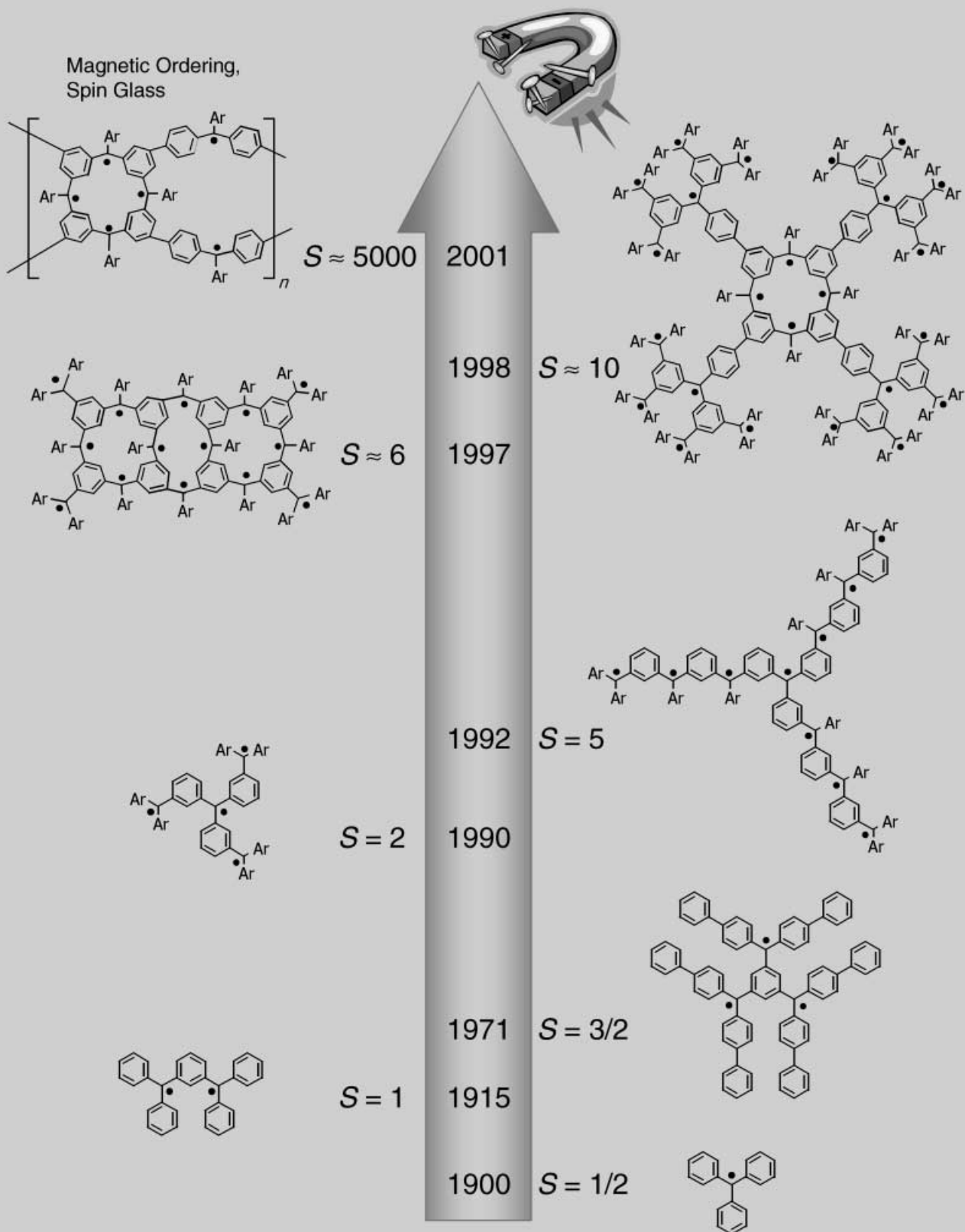


# From Gomberg's Triphenylmethyl to Polymer Magnets?



## From High-Spin Organic Molecules to Organic Polymers with Magnetic Ordering

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*Dedicated to Professor Andrew Streitwieser on the occasion of his 75th birthday.*

**Abstract:** This concept paper outlines the design of the first  $\pi$ -conjugated organic polymer with magnetic ordering. This rational, “bottom-up” macromolecular design is based on synthesis and study of polyarylmethyl polyradicals with increasing number of exchange-coupled unpaired electron spins. The prospects for attaining organic polymer magnets with stability at ambient temperature and/or higher magnetic ordering temperatures will be discussed.

**Keywords:** high-spin systems • magnetic properties • polymers • radicals

### Introduction

In typical magnetic materials, the source of electron spin are the d or f electrons of metals or metal ions. In the past decade, the first organic ferro- and ferrimagnets, based upon crystals of small radicals (e.g., mostly nitroxides) or charge transfer salts, have been prepared.<sup>[1–6]</sup> The Curie temperature ( $T_C$ ), that is, the temperature above which ferromagnetism is destroyed and the material becomes paramagnetic, is generally below 2 K,<sup>[1]</sup> with the exception of the C<sub>60</sub>-TDAE (TDAE = tetrakis(dimethylamine)ethylene) charge-transfer compound which has  $T_C = 16$  K.<sup>[2, 3]</sup> Rather weak through-space exchange coupling in these molecular solids leads to low Curie temperatures. In a molecular ferromagnet, radical pairs must effectively form a three-dimensional through-space network of pairwise exchange couplings, with each pair corresponding to a triplet ground state (ferromagnetic coupling). This is not a straightforward task, though occasionally assisted by crystal packing, because the unconstrained radical pairs would energetically prefer weak bonding, that is,

singlet ground state for each pair (antiferromagnetic coupling). Ferrimagnets, in which radicals of uneven spin (e.g.,  $S = 1$  diradical and  $S = \frac{1}{2}$  monoradical) are coupled antiferromagnetically, leading to a significant net magnetic moment, are also rare because of their inherently more complex design.<sup>[4, 5]</sup> In addition to ferro- and ferrimagnets, weak organic ferromagnets with relatively high  $T_C$  are known; in these molecular solids, unpaired electron spins have pairwise antiferromagnetic couplings though the spins are canted due to the spin-orbit coupling effects associated with the non-negligible spin density on heavier elements such as sulfur. The degree of canting is rather small, so the (spontaneous) magnetization at saturation is typically 1% or less of that in a ferromagnet.<sup>[7]</sup>

An alternative approach to organic magnets may rely on conjugated polymers.<sup>[8–13]</sup> In this approach pairwise exchange couplings between unpaired electron spin are mediated through  $\pi$ -conjugated system. Because very strong ferromagnetic couplings are found in selected conjugated diradicals, including ambient stable diradicals,<sup>[14–16]</sup> this approach offers a potential for magnets with  $T_C$  at or above room temperature. In order to realize this potential, one would have to prepare a conjugated polymer with truly three-dimensional connectivity (not just three-dimensional shape), in which these strong pairwise exchange couplings are maintained.<sup>[14]</sup> Considering the synthetic difficulties associated with such a lofty goal, it is useful to consider alternatives to three-dimensional conjugated polymer.

For isotropic exchange coupling (as found in most organic radicals), no bulk magnetism is theoretically predicted in strictly one- or two-dimensional polymers, for example, those proposed by Mataga three decades ago,<sup>[8]</sup> could still lead to magnetic ordering through magnetic dipole–dipole interactions between the polymer chains. In metal-containing molecule-based magnets, the dipole–dipole interactions between one-dimensional ferrimagnetic chains leads to  $T_C$ 's in cryogenic temperatures.<sup>[17]</sup>

Another strategy to attain magnetlike behavior may be based on blocking of magnetization (a significant barrier for inversion of magnetization) in superparamagnets or spin glasses.<sup>[18]</sup> In superparamagnets, time-dependent magnetic

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behavior and/or magnetic hysteresis are associated with magnetically independent individual molecules, one-dimensional chains, or particles. Thus, dimensionality is not an essential factor.<sup>[14, 19]</sup> Selected metal clusters with modest values of  $S$  ( $\leq 10$ ) and relatively large magnetic anisotropies show such “single-molecule magnet” behavior at cryogenic temperatures; also, a plethora of conventional magnetic materials in the form of superparamagnetic particles are known.<sup>[20, 21]</sup> In insulating spin glasses, the blocked magnetic moments are correlated with each other, leading to a phase transition; magnetic behavior is qualitatively similar to that of superparamagnets, though with somewhat different time dependence.<sup>[18]</sup> Both superparamagnets and insulating spin glasses rely on significant magnetic anisotropies for blocking of magnetization. There are two primary sources of anisotropy barrier (e.g., for inversion of magnetization) in magnetic materials: spin–orbit coupling and magnetic dipole–dipole interaction.<sup>[22]</sup> As spin-orbit couplings, especially in carbon-based organic radicals are rather small,<sup>[23]</sup> metal-free polymers (or molecules) may need to rely on the magnetic dipole–dipole interactions within the polymer chain. In that case, the shape anisotropy gives the anisotropy barrier  $E_A$  [in units of temperature; Eq. (1)]:<sup>[22, 24]</sup>

$$E_A = 0.5 NVM_s^2/k_B \quad (1)$$

In Equation (1),  $k_B$  is a Boltzmann constant,  $N$  is a shape factor (e.g.,  $0 \leq N \leq 2\pi$  with limiting values of 0 and  $2\pi$  for a sphere and infinite rod, respectively),  $V$  is volume of a polymer macromolecule, and  $M_s$  is magnetization at saturation (i.e., effectively, density of ferromagnetically coupled unpaired electron spins in a polymer macromolecule). In 1993, an order of magnitude estimate for superparamagnetic blocking in polyarylmethyl polyradicals was made; it was suggested that, for a moderately elongated shape macromolecule with  $N \approx 3$  (e.g., prolate ellipsoid with  $alb \approx 2$ ), about 200 ferromagnetically coupled electron spins (i.e.,  $S \approx 100$ ) are needed for anisotropy barrier of about 2 K.<sup>[25]</sup>

The key issue is how to attain large values of spin quantum number  $S$ , that is, ferromagnetic or ferrimagnetic correlation of large number unpaired electron spins within an organic macromolecule. Then, the attainment of three-dimensionality of exchange interactions or the problems associated with anisotropy barrier (e.g., magnetic dipole–dipole interactions) may be addressed.

During the past few years, rapid progress has been made in this field; the value of  $S$  in organic polymers or molecules has been increased from about 10 to 5000, leading to magnetic ordering.<sup>[9, 10, 26]</sup>

### Connectivity of the $\pi$ System

General guidelines for controlling the value of  $S$ , based upon connectivity of the  $\pi$  system, are reasonably well established.<sup>[14–16, 27–29]</sup> For example, 1,3-phenylene- and 3,3'-biphenylene-based diradicals are predicted to possess  $S=1$  (triplet) and  $S=0$  (singlet) ground states, respectively (Figure 1); the concepts of the ferromagnetic coupling unit (fCU) and the

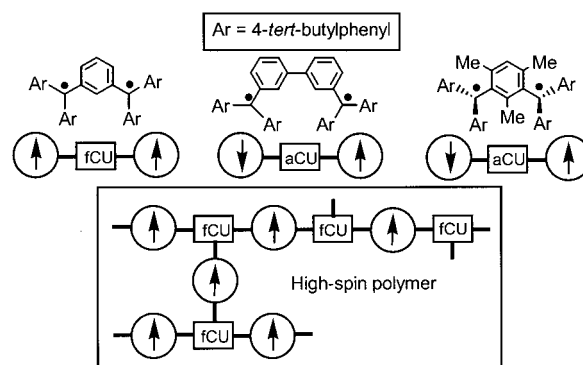


Figure 1. Ferro- and antiferromagnetic coupling units (fCU's and aCU's) in alkyl-substituted Schlenk–Braun hydrocarbons. Inset: conceptual depiction of a high-spin polymer with ferromagnetic coupling units alternating with radical sites (the ferromagnetic coupling scheme).

antiferromagnetic coupling unit (aCU) are very useful descriptors for  $\pi$  systems that connect the two radicals.<sup>[30]</sup> Moreover, in selected 1,3-phenylene-based diradicals, the triplet ground states are found to be almost exclusively populated at ambient temperature, that is, the singlet–triplet energy gaps ( $\Delta E_{ST}$ ) are significantly greater than thermal energy ( $RT$ ) at ambient temperature ( $\Delta E_{ST} > 0.6$  kcal mol<sup>-1</sup>).<sup>[14–16]</sup>

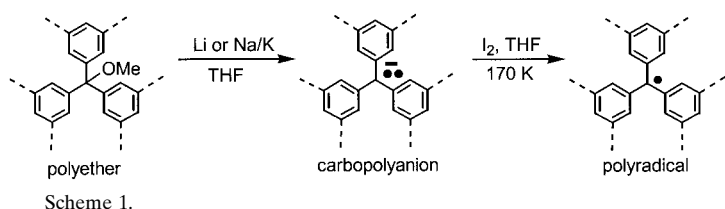
However, when  $\pi$  conjugation between the fCU and the radicals is diminished by near 90° out-of-plane twisting, the singlet ground states with relatively small  $\Delta E_{ST}$ 's (typically, less than 0.06 kcal mol<sup>-1</sup>) are found (Figure 1).<sup>[31]</sup>

Numerous “quasi-linear” and branched polymers, designed to possess large values of  $S$ , by using alternating connectivity between fCU's and radical sites have been reported. However, only relatively low values of spin,  $S \leq 5$ , were found.<sup>[11–13]</sup> A large body of experimental knowledge on  $S=1$  organic diradicals (including ambient stable diradicals), with  $\Delta E_{ST} > 0.6$  kcal mol<sup>-1</sup>  $\approx RT$  at room temperature, does not directly translate into magnetic material. Numerous claims of ferromagnetism in organic polymers at ambient conditions (typically with low concentration of radicals) turned out to be associated with metal impurities.<sup>[32]</sup>

### High-Spin Polyradicals with Ferromagnetic Coupling Scheme

High-spin polyradicals have multiple radical sites; these are coupled by exchange to produce large net values of  $S$  in the ground state. Typically, exchange coupling is mediated through a  $\pi$  system, though there are few notable exceptions.<sup>[33, 34]</sup> As all radicals are usually prepared in the final step of synthesis, it is essential that the yield per radical is near quantitative. This condition is satisfied by the carbanion method (Scheme 1)<sup>[35]</sup> for generation of triarylmethyl radicals, and has allowed for the preparation of star-branched polyradicals with values of  $S \leq 5$  (up to decaradicals).<sup>[36]</sup>

The typical implementation of the carbanion method yields the polyradical in tetrahydrofuran together with the by-products, such as alkali metal salts (iodides and, depending on concentration, variable amounts of alkoxides). Analogously,



an efficient solid-state photogeneration method for phenylcarbenes permitted the preparation of linear and branched polycarbenes with values of  $S \leq 9$ .<sup>[37]</sup>

Attempts to go beyond ten triarylmethyls ( $S > 5$ ) or nine phenylcarbenes ( $S > 9$ ) through the use of dendritic connectivities were not successful.<sup>[25, 38]</sup> For dendritic phenylcarbenes, evidence of interbranch C=C bond formation was reported.<sup>[39]</sup> For linear, star-branched, or dendritic connectivities, there is another fundamental problem associated with the presence of only one exchange pathway (through the  $\pi$  system) between any two remote radical sites.<sup>[14, 25]</sup> Therefore, a failure to generate a radical (a chemical defect) in the interior of a polyradical may interrupt the exchange pathway (by introducing an  $sp^3$ -hybridized atom) and effectively divide polyradical into two (or more) parts with relatively low values of  $S$ .<sup>[14, 25]</sup> A similar effect can be obtained by a large enough out-of-plane twisting of the  $\pi$  system connecting any two radical sites. In this case a strong fCU may be replaced with a weak aCU (a coupling defect) (Figure 2). There are two approaches to the problem of defects. Class I polyradicals, in which alternating coupling units and radical sites have macrocyclic connectivity, and class II polyradicals, in which pendant

radicals are attached to a coupling unit of the polymer (oligomer) backbone (Figure 2).<sup>[14]</sup>

In class I polyradicals with macrocyclic connectivity, a single chemical defect would lower the value of spin by only  $\frac{1}{2}$ , that is, the coupling is maintained between the remaining radicals (Figure 2).<sup>[40]</sup> Macrocycles may also provide sufficient conformational restriction to prevent significant out-of-plane twisting, minimizing the probability of coupling defects. However, not all macrocycles provide the polyradical with the persistence and exchange coupling required to maintain high spin. Macrocyclic calix[3]arene-based triradical **1**, the key building block of one of Mataga's polymers, readily forms C–C-bonded dimers, even at low temperature.<sup>[41]</sup> Calix[4]arene-based polyarylmethyls are found to possess sufficient persistence at low temperatures; ESR spectroscopy and SQUID magnetometry shows that the tetraradical **2** has a  $S = 2$  ground state, and no detectable population of the low-spin excited states is detected up to 80 K (Figure 2).<sup>[41]</sup>

The best class II polyradicals, developed by Nishide and co-workers, possess average values of  $S \leq 5$ .<sup>[13]</sup> The backbone  $\pi$  system of the fCU may include severely out-of-plane twisted conformations and the pendant radicals are typically depleted through chemical defects. Therefore, the coupling between the radicals may be weakened and even, for some pairs, changed from ferromagnetic to antiferromagnetic, leading to low values of  $S$ . Attaching pendants to a macrocyclic backbone  $\pi$  system may in part address this problem, though only a model  $S = \frac{3}{2}$  triradical has been reported so far.<sup>[13, 42, 43]</sup>

Annulation of calix[4]arenes, which are apparently reliable macrocycles for polyarylmethyls, could provide the desired resistance to multiple defects. Trimacrocyclic polyradical **4** (Figure 3) has a relatively high value of  $S \approx 6$  (vs  $S = 7$  for ferromagnetic coupling of all unpaired electrons), but chemical quenching studies indicate the presence of at least one chemical defect. Also, the low-spin excited states are populated at low temperature. This indicates significantly weakened exchange coupling relative to the parent tetraradical **2**.<sup>[44]</sup>

Iwamura and co-workers generated an  $S = 4$  tetracarbene and an  $S = 6$  hexacarbene based upon calix[ $n$ ]arene ( $n = 4$  and 6).<sup>[45]</sup> Systematic studies of exchange coupling through macrocyclic rings as a function of ring size and the use of stable radicals would be desirable. Such studies are important to find optimum approaches to highly annelated polyradicals and, ultimately, highly cross-linked conjugated polymer networks with strong and predictable exchange couplings.

Another approach to polyradicals with large values of  $S$  may rely on the attachment of additional radical sites to the macrocyclic (calix[4]arene) core.<sup>[26, 40, 46]</sup> One of these polyradicals, dendritic 24-radical **5**, with a value of  $S \approx 10$  (Figure 3), possesses the largest value of  $S$  among organic molecules in the literature.<sup>[26]</sup> The 3,4'-biphenylene-based weak fCU's, which link the strongly exchange-coupled macrocyclic core and the dendritic branches with 1,3-phenylene-based fCU's, allow for treatment of **5** as a pentamer of spins  $\frac{5}{2}$ ,  $\frac{5}{2}$ ,  $\frac{5}{2}$ , and  $\frac{5}{2}$  (Figure 3). Assuming pairwise ferromagnetic couplings between  $S = \frac{5}{2}$  and  $S = \frac{5}{2}$ , the Heisenberg Hamiltonian model is readily solvable. Numerical fitting of experimental magnetization as a function of temperature and

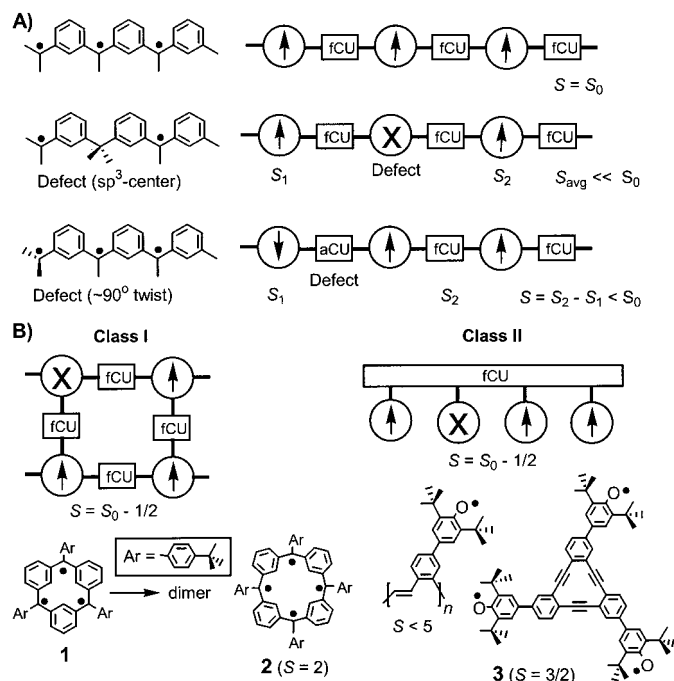


Figure 2. A) Effect of chemical defects ( $sp^3$  center) and coupling defects (out-of-plane twisting) on the values of spin in conjugated polyradicals, in which ferromagnetic coupling units (fCU's) alternate with radical sites. B) Circumvention of chemical defects in selected class I and class II polyradicals.

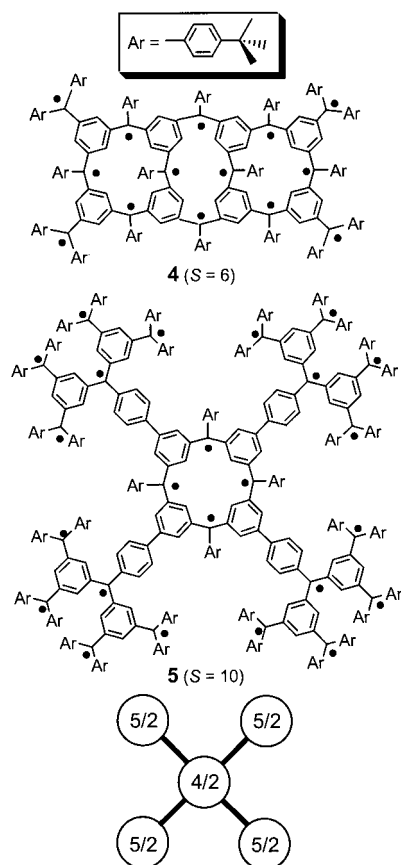


Figure 3. Macrocyclic and dendritic polyradicals **4** and **5**.

magnetic field to this model gives the exchange coupling constant through the 3,4'-biphenylene fCU as  $J/k = 7$  K ( $k$  = Boltzman constant).<sup>[26]</sup>

Dendrimer **5** has only four radical sites at which a single chemical defect may interrupt exchange coupling between the remaining radicals (biphenyl-substituted), drastically lowering the value of  $S$ . One plausible approach to address the discrepancy between the theoretical value of  $S = 12$  (for 24 ferromagnetically coupled unpaired electrons) and the experimental value is to assume the presence of chemical defects with only a 98% yield per radical site for generation of radicals.<sup>[26]</sup> However, more recent, qualitative magnetic measurements reveal that only 60–70% unpaired electrons are present at low temperature. (This estimate is obtained using the weight of the precursor 24-ether to calculate number of moles of **5**.) This may be reconciled with the average value of  $S = 10$  ( $S$ -weighed) by assuming presence of conformers of **5**, in which one or two  $S = \frac{5}{2}$  dendritic branches are antiferromagnetically coupled to the  $S = \frac{5}{2}$  macrocyclic core.<sup>[47]</sup> Monte Carlo conformational searches suggest that the lowest energy conformers have moderate torsional angles (40–50°) between the benzene rings of the biphenyl moieties, compatible with ferromagnetic coupling. However, the conformers, in which one of the biphenyls has the torsional angle near 90°, are not much higher in energy ( $\approx 5$  kcal mol<sup>-1</sup>).

### Polyradicals with Ferromagnetic–Ferrimagnetic Coupling Scheme: Calix[4]arene Macrocycles and Bis(biphenylene)methyl Linkers

The ferromagnetic coupling scheme outlined in the preceding paragraphs allows for an effective exchange coupling of no more than 20 unpaired electrons. In order to significantly increase values of  $S$  beyond 10, multiple exchange coupling pathways will have to be present to alleviate the problem of chemical defects. However, brute-force annelation, aimed at attaining everywhere in the network strong ferromagnetic coupling (like Mataga design), does not appear to be practical as shown by very limited studies. Out-of-plane twistings, reversing the sign of exchange coupling from ferromagnetic to antiferromagnetic, are difficult to avoid in model polyradicals. Although no systematic model studies are available, it is likely that the out-of-plane twistings may even be more intractable in large macromolecular polyradicals. Are very large values of  $S$  attainable in the presence of antiferromagnetic couplings?

The ferrimagnetic coupling scheme, that is, antiferromagnetic coupling of unequal spins leading to a large net spin (magnetic moment), was applied to the design of organometallic ferrimagnets. The relevant examples are antiferromagnetic couplings of  $S = \frac{5}{2}$  Mn<sup>II</sup> with  $S = \frac{1}{2}$  nitronyl nitroxides (or  $S = 1$ ,  $\frac{3}{2}$  di- and tri-nitroxides) in one-dimensional chains (or networks).<sup>[17, 48]</sup> In addition, there is an example of an  $S = 1$  tricarbene, which was interpreted in terms intramolecular antiferromagnetic coupling between  $S = 2$  and  $S = 1$ .<sup>[49]</sup>

We selected bis(biphenylene)methyl linker to connect calix[4]arene macrocycles. For just two macrocycles, this corresponds to a quasi-linear trimer of unequal spins,  $S_1 - \frac{1}{2} - S_1$ , for example,  $\frac{7}{2} - \frac{1}{2} - \frac{7}{2}$  for pentadecaradical **6** (Figure 4). Eigenvalues for the Heisenberg Hamiltonian (with nearest neighbor coupling) for such a spin cluster indicate that the energy gaps between the ground state and the excited state are relatively small (one unit of  $J$  compared to two units of  $J$  for the singlet–triplet gap in a diradical). The ground state has a total spin of  $S = 2S_1 + \frac{1}{2}$  and  $S = 2S_1 - \frac{1}{2}$  for ferromagnetic and antiferromagnetic couplings, respectively. Therefore, change from all-ferromagnetic to all-antiferromagnetic coupling through biphenylene coupling units will have only a small effect on the total value of  $S$  at low temperature. Although the unsymmetrical spin clusters, with one ferro- and one antiferromagnetic coupling, may have  $S = \frac{1}{2}$ , such clusters are likely to constitute only a fraction of the sample, especially if there is a preference for either ferromagnetic or antiferromagnetic couplings. For quasi-linear pentadecaradical **6** and 21-radical **7** (Figure 4), magnetic data at low temperature are quantitatively reproduced with a distribution of conformers (and chemical defects), in which exchange coupling through biphenylene moieties is ferro- (70–90%) or antiferromagnetic (10–30%). For **6** and **7**, such polydisperse mixtures of spin systems have average values of  $S = 5-6$  and  $7-9$ , respectively. These values are significantly below the theoretical values of 7.5 and 11 for ferromagnetically coupled, defect-free polyradicals. Because of antiferromagnetic couplings and chemical defects, only about 60% of unpaired electrons are present at low temperature. Similar

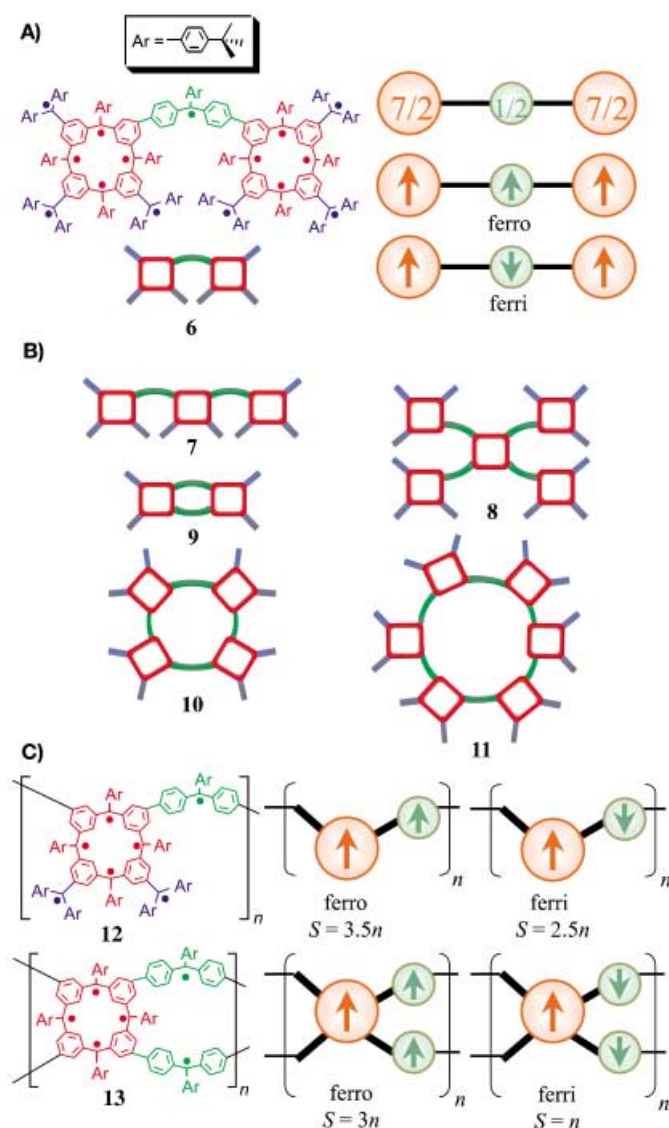


Figure 4. Polyradicals and polymers with the ferromagnetic–ferrimagnetic coupling scheme: A) pentadecaradical **6** as a trimer of spins  $7/2$ ,  $1/2$ ,  $7/2$ ; B) linear, branched, and annelated polyradicals **7–11**; C) polymers **12** and **13** with the ferromagnetic–ferrimagnetic coupling scheme with the macrocyclic ( $S=3$  and  $S=2$ ) and cross-linking ( $S=1/2$ ) modules.

trends for average values of spin (up to  $S=13$ ) and percentages of unpaired electrons are found for branched and macrocyclic polyradicals **8–11** (Figure 4).

For the less sterically encumbered bis(biphenylene)methyl-based tri- and pentaradicals, magnetic data may be interpreted in terms of ferromagnetically coupled quasi-linear trimers of spins ( $1/2 - 1/2 - 1/2$  and  $1 - 1/2 - 1$ ) with the high-spin ground states and  $J/k = 90$  K.<sup>[46]</sup>

Although a significant improvement over the  $S=10$  is not achieved by using bis(biphenylene)methyl-linked macrocycles, the viability of ferrimagnetic coupling scheme is demonstrated.

## Polymers with Ferromagnetic–Ferrimagnetic Coupling Scheme

The ferromagnetic–ferrimagnetic coupling scheme, based upon unequal spin modules, has been used for the design of two high-spin polymers **12** and **13**, in which bis(biphenylene)methyl groups link calix[4]arene macrocycles (Figure 4).

Polymer **12**, with  $S=3$  calix[4]arene macrocycles linked with  $S=1/2$  bis(biphenylene)methyls, may be viewed as a “quasi-linear” chain of unequal spins of  $S=3$  and  $S=1/2$  (Figure 4). (Also, conformations of polymer **12** may be “quasi-linear” due to the preference of calix[4]arene tetradical moiety for 1,3-alternate conformation.) Polymer **12** is found to possess an average value of  $S \approx 18$ , with 40–60% unpaired electrons present at low temperature. As polymer **12** is obtained from a polyether with  $M_w = 30$  kDa, an average value of  $S=50–60$  would be expected if all unpaired electron spin are ferromagnetically coupled and no chemical defects are present. Nevertheless, the value of  $S \approx 18$  exceeds the best values of  $S \approx 5$  obtained in other high-spin organic polymers.<sup>[6, 11–13]</sup>

Analogously to **12**, cross-linked polymers **13** may be viewed as network of unequal spins, that is, macrocyclic modules with  $S=2$  and linking modules with  $S=1/2$  (Figure 4). Cross-linked polymers **13** have an average value of  $S > 40$ , when prepared from soluble fractions of the corresponding polyether with  $M_w = 300–500$  kDa.<sup>[9]</sup> Values of  $S$  for polymer **13**, prepared from insoluble fractions of the polyether (gelled with  $[D_8]$ tetrahydrofuran), depend on polymerization time beyond the gel point for the polyether. When polymerization is stopped near the gel point, polymers **13** have values of  $S=600–1500$ ; for a longer polymerization time, values of  $S=3000–7000$  were obtained. It is estimated that approximately 50% of unpaired electrons are present at low temperature. This is consistent with the presence of chemical defects and ferromagnetic–ferrimagnetic coupling scheme.<sup>[10]</sup>

Magnetic properties beyond simple paramagnetism are observed for the first time in a conjugated organic polymer. The onset of magnetic ordering is observed near the temperature of 10 K; for a typical sample with a value of  $S \approx 5000$ , a sharp upturn in magnetic moment (an increase by two orders of magnitude) is found. Below 10 K, magnetization increases exceedingly fast with applied magnetic fields, and reaches near saturation at relatively small fields. The magnetization at saturation is about  $10 \text{ emu g}^{-1}$ , similar in magnitude to the paramagnetic magnetization at saturation for polyarylmethyl polyradicals. At zero field or very small fields on the order of earth’s field (0.5–1 Oe), magnetic blocking is found, that is, a significant barrier for inversion of magnetization is present. AC magnetic susceptibility studies suggest that the barrier is on the order of 15 K and the huge magnetic moments (corresponding to a value of  $S \approx 5000$ ) are frozen at low temperature with some degree of cooperativity. Overall, the magnetic properties of polymer **13** can be classified as being between insulating spin glasses and blocked superparamagnets, but are closer to spin glasses.<sup>[10]</sup> The soft magnetic behavior in polymer **13** is similar to the known small-molecule-based organic magnets, though the ordering temperature in polymer **13** is relatively high.<sup>[1–3, 5]</sup>

### Organic Polymer Magnets: Future Developments

Two major benchmarks have to be attained before polymer-based magnets can be made practical: 1) stability at ambient conditions and 2) magnetic ordering above room temperature.

The first objective could possibly be achieved by using polymers similar to **13**, in which stable radical moieties are used in the place of triarylmethyls. When di-coordinate radicals, such as nitroxides are used, the problems of solubility or gel-forming ability for the polymer would have to be addressed.

The second objective is much more difficult. The approach to increasing value of  $S$ , as described in the preceding sections, relies upon an effective weakening of exchange coupling by replacing 1,3-phenylene with 3,4'-biphenyl, and then bis(biphenylene)methyl as formal fCU's. Consequently, the temperature for the onset of magnetic ordering is drastically lowered when compared to the strength of pairwise ferromagnetic coupling through 1,3-phenylene fCU (triplet-singlet gap; i.e., 10 K vs >300 K). Nevertheless, the temperature of about 10 K is relatively high for an organic magnet, confirming the great potential of the macromolecular approach. Selected modifications to this design may involve macrocyclic modules with  $S > 2$  and/or increased connectivity between macrocycles (Figure 5).

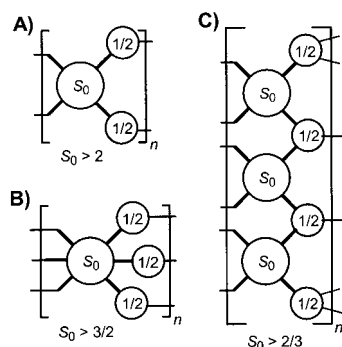


Figure 5. Selected examples of connectivities between the macrocyclic ( $S_0$ ) and cross-linking ( $S = 1/2$ ) modules for prospective magnetic polymers: A) macrocyclic module with increased value of spin; B) macrocyclic module with increased connectivity; C) cross-linking module with increased connectivity.

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