90, CDCl₃, ¹H-¹H COSY cross-peaks in the aromatic region): δ 7.714 (d, *J* = 2, 2 H, 7.311), 7.399 (d, *J* = 8, 2 H, 7.195), 7.350 (d, *J* = 2, 4 H, 7.206), 7.311 (t, *J* = 2, 1 H, 7.714), 7.235 (s, 16 H), 7.195 (d, *J* = 8, 2 H, 7.399), 7.206 (t, *J* = 2, 2 H, 7.350), 7.148 (d, *J* = 9, 16 H), 7.126 (d, *J* = 9, 8 H), 7.121 (d, *J* = 9, 8 H), 2.989 (s, 6 H), 2.798 (s, 3 H), 2.760 (s, 12 H), 1.291 (s, 36 H), 1.232 (s, 72 H). ¹³C{¹H}DEPT(135°)NMR (125 MHz, CDCl₃): δ aromatic quaternary region, expected, 12 resonances; found, 11 resonances at 149.5 (q), 149.1 (q), 144.3 (q), 143.0 (q), 142.8 (q), 142.3 (q), 141.44 (q), 141.41 (q), 141.0 (q), 139.5 (q), 139.4 (q); aromatic nonquaternary region, expected, 12 resonances; found 9 resonances at 129.3, 128.7, 128.4, 128.3, 127.0, 126.0, 124.4, 124.3, 124.0; aliphatic region, 86.86 (q), 86.83 (q), 52.08, 51.98, 51.95, 34.4 (q), 34.3 (q), 31.4. FABMS (3-NBA) cluster: *m/z* (% RA for *m/z* = 400–2320) at (M - OCH₃)⁺ 2166.5 (16), 2167.5 (24), 2168.5 (72), 2169.5 (100), 2170.5 (84), 2171.5 (43), 2172.5 (21); calcd for C₁₅₇H₁₈₇O₆ (M - OCH₃)⁺ 2168.4 (56), 2169.4 (100), 2170.4 (89), 2171.4 (53), 2172.4 (24). IR (cm⁻¹): 1594 (Ar), 1081 (C-O-C). Anal. Calcd for C₁₅₈H₁₉₀O₇: C, 86.21; H, 8.70. Found: C, 86.06; H, 8.90.

4-(OMe)₁₆. Following the general procedure for Suzuki coupling, starting from **12** (0.200 g, 0.126 mmol) and **13** (0.052 g, 0.029 mmol), reflux for 2 days in toluene/MeOH (8 mL) gave the crude product as a clear oil. Column chromatography (TLC grade silica gel, 7% ether in hexane), preparative TLC (7% ether in hexane with repeated developments), and treatment with boiling MeOH gave 19.9 mg of white glassy solid (15%). ¹H NMR (500 MHz, EM = -1.60, GB = 0.90, C₆D₆, 293 K): δ 8.180–7.080 (m, 128 H), 3.180 (s, 3 H), 2.999 (s, 3 H), 2.956 (s, 6 H), 2.936 (s, 18 H), 2.927 (s, 6 H), 2.921 (s, 3 H), 2.913 (s, 3 H), 2.886 (s, 3 H), 2.860 (s, 3 H), 1.238 (s, 9 H), 1.228 (s, 54 H), 1.226 (s, 18 H), 1.218 (s, 18 H), 1.215 (s, 18 H), 1.206 (s, 9 H), 1.200 (s, 18 H), 1.187 (s, 27 H), 1.180 (s, 9 H), 1.176 (s, 9 H), 1.172 (s, 9 H), 1.163 (s, 9 H), 1.151 (s, 9 H). ¹H NMR (500 MHz, EM = -1.50, GB = 0.90, C₆D₆, 328 K): δ 8.150–7.050 (m, 128 H), 3.168 (s, 3 H), 2.997 (s, 3 H), 2.990 (s, 3 H), 2.968 (s, 3 H), 2.955 (s, 6 H), 2.944 (s, 12 H), 2.941 (s, 6 H), 2.935 (s, 3 H), 2.931 (s, 3 H), 2.883 (s, 3 H), 2.875 (s, 3 H), 1.234 (s, 9 H), 1.228 (s, 72 H), 1.221 (s, 18 H), 1.219 (s, 18 H), 1.215 (s, 9 H), 1.195 (s, 18 H), 1.192 (s, 9 H), 1.191 (s, 9 H), 1.188 (s, 18 H), 1.184 (s, 9 H), 1.176 (s, 18 H), 1.159 (s, 9 H). ¹H NMR (500 MHz, EM = -1.50, GB = 0.90, C₆D₆, 348 K, ¹H-¹H COSY cross-peaks in aromatic region): δ 8.102 (t, *J* = 2, 1 H, 7.869, 7.561), 7.921 (t, *J* = 2, 1 H, 7.815, 7.484), 7.918 (t, *J* = 2, 1 H, 7.865, 7.795), 7.869 (t, *J* = 2, 1 H, 8.102, 7.561), 7.865 (t, *J* = 2, 1 H, 7.918, 7.795), 7.846 (d, *J* = 2, 2 H, 7.672), 7.839 (d, *J* = 2, 2 H, 7.680), 7.815 (t, *J* = 2, 1 H, 7.921, 7.484), 7.803 (d, *J* = 2, 2 H, 7.656), 7.795 (t, *J* = 2, 1 H, 7.918, 7.865), 7.736 (t, *J* = 2, 1 H, 7.684, 7.586), 7.684 (t, *J* = 2, 1 H, 7.736, 7.586), 7.680 (t, *J* = 2, 1 H, 7.839), 7.672 (t, *J* = 2, 1 H, 7.846), 7.656 (t, *J* = 2, 1 H, 7.803), 7.636 (d, *J* = 9, 2 H, 7.283), 7.586 (t, *J* = 2, 1 H, 7.736, 7.684), 7.561 (t, *J* = 2, 1 H, 8.102, 7.869), 7.43–7.51 (overlapped, 7.18–7.26), 7.503 (t or d, *J* = 2, 1 H or 2 H, 7.243), 7.484 (t, *J* = 2, 1 H, 7.921, 7.815), 7.464 (d, *J* = 9, 2 H, 7.283), 7.429 (d, *J* = 9, 2 H, 7.402), 7.404 (d, *J* = 9, 2 H, 7.362), 7.402 (d, *J* = 9, 2 H, 7.429), 7.362 (d, *J* = 9, 2 H, 7.404), 7.350 (d, *J* = 9, 2 H, 7.169), 7.342 (d, *J* = 9, 2 H, 7.127), 7.18–7.26 (overlapped, 7.43–7.51), 7.283 (d, *J* = 9, 2 H, 7.636), 7.283 (d, *J* = 9, 2 H, 7.464), 7.243 (d or t, *J* = 2, 2 H or 1 H, 7.503), 7.169 (d, *J* = 9, 2 H, 7.350), 7.127 (d, *J* = 9, 2 H, 7.342), 3.166 (s, 3 H), 3.017 (s, 3 H), 2.999 (s, 3 H), 2.981 (s, 3 H), 2.958 (s, 6 H), 2.952 (s, 18 H),

2.942 (s, 3 H), 2.940 (s, 3 H), 2.889 (s, 3 H), 2.886 (s, 3 H), 1.237 (s, 9 H), 1.233 (s, 72 H), 1.227 (s, 18 H), 1.226 (s, 18 H), 1.223 (s, 9 H), 1.202 (s, 9 H), 1.199 (s, 27 H), 1.195 (s, 27 H), 1.187 (s, 9 H), 1.182 (s, 9 H), 1.171 (s, 9 H). FABMS (3-NBA) cluster: m/z (% RA for $m/z = 800-4800$) at (M - OCH₃)⁺ 4604.1 (41), 4605.1 (79), 4606.1 (84), 4607.1 (100), 4608.1 (86), 4609.1 (64), 4610.1 (45); calcd for C₃₃₁H₃₈₉O₁₅ (M - OCH₃)⁺ 4604.0 (11), 4605.0 (42), 4606.0 (80), 4607.0 (100), 4608.0 (94), 4609.0 (71), 4610.0 (44), 4611.0 (24). IR (cm⁻¹): 1593 (Ar), 1083 (C-O-C). Anal. Calcd for C₃₃₂H₃₉₂O₁₆: C, 85.96; H, 8.52. Found: C, 85.08; H, 8.41.

Reactions of Heptaether 3-(OMe)₇ with Na/K and MeOH Quenching Product 3-(H)₇. A drop of Na/K alloy (multimolar excess) was added to a stirred polyether (15.2 mg) in THF (0.5 mL). After 3 days of stirring, MeOH (a few drops) was added. The usual aqueous workup with ether gave the crude product. Preparative TLC (2.5% ether in hexane) gave a clear oil (11.3 mg). Treatment with boiling ether/MeOH afforded a white solid (8.2 mg).³⁷

Preparation of Polyradicals for SQUID Magnetometry, ESR Spectroscopy, and Quenching Studies with MeOH and MeOD.^{3b}

Polyether (7–16 mg) was stirred for several days with excess Li metal (for 1-(OMe)₃, 2-(OMe)₅, 3-(OMe)₇) or Na/K alloy (for 2-(OMe)₅, 3-(OMe)₇, 4-(OMe)₁₆) in THF or THF-*d*₈ (0.5 mL). For 1-(OMe)₃, 2-(OMe)₅, and 3-(OMe)₇, carbopolyanions in THF were obtained in an argon-filled glovebox and, then, transferred to an oxidation vessel, which was modified by the replacement of the 4 mm with 5 mm o.d. quartz tube.²⁷ For 4-(OMe)₁₆, carbopolyanions in THF-*d*₈ (or THF) were prepared directly in a multicompartiment oxidation vessel, as described elsewhere.⁸ Addition of I₂, either as crystals under stream of argon or through vacuum transfer at low temperatures (168–178 K) gave the corresponding polyradicals in THF (or THF-*d*₈). A small portion of polyradical in THF (or THF-*d*₈) was transferred at low temperature to a 5 mm quartz tube. The tube possessed a thin flat bottom, located ca. 60 mm from the end of the tube.⁸ The tube was flame sealed and stored in liquid nitrogen for magnetization studies. Samples of tri- and pentaradicals **1** and **2** for ESR spectroscopy were diluted with 2-MeTHF several-fold prior to transfer to a 4 mm quartz tube. The remaining reaction mixture was treated with Na/K alloy or Li at 168–178 K for several hours and, then, at 195 K for several days. Subsequent addition of MeOD or MeOH was followed with usual aqueous workup. Separation by PTLC, 2.5% ether in hexane (2.0% ether in hexane for 4-(H)₁₆ and 4-(D)₁₆) gave clear oils of hydrocarbons 1-(H)₃, 2-(H)₅, and 4-(H)₁₆ and deuterated products 1-(D)₃, 2-(D)₅, 3-(D)₇, and 4-(D)₁₆.³⁷

SQUID Magnetometry. Quantum Design (San Diego, CA) MPMS5S was used. The sample tubes were inserted to the magnetometer at low temperature under helium atmosphere and, then, evacuated and purged with helium, as described elsewhere. Following the measurements, sample tubes were stored at ambient temperature for several weeks, until their magnetic moments were negligible. Such samples were carefully reinserted to the magnetometer, with the sample chamber at 200 K, and subjected to the identical sequence of measurements as the original sample. Such data were used for the point-by-point correction for diamagnetism.

Numerical Curve Fitting. The 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 follows: dependence = 1 - ((variance of the parameter, other parameters constant)/(variance of the parameter, other parameters changing)). Values close to 1 indicate overparametrized fit. Up to four variable parameters, J/k (spin coupling constant in Kelvin), N (number of moles of polyradical), θ (mean field parameter for small intermolecular magnetic interactions), M_{dia} (correction for diamagnetism) are used for fitting MT vs T data over wide range of T . For selected samples, accurate point-by-point correction for diamagnetism and/or negligible intermolecular magnetic interactions may eliminate M_{dia} and/or θ as variable parameters.

Equations for magnetization, $M(T, H)$, are obtained using the standard statistical mechanical procedures on energy eigenvalues, derived from the Heisenberg Hamiltonian. The following definitions are introduced for notation of all equations for M :

$$a = (1.345H)/(T - \theta)$$

$$c_k = 1 + 2 \sum_{i=1-k}^k \cosh(ia); k = 1, 2, \dots, S; \text{ for integral } S$$

$$c_k = 2 \sum_{i=1-k, \text{ odd}}^k \cosh(ia/2); k = 1, 3, \dots, 2S; \text{ for half-integral } S$$

$$s_k = \sum_{i=1-k}^k i(\sinh(ia)); k = 1, 2, \dots, S; \text{ for integral } S$$

$$s_k = \sum_{i=1-k, \text{ odd}}^k (i/2)(\sinh(ia/2)); k = 1, 3, \dots, 2S; \text{ for half-integral } S$$

$$e_m = \exp(-mb)/T; m = \text{integer}; b = J/k$$

$$e_m' = \exp(-mb')/T; m = \text{integer}; b' = J'/k = 500 \text{ K}$$

Equations for M for polyradicals **1–4** are as follows:

1 as $S' = 1/2, 1/2, 1/2$ trimer

$$M = (2(11180)NF_1) + M_{\text{dia}}; S = 3/2 \quad (1)$$

where

$$F_1 = [s_3 + s_1(e_3 + e_1)]/[c_3 + c_1(e_3 + e_1)]$$

2 as $S' = 1/2$, pentamer

$$M = (2(11180)NF_2) + M_{\text{dia}}; S = 5/2 \quad (2)$$

where

$$F_2 = \{s_5 + s_3[e_5 + e_1 + (2e_2'e_1)] + s_1[e_4 + e_2 + (2e_2'e_4) + (e_4'e_2)]\}/\{c_5 + c_3[e_5 + e_1 + (2e_2'e_1)] + c_1[e_4 + e_2 + (2e_2'e_4) + (e_4'e_2)]\}$$

3 as $S' = 5/2, 1/2$, dimer

$$M = (2(11180)NF_3) + M_{\text{dia}}; S = 7/2 \quad (3)$$

where

$$F_3 = [s_7 + s_5e_7 + s_3e_{12}]/[c_7 + c_5e_7 + c_3e_{12}]$$

4 as $S' = 5/2, 3, 5/2$ trimer

$$M = (2(11180)NF_4) + M_{\text{dia}}; S = 8 \quad (4)$$

where

$$F_4 = [s_8 + s_7(e_{16} + e_6) + s_6(e_{30} + e_{20} + e_{12}) + s_5(e_{42} + e_{32} + e_{24} + e_{18}) + s_4(e_{52} + e_{42} + e_{34} + e_{28} + e_{24}) + s_3(e_{60} + e_{50} + e_{42} + e_{36} + e_{32} + e_{30}) + s_2(e_{66} + e_{56} + e_{48} + e_{42} + e_{38}) + s_1(e_{60} + e_{52} + e_{46})]/[c_8 + c_7(e_{16} + e_6) + c_6(e_{30} + e_{20} + e_{12}) + c_5(e_{42} + e_{32} + e_{24} + e_{18}) + c_4(e_{52} + e_{42} + e_{34} + e_{28} + e_{24}) + c_3(e_{60} + e_{50} + e_{42} + e_{36} + e_{32} + e_{30}) + c_2(e_{66} + e_{56} + e_{48} + e_{42} + e_{38}) + c_1(e_{60} + e_{52} + e_{46}) + e_{54}]$$

Using M_{dia} from the MT vs T fit and/or point-by-point correction for diamagnetism, M vs H data at low temperatures ($T = 1.8, 3, 5 \text{ K}$) were corrected for diamagnetism. For tri- and pentaradicals **1** and **2**, fitting to a Brillouin function with mean field parameter, M vs $H/(T - \theta)$ were carried out;^{32,33} θ was adjusted until the two variable parameters, spin, S , and magnetization at saturation, M_{sat} , were identical for each T . For hepta- and hexadecaradicals **3** and **4**, $\theta = 0$ from the MT vs T fit, providing adequate fits to simple Brillouin function, M vs H/T , with two variable parameters, S and M_{sat} .³² Alternative procedure for **4**, involve fitting the M vs H/T data to a sum of Brillouin functions ($B(S_i)$) weighted with fractions (x_i) of spin systems with spin S_i in the sample

(37) See the Supporting Information.

of polyradical with 0–2 defects at the two 4-biphenyl-substituted sites (eq 5). Variable parameters are p and M_{sat} .

$$M/M_{\text{sat}} = \sum_i B(S_i)x_i / \sum_i x_i \quad (5)$$

For **4**, the following parameters are used: $x_i = p^2, 2p(1-p), (1-p)^2, 4[p(1-p) + (1-p)^2]$ and $S_i = 1 + 7p, 0.5 + 5p, 3p, p$, where $i = 1-4$. Average spin $\langle S \rangle$ is defined as follows (eq 6, Table 2):

$$\langle S \rangle = \sum_i S_i x_i / \sum_i x_i \quad (6)$$

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Supporting Information Available: A listing of NMR, MS, and IR data for hydrocarbons **1-(H)**₃, **2-(H)**₅, **3-(H)**₇, and **4-(H)**₁₆ and deuterated products **1-(D)**₃, **2-(D)**₅, **3-(D)**₇, **4-(D)**₁₆ (4 pages). See any current masthead page for ordering and Internet access instructions.

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