

CHAPTER 7

Conclusion

Abstract

This chapter represents general and comprehensive conclusions of all the previous chapters.

This final chapter deals with the general concluding remarks of all the previous chapters. In the first chapter, a brief introduction to the origin and advancement of research in the field of luminescence property, nonlinear optical property, and photovoltaic property of dye sensitized solar cell (DSSC) are extensively presented. Theoretical formulations also been given to comprehend the structure property relationship for designing efficient optoelectronic materials. It can be concluded that for the use of optical devices both conjugated organic systems and nanoclusters based systems possessing push-pull character are of enormous important.

The second chapter provides a brief theoretical framework related to fluorescence property, nonlinear optical property and photovoltaic property of dye sensitized solar cell (DSSC). Theoretical backgrounds of different spectroscopic property associated to fluorescence are also discussed here. Different models on the basis of quantum chemical approaches are discussed for theoretical determination of first hyperpolarizability (β). Few-states model, Sum over states (SOS) method, which are used in this thesis to quantify optical properties are also given in details. Various theoretical indices including working phenomena for DSSC applications are also explained in details.

Chapter Three presents theoretical study to gain information on the optoelectronic properties of five difluoroboron-naphthyridine analogs through DFT and TD-DFT study. All compounds were subjected to UV-Vis absorption and fluorescence studies in gas phase and in dichloromethane. Red shift is found in absorption and emission spectra with increasing electron delocalization. It is evident from this study that amine substituted BF_2 naphthyridine complex has lowest HOMO-LUMO energy gap and largest Stokes shift in gas phase as well as in solution phase. The emission property of amine substituted BF_2 -naphthyridine established high photoluminescence property compared to other molecules. The FMO analysis shows that HOMO and LUMO orbitals are more stabilized in polar environment. Naphthyridine ring also play a vital role in electron density delocalization and to enhance optical phenomena. In conclusion, this chapter reveals that difluoroboron complexes show significant photoluminescence behavior with the change of substitution

in the ketoiminate position. This outcome provides a practical direction towards fluorescent difluoroboron naphthyridine complexes for application in organic luminescence materials, biological sensing, and self illuminating fluorescence for in vivo studies.

Chapter Four provides theoretical studies on the newly designed molecules in search of better NLO materials which also show photovoltaic effect for dye sensitized solar cell (DSSC) application. We choose different D- π -A systems containing -CN and -COOH as electron acceptor group, indole as electron donor and thiazole ring with alkene or alkyne as π -conjugator. Our results illustrate that with increasing the strength of EWG at electron acceptor position, HOMO-LUMO gap decreases for both alkene and alkyne substituted systems. From FMO analysis we find that donor unit stabilizes the HOMO, whereas acceptor unit stabilizes the LUMO. Thiazole ring also provides additional stabilization to the LUMO. In case of alkene substituted dyes the HOMO is more stabilized by π -bridge than thiazole ring and in case of alkyne substituted dyes reverse order is found. Photophysical properties of the six compounds are evaluated examining the excited states. TDDFT results show that all the dye exhibit λ_{\max} in the visible region possessing low transition energy, high oscillator strength and LHE value. It has been found that first and second-order hyperpolarizabilities are more favoured in alkyne substituted π -linker systems and increases with the increase of strength of EWG. Polarizability and hyperpolarizability increases with the solvent polarity. Substitution of alkene π -linker by alkyne π -linker, all relevant properties for DSSC application like electron injection free enthalpy, LHE, dipole moment, open circuit voltage, charge transport character are favoured. This improvement assists to obtain high J_{SC} as well as high power conversion efficiency. In all the cases alkyne systems prove better than the alkene systems for NLO and DSSC applications. In summary we propose if these design molecules are synthesized, these should be efficient NLO material and organic sensitizer in DSSC application.

In the fifth chapter, photophysical properties are computed for novel zwitterionic BODIPY based molecules with pyridinium and imidazolium electron acceptors,

phenoxide unit as electron donor and various π -linkers for nonlinear optical application. DFT based methods are employed to explore their electronic structure, dipole moment, polarizability, hyperpolarizability, absorption property, IP, EA and reorganization energy of these molecules. Results reveal that with the introduction of different π -linkers in the D- π -A systems, planarity is maintained and HOMO-LUMO gap is systematically decreased. It is observed that thienothiophene groups reduce ΔE more than the other π -linkers. This observation is also supported by the excitation energy calculated with the TDDFT approach. Small HOMO-LUMO gaps of the molecules prompt the systems to absorb light in the NIR region. The intramolecular charge transfer from phenoxide unit to imidazolium unit through the π -conjugated backbone plays a significant role to obtain large NLO response. Imidazolium acceptor shows better NLO response than pyridinium acceptor. It is also to be noted that dipole moment, polarizability and hyperpolarizability are consistent with the HOMO-LUMO gap of the molecules. First hyperpolarizability of the molecules is found to respond dominantly in the z direction which indicates the course of charge transfer. A good correlation has been found between Δr index, TDM density, hyperpolarizability value and hole/electron transport property. As a whole, this chapter demonstrates that the structural modification of π -linkers and electron acceptors in designing D- π -A system is a significant approach to obtain of high performance NLO material.

Chapter Six propose donor-acceptor functionalized nanocluster as a valuable strategy to persuade significant NLO effect in the centrosymmetric $B_{12}N_{12}$ nanocluster. Different series of BN nanoclusters are considered here with different D-A group at their opposite ends. DFT based methods are used to investigate electronic structure, adsorption energy, dipole moment, hyperpolarizability and absorption property of the designed nanocluster. The result indicates complexations of $B_{12}N_{12}$ nanoclusters are remarkably sensitive to the electro-optical features. Good correlation was found with the HOMO-LUMO gap of the designed systems. Complexation of D-A group significantly narrows the HOMO-LUMO gap whereas enlarges the β value in several order. This result is also supported by the excitation energy calculation with the TDDFT approach. The negative adsorption energy values reveal that the complexations are energetically favourable and exothermic in nature. The lowest HOMO-LUMO gap found for the $PhNH_2$ - $PhCN$

decorated $B_{12}N_{12}$ nanocage. Doubly substituted D-A functionalized nanoclusters result large hyperpolarizability value compare to monosubstituted clusters which indicate the charge transfer from donor unit to acceptor unit. The intramolecular charge transfer from donor unit to acceptor unit through the $B_{12}N_{12}$ cluster plays a significant role to obtain large NLO response. Highest hyperpolarizability is obtained for $PhNH_2-B_{12}N_{12}-PhCN$ system with lowest excitation energy. A good correlation has been established among the Δr index, TDM density and hyperpolarizability. So, this chapter concluded that complexation of D-A with the BN nanocluster could be a significant strategy to design novel electro-optical BN-based material.