solvent in vacuo gave the desired enediyne (1.67 g, 93%) as a brown oil, which was used directly in the next step. 2) To the enediyne (1.67 g, 4.13 mmol) in MeOTMS (2.0 mL, 1.5 g, 15 mmol) was added TMSOTf (0.10 mL, 0.12 g, 0.52 mmol). After the reaction mixture had been stirred for 48 h at 25 °C, aqueous workup ($NaHCO_3$), removal of the solvent in vacuo, and filtration through silica gel (Et_2O/hexanes 1/1) gave the desired bis(acetal) (1.38 g, 74%) as a yellow oil. 3) To the bis(acetal) (7.34 g, 16.3 mmol) in MeOH (50 mL) was added K_2CO_3 ($\approx$100 mg). After the reaction mixture had been stirred for 15 min at 25 °C, aqueous workup, removal of the solvent in vacuo, and filtration through silica gel (Et_2O/hexanes 1/1) gave **6b** (5.80 g, 94%) as a yellow oil. It was diluted with THF (100 mL) and used directly in the next step.

7b: To **6b** (6.28 g, 16.6 mmol) in THF (100 mL) at −78 °C was added LiHMDS, which was prepared from $(Me_3Si)_2NH$ (3.50 mL, 2.68 g, 16.6 mmol) and 2.5 M *n*BuLi (6.60 mL, 16.6 mmol) in THF (15 mL). After 30 min CuBr (2.38 g, 16.6 mmol) was added, and the mixture warmed to 0 °C. To this solution was added 1,3,5-tris(bromoethynyl)benzene[1a] (2.03 g, 5.25 mmol). After the reaction mixture had been stirred for 12 h at 25 °C, aqueous workup ($NaHCO_3$) and removal of the solvent in vacuo gave a brown oil, which was purified by chromatography on silica gel (hexanes to hexanes/Et_2O 3/1) to afford **7b** (3.25 g, 48%) as a colorless foam.

8b: To **7b** (500 mg, 0.391 mmol) in THF (10 mL) was added five drops of H_2O followed by 1.0 M TBAF (2.0 mL, 2.0 mmol). The reaction mixture was stirred for 2 h, diluted with hexanes (50 mL), and filtered through silica gel (Et_2O). The resulting yellow fractions were concentrated to 5 mL and diluted with ODCB (400 mL) for the immediately following cyclization.

9b: To the solution of **8b** obtained above was added CuCl (119 mg, 1.20 mmol) followed by TMEDA (1.0 mL, 0.77 g, 6.6 mmol). After the reaction mixture had been stirred for 1 h under air, the solution was poured on top of a pad of silica gel and eluted with $CHCl_3$ to remove most of the ODCB. Elution with $Et_2O/CHCl_3$ (1/2) provided a yellow fraction with the desired product. The solvent was removed, and the brown oil purified by chromatography on silica gel ($Et_2O/CHCl_3$ 5/95). Removal of the solvent in vacuo gave cyclophane **9b** (150 mg, 48%) as a yellow foam.

3: Aliquots of **9b** (5 - 30 mg) were dissolved in trifluoroacetic acid (1–3 mL). Over 3–6 h a precipitate began to form (the reaction could be monitored by ^1H NMR spectroscopy in CF_3CO_2D). After 6–12 h the trifluoroacetic acid was removed in vacuo at 25 °C in the absence of light. [D_8]THF ($\approx$0.5 mL) was immediately added to the remaining orange-red solid under argon. This solution was used for ^{13}C NMR spectroscopy. For the LD-MS experiments, anhydrous CH_2Cl_2 or THF were added to dissolve the precipitate, and the solution was used immediately.

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A Dendritic Macrocyclic Organic Polyradical with a Very High Spin of $S = 10$**

Andrzej Rajca,* Jirawat Wongsriratanakul, Suchada Rajca, and Ronald Cerny

Organic molecules with a very high spin possess a large number of ferromagnetically coupled unpaired electrons.[1] The design and synthesis of such molecules must overcome the challenging problem of maintaining strong through-bond interactions between multiple sites within the molecule.[1d, 2] Highly efficient generation of unpaired electrons and/or multiple pathways for ferromagnetic coupling provided organic molecules with S greater than 5.[3–6] The highest spin for an organic molecule to date, a nonacarbene with $S = 9$, was reported by Iwamura and co-workers in 1993.[3]

Polyradical **1** was designed as an "organic spin cluster".[6, 7] Because ferromagnetic coupling through 1,3-phenylene is significantly stronger than that through a 3,4′-biphenylene unit, unpaired electrons in the four dendritic branches and the macrocyclic core can effectively be lumped into component spins (S').[6] Such a ferromagnetically coupled spin pentamer with $S' = 5/2, 5/2, 5/2, 5/2, 2$ should have a ground state with $S = 12$ (Scheme 1). We describe here the synthesis and magnetic studies of polyradical **1**.

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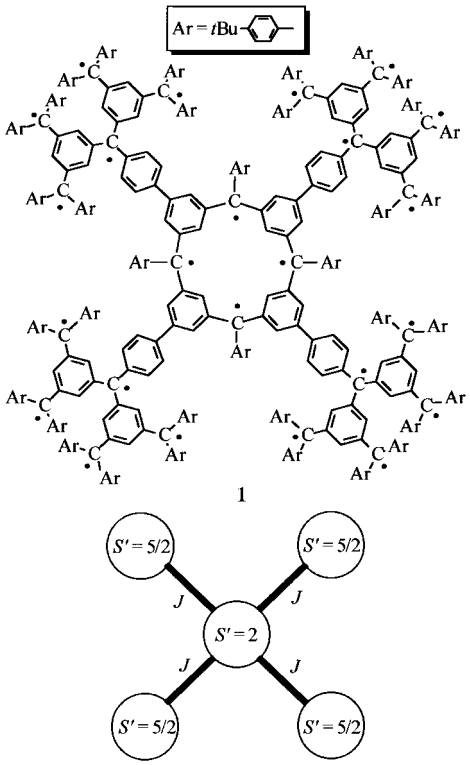
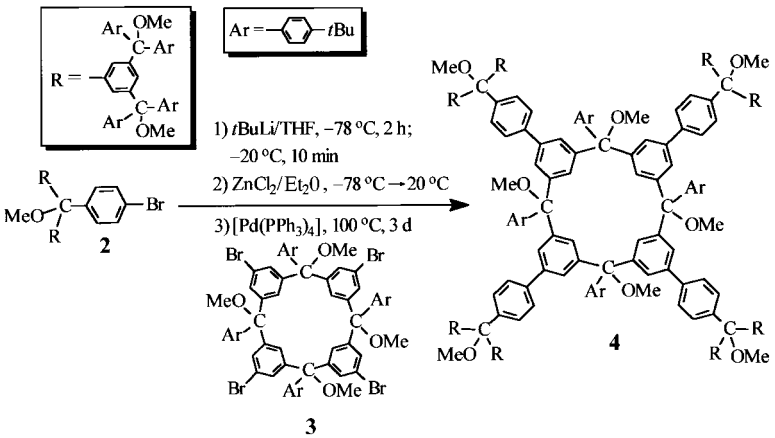


Scheme 1. Formula of the organic polyradical **1** (top) and the schematic representation of the coupling of the component spins S' in the spin pentamer with the coupling constant J (bottom).

The synthesis of **4**, the precursor to **1**, relies on the attachment of four dendritic branches **2** to the macrocyclic core **3**.[6, 8] Negishi coupling starting from an isomer of **3** that has fourfold symmetry gives **4** in 2% yield (Scheme 2).[9] The low-resolution fast atom bombardment (FAB) mass spectrum for **4** shows prominent cluster ions at $m/z = 7001$ and 3485 with similar fragmentation patterns; however, the spacings between the fragmentation ions and the widths of their isotopic envelopes for the region at $m/z = 3485$ are approximately half of those at $m/z = 7001$ (Figure 1). This suggests that the peaks at $m/z = 7001$ and 3485 correspond to singly and doubly charged ions $[M - OCH_3]^+$ and $[M - 2OCH_3]^{2+}$, respectively. In the high-resolution spectra, experimental isotopic intensities for $[M - OCH_3]^+$ and $[M - 2OCH_3]^{2+}$ ions



Scheme 2. Synthesis of **4**, a precursor to polyradical **1**.

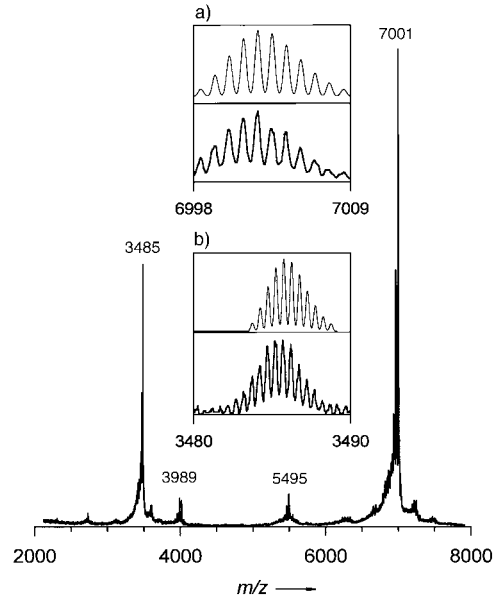
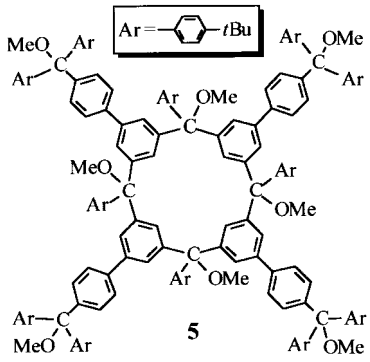


Figure 1. Section of the low-resolution FAB mass spectrum for polyether **4**. The peaks at $m/z = 7001$ and 3485 are assigned to the $[M - OCH_3]^+$ and $[M - 2OCH_3]^{2+}$ ion clusters, respectively. Their most prominent fragmentation patterns coincide with the consecutive loss of OCH_3 fragments. Weak-intensity clusters at $m/z = 5495$ and 3989 may correspond to either impurites or fragmentation ions with three and two dendritic branches, respectively. Inset: experimental high-resolution spectra (bottom in each case) for the $[M - OCH_3]^+$ (a) and $[M - 2OCH_3]^{2+}$ ion clusters (b) as well as their corresponding calculated spectra (top in each case) for the formulas $C_{503}H_{589}O_{23}$ (a) and $C_{502}H_{586}O_{22}$ (b) at natural isotopic abundance. The most intense isotopic peaks for the $[M - OCH_3]^+$ and $[M - 2OCH_3]^{2+}$ ion clusters are at $m/z = 7002.5$ and 3485.8, respectively. The intensity of the triply charged $[M - 3OCH_3]^{3+}$ ion is negligible.

are in satisfactory agreement with the calculated values (Figure 1). In the aromatic region of the ^1H NMR spectrum at 348 K, the COSY correlation shows two "singlet" off-diagonal peaks along with four well-resolved and four overlapping "quadruplet" off-diagonal peaks (Figure 2). The "singlet" peaks are associated with coupling of doublet (16 protons) and triplet resonances (8 protons; $J = 2$ Hz), corresponding to the eight 1,3,5-trisubstituted benzene rings of the dendritic branches. The "quadruplet" peaks result from the coupling of four doublet resonances (8 protons) with four further doublet resonances (32 protons; $J = 9$ Hz), accounting for all 1,4-disubstituted benzene rings. The two broad singlets (4 and 8 protons) furthest downfield do not show off-diagonal peaks; however, in less sterically congested **5**, analogous resonances appear at



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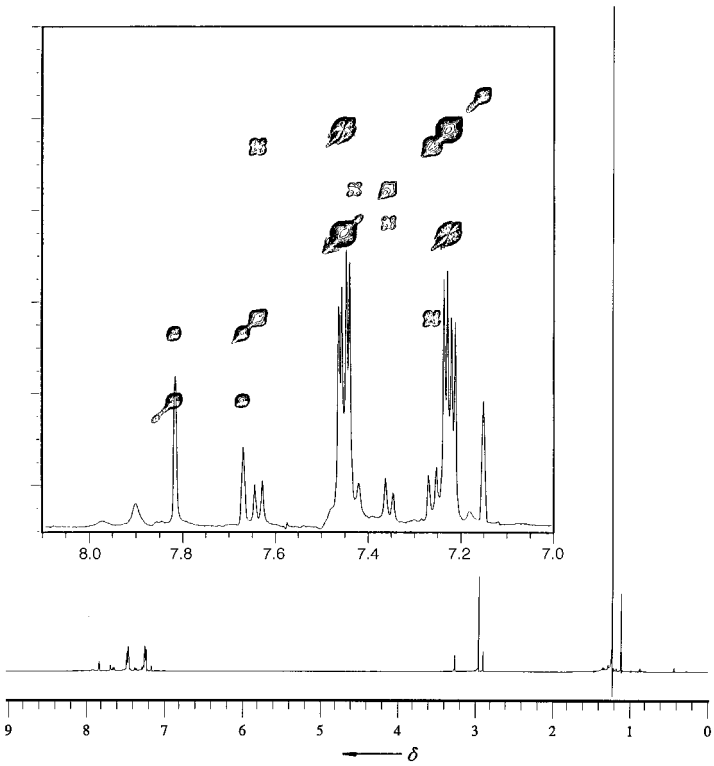

Figure 2. ^{1}H NMR spectrum (500 MHz, [D$_6$]benzene) for polyether **4** at 348 K with exponential (−1.2 Hz) and Gaussian multiplications (0.9 Hz). Inset: COSY ^{1}H–^{1}H NMR spectrum in the region of the arene resonances.

similar chemical shifts and do show off-diagonal peaks in the COSY correlation at ambient temperature. Therefore, these two resonances are assigned to the four 1,3,5-trisubstituted benzene rings of the calix[4]arene core (Figure 2). In the region of the MeO and *t*Bu resonances, two sets of three resonances each (intensitites 1:1:4 and 4:4:1, respectively) are resolved at 293 K. The fourfold symmetry of **4** is further corroborated by the ^{13}C NMR spectra in [D$_6$]benzene at 348 K.

When **4** (1–2 mg) was treated with Na/K alloy in [D$_8$]THF (80 μL), the reaction mixture briefly turned blue and subsequently deep purple-red.[6] After five days at 283 K, the reaction mixture was filtered into a quartz tube (outer diameter 5 mm). Iodine was added in small portions at 170–167 K until the reaction mixture turned blue, green, and finally red-brown.[6] The magnetization M of **1** was measured as a function of magnetic field H (0–5.0 T) and temperature T (1.8–160 K) in [D$_8$]THF. The values obtained at $H = 0.5$ T were plotted as MT versus T and fit to a model based on a pentamer of four spin carriers with $S = 5/2$ ferromagnetically coupled to one spin carrier with $S = 2$. Energy eigenvalues for the Heisenberg Hamiltonian were obtained by the vector-decoupling technique, and equations for magnetization, including saturation effects, were derived with standard formulas.[6, 10, 11] The following variable parameters were used for the numerical fits: J/k_B (spin coupling constant in Kelvin), N (number of moles of the polyradical), and, if needed, M_{dia} (correction for residual diamagnetism). The value $J/k_B = 7 \pm 1$ K, corresponding to a pairwise ferromagnetic coupling of spin carriers with $S = 5/2$ and 2 through a 3,4′-biphenylene moiety, was obtained for three samples of **1** (Figure 3). For an analogous triradical, in which three "colinear" spin systems with $S = 1/2$ are coupled through 3,4′-biphenylene moieties, $J/k_B = 90 \pm 20$ K is found.[6] Scaling of J/k_B values for **1** with the fraction of the spin sites with $S = 5/2$ and 2 adjacent to the 3,4′-biphenylene moiety gives $J/k_B = 70 \pm 10$ K, which is in satisfactory agreement with $J/k_B = 90 \pm 20$ K.[12]

The magnetic data for **1** in solution (0.003 M) at $T = 1.8$, 3, 5, and 10 K were fit to a Brillouin function (M versus H/T) with two variable parameters: S and magnetization at saturation (M_{sat}).[13] Values of S (≈ 10) slightly decreased at the lowest temperatures (e.g. S is smaller by 0.08 at 1.8 K than at 5 K). Such a change of S may be associated with very small intermolecular antiferromagnetic interactions, which may be described with a mean field parameter θ. The fit to a modified Brillouin function (M versus $H/(T-\theta)$ with $\theta = -0.03$ K)[14] gave $S = 10.0$ at 1.8, 3, and 5 K and $S = 9.8$ at 10 K (Figure 3). For a more dilute solution of **1** (0.002 M) $\theta = 0.00$ K was found; that is, fits to Brillouin functions (M versus H/T) give identical values of $S = 9.8$ in the range of 1.8–5 K.[15] When a solution of **1** in [D$_8$]THF (0.003 M) is measured after exposure to ambient temperature for 0.5 h, the magnetic data (M versus H) suggests sharply lowered spin of $S = 2-3$. The Brillouin function is not followed, as expected for a mixture of polyradicals with widely different values of S.[1d]

The value of $S = 10$ is a new record for the spin of an organic molecule. However, $S = 10$ for **1** is significantly less than the theoretical value of $S = 12$ expected for 24 ferromagnetically coupled unpaired electrons. This discrepancy is ascribed to the presence of a small density of defects, which results when the generation of unpaired electrons proceeds in less than 100% yield or when synthetic impurities are present in polyether **4**.[1d] The influence of these defects on the total spin is dependent on their positions in the molecule. One defect at the 4-biphenyl-substituted triarylmethyl spin sites and/or two defects at the macrocyclic sites would disrupt spin coupling and drastically lower the total spin of the defect polyradicals; however, defects at the outer triarylmethyl spin sites would lower the total spin in increments of 1/2 only. The sites in which a single defect would disrupt spin coupling are referred to as "defect-sensitive sites".[6] In **1**, such sites are substituted with stabilizing 4-biphenyl groups. Furthermore, there is a relatively small number of defect-sensitive sites in **1** (4 out of 24) compared to typical dendrimers (50%) or linear polymers (92% for a chain with 24 sites). A quantitative evaluation of defects in **1** can be obtained with a simple percolation model.[6] With the assumption of identical probability p for finding an unpaired electron at each triarylmethyl site ($100p$% yield per site), an approximate formula for average spin is $\langle S \rangle = 12p/(9-8p)$. Equating $\langle S \rangle = S$ or explicitly fitting magnetic data with a distribution of Brillouin functions gives $p = 0.98$, which corresponds to 98% yield per site for the generation of unpaired electrons. Adequate design of polyradical and very high chemical yields are prerequisites for maintaining strong through-bond interactions, such as ferromagnetic spin coupling, between multiple sites within a molecule.

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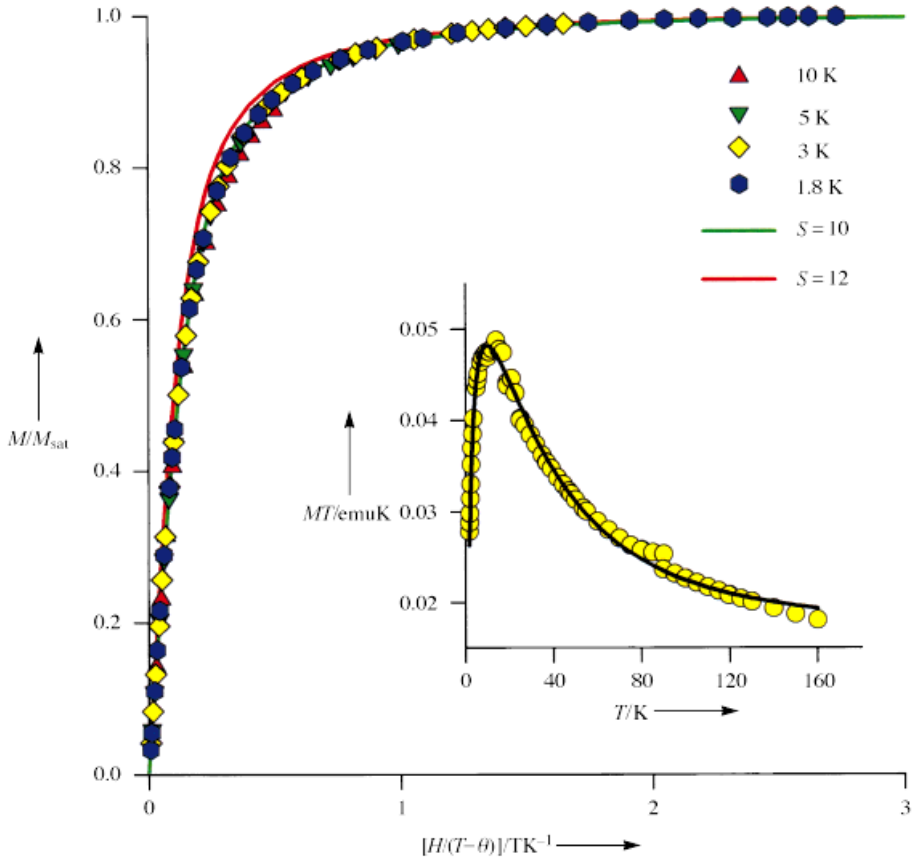

Figure 3. Superconducting quantum interference device (SQUID) magnetometry ($H = 0-5.0$ T) for polyradical **1** in [D_8]THF, $\theta = -0.03$ K. The experimental points at different temperature are represented by symbols, and Brillouin functions by lines. The fitting parameters for $T = 1.8$, 3, 5, and 10 K are $S = 10.0$, 10.0, 10.0, and 9.8 and $M_{sat} \times 10^2 = 2.01$, 2.01, 2.00, and 1.96 emu; the parameter dependence is 0.26, 0.34, 0.49, and 0.72, repectively. Inset: Plot of MT versus T at $H = 0.5$ T. The circles correspond to the experimental points, and the line is the numerical fit to the spin pentamer model. The fitting parameters (and their parameter dependencies) are $J/k_B = 6.6$ K (0.73), $N = 1.33 \times 10^{-7}$ mol (0.62), and $M_{dia} = 1.3 \times 10^{-5}$ emu (0.52). All experimental data are plotted after point-by-point and numerical corrections ($M_{dia} = 1.3 \times 10^{-5}$ emu) for diamagnetism.

In high-spin complexes containing a single transition metal or lanthanoid atom, maximum values of S are limited to 5/2 or 7/2 by (near) degeneracy in space of orthogonal 3d or 4f orbitals. In organic high-spin polyradicals, such a restriction is removed by the unlimited topological near degeneracy of nonbonding molecular orbitals. As long as spin coupling can be preserved in the presence of a small density of defects, "organic spin clusters" should be capable of significantly exceeding present values of S. The synthesis of higher homologues of **1**, in which dendritic branches are replaced with macrocycles, is in progress in our laboratory. This approach not only increases the number of unpaired electrons, but should improve the resistance of polyradicals to defects as well.

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