

ABSTRACT

Present developments in the field of materials chemistry show that, though inorganic materials are still the choices for many devices, interest in organic materials is growing day-by-day in view of the latter's adaptability to various kinds of applications. The field of nonlinear optics has attracted lot of interest in the past three decades not only because of the possible numerous applications in telecommunications, optical data storage etc., but also because of the fundamental research connected to issues like charge transfer, conjugation, polarization and crystallization into noncentrosymmetric lattices. In principle, nonlinear optics (NLO) deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields altered in frequency, phase or other physical properties. A variety of systems including inorganic materials, organometallic materials, organic molecules and polymers have been studied for NLO activity. Owing to the combination of chemical tunability and choice of synthetic strategies, organic molecules in particular have received much attention.

The purpose of the present research is the design of novel nonlinear optical (NLO) materials, capable of exhibiting enhanced Two-Photon Absorption (TPA) behavior. These materials have potential applications in biological imaging, microfabrication, sensing, photodynamic cancer therapy, optical limiting and ultrafast switching. Currently, only a limited number of 2PA fluorophores, specifically tailored for direct labeling of biomolecules for Two Photon induced fluorescence imaging studies, hence organic fluorescent probes with high Two Photon Absorption are highly desirable.

The objective of this work is to understand how the chemical structures of molecules relate to their electronic and optical properties, and use this understanding to design and synthesize novel organic arene compounds for two photon absorption which can be useful for bio-imaging applications. The requirements of molecules for these applications is high Two Photon Absorption cross sections, High fluorescence quantum yields, large transition dipole moments from ground to first excited state and from first excited to the higher excited state with low energy gaps.

This thesis entitled “Design and synthesis of organic arene compounds for Two Photon Absorption” is divided into four chapters.

CHAPTER 1

Chapter 1 provides an introduction of nonlinear optics, their origin, applications and various types of nonlinear optical effects. A special emphasis is given to the third order nonlinear optical property Two Photon Absorption (TPA) and their applications are discussed. Theoretical methods to determine the Two Photon Absorption cross-section (δ) and experimental techniques to estimate the magnitude of TPA activity are presented. The structure property relationships that can enhance the Two Photon absorption were described.

CHAPTER 2

In view of the importance of heterocycle-based chromophores and the interest in the development of TPA materials, in this chapter 2, five novel dipolar (D- π -A) molecules (**TA1-TA5**) based on the 1, 3, 5-triazine core as acceptor, including substituted anthracene as donor with a ethylenic bridge(C=C) as a spacer are synthesized. Linear and nonlinear optical property evaluations are presented. Experimental one photon absorption results have been compared with theoretical observations and fluorescence, electrochemical studies are carried out. Theoretical studies on TPA cross-sections were carried out based on the SACCI method. These molecules are with low TPA cross-sections and with negligible quantum yields due to the excitation in the molecule transfers to ICT state and subsequently to TICT state, which might be finally relaxing to the triplet state via cross-transfer process, this result in the weak PL emission. As high quantum yields are the prerequisite for bio-imaging applications these compounds may be useful as optical limiters and aimed for the synthesis of compounds with high quantum yields in the next chapters.

CHAPTER 3

Chapter 3 deals with the synthesis of bis (carbazole fluorene ethynyl) arene compounds C1–C5. Their electrochemical and photophysical properties are evaluated and compared with the theoretically calculated data. All compounds are

having high fluorescence quantum yields. All the compounds are quite thermally stable (355-490 °C) in the incident laser environment. Two Photon Absorption cross-section values are calculated theoretically and they showed large TPA cross-section values in the range of 728-5882 GM in the order of **C3** > **C1** > **C5** > **C4** > **C2**. Compound C3 with fluorene as a central bridge having high TPA value and compound C2 with anthracene as a bridge having low TPA value of 728 GM it may be due to lower transition dipole moments from the first excited state to the lowest allowed TPA state. As these compounds are with high fluorescence quantum yields and large theoretically predicted TPA cross-sections these compounds can be used as promising candidates for TPA with an application in bio-imaging.

CHAPTER 4

Chapter 4 explains about synthesis, photo physical and electrochemical properties of fluorenyl ethynyl pyrene derivatives (**P1-P5**) with different donor or acceptor substituents as a new series of pyrene based TPA chromophores. Their linear and nonlinear optical properties were investigated theoretically. The photophysical and electrochemical and theoretical data revealed that the energy gap decreases with increasing number of branches from **P1-P3**, i.e from mono to di to tetra substituted compounds. **P3-P5** the difference in energy gap is similar. All the molecules **P1-P5** showed high quantum yields of fluorescence. One photon and two photon absorption properties of these five newly synthesized compounds are theoretically analyzed by using SACCI method. The maximal one-photon absorption intensities for these compounds appear in the first excited state. It reveals that these are HOMO-1 to LUMO transitions. With the increase in the number of branches, the transition energies show red shift with increase in the intensities. From **P1** (180 GM) to **P2** (585 GM), the δ increased by 3-times and is increased by 4-times in **P3** (705 GM) and 7 and 8-times in **P4** (1113 GM) and **P5** (1408 GM). It indicates that the increase in size of the molecule with increased conjugation enhances TPA activity. Strong acceptor group like $-\text{NO}_2$ can enhance the transition dipole moment and decrease the transition energy which in turn enhances the magnitude of TPA cross-section. Compounds with acceptor substitution have large TPA cross-section than compounds with donor group substitution. This shed light into the significance of the pyrene derivatives as promising fluorescent probes with high TPA cross-sections which can be useful for bio-imaging application due to high fluorescence quantum yields.