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Optical Properties of Organic NLO Chromophores for Terahertz Applications

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

Doctor of Philosophy
in Physics

at

Massey University, Palmerston North,

New Zealand.

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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 $\sim 2$ 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.
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 go as well to the staff of the MacDiarmid Institute for Advanced Materials and Nanotechnology for the funding to attend international conferences.

Acknowledgements
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.
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