Photochemistry And Applications Of Diels-alder Adducts And Photoacids In Materials Science

2012

Valentine Johns
University of Central Florida

STARS Citation

http://stars.library.ucf.edu/etd/2496

This Doctoral Dissertation (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
PHOTOCHEMISTRY AND APPLICATIONS OF DIELS-ALDER ADDUCTS AND PHOTOACIDS IN MATERIALS SCIENCE

by

VALENTINE KEVIN JOHNS
B.S. Pune University, 2003
M.S. Pune University, 2005
M.S. University of Central Florida, 2012

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

Fall Term
2012

Major Professor: Yi Liao
ABSTRACT

In chapter I Photo-retro-Diels-Alder (PrDA) reactions of a variety of Diels Alder (DA) adducts were studied. Experimental results showed that the photoreactivity (quantum yield) depends on the electron-donating ability of the diene component and the electron-withdrawing ability of the dienophile component. The mechanism was studied by trapping the reaction intermediate, $O_2$ quenching and femtosecond time-resolved absorption spectroscopy. All the results support a mechanism that involves a charge-separated intermediate generated from a singlet excited state. The PrDA reaction may find applications in photoresponsive materials, photolithography, drug delivery and mechanistic research.

Chapter II shows two applications of the PrDA reaction. The first, being the formation of the 2$^{\text{nd}}$-ring DA adduct together with the central-ring adduct in a reaction of pentacene and tetracyanoethylene (TCNE) at room temperature. DFT calculations showed that the difference between the free energy of the two isomers is about 3.9 kcal/mol. Photo- and thermally induced isomerization between the central-ring adduct and the 2$^{\text{nd}}$-ring adduct were studied in solutions and in polymer films. In solution, the less stable 2$^{\text{nd}}$-ring adduct can be completely converted to the more stable central-ring adduct either thermally or photochemically, but the reverse transformation does not occur. In a polymer matrix, isomerization can be photochemically induced in both directions at different wavelengths, which results in a photoswitchable system. Formation of pentacene in the photochemical experiments was also observed, which supports an isomerization process involving a photo-retro-Diels Alder (PrDA) reaction.
The second application was the design and synthesis of a polymer with an anthracene diketone moiety which could undergo a PrDA reaction which should result in significant conductivity changes. Although the synthesis of this type of polymer was unsuccessful during this study, we still believe in the theoretical soundness of the synthesis and utility of this type of polymer.

Chapter IV undertakes the study of a class of photoacids which are based on a merocyanine core. These photoacids have been studied and characterized using UV-Vis spectroscopy and the pH of two photoacids have been shown to decrease by 2.0 units upon irradiation with blue light. In addition, the relaxation times of these photoacids have been studied in water and ethanol. We have taken one step further and synthesized and characterized three polymers which have a photoacid moiety in them. These polymers respond to visible light reversibly in solution and in solid state.
To my wife, Jaime, my parents, my sister and my brother without whose endless support and love this would not have possible.
ACKNOWLEDGMENT

I would like to extend my deep gratitude to my research advisor, Dr. Yi Liao. Never once has he turned me away; he has always been kind, thoughtful and accommodating. I remember when I had just joined his group, even when I asked the silliest questions he would be patient and explain things to me in great detail. Also, many reaction techniques were new to me and sometimes he would show me how to do things himself. There were countless times that I knocked on his door to ask his expert opinion and he would leave whatever he was doing and tend to my needs. In addition, Dr. Liao has been a great mentor, even at times when I needed his advice on personal matters. His patience and understanding have kept me from leaving my PhD program multiple times out of sheer frustration. His positive attitude and drive for doing research (even in times of adversity) have taught me to be positive and have a continued interest in academia.

I deeply appreciate my wife, Jaime for all her support during my studies. She has taken the time out of her busy schedule countless times to help me with my research, teaching, grading and even proof reading my manuscripts. Her wise words and objective insight have helped me immensely. She truly is the most understanding partner and friend; especially with me working evenings, nights and weekends to make finances as well as studies come to fruition on time. She has made my existence worthwhile with her endless love and I can only love her more deeply in return.

I would also like to extend my deep gratitude to Ruhai Tian, the post doctoral scholar who helped me with my experiments during the first couple of years in the program. Also, David
Richardson, the NMR specialist who taught me so much. They had nothing to gain by helping me.

I would like to thank the members of our group, past and present, who made my experience in the lab a pleasurable one. Zheng Shi, Daniel Rosenberg, Matthew McInnis, Candace Alber, Joe Dejesus, Sarah Lefave and Chris Ramirez are but a few names who have enriched my life as a graduate student.

I deeply appreciate my committee members who provided me with their experienced insight as well as questions, which made me think about problems in research more rationally. I would like to thank Dr. Miles in particular for being a friendly person who provided me with good advice and encouraging words when I needed them the most.

I would also like to thank the staff in the chemistry department; especially Maria, Lois, Mihaela, Niki and Josh. They always helped me with good advice, a smile and a helping hand.

I thank the people who work at the International Service Center and my friends who made my stay in the United States an enriching one. Their counsel and help will never be forgotten.

I would also like to acknowledge my new family (my wife’s parents and relatives) who have welcomed me into their lives with open hearts. They have always made me feel at home. I cannot thank them enough for their kindness and love.

Finally, my deepest gratitude goes to my parents who have always been supportive throughout my studies. Their words of encouragement and never-ending patience have always helped my morale. I can never repay them for their selflessness.
# TABLE OF CONTENTS

LIST OF FIGURES ............................................................................................................. xiii

LIST OF TABLES .................................................................................................................. xv

LIST OF SCHEMES ............................................................................................................ xvi

CHAPTER I: INTRODUCTION .............................................................................................. 1

  I.1 References .................................................................................................................. 8

CHAPTER II: A MECHANISTIC STUDY OF PHOTO RETRO-DIELS-ALDER REACTIONS
........................................................................................................................................... 10

  II.1 Introduction ................................................................................................................. 10

  II.2 Results and Discussion .............................................................................................. 11

  II.2.1 Synthetic Details for the Preparation of 2,6-Dimethoxyanthracene and
Tetramethyl-2,6-Diaminoanthracene .............................................................................. 12

  II.2.2 Quantum Yields ..................................................................................................... 12

  II.2.3 Electronic Effects of the Diene component ............................................................ 13

  II.2.4 Electronic Effects of the Dienophile Component ................................................... 14

  II.2.5 Determination of Structure of the Intermediate .................................................. 17

  II.2.6 Excited State Study ............................................................................................... 19

  II.3 Conclusion ................................................................................................................ 24

  II.4 References ................................................................................................................ 25

CHAPTER III: APPLICATION OF THE PRDA REACTION IN PHOTOSWITCHING IN
SMALL MOLECULES AND POLYMERS ........................................................................... 27

  III.1 Introduction .............................................................................................................. 27

  III.2 Results and Discussion ............................................................................................ 30

  III.2.1 Study of the Isomerization of Pentacene and TCNE DA Adducts ......................... 30
III.2.1.1 Synthesis and Analysis of DA Adducts ................................................................. 30
  III.2.1.1.1 NMR Analysis ............................................................................................... 31
  III.2.1.1.2 UV-Vis Analysis .......................................................................................... 32
III.2.1.2 Theoretical Studies ................................................................................................. 34
III.2.1.3 Photochemical Isomerization in Solution ................................................................. 34
III.2.1.4 Photo- and Thermally Induced Isomerisation in Polymer Thin Films ............... 35
III.2.1.5 Photo-Switching Cycles in Thin Films .................................................................. 36
III.2.2 Design and Attempted Synthesis of a Polymer which undergoes a PrDA Reaction
  with Change in Conductivity .......................................................................................... 38
   III.2.2.1 Synthesis of Anthracene Diketone Moiety ......................................................... 39
   III.2.2.2 Synthesis of the Tetrathiophene Monomer ......................................................... 42
   III.2.2.3 Attempted Synthesis of Polymer 2 .................................................................. 43
   III.2.2.4 Synthesis of Polymer 3 .................................................................................... 44
III.3 Conclusion .................................................................................................................... 45
III.4 References .................................................................................................................... 46

CHAPTER IV : SYNTHESIS AND CHARACTERIZATION OF PHOTOACIDS WITH
TUNABLE PROTON RELEASE RATES AND THEIR INCORPORATION IN POLYMERS 49

IV.1 Introduction ..................................................................................................................... 49
IV.2 Discussion of Previous Studies ......................................................................................... 50
IV.3 Synthesis of Photoacids ................................................................................................ 52
IV.4 Study of the Effect of Functional Groups on Photoacid Response ............................ 54
   IV.4.1 Effect of the Para Substituent ................................................................................. 54
      IV.4.1.1 UV-Vis Spectroscopic Studies ....................................................................... 54
      IV.4.1.2 pH Studies ..................................................................................................... 55
      IV.4.1.3 Hammett’s Constant and Trends ................................................................... 56
   IV.4.2 Effect of the Meta Substituent ................................................................................. 58
      IV.4.2.1 UV-Vis, pH Studies and Explanation .............................................................. 58
   IV.4.3 Solvent Studies ......................................................................................................... 59
      IV.4.3.1 Studies in Ethanol .......................................................................................... 59
IV.4.3.2 Studies in Mixtures of Ethanol and Water ......................................................... 61
IV.4.4 Kinetic Studies of Photoacids ............................................................................... 63
IV.5 Synthesis of Visible Light Responsive Reversible Photoacid Polymers .................. 65
   IV.5.1 Synthesis of Photoacid Monomer 7 ................................................................ 65
   IV.5.2 Synthesis and Characterization of Polymers ...................................................... 65
   IV.5.3 Photo-Responsiveness of Polymers ................................................................... 69
IV.6 Conclusion ............................................................................................................... 71
IV.7 References ............................................................................................................... 72

CHAPTER V : EXPERIMENTAL PROCEDURES ................................................................ 74

V.1 Instrumentation ......................................................................................................... 74
V.2 Photochemical Reaction Conditions for Pentacene/TCNE Experiments ................. 74
V.3 Synthesis and Characterization of Compounds in Chapter II .................................. 75
   V.3.1 Synthetic Procedures for DA Adducts of Maleic Anhydride and Substituted
       Anthracenes ............................................................................................................... 75
       V.3.1.1 2,6-Dibromoanthracene/Maleic Anhydride Adduct 2 ................................ 75
       V.3.1.2 2,6-Dimethylantracene/Maleic Anhydride Adduct 3 ............................... 76
       V.3.1.3 Tetramethyl-2,6-Diaminoanthracene/Maleic Anhydride Adduct 4.......... 76
       V.3.1.4 2,6-Dimethoxyanthracene/Maleic Anhydride Adduct 5 ...................... 76
   V.3.2 : Synthesis of N-methylmaleimide/Anthracene DA Adduct (7) ....................... 76
   V.3.3 : Synthesis of N-methylmaleimide/2,6-Dimethoxyanthracene DA Adduct (9) ... 77
   V.3.4 : Synthesis of Acrylonitrile/2,6-Dimethoxyanthracene DA Adduct (10) .......... 78
   V.3.5 : Synthesis of TCNE/Naphthacene Adduct (11) .............................................. 78
   V.3.6 : Characterization of Products after Irradiation of 12 ..................................... 79
V.4 Synthesis and Characterization of Compounds in Chapter III .................................. 79
   V.4.1 Synthesis of Central-Ring Pentacene/TCNE Adduct (1) ................................. 80
   V.4.2 Synthesis of Isomeric Mixture (1+2) ................................................................. 80
   V.4.3 Synthesis and Characterization of 5 ................................................................... 80
       V.4.3.1 Synthesis and Characterization of 2,6-Dibromo-9,10-dimethoxyanthracene .. 80
       V.4.3.2 Synthesis and Characterization of 2,6-Dibromo-9,10-dioctyloxyanthracene .. 81
LIST OF FIGURES

Figure I-1: Modified Jablonskii diagram showing the physical processes following excitation of a molecule. Radiative processes are shown by straight lines, radiationless processes by wavy lines. IC = Internal conversion, ISC = Intersystem crossing, vc = vibrational cascade, \( h\nu = \) absorbance, \( h\nu_f = \) fluorescence, \( h\nu_p = \) phosphorescence, \( S_0 = \) singlet ground state, \( S_1 = \) first singlet excited state, \( S_2 = \) second singlet excited state and \( T_1 = \) first triplet excited state. .........................................2

Figure II-1: Structures of the studied DA adducts. .................................................................................11

Figure II-2: UV absorption change during photo-irradiation of TCNE/anthracene adduct (6). (The linear relationship shown in the inserted figure indicates a “total absorption” condition in the early stage of the reaction, during which period the quantum yield can be calculated with chemical actinometry.) .................................................................................................................................15

Figure II-3: Proof of absence of triplet state participation in the PrDA reaction of TCNE/napthacene DA adduct 11.................................................................................................................20

Figure II-4: Absorption difference spectra obtained from the pump-probe spectrometry of 11 (left) and the biexponential decay of the absorption at 580 nm (right)......................................................21

Figure II-5: Time-resolved fluorescence spectra of 11 (left) and the exponential decay of the fluorescence (right). ............................................................................................................................................23

Figure III-1: \(^1\)H NMR spectra of (A) isomeric mixture of DA adducts of pentacene and TCNE and (B) the central-ring DA adduct of pentacene and TCNE.................................................................32

Figure III-2: UV-Vis spectra of mixture of 1 and 2. The inset shows the absorption of the anthracene moiety in 2 ...............................................................................................................................................33

Figure III-3: UV-Vis spectra of 1 ..................................................................................................................33
Figure III-4: Irradiation of a PMMA film doped with 1 at 254 nm for 5 min showing the formation of 2 in the UV-Vis spectrum. ..........................................................36

Figure III-5: UV-Vis spectra of a PMMA film doped with the isomeric mixture when the film was irradiated at 365nm and 254nm alternatively. The inset shows the absorption of pentacene formed during the experiment. ..................................................................................37

Figure IV-1: UV-Vis spectrum of 1..................................................................................52

Figure IV-2: Photoacids synthesized and studied...........................................................53

Figure IV-3: UV-Vis spectra of 5 before and after irradiation........................................55

Figure IV-4: Cycles of reversibility of pH of compound, 5 after irradiation at 470 nm for 40 seconds followed by recovery in the dark for 2 minutes..........................................................56

Figure IV-5: Solution of photoacid 6 in ethanol before irradiation at 470 nm (left) and after irradiation (right)........................................................................................................60

Figure IV-6: Cycles of reversibility of 6 in ethanol. Each irradiation was 5 minutes long and followed by a relaxation time of 1.5 hours. The electrode was not calibrated here. ............61

Figure IV-7: UV-Vis spectra of 6 showing the formation of MEH after irradiation (Initial concentration of 6 was 1.3 × 10^{-4} M. A scan was run every 5 minutes after irradiation) ........64

Figure IV-8: pMEH28M72 irradiated in solution..................................................................69

Figure IV-9: Cycles of irradiation of a film of pT18MEH22M50P10. .................................71
LIST OF TABLES

Table II-1: Quantum yields and Hammett para substituent constants of the DA adducts of substituted anthracenes and maleic anhydride.................................................................14

Table II-2: Quantum yields of the DA adducts studied to understand the electronic effects of the dienophile. .......................................................................................................................................16

Table IV-1: Hammett’s para substituent constants, pKₐ’s and photoactivity of para substituted photoacids ..................................................................................................................57

Table IV-2: Comparison of Hammett’s constants of meta substituted photoacids and their trends in photoactivity. ......................................................................................................59

Table IV-3: Comparison of irradiation and relaxation times of photoacid 6 in different combinations of ethanol and water. ........................................................................................................62

Table IV-4: Comparison of dissociation and re-association times of photoacids, 1, 5 and 6 and their Hammett para constants. These values are approximate and measured in ethanol. ........63

Table IV-5: Half-lives of photoacids 1, 5, 6 and 7. ...............................................................................................................................64
LIST OF SCHEMES

Scheme I-1: General DA reaction between anthracene and maleic anhydride and the rDA reaction of the adduct. The red bonds in the adduct will cleave during the rDA process. .................4
Scheme I-2: Photoacid 1 designed by our group showing its reversibility (above) and the role of the photoacid as a catalyst in an esterification reaction (below). .................................................7
Scheme II-1. Synthesis of 2,6-dimethoxy and tetramethyl-2,6-diaminoanthracene..................13
Scheme II-2: Trapping the charge-separated intermediate in the PrDA reactions of 11 and 12…18
Scheme II-3 Proposed mechanism of the PrDA reaction of 11.................................................24
Scheme III-1: Isomers of the DA adducts of pentacene and tetracyanoethylene undergo photo-isomerization back and forth with different wavelengths of light.................................28
Scheme III-2: A general DA reaction of pentacene with a dienophile to generate the central-ring and second-ring adduct.........................................................................................29
Scheme III-3: Reaction of pentacene and TCNE. (only 1 is formed in refluxing toluene while 1 and 2 are formed at room temperature).............................................................................31
Scheme III-4: Photo-decarbonylation of acene diketones.36 ......................................................38
Scheme III-5: Proposed polymer that can change its conductivity on irradiation with visible light. ...........................................................................................................................................39
Scheme III-6: Attempted synthesis of 8.......................................................................................40
Scheme III-7: Synthetic route to 9.............................................................................................41
Scheme III-8: Synthetic route to 16 ...........................................................................................42
Scheme III-9: Attempted synthesis of polymer 2........................................................................43
Scheme III-10: Synthesis of polymer 3.....................................................................................45
Scheme IV-1: Photoacid, 1 showing the generation of a proton upon irradiation .....................49
Scheme IV-2: Proposed mechanism of proton dissociation and re-association of photoacids. ....51
Scheme IV-3: General reaction scheme for synthesis of photoacids ....................................53
Scheme IV-4: Probable formation of a high energy spiropyran intermediate .......................57
Scheme IV-5: Proposed resonance form for photostability of 4 ........................................59
Scheme IV-6: Synthesis of pMEH28M72 ........................................................................66
Scheme IV-7: Synthesis of pMEH14M77P9 ......................................................................67
Scheme IV-8: Synthesis of pT18MEH22M50P10 .................................................................68
Scheme V-1: Synthesis of 7 .............................................................................................88
CHAPTER I: INTRODUCTION

Even though the sun’s energy has been harvested since ancient times, today’s “energy crisis” has driven scientists to develop new and more efficient ways to harness this energy. With the exponential growth of science, man has a better understanding of the fundamentals of solar energy. This can be evidenced by evolving technologies like photovoltaics, solar heating and solar thermal electricity which promise a cheaper, cleaner and greener source of energy. In fact, the Obama administration recently announced the first comprehensive plan in America to harvest solar energy on public land thereby promising enough power to over seven million homes over the next decade.\textsuperscript{1} The US has also aided a project for providing electricity to villagers in Pakistan using solar energy.\textsuperscript{2}

Researchers have put a lot of effort into effectively utilizing light energy to control the outcome of chemical reactions. This is of significant importance because key processes involve photochemistry. For example, one of the most fundamental processes in plants, photosynthesis, uses solar energy to convert carbon dioxide and water into glucose. Also, a photochemical reaction of rhodopsin is responsible for vision.\textsuperscript{3} Photochemical processes like these have made the study of photochemistry very interesting. This has resulted in many articles and books that provide an endless labyrinth of information about photo-processes. Photochemistry of organic compounds has been studied extensively due to its potential for use in materials, the biological
sciences and organic synthesis. It is therefore important to understand the processes a molecule undergoes upon excitation by light.

Figure I-1: Modified Jablonskii diagram showing the physical processes following excitation of a molecule. Radiative processes are shown by straight lines, radiationless processes by wavy lines. IC = Internal conversion, ISC = Intersystem crossing, vc = vibrational cascade, hv = absorbance, hv$_f$ = fluorescence, hv$_p$ = phosphorescence, S$_0$ = singlet ground state, S$_1$ = first singlet excited state, S$_2$ = second singlet excited state and T$_1$ = first triplet excited state.
Irradiation of a molecule enables it to absorb energy and go from a ground state to an electronically excited state, after which, it can undergo many physical processes to lose that energy which are described adequately by the Jablonskii diagram above.

Alternative to these processes, the molecule might undergo a photochemical reaction if the incident radiation is more than the dissociation energy of a bond. For example, a wavelength of 300 nm corresponds to an energy of approximately 399 kJ/mol. This is well above the energy needed for bond cleavage. Irradiation can also promote electrons to anti-bonding orbitals in the excited state which allows for reaction pathways that are inaccessible thermally. However, irradiation of organic molecules in the UV region normally results in lack of selectivity for cleavage of bonds due the fact that the energy in this region is high enough to target most bonds in the molecule. Hence, significant work is needed to design molecules which can selectively absorb energy at longer wavelengths. This would result in cleavage of only the weakest bonds (targeted bonds) thus giving photo-products in a controlled fashion.

In this thesis we have used the principles of photochemistry and applied it to study retro-Diels-Alder (rDA) reactions, ‘photo acids’ and certain cheletropic reactions.

The rDA reaction, the reverse of the Diels-Alder (DA) reaction is almost a century old now. Researchers have found innumerable ways to exploit the DA as well as the rDA reaction and many articles and reviews have been published in this area. While the mechanism for the concerted DA reaction has been well established and is in accordance with the rules put forward by Woodward and Hoffman, the mechanism of the rDA reaction continues to be the focus of research efforts. DA adducts tend to cleave their newly formed sigma bonds while undergoing
the rDA process. Kinetic studies indicate that these bonds are the weakest and bicyclic systems undergo the rDA reaction by cleaving them.\textsuperscript{6-7} For example, Figure 1 shows a well-known DA reaction between anthracene and maleic anhydride.

**Scheme I-1: General DA reaction between anthracene and maleic anhydride and the rDA reaction of the adduct. The red bonds in the adduct will cleave during the rDA process.**

The rDA reaction has been induced in a variety of different ways either thermally (heating neat or in solution, flash vacuum pyrolysis, shock tube, etc) or photochemically (direct, pulsed laser, sensitized, etc). Other methods like sonication, gamma-radiation, lewis acids and bases, etc have also been explored. Based on the reaction in question, the mechanism for this reaction can either be concerted or non-concerted. Rickborn clearly states that any broad generalization made to illustrate a ‘one fits all’ mechanism for the rDA reaction should not be made.\textsuperscript{8} It therefore makes sense that one should set up some boundaries for studying the rDA process for a certain class of reactions and then attempt to propose a mechanism for that particular kind of rDA reaction.

With this in mind we decided to study the photochemically induced rDA reaction of DA adducts of acenes with various dienophiles. Using light to affect the rDA process provides spatial and temporal control. The photo- retro-Diels-Alder (PrDA) reaction although reported in literature,\textsuperscript{9-12} has great potential that is yet to be exploited. Although many researchers have used the
thermal rDA reactions, few have used PrDA reactions and not much work has been put in to study the mechanism for this reaction or propose any kind of relationship between the structure of these adducts and their reactivity. There is no guide that one can use to predict the feasibility of a particular PrDA process. The first chapter of this dissertation presents a detailed study of the PrDA reaction of DA adducts of acenes and different dienophiles along with the proposed mechanism of this reaction. The aim of this study is to provide a tool to researchers who want to use this reaction to design photo-responsive materials. Once this study was complete, naturally, the next step was to apply the PrDA reaction to materials that can possibly switch their properties on irradiation. The design of photo-switchable electronics and photo-patternable materials was therefore our next focus.

The importance of organic electronic devices has expanded vastly over the last 20 years leaving us in the middle of an evolutionary process which promises a great future for new materials and applications with very few of these commercialized. However, in order to increase the acceptance of organic semiconductors, new materials need to be developed with superior performance and low fabrication costs. Higher acenes like pentacene and rubrene are worthy of mention since both are widely used in the fabrication of organic thin-film transistors (OTFT) and have the highest reported values of charge carrier mobilities. The main problem with using these materials in fabricating organic devices is their poor solubility and susceptibilities to oxidation. DA adducts of these acenes are very stable in air as well as have good solubilities in organic solvents. Many researchers have taken advantage of this by using the rDA reaction which regenerates the desired acene after the fabrication process is done. For instance, Afzali and coworkers reported using a thermal rDA reaction to regenerate pentacene from its soluble DA
precursor on a thin film and constructed an OTFT which exhibited a charge carrier mobility in the saturation regime of 0.89 cm$^2$ V$^{-1}$ s$^{-1}$\textsuperscript{13}

Even though small semiconductor molecules like pentacene have shown great promise in the field of organic electronics, problems like crystal defects, presence of impurities, stacking, etc are hurdles which need to be overcome for optimum device performance. McCullough and coworkers have shown that rational design of conducting polymers like poly-3-hexylthiophene (P3HT) can be used to circumvent the problems of small molecule semiconductors. Polyaniline is one of the most promising polymers, which has enormous potential for use in organic electronics. It has been shown by researchers that the rDA reaction with elimination of a small dienophile can change insulators to semi-conductors. In fact this kind of reaction can be used to design a photo-reactive polymer which can undergo the PrDA reaction to change its conductivity which might be able to make the process of microfabrication much simpler. Complex integrated circuits go through the process of photolithography up to 50 times. This can be shortened to just one time by using a polymer, which can be patterned using a laser in three dimensions. The PrDA reaction can not only be used to achieve this but the process can be spatially as well as temporally controlled. For example, Tian et al. demonstrated a 5 fold increase in conductivity of a pentacene diketone upon irradiation\textsuperscript{14}. We therefore decided to investigate the possibility of a reversible photoswitchable system based on pentacene and also investigate the synthesis of a polymer which could change from an insulator to a semiconductor upon irradiation irreversibly. The second chapter of this dissertation explores the thermal and photochemical isomerization of adducts of pentacene and tetracyanoethylene (TCNE) in order to test the possibility of a photoswitchable material (based on the PrDA and DA reaction). (See figure 2) and investigates the
possibility of using the PrDA reaction to change an insulating block co-polymer to a semiconductor by irradiating it with visible light.

The idea of using visible light to affect changes in properties of materials and polymers as well as in biological systems is very interesting. Being able to channel a ready and plentiful source of energy like visible light is ideal for this purpose. As seen in the previous paragraphs many molecules have the ability to absorb light to either break or rearrange bonds in a useful manner. Photoacids are one such class of molecules. These molecules become strong acids on irradiation. However, most of these molecules respond only to UV irradiation irreversibly and the few that do respond reversibly do not become acidic for a long enough period to affect a macroscopic event. Therefore, significant advances are needed in order to design photoacids that can respond in the visible region reversibly with minimal fatigue and become strong acids on irradiation. In fact, the realization of these molecules can be envisioned as a bridge between a photon and a proton.

**Scheme I-2: Photoacid 1 designed by our group showing its reversibility (above) and the role of the photoacid as a catalyst in an esterification reaction (below).**
With these requirements in mind, we envisioned the design of photoacid molecules that can release protons upon exposure to visible light and recapture them in the dark. This means that switching on a light will increase the acidity of the medium, while switching it off will decrease it. Recent work by our group also resulted in the design of a photoacid which can alter the pH of a solution by 2.2 units reversibly and also catalyze an esterification reaction upon irradiation by visible light.16 (see scheme 1) Spurred by these results we decided to investigate the response time, reversibility, fatigue and solvent effects on these kinds of photoacids. Furthermore, we also investigated the effects of incorporating a photoacid moiety onto a polymer backbone. Chapter four discusses the rational design and synthesis of photoacids with varying proton dissociation rates. In addition, the synthesis and characterization of three photoacid polymers have been investigated along with their potential to applications in visible light induced mechanical property changes in bulk materials.

I.1 References


CHAPTER II: A MECHANISTIC STUDY OF PHOTO RETRO-DIELS-ALDER REACTIONS

II.1 Introduction

The evolution of the retro-Diels-Alder (rDA) reaction into a powerful synthetic tool has given rise to a lot of applications in material science. DA adducts of acenes are interesting because they are non-conjugated structures which easily become conjugated by undergoing the rDA process. The rDA reaction thus can be utilized to effect significant changes in the electrical and optical properties of materials. In addition, this reaction can also be used to release ‘active small molecules’. The mechanism of the thermally induced rDA reaction is well understood. Woodward and Hoffmann proposed a set of rules, which applies to all reversible concerted thermal and photochemical process.\(^1\) These rules however, do not apply to stepwise or non-adiabatic processes, which are common to organic photoreactions. Photochemical reactions promise control in space and time for applications such as photolithography and drug delivery that require the use of strained chemicals that can be induced to undergo a favorable reaction upon irradiation. The sparsely reported photo-rDA (prDA) reaction.\(^2\)\(^-\)^\(^5\) is a reaction that if properly harnessed can provide a platform for the design of many reactive and metastable chemicals which can be made selectively responsive to different wavelengths of light. It therefore becomes essential to understand the structure/reactivity relationships that dictate favorable outcomes of prDA reactions.

This chapter undertakes the study of the structure/reactivity relationship and the mechanism of the prDA reactions in a systematic manner.
II.2 Results and Discussion

In order to understand the structure/reactivity relationship, a variety of aromatic DA adducts were chosen. Aromatic DA adducts were synthesized for two reasons; the first being that these adducts absorb significantly in the UV region of our choice (we chose 254 nm for measuring the quantum yields of these reactions) while the second reason is that the released aromatic diene from the prDA reaction can be detected even in trace amounts using UV-vis spectroscopy. The DA adducts (Figure 1) were prepared by mixing the corresponding dienophiles and aromatic dienes at room temperature or elevated temperatures. Some of the dienes were particularly problematic to synthesize and their syntheses is described in the following section. Details pertaining to specific DA adducts are given in the experimental section.

![Figure II-1: Structures of the studied DA adducts.](image-url)
II.2.1 Synthetic Details for the Preparation of 2,6-Dimethoxyanthracene and Tetramethyl-2,6-Diaminoanthracene

2,6-dimethoxyanthracene was synthesized according to scheme 1. 2,6-dihydroxyanthraquinone underwent an $S_N2$ reaction with dimethylsulfate in the presence of potassium carbonate as a base. The next step required the aromatization of the central ring. This was attempted using a refluxing mixture of zinc, ammoniumhydroxide and the quinone. However, this resulted in a mixture of products with incomplete reductions of one or both carbonyls. The separation of the desired product was problematic, hence this reaction was abandoned. The use of a refluxing aqueous mixture of zinc, sodium hydroxide as well as the quinone resulted in complete reduction of both carbonyls. (scheme 1) Tetramethyl-2,6-diaminoanthraquinone was attempted to be synthesized by an $S_N2$ reaction of 2,6-diaminoanthraquinone and methylidide with sodium carbonate as the base. This synthesis failed. So the quinone was refluxed in trimethylphosphate which gave a clean reaction. The tetra methylated quinone was then subjected to refluxing zinc and sodium hydroxide to yield tetramethyl-2,6-diaminoanthracene which was purified by column chromatography. (scheme 1)

II.2.2 Quantum Yields

Quantum yields of the DA adducts in acetonitrile were measured by chemical actinometry. The actinometer was uridine, which is hydrated under UV irradiation with a known quantum yield of 0.018 at 254 nm.$^{11,12}$ Millimolar solutions of the DA adducts were irradiated at 254 nm in an
inert atmosphere. The prDA products were analyzed by the long-wavelength UV-Vis absorption of the anthracene derivatives. An example is shown in Figure 2.

**II.2.3 Electronic Effects of the Diene component**

In order to study the electronic effects of the diene on the prDA reaction, 2,6-disubstituted anthracenes were chosen. The substituents were varied based on their electron accepting or donating abilities. (1 in Figure 1). Maleic anhydride was used as the common dienophile in this study because we found that the DA adduct of maleic anhydride and unsubstituted anthracene (1 in Figure 1) underwent the PrDA reaction with a moderate quantum yield of 0.0057 under 254 nm UV irradiation.
On introduction of electron donating substituents, the PrDA reactivity was enhanced. DA adducts of 2,6-dimethyl (3), tetramethyl-diamino (4), and dimethoxy (5) anthracenes showed quantum yields of 0.0068, 0.0157, and 0.023, respectively. The introduction of Br, a weak electron withdrawing group, made DA adduct 2 photostable. The quantum yields of the DA adducts and the Hammett para-substituent constants of the corresponding substituents are listed in Table 1. The trend of the PrDA reactivity is consistent with the trend of the Hammett substituent constants (Table 1).

Table II-1: Quantum yields and Hammett para substituent constants of the DA adducts of substituted anthracenes and maleic anhydride.

<table>
<thead>
<tr>
<th>DA adducts</th>
<th>Substituent</th>
<th>Hammett constant $\sigma_p$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Br</td>
<td>+0.232</td>
<td>$X^a$</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>0</td>
<td>0.0057 ± 0.0005</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>-0.170</td>
<td>0.0068 ± 0.0020</td>
</tr>
<tr>
<td>4</td>
<td>N(Me)$_2$</td>
<td>-0.205</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td>5</td>
<td>OMe</td>
<td>-0.268</td>
<td>0.023 ± 0.003</td>
</tr>
</tbody>
</table>

$^a$The quantum yield is too low to be measured because prolonged irradiation caused unidentified side reactions.

II.2.4 Electronic Effects of the Dienophile Component

Unsubstituted anthracene was chosen as a common diene to make DA adducts with dienophiles; acrylonitrile, N-methyl maleimide, maleic anhydride and tetracyanoethylene (TCNE). TCNE/anthracene adduct 6, underwent the prDA reaction with a quantum yield of 0.021 (Table 2). The change of absorption of 6 in the UV spectra is depicted in figure 2.
The maleic anhydride/anthracene adduct 1 underwent the prDA reaction with a quantum yield of 0.0057 which was significantly smaller than that of 6 while the N-methyl maleimide/anthracene and acrylonitrile/anthracene adducts, 7 and 8 were photostable.

Figure II-2: UV absorption change during photo-irradiation of TCNE/anthracene adduct (6). (The linear relationship shown in the inserted figure indicates a “total absorption” condition in the early stage of the reaction, during which period the quantum yield can be calculated with chemical actinometry.)
Table II-2: Quantum yields of the DA adducts studied to understand the electronic effects of the dienophile.

<table>
<thead>
<tr>
<th>DA adducts</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.021</td>
</tr>
<tr>
<td>1</td>
<td>0.0057</td>
</tr>
<tr>
<td>7</td>
<td>X&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>X&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>0.0094</td>
</tr>
<tr>
<td>10</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

<sup>a</sup>The quantum yield is too low to be measured.

The above results show that the prDA reaction is dependent on the electron donating nature of the diene component and the electron withdrawing nature of the dienophile component. If this structure/reactivity relationship is indeed the case, then DA adducts of weakly electron donating dienes may become photoactive when the dienophile is strongly electron withdrawing and vice-versa. To test this hypothesis, adducts of N-methyl-maleimide/2,6-dimethoxy-anthracene (9) and acrylonitrile/2,6-dimethoxy-anthracene (10) were synthesized and subjected to prDA reaction conditions (DA adducts of anthracene with N-methyl maleimide and acrylonitrile, 7 and 8 were previously shown to be photostable). Interestingly, these adducts 9 and 10 underwent the prDA reaction with quantum yields of 0.0094 and 0.0015.

This structure/reactivity relationship indicates that the mechanism of the prDA reaction may involve a charge separated intermediate with a positive charge stabilized on the electron-rich
diene while a negative charge is stabilized on the electron-poor dienophile. This relationship might also be the result of the relative thermal stabilities of the DA adducts due to a non adiabatic mechanism. To probe this, we compared the prDA reaction of TCNE/naphthacene (11) with that of 6. As expected, the more thermally stable 11 underwent the reaction much faster than 6 (6 decomposes slowly at room temperature) likely due to the extended aromatic character of 11 which stabilizes a positive charge in the intermediate. Moreover, conduction of the prDA reaction of 1 in dichloromethane, a less polar solvent gave a quantum yield of 0.0016 which is lower than that in acetonitrile (0.0057). A lower quantum yield in a less polar solvent indicates that the charge separated intermediate is less stabilized. Absence of a charged separated intermediate would give near identical quantum yields in both solvents irrespective of their polarity.

II.2.5 Determination of Structure of the Intermediate

A solution of 11 was prepared in large excess of methanol (25% methanol in acetonitrile) to trap the intermediate. This was irradiated and the solution was analyzed by GC-MS. Along with the expected products of the prDA reaction a peak with m/e = 259.0 showed up which is the mass of the cation resulting from fragmentation of the methanol trapped intermediate (a in scheme 2). The molecular ion peak did not shown up probably due to its low stability under the conditions of the GC-MS. Further evidence was obtained from the prDA reaction of 12, a DA adduct of TCNE and phencyclone in excess methanol. The methanol intermediate (b in scheme 2) was trapped, isolated and analyzed by $^1$H NMR.
Scheme II-2: Trapping the charge-separated intermediate in the PrDA reactions of 11 and 12.
II.2.6  Excited State Study

In order to determine if the excited states in this reaction involved a singlet or a triplet state, oxygen quenching experiments were carried out. A solution of 11 in acetonitrile was saturated with air and irradiated for 5 mins. Careful comparison of the UV spectra with that of a carefully degassed solution of 11 irradiated under identical conditions showed a slightly lower absorption of the photoproduct naphthacene than that of the degassed sample (See figure 3). Since, napthacene is known to oxidize rapidly in the presence of air it is not unreasonable to assume that some of the napthacene produced from the prDA reaction was oxidized thereby resulting in the lower absorption. Since oxygen (a triplet diradical) does not quench the reaction, therefore the prDA reaction must not involve a triplet state. Further evidence comes from the fact that DA adduct 2 was photostable which might be due to the presence of bromine which exhibits a heavy atom effect which likely favors intersystem crossing to the triplet state which would reduce prDA reactivity if it occurs from the singlet state. Therefore the intermediate must be in the singlet state.
Figure II-3: Proof of absence of triplet state participation in the PrDA reaction of TCNE/naphthacene DA adduct 11
Figure II-4: Absorption difference spectra obtained from the pump-probe spectrometry of 11 (left) and the biexponential decay of the absorption at 580 nm (right).

The excited states of 11 were further studied by femtosecond time-resolved absorption spectroscopy. The transient absorption spectra were recorded following a 266 nm excitation. Figure 4 shows the transient absorption spectra in a spectral region of 525 - 720 nm at a delay time of 3, 13, and 210 ps, respectively, after the excitation. The broad band spectra have an absorption maximum at ~610 nm with their spectral shape almost unchanged with the delay time. Figure 4 displays the corresponding kinetic decay curve probed at 580 nm. The decay process can be fit well into a biexponential decay with time constants of 8.3 ± 0.6 and 546 ± 12 ps. Previous study on the excited states in a photodecarbonylation reaction of an α-diketone, which has a structure similar to those of the DA adducts described here, showed a relaxation time of 5.4 ps for a vibrational cooling process in the S₁ state, and a lifetime of 218 ps for the S₁ state. The criteria for vibrational cooling in the S₁ state of this kind of compound is the invariance of the transient absorption spectra with the delay time. In
addition, a 12 ps time constant has also been observed in the fluorescence decay of the S\textsubscript{1} state of naphthacene, which was assigned to a vibrational cooling process\textsuperscript{16}. Therefore, we assign the two constants, 8.3 and 546 ps, to the vibrational cooling and excited-state decay of S\textsubscript{1} state, respectively. The assignment of the S\textsubscript{1} excited state was supported by time resolved fluorescence spectroscopy. Although the fluorescence is very weak, we have successfully acquired the time-resolved fluorescence spectra excited at 291 nm on a streak camera. This excitation wavelength locates at the red band side of the absorption spectrum of 11. Figure 5 shows the time-resolved fluorescence spectra at the initial time, 100 ps, and 200 ps delay after the excitation, and the kinetics of the fluorescence decay is also shown in Figure 5. Limited by the temporal resolution, the fast decay component was not observed by the streak camera, and thus the corresponding kinetics was fitted to a monoexponential decay with a time constant of 346 ± 4.3 ps. It is noteworthy that the shapes of the time-resolved fluorescence spectra are also independent of the delay time, which is similar to the time-resolved absorption spectra. In addition, the decay-time constant is close to the value obtained from the time-resolved absorption study. (The discrepancy between the two lifetimes may be due to the different fitting models used, i.e., biexponential and monoexponential models) Therefore, the fluorescence study supports that the transient absorption is from the S1 state.
Figure II-5: Time-resolved fluorescence spectra of 11 (left) and the exponential decay of the fluorescence (right).

On the basis of all the results, we propose that the mechanism of the PrDA reaction is as shown in Scheme 3. The DA adducts absorb the energy of irradiation and go to a higher excited states from which they undergo vibrational cooling to the $S_1$ state. This excited species then relaxes to the ground state, $S_0$ by undergoing bond dissociation to form a charge separated intermediate which can either reform the adduct or can undergo further dissociation to give the diene and dienophile photoproducts.
II.3 Conclusion

In conclusion a careful study of the prDA reaction of normal electron demand DA adducts was undertaken. Evidence strongly indicates that the reaction is facilitated by electron rich diene components and electron poor dienophile components. Trapping, oxygen quenching, time-resolved and fluorescence spectroscopy were used to study the mechanism of this reaction. The results of these experiments point to a charge separated intermediate arising from an excited singlet state. As was briefly mentioned in chapter 1, careful choice of
irradiation wavelengths is needed so as to avoid spectral overlap between reactants and photoproducts. Higher reaction yields might be achievable for some adducts if the wavelength of irradiation is changed. In our case 254 nm was chosen so that photoreactivites could be compared. Besides this, at 254 nm many adducts have the tendency to undergo photobleaching upon extended irradiation. A lot of these problems can be avoided by rational design of adducts which absorb in a different region of the spectrum than their products.

II.4 References


14. We understand that \( \text{N(Me)_2} \) is often deemed as a stronger electron donating group than \( \text{OMe} \). A more negative Hammett constant of \( \text{OMe} \) than that of \( \text{NMe}_2 \) may be due to partial protonization of \( \text{NMe}_2 \). Our result may be due to trace amounts of water in acetonitrile. However, through space interaction between the \( \text{NMe}_2 \) substituted anthracene and maleic anhydride during the photoreaction process may also affect the quantum yield.


CHAPTER III: APPLICATION OF THE PRDA REACTION IN
PHOTOSWITCHING IN SMALL MOLECULES AND POLYMERS

III.1 Introduction

After the success of the solution study of the PrDA reaction of DA adducts of different acenes with numerous dienophiles, we decided to test the feasibility of using the PrDA reaction in materials science. Currently, many research efforts are being put into studying the semi-conducting abilities of pentacene, one of the best organic semi-conductors.\textsuperscript{1-3} However, the fact that pentacene readily oxidizes in air along with its poor solubility in any solvent limit the widespread application of pentacene in organic semi-conductor applications. In order to combat this inherent problem, many groups have designed DA adducts of pentacene which are stable as well as very soluble in desirable solvents.\textsuperscript{4-11} These adducts readily undergo the rDA reaction to regenerate pentacene when required. Theoretical and experimental studies have shown that pentacene undergoes the DA reaction predominantly on the central ring.\textsuperscript{12-16} (See Scheme 1) For example, Mei-Fun Cheng \textit{et al.} conducted a study on the DA reactivity of pentacene and ethylene, and reported that the central -ring adduct is the most stable isomer.\textsuperscript{17} However, few studies have reported the formation of second-ring adducts of pentacene. This inspired us to probe deeper into the DA reactions of pentacene where second ring adducts formed and test the possibility of a photoswitchable system. It is therefore reasonable to propose that if the PrDA reaction can be used to regenerate high performance acenes or conjugated polymers when needed, these materials could be made to become conductive by simply switching a light on. In addition, if the process can be made reversible (a PrDA reaction followed by a fast DA reaction and vice-versa), then this reaction can be used by the material scientist to design photoswitchable systems.
responsive molecules which can change their optical and electronic properties drastically upon irradiation with different wavelengths of light. (Scheme 1)

**Scheme III-1:** Isomers of the DA adducts of pentacene and tetracyanoethylene undergo photo-isomerization back and forth with different wavelengths of light.

Realizing the potential of using the PrDA approach to design materials, which can become conjugated on photo-irradiation, we also decided to test the possibility of synthesizing polymers, which could change from insulators to semiconductors upon irradiation. Moreover, these polymers would be responsive to visible light (See Scheme 5). The design and synthesis of this type of material is discussed in the second part of the chapter.
Scheme III-2: A general DA reaction of pentacene with a dienophile to generate the central-ring and second-ring adduct.

During the course of our studies of the PrDA reaction we discovered that pentacene yields significant amounts of the second-ring DA adduct with TCNE when the reaction is carried out at room temperature. We wanted to determine what conditions influenced the formation of the second ring adduct over the central ring adduct or vice-versa. Groups that made fullerene DA adducts with pentacene reported the formation of second and fourth ring di-adducts of pentacene.\textsuperscript{18-19} Miller as well as Takahashi’s group have explored the effects of sterics on the 6,13 position of pentacene and have shown that pentacene can be made to form second ring adducts regioselectively.\textsuperscript{20-21}

These reports led us to conclude that steric hindrance plays a major role in formation of the second ring DA adduct of pentacene. However, our findings hinted at the fact that kinetics of the reaction is also key to the determination of the type of DA adduct formed. We therefore decided
to explore the photochemical and thermal isomerization of the second and central ring DA adducts of TCNE and pentacene by using the PrDA reaction.

III.2 Results and Discussion

III.2.1 Study of the Isomerization of Pentacene and TCNE DA Adducts

III.2.1.1 Synthesis and Analysis of DA Adducts

We first attempted to synthesize both DA adducts of TCNE and pentacene. We chose TCNE as our dienophile of choice as it has four strong electron with-drawing groups and is known to be a powerful dienophile for DA reactions with acenes.\textsuperscript{22} The central-ring adduct, 1 was easily synthesized by refluxing a 1:1 mixture of TCNE with pentacene in toluene. Filtration and extraction with acetonitrile yielded 1. Significant amounts of second-ring adduct, 2 was formed along with 1 when the reaction was conducted at room temperature. (See Scheme 3) Although many solvent systems (different combinations of dichloromethane, hexane, ethylacetate, acetonitrile, toluene) were tested to isolate 2 from the mixture, none of them could separate 1 and 2 on silica or alumina thin layer chromatography. Therefore we undertook to analyze 2 in the mixture by the differences in the UV-Vis and NMR spectra of 1 and the mixture.
Scheme III-3: Reaction of pentacene and TCNE. (only 1 is formed in refluxing toluene while 1 and 2 are formed at room temperature)

III.2.1.1.1 NMR Analysis

The peaks for the protons of 2 was carefully assigned by comparing the spectrum of the mixture with the spectra of 1 and anthracene, which is a moiety of 2 but not 1. The $^1$H NMR spectra of the 1 (see figure 1) shows an aromatic singlet at 8.09 for the second-ring protons and another singlet for the bridgehead protons at 5.27. Two aromatic multiplets show up at 7.92 and 7.62 which correspond to the protons on the aromatic rings at the ends. NMR of the mixture shows three aromatic singlets at 8.50, 8.20 and 8.09. On comparison with the spectra of 1 we can concluded that the peak at 8.50 corresponds to the protons of the central ring of the anthracene moiety in the 2 while 8.20 corresponds to the protons of the innermost ring of the anthracene moiety. Of the aromatic multiplets appearing at 8.05, 7.92, 7.66, 7.62, 7.57 and 7.52 four, viz; 8.05, 7.66, 7.57 and 7.52 were assigned to the four end ring protons of the 2. Lastly, the bridgehead protons were assigned the peak 5.19. In addition, the nitrile carbons of 1 and 2 appear at 110.78 and 110.72 ppm respectively in the carbon NMR spectra. The ratio of 1 and 2 was calculated to be 2:1 based on the integration of the peaks in the proton NMR of the mixture.
Figure III-1: $^1$H NMR spectra of (A) isomeric mixture of DA adducts of pentacene and TCNE and (B) the central-ring DA adduct of pentacene and TCNE.

III.2.1.1.2 UV-Vis Analysis

Analysis of the UV-Vis spectra of the isomeric mixture showed long-wavelength absorption maxima from 330-390 nm corresponding to an anthracene moiety in figure 2. This was an indication that the second-ring adduct, 2 had formed. This absorption is practically absent in the spectrum of 1 in figure 3.
Figure III-2: UV-Vis spectra of mixture of 1 and 2. The inset shows the absorption of the anthracene moiety in 2.

Figure III-3: UV-Vis spectra of 1.
III.2.1.2 Theoretical Studies
To gain insight into the formation of 2, we conducted a theoretical study on the relative stabilities of 1 and 2. Minimum energy structures of the two isomers (1 and 2) were located using the DFT method B3LYP in conjunction with a 6-311+G (d, p) basis set. Subsequent frequency calculations at the same level were performed to obtain zero-point energy and thermal corrections to total energy (at 298.15 K and 1 atm). The free energy difference between 1 and 2 was 3.90 kcal/mol. Our experimental results showed that the Diels-Alder reaction is kinetically controlled at room temperature, and thus a significant amount of the less stable isomer 2 forms. At 100 °C, according to the Boltzmann distribution, the ratio of 1 and 2 should be close to 197:1, if the thermal energy provided is higher than the energy barrier of the retro-Diels Alder reaction. This explains the predominant formation of 1 at elevated temperatures. This supported our observation that a solution of the mixture heated at 60°C did not isomerize while the same solution showed complete conversion of 2 to 1 at 110°C.

III.2.1.3 Photochemical Isomerization in Solution
According to our experiments described in chapter 2, the PrDA reactions of anthracene and napthacene DA adducts with TCNE occur with moderate quantum yields of 0.021 and 0.18 respectively. Our results suggest that the DA adduct of pentacene and TCNE should undergo the PrDA reaction with ease. Furthermore, based on the UV-Vis spectral differences of 1 and 2 (figure 2 and 3), we might be able to initiate a PrDA reaction in either direction selectively due to non-spectral overlap between both isomers. Moreover, since the DA reaction takes place even at room temperature, turning off the irradiation would involve a fast DA reaction to reform the isomers. To probe this hypothesis, we first measured the quantum yield of the PrDA reaction of 1
using the methods discussed in the previous chapter. We obtained a quantum yield of 0.019 seemed sufficient for the isomerization. Given that only 2 absorbs at 365 nm, photochemical conversion of 2 to 1 was conducted by irradiating a solution of the isomeric mixture in CDCl₃ using a 365 nm 8W UV lamp at room temperature under argon. Analysis of the NMR spectra of the solution before and after irradiation showed that the isomeric mixture was quantitatively converted to 1 after irradiation for 5 min. Since the isomerization does not occur at 60° C we safely concluded that the reaction must not be due to any photo-thermal effects. Likewise irradiation of 1 was carried out at 254 nm (Since 1 absorbs strongly at 254 nm). Interestingly, no production of 2 was observed in the NMR or the UV-Vis spectrum. In summary, in solution state, the relatively unstable second-ring adduct, 2 can be converted to the central-ring adduct 1 thermally or photochemically, but the reverse process does not occur.

### III.2.1.4 Photo- and Thermally Induced Isomerisation in Polymer Thin Films

The photo-isomerisation is solution suggests that we could test to see if we could affect isomerisation in thin films which could make these DA adducts viable candidates as photo-switchable materials. Therefore, films of the adducts in PMMA (poly-methylmethacrylate) were prepared. The thermal isomerisation was studied first. Heating a film doped with the isomeric mixture below 80° C showed no change in the composition of the mixture while raising the temperature to 100° C resulted in 2 being quantitatively converted to 1. These results were identical to our result in solution. However, when a film doped with 1 was irradiated at 254 nm, the anthracene moiety of 2 appeared in the UV-Vis spectrum. (Figure 4) As expected, when a film doped with the isomeric mixture was irradiated at 365 nm the absorption of 2 decreased however, 2 did not disappear completely even on prolonged irradiation. Both experiments
indicate that \( 2 \) is stabilized by the polymer matrix, which could be due to some local environments that favour \( 2 \). In comparison with the solution study, the greater entropy of the solvent and solute molecules likely disfavour the formation of \( 2 \) post PrDA.

![Absorbance vs Wavelength Graph](image)

**Figure III-4:** Irradiation of a PMMA film doped with \( 1 \) at 254 nm for 5 min showing the formation of \( 2 \) in the UV-Vis spectrum.

**III.2.1.5 Photo-Switching Cycles in Thin Films**

Even though more study is required to understand better what process favors the mechanism of the isomerisation in thin films, our results clearly suggest that the percentage \( 2 \) can be switched up or down by selective irradiation at 254 and 365 nm respectively. Indeed, as show in figure 5, when a PMMA film doped with the isomeric mixture was alternatively irradiated with 365 and 254 nm, the absorption was \( 2 \) reversible decreased and increased. Furthermore, we observed absorption peaks of pentacene appear in the UV-Vis spectrum.\(^{23-24}\) This observation supports the
hypothesis that a PrDA reaction followed by a fast DA reaction is involved in the isomerisation process. In addition, the tail that appears in figure 5 from 300 – 400 nm is likely due to oxidation of pentacene formed in the PrDA process. It might also benefit the reader to understand that pentacene molecules dispersed in a thin PMMA matrix have little resistance to aerial oxidation and is not known to undergo dimerization under 254 nm irradiation. (Although photoreactions were performed in a glove box filled with nitrogen, the UV-Vis spectra were taken in air.)

Figure III-5: UV-Vis spectra of a PMMA film doped with the isomeric mixture when the film was irradiated at 365nm and 254nm alternatively. The inset shows the absorption of pentacene formed during the experiment.
III.2.2 Design and Attempted Synthesis of a Polymer which undergoes a PrDA Reaction with Change in Conductivity.

Encouraged by our results we decided to explore the synthesis of a polymer which could switch on its conductivity upon irradiation.

The Strating-Zwanenburg decarbonylation reaction is a very efficient rDA reaction discovered in 1969 which was used as a tool to isolate the much elusive dimer of carbon monoxide. Even though the primary purpose of this reaction was not served, it has been exploited to synthesize acenes and higher acenes for semi-conductor applications. Neckers and coworkers studied the mechanism of this photodecarbonylation reaction and reported a quantum yield of 0.9 when the reaction was triplet sensitized with benzophenone. This efficient decarbonylation reaction (see scheme 4) and our demonstration of the photo-switchability of pentacene/TCNE DA adduct helped us envision a polymer (see scheme 5) with long alkyl chains to encourage solubility and an anthracene moiety with a diketone bridge which could undergo a PrDA (decarbonylation) reaction when required.

*Scheme III-4: Photo-decarbonylation of acene diketones.*

![Scheme III-4: Photo-decarbonylation of acene diketones.](image-url)
Scheme III-5: Proposed polymer that can change its conductivity on irradiation with visible light.

III.2.2.1  **Synthesis of Anthracene Diketone Moeity**

To achieve this, we undertook a multi-step synthesis of polymer 1. We attempted to synthesize an anthracene diketone moeity, compound 8 shown in scheme 6 which could be coupled readily by a Stille coupling to a tetrathiophene moeity to yield polymer 1. The synthesis of diketone 8 is described in scheme 6. Readily available 3 was subjected to a Sandmeyer reaction in the first step to yield crude 4 which was recrystallized in 1,4-dioxane to yield a greenish fluffy solid, 4. 4 was subjected to reduction with sodium dithionite and concomitant nucleophilic substitution with octylbromide to afford aromatized 5. Purification by silica gel chromatography afforded a bright yellow fluffy solid, 5. The next step involved a DA reaction of 5 with vinylene carbonate. This reaction surprisingly did not produce a good yield in refluxing m-xylene when the diene and dienophile were used in a 1:1 molar ratio. Using a 5 fold excess of vinylene carbonate and refluxing over a period of 48 hours yielded charry solids which were chromatographed on silica gel to yield the DA adduct 6 as a white solid. Stirring a solution of 6 in methanol, THF (tetrahydrofuran) and sodium hydroxide overnight hydrolyzed 6 which yielded an oil. Layering with hexane allowed for a white solid to precipitate which was filtered off and identified as
compound 7. 7 was subjected to a Swern oxidation to yield 8 as a crude oil. Unfortunately we could not purify 8 successfully either by column chromatography or recrystallization which resulted in us hitting a wall in our synthesis. We also tried other reagents for oxidation like, PCC (Pyridinium chlorochromate), MnO₂, IBX (2-Iodoxybenzoic acid) and DDQ (Dichlorodicyanobenzoquinone). All these resulted in the diketone bridge being cleaved and a dialdehyde being formed.

**Scheme III-6: Attempted synthesis of 8**

![Scheme III-6](image)

To understand the reason for the failure of isolation of compound 8, we decided to synthesize diketone 9. (See Scheme 7) Interestingly, 9 could be isolated using column chromatography. It is noteworthy, that 9 could be isolated only after being chromatographed twice in ether followed by
dichloromethane, Comparing the structure of 9 with that of 8 suggests that 8 should be more soluble in non-polar solvents hence more likely to co-exist with its side products thereby making isolation near impossible.

**Scheme III-7: Synthetic route to 9**

In order to continue our synthetic plan we decided to compromise on solubility of the final polymer so that we could affect a purification in the last step. Hence we undertook a similar synthesis of compound 10 an analogue of target compound 8, the only difference being that a methoxy group replaced the octyloxy group in 8. Following a similar pathway as shown in scheme 6 we ended up with an oil in the last step even after purification by chromatography. Proton NMR of the oil showed the presence of 10 along with some impurities. Hence, the oil was dissolved in dichloromethane and kept under high vacuum overnight. A fluffy orange solid resulted which was found to be pure by NMR.
III.2.2.2 Synthesis of the Tetrathiophene Monomer

Scheme III-8: Synthetic route to 16.

The second part of this project was synthesize a tetrathiophene block (16) which would ultimately copolymerized with the 10. Bithiophene, 11 was converted into a stille precursor, 12 by deprotonation with butyllithium followed by an immediate S\textsubscript{N}2 reaction of the lithiated bithiophene with tributylstannyl chloride. Meanwhile compound 13 was subjected to an electrophilic aromatic substitution with N-bromosuccinimide to introduce a bromine on the 2-position of the thiophene ring. Some problems we encountered during this reactions was that position 5 was competing for the bromine as well as a radical substitution of the side-chain was
likely. To minimize these side-reactions 13 was mixed with NBS in an equimolar ratio and stirred at room temperature in the dark for 48 hours. 14 was then isolated as a clear oil after silica gel chromatography using hexane as the eluent. 12 and 14 were then subjected to a Stille coupling to afford 15 which was purified on silica gel to yield a yellow oil which solidified in to a fluffy yellow solid on refrigeration. 15 was converted into another Stille precursor, 16 under the same conditions as 11 was converted to 12. Interestingly, 16 decomposes to 15 on silica gel and alumina thereby making it difficult to purify. However, washing with water and extraction with dichloromethane afforded 16 with reasonable purity for the next step.

III.2.2.3 Attempted Synthesis of Polymer 2

Scheme III-9: Attempted synthesis of polymer 2.
As shown in scheme 9 tetrathiophene, 16 was combined with diketone, 10 and subjected to a Stille cross-coupling. The result was an reddish intractable mixture and no purification of any sort was successful. An NMR analysis of the mixture showed the presence of a huge amounts of impurities. Moreover, an IR of the material showed no ketonic functionality indicating that the diketone did not survive the reaction conditions. Interestingly, we could not find any study stating that diketones did not survive Stille couplings. The reaction was attempted multiple times before we abandoned it. We also tried to synthesize a boronic ester as well as acid analogue of 16 but were unsuccessful, likely due to the decomposition of the boronic terathiophene during purification. Hence, a Suzuki coupling could not be attempted to make polymer 2. Various ring modifications were also carried out but none resulted in a polymer.

III.2.2.4 Synthesis of Polymer 3

Finally, we decided to synthesize a polymer without a diketone functionality using the same strategy and measure it’s properties. Since the tetrathiophene we synthesized was not of highest purity we decided to enhance the reactivity of the the anthracene monomer by replacing the bromines with iodines. As depicted in scheme 10, we used compound 3 to make compound 17 which was subsequently changed into compound 18 with ease following a similar synthesis as shown in scheme 6. 18 was then coupled with 16 to get polymer 3 as a dark red solid. Polymer 3 has a $M_n$ of 20,000. Proton NMR of polymer 3 showed that it was fairly pure. The charge carrier mobility of polymer 3 was found to be $1.22 \times 10^{-8}$ cm$^2$V$^{-1}$s$^{-1}$ using a SCLC (Space Charge Carrier Limited) technique. It is worth mentioning that this polymer had such a low mobility likely due to the impurity of the starting materials and low molecular weight. Thus, this may not be a good system for a photoswitchable material.
In conclusion, we have studied the isomerization of TCNE and pentacene DA adducts in solution and solid state. In solution, the less stable second-ring adduct is converted to the more-stable central-ring adduct photochemically as well as thermally irreversibly. In a polymer film, isomerization can be switched in both directions by photochemical means whereas thermally, isomerization occurs only from second-ring to central-ring adduct. The appearance of pentacene
is a strong indication of PrDA reaction. This study builds on the results of the previous chapter which proves that PrDA reactions can be used as a handy tool in materials science. In addition, an attempt was made to synthesize a polymer which can undergo the PrDA reaction in response to visible light irradiation. Unfortunately, this type of polymer could not be realized in our attempts. Future work might involve making a DA adduct of the polymer which can undergo an efficient PrDA reaction upon irradiation.

III.4 References


CHAPTER IV: SYNTHESIS AND CHARACTERIZATION OF PHOTOACIDS WITH TUNABLE PROTON RELEASE RATES AND THEIR INCORPORATION IN POLYMERS

IV.1 Introduction

Since the discovery of photoacids almost 40 years ago, the microelectronics industry has found great use for such compounds in photoresists.\textsuperscript{1-4} In particular, iodonium and sulfonium salts have found widespread use as photoinitiators in cationic polymerizations.\textsuperscript{5-10} However, such types of photoacids are generated only by high-energy UV irradiation, which leads to secondary reaction pathways therefore making the process irreversible.\textsuperscript{11} The reversible photoacids that are known are mostly aromatic alcohols that respond in the UV region\textsuperscript{12-13} as well (making them unsuitable for use in biological systems). Furthermore, their fast proton recapture rate inhibits the use of such photoacids as a tool to catalyze pH sensitive processes or affect bulk material properties. For optimal use in biological systems (for example; study of protein folding, liposomal drug delivery and mechanisms in confined volumes), the ideal photoacid should have a pKa > 8, should respond to a visible light source in nanoseconds and reprotonate very slowly (orders of magnitude slower).

Scheme IV-1: Photoacid, 1 showing the generation of a proton upon irradiation.
Recently, our group reported a photoacid (Photoacid, 1) that utilized an intramolecular photochromic reaction to extend the lifetime of the dissociated proton.\textsuperscript{14} Photoacid, 1 exhibited a half-life of 76s and a reversible pH change of 2.2 units (see scheme 1). It was also used to catalyze an esterification reaction and alter the volume of a pH sensitive hydrogel. These initial results encouraged us explore the structure-reactivity relationship of the photoacid. Furthermore, we decided to incorporate a photoacid moiety into a polymer and study the changes in bulk material properties upon irradiation.

**IV.2 Discussion of Previous Studies**

Previous studies indicate that photoacid, 1 releases protons according to the mechanism outlined in scheme 2.\textsuperscript{14} Irradiation with 419 nm light induces a trans to cis isomerization of. Deprotonation occurs rapidly giving rise to cis-ME via a thermal mechanism and the ring cyclizes to afford the spiropyran (SP). Inspection of the UV-Vis spectrum of 1 indicates that prior to irradiation there is some formation of a trans-ME which isomerizes on irradiation at longer wavelengths (570 nm) to yield the cis-ME as well. (See figure 1) It is unclear whether cis-ME gets deprotonated prior to ring closure or if the ring closes prior to the deprotonation.\textsuperscript{15}

Careful inspection of scheme 2 suggests that the nucleophilicity of the phenoxide (cis-ME) and the electrophilicity of the indoline are principle factors governing ring closure. Electron donors on the phenyl ring should favor the cis-MEH form over cis-ME while withdrawers should favor the phenoxide. In order to gain a better understanding, we synthesized and studied a variety of photoacids with electron donating and withdrawing groups para and meta to the OH on the benzene ring. We did not study any photoacids with ortho substituents as steric effects might complicate matters. Hence, photoacids 1 to 7 were synthesized.
Scheme IV-2: Proposed mechanism of proton dissociation and re-association of photoacids.

R = Electron donors or acceptors

trans-MEH

419 nm

cis-MEH

570 nm

Oxonium intermediate

trans-ME

cis-ME

 SP
IV.3 **Synthesis of Photoacids**

Photoacids, 1-7 (see figure 2) were synthesized. Starting material 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium was synthesized following a literature method.\(^\text{16}\) This was in turn coupled to the corresponding benzaldehyde via a dehydration reaction in refluxing ethanol to yield the corresponding photoacid (see scheme 3). Purification of the resulting compound was carried out by filtration of the precipitate and washing with cold ethanol (compound 7 was condensed in acetonitrile instead of ethanol due to unwanted hydrolysis of the ester product). This was advantageous as carrying out the same reaction in ethanol yield 4.
Figure IV-2: Photoacids synthesized and studied.

Scheme IV-3: General reaction scheme for synthesis of photoacids.
IV.4 Study of the Effect of Functional Groups on Photoacid Response

IV.4.1 Effect of the Para Substituent

First the effects of substituents para to the OH group were studied. All the compounds were soluble in water. Hence aqueous solutions of compounds, 2, 3, 5 and 6 were studied.

IV.4.1.1 UV-Vis Spectroscopic Studies

UV-Vis spectra of compounds 3, 5 and 6 showed an additional peak between 400 and 350 nm than that of the spectra of 1 and 2. (See figure 3) This is likely due to the increased tendency for formation of cis-MEH in the dark when there is an electron donor on the phenyl ring (This is not unreasonable, as the cis-MEH form should be conformationally twisted thereby resulting in a hypsochromic shift in the UV-Vis spectrum). This is corroborated by the observation that as the strength of the electron donor increases, the peak gets stronger in comparison to the trans-MEH peak. This might be explained by suggesting that the equilibrium between trans-MEH and cis-MEH is offset in the direction of cis-MEH in the dark. This could be because electron donors make the OH more nucleophilic which subsequently tends to get closer to the positive nitrogen in order to achieve greater stability hence becoming cis.

Irradiation of aqueous solutions of the photoacids revealed that 2 and 5 were photoactive, generating the SP form in less than 5 minutes (irradiation of samples were carried out in quartz cuvettes using a 470 nm LED source with power of 3 mWcm$^{-2}$ kept 3 inches away from the cuvette). Leaving them in the dark showed a complete reversal. Interestingly 3 and 6 were
photostable when irradiated for the same duration. Prolonged irradiation showed a little formation of SP, however the process was irreversible.

**Figure IV-3**: UV-Vis spectra of 5 before and after irradiation.

### IV.4.1.2 pH Studies

The pKₐ of 2 is 6.4 while that of 5 is 7.5 in the dark. This indicates that 2 is a stronger acid than 5, which is expected given the electron withdrawing nature of the nitro group in 2. Irradiation of a $3.4 \times 10^{-4}$ M solution of 2 shows a pH drop of 1.0 unit (initial pH = 4.9) while a $2.5 \times 10^{-4}$ M solution (1% DMSO in water) of 5 shows a pH drop of 2.0 units (initial pH = 6.0) on irradiation. Both compounds can undergo several cycles of pH change on irradiation, (figure 4 shows 5
undergoing cycles of pH changes), On the one hand the presence of a strong withdrawing group in 2 likely generates ME readily, prior to irradiation, which reduces the effective pH drop on irradiation while on the other hand, an electron donating methyl decreases the initial acidity of the photoacid but induces a larger pH drop on irradiation.

![pH Reversibility of 5](image)

**Figure IV-4:** Cycles of reversibility of pH of compound, 5 after irradiation at 470 nm for 40 seconds followed by recovery in the dark for 2 minutes.

### IV.4.1.3 Hammett’s Constant and Trends

Comparison with Hammett’s ($\sigma_p$) constant values, revealed that in compounds 3 and 6, OH and OMe in para positions are stronger electron donors than the methyl group. (See table 1) This makes the photoacid less acidic. Therefore, even though irradiation produces cis-MEH, it is less likely to cyclize as cis-ME is not formed. Even if cyclization does occur, a low energy oxonium
ion could form which may revert rapidly. On the other hand, this intermediate could be stabilized by strong electron donors which could push electrons towards the positive oxygen (see scheme 4). A better understanding could be had if ultrafast studies were performed on 3 and 6.

Table IV-1: Hammett’s para substituent constants, pKₐ’s and photoactivity of para substituted photoacids.

<table>
<thead>
<tr>
<th>Photoacid</th>
<th>Para group</th>
<th>pKₐ</th>
<th>σᵢ</th>
<th>Photoactive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>6.5</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>NO₂</td>
<td>6.4</td>
<td>0.78</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>-</td>
<td>-0.37</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>7.5</td>
<td>-0.17</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>OMe</td>
<td>9.0</td>
<td>-0.27</td>
<td>No</td>
</tr>
</tbody>
</table>

Scheme IV-4: Probable formation of a high energy spiropyran intermediate.
IV.4.2 Effect of the Meta Substituent

Next we decided to explore the effect of substituents meta to the OH. Compounds, 4 (meta hydroxyl) and 7 (meta acryloyl) were both found to be soluble in water.

IV.4.2.1 UV-Vis, pH Studies and Explanation

UV-Vis studies showed that 7 lacked the characteristic absorption previously absorbed in the case of para donors (between 350 – 400 nm). The pKa of 7 was 6.7 in the dark. Irradiation of a 1.4 × 10⁻⁴ M aqueous solution of 7 showed a pH drop of 1.7 units from an initial pH of 5.8. This cycle was also reversible. Surprisingly, even though the meta substituents in both compounds were withdrawing with respect to the OH that loses its proton, only 7 was photoactive while 4 was photostable. These observations suggest that the activity of the photoacids with meta substituents is dependent on a careful balance between the electron-withdrawing as well as the electron donating ability of the group at the meta position. Both groups in 4 and 7 withdraw electrons inductively making the OH acidic which is in accordance with the trend predicted by Hammett’s meta constants (σₘ).¹⁷, ¹⁸ (See table 2) Hence, in 7, the acryloyl group is more withdrawing than the OH in compound 4 making the phenolic oxygen more acidic. On the other hand, the donation of electrons by the meta OH to the positive nitrogen by resonance is far greater in 4 than the ester in 7 which is in accordance with Hammett’s para constants (σₚ). (See scheme 5) This reduces the electrophilicity of the nitrogen drastically which is why 4 is photostable.
Table IV-2: Comparison of Hammett’s constants of meta substituted photoacids and their trends in photoactivity.

<table>
<thead>
<tr>
<th>Photoacid</th>
<th>meta group</th>
<th>$\sigma_m$</th>
<th>$\sigma_p$</th>
<th>Photoactive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>0.00</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>OH</td>
<td>0.12</td>
<td>-0.37</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>OAc</td>
<td>0.38</td>
<td>0.31</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Scheme IV-5: Proposed resonance form for photostability of 4.

IV.4.3 Solvent Studies

**IV.4.3.1 Studies in Ethanol**

Wojtyk et al. showed that thermal reversion of spiropyrans to merocyanines occurs at different rates in different solvents\(^{19}\) while Keum et al. made the observation that non-polar solvents stabilize the SP form.\(^{20}\) Therefore, use of a less polar and more basic solvent like ethanol could; (i) make the phenolic oxygen more nucleophilic facilitating SP formation while (ii) the SP form should be more stable in less polar solvents therefore decreasing the rate of reversion. If the aforementioned points are valid then compounds, 3, 4 and 6 should become active in ethanol.
Therefore, an ethanolic solution of 6 was irradiated and subjected to UV-Vis analysis. Interestingly, the MEH peak in 6 disappeared after irradiation at 470 nm for 5 minutes along with a color change from orange to clear indicating formation of SP. (See figure 5) This process is reversible and it takes ~ 2 hours for the absorbance of the MEH peak to return to its initial value in the UV-Vis spectrum. This was very exciting as we learned that 6 becomes photoactive in ethanol. We proceeded to test if this change was accompanied by proton liberation. As expected, a $1.8 \times 10^{-4}$ M ethanolic solution of 6 showed a pHe (pHe = -log($\alpha_H$ in ethanol)) change of 1.6 on irradiation. This process was reversible and several cycles were performed over a week indicating unusual stability of the photoacid. (see figure 6) The pK$_a$ of 6 was also found to be 9.0. Compounds 3 and 4 were not tested. Further tests on these compounds might reveal more.

Figure IV-5: Solution of photoacid 6 in ethanol before irradiation at 470 nm (left) and after irradiation (right).
Figure IV-6: Cycles of reversibility of 6 in ethanol. Each irradiation was 5 minutes long and followed by a relaxation time of 1.5 hours. The electrode was not calibrated here.

IV.4.3.2 Studies in Mixtures of Ethanol and Water

Knowing that aqueous solutions of 6 are photostable in water (or maybe too fast) while ethanolic solutions of 6 are photoactive (the rate of reversion if relatively slower), it is not unreasonable to suggest that mixtures of ethanol and water might help tune the irradiation and relaxation times of 6. Hence solutions of 6 in different combinations of ethanol and water were irradiated and monitored by UV-Vis spectroscopy. The results are depicted in table 3.
Table IV-3: Comparison of irradiation and relaxation times of photoacid 6 in different combinations of ethanol and water.

<table>
<thead>
<tr>
<th>Ethanol (%)</th>
<th>Water (%)</th>
<th>Irradiation time (min)</th>
<th>Relaxation time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>5</td>
<td>NR (^a)</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>5</td>
<td>NR (^a)</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>5</td>
<td>NR (^a)</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>1.5</td>
<td>15</td>
</tr>
<tr>
<td>95</td>
<td>5</td>
<td>5</td>
<td>90</td>
</tr>
</tbody>
</table>

From table 3 it can be seen that as the percentage of ethanol is increased, the relaxation time (SP to MEH transformation) increases. In fact, a 30% ethanolic solution takes 2 minutes to relax as opposed to a 95% ethanolic solution which takes 90 mins. This is proof that the increased basicity of ethanol helps the oxonium intermediate form SP while the presence of electron donating groups makes the SP more nucleophilic and encourages MEH reversion by rapid proton re-association. In fact, an ethanolic solution of 5 with a weaker electron donor reverts in 6 hours while 1 with no substituents takes more than a day to revert completely. (See table 4)
Table IV-4: Comparison of dissociation and re-association times of photoacids, 1, 5 and 6 and their Hammett para constants. These values are approximate and measured in ethanol.

<table>
<thead>
<tr>
<th>Photoacid</th>
<th>Dissociation (MEH – SP)</th>
<th>Re-association (SP – MEH)</th>
<th>Hammett’s constant $\sigma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 sec</td>
<td>&gt; 24 hrs</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>5-10 sec</td>
<td>6 hrs</td>
<td>-0.17</td>
</tr>
<tr>
<td>6</td>
<td>4 min</td>
<td>2 hrs</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

**IV.4.4 Kinetic Studies of Photoacids**

Given that the photoacids show different rates for the reversion of SP to MEH, we tried to estimate the lifetime of the proton dissociated state by following the rate of formation of MEH by UV-Vis spectroscopy. A solution of the photoacid was irradiated and a scan was taken at fixed intervals during the relaxation process.(See figure 7) Due to a process being a reversible multistep one, it was not possible to fit the data into any a $0^{th}$, $1^{st}$ or $2^{nd}$ order rate law. Hence, the half-lives could only be estimated from the UV-Vis spectrum. (See table 5)
Figure IV-7: UV-Vis spectra of 6 showing the formation of MEH after irradiation (Initial concentration of 6 was $1.3 \times 10^{-4}$ M. A scan was run every 5 minutes after irradiation)

Table IV-5: Half-lives of photoacids 1, 5, 6 and 7.

<table>
<thead>
<tr>
<th>Photoacid</th>
<th>Solvent</th>
<th>Estimated half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>water</td>
<td>76 seconds</td>
</tr>
<tr>
<td>5</td>
<td>water</td>
<td>32 seconds</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol</td>
<td>29 minutes</td>
</tr>
<tr>
<td>7</td>
<td>Water</td>
<td>40 seconds</td>
</tr>
</tbody>
</table>
IV.5 Synthesis of Visible Light Responsive Reversible Photoacid Polymers

IV.5.1 Synthesis of Photoacid Monomer 7

After the observation that monomer 7 becomes a strong acid on irradiation we decided it was suitable for incorporation into polymers for testing material property changes upon irradiation. We therefore decided to graft 7 onto a polymer backbone. The next few pages describes the synthesis and testing of three random copolymers made from methyl acrylate as the principle component, photoacid 7 as the active light responsive part, triethyleneglycolmethylether acrylate to assist proton transfer and 5-thiazolemethacrylate as a weak base to induce ionic interactions.

IV.5.2 Synthesis and Characterization of Polymers

2,4-dihydroxybenzaldehyde, triethyleneglycolmonomethyl ether, and thiazole-5-methanol were esterified with acryloyl chloride to form the respective monomers according to a literature procedure.\textsuperscript{21} Polymer, pMEH28M72 (photoacid unit = 28 mol %, methylacrylate unit = 72 %) shown in scheme 6 was synthesized by reacting 4-formyl-3-hydroxyphenylacrylate with methyl acrylate using radical polymerization to form the precursor, pB28M72 (Benzaldehyde = 28 %, methylacrylate = 72%) The indolenine was then grafted on to the polymer by condensation in acetonitrile to give pMEH28M72. Likewise polymers, pMEH14M77P9 (photoacid = 14%, Methylacrylate = 77% and triethyleneglycol monomethylether acrylate = 9%) and pT18MEH22M50P10 (thiazole unit = 18 %, photoacid = 22 %, methylacrylate = 50% and triethyleneglycol monomethylether acrylate = 10%) were prepared as shown in scheme 7 and 8.
$^1$H NMR of the polymers showed that post grafting of the indolenine unit onto the benzaldehyde part of these polymers went to completion almost quantitatively and the mole percentages of the monomers in the polymers were determined by the proton ratios in the NMR spectrum. These polymers are readily soluble in acetonitrile, dimethylsulfoxide (DMSO) and N-methylpyrrolidone (NMP). GPC (gel permeation chromatography) was carried out on these polymers to reveal that $M_n$ of pMEH28M72 was 15000. $M_n$ of the other polymers were not measured.

**Scheme IV-6: Synthesis of pMEH28M72.**
Scheme IV-7: Synthesis of pMEH14M77P9.

$pMEH14M77P9$

$I = 14\%, m = 77\%, n = 9\%$

$pB14M77P9$

$I = 14\%, m = 77\%, n = 9\%$
Scheme IV-8: Synthesis of pT18MEH22M50P10.
Initially, pMEH28M72 was tested for photo-responsiveness. A solution of the polymer in 1:1 dichloromethane/ethanol solution was studied by UV-Vis spectroscopy as shown in figure 8. Irradiation with 470 nm for 5 minutes caused the solution to become clear while leaving in the dark caused the solution to regain its color in 3 hours. Several cycles of this were observed with no loss in fatigue. Films of the polymer showed a decrease of the MEH peak on irradiation however, the recovery was not good, presumably due to the poor quality and high crystallinity of the film. It is interesting that a weak electron withdrawing group on the ring actually decreases

Figure IV-8: pMEH28M72 irradiated in solution.
the relaxation time (SP – MEH) as opposed to what we previously observed. This might be due to the fact that the photoacid is a polymer and the proton is not able to drift too far away.

In order to assist proton transfer after dissociation and decrease the crystallinity of the film we decided to copolymerize triethyleneglycolmonomethylether acrylate with the aldehyde and methyl acrylate. This resulted in polymer, pMEH14M77P9 which had a lower percentage of MEH. The UV-Vis spectrum of films of this polymer showed the formation of SP upon irradiation and vice-versa in the solid state but the reversal was not good. It is likely that the poor film quality might be affecting the re-absorption of the proton.

We therefore decided to add another acryloyl monomer in the form of a thiazole acrylate which would serve two purposes. One would be that the resulting polymer would have a lower Tg while the other would be that the thiazole would function as a weak base. This would prevent the proton from drifting too far away while also helping induce ionic interactions at the same time. Hence, pT18MEH22M50P10 was prepared and films were irradiated with 470 nm and studied. UV-vis spectroscopy showed good reversibility. (See figure 9) Relaxation of the SP to the MEH form in the dark was extended to almost a day.

We finally decided to observe what would happen in a free standing film of this same material. The free standing film was a little difficult to make but seemed to respond to 470 nm irreversibly. Further work is in progress.
IV.6 Conclusion

We designed and synthesized a series of photoacids and studied their responsiveness in water and ethanol. We fully characterized these photoacids and found that their initial pKₐ’s can be raised by rational introduction of electron donors. In addition, it was observed that strong electron donors at the para position favor the MEH form hence rendering the photoacid inactive in aqueous solutions. These photoacids become active in less polar solvents like ethanol and aqueous mixtures of ethanol can be used to rationally tune the response of the photoacid. Substituents at the meta position inductively affect the acidity of the OH. If these groups are
ortho/para donors, then their ability to delocalize the positive charge on the nitrogen will determine if the photoacid will be active. A fuller understanding of the dissociative and re-associative pathways is currently underway.

We also synthesized three random copolymers with a photoacid moiety incorporated in each of them. This gives them the potential to change their properties upon irradiation with visible light. We observed some changes in the solid-state on irradiation as well. However, our understanding of this process is immature and we hope to understand these results better, which might help us design better polymers in future with faster response times and significant results.

IV.7 References


15. Later we discovered that irradiation with 470 nm (instead of 419 nm followed by 570 nm) can also achieve the same change


17. Hammett’s constants ($\sigma_m$) predict that an OAc group is more withdrawing by inductive effects than an OH. Since, the acryloyl group is structurally similar to an OAc functionality, it should be safe to assume that the effects of these groups are similar in a meta position.


CHAPTER V: EXPERIMENTAL PROCEDURES

V.1 Instrumentation
NMR (Nuclear Magnetic Resonance) spectra were recorded on a Varian VNMRS 500 MHz, a Varian Mercury 300 MHz and a Bruker AvanceIII 400 Mhz Spectrometers. IR (Infrared) spectra were obtained from a Bruker Vertex 70 ATR-IR (Attenuated Total Reflection-IR). pH measurements were done on a Fisher Scientific Accumet AR15 bench top meter and pH combination electrodes were used to measure the pH changes of photo acids. UV-vis spectra were obtained from a Varian Cary 50 Scan UV-vis spectrophotometer. Photoreactions were performed using a RPR-100 Rayonet photochemical reactor equipped with 16 lamps with variable emission wavelengths ranging from 254 nm to 570 nm. In addition, an LED (Light Emitting Diode) with an emission wavelength of 470 nm was used to irradiate the photoacids.

V.2 Photochemical Reaction Conditions for Pentacene/TCNE Experiments
Solutions (2 mg/1 mL) of Pentacene/TCNE adducts in CDCl₃ were degassed, stored in NMR tubes (quartz), and irradiated using an 8 W UV lamp with a wavelength of 365nm or 254 nm. Thin films of the adducts in PMMA were prepared by spin casting solutions of the adducts and PMMA (5 weight% of the adduct in PMMA) in acetonitrile on quartz slides. Both heating and irradiating the films were conducted in a glove box filled with nitrogen. The UV-vis spectrometer is not in the glove box and thus the UV-vis spectra were taken in air.
V.3 Synthesis and Characterization of Compounds in Chapter II

All starting materials for preparing the DA adducts were purchased and used without further purification. HPLC grade solvents were used without further purification except degassing. TCNE/anthracene (1), acrylonitrile/anthracene (8), TCNE/phencyclone (12), tetramethyl-2,6-diamino-anthracene, 2,6-dimethoxy-anthracene, 2,6-dimethyl anthracene were synthesized following literature procedures.

V.3.1 Synthetic Procedures for DA Adducts of Maleic Anhydride and Substituted Anthracenes

The substituted anthracene was mixed with 1 equivalent of maleic anhydride. The mixture was dissolved in just enough xylene and heated at 180 °C (bath temperature) for 45 min in a sealed tube under nitrogen. After cooling to room temperature, the tube was placed in an ice bath for 10 min. The precipitate was collected by filtration and then washed with a small amount of ethyl acetate and hexanes to yield the crude product. Recrystallization in toluene yielded the pure product.

V.3.1.1 2,6-Dibromoanthracene/Maleic Anhydride Adduct 2

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.55 (d, 1H, J=1.75Hz), 7.49 (d, 1H, J=1.74Hz), 7.37 (m, 2H), 7.26 (d, 1H, J=7.64Hz), 7.21 (d, 1H, J=7.94), 4.78 (m, 2H), 3.53 (m, 2H). HRMS (DART): 431.8990 (M$^+$, Expected = 431.8997), 432.9062 (M+H$^+$, Expected = 432.9075), 449.9305 (M+NH$_4^+$, Expected = 449.9340).
V.3.1.2 2,6-Dimethylanthracene/Maleic Anhydride Adduct 3

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.25 (m, 1H), 7.20 (d, 1H, J=7.41), 7.20 (m, 1H), 7.14 (m, 1H), 6.98 (m, 2H), 4.73 (m, 2H), 3.50 (m, 2H), 2.32 (s, 3H), 2.29 (s, 3H). HRMS (DART): 304.1099 (M$^+$, Expected = 304.1099), 305.1171 (M+H$^+$, Expected = 305.1178), 322.1445 (M+NH$_4^+$, Expected = 322.1443).

V.3.1.3 Tetramethyl-2,6-Diaminoanthracene/Maleic Anhydride Adduct 4

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.20 (d, 1H, J=8.26Hz), 7.14 (d, 1H, J=8.27Hz), 6.78 (d, 1H, J=2.12Hz), 6.67 (d, 1H, J=2.45Hz), 6.46 (dd, 2H, J$_1$=2.3Hz, J$_2$=8.3Hz) 4.62 (m, 2H) 3.49 (m, 2H), 2.92 (s, 6H), 2.90 (s, 6H). HRMS (DART): 362.1637 (M$^+$, Expected = 362.1630), 363.1710 (M+H$^+$, Expected = 363.1709).

V.3.1.4 2,6-Dimethoxyanthracene/Maleic Anhydride Adduct 5

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.27 (m, 1H), 7.23 (d, 1H, J=8.24Hz), 6.96 (d, 1H, J=2.47Hz), 6.89 (d, 1H, J=2.45Hz), 6.70 (m, 2H), 4.722(m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.51 (m, 2H). HRMS (DART): 336.0991 (M$^+$, Expected = 336.0998), 337.1064 (M+H$^+$, Expected = 337.1076), 354.1337(M+NH$_4^+$, Expected = 354.1341).

V.3.2 : Synthesis of N-methylmaleimide/Anthracene DA Adduct (7)

Anthracene (500 mg, 2.81 mmol), N-methyl maleimide (494 mg, 4.45 mmol) and chlorobenzene (2 mL) were added to a sealed tube equipped with a magnetic stirrer. The mixture was purged with nitrogen and sealed, and then allowed to reflux for 24 hours at 160$^\circ$C. The reaction mixture was cooled to room temperature. The precipitate was collected by filtration and
washed with methanol to yield a white solid as the product (520 mg, 70% yield). $^1\text{H}$ NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.37 (dd, 2H, $J_1$=8.57 Hz, $J_2$=2.12 Hz), 7.25 (dd, 2H, $J_1$=8.5 Hz, $J_2$=2.2 Hz), 7.17 (dd, 2H, $J_1$=8.6 Hz, $J_2$=2.25 Hz), 7.12 (dd, 2H, $J_1$=8.6 Hz, $J_2$=2.27 Hz), 4.78 [m (the doublets of the two protons on the respective chiral centers overlap), 2H], 3.21 [m (the doublets of the two protons on the respective chiral centers overlap), 2H], 2.50 [s, 3H]. HRMS (DART): 289.1116 (M$^+$, Expected = 289.1103), 290.1179 (M+H$^+$, Expected = 290.1181), 307.1445 (M+NH$_4^+$, Expected = 307.1147).

V.3.3: Synthesis of N-methylmaleimide/2,6-Dimethoxyanthracene DA Adduct (9)

N-methyl-maleimide (213 mg, 1.9 mmol), 2,6-dimethoxy-antracene (203 mg, 0.95 mmol), and chlorobenzene (1.5 mL) were added to a sealed tube equipped with a magnetic stirrer. The mixture was purged with nitrogen, sealed and heated to reflux for 2 hours at 160°C. The reaction mixture was cooled to room temperature. The white crystalline precipitate was collected and was added some dichloromethane. The cloudy solution (or dispersion) was filtered and the filtrate was added dropwise into methanol to yield the product as a white precipitate (290 mg, 97% yield). $^1\text{H}$ NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.25 (s, 1H), 7.14 (d, 1H, $J$=8.12 Hz), 6.94 (d, 1H, $J$=2.49 Hz), 6.82 (d, 1H, $J$=2.49 Hz), 6.66(d, 1H, $J_1$=2.5Hz, $J_2$=8.13 Hz), 6.62 (dd, 1H, $J_1$=8.13Hz, $J_2$=2.5 Hz), 4.66 (m, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.18 (m, 2H), 2.54 (s, 3H). HRMS (DART): 349.1309 (M$^+$, Expected = 349.1314), 350.1381 (M+H$^+$, Expected = 350.1392), 367.1652 (M+NH$_4^+$, Expected = 367.1658).
V.3.4 : Synthesis of Acrylonitrile/2,6-Dimethoxyanthracene DA Adduct (10)

Acrylonitrile (5 mL, 76.32 mmol), 2,6-dimethoxyanthracene (1 g, 4.2 mmol), m-xylene (15 mL), and hydroquinone (50 mg, 0.45 mmol) were added to a sealed tube equipped with a magnetic stirrer. The mixture was degassed, sealed and then heated at 175°C for 3 days. After, the reaction was cooled to room temperature, the solvent was evaporated under reduced pressure to yield a brown thick oil. About 4 mL of toluene was added to the oil and the solution was kept below 0°C overnight to yield light brownish precipitates. The precipitate contained the product and some hydroquinone. So it was further purified by adding small volume of methanol to form a paste, followed by adding water to the paste. The pure product was collected by filtration as a light brown solid (80 mg, 7% yield). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 7.19 (dd, 2H, J₁=5.7Hz, J₂=2.47 Hz), 6.98 (d, 1H, J=2.47Hz ), 6.85 (d, 1H, J=2.48 Hz), 6.7 ( dd, 1H, J₁=5.63 Hz, J₂=2.48 Hz), 6.64 (dd, 1H, J₁=5.84 Hz, J₂=2.49 Hz), 4.45 (d, 1H, J=2.48 Hz), 4.28 (t, 1H, J=2.62 Hz), 3.78 (s, 3H), 3.76 (s, 3H), 2.90(m, 1H), 2.19 (m, 1H), 1.95(m, 1H). HRMS (DART): 291.1256 (M⁺, Expected = 291.1259), 292.1333(M+H⁺, Expected = 292.1338), 309.1605(M+NH₄⁺, 309.1603).

V.3.5 : Synthesis of TCNE/Naphthacene Adduct (11)

Naphthacene (150 mg, 0.69 mmol) and 10 mL of toluene were added to a round bottom flask equipped with a magnetic stir bar. The flask was sealed and purged with Nitrogen then heated to 60°C. Tetracyanoethylene (104 mg, 0.8 mmol) was added to 6 mL of toluene and stirred leaving a small fraction of undissolved solid left. The liquid portion of this solution was extracted and
injected dropwise into the the hot naphthacene solution. The resulting mixture was maintained at 60°C with stirring for 30 minutes, then cooled to 0°C and vacuum filtered to obtain a white solid. (108 mg, 44% Yield) $^1$H NMR. (CDCl$_3$, 500MHz): $\delta$/ppm = 8.05 (s, 2H), 7.91 (q, 2H, J=3.31, 6.18), 7.63 (m, 4H), 7.49 (q, 2H, J=3.25, 5.46), 5.17 (s, 2H). HRMS (DART): 374.1404 (M+NH$_4^+$, Expected = 374.1406).

**V.3.6 : Characterization of Products after Irradiation of 12**

$^1$H NMR. (CDCl$_3$, 500MHz) : $\delta$/ppm = 3.15 (s, 3H), 8.77 (1H, d, J= 8.43 Hz), 8.73 (1H, d, J = 8.02 Hz), 8.30 (1H, d, J =7.58 Hz), 8.15 (s, 1H), 8.00 (1H, d, J = 7.81 Hz), 7.89 (d, 1H, J = 7.03 Hz), 7.68 – 7.58 (m, 7H), 7.53 (1H, m), 7.34 – 7.29 (3H, m), 7.16-7.14 (2H, m). HRMS = 542.1743 (M+, Expected)

**V.4 Synthesis and Characterization of Compounds in Chapter III**

All starting materials were purchased and used without further purification. Anhydrous toluene and CDCl$_3$ was degassed thoroughly by the freeze-pump-thaw method. CDCl$_3$ was purified by passing through an alumina column. HPLC grade acetonitrile was used for making films. THF was made anhydrous by distilling from Na and benzophenone. Triethylamine was freshly distilled from CaH$_2$ prior to performing the Swern oxidation. 2,6-Dibromoanthraquinone (4)$^7$, 9,10-Dihydro-9,10-ethanoanthracene-11,12-dione (9)$^8$ 5,5’-bis(tributylstannyl)-2,2’-bithiophene (12)$^9$, 2,6-Diiodoanthraquinone (17)$^{10}$ were prepared according to literature procedures.
V.4.1 Synthesis of Central-Ring Pentacene/TCNE Adduct (1)

50 mg (0.180 mmol) of Pentacene was finely crushed and added to 28 mg (0.216 mmol) of TCNE in 3.5 mL degassed and anhydrous toluene in a 10 mL round-bottomed flask fitted with a magnetic stirrer and a reflux condenser. The solution was refluxed under argon for 3 hours. The solution was cooled and the toluene was filtered off. The residue was dissolved in acetonitrile and filtered. The filtrate was collected and the solvent was evaporated to get 60 mg (yield = 82\% ) of central-ring adduct. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 8.09 (s, 4H), 7.92 (m, 4H), 7.62 (m, 4H), 5.27 (s, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 133.2, 129.9, 128.3, 128.0, 126.5, 110.8, 53.1, 46.5. HRMS (DART): 424.1557 (M+NH$_4^+$, expected = 424.1562)

V.4.2 Synthesis of Isomeric Mixture (1+2)

This was made in the same way as 1, except that the reaction was carried out at room temperature for 12 hours. For 2, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 8.50 (s, 2H), 8.20 (s, 2H), 8.05 (m, 2H), 7.66 (m, 2H), 7.57 (m, 2H), 7.52 (m, 2H), 5.19 (s, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 133.9, 132.7, 130.5, 130.3, 128.6, 128.2, 127.4, 126.9, 126.9, 126.6, 110.7, 53.0, 46.4.

V.4.3 Synthesis and Characterization of 5

V.4.3.1 Synthesis and Characterization of 2,6-Dibromo-9,10-dimethoxyanthracene

To a two neck round bottomed flask fitted with a magnetic stirrer was added 2.7 g of 3, followed by 2.16 g of tetrabutylammonium bromide. The mixture was purged with N$_2$ following which 2.7
g of Na$_2$S$_2$O$_4$ and 67.5 mL of degassed water were added. After 10 minutes of stirring, 81 mL of dichloromethane was syringed in, upon which the solution turned green. After 1 hour of stirring, 54 mL of a 20% NaOH aqueous solution was added. This was stirred for 2 hours following which, 4.5 mL of CH$_3$I was added. The resulting solution was stirred at room temperature overnight after which the reaction was dismounted and the dichloromethane layer was extracted. The aqueous layer was extracted thrice with dichloromethane. The organic layer was filtered and rotovaped. The residue was finally washed with MeOH to yield 1.9 g (yield = 65 %) of product.

$^1$H NMR (500 MHz, CDCl$_3$): δ/ppm = 8.43 (m, 2H), 8.14 (m, 2H), 7.55 (m, 2H), 4.09 (s, 6H).

V.4.3.2 Synthesis and Characterization of 2,6-Dibromo-9,10-dioctyloxyanthracene

2,6-Dibromo-9,10-dioctyloxyanthracene was made in an identical fashion as 2,6-dibromo-9,10-dimethoxyanthracene except that the product was purified by column chromatography using 1:4 ethylacetate : hexane as the solvent system. $^1$H NMR (500 MHz, CDCl$_3$): δ/ppm = 8.39 (m, 2H), 8.11 (m, 2H), 7.52 (m, 2H), 4.11 (t, 4H), 3.41 (t, 4H), 2.03 – 0.87 (m, 26H)

V.4.4 Synthesis and Characterization of 6

V.4.4.1 Synthesis and Characterization of DA Adduct of Vinylene Carbonate and 2,6-Dibromo-9,10-dimethoxyanthracene

Added 3.0 g of 2,6-dibromo-9,10-dimethoxyanthracene and 3.0 mL vinylene carbonate in a sealed tube fitted with a magnetic stirrer and allowed to reflux at 170°C for 3 days. Dismounted the reaction and directly loaded the charry solids onto a silica gel column and elueted with 5:2 hexane : dichloromethane. Collected the 2nd and 3rd fraction. Evaporated the solvent to leave
behind a white solid to give 4.1 g of product. (Yield = 85.5%). $^1$H NMR (500 MHz, CDCl$_3$): 
$\delta$/ppm = 7.73 (m, 2H), 7.46 (m, 4H), 5.11 (m, 2H), 3.96 (m, 6H).

V.4.4.2 Synthesis and Characterization of DA Adduct of Vinylene Carbonate and 2,6-Dibromo-9,10-dioctyloxyanthracene

The synthetic procedure was identical to the above procedure. $^1$H NMR (500 MHz, CDCl$_3$):
$\delta$/ppm = 7.65 (m, 2H), 7.38 (m, 2H), 5.09 (m, 2H), 4.09 (m, 4H), 1.98 – 0.92 (m, 26H).

V.4.5 Synthesis and Characterization of Diol 7

V.4.5.1 Synthesis and Characterization of Dimethoxy Diol

Took 1.0 g of the starting material in a round bottomed flask fitted with a magnetic stirrer. To this added 24.0 mL THF followed by 5 mL of MeOH and finally 4N NaOH (9.5 mL). Left this stirring vigorously overnight at room temperature. Then saturated with brine and extracted with dichloromethane. Dried with MgSO$_4$ and rotovaped the solvent off. An oily liquid was left behind. To this oil added a little hexane, triturated and sonicated. The oil slowly hardened. Kept repeating the trituration. Then filtered off to get a 0.8 g of a white powder. (Yield = 83 %) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.73 (m, 1H), 7.60 (m, 1H), 7.42 (m, 4H), 4.37 (m, 2H), 3.95 (m, 6H), 2.40 (m, 2H)

V.4.5.2 Synthesis and Characterization of Dioctyloxy Diol

The procedure was identical to above. It is worth mentioning here that the solidification of the oil in the end took a longer time than the dimethoxy diol presumably due to the longer alkyl chains $^1$H NMR (500 MHz, CDCl$_3$): The spectrum showed some impurities which made identification
of peaks difficult, however, based on a rough integration and positions of peaks we concluded that we have the right product.

V.4.6 Synthesis and Characterization of Diketone 10

To a 100 mL 3 neck RBF fitted with a magnetic stirrer was added 2.7 mL DMSO (Dimethyl sulfoxide) followed by 19.8 mL dichloromethane and set stirring under nitrogen at -70°C. Allowed the temperature to equilibrate for 15 minutes after which was added 4.8 mL trifluoroacetic anhydride dropwise. A white precipitate developed. Stirred for an additional 10 minutes and then added the starting diol (0.5 g) previously dissolved in a mixture of 2.3 mL DMSO and 3.35 mL dichloromethane dropwise. Let this stir at the same temp for 90 minutes. Then added 11.0 mL Triethylamine dropwise (a yellow color develops on addition) and let it stir for 90 mins more during which allowed it to warm up to –0 20˚C after which allowed it to warm to room temperature slowly. Then added 20.0 mL of 2N HCl and stirred for 5 minutes to quench the reaction. Then extracted once in dichloromethane. Washed the extract with water thrice. Then dried with MgSO₄ and filtered. Rotovaped to get an orange-yellow oil. Ran a slow column in 2:1 dichloromethane : hexane. Collected pure fractions which changed color under UV. So rotovaped to get an oil yet again. Pumping the oil under vacuum overnight still did not result in a solid so ran another column in 3:1 ether : hexane. which gave no separation. So rotovaped the solvent and dissolved in a little bit of dichloromethane and and kept under vacuum overnight. 0.2 g of a fluffy solid was left behind (Yield = 40.4 %) \(^1\)H NMR (500 MHz, CDCl₃): \(\delta/\text{ppm} = 7.78\) (m, 2H), 7.56 (m, 2H), 7.53 (m, 2H), 4.18 (s, 6H). ATR-IR = 1749 cm\(^{-1}\), 1439 cm\(^{-1}\), 1394 cm\(^{-1}\), 1271 cm\(^{-1}\).
V.4.7 Synthesis and Characterization of 2-Bromo-3-octylthiophene 14

Dissolved 5.0 g of 13 in 25.5 mL of DMF (Dimethyl formamide). Separately dissolved 4.59 g of NBS (N-bromosuccinimide) in 17.3 mL of DMF. Then added the NBS solution dropwise to the solution of 13 in the dark. Stirred for 48 hours. Then quenched the reaction in ice and extracted several times with ether. Dried with MgSO4 and ran a silica gel column in hexane to give 6.8 g of an 14 as an oil (yield = 97 %) 1H NMR (500 MHz, CDCl3): δ/ppm = 7.18 (m, 1H), 6.79 (m, 1H), 2.56 (m, 2H), 1.52-0.87 (m, 15H)

V.4.8 Synthesis and Characterization of Tetrathiophene 15

To a round bottomed flask fitted with a magnetic stirrer was added 2.7 g of 12, 3.0 g of 14, 0.0008 g of palladium(0) tetrakis followed by 10.8 mL DMF and 43.3 mL toluene. The mixture was purged with nitrogen and set to reflux for 24 hours after which the reaction was cooled down and quenched with water. Dichloromethane was used to extract the reaction mixture a couple of times. This was then washed with water and dried with MgSO4. A silica gel column was used to chromatograph the mixture using hexane as the eluent. The yellow fraction was collected and evaporated to yield 1.95 g of an oil which solidifies on refrigeration to a yellow solid. (yield = 96.7%). 1H NMR (500 MHz, CDCl3): δ/ppm = 7.19 (m, 2H), 7.13 (m, 2H), 7.03 (m, 2H), 6.95 (m, 2H), 2.79 (m, 4H), 1.66 (m, 4H), 1.45-0.87 (m, 26H).
V.4.9 Synthesis and Characterization of Tetrathiophene 16

1.0 gm of Tetrathiophene was taken in a two neck 100 mL round bottomed flask fitted with a magnetic stirrer and purged well with N₂. To this was added 12.5 mL dry THF and stirred well till a clear yellow solution with no layers is obtained. (This step is very important as the starting compound is a thick oil and tends not to mix with the THF. Then cooled down to -78°C in a dry ice-acetone bath and slowly added 1.7 mL of n-BuLi in THF (2.5M solution) drop wise slowly. (As the addition of n-BuLi proceeded, the color of the solution slowly changed from yellow to orange yellow to greenish yellow. Then allowed the reaction to stir for 1 hour (after this a cloudy yellow precipitate was observed) and then immersed in a water bath and stirred for another 1 hour and 15 minutes. Then cooled it down to -70°C and added 1.4 mL of Bu₃SnCl slowly drop wise. The color changed from dark murky orange to clear orange. Allowed it to stir for 15 minutes more at this temperature, then warmed it up to room temperature, and kept stirring overnight. Then added hexane to the reaction followed by 5% Na₂CO₃ (aq). The mixture was washed once more with 5% Na₂CO₃ (aq) and then twice with water. It was finally dried with MgSO₄ and then evaporated to get a 2.0 g of a dark brown viscous oil (yield = 98.0%). This was taken to the next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ/ppm = 7.10 (m, 2H), 7.01 (m, 2H), 6.96 (m, 2H), 2.80 (m, 4H), 1.62-0.86 (m, 84H)
V.4.10 Synthesis and Characterization of 2,6-Diiodo-9,10-dioctyloxyanthracene 18

2,6-Diiodo-9,10-dioctyloxyanthracene was made in an identical fashion as 2,6-dibromo-9,10-dioctyloxyanthracene. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 8.64 (m, 2H), 7.96 (m, 2H), 7.66 (m, 2H), 4.10 (t, 4H), 2.00 (quintet, 4H), 1.64 (quintet, 4H), 1.47-1.31 (m, 16H), 0.92 (t, 6H).

V.4.11 Synthesis and Characterization of Polymer 3

To a round bottomed flask fitted with a reflux condenser and a magnetic stirrer was added 0.13 g of 18 followed by 0.24 g of tetrathiophene 16 and 0.0008 g of palladium(0)tetrakis. To this was added 10.0 mL toluene and ~ 1.0 mL DMF. Purged the reaction mixture well with nitrogen and set to reflux 3.5 days. Then dismounted the reaction mixture and quenched it by adding 10.0 mL MeOH acidified with 1.5 mL of concentrated HCl dropwise with vigorous stirring. A red precipitate formed which was filtered off and washed multiple times with MeOH. Took the red solids and redissolved in dichloromethane and reprecipitated by dropping it into MeOH to yield 0.18 g of a red precipitate (yield = 98.0%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 8.46 (m, 2H), 8.29 (m, 2H), 7.75 (m, 2H), 7.36 (m, 2H), 7.17 (m, 4H), 4.21 (m, 4H), 2.86 (m, 4H), 2.12-0.86 (m, 60H), $M_n$ = 20,000.
V.5 Synthesis and Characterization of Compounds in Chapter IV

V.5.1 General Synthesis and Characterization of Compounds 4, 5, 6 and 7

V.5.1.1 Synthesis of 4, 5 and 6

2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium and the corresponding salicylaldehyde were added into anhydrous ethanol. The mixture was allowed to reflux overnight under nitrogen. Light orange solid to brick red solids were obtained by filtration followed by recrystallization in ethanol.

V.5.1.2 Characterization of 4

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 11.15 (s, 1H), 10.92 (s, 1H), 8.52 (m, 1H), 8.17 (m, 1H), 7.88 (m, 1H), 7.78 (m, 1H), 7.55 (m, 3H), 6.45 (m, 2H) 4.68 (t, 2H), 2.63 (t, 2H), 2.13 (m, 2H), 1.72 (s, 6H)

V.5.1.3 Characterization of 5

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 10.80 (s, 1H), 8.56 (d, 1H, J = 16.3 Hz), 8.12 (m, 1H), 8.00 (m, 1H), 7.84 (m, 2H), 7.62 (m, 2H), 7.28 (m, 1H), 6.93 (m, 1H), 4.81 (m, 2H), 2.65 (t, 2H), 2.29 (s, 3H), 2.18 (m, 2H), 1.76 (s, 6H)

V.5.1.4 Characterization of 6

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 10.60 (s, 1H), 8.60 (m, 1H), 7.97 (m, 2H), 7.83 (m, 2H), 7.61 (m, 2H), 7.08 (m, 1H), 6.97 (1H), 4.86 (m, 2H), 3.86 (s, 3H), 2.63 (m, 2H), 2.20 (m, 2H), 1.76 (s, 6H)
V.5.1.5 Synthesis of 7

7 was synthesized according to the scheme 1. 2,4-dihydroxybenzaldehyde was synthesized was esterified at the para position with acryloyl chloride according to a literature procedure.\textsuperscript{11} The resulting ester was very sensitive to polymerization and had a low melting point. Hence, after quick purification via silica gel chromatography, a little hydroquinone was added to inhibit any polymerization that might occur. The synthesis of compound 7 was then attempted by coupling the benzaldehyde ester with 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium in refluxing ethanol. This reaction failed because of uncontrolled hydrolysis of the ester. This however proved to be a convenient way to make compound 4. To circumvent this, acetonitrile was used instead of ethanol as the solvent. This resulted in the successful isolation of 7 which was recrystallized in acetonitrile.

Scheme V-1: Synthesis of 7.

V.5.1.6 Characterization of 7

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) : $\delta$/ppm = 11.44 (s, 1H), 8.56 (d, 1H, $J$ = 16.3 Hz), 8.35 (d, 1H, $J$ = 8.6 Hz), 8.01 (m, 1H), 7.86 (m, 2H), 7.61 (m, 2H), 6.85 (m, 2H), 6.59 (dd, 1H, $J_1$ = 1.3 Hz, $J_2$ =
17.3 Hz), 6.42 (dd, 1H, J1 = 10.3 Hz, J2 = 17.3 Hz), 6.18 (dd, 1H, J1 = 1.3 Hz, J2 = 10.3 Hz), 4.82 (m, 2H), 2.65 (m, 2H), 2.19 (m, 2H), 1.77 (s, 6H)

V.5.2 General Synthesis and Characterization of Polymers

To a round bottomed flask fitted with a magnetic stirrer was added the desired ratio of monomers followed by 3 mol % Initiator AIBN (Azobis-isobutyronitrile) and THF as the solvent. The reaction mixture was refluxed overnight following which the viscous solution was dropped into cold methanol. After letting the solution stand for a while the supernatant was decanted. Then the remaining think viscous liquid was dried under high vacuum for 2 hours. A white crusty solid resulted. This solid was condensed with 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium in acetonitrile by refluxing overnight. The resulting red solid was washed with cold ethanol and dried.

V.5.2.1 Characterization of pMEH28M72

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 11.48 (s, 1H), 8.70 – 7.52 (m, 7H), 7.00 – 6.55 (m, 2H), 5.06 – 4.51 (m, 2H), 3.59 (bs, 13H), 2.90 – 1.00 (m, 28H)

V.5.2.2 Characterization of pMEH14M77P9

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 11.51 (s, 1H), 8.57 – 7.50 (m, 9H), 6.90 – 6.60 (m, 2H), 4.90 – 4.58 (m, 3H), 4.23 – 4.00 (bs, 2H), 3.88 – 3.10 (m, 62H), 2.87 – 1.18 (m, 49H).
V.5.2.3 Characterization of pT18MEH22M50P10

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$/ppm = 11.47 (s, 1H), 9.11 (m, 1H), 8.60 – 7.26 (m, 4H), 6.92 – 6.62 (m, 2H), 5.31 (bs, 2H), 4.90 – 4.64 (m, 2H), 4.11 (bs, 1H), 3.85 – 3.07 (m, 27H), 2.87 – 1.19 (m, 11H).

V.6 References

APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER II
$^1$H NMR Spectrum of 2,6-Dibromo-anthracene/maleic anhydride adduct (2)
HRMS (DART) Spectrum of 2,6-Dibromo-anthracene/maleic anhydride adduct (2)

Theoretical $M^+ = 431.8991$

$[M+H]^+ = 432.9069$

$[M+NH_4]^+ = 449.9332$
$^1$H NMR Spectrum of 2,6-Dimethyl-anthracene/maleic anhydride adduct (3)
HRMS (DART) Spectrum of 2,6-Dimethyl-anthracene/maleic anhydride adduct (3)

Theoretical M+ = 304.1094
[M+H]+ = 305.1172
[M+NH4]+ = 322.1438
$^1$H NMR Spectrum of Tetramethyl-2,6-diamino-anthracene/maleic anhydride adduct (4)
HRMS (DART). Spectrum of Tetramethyl-2,6-diamino-anthracene/maleic anhydride adduct (4)
$^1$H NMR Spectrum of 2,6-Dimethoxy-anthracene/maleic anhydride adduct (5)
HRMS (DART) Spectrum of 2,6-Dimethoxy-anthracene/maleic anhydride adduct (5)

Theoretical $M_r = 336.0992$

$[M+H]^+ = 337.1071$

$[M+NH_4]^+ = 354.1386$
$^1$H NMR Spectrum of Anthracene/N-methyl maleimide DA adduct (7)
HRMS (DART) Spectrum of Anthracene/N-methyl maleimide DA adduct (7)

Theoretical $M^+ = 289.1097$

$[M+H]^+ = 290.1176$

$[M+N\text{H}_2]^+ = 307.1441$
$^1$H NMR of 2,6-Dimethoxy-anthracene/N-methylmaleimide DA adduct (9)
HRMS (DART) of 2,6-Dimethoxy-anthracene/N-methylmaleimide DA adduct (9)
$^1$H NMR of 2,6-Dimethoxy-anthracene/acrylonitrile DA adduct (10)
HRMS (DART) of 2,6-Dimethoxy-anthracene/acrylonitrile DA adduct (10)
$^1$H NMR of TCNE/naphthacene DA adduct (11)
HRMS (DART) of TCNE/naphthacene DA adduct (11)
$^1$H NMR of products (b) after irradiation of 12
GC-MS Spectrum of Fragmentation of 11 on irradiation in MeOH
APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER III
$^{13}$C NMR Spectrum of 1.

The $^{13}$C NMR data of 1 shows five peaks for the aromatic ring carbons at 133.23, 129.85, 128.34, 127.98, 126.52 ppm. The nitrile carbons appears at 110.78 ppm while the carbons between the nitriles appears at 53.07 ppm and the bridgehead carbon appears at 46.50 ppm.
$^{13}$C NMR Spectrum of mixture of 1 and 2.

$^{13}$C NMR spectra of the mixture of 1 and 2 in addition to the peaks for 1 show aromatic peaks at 133.90, 132.69, 130.46, 130.28, 128.64, 128.23, 127.41, 126.93, 126.90 and 126.62 ppm. The nitrile peaks for 2 appears at 110.72 ppm while the carbons between the nitriles appears at 53.04 ppm. Finally, the bridgehead carbons appear at 46.41 ppm.
Comparison $^{13}$C spectra used for structure deduction of 2
The nitrile peaks of the isomeric mixture of 1 & 2 (enlarged)
HRMS (DART) Spectrum for 1
$^1$H NMR Spectrum of 2,6-Dibromo-9,10-dimethoxyanthracene
$^1$H NMR Spectrum of 2,6-Dibromo-9,10-dioctyloxyanthracene
$^1$H NMR Spectrum of DA adduct of 2,6-Dibromo-9,10-dimethoxyanthracene and vinylene carbonate.
$^1$H NMR Spectrum of DA adduct of 2,6-Dibromo-9,10-dioctyloxyanthracene and vinylene carbonate.
$^1$H NMR Spectrum of Dimethoxy diol
$^1$H NMR Spectrum of Dioctyloxy diol
$^1$H NMR Spectrum of Diketo compound 10
ATR-IR Spectrum of Diketo compound 10
1H NMR Spectrum of 2-Bromo-3-octylthiophene 14
$^1\text{H NMR Spectrum of Tetrathiophene 15}$
$^1$H NMR Spectrum of Tetrathiophene 16
$^1$H NMR Spectrum of 2,6-Diiodo-9,10-dioctyloxyanthracene 18
$^1$H NMR Spectrum for Polymer 3
APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER IV
$^1$H NMR Spectrum for Photoacid 4
$^1$H NMR Spectrum for Photoacid 5
$^1$H NMR Spectrum for Photoacid 6
$^1$H NMR Spectrum for Photoacid 7
$^1$H NMR Spectrum for Photoacid Polymer pMEH28M72
$^1$H NMR Spectrum for Photoacid Polymer pMEH14M77P9
$^1$H NMR Spectrum for Photoacid Polymer pT18MEH22M50P10
UV-Vis spectra of 5 before and after irradiation. A scan was taken every 12 seconds after irradiation. Estimated half-life was determined from this plot.
UV-Vis spectra of 7 before and after irradiation. A scan was taken every 12 seconds after irradiation. Estimated half-life was determined from this plot.
pH cycles of photoacid 7