

ABSTRACT

Lot of works has been done on the magnetism and transport property of the molecules as evident from literature. The main objective of this thesis is to understand the magnetic and transport property of molecules from organic and inorganic domain. Magnetism and transport property of molecules are important in the modern technological applications like spintronics, spin valve etc. The studies in this work have been divided into seven chapters.

The chapter one describes the general introduction about the magnetism of organic radicals and charge transfer complexes. A prelude about the transport property of molecules is also given in this chapter. Literatures forming the background of the present thesis are categorically discussed. The objective of the present thesis is also highlighted in this chapter.

The chapter two depicts the theoretical background for the quantification of magnetic exchange coupling constant of the molecules. The theoretical background for the evaluation of transport property of molecules has also been discussed.

In chapter three, we theoretically design and investigate the photomagnetic property of azobenzene based diradical systems, where trans isomers convert into corresponding cis forms upon irradiation with light of appropriate wavelength. The coupling constant values have been estimated using broken symmetry approach in DFT framework. In each case, the trans isomer is found to be antiferromagnetic, while the cis form is ferromagnetic in nature. Therefore, photoinduced magnetic crossover from antiferromagnetic to ferromagnetic regime would be observed. This is a new observation in case of the systems of organic origin. Importance of such systems for photomagnetic switches, sensors, high density data storage, spin valves and semiconductor spintronic materials have also been discussed with support from density of state analysis, SOMO-SOMO energy gaps and spin density plots.

In chapter four, we have designed seven organic diradicals with polyacene coupler to show the effect of the configuration, aromaticity and HOMO-LUMO gap of the couplers on the exchange coupling constant of the diradicals. We have correlated aromaticity index NICS and HOMA to explain the change of aromaticity with the structures having same number of carbon and hydrogen atoms and rings. The linear coupler gives higher exchange coupling constant compared to the angular one in the diradicals. Here, we have found the HOMO-LUMO gap is the

determining factor of the extent of magnetic exchange coupling constant of the diradicals. Not only the energy value of LUMO, but also the occupation number and spatial position of the LUMO are important for magnetic exchange in diradicals. Thus, the role of LUMO in magnetic exchange has been firmly established through this work.

In chapter five the ferromagnetism in mixed-stack charge-transfer (CT) complexes is explained and evaluated through new theoretical framework of our own. In DFT framework, broken symmetry (BS) approach is adopted to evaluate J using spin projection technique. No overlap between singly occupied molecular orbitals (SOMOs) suggests a through-space ferromagnetic interaction between the donor and the acceptor in the ground state of the complexes. Apart from the ground state, the magnetic status of the molecules is studied by varying interlayer distance d , the extent of slippage (slipping distance r , r' , and deviation angle α), and rotational angle θ , which play a crucial role in magneto-structural correlation. Furthermore, it is categorically observed that the ferromagnetic interaction reaches its zenith at minimum energy crystallographic stacking mode resulting in maximum value of coupling constant in the ground state.

In chapter six, we have theoretically studied the effect of external electric field on biphenyl, methylene substituted biphenyl monoradical and diradical systems. It has been found that the molecular conformation changes with application of external electric field. Thus, it is possible to tune molecular conformation reversibly only by external electrical stimuli. The HOMO-LUMO gap of the diradical reduces under external electric field. The molecules with low HOMO-LUMO gap can be used as unimolecular rectifier if the HOMO and LUMO have different spatial location on the molecule. Either to be conductive, the molecule should have the HOMO and LUMO located on the same spatial position. It has been observed that the diradical can be used as both unimolecular rectifier and molecular conductor depending upon the field strength. Now, the insulator molecule can be switched to molecular rectifier or molecular conductor and vice versa by external electric field. The spin topology in a radical depends on the strength and direction of the applied electric field. Consequently the extent of magnetic coupling in diradical system changes with external electric field. We have calculated the transmission spectra and I - V curve for the diradical at different dihedral angles. At lower dihedral angle the diradical shows efficient spin filter behavior. It is now possible to use a single molecule for

multifarious application like unimolecular rectifier, spin filter and molecular conductor depending upon the strength of the applied electric field.

A comprehensive conclusions of all the chapters are given in the chapter seven.