

*"tvam hi praanaah shariire
baahute tumi maā shakti,
hridaye tumi maā bhakti"*

—Bankim Chandra Chatterjee

Dedicated to "Ma & Baba"

DECLARATION

I, Amrita Saha, hereby declare that the thesis entitled “Design, Synthesis and Characterization of Substituted Chalcone Based Compounds” has not been submitted either in whole or in part previously to any other institution for the award of any degree or qualification and does not contain any previously published material or written by another person, except where due reference is made in the text.

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INTEGRATED PRE PH.D. COURSE WORK EXAMINATION, 2012

MARK SHEET

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Preface

The fascinating field of nonlinear optics (NLO) has literally opened up a technological revolution. The application of NLO materials includes fiber optics, image applications using photorefractive crystals, frequency multipliers and mixers, parametric oscillators and optical switches etc. This wide range of application has intrigued extensive research work in the recent years. The organic NLO materials have higher nonlinear response compared to inorganic crystals. In the present work, chalcone based organic compounds were chosen because of their appealing properties like they (i) have high resistant to optical damage, (ii) have high mechanical hardness, (iii) can be synthesized through green chemistry in good yields (iv) exhibits good thermal and chemical stability. The core objective is to design chalcone based NLO chromophore, characterize their structural properties and finally, anextensive study on their linear and nonlinear optical properties.

This thesis consists of eight chapters.

Chapter 1 gives a brief overview of thenonlinear optical phenomenon, the basic difference between linear and nonlinear optics, and criterion for NLO compounds are discussed in this chapter. A discussion on NLO materials built from organic, semi-organic and inorganic materials and their applications are also included.

Chapter 2 presents the review of previous research work carried out on various organic NLO chromophores and their efficiency to produce anonlinear response. The review is mainly focused on chalcone derivatives with NLO property.

Chapter 3 deals briefly with the various analytical instrumentation techniques which are used throughout the research work to characterize the structure and properties of the compounds.

Chapter 4 points toward the synthesis of chalcones using Claisen Schmidt reaction and the synthesis of corresponding hydrazone derivatives. The ^1H NMR and ^{13}C NMR spectral analysis were carried out to identify the molecular structure. The linear optical properties were determined using UV-Visible and Fluorescence spectroscopy. The open aperture z-scan studies are also presented and the structure-property relationship was set up.

Chapter 5 contains the characterization, linear and nonlinear properties of chalcones with the heterocyclic core in the skeleton. A detailed study on their absorption and emission property was

done. Comparative study of the synthesized compounds and the nonlinear absorption coefficient is also presented to recognize suitable structures for nonlinear absorption.

Chapter 6 is devoted to the synthesis of various chalcones with naphthalene and anthracene core. Single crystals of chalcone having anthracene core were also grown. A qualitative relationship between the structure and NLA coefficient was also studied. Up-conversion photoluminescence studies were carried out on the naphthalene core chalcones in the near IR region.

Chapter 7 is meant for the synthesis of new branched chalcones, where asymmetrically substituted three chromophore units is linked through a common amino group. Up-conversion photoluminescence studies in the near IR region were also carried out.

Chapter 8 summarizes the results of the present investigation and goes a step further by listing out the possible future work on these compounds.

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LIST OF SYMBOLS AND ABBREVIATIONS

ϵ_0	Permittivity of free space
χ^1	Linear susceptibility
χ^2, χ^3	Nonlinear susceptibilities
$^{13}\text{C NMR}$	Carbon nuclear magnetic resonance
$^1\text{H NMR}$	Proton nuclear magnetic resonance
1PA	One-photon
2PA	Two-photon Absorption
3PA	Three photon Absorption
Å	Angstrom
A-D-A	Acceptor-donor-acceptor
Aq.	Aqueous
CDCl_3	Deuteriated chloroform
cm	centimeter
d	Doublet
D-A-D	Donor-acceptor-donor
DCM	Dichloromethane
dd	Double of doublet
DMF	Dimethylformamide
D- π -A- π -D	Donor-acceptor-donor
E	Electric Field Vector
EDF	Excitation Dependent Emission
Eg	bandgap
E _p	phonon characteristic energy
equiv.	Equivalents
esu	Electrostatic system of units
Et	Ethyl
ETOAc	Ethyl Acetate
fs	Femto Second
FT-IR	Fourier Transform Infrared

g	Gram (weight)
h	Hours
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
ICT	Intramolecular charge transfer
IR	Infrared
Is	Saturation Intensity
ISC	Intersystem charge transfer
ITO	Indium tin oxide
<i>J</i>	Coupling constant
KBr	Potassium Bromide
LIDAR	Light Detection And Ranging
LUMO	Lowest Unoccupied Molecular Orbital
M	Moles per litre
m	Multiplet
M.P.	Melting Point
Me	Methyl
MeOH	Methanol
mg	Milligram
min.	Minutes
ml	Millilitre
Mol	Moles
NaOH	Sodium Hydroxide
Nd - YAG	Neodymium Yttrium Aluminium Garnet
N_e	number of π electrons
NH ₂ NH ₂	Hydrazine Hydrazide
NIR	Near Infrared
NLA	Nonlinear Absorption
NLO	Nonlinear Optics
nm	Number
No.	Nanometer

o	Ortho
p	Para
<i>P</i>	Polarization
POCl ₃	Phosphorous Oxychloride
ppm	Parts per million
q	Quartet
R _f	Retention factor
rt	Room temperature
s	Singlet
Sc	Conjugation Signature
SHG	Second Harmonic Generation
t	Triplet
TICT	Twisted intramolecular charge transfer
TLC	Thin Layer Chromatography
TMS	Tetramethyl Silane
TPA/2PA	Two photon Absorption
UV	Ultraviolet
UV/Vis	Ultraviolet/Visible
XRD	X-Ray Diffraction
λ _{abs}	Absorption maximum
λ _{em}	Emission maximum
μJ	micro Joule
ν	Frequency
λ	Wavelength

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