

Review

# Recent Advances in Organic Radicals and Their Magnetism

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Academic Editor: Floriana Tuna

Received: 5 October 2016; Accepted: 22 November 2016; Published: 30 November 2016

**Abstract:** The review presents an overview of the organic radicals that have been designed and synthesized recently, and their magnetic properties are discussed. The  $\pi$ -conjugated organic radicals such as phenalenyl systems, functionalized nitronyl nitroxides, benzotriazinyl, bithiazolyl, aminyl-based radicals and polyradicals, and Tetrathiafulvalene (TTF)-based H-bonded radicals have been considered. The examples show that weak supramolecular interactions play a major role in modulating the ferromagnetic and antiferromagnetic properties. The new emerging direction of zethrenes, organic polyradicals, and macrocyclic polyradicals with their attractive and discrete architectures has been deliberated. The magnetic studies delineate the singlet-triplet transitions and their corresponding energies in these organic radicals. We have also made an attempt to collate the major organic neutral radicals, radical ions and radical zwitterions that have emerged over the last century.

**Keywords:** organic radicals; biradicals and polyradicals; magnetism; supramolecular interactions; self-assembly

## 1. Introduction

Organic molecules we frequently come across in our daily lives are comprised of closed-shell electronic structures with equal numbers of electrons with up- and down-spins. Therefore, most organic compounds are diamagnetic [1]. The paradigm-shifting discovery of the triphenylmethyl radical [2] by Moses Gomberg in 1900 was a major landmark in the 20th century, which set the stage for studies of molecules with unpaired electrons, i.e., systems with open-shell electronic structures. After this discovery, several classes of organic radical systems having one or more unpaired electrons have been synthesized [3]. These radical systems can be polyradicals, biradicals and diradicals. In the biradicals, the distance between the two unpaired electrons in the molecule is too large and the electron exchange interaction ( $J$ ) between them is negligible or nearly negligible [4,5]. On the other hand, when, in a molecule comprised of two unpaired electrons, the magnitude of the dipole-dipole interaction is large enough to produce two spin states, i.e., singlet and triplet, it is referred to as a diradical [4,6]. These novel organic radical systems have initiated a wide range of highly interesting applications in redox-catalysis [7,8], living radical polymerization [9–11] and particularly magnetochemistry [12,13], the topic which pertains to this review. In addition, radicals find new-age applications as components in batteries [14,15], molecular spintronics [16], and the kondo effect [17], as well as in chemical biology and medicine as spin-labeling agents, in electron paramagnetic resonance (EPR) imaging and also in the diverse areas of biochemistry [18,19].

The design of pure all-organic molecular materials with magnetic properties has been one of the challenges of the last few decades. In this context, the indispensable work of Cambi and Szego

on spin-crossover magnetic materials in 1930 [20] has been one of the essential reference points for chemists, physicists and materials scientists towards the generation of pure organic magnetic materials. In the pure organic compounds, as a result of the constituent light-weight elements, only the isotropic magnetic exchange interactions govern the magnetic behavior at temperatures above 0.1 K. The other magnetic interactions in organic radical systems, for example hyperfine or spin-orbit interactions, sources of magnetic anisotropies, are believed to be insignificant above this temperature. As a consequence, magnetic organic systems are described at zero applied magnetic field by the effective spin Hamiltonian approach by  $H = -2 \sum J_{ij} S_i S_j$  (1), where  $S_{ij}$  represents the effective exchange interaction parameter for the magnetic centers  $i$  and  $j$ , having total quantum spin numbers  $S_i$  and  $S_j$ , respectively, with the summation operating over the adjacent pair of centers. From eqn. (1), when  $S_{ij}$  is positive the magnetic interaction is ferromagnetic (FM), and if  $S_{ij}$  is negative the interaction is antiferromagnetic (AFM). In general, organic magnetic materials exhibit paramagnetic properties at high temperatures. The three aspects central to designing organic molecular materials with bulk magnetic properties which should be diligently considered are: (i) the permanence of the spin-containing moieties; (ii) the magnetic interaction mechanism or the coupling routes between the neighboring spin-possessing moieties; and (iii) the transmission of the magnetic interactions along the material [21]. Based on the different possibilities of the coupling routes, a FM interaction may originate if an orthogonal organization with a zero overall overlap integral between the two singly-occupied molecular orbitals (SOMOs) of the two interacting moieties is produced. In contrast, an AFM interaction results if such an integral is non-zero for non-degenerate orbitals. Magnetic interactions can take place in an intramolecular fashion between two (or more) spin-containing units within the same molecule, or in an intermolecular fashion between organic radicals governed by the isotropic exchange interactions between the unpaired electrons of the nearest molecules positioned on the respective SOMOs. Therefore, the creation of organic magnetic materials would require control over supramolecular interactions within the spin-containing sub-units, in order to promote the correct isotropic exchange interactions between the adjacent organic radicals. Supramolecular interactions such as hydrogen bonding,  $\pi$ - $\pi$  stacking, halogen bonding [22] and bridging of radical ions through the counter-ions are the majorly applied non-covalent intermolecular interactions to assemble such molecular building blocks.

In one of the earliest reports on an organic ferromagnet, Tamura et al. in 1991 reported the existence of FM intermolecular interactions in the crystals of *p*-nitrophenyl-nitronyl nitroxide [23], with a ferromagnetically ordered state below 0.65 K. After this pioneering report, diverse design strategies were applied towards the goal of realizing ferromagnetically ordered organic free radicals at the highest possible temperature. The result that has remained unsurpassed to date is a sulfur-nitrogen-based organic radical with a magnetic ordering at 36 K [24].

We have collated a list of diverse organic neutral radicals [25–71], radical anions [72–104], radical cations [105–131] and zwitterionic radicals [132–136] in Charts 1–3 according to the year of their report. It is to be noted that the list is not exhaustive. The goal has been to acquaint the reader with different classes of radicals that have emerged over time and to illustrate the growing interest towards creation of new organic radicals. Several of these radicals have been isolated and structural characterization has been carried out. Innovative design principles have led to radicals with unprecedented ambient stabilization and also a handful of radicals that can withstand even the acidic chromatography matrix during their purification. Also of tremendous interest to the synthetic radical chemistry community is to improve their opto-electronic properties, having the potential to exhibit multistability. Several of the radicals and radical ions outlined in Charts 1–3 have found tremendous applications as organic magnetic molecular materials. After presenting the collection of organic radicals, we have considered the recent (2011 until now) advances made in the design and magnetic studies of  $\pi$ -conjugated organic radicals such as phenalenyl systems, nitronyl nitroxides, benzotriazinyl, bisthiazolyl, aminyl-based radicals and polyradicals, and H-bonded Tetrathiafulvalene (TTF)-based radicals (Sections 2–7). The examples clearly show that weak noncovalent interactions play a major role in modulating