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# **Chapter 8**

## **Conclusions**

*A comprehensive conclusion on all the chapters of the thesis is given here.*

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# Conclusions

This part of the thesis deals with the concluding remarks among different aspects of design, characterisation and application of molecular magnetic systems particularly on the diradicals of organic origin, albeit theoretically. The origin of magnetism in an organic diradical arises due to the presence of unpaired electrons in the nonbonding molecular orbitals (NBMOs). Generally, designing of molecular magnetic entities means a strategy of constructing new tailor made molecules having essential desired characteristics. The bioactivity, insulation, transparency, photoactivity, spintronic properties and so on are such divergent areas of research which make organic diradical based magnetic molecules a promising field.

In Chapter 1 (**Chapter 1: Molecules Manifesting Magnetic Behavior**) we have discussed the general introduction of the thesis comprising about the molecules with magnetic characters. The background of the thesis work including the stable building blocks for the organic magnetic molecules, qualitative predictions of the ground state of organic diradicals is embodied in this chapter. The biological and technological applications of different relevant molecular magnetic systems are clearly stated. The objectives of the thesis are also categorically mentioned in this chapter.

The Chapter 2 (**Chapter 2: Theoretical Background**) portrays the theoretical background of magnetic exchange coupling constant ( $J$ ) in diradical species applying broken symmetry (BS) approach. The difference in energies between singlet and triplet state is related to the value of  $J$ . The magnetic molecules considered in this thesis are characterised by the sign and magnitude of  $J$  values. Positive and negative values of  $J$  indicate ferro- and antiferro-magnetic interactions respectively. Starting from the expression of Heisenberg effective spin Hamiltonian the popular Giensberg, Noodlemann and Davidson (GND) formula for the evaluation of  $J$  value is given. However, the GND equation is applicable where the overlap between the two magnetic orbitals is small. Another formula for the estimation of  $J$  proposed by Bencini, Ruiz and further justified by Illas is applied for a

system where the overlap between the orbitals is large enough. However, Yamaguchi formula is used for the calculation of  $J$  throughout my entire thesis work because of its suitability and wide applicability in all cases. The utility of zero field splitting (ZFS) parameters for the quantification of different applications especially related to the organic diradical based magnets are discussed. It is mentioned that, the ZFS parameters are associated with the magnetic anisotropy. The different electronic and geometric properties of radicals with  $S$  higher than  $\frac{1}{2}$ , are properly investigated through ZFS data. Although the spin-spin interaction and spin-orbit coupling of the ground state and the excited state are responsible for ZFS, however, the spin-spin coupling is the main source of ZFS in case of organic radicals. The ZFS value arising from the spin-spin interactions can be anticipated through effective spin Hamiltonian. The conventional methodologies for the determination of axial ZFS parameter ( $D$ ) and rhombic ZFS parameter ( $E$ ) are discussed. The formula for evaluating the static ZFS magnitude ( $a_2$ ) from the values of  $D$  and  $E$  is also mentioned.

In Chapter 3 (**Chapter 3: Magnetism in Bis-Oxoverdazyl Diradicals Coupled with Different Linkage Specific Aromatic Ring Spacers**), we have predicted intramolecular magnetic exchange coupling constants for 11 different linkage specific bis-oxoverdazyl diradicals divided into two groups (*meta* and *para*) with different aromatic ring couplers. All the molecules have been optimized at UB3LYP/6-311+G(d,p) level of theory and the  $J$  values are calculated using BS approach under DFT framework at the optimized level along with 6-311++G(d,p) basis set using the same methodology by single point calculations. The general observation shows that *meta* connected molecules are ferromagnetic, whereas the *para* connected ones are antiferromagnetic. The magnetic interactions are conveyed via  $\pi$ -conjugated path of the aromatic couplers as established by the spin density alternation rule. The figures of singly occupied molecular orbitals (SOMOs) are in good agreement with our predicted results. We also estimate hyperfine coupling constant (HFCC) values.

The Chapter 4 (**Chapter 4: Role of Linear Polyacene Spacers in Intramolecular Magnetic Exchange Coupling**) describes the theoretical investigation on 10 bis-oxo- and bis-thioxo-verdazyl diradicals with linear *meta* connected polyacenes (benzene to pentacene) of varying length as couplers. All the molecules are essentially ferromagnetic according to

the spin density alternation rule, as we have deliberately used *meta*-connected ring couplers. The evaluated magnetic exchange coupling constants ( $J$ ) decrease regularly when benzene, naphthalene and anthracene are used as couplers with the increase of coupler chain length, whereas for tetracene and pentacene couplers the  $J$  values are decreasing although the chain length is increased. This observation is explained in the light of open shell radicaloid character of the higher polyacenes. Nonetheless, the observed  $J$  values are in good agreement with the experimental findings. Magnetic aromaticity index, nuclear independent chemical shift (NICS) values for the each benzenoid ring at the ring plane [NICS(0)] and 1 Å above the plane of the ring surface [NICS(1)] of every coupler for all diradicals are evaluated. It is found that the central benzenoid rings of each coupler have higher NICS values compared to the terminal rings of the coupler. That is, a loss of benzenoid character is observed for the terminal rings. A relation between  $\Delta$ NICS (1) with that of  $J$  values is made. One should note that, the difference between average NICS(1)<sub>coupler</sub> and NICS(1)<sub>acene</sub> is represented by  $\Delta$ NICS(1).

The Chapter 5 (**Chapter 5: Influence of Aromaticity on the Magneto Structural Property of Heteroverdazyl Diradicals**) finds a theoretical correlation between the structural aromaticity index, harmonic oscillator model of aromaticity (HOMA) and magnetic aromaticity index NICS. These two indices are separately compared with the  $J$  values evaluated for the *meta*-phenylene and their corresponding *para*-phenylene coupled bis-heteroverdazyl diradicals as designed for this chapter. The HOMA index is estimated for the whole diradicals as well as for the aromatic six membered coupler fragments. On the other hand, the NICS index is evaluated only for the six membered coupler fragments of the diradicals. The HOMA and NICS values suggest that the increase of aromaticity is associated with the rise of ferromagnetism, that is, aromaticity favors ferromagnetic trend in such diradical systems. In this chapter, the low  $J$  values for bis-phosphoverdazyl diradicals are attributed due to the spin leakage phenomena associated with the phosphorus atom. A quantitative relation between SOMO–SOMO energy gaps with  $J$  values has been made for all molecules. The shapes of SOMOs also play a role to envisage the state of magnetism. The ground state stability of these diradicals has also been investigated and found that the ferromagnetic diradicals are more stable than their respective antiferromagnetic counterparts.

In Chapter 6 (**Chapter 6: Photoresponsive Magnetic Crossover**), the green fluorescent protein (GFP) chromophore based photoswitchable diradicals in two different structural isomeric forms (cis and trans) are theoretically designed and characterized. The cyan, blue and green variants of GFP chromophores are used as couplers to form the photomagnetic diradicals. These photochromic diradicals undergo antiferromagnetic (trans) to ferromagnetic (cis) crossover upon irradiation of appropriate wavelength of light associated with alteration in color, which are likely to be useful in the field of biomedical applications. From the time dependent density functional theory (TDDFT) measurement it is found that if the dark trans diradicals are exposed to the light of wavelength range 360 to 390 nm, the transformation to their puckered fluorescent cis form is observed. As far as the technological applications of these diradicals are concerned, we have made the density of states (DOS) plots and found that at the Fermi level the spins are highly polarized for ferromagnetic cis diradical indicating to show the spin valve effect. The HOMO-LUMO energy gap qualitatively indicates that these diradicals can be used in non linear optical (NLO) imaging, in organic light emitting diode (OLED) devices, high-density optical memories and switches. The efficiency of these diradicals to be used as magnetic resonance imaging contrast agents (MRICAs) and in many other biomedical cases are qualitatively justified. The ground state stability with the two different structural forms of all these diradicals are made and have shown that the cis fluorescent ferromagnetic molecules are more stable than their dark trans counterparts.

The quantification of the different variants of the fluoroprotein chromophore coupled diradicals which can be used as MRICAs are furnished in Chapter 7 (**Chapter 7: Possible Applications of Fluoro Protein Chromophore Coupled Photomagnetic Diradicals**). Here, the GFP chromophore based 6 photoswitchable diradicals are theoretically designed with bis-imino nitroxide (IN) as magnetic sites and a magnetic crossover is observed when irradiated with appropriate wave length of light. The extent of magnetic interactions in all these molecules has been quantified in terms of  $J$ . The choice of IN as radical sites in these diradicals is due to its water solubility, the ability to act as very effective spin levels and most importantly capacity to perform as MRICAs. The *in vivo* suitability of these diradicals has been tested by calculating these diradicals with 2-layer Our own N-layer Integrated

molecular Orbital molecular Mechanics (ONIOM) and Polarized Continuum Model (PCM) methods. Along with gas phase optimization, the ONIOM optimization for all diradicals is performed where the diradicals are treated as high level layer and the surrounding water molecules are selected as low level layer. However, for PCM optimization in *blood plasma medium* the dielectric constant,  $\epsilon = 58$  and reflective index,  $\mu_{ri} = 1.1315$  have been chosen. Like gas phase calculation a magnetic crossover from antiferromagnetic (trans, dark) state to ferromagnetic (cis, fluorescent) state is also observed for ONIOM and PCM methods. As a matter of fact, only visual inspection is required to understand the nature of magnetism; however, the extent of magnetism can be theoretically determined by applying the above methodologies. The photochemical properties of the diradicals in gas phase and in water solvated phases have been investigated using TDDFT method. The novel property of these diradicals is about their *in vivo* utilities as MRICAs. From our calculations it is found that all these designed fluoro protein chromophore coupled nitroxide based diradicals have axial zero field splitting (ZFS) parameter  $|D|$  in the range from  $1.2 \times 10^{-2}$  to  $1.7 \times 10^{-2} \text{ cm}^{-1}$ , which is essential to act as contrast agents in MRI. Moreover, the GFP chromophore is stable even at  $65^\circ\text{C}$ . Thereby, these fluorescent nano-magnetic moieties can have the utilities in magnetic hyperthermia treatment as  $42^\circ\text{C}$  temperature is required to destroy the required malignant sites. Being a good tagger, the magnetic separation of different biological entity with external magnetic field control is possible by the judicious use of these GFP based diradicals.

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