Polyarylmethyl Polyradicals as Organic Spin Clusters

Suchada Rajca and Andrzej Rajca

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304
E-mail: arajca1@unl.edu

IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

This overview describes the design for very high-spin organic polyradicals (polyarylmethyls), i.e., organic molecules and polymers with large values of spin quantum number S in the ground state. © 2001 Academic Press

Key Words: magnetic properties; radicals; macrocycles; polymers.

1. INTRODUCTION

Design and synthesis of nanometer-sized molecules with magnetic properties is one of the most exciting research areas in magnetism. Over the past decade, steady progress has been made in the synthesis and characterization of transition metal ion clusters (molecules) with large values of spin quantum number S. The highest value of S for transition metal ion clusters is $\frac{51}{2}$ (1). In several clusters with relatively large values of S and zero-field splitting parameter D, superparamagnetic blocking and/or quantum tunneling of magnetization at low temperatures were discovered (2). When the barrier for inversion of magnetization (superparamagnetic blocking), related to $S^2|D|$, significantly exceeds thermal energy at room temperature (kT), such clusters could function as single-molecule memory bits.

Purely organic molecules with unpaired electrons, i.e., polyradicals, offer an alternative approach to molecules with very large values of S (3–6). In this approach, multistep organic syntheses serve as a powerful tool for a reliable (though laborious) implementation of rational designs for such molecules.

2. DESIGN OF VERY HIGH-SPIN ORGANIC MOLECULES AND POLYMERS

The most fundamental prerequisite for a high-spin ($S > \frac{1}{2}$) organic molecule is attaining ferromagnetic coupling between unpaired electrons (7). Connecting two spin sites for an unpaired electron to a ferromagnetic coupling units (fCUs) gives rise to a high-spin diradical with $S = 1$ ground state (8). An example is the Schlenk hydrocarbon (9), in which two arylmethyl spin sites are connected to a 1,3-phenylene fCU. The conceptual extension to a high-spin molecule relies on connecting in an alternating mode spin sites and fCUs (Fig. 1).

The goal is to build up large macromolecules with very large numbers of interacting spin sites. Well-defined molecular sizes and shapes are very desirable. Fractals with well-defined dimensions, highly annelated polymacrocyclic molecules, and polymers are among fascinating targets.

2.1. Ensembles of Alternating Spin Sites and fcus

Simple molecular designs for ensemble of alternating spin sites and fCUs are linear, dendritic, and macrocyclic structures (Fig. 2) (3). These structures could be modified with functional groups for polymerization. More sophisticated designs involve molecules with multiple dendritic and macrocyclic modules as well as annelated macrocycles (10).

For the linear and dendritic structures, attempts to obtain molecules and polymers with $S > 5$ were not successful. Increasing the number of sites for unpaired electrons beyond 7–10 in such molecules and polymers leads to more complicated mixtures of spin systems with relatively low values of S; e.g., for a dendritic pentadecaradical with 15 sites for unpaired electrons, an average spin value of $\frac{7}{2}–\frac{5}{2}$ was found (Fig. 3) (11).

To obtain the expected values of spin, generations of unpaired electrons at the radical sites must be perfect. A failure in generation of an unpaired electron (i.e., a defect) interrupts π-conjugation, and consequently the spin couplings. In linear or dendritic structures, there is only one pathway for π-conjugation between the spin sites. A defect at one of the sites in the interior of the molecule will cut the π-conjugated system into noninteracting segments, with low values of S (Fig. 3). However, a defect at one of the terminal
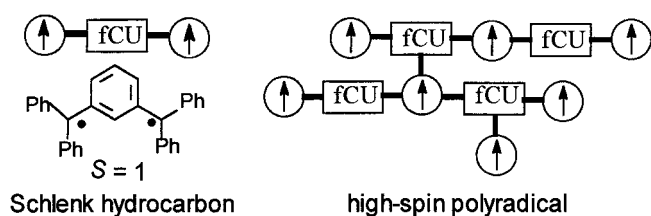
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FIG. 1. High-spin diradical and polyradical.

FIG. 2. Examples of simple molecular designs for ensembles of alternating spin sites (circle) and fCUs (line).

sites will not interrupt interaction between the remaining unpaired electrons, slightly decreasing the value of S to $S - \frac{1}{2}$. Linear chains have only two terminal sites, compared to typical dendrimers with about half-terminal and half-inner sites.

In a macrocyclic structure, there are two pathways for spin couplings (12). A defect would decrease the value of S to $S - \frac{1}{2}$ (Fig. 4). However, to obtain very large values of S, a polyradical must contain a large number of spin sites; as the number of spin sites increases, the probability of having two or more defects becomes greater. In a macrocyclic structure, two or more defects may cut the molecule into segments, giving a mixture of spin systems. As a result, large macrocyclic structures are not the optimum molecular design for very high-spin systems. So far, only high-spin polyarylmethyls based on macrocyclic calix[4]arene ring were reported but the limit of the ring size has not been determined (13).

Dendritic–macrocyclic and macrocyclic–macrocyclic structures provide a good compromise between the feasibility of their synthesis and the problem of defects. An organic spin cluster approach was employed in the design of these novel classes of high-spin macromolecules.

2.2. Organic Spin Clusters

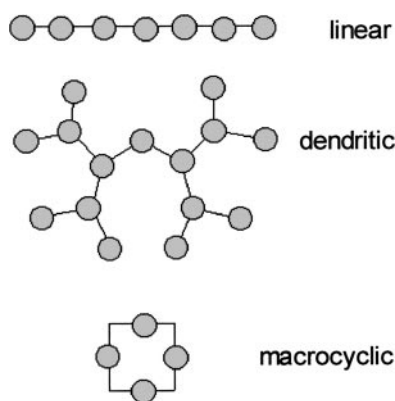In the organic spin cluster approach, fCUs with two different coupling strengths are used such that groups of the spins $\frac{1}{2}$ may be effectively combined into larger component spins; i.e., strong fCUs or high-spin modules are linked with weak fCUs to form simple spin clusters (14–16). In the implementation of this design in the polyarylmethyl polyradicals, the spins $\frac{1}{2}$ are strongly coupled through 1,3,5-phenylyne units and the component spins are weakly coupled through the 3,4'-biphenylene units (17). Because such spin systems may be viewed as simple spin clusters, their magnetic data can be analyzed in more detail (Fig. 5).

2.2.1. Dendritic–macrocyclic structures.
Dendritic–macrocylic structures consist of a macrocyclic core and dendritic branches. A calix[4]arene ring was selected for the core and dendrimer with five spin sites for the branches. Connection of the dendritic branches to the macrocyclic core can be accomplished via modular synthetic routes involving biphenyl CC-bond-forming reactions. Such polyradicals possess only very few triarylmethyl sites for which a single defect may interrupt π-conjugation (defect-sensitive sites); also, these defect-sensitive sites are protected by the 4-biphenyl substituents. The terminal spin sites correspond to significantly more than 50% of all spin sites. The
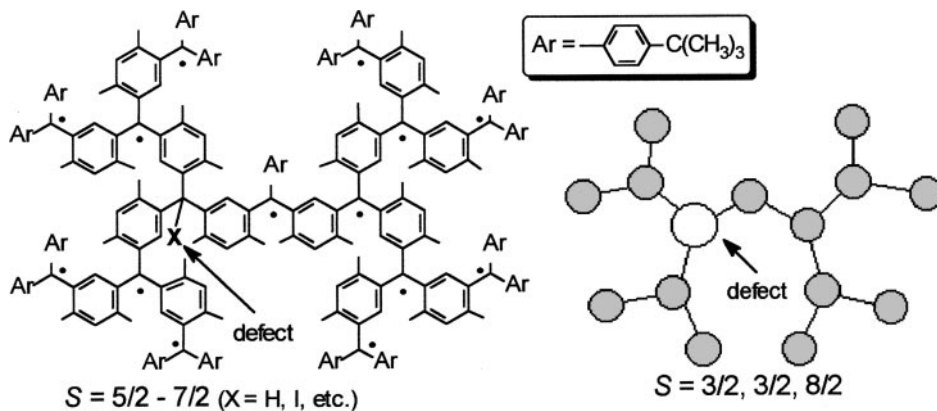

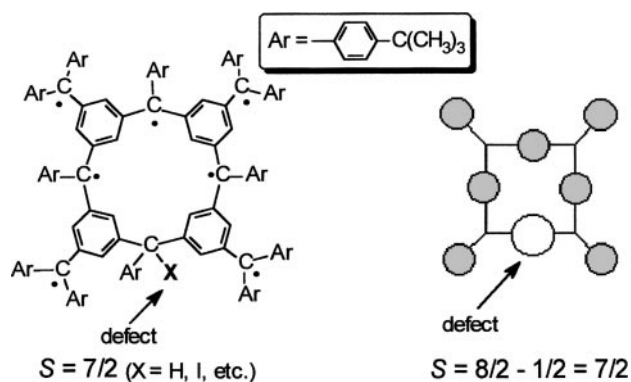**FIG. 3.** Dendritic pentadecaradical with one defect at an inner site.

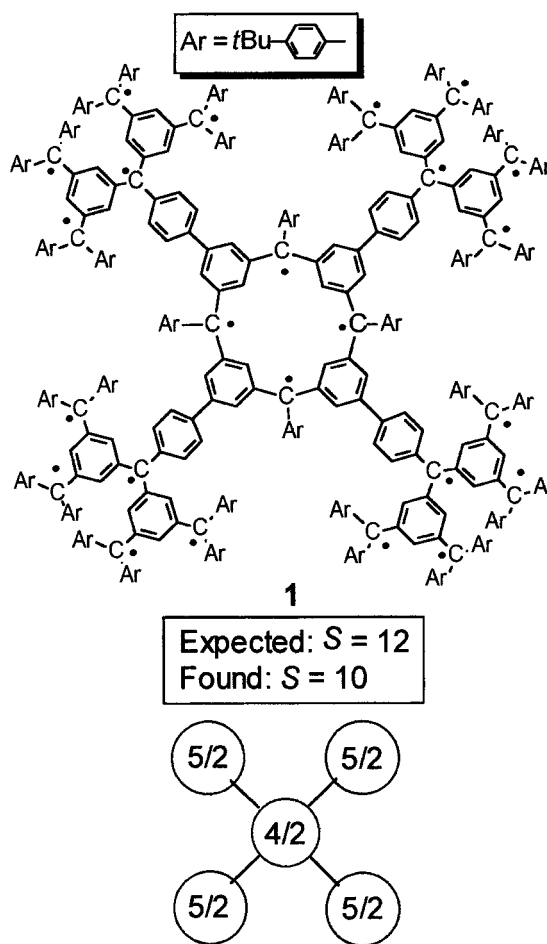**FIG. 4.** Macrocyclic octaradical with one defect at an inner site.

4-biphenyl substitution also provides distinct color change of carbopolyanion upon oxidation to a polyradical, allowing for more accurate titration. The average yield per site for unpaired electrons can be improved up to 98% (15, 16).

24-Radical **1** possesses an average value of $S = 10$, the highest spin organic molecule to date (Fig. 6) (16). For a polyradical with 24 ferromagnetically coupled unpaired electrons, $S = 12$ is expected. A small density of defects may cause the discrepancy between the two values (16). It should be noted that **1** has only 4 defect sensitive sites (out of 24), which is a relatively small percentage compared to typical dendrimers (50%) or linear chains (92% for 24 sites). Despite the small density of defects in **1**, its magnetic data qualitatively conform to the organic spin cluster model, i.e., a ferromagnetically coupled pentamer of component spin $\frac{5}{2}, \frac{5}{2}, \frac{5}{2}, \frac{5}{2}, \frac{4}{2}$ (Fig. 6) (16).

24-Radical **1** has an overall shape of a prolate ellipsoid with diameters of 4 and 2 nm, as determined by Monte Carlo conformational searches (Macromodel) and small-

FIG. 5. Concept of an organic spin cluster. A complex octamer of spin $\frac{1}{2}$ may be reduced to a simple dimer of spin $\frac{3}{2}$ and spin $\frac{5}{2}$.

1

Expected: $S = 12$
Found: $S = 10$

FIG. 6. Dendritic–macrocyclic spin cluster polyradical.

angle neutron scattering experiments. It remains to be seen whether superparamagnetic blocking can be observed at very low temperatures for such elongated shape organic high-spin polyradicals (3).
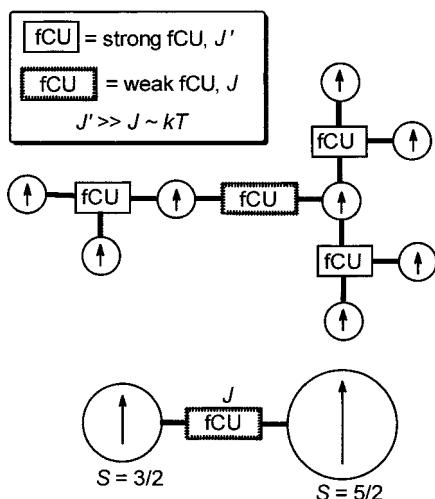
2.2.2. Macrocyclic–macrocyclic structures. Connection between macrocyclic rings may provide macromolecules with well-defined dimension as well as a polymacrocyclic network.

Fractals with well-defined dimensions are among the fascinating geometries in the design of nanometer-sized molecules. Because dimensionality is one of the central issues in magnetism, a fractal is a very attractive geometry to be adopted in the design of very high-spin molecules. The macrocyclic ring structure of calix[4]arene accommodates the square fractal geometry, corresponding to the zeroth-generation square. Pentacalix[4]arene **2** may be viewed as the first-generation five squares (Fig. 7).

36-Radical **2** has an average value of $S = 13$, significantly below the theoretical value of $S = 18$ for 36 ferromagnetically coupled unpaired electrons (Fig. 7). It should be noted

that the fraction of defect sensitive sites in **2** (4 out 36) is significantly lower than that in **1** (4 out of 24). However, the mixtures of the spin systems for **2** are more polydisperse than those for **1**. Also, magnetic data suggest the presence of conformations with antiferromagnetic couplings between the branches and the core.

Polymerization of multifunctionalized macrocycles may produce numerous annelated macrocyclic structures, leading to networks. Considering the problem of defects, annelated macrocyclic structures are very desirable. Great improvements in S values are expected for network polyradicals. Although the synthesis of such network polyradicals is much more straightforward than that of the square fractal polyradical, structural complexity of the products is the major drawback. Polymerization of two macrocyclic and tetrafunctionalized modules (tetrabromocalix[4]arene and calix[4]arene with four linkers) may lead to the following limiting structures for the polymer network, a precursor to polyradicals **3** (Fig. 8) (18).

Polyradicals **3** are generated from both soluble and insoluble portions of a polymer network. As the distributions of spin systems are highly polydisperse, two averages of S are defined, i.e., the number-average (S_n) and the spin-average (S_s). (S_n and S_s are defined analogously to their molecular mass averages counterparts, M_n and M_w, widely used for polymers.) From the soluble part of the polymer network, polyradical **3** with $S_n \geq 40$ is reproducibly obtained; the best sample has $S_n = 48$ (18). For the insoluble part, polyradicals **3** with S_n exceeding 300 are obtained; notably, magnetic data suggest an onset of superparamagnetic blocking at low temperatures.

The origin of such extraordinary values of S in organic polyradicals **3** is studied using several well-defined molecular polyradicals—molecular models for the limiting structures of **3** are shown in Fig. 8. Polyradical **2** represents one of the models for the limiting structures of **3**. Values of S for all model polyradicals, including those with annelated macrocycles connectivities, are significantly below those theoretically predicted for all ferromagnetically coupled unpaired electrons. Also, antiferromagnetic interactions between the spin modules can be detected. These results are consistent with the organic spin cluster model for polyradical **3**, in which the alternating connectivity of two types of radical modules with unequal spins (2 and $\frac{1}{2}$) facilitates large net values of S for either ferromagnetic or antiferromagnetic coupling between the modules (Fig. 8) (18).

3. MAGNETIC CHARACTERIZATION OF ORGANIC SPIN CLUSTERS

The experimental measurement of the temperature (T) dependence of magnetization (M) may estimate the strength of magnetic interactions via the determination of the thermal population of states with different values of S (energy

gaps $\approx kT$). For a polyradical with a large number of unpaired electrons and complex spin connectivity, the organic spin cluster design provides much simplified analysis of magnetic data; i.e., the numerical fit to the experimental magnetic data, using relatively few variable parameters, is feasible.

The Heisenberg Hamiltonian

$$H = -2\sum_{i>j} J_{ij}\mathbf{S}_i\mathbf{S}_j \qquad [1]$$

provides an approximate description of its dominant magnetic interaction in term of isotropic exchange coupling between unpaired electrons. The coupling constants, J_{ij}, between the nearest-neighbor spins $\mathbf{S}_i$ and $\mathbf{S}_j$ may correspond to either ferromagnetic ($J_{ij} > 0$) or antiferromagnetic ($J_{ij} < 0$) couplings.

The Heisenberg Hamiltonian may be used to obtain energy eigenvalues for states with various S in terms of J_{ij} (19). For relatively simple organic polyradicals with a cluster of spins $\frac{1}{2}$, exact solutions for the Heisenberg
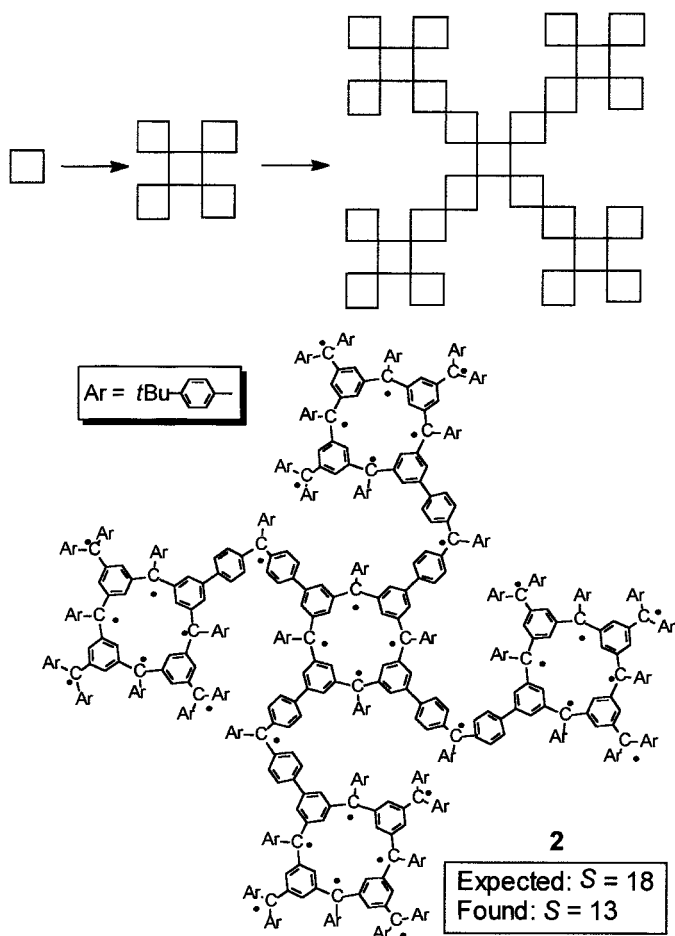

FIG. 7. Fractal generations (dimension, $D = \ln 5/\ln 3$): 0, 1, and 2 (top) and a macrocyclic–macrocyclic spin cluster polyradical as the first-generation fractal (bottom).
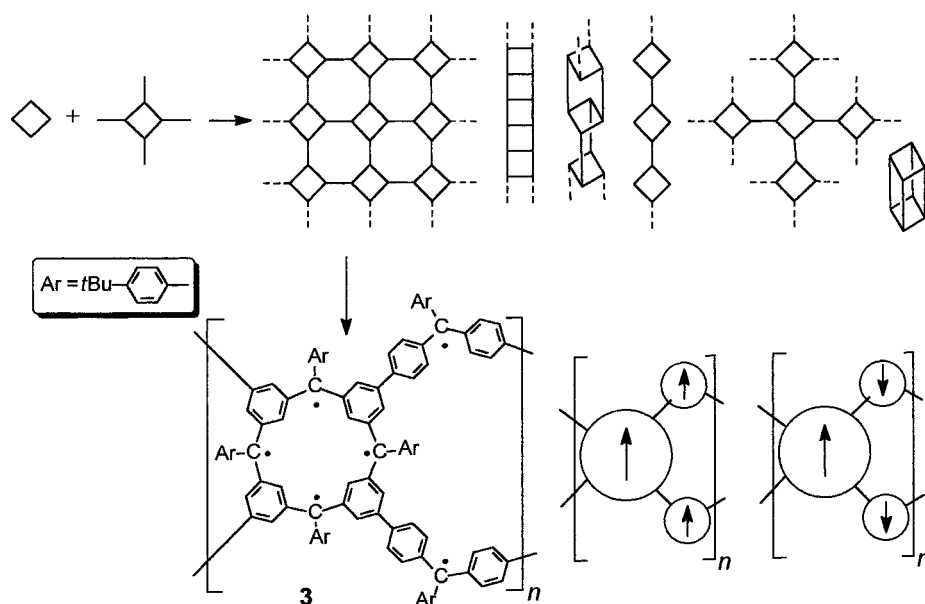
FIG. 8. Possible structures from polymerization of two macrocyclic and tetrafunctionalized modules (top). Network polyradical **3** as a spin cluster with unequal spin modules (bottom).

Hamiltonian (Eq. [1]) are possible. In large organic spin clusters, in which fCU's with two different coupling strengths are used, the strongly coupled spins $\frac{1}{2}$ (through 1,3-phenylenes) may be combined into component spins. With this approximation, a solution for the energy eigenvalues in Eq. [1] can readily be obtained for the weakly coupled component spins (through the 3,4′-biphenylene). In order to obtain correct spacing between energy eigenvalues, J_{ij} must be scaled. For example, in the case of J'(1,3-phenylene) $= 6J$(3,4′-biphenylene) $\approx kT$, examination of simple model spin clusters suggests that J_{ij} should approximately be scaled by the fraction of the component spin (the fraction of arylmethyl spin sites) directly involved in pairwise couplings through 3,4′-biphenylenes (4, 15, 20). M as a function of T and magnetic field (H) can be obtained from the energy eigenvalues. The agreement between the experimental and calculated plots of MT vs T is excellent, even in the presence of a small density of defects (15, 16).

Under the conditions such that the ground state of a high-spin polyradical is 100% populated at low T, the experimental measurement of the H dependence of M may estimate the S value for the ground state. For a polyradical with a large number of unpaired electrons, even a small density of defects leads to a mixture of spin systems and a significantly lowered average value of S. When the mixture of a spin system is almost monodisperse in S, the M vs H data may be fitted to a single Brillouin function with a variable S (and, typically, magnetization at saturation, M_{sat}). For a polydisperse mixture of spin systems, the M vs H curve deviates from any single Brillouin function; i.e., it is dominated by large and small S at small and large H, respectively (11).

Consequently, an appropriate linear combination of the Brillouin functions must be used. Percolation models, typically assuming identical yield per site for a generation of radicals ($p100\%$), permit a generation of such linear combinations of the Brillouin functions; variable parameters are p and, typically, M_{sat}. The number average value of S can be calculated from p (3, 18).

4. CONCLUSION

The organic spin cluster approach provides a novel design of nanostructured very-high-spin molecules with well-defined sizes and shapes, which are prepared by efficient modular syntheses. Analogous cluster design is applied to the synthesis of polymer network polyradicals. For both organic molecules and polymers, the highest values of spin quantum number S are attained. The next challenges are: (1) implementation of these design rules in synthesis of polyradicals, which are stable at ambient conditions, and (2) development of a rational approach to increase the blocking temperatures.

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