ABSTRACT

The first chapter describes a brief history of magnetism and the origin of magnetism in different types of magnetic materials. Starting from the early paradigm of magnets which was first observed in a type of mineral magnetite, the discussion moves forward according to the requisite of novel kind of magnetic materials. This chapter also deals with the transport property of spin polarized molecular systems. Transport property of different types of metal complexes, Single Molecule Magnets (SMMs) and different organic radical systems coupled with electrodes are discussed here. A detailed analysis of literature along with the objectives of the thesis is stated in this chapter.

The second chapter depicts the theoretical background for the estimation of magnetic exchange coupling constant (*J*) of molecules. Among different variety of methodologies, the broken symmetry (BS) formalism in density functional theory (DFT) framework is found to come up with the optimal solution for the determination of *J*. The theoretical background for the estimation of transport property of molecules through green function-based technique in DFT framework has also been discussed here.

The crux of the third chapter is to study the effect of length of unsaturated organic molecular wires and radical substituted wires on the electrical transport properties. Extended π-conjugated systems are known to have interesting applications as memory devices, conducting nanowires, and diodes. In this chapter, the investigation of the transport property of two molecular wires of different length shows that the molecular wires of smaller length have higher transmission, i.e., higher conduction. The magnetic exchange coupling constant of the radical substituted molecular wires (substituting the molecular wire with two methylene radical centers at two different positions) depend only on the distance between the spin centers, not on the outsider substitution. The transmission characteristics of the radical substituted molecular wires (for ferromagnetically coupled diradicals) show similar observation as that of the wires without radical substitution. But for antiferromagnetically coupled diradical substituted molecular wires, there is a small variation in transmission characteristics.

In fourth chapter, the magnetic property of diradical-based organic molecules with allene and chiral cumulene couplers has been studied theoretically. Generally, for most of the diradicals, *J* value decreases with the increase in distance between radical centers. However, the designed diradicals show ferromagnetic interaction with conflicting behavior i.e., *J* value increases with the increase in distance between radical centers. Moreover, spin density within the coupler increases remarkably as

length of the coupler increases which is quite contradictory from the normal concept that spin density within the coupler decreases with the increase in length of the coupler. A large accumulation of spin density within the coupler overcomes the distance factor between radical centers that results higher magnetic exchange coupling for longer coupler in the designed diradicals. Moreover, addition of chiral centers within the coupler lowers the energy of lowest unoccupied molecular orbital (LUMO) and a smaller HOMO (highest occupied molecular orbital) - LUMO gap facilitates a stronger magnetic coupling. From natural orbital occupancies it is found that, with increasing chain length of chiral coupler the occupancy of LUMO increases. Therefore, a correlation between the LUMO occupation and magnetic exchange coupling constant is intuited. These designed molecules may be used as molecular building blocks for organic chiral magnetic solids.

The key issue of the fifth chapter is to investigate the magnetic and transport properties of diradicals attached by a range of linear conjugated and cumulene couplers focusing on the unusual π-interaction properties within the couplers. Generally, chains containing *sp*-hybridized carbon atoms are interesting for their unique linear structure and physical properties. On the other hand, linear chains of carbon atoms have been anticipated to have excellent properties for several transport related applications. In this chapter, it is observed that the spin density within the couplers, distance between radical centers, dihedral angles between the plane of the coupler and radical centers influence the strength of magnetic coupling for all the diradicals. It is established that the strength of magnetic interaction in cumulated and conjugated systems varies in a different way as the length of the coupler increases. Transport calculations show that with the increase in chain length, diradicals based on even cumulene couplers act as better conductor than odd cumulenes couplers. However, in conjugated coupler based diradicals, transmission does not vary in a sequential way.

The sixth chapter has embodied the study of magnetic property of heteroallene (>C=C=X−) and heterocumulene (>C=C=C=X−) based *tert*-butyl nitroxide diradicals (X is P/As) by density functional theory based methods. Different research works show that the presence of heteroatom in the exchange pathway significantly influences magnetic exchange coupling. Moreover, heteroallene and heterocumulene (with 4 atoms in backbone chain) containing double bonded heavy elements have attracted interest from a theoretical point of view because of their peculiar physicochemical properties. In this chapter a theoretical investigation on the potential effect of P/As atom substitution within the allene and cumulene couplers in mediating the exchange interaction between the two radical centers has been carried out. Calculation of magnetic exchange coupling constant (J) shows ferromagnetic interactions in heteroallene based diradicals. Interestingly, in heterocumulene based diradicals, tuning of J value from antiferromagnetic to ferromagnetic state is observed from *Z*- to *E*- isomer. The essence of all findings is further explored by the structural effects, spin density distributions and molecular orbital analysis. Delocalization of spin density from *tert*-butyl nitroxide radical site to the coupler (in planar arrangement) is observed in the spin distribution analysis. Moreover, the shapes of singly occupied molecular orbitals (SOMOs) advocate the delocalization of spin from radical center to the coupler. The J value of all the diradicals strongly depends on the dihedral angle between the radical center and the coupler. Magneto-structural correlation shows that the change in dihedral angle tunes the magnetic property between ferromagnetic and antiferromagnetic states for both the *Z*- and *E*- isomers of heterocumulene based diradicals depending on the spin accumulation on two nearby magnetic centers. The energy gap between two consecutive SOMOs also supports this observation such that when this energy gap is low, ferromagnetic interaction is observed and for higher value of the energy gap antiferromagnetic situation arises in heterocumulene based diradicals.

A comprehensive remark, summarizing all the works done, is put in the seventh chapter.