ABSTRACT

Photophysical properties of organic and inorganic molecules have attracted considerable interest due to their potential application in diverse fields. By understanding the excited state properties various phenomenon transpiring in the system can be explored. The first chapter conveys a brief history and significant development in the field of optical properties. This chapter includes origin of several optoelectronic properties like photoluminescence, nonlinear optical property, and highlights of the progress in research on designing new molecular systems with enhanced optical properties. Special attention is given to the luminescent materials for their applicability as fluorescent molecules for organic light emitting diodes (OLEDs). This chapter also includes different photovoltaic properties for dye sensitized solar cell (DSSC) application. These optical properties are investigated from the perspective of electronic structure theory for proper understanding of the structure-property relationship.

The second chapter addresses a concise description of basic theoretical background related to various optical properties along with theoretical techniques. Principle of fluorescence process in gas phase model and solvent model are clearly discussed. For theoretical estimation 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. Working principle of DSSC and mathematical expression of various photovoltaic properties of dye sensitized solar cell are also discussed in this chapter.

The third chapter contains the results and analysis of the theoretical study of photophysical properties of five napthyridine-based fluorine-boron (BF_2-napthyridine) conjugate compounds. Influence of electron-donating and electron-withdrawing groups attached with the N^C^O moiety of BF_2-napthyridine molecule has been interpreted. The optoelectronic properties, including absorption spectra and emission spectra of the BF_2-napthyridine derivatives are studied using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) based methods. Different characteristics, such as HOMO-LUMO gap, molecular orbital density,

ionization potential, electron affinity, and reorganization energy for hole and electron, are calculated. It is found that introduction of an electron-donating group into the BF_2-napthyridine complex improves the hole transport properties and provides useful clues in designing new materials for organic light emitting diodes (OLED). As a whole, this work demonstrates that electron-donating and electron-withdrawing groups in BF_2 derivatives can extend their effectiveness toward designing of OLED materials, vitro cellular studies, ex vivo assays, and in vivo imaging agents.

In fourth chapter indole based thiazole substituted donor-π-acceptor molecules are designed and their nonlinear optical properties (NLO) are evaluated theoretically. Different electron withdrawing groups and π-linkers are used to understand their role in tuning the NLO properties. The NLO properties of the molecules are analyzed in gas phase and solvent phases through the dipole moment, polarizability and hyperpolarizability. NLO efficiency is studied through HOMO-LUMO gap, frontier molecular orbitals, light harvesting efficiency, ionization potential, electron affinity and reorganization energy for hole and electron. It is found that hyperpolarizability increases with increasing strength of the electron withdrawing group. We also calculate relevant parameters related to photovoltaic cells for the designed dyes which emerge suitable for this purpose. Photovoltaic parameters such as electron injection efficiency, exciton binding energy, and open circuit photovoltage are evaluated for dye sensitized solar cells (DSSC) applications. It is found that alkyne π-linkers are better than alkene π-linkers for desired applications. This chapter highlights the optical and photovoltaic nature of the dyes and reveals the influence of different π-linkers and electron acceptors in designing new materials for NLO and DSSC applications.

The fifth chapter deals with boron dipyromethane (BODIPY) based push-pull systems that have been designed with zwitterionic donor-acceptor groups and their NLO properties have been evaluated using density functional theory based approach. Different π-conjugated linkers and electron acceptor groups are taken to understand their role in tuning the NLO properties. The molecules are analyzed through HOMO-LUMO gap, frontier molecular orbitals, polarizability, hyperpolarizability, Δr index, transition dipole moment density, ionization potential, electron affinity and reorganization energy for hole and electron. These observations are well correlated with the computed absorption spectra of the molecules. It is found that compared to

pyridinium acceptor group, imidazolium acceptor group in the BODIPY systems amplifies NLO response to a larger extent. This chapter highlights that π-conjugated linkers and electron acceptor groups can be used judiciously to design new molecular systems for optoelectronic application.

The sixth chapter provides a comprehensive study on the nonlinear optical property of $B_{12}N_{12}$ nanocluster functionalized donor-acceptor (D-A) groups using density functional theory. We study the effect of bonding of electron acceptor ligands and donor ligands positioned at opposite end of $B_{12}N_{12}$ nanocluster in gas phase. Designed systems are analyzed through HOMO-LUMO gap, frontier molecular orbital, hyperpolarizability, Δr index, transition dipole moment density and molecular electrostatic potential. The obtained results are well correlated with the computed absorption spectra of the molecule. It is found that phenyl ring incorporated D-A groups amplifies NLO response to a larger extent. As a whole this chapter provides a direction to the researchers that the right choice of substitution can considerably impact the nonlinear optical property of the BN nanocluster.

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