**Synthesis and Stability Studies of Z- β -(1-Substituted-4-Pyridinium)- α -
Cyano-4-Styryldicyanomethanide Nonlinear Optical Chromophores**

By Cara A. M. Weir

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the requirements

for the degree of

Masters of Science

Carleton University
Department of Chemistry
1125 Colonel By Drive
Ottawa, Ontario, Canada

January 2003

©2003, Cara A. M. Weir

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-79824-0

Canada

The undersigned recommend to the
Faculty of Graduate Studies and Research
acceptance of the thesis

**Synthesis and Stability Studies of Z- β -(1-Substituted-4-Pyridinium)- α -Cyano-4-
Styryldicyanomethanide Nonlinear Optical Chromophores**

Submitted by
Cara A. M. Weir

in partial fulfillment of the requirements for the
degree of Masters of Science

Dr. Z. Y. Wang, Thesis Supervisor

Dr. G. W. Buchanan, Chair, Department of Chemistry

Carleton University

January 2003.

Abstract

Z- β -(1-substituted-4-pyridinium)- α -cyano-4-styryldicyanomethanide NLO chromophores have shown potential for use in electro-optic (EO) materials but have long been dismissed due to the low yields (15 to 30 %) and long reaction times (5 to 14 days) associated with synthesis. The objectives were to make the chromophores available by a high-yield cost-effective pathway and to assess the stability of the chromophores to processing and device operating conditions.

By varying the ratio of reactants and with the use of an amine base, the synthesis was improved up to 97 % with a reaction time of 14 hours. The chromophores in solution decomposed when exposed to oxygen, and were sensitive to white light and high temperatures. In doped polymer films using poly(ether sulfone) the chromophores were stable to oxygen and high temperatures, but were light-sensitive indicating that the materials would require protection from white light if used in EO devices. The mechanism of decomposition was established providing the information required to design a more stable chromophore.

Acknowledgements

I would like to thank my supervisor Dr. Wayne Wang for all of the guidance and support he has given me over the years. I would also like to thank Dr. Jane Gao and Dr. Ted Edwards, you were both a tremendous help throughout the duration of my project. I would like to acknowledge the other members of the modulators team, Andrew Beaudin, David Song and Tayebbeh Hadizad. It was a pleasure collaborating with you, thank you for all of the help you gave me along this project, I could not have done it without you. I would like to thank all of my other labmates, especially Maria Birau, Connie Kuang, and Sean MacKinnon. Thank you all for your friendship over the years.

Thank you Keith Bourque for running all the NMR spectra for this work, Clem at U of O for running the mass spectra, and Lisa Men for the EO measurements.

I would like to thank NSERC and Nortel Networks for the financial support I received over the past two years. I would also like to thank sincerely Michal Tencer (Nortel) and Diane Berezowski for all of your help in this area.

Thank you to my family, especially Mom and Gerry, Dad and Ann, and my sister Kyla. You have all been incredibly supportive over the years, I could not have made it through this project without your help and encouragement.

Finally I would like to thank my best friends. You have all been there when I needed you, I consider myself incredibly lucky to have friends like you. Thank you Stephanie Doyle, Melanie Berljawsky, Mireille Chaput, Christine Pratley Moore, Cari Segat, Lori Gordon and Christy Nichol.

Last but not least, thank you Adam for being so patient, understanding and supportive over the last few months.

Table of Contents

Chapter 1: Introduction to Nonlinear Optical Materials.....	pg. 1
1.1 Nonlinear Optical Materials and Applications.....	pg. 1
1.2 Organic Nonlinear Optical Materials.....	pg. 1
1.3 Rationale and Objectives.....	pg. 7
Chapter 2: Study of the Factors Affecting Chromophore Synthesis.....	pg. 9
2.1 Choice of Solvent.....	pg. 9
2.2 Using an Amine Base.....	pg. 10
2.3 Ratio of Reactants.....	pg. 12
2.4 Reaction Mechanism.....	pg. 13
Chapter 3: Chromophore Decomposition Studies.....	pg. 22
3.1 Solution Decomposition.....	pg. 22
3.2 Mechanism of Decomposition.....	pg. 26
3.3 Solid State Decomposition.....	pg. 29
Chapter 4: Experimental.....	pg. 35
4.1 Materials.....	pg. 35
4.2 Instruments and Characterization.....	pg. 35
4.3 Experimental Procedures.....	pg. 36
4.3.1 Synthesis Procedures.....	pg. 36
4.3.2 Chromophore Decomposition in Solution.....	pg. 42
4.3.3 Solid State Chromophore Decomposition.....	pg. 44
Conclusions.....	pg. 47

Contribution to Knowledge.....	pg. 48
Appendices.....	pg. 49
Appendix A. Spectra of Synthesized Reactants and Products.....	pg. 49
Appendix B. Spectra from Solution Decomposition Studies.....	pg. 65
Appendix C. Spectra from Solid-State Decomposition Studies.....	pg. 70

List of Tables

Table 2.1 Preliminary Reactions Investigating Choice of Base..... pg. 11

Table 2.2 Molar Equivalents of Reactants Used and the Isolated Yields for **2a**... pg. 12

List of Figures

Figure 1.1 Charge-transfer zwitterionic chromophore DEMI.....	pg. 3
Figure 1.2 Arrangement of dipolar chromophores: a) electric-field induced noncentrosymmetry; b) preferred dipole-dipole orientation of zwitterionic chromophores.....	pg. 3
Figure 1.3 Schematic of electric-field poling set-up.....	pg. 3
Figure 1.4 Z- β -(1-R-pyridinium)- α -cyano-4-styryldicyanomethanide.....	pg. 7
Figure 2.1 UV-vis spectrum of 2a in DMF (4.36×10^{-4} M, $\lambda_{\text{max}} = 654$ nm, $\epsilon = 17525 \text{ M}^{-1} \text{ cm}^{-1}$).....	pg. 14
Figure 2.2 IR spectrum of 2a (KBr).....	pg. 14
Figure 2.3 ^1H NMR spectrum of 2a (DMSO- d_6 , 400 MHz).....	pg. 15
Figure 2.4 ^{13}C NMR spectrum of 2a (DMSO- d_6 , 100 MHz).....	pg. 15
Figure 2.5 a) Reaction profile of 2a (arrows indicate the direction of change over time); b) UV-vis spectrum of LiTCNQ (DMF, $\lambda_{\text{max}} = 849$ nm).....	pg. 19
Figure 2.6 UV-vis spectra of disproportionating LiTCNQ and formation of 3 (DMF).....	pg. 19
Figure 3.1 UV-vis spectra of 2a decomposing over time at 125°C , in the dark, under nitrogen (DMF, 4.36×10^{-4} M, control reaction).....	pg. 23
Figure 3.2 UV-vis spectra of 2a decomposing upon exposure to air, heated for a period of a) 0 min.; b) 50 min; c) 90 min; d) 120 min; e) 145 min.....	pg. 23

Figure 3.3 Absorbance of λ_{max} vs. time for decomposing 2a under different conditions: a) at 25 °C; b) at 125 °C, under nitrogen, protected from light; c) exposed to light; d) exposed to atmospheric oxygen.....	pg. 25
Figure 3.4 Absorbance of λ_{max} vs. time for 2a at various temperatures, protected from light, under nitrogen; (●) 25 °C; (□) 65 °C; (▲) 80 °C; (◇) 100 °C; (■) 125 °C.....	pg. 25
Figure 3.5 UV-vis absorption spectra of 2a decomposing over time at 100 °C, under nitrogen and protected from light (DMF).....	pg. 27
Figure 3.6 UV-vis spectra of 2a decomposing over time in the presence of atmospheric oxygen, in the dark at 125 °C (250 nm to 1000 nm).....	pg. 28
Figure 3.7 UV-vis spectra of final decomposed product and 2-pyridinecarboxaldehyde (DMF).....	pg. 28
Figure 3.8 UV-vis spectra of 2a in solution (DMF) and doped into PES (1 %)...	pg. 30
Figure 3.9 UV-vis spectra of a 1 % film of 2a in PES at 210 °C, under nitrogen and in the dark (over 8 hours).....	pg. 30
Figure 3.10 UV-vis spectra of a 1 % film of 2a in PES at 210 °C, protected from light and exposed to atmospheric oxygen (over 8 hours).....	pg. 30
Figure 3.11 Decomposition of a 1 % film of 2a in PES upon exposure to a) light; b) light and atmospheric oxygen (over 8 hours).....	pg. 32
Figure 3.12 Absorbance of λ_{max} vs. time for films decomposing at 210 °C : a) exposed to oxygen; b) in the dark under N ₂ (g); c) exposed to light; d) exposed to light and oxygen.....	pg. 32

List of Schemes

Scheme 2.1 Chromophore 2 synthesis.....	pg. 9
Scheme 2.2 Reaction of <i>N</i> -octyl-4-quinolinium bromide, TCNQ and piperidine.	pg. 10
Scheme 2.3 Proposed mechanism for the synthesis of 2 from LiTCNQ and the pyridinium salt in the presence of a tertiary amine base.....	pg. 16
Scheme 2.4 Disproportionation of LiTCNQ.....	pg. 16
Scheme 2.5 Reaction of TCNQ ²⁻ with oxygen.....	pg. 18
Scheme 3.1 Proposed mechanism of the decomposition of 2a in solution.....	pg. 27

List of Abbreviations

β	nonlinear second-order molecular hyperpolarizability
EO	electro-optic
esu	electrostatic units
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCTC ⁻	α,α -dicyano- <i>p</i> -toluoylcyanide anion
DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DMSO-d ₆	deuterated DMSO
IR	infrared
KBr	potassium bromide
LiTCNQ	lithium-TCNQide
M	moles/litre
MeCN	acetonitrile
μ	dipole moment
NLO	nonlinear optical
OCN ⁻	cyanate ion
PMMA	poly(methyl methacrylate)
r ₃₃	EO coefficient
TCNQ	7,7,8,8-tetracyanoquinodimethane
T _g	glass transition temperature
UV-Vis	ultraviolet-visible

Chapter 1. Introduction to Nonlinear Optical Chromophores and Materials

1.1 Nonlinear Optical Materials and Applications.

Electro-optic (EO) and second harmonic generation (frequency doubling) materials each belong to the larger class of second-order nonlinear optical (NLO) materials. EO activity refers to the ability to change the refractive index of a material upon the application of voltage. The refractive index is related to the velocity of light propagating through a material, thus an electric field dependent change in the refractive index results in a phase shift of the light.¹

Such materials are used in devices such as EO modulators used for optical switching, electric-to-optical signal transduction, and ultrafast analogue-to-digital signal conversion in optical telecommunications industry.¹ The most effective way to rapidly transfer data over large distances is through the transmission of light signals through optical fibers.² The EO modulator impresses electronic data signals onto a laser beam by modulating the phase and amplitude of the light passing through it.^{1,2} It acts as an ultrafast shutter by blocking and un-blocking the laser beam, thereby creating the signal. The current industry standard uses lithium niobate crystals (EO coefficient $r_{33} = 30 \text{ pm/V}$, see equation 1 pg. 2) as the EO material in modulators which operate at bandwidths of 10 to 40 GHz. Researchers anticipate the future growth in data traffic will require EO coefficients greater than 100 pm/V and bandwidths greater than 100 GHz, creating a need for new materials other than lithium niobate able to sustain higher bandwidths.^{1,2}

1.2 Organic Nonlinear Optical Materials.

Current research efforts are directed towards organic second-order NLO materials to meet the future requirements of broadband optical communications. Organic materials

have been able to achieve higher EO coefficients (~ 70 pm/V), higher bandwidths (up to 150-200 GHz) and are easier to prepare and process than inorganic materials.^{1,2} Organic materials are prepared by incorporating second-order NLO chromophores into passive polymer matrices. Charge-transfer donor-(π electron bridge)-acceptor chromophores (Figure 1.1) arranged in noncentrosymmetric lattices throughout the material undergo a change in charge distribution resulting from an applied electric field. The electric field acts to change the mixing of the neutral and charge-separated states of the chromophore, which alters the refractive index and hence the light velocity.¹

The noncentrosymmetric arrangement is required since randomly ordered dipolar chromophores tend to dimerize, cancelling their influence as light passes through the material (Figure 1.2).³ When the chromophores are aligned in the direction of an applied field then there is an additive effect of the chromophores and the material is EO active.

The EO coefficient (r_{33}) is described by equation 1:

$$r_{33} = 2N\beta f(\omega)/n^4 \quad (1)$$

where N is the chromophore number density, β (nonlinear second-order molecular hyperpolarizability) is related to the charge transfer between the neutral and charge-separated states of the chromophore, $f(\omega)$ represents local field factors of the chromophore in the applied field, and n is the refractive index.¹ Equation 1 shows that an increase in either chromophore content in a material or the chromophore β value would increase the magnitude of the EO coefficient.

One method to determine r_{33} is to use the reflection method established by Teng and Man.⁴ Organic thin films are cast onto on indium tin oxide (ITO) coated glass which is

Figure 1.1 Charge-transfer zwitterionic chromophore DEMI.⁵

Figure 1.2 Arrangement of dipolar chromophores³: a) electric-field induced noncentrosymmetry; b) preferred dipole-dipole orientation of zwitterionic chromophores.

Figure 1.3 Schematic of electric field poling set-up.

conductive and serves as one of the electrodes in the poling step.⁴ Following film preparation a second electrode is applied by thermal evaporation of gold on top of the EO polymer as outlined in Figure 1.3 and the material is electrically poled to induce the chromophores to align in the direction of the applied field, resulting in the EO activity.⁴ The EO measurement is then carried out by the Teng-Man simple reflection technique which measures the output intensity (I_o), r_{33} can then be calculated using equation 2.⁴

$$r_{33} = \frac{3\lambda I_m (n^2 - \sin^2\theta)^{3/2}}{4\pi V_m n^2 I_o (n^2 - 2\sin^2\theta) \sin^2\theta} \quad (2)$$

The wavelength (λ), amplitude of modulation (I_m), angle of the incident beam (θ) and modulation voltage (V_m) are all fixed during measurement, and the refractive index (n) of the film can be measured prior to analysis.⁴ The derivation of equation 2 was possible with the assumption that the refractive indices perpendicular (n_c) and parallel (n_o) to the plane of the polymer film are approximately equal to one another ($n_o \approx n_c \approx n$).⁴ A second assumption is that no prior axial order existed, thus $r_{33} = 3r_{31}$ where r is the EO tensor, 3 represents the direction perpendicular to the film and 1 the direction parallel to the film.⁴ It should also be noted that any induced birefringence in the film is negligible when using the Teng-Man set-up.⁴

There are different approaches to incorporating the NLO chromophore into the organic thin film to produce EO materials. Ashwell et al. recently reported the preparation of Langmuir-Blodgett films which have an inherent noncentrosymmetric alignment and contained 30-50% of an NLO chromophore with r_{33} values of 30-40 pm/V.⁶ Most often the NLO chromophore is doped into a passive polymer matrix, and there have also been examples of direct grafting of the chromophore to the polymer. The current trend has shifted toward using a polymer containing pendant groups that can be

crosslinked following the poling step to lock chromophores into the induced noncentrosymmetric alignment. This was an important innovation since most chromophores relax back to the original state when the electric field is removed and hence EO activity is lost. Researchers for Bell Laboratories-Lucent Technologies recently published details of an EO modulator made using the commercial dye disperse red 1 doped into a crosslinkable PMMA copolymer. The material contained 20% chromophore by weight, had an r_{33} value between 5 and 7 pm/V, and the resultant device modulated light at a bandwidth of 150-200 GHz.² Dalton et al. grafted an NLO chromophore to a series of crosslinkable polymers in 30-40% chromophore by weight. The r_{33} values ranged from 10 to 15 pm/V.⁷

A number of criteria must be met in order for an organic chromophore to be considered for an EO material. Equation 1 showed β is directly proportional to the EO coefficient, thus a high β chromophore should be used. It is normally the $\mu\beta$ value that is reported for NLO chromophores. The scalar $\mu\beta$ represents the averaged orientation of the chromophore in poled media where μ is the ground state dipole moment and β is the nonlinear second-order molecular hyperpolarizability.^{8,9} To be useful in EO materials the chromophore should have a $\mu\beta$ value of 2000×10^{-48} esu or greater.¹ The $\mu\beta$ value of the chromophore in Figure 1.1 is 9500×10^{-48} esu.⁶ In addition to a high $\mu\beta$ value the chromophore must have the chemical and thermal stability to withstand film processing as well as device operating conditions. The chromophore should also be available by high yield inexpensive pathways to be potentially useful for a commercial device.¹

The glass transition temperature (T_g) of the polymer needs to be considered for doping experiments since the chromophore dopant would have a plasticizing effect, resulting in a

material with a T_g lower than that of the original polymer. To avoid sublimation of the chromophore poling most often takes place between 90 to 140 °C, so the host polymer should have a T_g in the range of 150 to 250 °C.¹

The chromophore and polymer must share solubility in a good casting solvent, and they must be compatible otherwise phase separation would occur. Once these considerations have been met the loading limit would need to be determined. The greater the incorporation of the chromophore into the polymer matrix the greater the chromophore number density (N) which contributes to the EO coefficient as described by equation 1. The loading limit is the point at which increased chromophore incorporation would lead to phase separation and/or aggregation of the dopant. If the loading limit were too low for a given chromophore/polymer system the material would not be EO active.

After screening the materials as outlined above a thin film would be prepared and another set of criteria would need to be met. Once the material was confirmed to be EO active the chemical, thermal, photochemical and electrochemical stability would need to be determined.^{1,10} Commonly if the material is unstable the chromophore will decompose as the result of attack at its reactive positions by the normal pathways of organic chemistry. Decomposition can be prevented or at least significantly slowed if the polymer media used has a high density since a dense polymer film would slow the rates of diffusion.¹ A material that is found to have good stability and EO activity can then be considered for use in an EO device such as a modulator.

1.3 Rationale and Objectives.

The long term team objective was to functionalize an NLO chromophore so that it could be grafted onto a polymer capable of being crosslinked following the poling step, producing an EO material resistant to chromophore relaxation outside the electric field. Based on the similarity in structure to one of the highest $\mu\beta$ chromophores known (DEMI, Figure 1.1) the class of chromophores shown in Figure 1.4 (2) was selected for the investigation.⁵ Unfortunately the literature procedures available for the synthesis of **2** reported yields of only 15 to 30%, and the reaction times when repeated were upwards of 5 to 14 days.^{8,11} The literature made no reference to the stability of the chromophores, but the characterization to determine the r_{33} of some preliminary graft materials using **2** in our group showed small but notable decomposition.

The objectives were to develop a high-yield cost effective synthesis of **2** and to assess the stability of the chromophores in both solution and solid state to mimic to processing and device operating conditions. The information gathered from stability studies would help establish the whether the materials would be worthwhile pursuing for use in EO devices, and the results could give information on how to design a more stable chromophore.

Figure 1.4 Z- β -(1-R-4-pyridinium)- α -cyano-4-styryldicyanomethanide.

References

1. Dalton, L. *Polymers for Photonics Applications I*, Advances in Polymer Science, **158**, **2002**, 1-86.
2. Lee, M., Katz, H. E., Erben, C., Gill, D. M., Gopalan, P., Herber, J. D., McGee, D. J. *Science* **2002**, 298, 1401-1403.
3. Würthner, F., Yao, S. *Angew. Chem. Int. Ed.* **2000**, 39, 11, 1978-1981.
4. Teng, C. C., Man, H. T. *Appl. Phys. Lett.* **1990**, 56, 1734-1736.
5. Szablewski, M., Thomas, P. R., Thornton, A., Bloor, D., Cross, G. H., Cole, J. M., Howard, J. A. K., Malagoli, M., Meyers, F., Bredas, J., Wenseleers, W., Goovaerts, E. *J. Am. Chem. Soc.* **1997**, 119, 3144-3154.
6. Ashwell, G. J., Zhou, D., Skjonnemand, K. *IEICE Trans. Electron.* **2000**, E83-C, 7, 1057-1061.
7. Mao, S. S. H., Ra, Y., Guo, L., Zhang, C., Dalton, L. R., Chen, A., Garner, S., Steier, W. H. *Chem. Mater.* **1998**, 10, 146-155.
8. Ashwell, G. J. *Thin Solid Films* **1990**, 186, 155-165.
9. Chen, A., Chuyanov, V., Garner, S., Zhang, H., Steier, W. H., Chen, J., Zhu, J., Wang, F., He, M., Mao, S. S. H., Dalton, L. R. *Optics Lett.* **1998**, 23, 6, 478-480.
10. Ren, Y., Szablewski, M., Cross, G. H. *Appl. Optics* **2000**, 39, 15, 2499-2506.
11. Ashwell, G. J. Eur. Patent EP 0 391 631 A1, 1990.

Chapter 2: Study of the Factors Affecting Chromophore Synthesis

To improve the synthesis of chromophore **2** the reaction conditions, reactants, products and mechanism were studied closely. The reactions were carried out according to Scheme 2.1. Different reaction solvents and tertiary amine bases were tested for the syntheses of **2a-c**. The relative proportion of reactants were studied more closely for **2a** and the optimized synthesis conditions were attained.

Scheme 2.1 Chromophore **2** synthesis.

2.1 Choice of Solvent.

The reactions designed to identify the best reaction solvent were done by another member of the Wang group.^a Each solvent screening reaction was carried out using *N*-(3-hydroxypropyl)-4-pyridinium bromide (**1b**), lithium-TCNQ adduct (LiTCNQ) and *N*-(2-hydroxyethyl)piperidine as the amine base. Based on literature procedures reactions were first attempted using chlorobenzene and ethanol/chlorobenzene but the resulting yields were only 1 and 2 % respectively.¹ A third reaction using DMF resulted in no recovery of chromophore **2b**. The chromophore had started to form as indicated by the large peak

^aAndrew Beaudin, from Wang, Z. Y., Song, N., Beaudin, A., Weir, C., Cross, G., Szablewski, M. "Functionalized Zwitterionic Nonlinear Optical Materials and Polymers Derived Therefrom", US and Canadian Patents (filed March 2002)

at 650 nm in the UV-vis absorption spectrum, but within 1 hour the chromophore had fully decomposed. An additional reaction using MeCN as the solvent resulted in 30 % yield, thus it was used as the solvent for all further reactions.

Later experiments discussed in Chapter 3 suggest that the poor yields associated with chlorobenzene (bp. 132 °C) and DMF (bp. 153 °C) were due to the high reaction temperatures. In each case the reactions were carried out at the reflux temperature of the solvent. It was later discovered that the stability of the chromophore in solution is compromised over 100 °C. The boiling point of MeCN is only 80 °C providing a more stable reaction environment.

2.2 Using an Amine Base.

Ashwell et al. reported a drastic improvement in reaction time from 2 weeks to 8 hours for the chromophore synthesized from *N*-octyl-4-quinolinium bromide and TCNQ in the presence of piperidine (Scheme 2.2).² They later reported however that the yield for that reaction was compromised as a result of an additional substitution reaction involving piperidine.³ In a well documented process primary and secondary amines act as nucleophiles and displace one or two cyano groups of TCNQ.⁴

Scheme 2.2 Reaction of *N*-octyl-4-quinolinium bromide, TCNQ and piperidine.²

Based on those findings different tertiary amine bases were tested. *N*-(2-hydroxyethyl)piperidine was used with one equivalent of LiTCNQ and one equivalent of

N-(6-hydroxyhexyl)-4-methylpyridinium bromide (**1c**). After only 10 hours the colour had changed from green to blue, marking the end-point of the reaction according to literature.³ This was a drastic improvement from previous reactions done without the use of a base that had shown no reaction in 5 days.

Based on the price of *N*-(2-hydroxyethyl)piperidine, two other less expensive tertiary amine bases were tested to see if the same improvement in reaction time could be achieved. Initial experiments using 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the synthesis of **2b** showed even shorter reaction times than with *N*-(2-hydroxyethyl)piperidine. Table 2.1 shows a comparison of reactions using each of the three bases. The results showed that the end-point was reached in the shortest amount of time using the strongest base DBU ($pK_a = 12$). Based on this result DBU was chosen for all remaining investigations.

Table 2.1 Preliminary Reactions Investigating Choice of Base

Base	pK_a	Chromophore	Equiv.	Equiv.	Equiv. of Base	Reaction Time ^a (hrs)
			Pyridine Salt	LiTCNQ		
Pip-EtOH ^b	9	2c	1	1	1.7	10
DABCO	9	2b	1	1	2.6	3.5
DBU	12	2b	1	1	2.0	1.5

^aReaction time based solely on time required for the reaction solution to turn blue in colour

^b*N*-(2-hydroxyethyl)piperidine

The amount of base required in the reaction was misjudged during these trials. It became evident after further investigation that too much base was used, which led to mostly decomposed products. A small amount of **2c** was attained in 0.9 %, but no product could be isolated for the **2b** reactions.

The manner in which the base was added to the reaction was also very important. For the reactions described in Table 2.1 the base was added to the solution all at once. It was

found that adding the base slowly to the reaction in increments of 3-5 drops every 15-30 minutes greatly reduced decomposition of the final product and the blue colour was reached more quickly.

It was also found that the end-point was better judged by monitoring the disappearance of LiTCNQ by UV-vis analysis, the colour change from green to blue gauged the beginning of chromophore formation but LiTCNQ would continue to be used up over time.

2.3 Ratio of Reactants.

In order to maximize the yield the synthesis of **2a** was repeated several times, varying the amounts of starting material for each reaction. Table 2.2 outlines the variables and resulting yields.

Table 2.2 Molar Equivalents of Reactants Used and the Isolated Yields for **2a**

Equiv. of 1a	Equiv. of LiTCNQ	Equiv. of TCNQ	Equiv. of DBU	% Yield	Reaction Time (hours)
1	1	-	0.1	24 ^a	26
1	1	-	2	-	5.5
1	2	-	1	62 ^a	18
1	2	-	2	97 ^b	14
1	-	2	2	34 ^a	18.5
1	1	1	2	50 ^a	16

^aAfter one purification

^bAfter four purifications

The conditions providing the best yield of **2a** used 1 equivalent of *N*-octyl-4-methylpyridinium bromide (**1a**), 2 equivalents of LiTCNQ and 2 equivalents of DBU. The reactants were dissolved in MeCN and DBU was added to the refluxing solution slowly in intervals of 3 drops every 15 minutes over a period of 1.5 hours. The reaction

proceeded for a total of 14 hours and the product that had precipitated from solution was collected. Following purification in which the crude product was washed repeatedly with boiling methanol, **2a** was obtained in 97% yield. The UV-vis absorption spectrum in DMF showed absorbances at $\lambda_{\text{max}} = 654 \text{ nm}$ and 333 nm (Figure 2.1). The IR spectrum (Figure 2.2) of **2a** showed the $\text{C}\equiv\text{N}$ peaks at 2132 and 2175 cm^{-1} , suggesting the compound was zwitterionic in character based on the difference in position between the $\text{C}\equiv\text{N}$ absorptions of LiTCNQ (2196 and 2182 cm^{-1}) and neutral TCNQ (2225 cm^{-1}).² The chromophore was also characterized by ^1H NMR (Figure 2.3), ^{13}C NMR (Figure 2.4) and by mass spectral analysis (pg. 60, Appendix A).⁵

The results from Table 2.2 showed that using two equivalents of LiTCNQ relative to one equivalent of **1a** led to higher yields. The base led to faster reaction times and contributed positively to the yield when used in excess of **1a**. However when base was used in excess of LiTCNQ as with the reaction using one equivalent of **1a**, one equivalent of LiTCNQ and two equivalents of DBU, the product fully decomposed and no chromophore could be isolated. A comparison of reactions using neutral TCNQ versus LiTCNQ revealed that higher yields were attained using the charged adduct. Therefore using two molar equivalents of both charged LiTCNQ and DBU in excess to only one molar equivalent of the pyridinium salt provided significantly higher yields and shorter reaction times than previously reported for type **2** chromophores.

2.4 Reaction Mechanism.

Based on the findings from the series of reactions carried out in Section 2.3 (Table 2.2), a possible reaction mechanism was devised. The radical mechanism (Scheme 2.3) would seemingly explain why the second equivalent of LiTCNQ is required to achieve a

Figure 2.1 UV-vis spectrum of **2a** in DMF (4.36×10^{-4} M, $\lambda_{\text{max}} = 654$ nm, $\epsilon = 17525$ M⁻¹ cm⁻¹).

Figure 2.2 IR spectrum of **2a** (KBr).

Figure 2.3 ^1H NMR spectrum of **2a** (DMSO-d_6 , 400 MHz).

Figure 2.4 ^{13}C spectrum of **2a** (DMSO-d_6 , 100 MHz).

Scheme 2.3 Proposed mechanism for the synthesis of **2** from LiTCNQ and the pyridinium salt in the presence of a tertiary amine base.

Scheme 2.4 Disproportionation of LiTCNQ in solution.¹³

yield greater than 50 %, as well as the need for the second equivalent of DBU. The first step is deprotonation of the pyridinium salt to form the unsaturated product, followed by radical addition of LiTCNQ to the newly formed double bond. The unpaired electron, delocalized by adjacent double bonds, is then transferred to a second equivalent of LiTCNQ, resulting in TCNQ^{2-} and the precursor to **2**. A second equivalent of base then attacks the proton leading to the elimination of CN^- and the unsaturated product **2**. The electron transfer from radicals to give ionic products is well documented, especially for highly conjugated systems.⁶⁻¹⁰

Every synthesis reaction outlined in Tables 2.1 and 2.2 proceeded according to the profile outlined in the UV-vis spectra of Figure 2.5 a) (in DMF). Over time the LiTCNQ ($\lambda_{\text{max}} = 849 \text{ nm}$, Figure 2.5 b) concentration would decrease, the chromophore peaks at 654 nm and 333 nm would increase, and an additional peak at 490 nm would also form and increase in absorbance intensity. The pyridinium salts and DBU were not present in Figure 2.5 a) as they each absorb below the solvent cutoff point. The cause of the peak at 490 nm was unknown and was initially assumed to be either a reaction intermediate or the product of the chromophore decomposing *in situ*, but both possibilities were ruled out. The synthesis of **2a** in 97 % yield (Table 2.2) showed the peak at 490 nm increased steadily throughout the reaction (an intermediate would eventually decrease), and the crude product showed the peaks at 490 nm and 654 nm to be of approximately equal intensity, implying the formation of a by-product. A great deal of time was spent trying to isolate the product responsible for the peak at 490 nm to no avail, and as such a full characterization was not possible.

Following a literature search it was found that the α,α -dicyano-*p*-toluoylcyanoide ion (DCTC⁻), a derivative of LiTCNQ that can form in the presence of oxygen, absorbs close to 490 nm (483 nm, 333 nm and 274 nm in MeCN).¹¹⁻¹³ As shown in Scheme 2.4 a solution of LiTCNQ will disproportionate over time to give neutral TCNQ⁰ and TCNQ²⁻, and in the presence of oxygen TCNQ²⁻ reacts to give DCTC⁻ (**3**).¹³ To verify where DCTC⁻ absorbs in DMF, a solution of LiTCNQ was allowed to disproportionate in the presence of atmospheric oxygen. Figure 2.6 shows the absorbance of **3** at 490 nm in DMF. TCNQ⁰ has a distinct peak in DMF at 393 nm, this peak was not observed in Figure 2.6 since it absorbs in the same region as LiTCNQ. The DCTC⁻ generated could not be isolated from solution as is always the case for salts of **3**, explaining why it could not be isolated for the synthesis reactions.^{11,13} Since there was clearly no absorbance at 393 nm during chromophore syntheses (Figure 2.5 a) disproportionation can be ruled out, indicating LiTCNQ does not provide the source of TCNQ²⁻ in the reactions.

Scheme 2.5 Reaction of TCNQ²⁻ with oxygen.¹²

Figure 2.5 a) Reaction profile of **2a** (arrows indicate the direction of change over time);
b) UV-vis spectrum of LiTCNQ (DMF, $\lambda_{\text{max}} = 849 \text{ nm}$).

Figure 2.6 UV-vis spectra of disproportionating LiTCNQ and formation of **3** (DMF).

The generation of TCNQ^{2-} (λ_{max} 330 MeCN) in the chromophore reaction likely occurs as shown in Scheme 2.3, following the one-electron transfer to the second equivalent of LiTCNQ.¹² It is well documented that in the presence of trace amounts of oxygen, TCNQ^{2-} undergoes reaction to DCTC⁻ (**3**) as depicted in Scheme 2.5.¹¹⁻¹³ Although the reactions were carried out under nitrogen, the system was frequently opened to remove samples for analysis providing the source of oxygen.^{12,13} The production of **3** does not hinder the chromophore synthesis, and its presence helps to reinforce the proposed mechanism.

References

1. Szablewski, M., Thomas, P. R., Thorton, A., Bloor, D., Cross, G. H., Cole, J. M., Howard, J. A. K., Malagoli, M., Meyers, F., Bredas, J. L., Wenseleers, W., Goovaerts, E. *J. Amer. Chem. Soc.* **1997**, *119*, 3144-3154.
2. Bell, N. A., Broughton, R. A., Brooks, J. S., Jones, T. A., Thorpe, S. C., Ashwell, G. *J. J. Chem. Soc., Chem. Commun.* **1990**, 325-326.
3. Ashwell, G. J. *Thin Solid Films* **1990**, *186*, 155-165
4. Hertler, W. R., Hartzler, H. D., Acker, D. S., Benson, R. E. *J. Amer. Chem. Soc.* **1962**, *84*, 3387-3393.
5. Gottlieb, H. E., Kotlyar, V., Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.
6. Edwards, O. E., Grue-Sorensen, G., Blackwell, B. A. *Can. J. Chem.* **1997**, *75*, 857-872.
7. Pincock, J. A. *Acc. Chem. Res.* **1997**, *30*, 43-49.
8. Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131-137.
9. Zimmerman, H. E. *Angew. Chem. Intl. Ed.* **1969**, *8*, 1-11.
10. Edwards, O. E., Ho, P. T. *Can. J. Chem.* **1978**, *56*, 733-742.
11. Grossel, M. C., Duke, A. J., Hibbert, D. B., Lewis, I. K., Seddon, E. A., Horton, P. N., Weston, S. C. *Chem Mater.* **2000**, *12*, 2319-2323.
12. Suchanski, M. R., Van Duyne, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 250-252.
13. Lombardo, A., Fico, T. R. *J. Org. Chem.* **1979**, *44*, 2, 209-212.

Chapter 3: Chromophore Decomposition Studies

Preliminary EO measurements of a polymer grafted with isolated chromophore (**2b**) and cast as a film showed the chromophore decomposed leading to the formation of a peak centering around 490 nm by UV-vis analysis, signaled by a colour change in the film from blue to green. Since the stability of the chromophore and resulting material is imperative if it were to be incorporated into an EO device, a series of reactions were designed to study the effects of light, temperature and atmospheric oxygen on the decomposition of the chromophore.

3.1 Solution Decomposition.

The experiments were each carried using the same concentration of **2a** in DMF (4.36×10^{-4} M). Decomposition of the chromophore was monitored by UV-vis analysis of undiluted reaction solution using a cuvette with a pathlength of 0.1 cm. A control experiment was carried out in a closed system under a steady stream of nitrogen with the reaction vessel protected from the light. The temperature was raised to 125 °C and the decomposition of the chromophore in the blue solution was monitored by UV-vis analysis. Figure 3.1 shows the changing spectra over time. The chromophore **2a** appeared stable up to 7 hours, at 20 hours the main chromophore peak at $\lambda_{\text{max}} = 654$ nm had dropped in absorbance and the decomposition peak at 490 nm had started forming. After 2 days there was a significant drop in chromophore absorbance at 654 nm, the peak at 490 nm was present but not well defined, an additional peak at around 410 nm had formed, and the peak at 333 nm had approximately the same absorbance intensity as the original chromophore solution. The final colour of the reaction solution was dark brown/green.

Figure 3.1 UV-vis spectra of **2a** decomposing over time at 125 °C, in the dark, under nitrogen (DMF, 4.36×10^{-4} M, control reaction).

Figure 3.2 UV-vis spectra of **2a** decomposing upon exposure to air, heated for a period of a) 0 min.; b) 50 min.; c) 90 min.; d) 120 min.; (e) 145 min.

To investigate the effect of oxygen on chromophore decomposition the experiment was repeated in the same manner as the control experiment except that the system was open to air/moisture. The temperature was maintained at 125 °C and the reaction vessel was protected from light. Figure 3.2 shows that the peak at 490 nm began to form after 90 minutes, and the product had fully decomposed within 145 minutes as shown by the complete disappearance of the chromophore peak at 654 nm. The final colour of the reaction solution was orange. In only 145 minutes **2a** had decomposed more fully than the control experiment had after 2 days, implying that exposure to air/moisture had a very significant impact on the rate of decomposition.

To assess the effect of exposure to light the experiment was repeated in the same manner as the control experiment except that a 60 W white light lamp was focused on the reaction vessel. The temperature was maintained at 125 °C and the closed system was under a steady stream of nitrogen. After 18 hours there was a significant drop in the absorbance intensity of the peak at 654 nm and the decomposition peak at 490 nm had started to form. The chromophore was showing increased decomposition compared to the control experiment, but the effect was secondary compared to exposure to air/moisture. Figure 3.3 shows a comparison of the effects of air, light and temperature on the decomposition of **2a** compared to the control experiment.

The effect of temperature on the decomposition of **2a** was investigated more thoroughly by repeating the reaction in the same manner as the control experiment at several different temperatures, under nitrogen in a closed system protected from light. Figure 3.4 shows the relative decrease in intensity of the chromophore peak at $\lambda_{\text{max}} = 654$ nm over time as a function of temperature. The reactions carried out at 25, 65, 80, 100

Figure 3.3 Absorbance of $\lambda_{\max}$ vs. time for decomposing **2a** under different conditions: a) at 25 °C; b) 125 °C, under nitrogen, protected from light; c) exposed to light; d) exposed to atmospheric oxygen.

Figure 3.4 Absorbance of $\lambda_{\max}$ vs. time for **2a** at various temperatures, protected from light, under nitrogen; (●) 25 °C; (□) 65 °C; (▲) 80 °C; (◇) 100 °C; (■) 125 °C.

and 125 °C showed **2a** was stable up to 65 °C. The experiment at 80 °C was stable up to 28 hours, at which point a shoulder around 490 nm had started to form and the chromophore peak decreased slightly in intensity. There was no significant change in the spectra between 28 and 48 hours. Above 100 °C there was more significant decomposition as shown in Figure 3.5. The UV-vis spectra indicated that by the 8 hour mark the peak at 654 nm was decreasing and the decomposition peak at 490 nm had formed. After 52 hours there was very little chromophore remaining in the mixture that was brown in colour.

The results of the solution state reactions indicated that exposure to oxygen has the largest impact on the decomposition of **2a**. Light and temperatures over 80 °C also accelerate decomposition but to a much smaller degree. Therefore to protect against decomposition the synthesis reactions, the processing of doped polymer films, and in chromophore/polymer grafting reactions, the processes should be carried out in an inert atmosphere, protected from light and at temperatures of 80 °C or lower.

3.2 Mechanism of Decomposition.

Exposure to oxygen from the atmosphere was the primary factor that contributed to the decomposition of the **2a** in solution. Based on those results and the fact that the decomposed peak absorbs at 490 nm by UV-vis, a mechanism was devised with attack at the allylic bridge (Scheme 3.1) similar to the attack of oxygen on TCNQ²⁻ shown in Scheme 2.5 (Chapter 2). The chromophore is proposed to decompose into DCTC⁻ (**3**) and *N*-octyl-4-pyridinecarboxaldehyde (**4**). The UV-vis absorption spectrum of 2-pyridinecarboxaldehyde shows λ_{max} to be 268 nm, which falls below the measured

Figure 3.5 UV-vis absorption spectra of **2a** decomposing over time at 100 °C, under nitrogen and protected from light (DMF).

Scheme 3.1 Proposed mechanism of the decomposition of **2a** in solution.

Figure 3.6 UV-vis spectra of **2a** decomposing over time in the presence of atmospheric oxygen, in the dark at 125 °C (250 nm to 1000 nm).

Figure 3.7 UV-vis spectra of final decomposed product and 2-pyridinecarboxaldehyde (DMF).

range in the decomposition reactions. The solution decomposition of **2a** exposed to atmospheric oxygen was repeated monitoring the full range and the results showed the formation of the additional peak at 268 nm (Figure 3.6). The UV-vis absorption spectra of the decomposed product and 2-pyridinecarboxaldehyde are compared in Figure 3.7. The additional peak that appears at 410-420 nm in Figure 3.6 is attributed to the decomposition of DCTC⁻, which is known to be unstable in solution.¹ The peak at around 333 nm does not change drastically because the chromophore, DCTC⁻ and decomposing DCTC⁻ all share absorbances in this region.¹ The evidence supports the proposed mechanism and suggests the chromophore decomposition peak at 490 nm was in fact DCTC⁻. A more stable chromophore can now be designed based on protecting the allylic bridge from attack by oxygen.

Based on the results of the decomposition reactions, future syntheses of Z- β -(1-substituted-4-pyridinium)- α -cyano-4-styryldicyanomethanide chromophores (**2**) should be carried out at temperatures of 80 °C or below, protected from light and in an inert atmosphere to prevent *in situ* decomposition of the chromophore.

3.3 Solid State Decomposition.

Films of 1% incorporation of **2a** in polyether sulfone (PES) were prepared to carry out the solid state investigations. Higher incorporation of the chromophore in PES resulted in aggregation as **2a** is highly crystalline. The UV-vis spectrum of the blue polymer material was the same as the chromophore except the peaks were shifted to longer wavelengths as shown in Figure 3.8. The glass transition temperature (T_g) of the film was 220 °C (PES T_g = 230 °C). Since poling of the polymer films is normally carried out 10

Figure 3.8 UV-vis spectra of **2a** in solution (DMF) and doped into PES (1 %).

Figure 3.9 UV-vis spectra of a 1 % film of **2a** in PES at 210 °C, under nitrogen and in the dark (over 8 hours).

Figure 3.10 UV-vis spectra of a 1 % film of **2a** in PES at 210 °C, protected from light and exposed to atmospheric oxygen (over 8 hours).

°C below T_g , the temperature used for the decomposition studies was 210 °C. The control experiment was set up with the film heated on a digital hot stage under a steady stream of nitrogen and protected from the light. The film was heated over 8 hours and the UV-vis spectra showed no decrease in the absorbance intensity of the chromophore peak ($\lambda_{max} = 710$ nm) and no decomposition peak (Figure 3.9). The film was not the same initial blue colour, it was slightly blue-green.

To test the effect of oxygen the experiment was carried out with the system open to air, at 210 °C and protected from the light. Unlike the solution reaction exposed to air, there was no significant decomposition observed by UV-vis (Figure 3.10) after 8 hours. PES has a high density and a very low O₂ permeability value in the film form, which is the likely reason the chromophore did not decompose. The film had changed slightly in colour to blue-green as with the standard reaction.

The effect of light was investigated by repeating the experiment with a 60 W white light lamp focused on the film. The system was closed under a steady nitrogen flow and the temperature was 210 °C. Unlike the previous experiment there was a more significant change in the UV-vis spectra shown in Figure 3.11 a). Within 1 hour the peak at 710 nm was decreasing in intensity and a shoulder was starting to form around 500 nm. Over the 8 hour period the film showed a moderate amount of decomposition, reminiscent of the solution decomposition exposed to light. The final colour of the film was green.

A final experiment was carried out exposing the film to both light and oxygen with the temperature at 210 °C. The UV-vis spectra in Figure 3.11 b) showed that within 1 hour the chromophore peak at 710 nm had decreased significantly and the peak at 500 nm had

Figure 3.11 Decomposition of a 1 % film of **2a** in PES upon exposure to a) light; b) light and atmospheric oxygen (over 8 hours).

Figure 3.12 Absorbance of $\lambda_{\max}$ vs. time for films decomposing at 210 °C: a) exposed to oxygen; b) in the dark under N_2 (g); c) exposed to light; d) exposed to light and oxygen.

formed. After 6.5 hours there was very little chromophore remaining so the experiment was stopped. The final colour of the film was light brown. The decomposition upon exposure to both light and oxygen was much stronger than for either factor individually. Figure 3.12 shows the change in absorbance of the main chromophore peak ($\lambda_{\text{max}} = 710$ nm) over time for the different factors.

The chromophore/PES film is susceptible to decomposition upon exposure to light and more so in the presence of both light and oxygen. The chromophore incorporated in the polymer matrix was quite stable to oxygen as the result of the low permeability of PES to $\text{O}_2(\text{g})$. To protect a film containing **2a**, poling and testing should be carried out with light and oxygen excluded. Under those conditions **2a** is stable up to 210 °C doped into PES.

Reference

1. Grossel, M. C., Duke, A. J., Hibbert, D. B., Lewis, I. K., Seddon, E. A., Horton, P. N., Weston, S. C. *Chem. Mater.* **2000**, *12*, 2319-2323.

Chapter 4. Experimental

4.1 Materials.

All chemicals were purchased from Aldrich Chemical Co. and were used as received. Acetone, acetonitrile, DMF, DMAc, diethyl ether and methanol were purchased from Caledon and were used as received. Anhydrous ethanol was purchased from Commercial Alcohols, Inc. Deuterated DMSO was purchased from CDN Isotopes. Poly(ether sulfone) (Ultrason®) was purchased from BASF. The microscope cover glasses (1 oz, 22X22 mm) were purchased from VWR Scientific, Inc. The syringe filters (0.45 µm, PTFE) were TITAN® brand.

4.2 Instruments and Characterization.

IR spectra were recorded using a Bomem Michelson 120 FTIR Spectrometer. ¹H and ¹³C NMR spectra were recorded using a Bruker-400 Spectrometer. UV-vis absorption spectra were recorded using a Perkin Elmer Lambda 900 Spectrometer. Mass spectra were recorded at the University of Ottawa using either a Kratos Concept IIIH (HRMS, EI) or a Fisons Quattro (LCMS, ESI) spectrometer. Glass transition temperatures were measured using either a TA Instruments DSC 2920 or a Seiko SSC-5200, using a heating rate of 10 °C/min under nitrogen flow of 50 mL/min. Decomposition temperatures were analyzed using a Seiko SSC-5200 TG/DTA using a heating rate of 10 °C with a nitrogen flow of 50 mL/min. A PACE H38-HOTP hotstage was used with a PACE Heat Wave H50-HOTP digital heat control.

4.3 Experimental Procedures.

4.3.1 Synthesis Procedures.

***N*-Octyl-4-Methylpyridinium Bromide (1a).**

4-Picoline (9.57 g, 0.103 mol) was dissolved in 55 mL of anhydrous ethanol in a 1-neck 250 mL round-bottomed flask fitted with a CaCl₂ drying tube. Just before temperature reached reflux, 1-bromooctane (25.8 g, 0.134 mol) was added to the mixture. The reaction was stopped after 48 hours and the solvent was removed by rotary evaporation. The yellow viscous liquid was extracted with 5 x 25 mL of diethyl ether. Upon removal of residual ether following the work-up, the product precipitated from the solution to give an off-white powder, which was washed repeatedly with chilled ethanol and ether. The final product was an off-white amorphous powder collected in 94 % yield (27.7 g) with a very low melting point of 32-33°C, thus the product required refrigeration.

1a: ¹H NMR (DMSO-d₆, 400 MHz): δ 0.81 (t, 3H, *J* = 6.8 Hz), 1.22 (m, 10 H), 1.85 (m, 2 H), 2.58 (s, 3H), 4.52 (t, 2H, *J* = 7.3 Hz), 7.96 (d, 2H, *J* = 6.6 Hz), 8.92 (d, 2H, *J* = 6.7 Hz); ¹³C NMR (DMSO-d₆, 100 MHz): δ 14.1, 21.5, 22.2, 25.5, 28.5, 28.6, 30.8, 31.3, 60.1, 128.5, 143.8, 159.0; MS (SI, MeCN, *m/e*) 206 (*M*⁺); IR (CHCl₃, cm⁻¹): 1641 (C=N), 1576, 1469 (C=C).

***N*-Hydroxypropyl-4-Methylpyridinium Bromide (1b).**

3-Bromo-1-propanol (60.0 g, 0.432 mol) was dissolved in 250 mL of anhydrous ethanol in a 2-neck 1L round-bottomed flask flushed with nitrogen. 4-Picoline (43.8 g, 0.470 mol) was added and the mixture was heated to reflux. The reaction was stopped after 48 hours and the solvent was removed by rotary evaporation. The residue was

extracted with 5 x 50 mL of diethyl ether. The final product was a viscous yellow liquid with 96% yield (96.6 g). **1b**: ^1H NMR (DMSO- d_6 , 400 MHz): δ 2.06 (m, 2H), 2.62 (s, 3H), 3.44 (t, 2H, $J = 5.9$ Hz), 4.62 (t, 2H, $J = 7.0$ Hz), 7.99 (d, 2H, $J = 6.5$ Hz), 8.94 (d, 2H, $J = 6.7$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 21.2, 33.1, 57.0, 57.7, 128.1, 143.9, 158.6; MS (SI, MeCN, m/e) 152 (M^+); IR (neat, cm^{-1}): 3332 (O-H), 1642 (C=N), 1572, 1475 (C=C).

N-Hydroxyhexyl-4-Methylpyridinium Bromide (1c).

6-Bromo-1-hexanol (5.00 g, 27.6 mmol) was dissolved in 16 mL of anhydrous ethanol in a three-necked 50 mL round-bottomed flask flushed with nitrogen. 4-Picoline (2.80 g, 30.1 mmol) was added and the solution was heated to reflux. The reaction was stopped after 48 hours, cooled to room temperature and the ethanol was removed by rotary evaporation. The residue was extracted with 6 x 20 mL of diethyl ether. The final product was obtained as an orange-yellow viscous liquid in 100% yield (6.41 g).

1c: ^1H NMR (DMSO- d_6 , 400 MHz): δ 1.21-1.44 (m, 6H), 1.87 (m, 2H), 2.59 (s, 3H), 3.35 (t, 2H, $J = 6.2$ Hz), 4.52 (t, 2H, $J = 7.3$ Hz), 7.98 (d, 2H, $J = 6.6$ Hz), 8.94 (d, 2H, $J = 6.7$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 21.3, 24.9, 25.2, 30.6, 32.1, 59.9, 60.4, 128.3, 143.7, 158.8; MS (SI, MeCN, m/e) 194 (M^+); IR (neat, cm^{-1}): 3361 (O-H), 1641 (C=N), 1572, 1475 (C=C).

Lithium-TCNQide.

TCNQ (7.27 g, 35.6 mmol) was dissolved in 370 mL of MeCN in a 2-neck 1L round-bottomed flask. A solution of lithium iodide (7.96 g, 59.4 mmol) in 60 mL of acetone was added to the mixture, which immediately changed colour from yellow to blue-green, then to a dark brown. The reaction was stopped after 12 hours. The crude product was

filtered and washed with fresh MeCN until the washings were bright green. The purple amorphous powder was recovered in 93% yield (7.0025 g).

LiTCNQ: ^1H NMR (DMSO- d_6 , 400 MHz): δ 6.84 (d, 2H, $J = 7.0$ Hz), 7.64 (d, 2H, $J = 7.9$ Hz); MS (EI, m/e) 204 ($\text{M}^{+\bullet}$); IR (KBr): 2197, 2182 ($\text{C}\equiv\text{N}$), 1579 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 849$ nm.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

LiTCNQ (2.570 mmol) was dissolved in 20 mL of MeCN and the solution was brought to reflux. Once dissolved a solution of *N*-octyl-4-pyridinium bromide (1.283 mmol) in 5 mL of MeCN was added. DBU (2.570 mmol) was added in increments of 3 drops every 15 minutes. After 14 hours the reaction was stopped and the precipitate was filtered, washed with MeCN and dried under vacuum. The crude product was purified by washing with boiling MeOH (70 mL) added dropwise. The undissolved portion was filtered and washed with a further 70 mL increment of boiling MeOH. The undissolved portion was filtered, dried and analyzed. This was repeated four times before the product was pure. The final product was a blue amorphous powder collected in 97% yield (481.0 mg), $T_d = 271$ °C.

2a: ^1H NMR (DMSO- d_6 , 400 MHz): δ 0.83 (m, 3H), 1.24 (m, 10H), 1.89 (m, 2H), 4.48 (t, 2H, $J = 7.2$ Hz), 6.84 (d, 2H, $J = 8.6$ Hz), 7.56 (d, 2H, $J = 8.5$ Hz), 7.83 (s, 1H), 8.29 (d, 2H, $J = 6.4$ Hz), 8.95 (d, 2H, $J = 6.6$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 13.9, 22.0, 25.4, 28.2, 28.4, 30.4, 31.1, 59.9, 116.8, 118.4, 119.6, 121.0, 123.1, 125.1, 125.5, 127.4, 144.2, 147.1, 149.5; MS (EI, m/e) 382 ($\text{M}^{+\bullet}$); IR (KBr, cm^{-1}): 2132, 2175 ($\text{C}\equiv\text{N}$), 1637 ($\text{C}=\text{N}$), 1606, 1578 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 654$ nm.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

N-octyl-4-pyridinium bromide (2.593 mmol), LiTCNQ (2.593 mmol) and DBU (0.259 mmol) were reacted in the same manner as above, only the amounts of starting materials were changed. The reaction was stopped after 25 hours and the product was purified once by washing with boiling MeOH as above. The final product was an amorphous blue-purple powder in 24% yield (237.4 mg).

2a: ^1H NMR (DMSO- d_6 , 400 MHz): δ 0.84 (m, 3H), 1.28 (m, 10H), 1.90 (m, 2H), 4.48 (t, 2H, $J = 6.9$ Hz), 6.86 (d, 2H, $J = 8.3$ Hz), 7.57 (d, 2H, $J = 8.3$ Hz), 7.84 (s, 1H), 8.30 (d, 2H, $J = 6.3$ Hz), 8.96 (d, 2H, $J = 6.4$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 13.9, 22.0, 25.4, 28.3, 28.4, 30.4, 31.1, 60.0, 116.8, 118.5, 119.6, 121.1, 123.1, 125.1, 125.6, 127.5, 144.2, 147.1, 149.5; MS (SI, 1:1 MeCN:MeOH, m/e) 383 ($M + H$) $^+$; IR (KBr, cm^{-1}): 2123, 2172 ($\text{C}\equiv\text{N}$), 1640 ($\text{C}=\text{N}$), 1604, 1570 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 655$ nm.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

N-octyl-4-pyridinium bromide (2.511 mmol), LiTCNQ (2.511 mmol) and DBU (5.023 mmol) were reacted in the same manner as above. Within only 2.5 hours the chromophore started to form but then decomposed fully. UV-vis absorption spectra showed the appearance and disappearance of the peak at 654 nm, leaving residual LiTCNQ and a large peak at 490 nm. No chromophore could be isolated.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

N-octyl-4-pyridinium bromide (1.689 mmol), LiTCNQ (3.377 mmol) and DBU (1.689 mmol) were reacted in the same manner as above. The reaction was stopped after 18 hours and the product was purified once by washing with boiling MeOH as above. The final product was an amorphous blue powder in 62% yield (397.1 mg).

2a: ^1H NMR (DMSO- d_6 , 400 MHz): δ 0.84 (t, 3H, J = 6.8 Hz), 1.25 (m, 10H), 1.91 (m, 2H), 4.48 (t, 2H, J = 7.3 Hz), 6.85 (d, 2H, J = 8.9 Hz), 7.57 (d, 2H, J = 8.9 Hz), 7.82 (s, 1H), 8.29 (d, 2H, J = 6.9 Hz), 8.95 (d, 2H, J = 7.0 Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 13.9, 22.0, 25.4, 28.3, 28.4, 30.4, 31.1, 60.0, 116.8, 118.5, 119.6, 121.1, 123.1, 125.1, 125.6, 127.5, 144.2, 147.1, 149.5; MS (SI, 1:1 MeCN:MeOH, m/e) 383 ($M + H$) $^+$; IR (KBr, cm^{-1}): 2131, 2173 ($\text{C}\equiv\text{N}$), 1637 ($\text{C}=\text{N}$), 1604, 1569 ($\text{C}=\text{C}$); UV-vis (DMF) λ_{max} = 655 nm.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

N-octyl-4-pyridinium bromide (1.178 mmol), neutral TCNQ (2.356 mmol) and DBU (2.356 mmol) were reacted in the same manner as above. The reaction was stopped after 18.5 hours and the product was purified once by washing with boiling MeOH as above. The final product was an amorphous blue powder in 34% yield (150.9 mg).

2a: ^1H NMR (DMSO- d_6 , 400 MHz): δ 0.85 (t, 3H, J = 6.9 Hz), 1.26 (m, 10H), 1.90 (m, 2H), 4.48 (t, 2H, J = 7.4 Hz), 6.85 (d, 2H, J = 8.7 Hz), 7.57 (d, 2H, J = 8.7 Hz), 7.84 (s, 1H), 8.29 (d, 2H, J = 6.6 Hz), 8.95 (d, 2H, J = 6.7 Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 13.9, 22.0, 25.4, 28.3, 28.4, 30.4, 31.1, 60.0, 116.8, 118.5, 119.6, 121.0, 123.1, 125.1, 125.5, 127.4, 144.2, 147.1, 149.5; MS (SI, 1:1 MeCN:MeOH, m/e) 383 ($M + H$) $^+$; IR (KBr, cm^{-1}): 2130, 2172 ($\text{C}\equiv\text{N}$), 1637 ($\text{C}=\text{N}$), 1604, 1582 ($\text{C}=\text{C}$); UV-vis (DMF) λ_{max} = 654 nm.

Z- β -(1-Octyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2a).

N-octyl-4-pyridinium bromide (1.188 mmol), LiTCNQ (1.188 mmol), neutral TCNQ (1.188 mmol) and DBU (2.377 mmol) were reacted in the same manner as above. The reaction was stopped after 16 hours and the product was purified once by washing with

boiling MeOH as above. The final product was an amorphous blue powder in 50% yield (230.9 mg).

2a: ^1H NMR (DMSO- d_6 , 400 MHz): δ 0.83 (m, 3H), 1.25 (m, 10H), 1.92 (m, 2H), 4.48 (t, 2H, $J = 6.7$ Hz), 6.85 (d, 2H, $J = 8.6$ Hz), 7.57 (d, 2H, $J = 8.5$ Hz), 7.84 (s, 1H), 8.29 (d, 2H, $J = 6.4$ Hz), 8.95 (d, 2H, $J = 6.5$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 14.0, 22.0, 25.4, 28.3, 28.4, 30.4, 31.1, 60.0, 116.8, 118.5, 119.6, 121.1, 123.2, 125.2, 125.6, 127.5, 144.2, 147.1, 149.5; MS (SI, 1:1 MeCN:MeOH, m/e) 383 ($M + H$) $^+$; IR (KBr, cm^{-1}): 2132, 2174 ($\text{C}\equiv\text{N}$), 1637 ($\text{C}=\text{N}$), 1607, 1579 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 654$ nm.

Z- β -(1-Hydroxypropyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2b).

LiTCNQ (7.10 mmol) and N-(3-hydroxypropyl)-4-pyridinium bromide (7.10 mmol) were dissolved in 100 mL of MeCN in a round-bottomed flask flushed with nitrogen. Once reflux temperature was reached, 1-(2-hydroxyethyl)piperidine (11.296 mmol) was added to the mixture. The reaction was stopped after 20 hours, the reaction was stopped and the crude precipitate was filtered and recrystallized from MeCN. The final product was a blue amorphous powder in 30 % yield.

2b: ^1H NMR (DMSO- d_6 , 400 MHz): δ 2.1 (m, 2H), 3.5 (m, 2H), 4.5 (m, 2H), 6.8 (d, 2H, $J = 8.1$ Hz), 7.5 (d, 2H, $J = 8.0$ Hz), 7.8 (s, 1H), 8.3 (d, 2H, $J = 5.4$ Hz), 8.8 (d, 2H, $J = 5.2$ Hz); MS (SI, 1:1 MeCN:MeOH, m/e) 329 ($M + H$) $^+$; IR (KBr, cm^{-1}): 3403 (O-H), 2132, 2174 ($\text{C}\equiv\text{N}$), 1633 ($\text{C}=\text{N}$), 1604, 1565 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 650$ nm.

Z- β -(1-Hydroxyhexyl-4-Pyridinium)- α -Cyano-4-Styryldicyanomethanide (2c).

N-(6-Hydroxyhexyl)-4-pyridinium bromide (6.555 mmol) and LiTCNQ (6.555 mmol) were dissolved in 25 mL of MeCN in a 3-neck round-bottomed flask flushed with $\text{N}_2(\text{g})$. 1-(2-Hydroxyethyl)piperidine (11.296 mmol) was added and the solution was brought to

reflux. The reaction was stopped after 15 hours, the precipitate was filtered. The crude product was purified by washing with 100 mL of boiling MeOH added dropwise. The undissolved portion was filtered and a further 100 mL of MeOH was added. The product was filtered and dried under vacuum. The final product was an amorphous blue powder in 0.9% yield (21.6 mg).

2c: ^1H NMR (DMSO- d_6 , 400 MHz): δ 1.32-1.42 (m, 6H), 1.92 (m, 2H), 3.39 (m, 2H), 4.38 (m, picoline salt), 4.50 (m, 2H), 6.85 (d, 2H, $J = 8.5$ Hz), 7.57 (d, 2H, $J = 7.8$ Hz), 7.83 (s, 1H), 8.30 (d, 2H, $J = 6.1$ Hz), 8.97 (d, 2H, $J = 4.4$ Hz); MS (SI, 1:1 MeCN:MeOH, m/e) 371 ($M + H$) $^+$; IR (KBr, cm^{-1}): 3433 (O-H), 2129, 2175 ($\text{C}\equiv\text{N}$), 1637 ($\text{C}=\text{N}$), 1604, 1579 ($\text{C}=\text{C}$); UV-vis (DMF) $\lambda_{\text{max}} = 654$ nm.

4.3.2 Chromophore Decomposition in Solution.

All solution decomposition reactions were carried out using **2a** dissolved in DMF with a concentration of 4.36×10^{-4} M. UV analysis was carried out by removing approximately 0.4 mL of the reaction solution used undiluted in a quartz cuvette of 0.1 cm pathlength. The sample was replaced in the reaction vessel following each analysis.

Reaction at 125 °C, under nitrogen and in the dark (control).

Chromophore **2a** (5.9 mg) was dissolved in 35.4 mL of DMF in a 3-necked round-bottomed flask flushed with $\text{N}_2(\text{g})$ in a dark fumehood. The blue solution was heated to 125 °C and the reaction was monitored over the course of 48 hours, at which point the reaction was stopped. The final solution was dark brown/green in colour, and the UV-vis spectrum showed the decomposition peaks at 490 and 410 nm as well as a large decrease in the absorption of the chromophore peak at 654 nm.

Exposure to air.

The reaction was repeated with the system open to air, in the dark, at 125 °C using a solution of 4.4 mg of **2a** in 26.4 mL of DMF. The reaction was monitored by UV-vis over the course of 2.5 hours, at which point the reaction was complete. The final solution was orange in colour, and the UV-vis spectrum showed the complete disappearance of the chromophore peak and the decomposition peak at 490 nm.

Exposure to air.

The reaction was repeated in the same manner using 4.4 mg of **2a** in 26.4 mL of DMF. The reaction was monitored over the course of 48 hours, at which point the only remaining product by UV-vis was the 4-pyridinecarboxaldehyde derivative at 268 nm.

Exposure to light.

The reaction was repeated under nitrogen, at 125 °C and exposed to a 60 W white light lamp focused on the flask containing a solution of **2a** (6.0 mg) in 36 mL of DMF. The reaction was monitored by UV-vis over 45 hours at which time the reaction was stopped. The final solution was brown in colour. The last UV-vis spectrum showed the chromophore peak was almost completely gone, and the presence of the decomposition peaks at 490 and 410 nm.

Reaction at room temperature.

The reaction was repeated at room temperature, under nitrogen and protected from light using a solution of 6.0 mg of **2a** in 36 mL of DMF. After 4 days there was no change in the UV-vis spectra and the solution colour was still the original blue colour.

Reaction at 65 °C.

The reaction was repeated at 65 °C, under nitrogen and in the dark using a solution of **2a** (4.3 mg) in 25.8 mL of DMF. There was no change in the UV-vis spectra after 48 hours and the solution remained the original blue colour, thus the reaction was stopped.

Reaction at 80 °C.

The reaction was repeated at 80 °C, under nitrogen and in the dark using a solution of 5.3 mg of **2a** in 31.8 mL of DMF. The reaction proceeded for 48 hours, at which point the solution colour was a darker blue colour and the UV-vis spectrum showed a slight decrease in the chromophore peak as well as a small shoulder appearing at 490 nm.

Reaction at 100 °C.

The reaction was repeated at 100 °C, under nitrogen and in the dark using a solution of 4.7 mg of **2a** in 28.2 mL of DMF. After 48 hours the solution was brown in colour, the chromophore peak had decreased significantly and the decomposition peaks were present at 490 and 410 nm.

4.3.3 Solid State Chromophore Decomposition.

To study the chromophore stability in the solid state, a series of 6 films were prepared. The first 5 films (1-5) were 1% (w/w) of **2a** in poly(ether sulfone) (PES), and the last film (6) was a 100% PES film prepared in order to calibrate the UV-vis spectrophotometer for analyzing the films. A mixture of **2a** (1.0 mg) and PES (100 mg) was dissolved in DMAc (1.00 g) using a stirring bar, making a 10% (w/w) solution in DMAc. The solution was filtered through a 0.45 µm syringe filter, and 0.1 mL of the solution was cast onto each of 5 microscope slip covers. A second 10% (w/w) solution of PES (40 mg) in DMAc (400 mg) was dissolved, filtered and 0.1 mL of the solution was cast on a

microscope slip cover in the same manner. The films were dried for 24 hours on a temperature-controlled hotstage flushed with $N_2(g)$ at $40^\circ C$, then for a second 24 hour period at $80^\circ C$. The films were light blue in colour.

Film decomposition at $210^\circ C$, under $N_2(g)$ and protected from light (control).

The film (3) was tested by UV-vis for the initial absorbance value, then was placed on a controlled-heating hotstage set to $210^\circ C$, covered with a glass bell jar with $N_2(g)$ flushing through the closed system in a dark fumehood. The film was removed from the hotstage after 1 hour, analyzed by UV-vis, and was then replaced on the hotstage. The reaction was monitored over 8 hours, at which point the reaction was stopped. The final colour of the film was cyan, and the UV-vis showed a decrease in the chromophore peak around 710 nm as well as a shoulder around 500 nm.

Exposure to air.

The film (4) was tested in the same way as above at $210^\circ C$, protected from light with the system open to air. The film was monitored by UV-vis over a period of 8 hours, at which point the reaction was stopped. The final colour of the film was cyan, and the UV-vis showed a decrease in the chromophore peak around 710 nm as well as a shoulder around 500 nm.

Exposure to light.

The film (2) was tested in the same way as above at $210^\circ C$, under nitrogen with the system exposed to light from a 60W white light lamp focused on the sample. The film was monitored by UV-vis over a period of 7.5 hours, at which point the reaction was stopped. The final colour of the film was green, and the UV-vis spectra showed a significant decrease in the chromophore peak around 710 nm as well as a peak at 500 nm.

Exposure to light and air.

The film (1) was tested in the same manner described above at 210 °C, with the system open to air and exposed to light from a 60W white light lamp. The film was monitored over the course of 6.5 hours at which point the reaction was stopped. The final colour of the film was beige-brown. The final UV-vis spectrum showed the chromophore peak had almost completely disappeared as well as the decomposition peak at 500 nm.

Conclusions

The synthesis of **2a** was improved drastically by using a base, and when two molar equivalents of each LiTCNQ and DBU were used with one equivalent of the pyridinium salt (**1a**) the product was obtained in 97 % yield in only 14 hours. The stability of **2a** in solution was compromised by attack of oxygen at the allylic bridge, resulting in decomposition to the DCTC⁻ anion and most likely *N*-octyl-4-pyridiniumcarboxyaldehyde. A new derivative of **2** containing bulky groups that would protect the allylic bridge should reduce or eliminate reaction with oxygen, producing a more stable NLO chromophore. The chromophore in solution is stable in an inert atmosphere, protected from light and at temperatures below 80 °C. The chromophore doped into solid-state poly(ether sulfone) films showed a great improvement in stability to oxygen and temperature up to 210 °C, but only in the absence of white light. The stability to oxygen stems from the high density and low oxygen permeability of PES, other more permeable polymers could show very different results. The chromophore would therefore be useful in EO materials prepared from a high density polymer as long as the material were protected from white light.

Contributions to Knowledge

1. Established an efficient synthetic pathway to Z- β -(1-substituted-4-pyridinium)- α -cyano-4-styryldicyanomethanide NLO chromophores.
2. Proposed the mechanism of chromophore decomposition to α,α -dicyano-*p*-toluoylcyanide (DCTC) and *N*-octyl-4-pyridiniumcarboxaldehyde.
3. Confirmed the chromophore as having good stability to oxygen and high temperatures when doped into poly(ether sulfone), but is sensitive to white light.

Publications.

1. Zhi Yuan Wang, Naiheng Song, Andrew Beaudin and Cara Weir, Graham Cross and Marek Szablewski, "Functionalized Zwitterionic Nonlinear Optical Materials and Polymers Derived Therefrom", US and Canadian Patents (filed in March 2002).
2. Weir, C. A. M., Hadizad, T., Beaudin, A. M. R., Wang, Z. Y. "Improved Synthesis and a Decomposition Study of Optically Nonlinear Adducts of Tetracyanoquinodimethane", submitted for publication to *Tetrahedron Letters*, December 2002.
3. Wang, Z. Y., Men, L., Song, N., Beaudin, A. M. R., Weir, C. A. M., Gao, J. P., Cross, G., Szablewski, M. "Development of a New Class of Nonlinear Optical Polymers with High Electro-Optic Coefficients", submitted for publication to *SPIE Proceedings*, November 2002.
4. Andrew Beaudin, Tayebah Hadizad, David Song, Cara Weir and Wayne Wang. "Organic Nonlinear Optical Materials: Synthesis, Properties and Applications." Chemistry Research Day, Carleton University, Ottawa, Ontario, March 2002.

Appendix A. Spectra of Synthesized Reactants and Products

1a**Figure A1.** IR spectrum of **1a** (KBr) **Figure A2.** ¹H NMR spectrum of **1a** (DMSO-d₆, 400 MHz)

Figure A3. ^{13}C NMR spectrum of **1a** (DMSO- d_6 , 100 MHz)

Figure A4. Mass spectrum of **1a** (SI, m/e 206)

Figure A5. UV-vis absorption spectrum of **1a** (MeCN, $\lambda_{\text{max}} = 215, 253 \text{ nm}$)

1b**Figure A6.** IR spectrum of **1b** (neat) **Figure A7.** ¹H NMR spectrum of **1b** (DMSO-d₆, 400 MHz)

Figure A8. ^{13}C NMR spectrum of **1b** (DMSO- d_6 , 100 MHz)

Figure A9. Mass spectrum of **1b** (SI, m/e, 152)

1c**Figure A10.** IR spectrum of **1c** (neat) **Figure A11.** ¹H NMR spectrum of **1c** (DMSO-d₆, 400 MHz)

Figure A12. ^{13}C NMR spectrum of **1c** (DMSO- d_6 , 100 MHz)

Figure A13. Mass spectrum of **1c** (SI, m/e 194)

LiTCNQ**Figure A14.** IR spectrum of LiTCNQ (KBr) **Figure A15.** ¹H NMR spectrum of LiTCNQ (DMSO-d₆, 400 MHz)

Figure A16. Mass spectrum of LiTCNQ (EI, m/e 204)

Figure A17. UV-visible absorption spectrum of LiTCNQ (DMF)

2a**Figure A18.** IR spectrum of **2a** (KBr) **Figure A19.** ¹H NMR spectrum of **2a** (DMSO-d₆, 400 MHz)

Figure A20. ^{13}C NMR of **2a** (DMSO- d_6 , 100 MHz)

Figure A21. Mass spectrum of **2a** (EI, m/e 382)

Figure A22. UV-vis absorption spectrum of **2a** (DMF, $\lambda_{\text{max}} = 654$ nm)

2b**Figure A23.** IR spectrum of **2b** (KBr) **Figure A24.** ¹H NMR spectrum of **2b** (DMSO-d₆, 400 MHz)

Figure A25. ^{13}C NMR spectrum of **2b** (DMSO- d_6 , 100 MHz)

Figure A26. Mass spectrum of **2b** (SI, m/e 327)

Figure A27. UV-vis absorption spectrum of **2b** (DMF, $\lambda_{\text{max}} = 651 \text{ nm}$)

Appendix B. Spectra from Solution Decomposition Studies

Figure B1. UV-vis absorption spectra of **2a** decomposing over time at 125 °C, in the dark, under nitrogen (DMF, 4.36×10^{-4} M, control reaction, monitored over 48 hours).

Figure B2. UV-vis absorption spectra of **2a** decomposing upon exposure to air, heated for a period of a) 0 min.; b) 50 min.; c) 90 min.; d) 120 min.; (e) 145 min.

Figure B3. UV-vis absorption spectra of **2a** decomposing over time exposed to white light, under nitrogen at 125 °C (over 45 hours).

Figure B4. UV-vis absorption spectra of **2a** over time at 25 °C, protected from light, under nitrogen (over 4 days).

Figure B5. UV-vis absorption spectra of **2a** over time at 65 °C, protected from light, under nitrogen (over 48 hours).

Figure B6. UV-vis absorption spectra of **2a** over time at 80 °C, protected from light, under nitrogen (over 48 hours).

Figure B7. UV-vis absorption spectra of **2a** decomposing over time at 100 °C, under nitrogen and protected from light (over 48 hours).

Appendix C. Spectra from Solid-State Decomposition Studies

Figure C1. UV-vis absorption spectra of a 1 % film of **2a** in PES at 210 °C, under nitrogen and in the dark (over 8 hours).

Figure C2. UV-vis absorption spectra of a 1 % film of **2a** in PES at 210 °C, protected from light and exposed to atmospheric oxygen (over 8 hours).

Figure C3. UV-vis absorption spectra of a 1 % film of **2a** in PES decomposing in the presence of light (over 8 hours).

Figure C4. UV-vis absorption spectra of a 1 % film of **2a** in PES decomposing in the presence of light and oxygen (over 8 hours).