Acknowledgement

Dr. K Sreekumar - My supervising guide and Head of the Department - For his constant inspiration and guidance all through this work
Prof. K Girish Kumar - Former Head of the Department and Doctoral committee member - For the assistance during period of research
Prof. M R Prathapachandra Kurup - Former Head of the Department - For the help and for all the facilities
All the faculty members and non-teaching staff of the department - For their timely help and co-operation
Prof. Swapan K Pati, JNCASR, Bangalore - Our collaborator
Prof. P K Das, IISc, Bangalore - For NLO measurements
Dr. Ayan Datta, IISER Trivandrum; Dr. Manoj, IIITMK Trivandrum - For their valuable discussions and suggestions
STIC - CUSAT, NRC- IISc - Bangalore, SAIF - IIT Madras, NIIST - Trivandrum, Department of Physics-CUSAT - For Spectral Analysis
My Labmates - For their love and co-operation
Friends from Theoretical Science Unit, JNCASR, Bangalore - For their help during my work in JNCASR
Athulya hostel inmates - For their love, support and help
Friends of Department of Applied Chemistry - For their help and care
Research scholars from Department of Physics, Polymer Science and Rubber Technology Department, International School of Photonics - For their help during research
Friends and Teachers from Mar Thoma College, Perumbavoor, Sree Sankara Vidhyapeedam College, Valayanchirangara, C M S College Kottayam - For their love support and blessings
DRDO and CUSAT - For financial support to carry out the research work
My family - For their love, prayers, patience, support and interest

Elizabeth
The development of materials with high nonlinear optical (NLO) properties is a key to control the propagation of light by optical means. In particular, the response of the materials to the electric field has found tremendous application in designing materials for NLO devices. These devices are being used in numerous applications, from lasers to optical switches and electronics. Some of the best NLO properties are displayed by organic and polymer systems. These materials are of great interest because of their low cost, ease of fabrication and integration into devices. The necessary and essential conditions for the existence of second order nonlinear optics include the attainment of charge and spatial asymmetry. Such requirements are best met by dipolar, highly polarizable donor-acceptor systems, showing charge transfer between electron donating and electron withdrawing groups. When such structures extent to macroscopic dimensions, the poling of chromophores can be achieved through chemical synthesis, and there is no need for external poling. The permanent dipole moment of such structures can be very large because of the coherent addition of dipole moments achieved by a high degree of polar order.

Another way of ensuring noncentrosymmetry in polymer system is the incorporation of chiral molecules in polymer structure. Optically pure materials, which have only left-handed or right-handed symmetry, are inherently noncentrosymmetric. Such compounds are, in fact, readily available in the nature (amino acids, sugars and alkaloids are well known examples existing only in a single enantiomer). Thus polymers with these molecules are expected to be NLO active. The present work emphasizes chirality as an efficient tool to synthesize new class of second order nonlinear optical polymers. The nonlinear optical properties of polymers have been studied theoretically and experimentally.

Objectives of the present study

1. Theoretical investigation of NLO properties of organic molecules and polymers.
2. Theoretical designing of bifunctional and multifunctional polymers with high second-order NLO properties.
3. Synthesis and characterization of the designed bifunctional and multifunctional polyesters and polyurethanes.
4. Experimental evaluation of NLO efficiency of the polymers.
5. Theoretical and experimental correlations.

Chapter 1: Nonlinear optical properties of organic and polymer systems

This chapter presents a general introduction on the nonlinear optical (NLO) properties, theoretical background and various applications of NLO materials. It also gives a brief review of the important nonlinear optical polymers such as side chain, main chain, guest host systems, crosslinked systems etc. developed with high NLO coefficients.

Chapter 2: Computational studies on the stability and spectroscopic properties of porphyrin, chlorin, bacteriochlorin and their few metal complexes

This chapter discusses the stability of metal incorporated porphyrin, chlorin and bacteriochlorin. The metals with +2 oxidation state (Be, Mg, Ca, Sr, Ba, Zn and Cd) are used for the stability studies. The theoretical calculations were done to investigate the metal-ligand stability by means of Density Functional Theory and Time Dependent Density Functional Theory. Various spectroscopic properties (UV-Vis, IR, Raman) including NLO properties of metal free and metal incorporated porphyrin, chlorin and bacteriochlorin were investigated. This chapter mainly describes the effect of changes in electronic structure, bond order, formation energy, aromaticity and charge distribution on the stability of the metal encapsulated complexes. The stability order of metal complexes is predicted.

Chapter 3: Nonlinear optical properties of organic molecules: Theoretical investigation

This chapter describes the theoretical calculation of NLO properties of organic molecules. The chapter is divided into four parts. The first part deals with nonlinear optical properties of chromophore (D-n-A) and bichromophore (D-n-A-A-n-D) systems by making use of DFT and semiempirical calculations. Second part of this chapter deals with the odd-even effects in D-A groups of amidodiols obtained by the aminolysis of ε-caprolactone. Extensive theoretical evaluation was done on the effect of spacer length enhancement on the second-order NLO properties of twin donor-acceptor molecules having amido units bridged by CH₂
spacers. ZINDO/CV method was adopted for the NLO property calculations. The third part describes the odd even effect of D-A groups of amidodiols obtained by the aminolysis of γ-butyrolactones. The fourth part of this chapter deals with the theoretical investigation on the Diels-Alder reactions of fulgides with maleic anhydride. The spectroscopic properties of fulgides obtained by the Stobbe condensation of acetone, acetophenone and benzophenone with diethyl succinate and the theoretical studies regarding the feasibility of Diels-Alder reaction with maleic anhydride were performed by computational methods. DFT/B3LYP/6-31G (d, p) basis set was used for the theoretical evaluation of the transition states.

Chapter 4: Nonlinear optical polymers from natural resources: Theoretical and experimental studies on cardanol based polyurethanes

This chapter describes the synthesis of a series of polyurethanes incorporating chiral and achiral diols obtained from natural resources. The bifunctional and multifunctional polymers were designed computationally and the NLO activity was predicted. The achiral diol used for polymer synthesis was prepared by the condensation of formaldehyde with cardanol. The bifunctional and multifunctional polymers were synthesized by varying the composition of chiral and achiral diols. The NLO activity of the chiral polyurethanes was determined experimentally and the chapter concludes with correlating the experimental and theoretical results.

Chapter 5: Nonlinear optical properties of main chain chiral polyurethanes containing bisazo chromophores: Theoretical and experimental investigations

Chapter 5 deals with the theoretical and experimental studies of polyurethanes having main chain chirality and push-pull (donor-acceptor) azobenzene moiety. The azo polymers were designed as the polyaddition product of chromophores 2, 4-toluene diisocyanate (TDI) with azo diols, bis (4-hydroxy phenylazo)-2, 2′-dinitrodiphenylmethane, bis (8-hydroxy quinolinazo)-2, 2′-dinitro- diphenylmethane, bis (4-hydroxy-3-methylphenylazo)-2, 2′-dinitrodiphenylmethane (obtained by the diazo coupling of 4, 4′ diamino-2, 2′-dinitrodiphenylmethane with phenol, 8-hydroxy quinoline and o-Cresol) and chiral diols (isosorbide, (2R, 3R)-diethyl tartrate and isomannide) with 2, 4-toluene diisocyanate. The SHG efficiency of the polyurethanes was found to be considerably high as predicted by theoretical calculations.
Chapter 6: Main chain chiral polyesters with amidodiol monomers derived from γ-Butyrolactone: Theoretical and experimental investigations

This chapter deals with the theoretical and experimental investigation of nonlinear optical properties of polyesters obtained by the condensation polymerization of terephthaloyl chloride with chiral diols and achiral diols. The polyesters were computationally designed and NLO properties of the bifunctional and multifunctional polymers were studied using ZINDO/CV methods. The designed polymer molecules were synthesized and the SHG efficiency of the molecules was evaluated. One part of the chapter describes the polyester synthesis using isosorbide as chiral moiety. The amidodiols obtained by the aminolysis of γ-Butyrolactone was used as the achiral diol for the present synthesis. The second and third parts of the chapter deal with synthesis of polyesters from (2R, 3R)-diethyl tartrate and isomannide as chiral molecules and SHG efficiency was experimentally determined.

Chapter 7: Main chain chiral polyurethanes with amidodiol monomers derived from ε-Caprolactone: Theoretical and experimental investigations

This chapter discusses the NLO properties of chiral polyurethanes obtained by the polyaddition of achiral amidodiols and chiral diols with 2, 4-toluene diisocyanate. The amidodiol monomers used for the synthesis was prepared by the aminolysis of ε-Caprolactone. The polymers were first designed and the NLO properties were predicted by computational tools. The designed bifunctional and multifunctional polyurethanes were synthesized by varying the chiral-achiral diol compositions. The SHG efficiency of the polymers predicted by theoretical calculations correlated with the experimental measurements.

Chapter 8: Conclusions

This chapter presents the summary and important conclusions of the work done. References are given to the end of each chapter.