ABSTRACT

The first chapter addresses a concise history and momentous advances in the field of characterization of optical properties. This chapter introduces origin of several optical properties like nonlinear optical property, luminescence property, two-photon absorption property and also highlights current advancement in researches on designing of materials with improved optical properties. These optical properties are analyzed from the viewpoint of electronic structure theory for proper understanding of the structure property relationship. Special attention is given to the luminescent materials for their applicability as phosphorescent emitters for organic light emitting diodes (OLEDs) along with basic setup and working principles of OLED devices.

The second chapter represents a brief description of the basic theoretical background related to various optical properties along with theoretical techniques to quantify hyperpolarizability (β) and two-photon absorption cross section (σ). For theoretical determination of first hyperpolarizability (β), early models, equivalent field model (EIF), additivity model and two-state model along with quantum chemical approaches *viz.*, sum over states (SOS) methods and coupled perturbed HF (CPHF) methods are discussed here. A short description of available methods *viz.*, few-states model for quantifying two-photon absorption cross section (σ), is also presented. In case of luminescent materials, principles of computational phosphorescence are clearly stated.

The third chapter contains the results and analysis of the theoretical study on the NLO property of two synthesized aryl extended thiophene fused Nickel dithiolenes. Based on these two systems, a systematic modification of the molecules is done by substituting neutral and zwitterionic donor acceptor group at the aryl (phenyl and thenyl) ring to find their effect on NLO responses. Among the four designed systems, zwitterionic donor-acceptor group significantly reduces the HOMO-LUMO energy gap resulting an enormous increase in the first hyperpolarizability (β) values. To judge their high NLO response, transition dipole moment (TDM) density is also plotted and it is found that electron dissipation occurs from one donor part to the acceptor part with a large Δr index value which is the quantitative measurement to understand the type of transitions. A charge transfer transition is also observed in case of zwitterionic systems. In order to highlight the NLO active segment in a molecule, a beta density analysis is also presented.

In fourth chapter six different diradical systems based on azulene coupler and nitronyl nitroxide radical moieties are studied theoretically. Among them, three ferromagnetic diradicals are chosen for further calculation to assess their usability in different biological applications such as two-photon absorption photodynamic therapy (TPA-PDT) and magnetic resonance imaging contrast agents (MRICA). The TPA cross-section values are calculated to judge their efficiency as TPA-PDT photosensitizing agents. Calculated values of TPA cross-section lie in the range of commonly used photosensitizers for PDT. It is seen that the ferromagnetic diradicals can act as very good MRI contrast agents due to their high magnetic anisotropy characteristics. The magnetic anisotropy is quantified in terms of zero-field splitting parameter using DFT. It is found that the proposed diradicals can show good relaxation behaviour and consequently act as efficient MRI contrast agents. Thus, one can anticipate the multifunctional biological activity of these diradicals.

The fifth chapter deals with designing of efficient luminescent materials based on octahedral hexaaminechromium(III) complex. It is found that distortion of the octahedral symmetry of $[Cr^{III}(NH_3)_6]^{3+}$ by replacing the axial ligands with weaker halides influences the stability of the doublet state with respect to the quartet ground state. This replacement affects the doublet to quartet transition responsible for phosphorescence. The relative positions of the halides and ammonia in the spectrochemical series play an important role in tuning of emission wave length. The proximity of fluorine and ammonia in the spectrochemical series causes blue-shift in the emission wavelength and thus provides a rational way for designing blue emitting phosphorescent materials, essential in OLED application for full color display.

The sixth chapter provides a comprehensive study of molecular mechanism of excited state relaxation induced by intermolecular hydrogen-bond formation. The absorption and fluorescence property of 2-amino pyridine (2-AP) and its dimer $(2\text{-AP})_2$ are analyzed theoretically in order to unveil the effect of intermolecular H-bonding interaction in the photochemical behavior of 2-AP. All the calculations (DFT and TDDFT) are performed using ADF suit of program with dispersion corrected methods (DFT-D). To reveal the cooperativity due to H-bonding, a decomposition analysis (EDA) in the framework of the Kohn-Sham molecular orbital (MO) model is performed. The ETS-NOCV calculations are performed for the equilibrium geometries of the ground and excited states of the dimer. The formation of H-bond has been confirmed by the calculation of synergy (ΔE_{syn}) from the difference of interaction energy (ΔE_{int}) with and without H-bond interactions. H-bond interaction affects the energy of the electronic excited state of the dimer resulting red-shift in the emission spectrum.

General and comprehensive conclusions of all the chapters are given in the final chapter.