ABSTRACT

A substantial amount of work has already been done on molecule based magnetism as evident from the existing literature. The main objective of this thesis is to study the properties as well as the applications of the designed molecular magnets particularly of organic domain. Transparency, photo activity, low toxicity and biocompatibility are the properties which make the field of molecule based magnetism to rise over traditional magnetism. The studies described in the thesis are divided into eight chapters.

The **Chapter 1** describes the general introduction of this work based on magnetic molecules. The background of this thesis is clearly described. This chapter also categorically portrays the different objectives of this thesis.

The **Chapter 2** depicts the theoretical background of how the magnetic exchange coupling constant (J) is evaluated by broken symmetry (BS) approach in the unrestricted density functional theory (UDFT) framework. The theoretical background of estimation of axial spin-spin zero field splitting (ZFS) parameter (D), the rhombic ZFS parameter (E) and ZFS magnitude (a_2) are also discussed here.

The **Chapter 3** describes our investigation on different linkage specific oxoverdazyl diradicals. Here, we have used *meta-* and *para-*connected aromatic cyclic ring couplers in between two oxoverdazyl moieties to form the desired diradicals. Their J values are then evaluated at UB3LYP/6-311++G(d,p) level of theory. A correlation between sign and magnitude of J with respect to their connectivity is also made. The ferromagnetic and antiferromagnetic interactions are observed for *meta-*connected and *para-*connected diradicals respectively. After that, the estimated J values are clarified using spin polarization maps and magnetic orbitals. The hyperfine coupling constant values are also computed to support the intramolecular magnetic interactions. Figure 1 is the representative of two such *meta-* and corresponding *para-*connected systems.

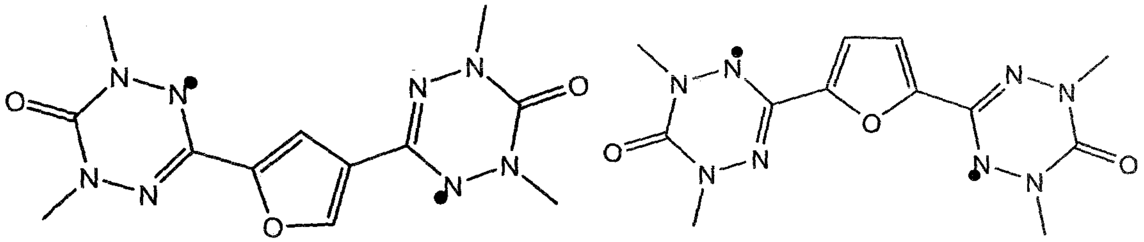


Figure 1. Bis-oxoverdazyl diradicals where *meta*- and *para*-connected furan is used as couplers.

The **Chapter 4** encompasses the intramolecular magnetic exchange coupling constant for different high spin diradicals using BS-UDFT treatment. The role of linear polyacenes of varying length which are used as couplers in these bis-oxo- and bis-thioxo-verdazyl diradicals is discussed. The spin density distribution as well as an analysis made by "magnetic" orbitals is used to explain their magnetic character. The Nuclear Independent Chemical Shift (NICS) values have been correlated with J values. Figure 2 shows a general schematic representation of the diradicals investigated in **Chapter 4**.

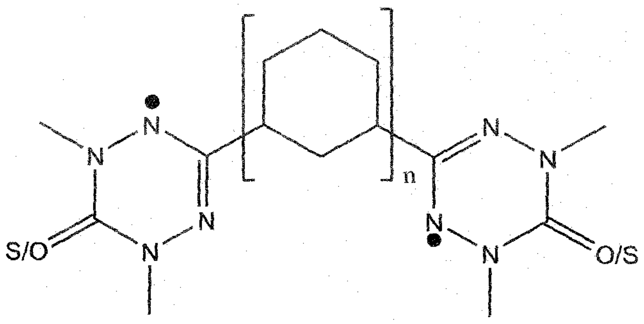


Figure 2. Bis-oxo- and bis-thioxo-verdazyl diradicals where *meta* connected linear polyacenes are used as couplers, where n is the number of benzenoid rings.

In **Chapter 5** geometry based aromaticity index harmonic oscillator model of aromaticity (HOMA) along with magnetic aromaticity index NICS has been evaluated. Here we have taken so called heteroverdazyl diradicals where *meta*- and *para*-phenylene coupled high spin and the corresponding low spin diradicals (Figure 3) are used. The result of the spin leakage phenomena on J and that on HOMA and NICS values of certain phosphaverdazyl systems has been unequivocally argued. However, the main novelty of this work stands upon the consideration of the aromatic behavior by means of the geometrical global and local aromaticity index HOMA.

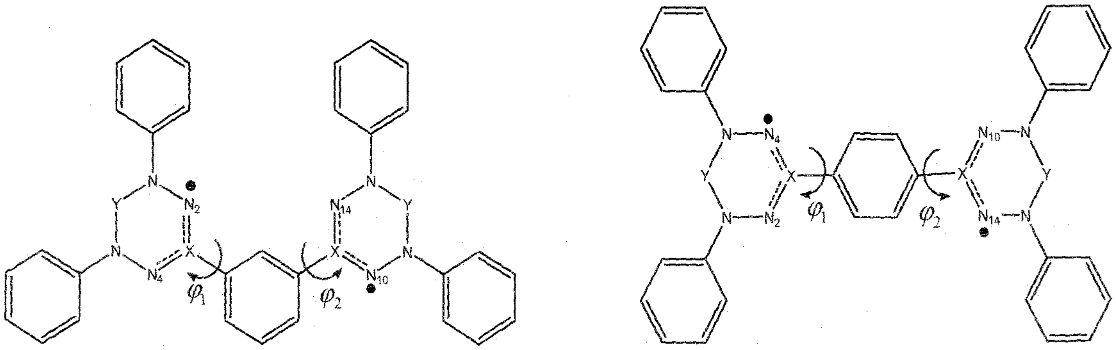
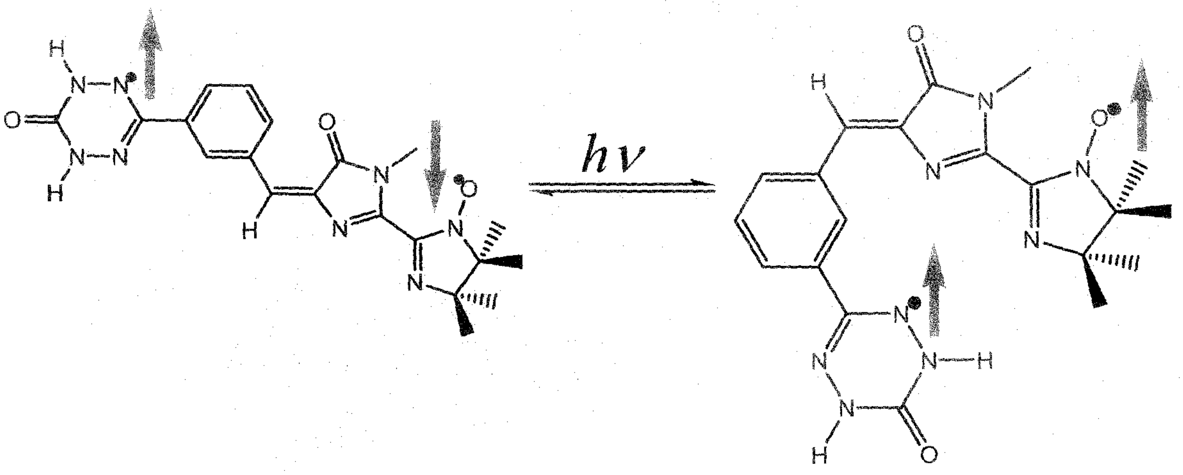


Figure 3. Substitution at X and Y position gives rise to different "so called" *meta-* and corresponding *para*-phenylene coupled heteroverdazyl diradicals. The φ_1 and φ_2 denote two different relevant dihedral angles.

The **Chapter 6** has embodied the study of different variants of green fluorescent



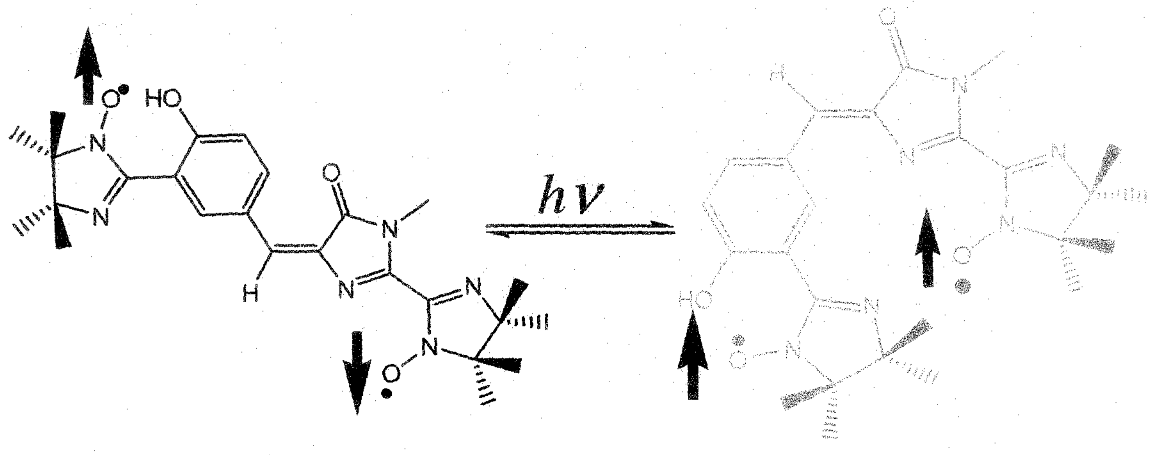
Dark, antiferromagnetic and trans

Blue fluorescent, ferromagnetic and cis

Figure 4. The trans (antiferromagnetic) and the respective photoconverted cis (ferromagnetic) diradicals, where the blue variant of GFP chromophore (BFPF) is used as coupler. Here, IN and oxo-verdazyl radicals are used as mixed magnetic sites. The up and down arrows show α and β spin respectively.

protein (GFP) chromophore coupled diradicals where imino nitroxide (IN) and IN or oxo- or phospha-verdazyl radical moieties are used as magnetic centers. A spin crossover from antiferromagnetic to ferromagnetic state is observed as the trans diradicals are converted into their cis state by the irradiation of appropriate wave length of light, which is estimated by the time dependent DFT calculation. The most novel property observed here is that the dark trans diradicals turn into their fluorescent cis isomers upon irradiation of appropriate light. As a result, only visual inspection is required to know the magnetic status of these diradicals (Figure 4).

The **Chapter 7** describes biomedical applications of different analogues of GFP chromophores coupled diradicals where we have introduced bis-IN as radical sites. To confirm their biomedical uses we have optimized them not only in gas phase but also in water and *blood plasma medium* by adopting 2-layer our own N-layer integrated molecular orbital and molecular mechanics (ONIOM) method and polarized continuum model (PCM) method respectively. In ONIOM method the water molecules are treated as



Antiferromagnetic, trans and dark

Ferromagnetic, cis and green fluorescent

Figure 5. The antiferromagnetic planar trans (dark) and corresponding photoconverted puckered cis fluorescent (green) bis-IN diradicals where GFP chromophore is used as couplers. These diradicals are used as contrast agents in MRI experiment. The α and β spins are represented by the up and down arrows.

low level layer whereas the diradicals are treated as high level layer. The magnetic nature of these diradicals is estimated by ONIOM-BS [where BS calculations are done for inner high level layer (diradical system) keeping the outer water layer at low level] and in PCM-BS methodology. Their suitability to be used as magnetic resonance imaging contrast agent (MRICA) has been quantified by the estimation of the axial zero field splitting (ZFS) parameter (D), rhombic ZFS parameter (E) and ZFS magnitude (a_2) for each ferromagnetic species in three different media. One can ambitiously expect from our calculations that if these diradicals are synthesized then they can be used as successful, non-hazardous MRICA in place of other metal based contrast agents. Figure 5 shows the photoconversion of antiferromagnetic dark planar trans and their corresponding fluorescent (green) puckered cis diradicals where GFP chromophore is used as couplers between two IN moieties.

A comprehensive conclusion of the total thesis work is given at the end in **Chapter 8.**