

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

OPTICAL PROPERTIES OF
ORGANIC NLO CHROMOPHORES
FOR TERAHERTZ APPLICATIONS

A Thesis Presented in Partial Fulfilment of the Requirements
for the Degree of

Doctor of Philosophy
in Physics

at

Massey University, Palmerston North,
New Zealand.

YASAR KUTUVANTAVIDA

2012

Abstract

This thesis was motivated by the potential of organic nonlinear optical (NLO) zwitterionic chromophores to be used as active components in THz emitters and detectors. This study presents the results from measurements of the electro-optic (EO) coefficient, photostability and the THz properties of organic NLO chromophores.

An EO coefficient of over 700 pm/V was measured for some EO polymers using the Teng-Man modulation ellipsometry technique at low frequencies. A roll off in the value of the EO coefficient was observed for frequencies over 10 kHz and converging to the theoretically estimated value of ~ 2 pm/V. The large over estimate of the EO coefficient at low frequencies using the Teng-Man method is attributed to contributions from the cavity resonance and interference effects.

The EO coefficient was also measured using a new method based on the electric field induced modulation of diffraction gratings. The measured EO coefficient using this technique is an order of magnitude lower than that measured using the Teng-Man method but it is an order of magnitude higher than the theoretically expected value. By investigating DC and AC measurements it was possible to deduce that the large apparent EO coefficient is due to the inverse piezoelectric effect and thin film interference. The large EO coefficient at low frequencies may also have a contribution from dipole clusters. The small EO coefficient at high frequency shows that the chromophores may not be particularly useful for THz applications. However, they have potential in low frequency applications such as modulators, and dense wavelength division multiplexing.

The current photodegradation models are shown to be inadequate and the photodegradation can be modeled by considering a distribution in the photodegradation quantum efficiencies. The addition of a singlet oxygen quencher has been found to enhance the photostability of some chromophores by up to 6 times. Structural modifications also affect the photostability. A correlation between the photostability

and bond length alternation (BLA) was found where there is a trade-off between the chromophores molecular NLO effect and photostability.

Calculations based on the THz dielectric properties showed that the EO polymers have a reasonable coherence length for THz generation using optical rectification. Low wavenumber Raman spectroscopy measurements made on recrystallised compounds exposed some theoretically predicted modes that were not been reported found experimentally. Low temperature and low energy Raman spectroscopy measurements made on some selected organic compounds showed a strong temperature dependence of the low energy vibrational modes. The temperature dependent red-shift and line broadening have been primarily attributed to thermal expansion and a distribution in the distance between monomers.

Acknowledgements

I would like to express my sincere gratitude to my day-to-day supervisor Dr Grant Williams at the School of Chemical and Physical Sciences, Victoria University of Wellington. His enthusiastic supervision, constant encouragement and useful discussions made this thesis possible. My sincere thanks to my Massey University supervisor Associate Professor Mark Waterland for his support and help ensuring my thesis was on track.

I gratefully acknowledge the support of Dr Sebastiampillai Raymond at Industrial Research Limited during this study. My sincere thanks to Dr Delower Bhuiyan and Dr Andrew Kay at Industrial Research Limited for their invaluable help, including the supply of organic compounds used in this study.

My sincere thanks to Professor Roger Lewis at University of Wollongong for the THz laboratory facility, Jessianta Anthony at University of Auckland for providing THz-TDS data of electro-optic polymers, Professor Pablo Etchegoin at Victoria University of Wellington for the Raman facility, and Dr Graeme Gainsford at Industrial Research Limited for the crystallography data.

I am indebted to those who helped me proof read this thesis, especially, Damian Carder, Adam Swanson, Robert Breukers, James Quilty and Jibu Stephen at Industrial Research Limited. My sincere thanks to the rest of the current and former Photonics team at Industrial Research Limited - Ayla Middleton, David Clarke, Mohamed Ashraf, Victoria Peddie, Christin Gaedtke, Stefaan Janssens and Tra My Do for their support during this thesis.

I would like to gratefully acknowledge the PhD scholarship by the Industrial Research Limited from the project “Photonic Imaging and Sensing Program” funded by the New Zealand Ministry of Research and Innovation. My sincere thanks to the MacDiarmid Institute for Advanced Materials and Nanotechnology for the funding to attend international conferences. My sincere thanks go as well to the staff of

the Institute of Fundamental Sciences, Massey University for the administrative support.

Finally, I wish to thank my family and friends for their support and encouragement throughout my stay in New Zealand.

Contents

1	Introduction	1
2	Basic Concepts	5
2.1	Nonlinear optics	5
2.2	Electro-optic effect	6
2.2.1	Linear electro-optic coefficient	8
2.2.2	Optical rectification and frequency mixing	9
2.3	Electro-optic materials	10
2.3.1	Electro-optic polymers	11
2.3.2	Electro-optic polymer systems	11
2.3.3	Glass transition temperature	14
2.4	Organic nonlinear optical chromophores	14
2.4.1	Microscopic NLO effect	15
2.4.2	Bond length alternation	17
2.5	Absorption	19
2.5.1	Linear absorption	19
2.5.2	Two-photon absorption	19
2.5.3	Kramers-Kronig relation	20
2.6	Aggregation	21
2.7	Solvatochromism	22
2.8	THz radiation	23
2.8.1	EO effect in THz technology	24
2.9	Interaction of photons with phonons	25
2.9.1	Infrared absorption	25
2.9.2	Raman scattering	27

3	Instruments and Techniques	29
3.1	Spin coater	29
3.2	UV-Vis-NIR spectroscopy	29
3.2.1	Lambda 1050 UV/Vis/NIR spectrophotometer	30
3.2.2	Varian Cary 50	31
3.2.3	Fibre optic spectrometer	31
3.3	Measurement of thickness and refractive index	31
3.3.1	Prism coupler	31
3.3.2	DekTak profilometer	33
3.3.3	Interferometry technique	33
3.4	Poling apparatus	35
3.5	Teng-Man apparatus	35
3.6	DSC-TGA	37
3.7	Infrared spectroscopy	38
3.7.1	Nicolet TM FTIR spectrometer	39
3.8	THz time domain spectroscopy	39
3.9	Raman spectroscopy	40
3.10	Lasers	41
4	Fabrication and Processing of EO Polymers	43
4.1	Preparation of ultra-clean substrates	43
4.2	Polymer thin film fabrication	45
4.2.1	Host polymer	45
4.2.2	Preparation of solution	46
4.2.3	Solution casting for thick films	48
4.2.4	Spin coating for thin films	49
4.3	Measurement of thickness and refractive index	51
4.3.1	Refractive index dispersion	52
4.4	Chromophore concentration in films	53
4.5	Poling to induce electro-optic effect	54
4.5.1	Poling techniques	56
4.5.2	Contact electrode poling	58
4.5.3	Optimising poling conditions	58
4.5.4	Dielectric breakdown	60

5	Measurement of r_{33} Using Modulation Ellipsometry	63
5.1	Teng-Man apparatus for the measurement of r_{33}	63
5.1.1	Teng-Man apparatus optimisation	67
5.2	Temporal stability of induced EO effect	69
5.2.1	Relaxation of the induced r_{33} of a PYR-3 system	70
5.2.2	Analysis of the relaxation process	72
5.3	Structural alterations for improved molecular nonlinearity	74
5.3.1	Effects of donor strength	75
5.3.2	Effects of conjugation length	76
5.3.3	Effects of ring-locking	77
5.3.4	Effects of bulky group substitution	78
5.4	Effects of structural alternations at the macroscopic level	79
5.4.1	Bulky substitution in PYR-3	80
5.4.2	Bulky substitution in IND-5	81
5.4.2.1	Hydrogenated bulky group	82
5.4.2.2	Fluorinated bulky group	83
5.4.2.3	Mixed bulky groups	83
5.4.3	Ring-locking of QUN-7 and IND-7	84
5.5	Theoretical calculation of r_{33}	84
5.5.1	Translating microscopic quantities to r_{33}	86
5.5.2	Calculation of r_{33} for a PYR-3/APC system	87
5.5.3	Mismatch between experiment and calculation	88
5.6	Analysis of the mismatch between experimental and calculated r_{33}	89
5.6.1	Frequency response of r_{33}	89
5.6.2	Contribution from acoustic and optical phonons	91
5.6.3	Contribution from piezoelectric effect	93
5.6.4	Effects of acoustic velocity in the host polymer	95
5.6.5	Contribution from the formation of chromophore clusters	95
5.7	Conclusions	96
6	Measurement of r_{33} Using Diffraction Method	99
6.1	Diffraction gratings	100
6.2	Diffraction efficiency	101
6.2.1	Small Q: “thin” grating	102
6.2.2	Large Q: “thick” grating	104

6.2.3	Sinusoidal grating with small modulation	105
6.3	Periodic gratings on poled polymers	106
6.3.1	Grating inscription using interferometry	106
6.3.2	Modulation of refractive index	108
6.3.3	Skin depth	111
6.3.4	Estimation of diffraction efficiency	112
6.4	Estimation of r_{33} from diffraction efficiency	114
6.4.1	Condition of validity	115
6.5	Experiment using DC modulating field	116
6.5.1	Estimation of EO coefficient using DC field	117
6.6	Experiment using AC modulating field	119
6.6.1	Estimation of EO coefficient using AC field	120
6.7	Analysis of diffraction technique	121
6.7.1	Effects of modulating frequency	121
6.7.2	Change in diffraction efficiency with lock-in phase settings	122
6.7.2.1	Inverse piezoelectric effect	123
6.7.2.2	Interference effect	124
6.8	Conclusions	126
7	Photostability of NLO Chromophores	129
7.1	Light induced degradation of NLO chromophores	130
7.1.1	Photodegradation mechanism	132
7.1.2	Photochemistry of photo-oxidation	134
7.1.3	Basic photodegradation model	135
7.2	Experimental setup	136
7.3	Effects of light intensity and oxygen partial pressure	138
7.4	Modified model of photodegradation	141
7.4.1	Model based on multiple photodegradation pathways	143
7.5	Effects of film thickness	148
7.6	Effects of chromophore concentration	149
7.7	Strategies to achieve high photostability	151
7.7.1	Bulky substitution on PYR-3	152
7.7.2	Partial ring-locking on IND-7 and QUN-7	153
7.7.3	Addition of singlet oxygen quencher	155
7.8	Influence of bond length alternation on photostability	157

7.8.1	Effects of ring-locking on the BLA of IND-7	158
7.8.2	Effects of ring-locking on the BLA of QUN-7	159
7.8.3	Trade-off between hyperpolarisability and photostability . . .	161
7.9	Conclusions	162
8	Material Characterisation at THz Frequencies	165
8.1	THz generation and detection using EO polymers	166
8.1.1	Phase matching	167
8.1.2	Phase matching for THz generation	167
8.1.3	Phase matching for THz detection	169
8.2	Properties of polymers in THz region	169
8.2.1	THz time domain spectroscopy	170
8.2.2	Absorption in the THz region	172
8.2.3	THz refractive index	172
8.2.4	Coherence length for THz generation using PYR-3/APC . . .	173
8.2.5	Raman and IR on APC film	174
8.3	Low energy vibrational spectra of organic crystals	175
8.3.1	Experimental details	175
8.3.2	Spectrum of benzoic acid derivatives	176
8.3.3	Spectrum of aspirin	177
8.3.4	Spectrum of nitro derivatives of toluene	179
8.4	Temperature dependence of low energy vibrational modes	180
8.4.1	Temperature dependence in salicylic acid	181
8.4.2	Temperature dependent Raman in 2,4-DNT	182
8.5	Conclusions	182
9	Summary	185
	Bibliography	189
	List of Publications	205

List of Figures

2.1	Polarisation as a function of electric field in a linear and a nonlinear medium.	6
2.2	Refractive index as a function of applied electric field in (a) a linear EO medium and (b) a quadratic EO medium.	8
2.3	An example scheme of a Pockels cell showing the change in polarisation of a wave through an EO material in the presence of an external electric field. Arrows indicate the polarisation direction.	8
2.4	Electro-optic polymer systems: (a) Host-guest, (b) Side-chain, (c) Main-chain and (d) Cross-linked polymer systems.	12
2.5	(left) Schematic of a push-pull molecule (chromophore) with an electron donor (D) and an electron acceptor (A) connected by a conjugated π -bridge. (right) An example structure of an NLO chromophore.	15
2.6	Definition of regions of BLA correspond to the degree of mixing the neutral (N) and charge-separated (CS) resonance structures to the ground state. The nature of the conjugated π -bridge changes from neutral polyene-like (1) to polar cyanine-like (3) to very polar charge separated polyene-like (5).	18
2.7	Energy level diagram showing excitation of chromophores; ISC represents inter system crossing.	20
2.8	Schematics of H- and J- aggregated chromophores.	22
2.9	Energy level diagram showing the transitions involved in IR absorption and Raman scattering.	26
3.1	A WS-400E-6NPP-LITE spin processor by Laurell Technologies Corporation. (a) Front view and (b) Rear-view of the instrument. . . .	30

3.2	Schematic of the measurement of film thickness using prism coupler. Left side is the schematic of geometry of the apparatus and shown right is the example for the coupling modes.	32
3.3	Schematic of the transmission through a thin film on a glass substrate.	34
3.4	Photograph of the poling apparatus being used in our laboratory; shown inset is the film with electric field applied across the block electrode and ITO layer over the glass.	35
3.5	Schematic of the Teng-Man modulation ellipsometry apparatus. . .	36
3.6	Teng-Man experimental set-up used in our laboratory at IRL. . . .	37
3.7	Schematic of a THz-TDS system using optical rectification technique for THz generation and electro-optic sampling method for THz detection.	40
4.1	Structures of the organic NLO chromophores used in the experiments in this thesis.	47
4.2	Effects of spin speed and viscosity of the solution on determining the thickness of spin-processed films of APC in 1,1,2-TCE.	50
4.3	Interferometry method to estimate film thickness.	52
4.4	(a) Absorption coefficient of a $2\mu\text{m}$ polymer film containing 5 wt% PYR-3 in APC. (b) Dispersion of change in refractive index Δn with wavelength calculated using the Kramers-Kronig transform from the absorption coefficient. (c) Refractive index dispersion of the host polymer APC estimated using first order Sellmeier equation on the measured values at 633, 1300 and 1550 nm, and the total effective refractive index of the polymer film.	53
4.5	Schematic of chromophore orientation in the polymer films before, during and after poling.	56
4.6	Schematic of an <i>in situ</i> contact electrode poling system.	59
4.7	Current flow across the film and temperature as a function of time during poling.	61
5.1	Output laser intensity (I_O) and modulated intensity (I_M) as a function of SBC retardation.	65
5.2	Modulated intensity as a function of modulating voltage on a poled film containing 5 wt.% PYR-3B in APC.	69

5.3	Optical bias curve and modulated intensity obtained as a function of compensator position correspond to the phase retardation induced by the compensator.	70
5.4	Analysis of the Teng-Man ellipsometry data from a poled polymer.	71
5.5	Relaxation of r_{33} of a poled 5 wt.% PYR-3/APC film.	71
5.6	Structures of the PYR-3, QUN-3 and IND-3 chromophores.	76
5.7	Structure of PYR-3 chromophore and its bulky group derivative PYR-3B.	80
5.8	(a) Plot of the molar extinction coefficient of PYR-3B in solutions. (b) Plot of the optical absorption coefficient of PYR-3B in films.	81
5.9	Plot of the measured r_{33} of a poled 8 wt.% PYR-3B/APC film against time and a bi-exponential fit to the data.	82
5.10	Structures of the IND-5 chromophore and its bulky group derivatives.	82
5.11	Structures of the QUN-7 and IND-7 chromophores and their ring-locked structures QUN-7R and IND-7R.	84
5.12	Dependence of the EO coefficient on the modulation frequency measured at $\lambda = 1314$ nm for a $4 \mu\text{m}$ film made of 5 wt% PYR-3/APC.	90
5.13	Small angle XRD data of a 5 wt.% PYR-3/APC film on (a) glass and (b) ITO coated glass substrate.	93
6.1	The geometry of a thick periodic grating; I_{inc} is the incident wave, \mathbf{K} is the grating vector, Λ is the grating period, I_0 is the zeroth order beam, I_1 is the first order diffracted beam, d is the thickness of grating and θ is the angle corresponding to each beams.	100
6.2	Experimental set up used to inscribe Bragg grating on polymer thin films using two coherent interfering beams.	107
6.3	(a) Absorption coefficient of a $\sim 6 \mu\text{m}$ PYR-3/APC film at 488 nm during the grating inscription. (b) The first order diffraction efficiency measured during the the grating inscription.	108
6.4	(a) $\Delta\alpha$ as a function of wavelength and (b) the refractive index dispersion estimated for a 5 wt.% PYR-3/APC film using Kramers-Kronig approximation on $\Delta\alpha$	109
6.5	Change in $\Delta\alpha$ with incident energy when the grating inscribed on a 5 wt.% PYR-3/APC film using two-beam interference.	110

6.6	Skin depth, δ_p , estimated for a 5 wt.% PYR-3/APC film in the visible spectrum.	112
6.7	(a) Q factor of a 5 wt.% PYR-3/APC thin film with thickness $6.08 \mu\text{m}$ and grating period $2.85 \mu\text{m}$. (b) Diffraction efficiency estimated for for small modulation.	113
6.8	Schematic of the experimental set up to estimate EO coefficient using diffraction technique with DC modulating field.	116
6.9	(a) Diffraction efficiency for the first order diffracted beam, η as a function of applied DC field for a $6.06 \mu\text{m}$ film of 5 wt% PYR-3/APC. (b) $\Delta\eta(E)/\eta_0$ vs. E for the same data.	117
6.10	(a) Diffraction efficiency as a function of applied DC field for a $6.1 \mu\text{m}$ film of 5 wt.% PYR-3/APC with 170 pm/V when measured using Teng-Man modulation ellipsometry. (b) $\Delta\eta(E)/\eta_0$ vs. electric field for the same data.	118
6.11	Schematic of the experimental set up to estimate r_{33} using diffraction technique with an AC modulating field with a modulating frequency of 1 kHz.	119
6.12	(a) Diffraction efficiency as a function of applied field for a poled $\sim 6 \mu\text{m}$ thick 5 wt.% PYR-3/APC film. (b) $\Delta\eta/\eta$ as a function of applied AC modulating field.	120
6.13	Plot of the effect of AC modulation on the zeroth order beam. This kind of strong modulation on zeroth order was not observed during the measurements using DC field.	121
6.14	(a) Diffraction efficiency as a function of modulating frequency for a $6.1 \mu\text{m}$ PYR-3/APC film for a 760 nm beam. The modulating field was $0.82 \text{ V}/\mu\text{m}$. (b) A similar effect observed in the r_{33} measurement using Teng-Man modulation ellipsometry.	122
6.15	(a) Change in the effective transmittance simulated for a $6.0 \mu\text{m}$ and a $6.1 \mu\text{m}$ PYR-3/APC film due to the thin film interference effect; vertical dashed line shows the wavelength of interest, 760 nm . (b) Change in effective transmittance at 760 nm for a PYR-3/APC film for a small variation in thickness from $6.1 \mu\text{m}$. (c) The same as in (b) for $6.0 \mu\text{m}$	124

7.1	Absorption spectra during progressive bleaching of of IND-7 solution in CHCl_3 by exposure to UV radiation at 365 nm.	131
7.2	Absorption spectrum of IND-7 solution in CHCl_3 at different concentrations.	131
7.3	(a) Absorbance of a 3% IND-7/APC film while progressive bleaching using a 655 nm beam, arrow indicates increasing bleaching time (b) Normalised absorbance.	131
7.4	Energy level diagram for a chromophore molecule, where S_0 is the ground state (with lifetime τ_g), S_1 the singlet excited state (with lifetime τ_1), T_1 the triplet excited state (with lifetime τ_T) of the chromophore molecule, ISC is the inter system crossing.	133
7.5	(a) The trans and (b) the cis form of a PYR-3 chromophore (c), (d) and (e) the expected products formed after photo-oxidation process. .	134
7.6	Photodegradation experimental set up.	136
7.7	Picture of a photodegradation experimental set using a 532 nm Nd:YVO ₄ laser beam.	137
7.8	Transmittance as a function of time while photodegrading a 2.4 μm , 5 wt% PYR-3/APC film with a 1 mW/mm ² 532 nm laser beam. . . .	137
7.9	$F(\beta)$ against β plot for the photodegradation data obtained by optically degrading a 5 wt.% IND-7/APC film at different light intensities.	139
7.10	Plot of photodegradation quantum efficiency as a function of light intensity.	140
7.11	Plot of the transmittance $T(t)$ against time during illumination at 532 nm for (a) a 2.4 μm 5% PYR-3/APC film with an incident intensity 1 mW/mm ² , and (b) a 2.05 μm 15% PYR-3/APC film with an incident intensity 0.47 mW/mm ²	143
7.12	Plot of the transmittance against $\beta/2.67 \times 10^{19}$ (solid curves) for (a) a 2.4 μm thick 5% PYR-3/APC films and (b) a 2.05 μm thick 15% PYR-3/APC film.	145
7.13	Plot of the photostability enhancement factor, η , against light intensity at 532 nm.	148
7.14	Transmittance data when photodegrading 5 wt% PYR-3/APC films of 2.4 μm , 3.84 μm and 7.5 μm using 532 nm and intensity 50 mW/mm ² .	

7.15	Plot of $F(\beta)$ against β plot for three concentrations of IND-7 chromophores in APC with $2.1\mu\text{m}$ thickness when photodegradating with 655 nm laser and intensity 15.7 mW/mm^2 . Inset is the plot of $\beta_{1/e}$ against chromophore loading by wt% in APC.	150
7.16	Absorption spectra of 1%, 3%, 5% and 8% IND-7 film in APC.	150
7.17	Structures and absorption spectra of PYR-3 and PYR-3B in the films made of similar chromophore concentration and thicknesses in APC. Dashed line indicates the wavelength used to degrade the chromophores.	152
7.18	Plot of the transmittance at 532 nm against incident photon flux for a 8 wt.% PYR-3B/APC film with incident laser intensities of 1 mW/mm^2 and 5 mW/mm^2	153
7.19	Structures and absorption spectra of IND-7 and IND-7R in the films made of mixing similar chromophore concentrations, 5 %, and thicknesses, $2.2\mu\text{m}$, in APC.	154
7.20	(a) Plot of the transmittance at 655 nm against time for a $2.2\mu\text{m}$ thick 5 wt.% IND-7/APC film (green solid curve) and a $2.1\mu\text{m}$ thick 5 wt.% IND-7R/APC film (red dashed curve) for incident laser intensity of 35 mW/mm^2 (b) Plot of $F(\beta)$ against β	154
7.21	Structures and absorption spectra of QUN-7 and QUN-7R in the films made of mixing similar chromophore concentrations in APC.	155
7.22	(a) Plot of the Plot of $F(\beta)$ against β at 760 nm for a $5.1\mu\text{m}$ thick 5 wt.% QUN-7/APC film (black solid curve) and a $5.06\mu\text{m}$ thick 5 wt.% QUN-7R/APC film (red solid curve) for incident laser intensity of 10 mW/mm^2 (b) Plot of transmittance against time.	155
7.23	Structure of trans- and cis- isomers of β -carotene.	156
7.24	Energy level diagram showing excitation of the PYR-3 chromophore (left) to the S_1 state, inter-system crossing (ISC) to the T_1 state, energy transfer to β -carotene (middle) that leaves PYR-3 in the ground S_0 state and β -carotene in the triplet excited state, and finally multiphonon decay from the β -carotene excited triplet state to the singlet ground state.	157
7.25	Absorption coefficient and photodegradation experimental data for films containing 5% PYR-3/APC and 0%, 1%, 5% and 10% β -carotene.	158

7.26	Absorption spectra of (a) IND-7 and (b) IND-7R in solutions of different $E_T(30)$ values.	159
7.27	Normalised absorption spectra of (a) QUN-7 and (b) QUN-7R in solutions of different $E_T(30)$ values.	160
7.28	Schematic of the relation between first hyperpolarisability, β_0 and photostability, B	161
8.1	Scheme of THz-TDS in transmission mode.	170
8.2	Time domain THz data collected for a $320\ \mu\text{m}$ 5 wt.% PYR-3/APC film with air as reference. Time delays are relative to each another.	171
8.3	Absorption spectrum of a 5 wt% PYR-3/APC film between 0.2 and 1.1 THz estimated from THz-TDS data.	172
8.4	Refractive index of a 5 wt% PYR-3/APC for the range 0.2 to 1.1 THz.	173
8.5	Low wavenumber Raman spectra of APC.	174
8.6	Structures of the compounds considered for this study; Benzoic acid (a) monomer and (b) dimer, (c) 2-hydroxy benzoic acid, and (d) 3-hydroxy benzoic acid.	176
8.7	Raman spectra of benzoic acid, 2-hydroxy benzoic acid, and 3-hydroxy benzoic acid for energies corresponding to the THz region.	177
8.8	Infrared absorption spectra of benzoic acid, 2-hydroxy benzoic acid, and 3-hydroxy benzoic acid for the THz region. Also shown is the spectra of PB100XF (dash-dotted curve).	179
8.9	Low wavenumber Raman spectrum of Aspirin and Salicylic acid. Structure the monomer units of both compounds are shown inset.	180
8.10	Low wavenumber Raman on 4-nitro toluene (4-NT) and 2,4-dinitro toluene (2,4-DNT) in the THz frequency range.	180
8.11	Temperature dependent low wavenumber Raman spectrum of Salicylic Acid.	181
8.12	Temperature dependent low wavenumber Raman spectrum of 2,4-DNT.	182

List of Tables

4.1	Physical properties of Bayer APEC 9389 Amorphous Polycarbonate (APC).	46
5.1	Effect of varying donor groups on the molecular NLO response of chromophores. β_{zzz} was measured at 1314 nm.	76
5.2	Effect of conjugation length on the molecular NLO response of chromophores. β_{zzz} was measured at 1314 nm.	77
5.3	Effect of partial ring-locking at the conjugated π -bridge on the molecular NLO response IND-7 chromophore, β_{zzz} was measured at 1314 nm.	77
5.4	Effect of bulky substitution on the molecular NLO response of PYR-3 chromophore, β_{zzz} was measured at 1314 nm.	78
5.5	Effect of bulky substitution on the macroscopic EO response of IND-5 chromophore.	83
5.6	Effects of ring-locking on the EO coefficient of IND-7 and QUN-7 chromophores.	84
5.7	Physical quantities used in the calculation of r_{33} in electrostatic and SI units.	87
5.8	Physical properties of the PYR-3 chromophore used in the calculation of r_{33}	87
6.1	Diffraction efficiency for the first order beam of a 6.1 μm , 5 wt % PYR-3/APC film with grating period, $\Lambda = 2.85 \mu\text{m}$. n_{av} is the average refractive index of the film.	113
6.2	Measured and estimated values of diffraction efficiencies at 16 V/ μm for a 5 wt.% PYR-3/APC film.	118

7.1	Chromophore number densities correspond to the chromophore loading in APC.	138
7.2	Table of parameters used to model the transmittance data in Fig. 7.11 and Fig. 7.12 for 2.4 μm thick 5% PYR-3/APC films at 532 nm. . . .	146
7.3	Table of parameters used to model the transmittance data in Fig. 7.11 and Fig. 7.12 for 2.05 μm thick 15% PYR-3/APC films at 532 nm. . .	147
7.4	Structural and electronic properties of IND-7 and IND-7R. Absorption maxima, λ_{max} , in films and in selected solvents having different $E_T(30)$ values are summarized.	159
7.5	Structural and electronic properties of QUN-7 and QUN7R. Absorption maxima, λ_{max} , in films and in selected solvents having different $E_T(30)$ values.	160
7.6	Relationship between the magnitude of BLA values and corresponding photostability (B) of IND-7 & IND-7R ($\sim 2 \mu\text{m}$ thick, light intensity 35 mW/mm ²), and QUN-7 & QUN-7R ($\sim 5 \mu\text{m}$ thick, light intensity 10 mW/mm ²) for similar chromophore loading.	161
8.1	Summary of the experimental and calculated vibrational modes of benzoic acid, 2-hydroxy benzoic acid and 3-hydroxy benzoic acid. . .	178