April 2014

Design and Syntheses of Donor-Acceptor Dyads and Triads for Improved Light Harvesting in Organic Photovoltaics

Andrea Della Pelle

*University of Massachusetts - Amherst*

Follow this and additional works at: https://scholarworks.umass.edu/dissertations_2

Part of the Chemistry Commons

**Recommended Citation**


https://scholarworks.umass.edu/dissertations_2/36

This Open Access Dissertation is brought to you for free and open access by the Dissertations and Theses at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
DESIGN AND SYNTHESSES OF DONOR-ACCEPTOR DYADS AND TRIADS FOR IMPROVED LIGHT HARVESTING IN ORGANIC PHOTOVOLTAICS

A Dissertation Presented

by

ANDREA M. DELLA PELLE

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2014

Department of Chemistry
DESIGN AND SYNTHESSES OF DONOR-ACCEPTOR DYADS AND TRIADS FOR IMPROVED LIGHT HARVESTING IN ORGANIC PHOTOVOLTAICS

A Dissertation Presented
by
ANDREA M. DELLA PELLE

Approved as to style and content by:

________________________________________
Sankaran Thayumanavan, Chair

________________________________________
Paul M. Lahti, Member

________________________________________
Michael D. Barnes, Member

________________________________________
Ryan C. Hayward, Outside Member

____________________________
Craig T. Martin, Department Head
Chemistry
DEDICATION

To my family: the one I was born into and the one that I have made for myself,
especially my angels in heaven: FL, RC, and LL.
ACKNOWLEDGMENTS

There are so many people that I need to thank and acknowledge for their contributions to this thesis.

Firstly, I could not have done this without the support and guidance of my advisor Prof. Thayumanavan. There are so many things that I admire and respect about Prof. Thai, most notably are probably his passion for science and his commitment to his research group. I have to thank him for always believing in me especially when I didn’t believe in myself.

I would also like to thank my committee members, Prof. Lahti, Prof. Barnes, and Prof. Hayward, for their contributions and insights throughout the years. I would also like to thank my undergraduate research advisor Prof. L. Kraig Steffen, and all the professors at Fairfield University, who believed in me, still check in on me, and have helped me to get to where I am today.

I need to thank all of my collaborators: Ambata Poe, Youngju Bae, Paul Homnick, Dr. Akshay Kokil, Dr. Supravat Karak, Jacob, Harvey, and Prof. Alexander Sidorenko. I especially need to thank Dr. Ashok Maliakal for the amazing internship opportunity. I have also been lucky to mentor some of the brightest undergraduate students, all of whom have contributed to the work in this thesis: Elle Jefferies, Laura Stirchak, and Sean Byrnes.

I also need to thank all current and past members of the Thai Group Family and Energy Subgroup especially, Ambata Poe (I had to mention you twice!), Jing Guo, Krishna Raghupathi, Jiaming Zhuang, Kishore Raghupathi, Piyachai Khomein,
Pryiaa Prasad, Dr. Reuben Chacko, Dr. Tejaswini Kale, Dr. G. Balaji, Dr. Daniella Gonzalez Toro, Dr. Siriporn Jiwpanich, Dr. Sompit Wanwong, Dr. Ayyagari Venkata Subrahmanyan and Dr. A. Chandrasekaran. A very special thank you to all of my classmates who have been there with me through every second: Diego Fernando Amado Torres, Feng Wang, and Rajasekhar Rami Reddi. I will greatly miss our subgroup meetings and hot pot!

I need to thank all my friends outside of the Thai Lab for all of their support throughout my five years here: Dr. Gitanjeli Prasad, Dr. Austin Cyphersmith, Dr. Sravan Surampudi, Lalitha Surampudi, Jeffrey Lucas, and my past and present “every other Wednesday” sisters.

I would not have been able to get to this point without the help of the entire staff of the Chemistry Department especially Robert Sabola, Ryan Feyrer, Marvin Ellin, Dennis Glick, and my lab mom Karen Hakala.

Last, but definitely not least, I need to thank the entire Della Pelle, LaFrazia, and Contrado families in addition to our friends who have become family. Your love and support mean more to me than I could ever express or you could ever know. I am where I am today because you believed in me. Each and every one of you has shaped the person that I am today and I am truly blessed to have you as my family. No matter where this crazy career takes me, remember that you are always in my heart and I will always just be the loud Italian girl drinking CC & ginger and singing Piano Man. I would also like to thank my angels in Heaven who I turn to constantly for strength and guidance, especially Papa, Cousin Ralphie, and Laura.
To my mother, Patricia, my father, Peter, and my big sister, Angela: I hope that I have made you all so proud of me. I know now that I have the greatest family ever. You have always supported me and challenged me to be the best person that I can be. Since the days of the dreaded red pen, you have insisted that I never settle for anything but my best. I know that you never understood what I was doing in graduate school but you were always there to listen. It is because of you that I have made it this far and I share my success with you, because this thesis is not just mine, but yours as well.
ABSTRACT

DESIGN AND SYNTHESIS OF DONOR-ACCEPTOR DYADS AND TRIADS FOR IMPROVED LIGHT HARVESTING IN ORGANIC PHOTOVOLTAICS

FEBRUARY 2014

ANDREA M. DELLA PELLE, B.S., FAIRFIELD UNIVERSITY
Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Sankaran Thayumanavan

All organic photovoltaics (OPVs) undergo four major processes to convert sunlight in electrical energy. The first process is the absorbance of sunlight. Due to the limit of available acceptor molecules, the burden of light absorbance weighs heavily on the donor material. This thesis focuses heavily on the development of dyes consisting of donor-acceptor dyads and triads for improved light harvesting in OPVs.

Squaraine dyes show impressive light harvesting properties with absorbances in the UV to near IR region with extinction coefficients on the order of $10^5$ M$^{-1}$ cm$^{-1}$. Unfortunately, improved light harvesting is not enough to insure optimized OPVs. Energy level tuning to increase $V_{oc}$ and insure efficient exciton dissociation is also required. Functionalizing squaraine dyes with electron donating or electron withdrawing groups allow for the systematic tuning of the HOMO energy levels. This tunability allows for the concurrent optimization of bandgap and $V_{oc}$.

Cyanine dyes have been explored for small molecule OPVs due to their impressive absorbance properties. The absorbance of ketocyanine dyes can be tuned by manipulating the strength of the acceptor moiety. Stronger acceptors are better able to stabilize the negative charge in the charge separated state of the dye.
This stabilization allows for a greater contribution from the cyanine structure of the dye, thus red shifting the absorbance. Stronger acceptors also increase the communication between the two amine functionalities as demonstrated by cyclic voltammetry.

Block copolymers show impressive morphological control through the tuning of the molecular weight of the blocks as well as the compatibility of the functional groups. This allows for the access of morphologies with small, well ordered, and continuous domains thought to be beneficial in the active layer of OPVs. Unfortunately, block copolymers often show inferior light harvesting compared to their conjugated polymer counterparts. Donor-acceptor systems are explored as sensitziers for block copolymer OPVs. Small molecules without twists or bends or acetylene linkers were found to be most effective for lowering the bandgap and aligning the energy levels.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xx</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Photovoltaics</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Processes in Organic Photovoltaics</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 Light Harvesting</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2 Exciton Diffusion and Dissociation</td>
<td>5</td>
</tr>
<tr>
<td>1.2.3 Charge Migration and Collection</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Device Parameters of Organic Photovoltaics</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Polymer Photovoltaics</td>
<td>9</td>
</tr>
<tr>
<td>1.5 Small Molecule Photovoltaics</td>
<td>13</td>
</tr>
<tr>
<td>1.6 Summary and Dissertation Overview</td>
<td>14</td>
</tr>
<tr>
<td>1.7 References</td>
<td>16</td>
</tr>
<tr>
<td>2. ENERGY LEVEL TUNING IN SQUARAINES DYES FOR IMPROVED LIGHT HARVESTING AND OPEN CIRCUIT VOLTAGE FOR ORGANIC PHOTOVOLTAICS</td>
<td>22</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>22</td>
</tr>
<tr>
<td>2.2 Results and Discussion</td>
<td>24</td>
</tr>
<tr>
<td>2.2.1 Molecular Design</td>
<td>24</td>
</tr>
<tr>
<td>2.2.2 Optoelectronic Properties</td>
<td>29</td>
</tr>
<tr>
<td>2.2.3 Charge Transport Properties</td>
<td>34</td>
</tr>
<tr>
<td>2.2.4 Photovoltaic Properties</td>
<td>38</td>
</tr>
<tr>
<td>2.3 Summary</td>
<td>41</td>
</tr>
<tr>
<td>2.4 Experimental</td>
<td>42</td>
</tr>
</tbody>
</table>
2.4.1 Synthesis of 3,5-dimethoxy-N,N-diphenylaniline ........................................... 42
2.4.2 Synthesis of 5-(diphenylamino)benzene-1,3-diol ........................................ 43
2.4.3 Synthesis of 2,4-bis(4- (diphenylamino)-2,6-
dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate)
(Sq-TAA-H) ........................................................................................................... 43
2.4.4 Synthesis of N,N-bis(4-fluorophenyl)-3,5-
dimethoxyaniline .................................................................................................. 44
2.4.5 Synthesis of 5-(bis(4-fluorophenyl)amino)benzene-1,3-
diol ............................................................................................................................ 44
2.4.6 Synthesis of 2,4-bis(4- (bis(4-fluorophenyl)amino)-2,6-
dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate)
(Sq-TAA-F) ............................................................................................................. 45
2.4.7 Synthesis of bis(4-hexylphenyl)amine ............................................................ 46
2.4.8 Synthesis of N,N-bis(4-hexylphenyl)-3,5-
dimethoxyaniline .................................................................................................. 46
2.4.9 Synthesis of 5-(bis(4-hexylphenyl)amino)benzene-1,3-
diol ............................................................................................................................ 47
2.4.10 Synthesis of 2,4-bis(4- (bis(4-hexylphenyl)amino)-2,6-
dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate)
(Sq-TAA-C6H13) ....................................................................................................... 48
2.4.11 Synthesis of 3,5-dimethoxy-N,N-bis(4-
methoxyphenyl)aniline ........................................................................................ 49
2.4.12 Synthesis of 5-(bis(4-hydroxyphenyl)amino)benzene-
1,3-diol ...................................................................................................................... 49
2.4.13 Synthesis of 2,4-bis(4- (bis(4-hydroxyphenyl)amino)-
2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate)
(Sq-TAA-OH) ......................................................................................................... 50
2.4.14 Synthesis of N,N-bis[3,5-bis(trifluoromethyl)phenyl]-
3,5-dimethoxyaniline ............................................................................................ 51
2.4.15 Synthesis of 5-(bis[3,5-
bis(trifluoromethyl)phenyl]amino)benzene-1,3-diol ....................................... 51
2.4.16 Synthesis of 2,4-bis(4- (bis[3,5-
bis(trifluoromethyl)phenyl]amino)-2,6-
dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate)
(Sq-TAA-CF3) ......................................................................................................... 52
2.4.17 Solution and Thin Film Absorbance .............................................................. 53
2.4.18 Cyclic Voltammetry and Energy Level Estimation ........................................ 53
2.4.19 Thin Film Transistor Fabrication and Measurements ................................. 53
2.4.20 Photovoltaic Fabrication and Measurements ................................................ 54

2.5 References .......................................................................................................... 60

3. EFFECT OF ACCEPTOR STRENGTH ON KETO CYANINE DYES ................. 63
3.1 Introduction .................................................................................................................. 63
3.2 Results and Discussion ............................................................................................... 66
    3.2.1 Molecular Design ................................................................................................. 66
    3.2.2 Absorbance Properties ......................................................................................... 70
    3.2.3 Nuclear Magnetic Resonance Studies ................................................................. 72
    3.2.4 Field Effect Transistor Measurements ............................................................... 76

3.3 Summary ...................................................................................................................... 77
3.4 Experimental .............................................................................................................. 78
    3.4.1 Synthesis of 3,6-dibromophenanthrene-9,10-dione ........................................... 78
    3.4.2 Synthesis of 3,6-dibromo-9H-fluoren-9-one ..................................................... 78
    3.4.3 Synthesis of 3,6-bis(diphenylamino)-9H-fluoren-9-one (DAA-Fl) ................. 79
    3.4.4 Synthesis of 2-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)malononitrile (DAA-Fl-CN) ................................................................. 80
    3.4.5 Synthesis of 5-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (DAA-Fl-6O) ......................... 80
    3.4.6 Synthesis of 5-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (DAA-Fl-6S) ................. 81
    3.4.7 Synthesis of 2-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1H-indene-1,3(2H)-dione (DAA-Fl-In)................................................................. 82
    3.4.8 Synthesis of 4-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-3-phenylisoxazol-5(4H)-one (DAA-Fl-PI) ......................................................... 83
    3.4.9 Solution Absorbance ........................................................................................... 83
    3.4.10 Thin Film Transistor Fabrication and Measurements ........................................ 84
    3.5 References ............................................................................................................... 90

4. DONOR ACCEPTOR SYSTEMS AS SENSITIZERS FOR BLOCK COPOLYMER PHOTOVOLTAICS ...................................................................................................................... 94

4.1 Introduction ............................................................................................................... 94
4.2 Results and Discussion ............................................................................................. 96
    4.2.1 Molecular Design ............................................................................................... 96
    4.2.2 Absorbance Properties ..................................................................................... 102
    4.2.3 Electrochemical Properties .............................................................................. 103
    4.2.4 Design Rules ..................................................................................................... 107

4.3 Summary .................................................................................................................. 108
4.4 Experimental .......................................................................................................... 108
4.4.1 Synthesis of 2,9-bis(2-ethylhexyl)-5-(4-hexyl-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)anthra[2,1,9-def:6,5,10-d'e']diisoquinoline-1,3,8,10(2H,9H)-tetraene (DTP-PDI) .......................................................... 109
4.4.2 Synthesis of 2-butyl-6-(9H-carbazol-9-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-NI) ...................... 110
4.4.3 Synthesis of 2-butyl-6-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (EDOT-NI) .............................................................. 111
4.4.4 Synthesis of 2-butyl-6-(4-(4-hexylphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (DTP-NI) .......................... 112
4.4.5 Synthesis of 2-butyl-6-([9-hexyl-9H-carbazol-3-yl]ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-a-NI) .................................................. 113
4.4.6 Synthesis of 2,7-bis(2-ethylhexyl)-4,9-bis([9-hexyl-9H-carbazol-3-yl]ethynyl)benzo[1,5mn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraene (CBZ-a-NDI-a-CBZ) .............. 114
4.4.17 Absorbance Measurements ..................................................... 114
4.4.18 Cyclic Voltammetry and Energy Level Estimation .................. 115

4.5 References .................................................................................. 122

5. SUMMARY AND FUTURE DIRECTIONS ............................................. 127
5.1 Summary .................................................................................... 127
5.2 Future Directions ......................................................................... 129

5.2.1 Squaraine Dyes for Organic Photovoltaics ....................... 129
5.2.2 Ketcyanine Dyes for Organic Photovoltaics ..................... 130
5.2.3 Sensitized Block Copolymers for Organic Photovoltaics .... 131

5.3 References .................................................................................. 132

APPENDIX: EFFECT OF TITANIUM OXIDE–POLYSTYRENE NANOCOMP OSITE DIELLECTRICS ON MORPHOLOGY AND THIN FILM TRANSISTOR PERFORMANCE FOR ORGANIC AND POLYMERIC SEMICONDUCTORS .......... 137

BIBLIOGRAPHY .................................................................................. 152
LIST OF TABLES

Table | Page
---|---
2.1: Average hole mobilities and standard deviations of Sq-TAA-OH TFTs with varying channel lengths | 34
2.2: Average hole mobilities and standard deviations of Sq-TAA-C$_6$H$_{13}$ TFTs with varying channel length. The mobility increased with annealing confirming the increase in organization that was seen in the annealed thin film absorbance | 35
2.3: Average hole mobilities and standard deviations of Sq-TAA-H TFTs with varying channel length | 36
2.4: Average a) hole and b) electron mobilities and standard deviations of Sq-TAA-F TFTs with varying channel length. It has been shown in literature that installing fluorine groups onto a p-type semiconductor often results in ambipolar or electron transport behavior | 36
2.5: Average electron mobilities and standard deviations of Sq-TAA-CF$_3$ TFTs with varying channel length | 37
2.6: Summary of the parameters of the bilayer OPV devices. It can be seen that the efficiency of Sq-TAA-H is the highest. The lowest $V_{OC}$ is for Sq-TAA-OH which is expected from the HOMO energy level | 40
3.1: Summary of the absorbance data. It can be seen that as the charge separated structure is stabilized, the difference between the $\lambda_{\text{max}}$ of the $\pi-\pi^*$ and CT peaks increases | 72
3.2: NMR peaks for the fluorenone protons of the ketocyanine dyes. Peak 1 shifts down field with increasing acceptor strength, while peaks 2 and 4 shift upfield | 73
3.3: Maximum mobility of each dye determined using bottom contact FET configuration. All dyes show hole mobility, while DAA-FI-PI shows ambipolar charge transport | 77
4.1: Summary of the absorbance properties of the D-A systems and their parent donor and acceptor moieties | 103
A.1: The surface roughness and contact angle of the nanocomposite films remains constant across the entire range of blends studied | 140
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A summary of the best reported efficiencies of various types of photovoltaic devices. Crystalline silicon is shown in blue. OPVs can be seen in the bottom right corner in red.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>The solar irradiance spectrum covers a large range of wavelength but weighs heavily in the 400 nm – 1100 nm range. Organic molecules can be tuned in order to absorb light in this region.</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>The two resonance forms, shown on the left and right, are identical in structure minimizing the energy difference between the two and minimizing the bond length alternation.</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>Shows the dissociation of the exciton formed in the donor material. Here the electron in the LUMO of the excited state donor is transferred to the LUMO of the acceptor as long as the energy level difference between the two LUMOs is at least 0.3 eV.</td>
<td>6</td>
</tr>
<tr>
<td>1.5</td>
<td>Typical J-V characteristics of an OPV. The critical device parameters (V_{OC}, J_{SC}, V_{mpp}, and J_{mpp}) are pointed out. The FF is equal to the ratio of the grey square to the square made by the dotted line.</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>Schematic representation of a BHJ OPV. The BHJ architecture provides greater interfacial area for the dissociation of excitons within the exciton diffusion distance.</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Chemical structures of some of the better performing polymer OPVs to date. P3HT shows efficiencies around 5%. These donor acceptor polymers all show efficiencies about 6.8%.</td>
<td>11</td>
</tr>
<tr>
<td>1.8</td>
<td>Recent progress in small molecule OPVs have resulted in quickly rising efficiencies nearing those of polymer OPVs.</td>
<td>13</td>
</tr>
<tr>
<td>1.9</td>
<td>Small molecules which show high efficiencies. The first row is dyes and the bottom two rows are D-A systems. All show PCE about 6%.</td>
<td>14</td>
</tr>
<tr>
<td>2.1</td>
<td>Low bandgap materials offer enhanced light absorption for organic photovoltaics devices. Raising the HOMO of the chromophore would compromise the V_{OC} of the resulting device. The LUMO can only be lowered to 0.3 eV above the LUMO of the acceptor to allow for exciton dissociation. Energy level tuning is essential for the optimization of OPVs.</td>
<td>23</td>
</tr>
</tbody>
</table>
2.2: Molecular design of squaraine dyes with tunable bandgaps and HOMO energy levels. Sq-TAA-H offers a control molecule for reference. Sq-TAA-C₆H₁₃ and Sq-TAA-OH are squaraine dyes with increasing electron donor strength. Sq-TAA-F and Sq-TAA-CF₃ are squaraine dyes with increasing electron withdrawing strength

2.3: Solution absorbance spectra of the squaraine dyes in DCM. The spectra are plotted with respect to molar absorptivity to indicate the extinction coefficient of each dye. It can be seen that as the electron donation character of the dye is increased, the absorbance red shifts

2.4: Solution absorbance spectra of the squaraine dyes in THF. It can be seen that a high energy peak emerges as a result of the solvent hydrogen bonding with the dye and causing a break in the conjugation due to the twist in the backbone

2.5: Thin film absorbance of the squaraine dyes are red shifted and broadened as compared to the solution absorbance

2.6: Annealing the films do not appear to have any major effect on the absorbance with the exception of Sq-TAA-C₆H₁₃. WhenSq-TAA-C₆H₁₃ is annealed a low energy peak emerges at about 800 nm. This suggests further organization of the film upon thermal annealing

2.7: HOMO and LUMO energy levels of the squaraine dyes calculated electrochemically. LUMO of CF₃ is estimated from the optical bandgap. The bandgap is tuned by variations in the HOMO energy levels, while the LUMO energy levels remain relatively constant

2.8: HOMO and LUMO energy levels of Sq-TAA-OH and Sq-TAA-CF₃ as determined theoretically by DFT using Gaussian 09 with B3LYP level of theory and 6-311g(d, p) basis set

2.9: J-V curves of bilayer OPV devices of a) Sq-TAA-OH, b) Sq-TAA-H, and c) Sq-TAA-F with PCBM

2.10: J-V curve of Sq-TAA-OH: PC₇₁BM bulk heterojunction device. Optimized efficiency is a result of a mixed solvent system (THF: CB, 70:30) and solvent additive (DIO, 0.4 vol%)
3.1: Generic structure of cyanine dye. The odd number of methine groups allow for resonance stabilization between the amine and the iminium ................................................................. 63

3.2: Generic structure of merocyanine dye. Merocyanine dyes are asymmetric charge neutral and consist of a nitrogen donor and an oxygen acceptor connected through a polyethylene chain .......... 64

3.3: Generic structure of ketocyanine dye. Ketocyanine dyes have a symmetric charge neutral structure, where the two nitrogens only communicate in the charge separated resonance structure...... 65

3.4: Structures of cyanine dyes successfully used in the active layer of OPVs ................................................................. 65

3.5: Resonance structures of ketocyanine dyes. In the ground state the two amines are not in electronic communication. In the charge separated state the two amines are allowed to communicate with each other .................................................................... 66

3.6: Chemical structures of the ketocyanine dyes reported in this chapter. The acceptor strength is tuned while the amine portion of the dyes remains constant ................................................................. 67

3.7: Absorbance spectra of the ketocyanine dyes. The absorbances of the dyes are red shifted as the acceptor strength increases suggesting that the cyanine form is more stabilized by the stronger acceptors ................................................................ 70

3.8: Image of ketocyanine dye solutions in DCM. Each dye structure is color matched to the representative dye solution. The color change of the dyes can be seen by the naked eye ............................................ 72

3.9: 1H NMR of DAA-Fl-6O ........................................................................................................................................ 73

3.10: Resonance structures can be used to explain the trends seen in the NMR. The carbons that have a negative charge in the shown resonance forms are upfield shifted, while the one with a positive charge is downfield shifted ................................. 74

3.11: Comparison of 1H NMR of DAA-Fl-6O and DAA-Fl-PI .......................... 75

3.12: Chemical structure of the charge separated state of DAA-Fl-PI ........... 75
3.13: HOMO energy levels of DAA-Fl-6O and DAA-Fl-PI as calculated from DFT .................................................................................. 76

4.1: Schematic representation of a donor-acceptor block copolymer linked through a D-A sensitizer for improved light harvesting. The system requires specific energy level alignment to achieve efficient exciton dissociation ........................................................................ 97

4.2: Molecular designs of small molecule D-A systems as sensitizers for block copolymers .................................................................................................................. 98

4.3: Energy levels of DTP, DTP-PDI, and PDI. DTP-PDI has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of DTP-PDI is lower than PDI ........................................................................................................ 104

4.4: Energy levels of CBZ, CBZ-NI, and NI. CBZ-NI has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-NI is lower than NI .......... 105

4.5: Energy levels of EDOT, EDOT-NI, and NI. EDOT has a lower bandgap than EDOT-NI. The energy levels align appropriately ......................... 105

4.6: Energy levels of DTP, DTP-NI, and NI. DTP-NI has bandgap similar to DTP. The HOMO levels align appropriately ........................................ 106

4.7: Energy levels of CBZ, CBZ-a-NI, and NI. CBZ-a-NI has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-a-PNI is lower than NI ......................................................................................... 106

4.8: Energy levels of CBZ, CBZ-a-NDI-a-CBZ, and NDI. CBZ-a-NDI-a-CBZ has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-a-NDI-a-CBZ is lower than NDI ................................................................. 107

5.1: Croconium dye polymers with pyrrole and dithienopyrrole acceptors. The absorbance of these dyes are significantly broadened and red shifted with absorbances reaching into the NIR ........................................ 130

5.2: BODIPY dye sensitized block copolymer ......................................................... 132
A1: Schematic representation of the TiO$_2$-PS nanocomposite; a) represents the core-shell approach taken for flexible dielectrics with high dielectric constants; b) the polystyrene shell is covalently attached to the TiO$_2$ nanorod through a ligand exchange reaction between a phosphonate terminated polymer chain and a oleic acid coated nanorod..........................................................138

A2: a) Schematic representation of the blending of the TiO$_2$-PS nanocomposite with the PS matrix resulting in the tuning of the dielectric constant of the resulting film; b) the dielectric constant of the resulting films increases with increasing concentration of the TiO$_2$-PS nanocomposite ..................................................139

A3: a) Chemical structure of pentacene, a crystalline small molecule semiconductor; b) the mobility of the pentacene devices increases with increasing dielectric constant ............................................140

A4: AFM images of the pentacene films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite............................................141

A5: a) Chemical structure of sexithiophene (α-6T); b) device architecture of the thin film transistor ..................................................................................141

A6: The mobility of the α-6T devices increases with increasing dielectric constant..................................................................................................................142

A7: AFM images of the α-6T films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite............................................142

A8: Film transfer method for the fabrication of P3HT thin film transistors. The film transfer method allows for the solvent free deposition of the P3HT film onto the nanocomposite dielectric.................................144

A9: The mobility of the P3HT devices on dielectric films with increasing concentrations of TiO$_2$-PS nanocomposite show no consistent trend in mobility both a) before and b) after annealing......................145

A10: AFM images of the P3HT films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite both before and after annealing.................................................................145

xix
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1: Scheme for the synthesis of Sq-TAA-H</td>
<td>26</td>
</tr>
<tr>
<td>2.2: Scheme for the synthesis of Sq-TAA-OH</td>
<td>26</td>
</tr>
<tr>
<td>2.3: Scheme for the synthesis of Sq-TAA-C_{6}H_{13}</td>
<td>27</td>
</tr>
<tr>
<td>2.4: Scheme for the synthesis of Sq-TAA-F</td>
<td>28</td>
</tr>
<tr>
<td>2.5: Scheme for the synthesis of Sq-TAA-CF$_{3}$</td>
<td>28</td>
</tr>
<tr>
<td>3.1: Synthesis of DAA-F1</td>
<td>68</td>
</tr>
<tr>
<td>3.2: Synthesis of DAA-F1-CN</td>
<td>68</td>
</tr>
<tr>
<td>3.3: Synthesis of DAA-F1-In</td>
<td>69</td>
</tr>
<tr>
<td>3.4: Synthesis of DAA-F1-6O</td>
<td>69</td>
</tr>
<tr>
<td>3.5: Synthesis of DAA-F1-6S</td>
<td>69</td>
</tr>
<tr>
<td>3.6: Synthesis of DAA-F1-PL</td>
<td>70</td>
</tr>
<tr>
<td>4.1: Scheme for the synthesis of DTP-PDI</td>
<td>99</td>
</tr>
<tr>
<td>4.2: Scheme for the synthesis of CBZ-NI</td>
<td>99</td>
</tr>
<tr>
<td>4.3: Scheme for the synthesis of EDOT-NI</td>
<td>100</td>
</tr>
<tr>
<td>4.4: Scheme for the synthesis of DTP-NI</td>
<td>100</td>
</tr>
<tr>
<td>4.5: Scheme for the synthesis of CBZ-a-NI</td>
<td>101</td>
</tr>
<tr>
<td>4.6: Scheme for the synthesis of CBZ-a-NDI-a-CBZ</td>
<td>102</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Photovoltaics

It has been estimated that the sun supplies more energy to the earth in one hour as the human population can consume in a year\(^1\). If even a portion of this solar energy can be harvested, the dependence on fossil fuels can be greatly reduced. Therefore, it should come as no surprise that photovoltaics (PVs) have garnered much attention over the past several years\(^2\)\(^-\)\(^8\). The photovoltaic effect was first reported in 1893\(^9\), however, it wasn’t until 1954 that the first silicon solar cell was made which showed 6% efficiency\(^10\). A majority of the solar cells that are commercially available are made out of highly crystalline silicon and exhibit efficiencies near 27.6%\(^11\). Despite silicon’s current popularity, photovoltaics based on highly crystalline silicon suffer from major drawbacks: i) difficult processing conditions and necessary high purity prevent the fabrication of large area devices and also make silicon-based photovoltaics expensive\(^12\); ii) low absorption of silicon necessitates the use of thick layers in order to absorb sunlight which also increases the weight of the device\(^13\); iii) silicon does not allow for the fabrication of flexible devices limiting the use of photovoltaics to flat surfaces which can withhold the weight of such devices.

Organic photovoltaics (OPVs) offer an exciting alternative to silicon solar cells. Unlike silicon-based devices, OPVs offer the potential for fabricating low cost,
large area, lightweight, and flexible devices\textsuperscript{8}. Organic photovoltaics can be solution processed removing the need for difficult and expensive processing techniques. This not only reduces the cost of fabrication of devices, but also allows for the fabrication of large area devices. Tunable absorbance and high extinction coefficients allow for the utilization of significantly thinner films as compared to silicon, while retaining the same light absorption\textsuperscript{14}. Thinner films also result in flexible active layers allowing for the potential of lightweight and flexible devices. Despite the major interest in OPVs, the efficiencies of such devices are still significantly lower than silicon-based devices. A chart showing the record efficiencies in each class of photovoltaics\textsuperscript{11} is shown in Figure 1.1.

In order to improve the efficiencies of OPVs, each step in the conversion of sunlight into electrical current must be understood and optimized. Every OPV requires four steps in order to complete this conversion\textsuperscript{15}: i) absorption of light generating excitons; ii) exciton dissociation resulting in free charges; iii) transport of free charges through the active layer towards their respective electrodes; and iv) charge collection at the electrodes. In the next sections, each of these processes will be explored.

1.2 Processes in Organic Photovoltaics

1.2.1 Light Harvesting
Figure 1.1: A summary of the best reported efficiencies of various types of photovoltaic devices. Crystalline silicon is shown in blue. OPVs can be seen in the bottom right corner in red\textsuperscript{11}.

All photovoltaic devices start with the process of light absorption. In inorganic solar cells, the absorption of sunlight results in the immediate generation of free charge carriers due to the larger dielectric constant compared to organic materials. This differs from OPVs in that absorption of light produces a coulombically bound electron-hole pair referred to as an exciton, which is charge neutral\textsuperscript{16}. OPVs typically consist of conjugated materials because they display desirable absorption profiles. The absorbance of conjugated molecules are often intense and broad and extend into the visible and near infrared regions\textsuperscript{14}. This provides an extensive overlap with the solar spectrum, seen in Figure 1.2, and when coupled with the large molar absorptivity of such molecules, allows for the utilization of thinner films (100 – 200 nm).
Figure 1.2: The solar irradiance spectrum covers a large range of wavelength but weighs heavily in the 400 nm – 1100 nm range. Organic molecules can be tuned in order to absorb light in this region$^{17}$.

In order to improve the light harvesting of photovoltaic devices, significant emphasis has been put on utilizing low bandgap small molecules and polymers$^{17-23}$. Reducing the bandgap of a material can be achieved simply by extending the conjugation of the material$^{24-26}$. Another strategy for lowering the bandgap is to minimize the bond length alternation. Minimizing the energy level difference between the benzenoid and quinoid resonance structures will result in a lower bandgap$^{27,28}$. Some dyes, such as squaraine dyes, exist in a partial benzenoid and partial quinoid form, seen in Figure 1.3. When these molecules are symmetric, the bond length alternation is at a minimum providing a low bandgap$^{29}$. Minimizing bond length alternation can also be achieved by the charge stabilization that occurs from alternating donor and acceptor molecules in a small molecule or polymer$^{18,21,30}$. The bandgap of such a molecule can often be tuned by varying the donor and acceptor strength$^{22,31}$. 
1.2.2 Exciton Diffusion and Dissociation

The absorption of light in OPVs does not produce free charges but rather a charge neutral exciton. In order to generate free electrons and holes, the exciton must travel to an interface between the donor and acceptor material where the exciton can be split\textsuperscript{32}. Due to the fact that the exciton is charge neutral, it is unaffected by electrical field and therefore diffuses randomly throughout the active layer. The exciton must reach an interface within its lifetime (10 – 20 nm) or it will decay back to the ground state\textsuperscript{32}. This necessitates small and regular domains of donor and acceptor materials. Bulk heterojunction (BHJ) devices, where the donor and acceptor are blended together and cast from the same solution, is one of the great advances in OPVs because it provides such a morphology in the active layer\textsuperscript{33-36}. Alternately, the donor and acceptor molecules can be covalently attached to each other to guarantee and donor and acceptor interface within the lifetime of the exciton\textsuperscript{37}.

Once the exciton reaches an interface, it must then dissociate into free charges. This process is depicted in Figure 1.4. As mentioned above, the charge separation is fueled by the energy level difference in the LUMOs of the donor and
the acceptor\textsuperscript{32,35,38}. It has been suggested that this energy level offset must be at least 0.3 eV to allow for facile charge separation\textsuperscript{38}. Therefore, special care must be taken in the design of the active layer materials to ensure appropriate energy level alignment.

![Diagram of exciton dissociation](image)

Figure 1.4: Schematic representation of the dissociation of the exciton formed in the donor material. Here the electron in the LUMO of the excited state donor is transferred to the LUMO of the acceptor as long as the energy level difference between the two LUMOs is at least 0.3 eV.

### 1.2.3 Charge Migration and Collection

Once the free charges have been generated, the electrons and holes will move through the active layer towards their respective electrodes. The efficiency at which these charges reach the electrodes will depend on the mobility and the molecular packing of the materials. Crystalline small molecules, such as pentacene, exhibit enhanced molecular packing and high mobilities\textsuperscript{39}. However, these small molecules are often not soluble and require difficult processing techniques. Polymers, on the other hand, can be solution processed but typically show lower mobilities than their small molecule counterparts. Additionally, the electron and hole mobility must be
balanced in OPVs because slow and unbalanced charge transport results in lower efficiencies\(^{40,41}\). The bulk morphology of the device will also affect the efficiency of charges reaching the electrodes\(^{42,43}\). There must be clear paths for the charges to travel without encountering isolated domains. Therefore the donor and acceptor domains should not only be small and regular but also continuous from electrode to electrode.

Charge collection at the electrodes requires appropriate alignment of the work function of the electrodes with the energy levels of the active layer. The interface between the active layer and the electrodes is also a critical parameter in the fabrication of OPVs. Significant focus has been placed on the design of these interfaces to enhance contact between the incompatible organic and inorganic layers. The most common surface modification is the utilization of poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate (PEDOT:PSS), which is used as an electron blocking layer between a metal oxide electrode and the active layer\(^{44}\).

### 1.3 Device Parameters of Organic Photovoltaics

In order to characterize the performance of the device, standardized illumination conditions are typically used. A light source (AM 1.5G) is used to simulate the solar spectrum with an intensity of 100mW/cm\(^2\). This is meant to mimic the average intensity of the sunlight over a year at mid-latitudes. An example of a J-V curve is shown in Figure 1.5. The efficiency of a PV device is determined using three parameters: the open circuit voltage (\(V_{oc}\)), the short-circuit current
density ($J_{sc}$), and the fill factor (FF). Each of these parameters are closely related to the material used in the device as well as the device architecture and morphology.

![Figure 1.5: Typical J-V characteristics of an OPV. The critical device parameters ($V_{oc}$, $J_{sc}$, $V_{mpp}$, and $J_{mpp}$) are pointed out. The FF is equal to the ratio of the grey square to the square made by the dotted line.]

The $V_{oc}$ is the maximum voltage possible across a photovoltaic cell and occurs when no current is flowing. In organic photovoltaics, this value is directly related to the energy level difference between the HOMO of the donor and the LUMO of the acceptor. Therefore a donor material with a low HOMO would be desirable for maximizing the $V_{oc}$ of the device. Unfortunately, as the $V_{oc}$ is optimized, the bandgap, and thus the light harvesting, of the device is compromised. Careful tuning of the energy levels of the active layer materials is essential for the optimization of the $V_{oc}$.

The $J_{sc}$ is the maximum current density that a solar cell can produce and is the current that flows through a solar cell when there is no external resistance. The $J_{sc}$ relates to the generation and collection of light generated charge carriers. For OPVs, the $J_{sc}$ depends on the efficiency of each step discussed in Section 1.2:
light absorption, exciton diffusion and dissociation, charge transport, and charge collection. As far as the active layer is concerned, the $J_{SC}$ is improved if the absorbance of the film is improved. Therefore materials with low bandgaps and high extinction coefficients are desirable. The $J_{SC}$ is also improved if the materials in the active layer have high charge mobility and appropriate morphology.

The FF is the ratio of the maximum power output to the theoretical power output. The maximum power output is given as the point on the J-V curve where the maximum power is produced. On the J-V curve this is represented as a rectangle with an area equal to the product of the $J_{mpp}$ and the $V_{mpp}$. The theoretical power output is given as the product of the $J_{SC}$ and the $V_{OC}$. Therefore the equation for calculating the FF of an OPV is:

$$\text{FF} = \frac{J_{mpp} V_{mpp}}{J_{SC} V_{OC}}$$

The power conversion efficiency (PCE) of a photovoltaic device is the ratio of the power output to the power input. The equation for determining the PCE is:

$$PCE = \frac{J_{max} V_{max}}{P_{in}} = \text{FF} \frac{J_{SC} V_{OC}}{P_{in}}$$

1.4 Polymer Photovoltaics

To date, the most successful OPVs have implemented a BHJ architecture utilizing a conjugated donor-acceptor (D-A) polymer as the donor and a soluble fullerene derivative, most commonly [6,6]-phenyl-C61-butyric acid methyl ester (PC_{61}BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC_{71}BM) as the acceptor.45
A schematic representation of a BHJ OPV can be seen in Figure 1.6. Most commonly, BHJ devices are built on an ITO-glass substrate, which acts as both a trans

![Schematic representation of a BHJ OPV](image)

**Figure 1.6:** Schematic representation of a BHJ OPV. The BHJ architecture provides greater interfacial area for the dissociation of excitons within the exciton diffusion distance.

parent substrate and electrode. The substrate is typically coated with an interfacial layer, PEDOT:PSS, which is a transparent conductive polymer and provides an improved interface between the ITO and the active layer while acting as an electron blocking layer\(^44\). The polymer:fullerene layer is deposited onto the PEDOT:PSS layer followed by the deposition of a metal cathode, most commonly aluminum.

Polymers have many beneficial qualities that make them suitable for the fabrication of OPVs. Firstly, polymerization provides an extended conjugation which allows for good light harvesting. Additionally, conjugated polymers are often rigid and planar which allows for good pi-orbital overlap, which facilitates charge transport. Polymers are often utilized for their good film forming properties and solubility, which allow them to be used in fabrication techniques appropriate for large areas such as roll-to-roll processing\(^46\).
As mentioned previously, the most common strategy for the design of low bandgap polymers is to alternate electron rich donors with electron poor acceptors in the polymer backbone. This results in a red-shifted absorbance into the region where the solar photon flux is most intense\(^4\). Conjugated polymers have been studied extensively in order to optimize light absorption as well as charge transport and morphology control in BHJ OPVs\(^{17,21,23,30,48-54}\). Figure 1.7 shows the structures of some polymers, which have demonstrated the highest efficiencies thus far.

![Chemical structures of some of the better performing polymer OPVs to date. P3HT shows efficiencies around 5%. These donor acceptor polymers all show efficiencies about 6.8%\(^{53,54,55}\).](image)

Poly(3-hexylthiophene) (P3HT) is considered the gold standard of OPVs and has been studied extensively\(^6,42,52,53\). P3HT demonstrates high hole mobility as a result of its good self-assembly properties and crystallinity. P3HT:PC\(_{61}\)BM BHJ
devices have reported PCE values of 4.5%\textsuperscript{64,52,53}. Although P3HT is by far the most widely studied donor polymer for OPVs, it is not the most ideal polymer. P3HT has a bandgap of 2 eV, which is not suitable for the absorbance of a significant portion of the solar photon flux. Additionally, P3HT has a high lying HOMO, which makes it oxidatively unstable and compromises $V_{\text{OC}}$.

D-A polymers offer a significant improvement in bandgap over P3HT. One of the most used and successful techniques is to implement weak or moderate donors with strong acceptors\textsuperscript{22,31}. As mentioned in earlier sections, both a low bandgap and a high $V_{\text{OC}}$ are desirable for high efficiency OPVs. Utilizing a weak donor maintains a low lying HOMO energy level, while a strong acceptor promises a low bandgap. Examples of such polymers can be seen in Figure 1.7. These polymers have shown efficiencies up to 8%, making them some of the highest efficiency OPVs\textsuperscript{54,55}.

There are also some drawbacks to polymer OPVs. Conjugated polymers, especially at high molecular weights, are not readily soluble. This makes the processing of these polymers increasingly difficult. Additionally, polymers often contain impurities due to insufficient purification techniques. Impurities have been shown to greatly affect the efficiency of OPVs by acting as charge traps and compromising device morphology. Polymers also have a variation in molecular weight, which prevent consistent batch to batch processing and make the study of structure-property relationships increasingly difficult\textsuperscript{56,57}. 
1.5 Small Molecule Photovoltaics

Polymers have been the main focus of OPVs for several years, however, more recently, small molecule OPVs have shown great promise\textsuperscript{2,5,19,20,58-61}. Perhaps one of the greatest advantages of small molecule OPVs is their consistency from batch to batch. Small molecules have a well defined molecular structure which can be characterized by several techniques. Unlike their polymer counterparts, small molecules have a definite molecular weight and can be synthesized with very high purity. This facilitates the study of the structure-property relationship of such systems. As seen in Figure 1.8, the efficiencies of small molecule OPVs are rapidly climbing and coming within reach of their polymer counterparts.

![Graph showing PCE (%) vs Year for Polymer and Small Molecule OPVs.](image)

Figure 1.8: Recent progress in small molecule OPVs have resulted in quickly rising efficiencies nearing those of polymer OPVs.

Out of all of the small molecule semiconductors reported, small molecule dyes have by far shown the most promise for OPVs. Most dyes are made of push pull systems, which show desirable absorptions at long wavelengths with high
extinction coefficients. Additionally, by manipulating the chemical structure, a large degree of variability can be seen in the energy levels.

In addition to dye molecules, a few extended D-A small molecule systems have also shown promise for OPVs. Similar to D-A polymers, these small molecules show improved light harvesting due to the electron rich and electron poor nature of the molecule. A few examples of these small molecule dyes and D-A systems can be seen in Figure 1.9. Each of these dyes show PCE of at least 6%, with some reaching to nearly 7%\(^{62-66}\).

![Figure 1.9: Small molecules which show high efficiencies. The first row is dyes and the bottom two rows are D-A systems. All show PCE about 6%\(^{62-66}\).](image)

### 1.6 Summary and Dissertation Overview

In this chapter, an introduction into OPVs has been discussed. Conventional PVs are made from silicon and are commercially available with efficiencies nearing 28%. The absorbance of silicon greatly limits improvements to the efficiency, and
the high purity of silicon and the processing techniques necessary for fabrication make the devices costly. OPVs on the other hand offer some benefits over traditional silicon based devices including tunable absorbance with high extinction coefficients, and the potential for fabricating low cost, large area, flexible devices. OPVs however operate by more complicated processes, which have thus far limited them from reaching high efficiencies.

There are multiple processes that an OPV device must undergo in order to convert sunlight into electrical current. Optimization of these processes through molecular design or device manipulation will bring the realization of commercially viable high efficiency OPVs. As discussed in this chapter, the processes that the active layer materials undergo are interrelated to one another and therefore require a fine balancing act to reach high efficiencies. Device parameters are also influenced by multiple processes meaning that changing one property of the molecular design of the active layer, will have multiple effects on the device properties.

Examples of both polymer and small molecule OPVs are also discussed. Polymers offer superior processing and morphological control over small molecules. Small molecules, on the other hand, offer a greater control over structure-property relationship studies. Although polymers have shown greater efficiencies to date, small molecules are quickly catching up with their polymer counterparts.

In this dissertation, the focus is on the application of small molecules for OPVs and the potential application of small molecules in sensitizing polymer OPVs. In Chapter 2, squaraine dyes for OPVs will be discussed. The energy levels of triarylamine squaraine dyes will be tuned in order to optimize the fine balance
between enhanced light harvesting and increased $V_{OC}$. In Chapter 3, the tunability of the absorbance of ketocyanine dyes is explored. The acceptor strength of the dyes are tuned in order to increase the cyanine character of the dye resulting in shifts in the absorbance. In Chapter 4, the design properties of D-A systems as sensitizers are explored and their application in improving the light harvesting of block copolymers is discussed. Finally, in Chapter 5, the general conclusions of the dissertation will be given and future directions for each of the projects will be proposed.

1.7 References


CHAPTER 2

ENERGY LEVEL TUNING IN SQUARAINES FOR IMPROVED LIGHT HARVESTING AND OPEN CIRCUIT VOLTAGE FOR ORGANIC PHOTOVOLTAICS

2.1 Introduction

Organic photovoltaics (OPVs) undergo four major processes in order to convert solar energy into electricity: i) absorption of a photon generating an exciton; ii) exciton dissociation generating free charge carriers; iii) charge transport through the active layer; and iv) charge collection at the electrodes. Improving the efficiency of a PV device does not simply require the improvement of each step, but also the optimization of each step with respect to the entire process.

To improve the light absorbance of the active layer, low bandgap materials, which absorb well into the near IR region, are often utilized\textsuperscript{1-4}. In order to lower the bandgap of a material, either the HOMO can be raised and/or the LUMO can be lowered. Even though raising the HOMO would result in a low bandgap, it can have negative effects on the device performance. The open circuit voltage ($V_{oc}$) is directly related to the energy level difference between the HOMO of the donor and the LUMO of the acceptor\textsuperscript{5,6}. As seen in Figure 2.1, raising the HOMO of the donor material would lower the theoretical maximum $V_{oc}$ that can be achieved. Additionally, raising the HOMO can also compromise the oxidative stability of the donor material. Alternately, lowering the LUMO of the donor material will compromise the exciton dissociation process. It has been estimated that in order for facile exciton dissociation, the LUMO of the donor must be at least 0.3 eV above the LUMO of the acceptor\textsuperscript{7}. Therefore this energy level difference must be preserved.
Figure 2.1: Low bandgap materials offer enhanced light absorption for organic photovoltaics devices. Raising the HOMO of the chromophore would compromise the \( V_{OC} \) of the resulting device. The LUMO can only be lowered to 0.3 eV above the LUMO of the acceptor to allow for exciton dissociation. Energy level tuning is essential for the optimization of OPVs.

Currently, most OPV devices are fabricated using some fullerenes derivative as the electron acceptor. Most commonly, phenyl-C\textsubscript{61}-butyric-acid-methyl ester (PC\textsubscript{61}BM) and phenyl-C\textsubscript{71}-butyric-acid-methyl ester (PC\textsubscript{71}BM) are used. There are very few alternative n-type materials that have shown as much promise as these, and therefore, the burden of optimization often falls on the donor material. It is therefore imperative that the energy levels of the donor can be tuned to optimize the characteristics of the material, such as light absorption and exciton dissociation, as well as device parameters such as \( V_{OC} \).

Low bandgap polymers have been extensively studied as donor materials in OPVs\textsuperscript{4,5,8,9}. Decreasing bandgap is often a result of extended conjugation as well as alternating donor and acceptor moieties in the backbone of the polymer. Identifying low bandgap small molecules is often more problematic because exploiting extended conjugation is not an option. Recently, investigation into the use of various dye molecules, have revealed promising candidates for small molecule OPVs\textsuperscript{2,3,10-14}. 
Squaraines are a class of dyes resulting from the condensation of squaric acid, a small and planar electron acceptor, with two electron-donating materials. Squaraine dyes typically consist of a donor-acceptor-donor configuration with an electron deficient core flanked by two electron rich groups. Squaraine dyes typically have a strong absorbance in the visible to near IR region of the spectrum, with molar extinction coefficients on the order of $10^4 - 10^5 \text{ M}^{-1}\text{cm}^{-1}$. Recently, squaraine dyes have showed promise in the field of small molecule photovoltaics with efficiencies reaching $6\%_{11,14,17-20}$.

2.2 Results and Discussion

2.2.1 Molecular Design

A squaraine dye based on triarylamine donor molecules was recently published showing promising results for small molecule OPVs$^{11,13}$. This molecule (Sq-TAA-H), shown in Figure 2.2, is an excellent candidate for studying the effect of the energy level tuning of the small molecule. Triarylamine is typically considered as a weak donor. Molecules combining weak donors and strong acceptors have been shown to be advantageous for push-pull systems and therefore for photovoltaics$^{21,22}$.

In order to tune the energy levels of the squaraine small molecules, electron donating or electron withdrawing groups have been installed onto the triarylamine moieties. Installing electron donating groups onto triarylamines has been shown to destabilize the HOMO energy level. Alternatively, installing electron withdrawing groups have been shown to stabilize the HOMO energy level. By tuning the strength
of the electron donating or electron withdrawing groups, the HOMO energy level can be tuned over a range\textsuperscript{23,24}.

As seen in Figure 2.2, two different electron donating and electron withdrawing groups will be used to tune the HOMO of the squaraine dye. The expected trend in HOMO energy level should follow that of the most electron donating to the most electron withdrawing: Sq-TAA-OH > Sq-TAA-C\textsubscript{6}H\textsubscript{13} > Sq-TAA-H > Sq-TAA-F > Sq-TAA-CF\textsubscript{3}. By selectively tuning the HOMO, the bandgap can be optimized while maintaining appropriate \(V_{OC}\) and exciton dissociation.

![Molecular design of squaraine dyes with tunable bandgaps and HOMO energy levels.](image)

**Figure 2.2:** Molecular design of squaraine dyes with tunable bandgaps and HOMO energy levels. Sq-TAA-H offers a control molecule for reference. Sq-TAA-C\textsubscript{6}H\textsubscript{13} and Sq-TAA-OH are squaraine dyes with increasing electron donor strength. Sq-TAA-F and Sq-TAA-CF\textsubscript{3} are squaraine dyes with increasing electron withdrawing strength.

The synthesis of Sq-TAA-H can be seen in Scheme 2.1. 3,5-dimethoxy-N,N-diphenylaniline was synthesized by a palladium catalyzed Buchwald coupling of 3,5-dimethoxyaniline and bromobenzene. 3,5-dimethoxy-N,N-diphenylaniline was deprotected with BBr\textsubscript{3} to yield 5-(diphenylamino)benzene-1,3-diol. The hydroxyl groups are a synthetic necessity as they active the carbon between them for the
subsequent condensation reaction. The hydroxyl groups on the triarylamino play another role in the squaraine dye; the hydroxyl groups are hydrogen bonded with the oxides in the central ring resulting in a planarization of the molecule. Sq-TAA-H was synthesized by condensation of 5-(diphenylamino)benzene-1,3-diol and squaric acid.

Scheme 2.1: Scheme for the synthesis of Sq-TAA-H.

The synthesis of Sq-TAA-OH can be seen in Scheme 2.2. A copper catalyzed Ullmann coupling of 3,5-dimethoxyaniline and iodoanisole followed by deprotection with BBr₃ yields 5-(bis(4-hydroxyphenyl)amino)benzene-1,3-diol. Sq-TAA-OH was

Scheme 2.2: Scheme for the synthesis of Sq-TAA-OH.
synthesized by condensation of 5-(bis(4-hydroxyphenyl)amino)benzene-1,3-diol and squaric acid.

The synthesis of Sq-TAA-C$_6$H$_{13}$ can be seen in Scheme 2.3. Bis(4-hexylphenyl)amine was synthesized by a palladium catalyzed Buchwald coupling of 1-bromo-4-hexylbenzene and 4-hexylaniline. A palladium catalyzed Buchwald coupling of 1-bromo-3,5-dimethoxybenzene and bis(4-hexylphenyl)amine followed by deprotection with BBr$_3$ yields 5-(bis(4-hexylphenyl)amino)benzene-1,3-diol. Sq-TAA-C$_6$H$_{13}$ was synthesized by condensation of 5-(bis(4-hexylphenyl)amino)benzene-1,3-diol and squaric acid.

Scheme 2.3: Scheme for the synthesis of Sq-TAA-C$_6$H$_{13}$.

The synthesis of Sq-TAA-F can be seen in Scheme 2.4. A palladium catalyzed Buchwald coupling of 3,5-dimethoxyaniline and 1-bromo-4-fluorobenzene followed by deprotection with BBr$_3$ yields 5-(bis(4-fluorophenyl)amino)benzene-1,3-diol. Sq-TAA-F was synthesized by condensation of 5-(bis(4-fluorophenyl)amino)benzene-1,3-diol and squaric acid.
Scheme 2.4: Scheme for the synthesis of Sq-TAA-F.

The synthesis of Sq-TAA-CF$_3$ can be seen in Scheme 2.5. N,N-bis(3,5-bis(trifluoromethyl)phenyl)-3,5-dimethoxyaniline was synthesized by a palladium catalyzed Buchwald coupling of 3,5-dimethoxyaniline and 1-bromo-3,5-bis(trifluoromethyl)benzene. The triarylamine was deprotected with BBr$_3$ to yield 5-(bis(3,5-bis(trifluoromethyl)phenyl)amino)benzene-1,3-diol which was condensed with squaric acid to yield Sq-TAA-CF$_3$.

Scheme 2.5: Scheme for the synthesis of Sq-TAA-CF$_3$. 
2.2.2 Optoelectronic Properties

The absorbance of each dye was taken in dichloromethane (DCM) and can be seen in Figure 2.3. Each of the dyes absorb significantly at long wavelengths. This is desirable as it better overlaps with the solar irradiance spectrum. The absorbance spectra are plotted with respect to the molar absorptivity demonstrating that the extinction coefficients of the dyes range from $5 \times 10^4$ – $2.5 \times 10^5$ M$^{-1}$cm$^{-1}$.

![Absorbance Spectra](image)

Figure 2.3: Solution absorbance spectra of the squaraine dyes in DCM. The spectra are plotted with respect to molar absorptivity to indicate the extinction coefficient of each dye. It can be seen that as the electron donation character of the dye is increased, the absorbance red shifts.

It can also be seen that the onset of the absorbance shifts towards longer wavelengths as the electron donating character increases. The absorbance onset is often used as an estimation of the bandgap of the material. This follows the expected trend where the band gap increases in the following manner: Sq-TAA-CF$_3$ > Sq-TAA-F > Sq-TAA-H > Sq-TAA-C$_6$H$_{13}$ > Sq-TAA-OH.

The absorbance spectra in tetrahydrofuran (THF) can be seen in Figure 2.4. It can be seen that when the dyes are dissolved in THF, a high-energy band emerges.
THF is capable of hydrogen bonding with the hydroxyl groups on the triarylamines. This could potentially reduce the hydrogen bonding between the hydroxyl groups and the squaric acid core, resulting in the twisting of the molecule. If this were the case, then this twist will cause a break in the conjugation resulting in a blue-shifted peak in the absorbance. The emergence of this peak is least pronounced in

![Solution absorbance spectra of the squaraine dyes in THF.](image)

Figure 2.4: Solution absorbance spectra of the squaraine dyes in THF. It can be seen that a high energy peak emerges as a result of the solvent hydrogen bonding with the dye and causing a break in the conjugation due to the twist in the backbone.

Sq-TAA-C₆H₁₃ and most pronounced in Sq-TAA-CF₃, where the low energy peak is essentially gone replaced by a peak with a λ_max of approximately 400 nm. Additionally, the color of the solution changes from a deep blue color when dissolved in DCM to a pale yellow when dissolved in THF. This pale yellow color is characteristic of the triarylamine itself, suggesting that the change in color is due to the break in conjugation resulting from THF hydrogen bonding with the squaraine dye.
As mentioned above, increasing the electron withdrawing character results in a more pronounced high-energy band. This could be a result of the electron withdrawing groups pulling electron density out of the central squaraine ring weakening the hydrogen bond acceptor strength of the oxides. Additionally, pulling electron density out of the phenyl ring attached to the squaraine core will make the hydroxyl groups more acidic making them stronger hydrogen bond donors. Therefore, the hydroxyl groups will most likely hydrogen bond with the THF resulting in the break of conjugation.

The thin film absorbance of the dyes, compared to that of the solution absorbance, can be seen in Figure 2.5. In all cases it can be seen that the thin film absorbance is red shifted and broadened compared to the solution UV. This suggests that there is some aggregation of the molecules in the film. These changes to the absorbance are beneficial for the light harvesting aspects of OPVs. Additionally, aggregation can help with the charge transport in the active layer.

![Graph](image)

Figure 2.5: Thin film absorbance of the squaraine dyes are red shifted and broadened as compared to the solution absorbance in DCM.
As can be seen in Figure 2.6, annealing has very little effect on the absorbance of the squaraine dyes with the exception of Sq-TAA-C6H13. All of the squaraine dyes seem to be crystalline, but only Sq-TAA-C6H13 has solubilizing groups. These groups most likely reorient themselves during the annealing process allowing for further packing of the molecule. The effect of this reorganization can be seen by the emergence of the low energy peak in the annealed film of Sq-TAA-C6H13.

![Graph showing absorbance and wavelength](image)

Figure 2.6: Annealing the films do not appear to have any major effect on the absorbance with the exception of Sq-TAA-C6H13. When Sq-TAA-C6H13 is annealed a low energy peak emerges at about 800 nm. This suggests further organization of the film upon thermal annealing.

The HOMO and LUMO energy levels were determined electrochemically by using thin film cyclic voltammetry (CV) in dry acetonitrile or DCM using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the standard. HOMO and LUMO energy levels were calculated with respect to vacuum using the peak onsets using the equations:

\[ \text{HOMO} = -(4.8 + E_{\text{ox onset}}) \]

\[ \text{LUMO} = -(4.8 + E_{\text{red onset}}) \]
These energy levels are shown in Figure 2.7. Electron donating groups result in a destabilization of the HOMO energy level as a result of pushing electron density into an already electron rich system. This causes a rise in the HOMO. Electron withdrawing groups result in a stabilization of the HOMO energy level as a result of removing some of the electron density from the electron rich system. This causes a decrease in the HOMO. The LUMO energy levels are not affected as much and therefore the band gap increases moving from least electron withdrawing to most electron withdrawing. It should be noted that the HOMO energy level of the Sq-TAA-CF₃ molecule could not be calculated electrochemically. Changes in the solubility and the color of the molecule suggest that there is a chemical change occurring upon oxidation. It has been shown in literature that when triarylamines with electron withdrawing groups are oxidized, dimerization is more common due to the ease of deprotonation of the radical cation²⁵. Therefore the HOMO energy level of Sq-TAA-CF₃ is calculated using the optical band gap. The optical band gap

![Figure 2.7: HOMO and LUMO energy levels of the squaraine dyes calculated electrochemically compared to ferrocene. LUMO of CF₃ is estimated from the optical bandgap. The bandgap is tuned by variations in the HOMO energy levels, while the LUMO energy levels remain relatively constant.](image-url)
can be estimated from the onset of the absorbance spectra using the equation $E_{\text{g,}\text{opt}} = 1240 \text{ eV nm/} \lambda_{\text{onset}}$. Subtracting the band gap from the electrochemically determined LUMO energy level gives the HOMO energy level.

### 2.2.3 Charge Transport Properties

All of the squaraine dyes were investigated for their charge transport properties using bottom contact field effect transistors. The devices were measured both before and after annealing at various channel lengths. All molecules were investigated both for n-type and p-type mobility.

Sq-TAA-OH was found to be strictly hole transporting. The average measured mobilities are reported in Table 2.1. As the channel length increases, the mobility decreases. This is often seen in films that have defects, which often arise from the attempt to spin coat molecules that are crystalline. The channel length

<table>
<thead>
<tr>
<th>Sq-TAA-OH</th>
<th>Charge Carrier</th>
<th>$L = 2.5 \mu m$</th>
<th>$L = 5 \mu m$</th>
<th>$L = 10 \mu m$</th>
<th>$L = 20 \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Is</td>
<td>Hole (cm² V⁻¹ s⁻¹)</td>
<td>$1.90 \times 10^{-5}$</td>
<td>$6.96 \times 10^{-6}$</td>
<td>-</td>
<td>$5.90 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 7.40 \times 10^{-6}$</td>
<td>$\pm 6.40 \times 10^{-7}$</td>
<td>-</td>
<td>$\pm 2.20 \times 10^{-7}$</td>
</tr>
<tr>
<td>Annealed</td>
<td>Hole (cm² V⁻¹ s⁻¹)</td>
<td>$1.91 \times 10^{-5}$</td>
<td>$1.26 \times 10^{-5}$</td>
<td>$7.86 \times 10^{-6}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 6.60 \times 10^{-6}$</td>
<td>$\pm 5.00 \times 10^{-8}$</td>
<td>$\pm 1.12 \times 10^{-6}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.1: Average hole mobilities and standard deviations of Sq-TAA-OH TFTs with varying channel lengths.

represents the distance that the charge must travel between the source and the drain electrode. The larger distance increases the probability that the charge will reach a defect or a trap lowering the overall mobility. Annealing the film does not
show any major changes indicating that there is no major reorganization as a result of the annealing.

Sq-TAA-C$_6$H$_{13}$ was found to be strictly hole transporting. The average measured mobilities are reported in Table 2.2. Annealing the film results in major increases in the hole mobility suggesting a significant reorganization of the film upon annealing. This reorganization can also be seen in the absorbance of the films where annealing the Sq-TAA-C$_6$H$_{13}$ film shows the emergence of a long wavelength peak.

Sq-TAA-H was found to be strictly hole transporting. The average measured mobilities are reported in Table 2.3. Similar to the Sq-TAA-OH transistor, annealing the film does not show any major changes indicating that there is no major reorganization as a result of the annealing.

<table>
<thead>
<tr>
<th>Sq-TAA-C$<em>6$H$</em>{13}$</th>
<th>Charge Carrier</th>
<th>L = 2.5 μm</th>
<th>L = 5 μm</th>
<th>L = 10 μm</th>
<th>L = 20 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Is</td>
<td>Hole</td>
<td>4.17 x 10$^{-6}$</td>
<td>1.51 x 10$^{-5}$</td>
<td>3.73 x 10$^{-6}$</td>
<td>2.79 x 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>(cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>± 6.50 x 10$^{-8}$</td>
<td>± 1.18 x 10$^{-5}$</td>
<td>± 2.95 x 10$^{-7}$</td>
<td>± 4.05 x 10$^{-7}$</td>
</tr>
<tr>
<td>Annealed</td>
<td>Hole</td>
<td>2.54 x 10$^{-3}$</td>
<td>9.66 x 10$^{-4}$</td>
<td>1.53 x 10$^{-4}$</td>
<td>1.76 x 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>± 8.25 x 10$^{-4}$</td>
<td>± 1.05 x 10$^{-4}$</td>
<td>± 9.44 x 10$^{-5}$</td>
<td>± 1.28 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

Table 2.2: Average hole mobilities and standard deviations of Sq-TAA-C$_6$H$_{13}$ TFTs with varying channel length. The mobility increased with annealing confirming the increase in organization that was seen in the annealed thin film absorbance.
<table>
<thead>
<tr>
<th>Sq-TAA-H</th>
<th>Charge Carrier</th>
<th>$L = 2.5 , \mu m$</th>
<th>$L = 5 , \mu m$</th>
<th>$L = 10 , \mu m$</th>
<th>$L = 20 , \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Is</td>
<td>Hole</td>
<td>$6.78 \times 10^{-4}$</td>
<td>$4.89 \times 10^{-4}$</td>
<td>$9.63 \times 10^{-4}$</td>
<td>$6.72 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$\pm 1.05 \times 10^{-4}$</td>
<td>$\pm 8.50 \times 10^{-6}$</td>
<td>$\pm 1.99 \times 10^{-4}$</td>
<td>$\pm 8.90 \times 10^{-5}$</td>
</tr>
<tr>
<td>Annealed</td>
<td>Hole</td>
<td>$7.78 \times 10^{-4}$</td>
<td>$4.00 \times 10^{-4}$</td>
<td>$5.71 \times 10^{-4}$</td>
<td>$4.89 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$\pm 5.20 \times 10^{-5}$</td>
<td>$\pm 6.50 \times 10^{-6}$</td>
<td>$\pm 2.25 \times 10^{-5}$</td>
<td>$\pm 3.00 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 2.3: Average hole mobilities and standard deviations of Sq-TAA-H TFTs with varying channel length.

Sq-TAA-F was found to be ambipolar, meaning that it shows both hole and electron mobility. The average measured mobilities are reported in Table 2.4. Sq-TAA-CF$_3$ was found to be strictly electron transporting. The average measured mobilities are reported in Table 2.5. In literature, squaraine dyes have been utilized as hole transporters rather than electron transporters. However, it is not uncommon in literature to see that installing fluorine atoms into a hole transporting
dye results in a change in the charge carrier mobility\textsuperscript{26-31}. Several papers have attributed a change in charge carrier mobility to the lowering of the LUMO energy level, allowing for easier reduction, thus opening up the electron transporting channel\textsuperscript{30}. Similar to the squaraine dyes reported here, it has been shown that this phenomenon also occurs when the LUMO energy level is relatively unaffected by installing fluorine atoms\textsuperscript{29}. Despite the several reported molecules that exhibit this change, the cause is still unknown.

In attempts to determine the cause of the change in the polarity of the charge carrier, the molecules were investigated by DFT using Gaussian 2009\textsuperscript{32} with B3LYP level of theory and a 6-311g(d,p) basis set. The calculated surfaces of the HOMO and LUMO energy levels for Sq-TAA-OH and Sq-TAA-CF\textsubscript{3} are shown in Figure 2.8. There does not appear to be any major difference in the HOMO or LUMO energy levels upon installation of the fluorine atoms. Further investigation into this change in charge carrier polarity is therefore necessary to understand the effect that fluorine

<table>
<thead>
<tr>
<th>Sq-TAA-CF\textsubscript{3}</th>
<th>Charge Carrier</th>
<th>L = 2.5 μm</th>
<th>L = 5 μm</th>
<th>L = 10 μm</th>
<th>L = 20 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Is</td>
<td>Electron</td>
<td>6.11 × 10\textsuperscript{-6} ± 1.13 × 10\textsuperscript{-6}</td>
<td>2.65 × 10\textsuperscript{-6} ± 4.55 × 10\textsuperscript{-7}</td>
<td>1.20 × 10\textsuperscript{-6} ± 8.50 × 10\textsuperscript{-8}</td>
<td>1.51 × 10\textsuperscript{-6} ± 2.00 × 10\textsuperscript{-8}</td>
</tr>
<tr>
<td>Annealed</td>
<td>Electron</td>
<td>7.29 × 10\textsuperscript{-6} ± 5.55 × 10\textsuperscript{-7}</td>
<td>2.65 × 10\textsuperscript{-6} ± 1.95 × 10\textsuperscript{-7}</td>
<td>1.57 × 10\textsuperscript{-6} ± 3.70 × 10\textsuperscript{-7}</td>
<td>1.55 × 10\textsuperscript{-6} ± 3.90 × 10\textsuperscript{-7}</td>
</tr>
</tbody>
</table>

Table 2.5: Average electron mobilities and standard deviations of Sq-TAA-CF\textsubscript{3} TFTs with varying channel length.
atoms have on the squaraine dyes.

Figure 2.8: HOMO and LUMO energy levels of Sq-TAA-OH and Sq-TAA-CF₃ as determined theoretically by DFT using Gaussian 09 with B3LYP level of theory and 6-311g(d, p) basis set.

2.2.4 Photovoltaic Properties

In order to determine the photovoltaic properties of these dyes, both bilayer and bulk heterojunction devices have been investigated. Bilayer devices are fabricated by spin coating a solution of the squaraine dye onto an indium tin oxide-glass (ITO-glass) substrate followed by subsequent thermal evaporation of the acceptor molecule and aluminum electrodes. Bilayer devices are fabricated by spin coating a solution of squaraine dye and acceptor onto an ITO-glass substrate followed by the evaporation of aluminum electrodes.

The J-V curves for the bilayer devices of Sq-TAA-OH:PC₆₁BM, Sq-TAA-H:PC₆₁BM, and Sq-TAA-F:PC₆₁BM can be seen in Figure 2.8 a, b, and c, respectively.
A summary of the PV parameters can be seen in Table 2.6. The Sq-TAA-OH:PC$_{61}$BM device has the lowest $V_{OC}$ most likely due to its destabilized HOMO energy level. This could be one of the reasons that the Sq-TAA-OH:PC$_{61}$BM device has lower efficiency than the Sq-TAA-H:PC$_{61}$BM device despite the lower bandgap of Sq-TAA-OH. The Sq-TAA-H:PC$_{61}$BM device and Sq-TAA-F:PC$_{61}$BM device have higher $V_{OC}$ than Sq-TAA-OH:PC$_{61}$BM due their more stabilized HOMO energy levels. Sq-TAA-H:PC$_{61}$BM has a higher efficiency than Sq-TAA-F:PC$_{61}$BM. This could result from the larger bandgap of Sq-TAA-F despite the similar $V_{OC}$.

Figure 2.9: J-V curves of bilayer OPV devices of a) Sq-TAA-OH, b) Sq-TAA-H, and c) Sq-TAA-F with PCBM.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_g$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sq-TAA-OH</td>
<td>0.77</td>
<td>0.32</td>
<td>7.69</td>
<td>0.35</td>
<td>0.93</td>
</tr>
<tr>
<td>Sq-TAA-H</td>
<td>1.68</td>
<td>0.47</td>
<td>6.00</td>
<td>0.61</td>
<td>1.71</td>
</tr>
<tr>
<td>Sq-TAA-F</td>
<td>1.86</td>
<td>0.44</td>
<td>5.05</td>
<td>0.40</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 2.6: Summary of the parameters of the bilayer OPV devices. It can be seen that the efficiency of Sq-TAA-H is the highest. The lowest $V_{OC}$ is for Sq-TAA-OH which is expected from the HOMO energy level.

Figure 2.9 shows the current density vs. voltage (J-V) characteristics of the Sq-TAA-OH:PC$_{71}$BM bulk heterojunction device under 100 mWcm$^{-2}$ AM 1.5 simulated solar irradiation conditions. Using PC$_{71}$BM and 1,8-diiodooctane (DIO), a solvent additive, improves the efficiency to nearly 5%. The samples exhibit a short-

![J-V curve](image)

Figure 2.10: J-V curve of Sq-TAA-OH: PC$_{71}$BM bulk heterojunction device. Optimized efficiency is a result of a mixed solvent system (THF: CB, 70:30) and solvent additive (DIO, 0.4 vol%).

circuit current density ($J_{SC}$) of 12.56 mAcm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.79 V and a fill factor (FF) of 47.9% which lead to a power conversion efficiency (η) of
~4.82%. Bulk heterojunction devices offer advantages over bilayer devices because of the increased donor-acceptor interfacial area. This improves the exciton dissociation of the device, as an exciton is more likely to reach an interface within its lifetime in the bulk heterojunction architecture. This could be the cause of the major increase in efficiency. Bulk heterojunction devices of the other squaraine dyes are currently under investigation.

2.3 Summary

Squaraine dyes are promising molecules for use in organic electronic devices. They have substantial absorbance in the visible to near IR region. Squaraine dyes utilizing electron rich triarylamine moieties offer a unique platform for tuning the energy levels of the squaraine dye. Installing electron donating or electron withdrawing groups onto triarylamine donors results in squaraines with tunable HOMO energy levels. Tunable energy levels allow for optimization of photovoltaics parameters such as light harvesting and \( V_{oc} \). The thin film absorbance of the dyes are red shifted and broadened with respect to the solution as a result of aggregation and organization of the molecules. Sq-TAA-C\(_6\)H\(_{13}\) shows further organization upon annealing most likely owing to the alkyl chains. This may offer added benefits in the light harvesting and charge mobility of PV devices. Traditionally, squaraine dyes are hole transporting but installing fluorine atoms onto the triarylamines results in ambipolar transport for Sq-TAA-F and electron transport for Sq-TAA-CF\(_3\). Preliminary photovoltaic devices have shown that tuning the energy levels of the dyes does affect the \( V_{oc} \) of the resulting device. Future work will focus on identifying
an appropriate acceptor molecule and device architecture for device optimization and to determine the effect of electron donating or withdrawing groups on light harvesting, $V_{oc}$, and PCE.

2.4 Experimental

2.4.1 Synthesis of 3,5-dimethoxy-N,N-diphenylaniline

![Chemical structure of 3,5-dimethoxy-N,N-diphenylaniline]

3,5-dimethoxy-N,N-diphenylaniline was synthesized using a previously reported procedure\textsuperscript{11}. Pd\textsubscript{2}(dba)\textsubscript{3} (0.6 g, 0.065 mmol), P(tBu)\textsubscript{3}HBF\textsubscript{4} (0.38 g, 1.31 mmol), and NaOtBu (3.76 g, 39.17 mmol) was suspended in 25 mL degassed toluene and stirred at room temperature for 10 mins. 3,5-dimethoxyaniline (2.0 g, 13.06 mmol) and bromobenzene (4.5 g, 28.72 mmol) were added and the reaction was refluxed overnight. The toluene was removed under vacuum and the crude product was purified on CombiFlash (73%). $^1$H NMR (400MHz, acetone-d$_6$): $\delta$ 7.29 (t, 4H, $J =$ 8 Hz, a), 7.06 (m, 6H, b/c), 6.19 (t, 1H, $J =$ 4 Hz, d), 6.15 (d, 2H, $J =$ 4 Hz, e), 3.67 (s, 6H, f).
2.4.2 Synthesis of 5-(diphenylamino)benzene-1,3-diol

![Chemical Structure]

5-(diphenylamino)benzene-1,3-diol was synthesized from a previously reported procedure. 3,5-dimethoxy-N,N-diphenylaniline (3.5 g, 11.5 mmol) was dissolved in 20 mL DCM. The mixture was placed in a dry ice – acetone cooling bath for several minutes. BBr₃ (2.2 mL, 23 mmol) was added and the reaction was allowed to stir overnight coming to room temperature. The mixture was then poured into 200 mL water cooled in an ice bath. The reaction was extracted into DCM, dried over sodium sulfate and the DCM was removed under vacuum. The product was used without further purification. ¹H NMR (400 MHz, acetone-d₆): δ 7.28 (t, 4H, J = 8 Hz, a), 7.04 (m, 6H, b/c), 6.06 (s, 1H, d), 6.00 (s, 2H, e).

2.4.3 Synthesis of 2,4-bis(4-(diphenylamino)-2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate) (Sq-TAA-H)

![Chemical Structure]

Sq-TAA-H was synthesized using a previously reported procedure. 5-(diphenylamino)benzene-1,3-diol (500 mg, 1.8 mmol) and squaric acid (103 mg, 0.9 mmol) was dissolved in 5 mL toluene and 5 mL n-BuOH and refluxed overnight. The solid precipitate was collected and washed with methanol (61%). ¹H NMR
(400MHz, CDCl₃): δ 10.98 (s, 4H, a), 7.38 (t, 8H, J = 8 Hz, b), 7.27 (t, 4H, J = 8 Hz, c),
7.21 (d, 8H, J = 8 Hz, d), 5.86 (s, 4H, e).

2.4.4 Synthesis of N,N-bis(4-fluorophenyl)-3,5-dimethoxyaniline

\[
\begin{array}{c}
\text{MeO} \\
\text{c} \\
\text{d} \\
\text{b} \\
\text{MeO} \\
\text{N} \\
\text{F} \\
\end{array}
\]

Pd₂dba₃ (0.64 g, 0.07 mmol), P(tBu)₃BF₄ (0.38 g, 1.3 mmol), and NaOtBu (3.8 g, 39.3 mmol) were suspended in 25 mL degassed toluene and stirred at room
temperature for 10 mins. 1-bromo-4-fluorobenzene (3.1 mL, 28.8 mmol) was added
and the reaction was heated to 60 °C and stirred for 10 mins. 3,5-dimethoxyaniline
(2.0 g, 13.1 mmol) was added and the reaction was refluxed overnight. The toluene
was removed under vacuum and the crude product was purified on CombiFlash
(67%). ¹H NMR (400MHz, CDCl₃): δ 7.04 (d, 4H, J = 8 Hz, a), 6.96 (d, 4H, J = 8 Hz, b),
6.10 (s, 3H, c), 3.68 (s, 6H, d). ¹³C NMR (100MHz, CDCl₃): δ 161.4, 160.3, 157.9,
149.9, 143.7, 143.7, 126.6, 126.5, 116.3, 116.0, 101.0, 94.2, 55.3. m/z calculated for
C₂₀H₁₇F₂NO₂: 341.1 found by FAB: 341.1.

2.4.5 Synthesis of 5-(bis(4-fluorophenyl)amino)benzene-1,3-diol

\[
\begin{array}{c}
\text{OH} \\
\text{c} \\
\text{OH} \\
\text{b} \\
\text{a} \\
\text{N} \\
\text{F} \\
\end{array}
\]
N,N-bis(4-fluorophenyl)-3,5-dimethoxyaniline (2.0 g, 5.9 mmol) was dissolved in 20 mL DCM. The mixture was placed in a dry ice – acetone cooling bath for several minutes. BBr₃ (1.2 mL, 11.8 mmol) was added and the reaction was allowed to stir overnight coming to room temperature. The mixture was then poured into 200 mL water cooled in an ice bath. The reaction was extracted into DCM, dried over sodium sulfate and the DCM was removed under vacuum. The product was used without further purification. ¹H NMR (400MHz, acetone-d₆): δ 7.08 (d, 8H, J = 8 Hz, a/b), 6.02 (t, 1H, J = 4 Hz, c), 5.92 (d, 2H, J = 4 Hz, d). ¹³C NMR (100MHz, CDCl₃): δ 206.4, 160.9, 159.9, 158.5, 150.7, 144.9, 144.9, 127.4, 127.4, 116.8, 116.6, 101.9, 98.0. m/z calculated for C₂₀H₁₇F₂NO₂: 313.1 found by FAB: 313.1.

2.4.6 Synthesis of 2,4-bis(4-(bis(4-fluorophenyl)amino)-2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bisolate (Sq-TAA-F)

5-(bis(4-fluorophenyl)amino)benzene-1,3-diol (500 mg, 1.6 mmol) and squaric acid (91 mg, 0.8 mmol) was dissolved in 5 mL toluene and 5 mL n-BuOH and refluxed overnight. The solid precipitate was collected and washed with methanol (53%). ADP_3_172 ¹H NMR (400MHz, CDCl₃): δ 11.00 (s, 2H, a), 7.19 (d, 8H, J = 8 Hz, b), 7.09 (d, 8H, J = 8 Hz, c), 5.77 (s, 4H, d). ¹³C NMR (100MHz, CDCl₃): δ 182.0, 164.4,
163.5, 150.6, 140.0, 129.4, 129.3, 117.2, 117.0, 98.5. m/z calculated for C₄₀H₂₄F₄N₂O₆: 704.2 found by FAB: 705.2.

2.4.7 Synthesis of bis(4-hexylphenyl)amine

\[
\begin{align*}
\text{Pd}_2(\text{dba})_3 (1.29 \text{ g}, 1.41 \text{ mmol}), \text{P(tBu)}_3\text{HBF}_4 (0.82 \text{ g}, 2.82 \text{ mmol}), \text{and NaOtBu} \\
(8.13 \text{ g}, 84.6 \text{ mmol}) \text{ were suspended in 25 mL degassed toluene and stirred at room} \\
\text{temperature for 10 mins. 1-bromo-4-hexylbenzene (5.8 mL, 28.2 mmol) was added} \\
\text{and the reaction was heated to 60 °C and stirred for 10 mins. 4-hexylaniline (5.0} \\
\text{mL, 28.2 mmol) was added and the reaction was refluxed overnight. The toluene} \\
\text{was removed under vacuum and the crude product was purified on CombiFlash} \\
(63\%). \quad \text{^1H NMR (400MHz, CDCl₃):} \ & \delta 7.07 (d, 4H, J = 8 \text{ Hz, a}), 6.97 (d, 4H, J = 8 \text{ Hz, b}), \\
5.54 (br, 1H, c), 2.55 (t, 4H, J = 8 \text{ Hz, d}), 1.63-1.55 (m, 4H, e), 1.38-1.27 (m, 12H, f), \\
0.88 (t, 6H, J = 10.0 \text{ Hz, g}). \quad \text{^13C NMR (100MHz, CDCl}_3\text{):} \ & \delta 141.3, 135.2, 128.9, 117.8, \\
35.3, 31.9, 31.8, 29.1, 22.8, 14.2. \quad \text{m/z calculated for C}_{24}\text{H}_{35}\text{N:} \ & 337.3 \text{ found by FAB:} \\
337.3.
\end{align*}
\]

2.4.8 Synthesis of N,N-bis(4-hexylphenyl)-3,5-dimethoxyaniline

\[
\begin{align*}
\text{MeO a}
\end{align*}
\]
Pd$_2$(dba)$_3$ (0.44 g, 0.45 mmol), P(tBu)$_3$HBF$_4$ (0.28 g, 0.96 mmol), and NaOtBu (2.8 g, 28.8 mmol) were suspended in 25 mL degassed toluene and stirred at room temperature for 10 mins. 1-bromo-3,5-dimethoxybenzene (3.13 g, 14.4 mmol) was added and the reaction was heated to 60 °C and stirred for 10 mins. bis(4-hexylphenyl)amine (3.24 g, 9.60 mmol) was added and the reaction was refluxed overnight. The toluene was removed under vacuum and the crude product was purified on CombiFlash (72%). 7.04 (d, 4H, J = 8 Hz, a), 7.01 (d, 4H, J = 8 Hz, b), 6.17 (d, 2H, J = 2.2 Hz, c), 6.07 (t, 1 H, J = 2.2 Hz, d), 3.67 (s, 6H, e), 2.54 (t, 2 H, J = 8 Hz, f), 1.59-1.57 (m, 2H, g), 1.34-1.25 (m, 12H, h), 0.88 (t, 6H, J = 8 Hz, i). $^{13}$C NMR (100MHz, CDCl$_3$): δ 161.2, 150.3, 145.3, 137.9, 129.2, 125.0, 101.2, 93.8, 55.5, 35.5, 31.9, 31.6, 29.2, 22.8, 14.2. m/z calculated for C$_{32}$H$_{43}$NO$_2$: 473.3 found by FAB: 473.7.

2.4.9 Synthesis of 5-(bis(4-hexylphenyl)amino)benzene-1,3-diol

\[
\text{N,N-bis(4-hexylphenyl)-3,5-dimethoxyaniline (0.92 g, 1.94 mmol) was dissolved in 20 mL DCM. The mixture was placed in a dry ice – acetone cooling bath for several minutes. BBr}_3 \text{ (3.0 mL, 4.27 mmol) was added and the reaction was allowed to stir overnight coming to room temperature. The mixture was then poured into 200 mL water cooled in an ice bath. The reaction was extracted into DCM, dried over sodium sulfate and the DCM was removed under vacuum. The}
\]
product was used without further purification. $^1$H NMR (400MHz, CDCl$_3$): δ 7.06 (d, 4H, J = 8 Hz, a), 7.01 (d, 4H, J = 8 Hz, b), 6.02 (d, 2H, J = 2 Hz, c), 5.90 (t, 1H, J = 2 Hz, d), 4.85 (br, 2H, e), 2.55 (t, 4H, J = 8 Hz, f), 1.62-1.58 (m, 4H, g), 1.38-1.29 (m, 12H, h), 0.90 (d, 6H, J = 8 Hz, i). $^{13}$C NMR (100MHz, CDCl$_3$): δ 157.1, 150.6, 145.1, 138.2, 129.2, 125.4, 101.7, 96.2, 35.5, 31.9, 31.6, 29.2, 22.7, 14.2. m/z calculated for C$_{30}$H$_{39}$NO$_2$: 445.3 found by FAB: 445.3.

2.4.10 Synthesis of 2,4-bis(4-(bis(4-hexyphenyl)amino)-2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate) (Sq-TAA-C$_6$H$_{13}$)

5-(bis(4-hexyphenyl)amino)benzene-1,3-diol (400 mg, 2.75 mmol) and squaric acid (157 mg, 1.37 mmol) was dissolved in 5 mL toluene and 5 mL n-BuOH and refluxed overnight. The solid precipitate was collected and washed with methanol (91%). YB_1_136 $^1$H NMR (400MHz, CDCl$_3$): δ 10.96 (s, 4H, a), 7.17 (d, 8H, J = 8 Hz, b), 7.10 (d, 8H, J = 8 Hz, c), 5.84 (s, 4H, d), 2.59 (t, 8H, J = 8 Hz, e), 1.61-1.59 (m, 8H, J = 8 Hz, f), 1.35-1.25 (m, 24H, g), 0.89 (t, 12H, J = 8 Hz, h). $^{13}$C NMR (100MHz, CDCl$_3$): δ 181.5, 163.0, 162.8, 159.6, 142.1, 141.8, 129.8, 127.4, 104.8, 98.5, 35.7, 31.8, 31.4, 29.2, 22.7, 14.2. m/z calculated for C$_{64}$H$_{76}$N$_2$O$_6$: 968.6 found by FAB: 970.1.
2.4.11 Synthesis of 3,5-dimethoxy-N,N-bis(4-methoxyphenyl)aniline

![Chemical Structure]

3,5-dimethoxyaniline (0.55 g, 3.62 mmol), iodoanisole (2.54 g, 10.9 mmol), Cu (0.05 g, 0.72 mmol), CuSO₄ (0.057 g, 0.36 mmol), sodium ascorbate (0.071 g, 0.36 mmol), and K₂CO₃ (1.15 g, 8.33 mmol) were dissolved in 20 mL of o-dichlorobenzene and the reaction mixture heated at 230 °C for three days. The reaction mixture was allowed to cool to room temperature, filtered through Celite, and concentrated under vacuum. The crude mixture was purified on silica (64 %).

¹H NMR (400 MHz, DMSO-d₆): δ 7.01 (d, 4H, J = 8 Hz, a), 6.89 (d, 4H, J = 8 Hz, b), 6.02 (t, 1H, J = 2 Hz, c), 5.84 (d, 2H, J = 2 Hz, d), 3.73 (s, 6H, e), 3.59 (s, 6H, f). ¹³C NMR (100MHz, DMSO-d₆): δ 160.9, 155.8, 150.2, 139.9, 127.0, 114.8, 98.0, 91.9, 55.2, 54.9. m/z calculated for C₂₂H₂₃NO₄: 365.2 found by FAB: 365.2.

2.4.12 Synthesis of 5-(bis(4-hydroxyphenyl)amino)benzene-1,3-diol

![Chemical Structure]

3,5-dimethoxy-N,N-bis(4-methoxyphenyl)aniline (1.2 g, 3.3 mmol) was dissolved in 16 mL DCM. The mixture was placed in a dry ice – acetone cooling bath for several minutes. BBr₃ (1.3 mL, 13.2 mmol) was added and the reaction was
allowed to stir overnight coming to room temperature. The mixture was then poured into 200 mL water cooled in an ice bath. The reaction was extracted into DCM, dried over sodium sulfate and the DCM was removed under vacuum. The product was used without further purification. \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 9.26 (s, 2H, a), 8.84 (s, 2H, b), 6.88 (d, 4H, \(J = 8\) Hz, c), 6.70 (d, 4H, \(J = 8\) Hz, d), 5.61 (t, 1H, \(J = 2\) Hz, e), 5.56 (d, 2H, \(J = 2\) Hz, f). \(^13\)C NMR (100 MHz, DMSO-d\(_6\)): \(\delta\) 158.5, 153.9, 150.8, 138.9, 127.6, 115.9, 96.9, 94.3. m/z calculated for \(\text{C}_{18}\text{H}_{15}\text{NO}_{4}\): 309.1 found by FAB: 309.1.

### 2.4.13 Synthesis of 2,4-bis(4-(bis(4-hydroxyphenyl)amino)-2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate) (Sq-TAA-OH)

![Structure Diagram]

5-(bis(4-hydroxyphenyl)amino)benzene-1,3-diol (1.18 g, 3.81 mmol) and squaric acid (0.22 g, 1.91 mmol) was dissolved in 10 mL of toluene and 10 mL of n-BuOH and refluxed overnight. The precipitate was collected and washed thoroughly with toluene, then hexanes (75 %). \(\text{PfH}_3\text{14I}\) \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 11.3 (s, 4H, a), 9.76 (s, 4H, b), 7.14 (d, 8H, \(J = 8\) Hz, c), 6.82 (d, 8H, \(J = 8\) Hz, d), 5.47 (s, 4H, d). \(^13\)C NMR (100 MHz, DMSO-d\(_6\)): \(\delta\) 180.6, 164.4, 162.2, 159.2, 156.6, 135.1, 128.7, 116.4, 103.3, 95.8. m/z calculated for \(\text{C}_{40}\text{H}_{28}\text{N}_{2}\text{O}_{10}\): 696.2 found by FAB: 696.2.
2.4.14 Synthesis of N,N-bis(3,5-bis(trifluoromethyl)phenyl)-3,5-dimethoxyaniline

\[
\begin{array}{c}
\text{N} \\
\text{CF}_3
\end{array}
\]

Pd\(_2\)(dba)\(_3\) (0.6 g, 0.65 mmol), P(tBu)\(_3\)HBF\(_4\) (0.38 g, 1.3 mmol), and NaOtBu (3.77 g, 39.18 mmol) were suspended in 25 mL degassed toluene and stirred at room temperature for 10 mins. 1-bromo-3,5-bis(trifluoromethyl)benzene (4.5 mL, 26.12 mmol) was added and the reaction was heated to 60 °C and stirred for 10 mins. 3,5-dimethoxyaniline (2.0 g, 13.06 mmol) was added and the reaction was refluxed overnight. The toluene was removed under vacuum and the crude product was purified on CombiFlash (81%). \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.55 (s, 2H, a), 7.49 (s, 4H, b), 6.40 (t, 1H, J = 4 Hz, c), 6.25 (d, 2H, J = 4 Hz, d), 3.76 (s, 6H, e). \(^{13}\)C NMR (100MHz, CDCl\(_3\)): δ 162.5, 147.9, 146.6, 133.8, 133.5, 133.2, 132.8, 127.2, 124.5, 122.9, 121.7, 119.0, 117.0, 117.0, 116.9, 104.6, 98.7, 55.7. m/z calculated for C\(_{24}\)H\(_{15}\)F\(_{12}\)NO\(_2\): 577.1 found by FAB: 577.2.

2.4.15 Synthesis of 5-(bis(3,5-bis(trifluoromethyl)phenyl)amino)benzene-1,3-diol

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

N,N-bis(3,5-bis(trifluoromethyl)phenyl)-3,5-dimethoxyaniline (2.0 g, 5.9
mmol) was dissolved in 20 mL DCM. The mixture was placed in a dry ice – acetone cooling bath for several minutes. BBr₃ (1.2 mL, 11.8 mmol) was added and the reaction was allowed to stir overnight coming to room temperature. The mixture was then poured into 200 mL water cooled in an ice bath. The reaction was extracted into DCM, dried over sodium sulfate and the DCM was removed under vacuum. The product was used without further purification. ¹H NMR (400MHz, CDCl₃): δ 7.57 (s, 2H, a), 7.47 (s, 4H, b), 6.25 (s, 1H, c), 6.19 (s, 2H, d), 5.10 (s, 2H, e). ¹³C NMR (100MHz, CDCl₃): δ 158.3, 147.7, 147.2, 133.9, 133.6, 133.3, 132.9, 127.1, 124.4, 123.1, 121.7, 118.9, 117.3, 117.3, 117.3, 105.8, 101.4. m/z calculated for C₂₂H₁₁F₁₂NO₂: 549.1 found by FAB: 549.4.

2.4.16 Synthesis of 2,4-bis(4-(bis(3,5-bis(trifluoromethyl)phenyl)amino)-2,6-dihydroxyphenyl)cyclobuta-1,3-diene-1,3-bis(olate) (Sq-TAA-CF₃)

5-(bis(3,5-bis(trifluoromethyl)phenyl)amino)benzene-1,3-diol (500 mg, 0.91 mmol) and squaric acid (49 mg, 0.43 mmol) was dissolved in 5 mL toluene and 5 mL n-BuOH and refluxed overnight. The solid precipitate was collected and washed with methanol (46%). SQR_1_52 ¹H NMR (400MHz, acetone-d₆): δ 8.19 (s, 8H, a), 8.05 (s, 4H, b), 5.94 (s, 4H, c). ¹³C NMR (100MHz, acetone-d₆): δ 181.6, 145.7, 140.7, 134.1, 133.8, 129.7, 125.3, 122.8, 112.9, 101.0. m/z calculated for C₄₈H₂₀F₂₄N₂O₆: 1176.1 found by FAB: 1177.4.
2.4.17 Solution and Thin Film Absorbance

Solution absorbance spectra were recorded on a Cary 100 spectrophotometer. All extinction coefficients were determined from a linear fit of five data points. Thin film absorbance spectra were recorded on a Shimadzu UV 3600. Concentrated solutions of the squaraines were spin coated onto glass cover slips and the absorbance was taken. Films were annealed at 100 °C for 1 hour and then measured again.

2.4.18 Cyclic Voltammetry and Energy Level Estimation

Thin film cyclic voltammetry experiments were carried out using a BASi C3 cell stand fitted with three electrodes: a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag+ reference electrode. The film was drop cast onto the working electrode from a concentrated solution of the squaraine dye in DCM. The voltammograms were recorded in dry acetonitrile (Sq-TAA-H, Sq-TAA-C6H13, Sq-TAA-F) or dry DCM (Sq-TAA-OH, Sq-TAA-CF3) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the standard. HOMO and LUMO energy levels were calculated using the peak onsets using the equations:

\[ \text{HOMO} = -(4.8 + E_{\text{ox onset}}) \]

\[ \text{LUMO} = -(4.8 + E_{\text{red onset}}) \]

2.4.19 Thin Film Transistor Fabrication and Measurements

All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer. The field effect transistors
were constructed using pre-patterned substrates made of heavily n-doped silicon substrate with a 230 nm silicon dioxide layer and a capacitance of 14.9 nF/cm². The gold source and drain electrodes were deposited on the gate oxide layer resulting in bottom contact FETs. Before the squaraine films were spin coated onto the surface, the substrates were cleaned with acetone and dried with an argon stream. Solutions of 10mg/ mL in chloroform (Sq-TAA-H, Sq-TAA-C₆H₁₃, Sq-TAA-F) or THF (Sq-TAA-OH, Sq-TAA-CF₃) were spin coated onto the surface (1500 rpm for 45 seconds). The devices were measured both before and after annealing at 80 °C for 30 mins. The channel width of all transistors was 10 mm and channel lengths were 2.5 μm, 5 μm, 10 μm, and 20 μm. Mobilities were determined from the saturated regime and averaged and standard deviations are reported.

2.4.20 Photovoltaic Fabrication and Measurements

The bilayer solar cells were prepared and measured by Akshay Kokil. The preparation was achieved by spin coating a solution of the dyes, prepared in 1,2-dichlorobenzene (5 mg/mL) at 80 °C, on cleaned ITO coated glass slides (50 Ω/sq) at 800 rpm. The PC₆₁BM layer was thermally evaporated on the squaraine layer at a base pressure of 3×10⁻⁷ Torr. The active layer was solvent annealed at ambient temperature in a sealed chamber containing dichloromethane for 3 min. The aluminum cathode (100 nm) was then thermally evaporated on the active layer. The device characteristics were measured at ambient temperatures under AM 1.5G illumination.
The bulk heterojunction solar cells were prepared and measured by Supravat Karak through the optimization of several parameters. The ITO-glass substrate (20 Ω/sq) was cleaned by subsequent sonication in detergent, acetone, and isopropyl alcohol. The cleaned ITO-glass was then exposed to UV/ozone treatment for 20 min followed by spin coating PEDOT:PSS (2000 rpm for 2 min). The SQ-BDHOPA:PC$_{71}$BM (donor:acceptor) blend solution was prepared with a weight ratio of 1:5 and a final concentration of 30 mg/ml in a mixed solvent system of THF:CB (70:30 vol%) with 0.4 vol% of DIO additive. After stirring overnight at 55 °C, the blend was heated to 90 °C for 15 min before spin coating. The bulk heterojunction film was obtained from spin casting the solution at 1500 rpm for 60 s. The coated bulk heterojunction films were baked to 80 °C for 10 min to evaporate the residual solvent. LiF (1.5 nm) was thermally evaporated as a buffer layer followed by deposition of a 100 nm aluminum cathode with an effective device area of 0.06 cm$^2$. The J–V characteristics of the solar cells were measured by a Keithley 2400 sourcemeter unit. The light source was calibrated by using silicon reference cells with an AM 1.5 G solar simulator with an intensity of 100 mW/cm$^2$. All solar cells were tested under ambient conditions.
$^{1}$H and $^{13}$C NMR of Sq-TAA-F.
$^1$H and $^{13}$C NMR of Sq-TAA-$C_6H_{13}$. 
$^1$H and $^{13}$C NMR of Sq-TAA-OH.
$^1$H and $^{13}$C NMR of Sq-TAA-CF$_3$. 
2.5 References


CHAPTER 3
EFFECT OF ACCEPTOR STRENGTH ON KETO CYANINE DYES

3.1 Introduction

Cyanine dyes are a specific type of polymethine dye that contains two nitrogen atoms bridged by an odd number of methine groups\(^1\). One of the nitrogen atoms is positively charged and the odd number of methine groups allow for resonance stabilization, shown in Figure 3.1. In this case, the two nitrogen containing end groups are identical and therefore there is no energy difference between the two resonance forms. The equal contribution from both resonance structures minimizes the bond length alternation to the cyanine limit\(^2\). The minimal structural change between the two states results in a red shifted absorption with high extinction coefficients\(^3\). Their intense absorbance motivates their use as dyes in biological imaging\(^4-7\).

![Figure 3.1: Generic structure of cyanine dye. The odd number of methine groups allow for resonance stabilization between the amine and the iminium.](image)

Merocyanine dyes differ from conventional cyanine dyes in that they consist of a neutral asymmetrical structure consisting of a donor and acceptor portion\(^8,9\). A generic structure of merocyanine dye can be seen in Figure 3.2, where a nitrogen containing donor and a oxygen containing acceptor are linked through a polyethylene chain. This results in a push-pull system similar to typical donor-acceptor type molecules. Merocyanine dyes are excellent detectors of
microenvironments as they are indicators of both polarity and pH. The charge separated state can be stabilized by an increase in the polarity of the solvent. In a similar way, protonation of the oxygen anion under acidic conditions will likewise promote the charge separated state. Both increasing polarity and decreasing pH will often result in a red shift of the absorbance of these dyes. Merocyanine dyes functionalized with crown ethers can coordinate biologically relevant counter ion such as Na⁺, K⁺, Ca²⁺ or Mg²⁺, making them promising candidates as cation indicators.

Ketocyanine dyes combine the benefits of traditional cyanine dyes with those of merocyanine dyes. As seen in Figure 3.3, ketocyanine dyes are neutral, symmetrical, and consist of two amine containing donors as well as an oxygen containing, or other electron withdrawing acceptor. Similar to merocyanine dyes, ketocyanine dyes also exhibit solvatochromic as well as halochromic behavior.

Various cyanine and merocyanine dyes have also been explored for applications in layered and bulk heterojunction organic photovoltaics. These dyes possess high absorption coefficients with tunable absorbance, which make
Figure 3.3: Generic structure of ketocyanine dye. Ketocyanine dyes have a symmetric charge neutral structure, where the two nitrogens only communicate in the charge separated resonance structure.

them desirable for light harvesting. These dyes have also been also utilized for the fabrication of dye sensitized solar cells\textsuperscript{32}. Examples of some high efficiency OPV devices with cyanine active layers are shown in Figure 3.4.

Figure 3.4: Structures of cyanine-type dyes successfully used in the active layer of OPVs.
3.2 Results and Discussion

3.2.1 Molecular Design

The ketocyanine dyes reported here consist of a donor-acceptor-donor architecture where diphenylamine will act as the electron donating moiety and fluorenone will act as the electron accepting moiety. As seen in Figure 3.5, in the ground state of this molecule the two amines are not in electronic communication with each other, however, in the charge separated state, the molecule accesses a partial benzenoid-partial quinoid form allowing electronic communication between the two amines. In the charge separated state of the molecule, there is a positive charge localized on one of the nitrogen atoms of the diphenylamine and a negative charge localized on the oxygen atom of the fluorenone. Increasing the acceptor strength in this ketocyanine dye should stabilize the negative charge in this form and result in a greater contribution from this resonance form. In order to test this hypothesis, a series of ketocyanine dyes with acceptors of varying strengths were

Figure 3.5: Resonance structures of ketocyanine dyes. In the ground state the two amines are not in electronic communication. In the charge separated state the two amines are allowed to communicate with each other.
synthesized, and can be seen in Figure 3.6. The acceptor strength increases with the following trend: ketone < malononitrile < 1,3-indandione < 1,3-dimethylbarbituric acid < 1,3-diethyl-2-thiobarbituric acid\textsuperscript{33-35}. It is not clear where 3-phenyl-5-isoxazolone falls into this list because, unlike the other acceptors, it adopts an aromatic form when stabilizing the negative charge\textsuperscript{36}. This sets 3-phenyl-5-isoxazolone apart from the other acceptors and therefore DAA-Fl-Pl cannot always be compared with the other molecules.

Figure 3.6: Chemical structures of the ketocyanine dyes reported in this chapter. The acceptor strength is tuned while the amine portion of the dyes remains constant.

DAA-Fl was synthesized according to a previously published procedure\textsuperscript{37} and is shown in Scheme 3.1. Briefly, 3,6-dibromo-9H-fluoren-9-one was synthesized from the bromination and subsequent ring contraction of 3,6-dibromophenanthrene-9,10-dione. 3,6-dibromo-9H-fluoren-9-one was then subjected to a Buchwald coupling with diphenylamine to synthesize DAA-Fl as an orange solid. The remaining ketocyanine dyes were synthesized by condensing
various acceptors with DAA-Fl.

![Scheme 3.1: Synthesis of DAA-Fl.]

DAA-FL-CN was synthesized by a piperidine catalyzed Knoevenagle condensation of DAA-Fl with malononitrile resulting in a brown solid. The synthetic scheme can be seen in Scheme 3.2.

![Scheme 3.2: Synthesis of DAA-Fl-CN.]

DAA-Fl-In was synthesized by the condensation of DAA-Fl with 1,3-indandione in the presence of acetic acid and acetic anhydride yielding a purple colored solid. The synthesis of DAA-Fl-In can be seen in Scheme 3.3.
Scheme 3.3: Synthesis of DAA-Fl-In.

The acetic acid-acetic anhydride condensation of DAA-Fl with barbituric acid yielded DAA-FL-6O, a blue solid. The synthesis is shown in Scheme 3.4.

Scheme 3.4: Synthesis of DAA-Fl-6O.

Scheme 3.5 shows the synthesis of DAA-Fl-6S. DAA-Fl was condensed with thiobarbituric acid in the presence of acetic acid and acetic anhydride resulting in a green solid.

Scheme 3.5: Synthesis of DAA-Fl-6S.

DAA-Fl-PI was synthesized by the condensation of DAA-Fl with 3-Phenyl-5-isoxazolone in the presence of acetic acid and acetic anhydride yielding a purple
colored solid. The synthesis of DAA-Fl-PI can be seen in Scheme 3.6.

Scheme 3.6: Synthesis of DAA-Fl-PI.

### 3.2.2 Absorbance Properties

The absorbance of each dye was measured in dichloromethane (DCM) and can be seen in Figure 3.7. Each of the dyes has significant absorbance over a wide range of wavelengths. There are two major peaks for each of the dyes which correspond to the π-π* and charge transfer transitions. The absorbance spectra are

Figure 3.7: Absorbance spectra of the ketocyanine dyes. The absorbances of the dyes are red shifted as the acceptor strength increases suggesting that the cyanine form is more stabilized by the stronger acceptors.
plotted with respect to the molar absorptivity demonstrating that the extinction coefficients of the dyes range from $4 \times 10^3 - 3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ for the $\pi-\pi^*$ transition.

It can be seen that as the acceptor strength increases there is a red shift in the absorbance of both the $\pi-\pi^*$ and charge transfer bands. The hypothesis is that increasing the acceptor strength will stabilize the negative charge promoting the charge separated state, providing red shifted absorbance. DAA-FI-PI has a $\lambda_{\text{max}}$ and $\lambda_{\text{onset}}$ that lies between DAA-FI-In and DAA-FI-60. This suggests that the acceptor strength of PI lies between that of In and 60. The energy difference between the $\pi-\pi^*$ and charge transfer bands increases with increasing acceptor strength. The $\Delta \lambda_{\text{max}}$ gradually increases by approximately 160 nm over the range of acceptors studied. This difference is most pronounced in DAA-FI-PI. The charge transfer band is believed to correspond to an intramolecular charge transfer from the amine to the iminium through the backbone of the dye. In the case of the stronger acceptors, the cyanine structure is more pronounced allowing for a greater stabilization of this charge transfer band resulting in the greater shift in absorbance between the maximum of the $\pi-\pi^*$ and the charge transfer peaks. In the case of the DAA-FI-PI dye, the charge separated structure is significantly stabilized due to the aromatization of the acceptor. Therefore this charge transfer band is significantly red shifted compared to the $\pi-\pi^*$ peak. The absorbance data is summarized in Table 3.1. It can also be seen from Figure 3.8, that the color change is visible.
Table 3.1: Summary of the absorbance data. It can be seen that as the charge separated structure is stabilized, the difference between the $\lambda_{\text{max}}$ of the $\pi-\pi^*$ and CT peaks increases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon$ (10$^6$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{max}}$ (nm) $\pi-\pi^*$</th>
<th>$\lambda_{\text{max}}$ (nm) $\text{ICT}^a$</th>
<th>$\Delta \lambda_{\text{max}}$ (nm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAA-Fi</td>
<td>1.66</td>
<td>397</td>
<td>475</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>DAA-Fi-CN</td>
<td>2.50</td>
<td>490</td>
<td>592</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>DAA-Fi-In</td>
<td>3.29</td>
<td>564</td>
<td>676</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>DAA-Fi-6O</td>
<td>2.25</td>
<td>605</td>
<td>742</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>DAA-Fi-6S</td>
<td>0.44</td>
<td>638</td>
<td>791</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td>DAA-Fl-PI</td>
<td>2.99</td>
<td>583</td>
<td>822</td>
<td>239</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Charge transfer band. $^b$ $\Delta \lambda_{\text{max}} = \lambda_{\text{max}}$ $\text{ICT} - \lambda_{\text{max}}$ $\pi-\pi^*$

Figure 3.8: Image of ketocyanine dye solutions in DCM. Each dye structure is color matched to the representative dye solution. The color change of the dyes can be seen by the naked eye.

3.2.3 Nuclear Magnetic Resonance Studies

In order to gain further insight into the structure of the cyanine dyes, proton nuclear magnetic resonance ($^1$H NMR) spectra were taken and compared. The NMR of DAA-Fi-6O can be seen in Figure 3.9. It can be seen from this NMR that the
structure is symmetric suggesting delocalization along the backbone of the structure. There are shifts in the peaks assigned to the fluorenone protons, which are summarized in Table 3.2. It can be seen that the peak that originates at 7.43 ppm shift downfield when stronger acceptors are installed. Alternatively, with stronger acceptors, the peaks that originate at 7.12 ppm and 6.75 ppm both shift upfield. These shifts can be explained by looking at the resonance structures of a
generic ketocyanine dye, shown in Figure 3.10. In the first two resonance structures, the negative charge is delocalized to the two and four positions of the fluorenone.

![Resonance structures](image)

**Figure 3.10:** Resonance structures can be used to explain the trends seen in the NMR. The carbons that have a negative charge in the shown resonance forms are upfield shifted, while the one with a positive charge is downfield shifted.

Increased electron donating character at these positions, as a result of the charge separated cyanine state, results in an upfield shift of the protons at these two positions. In the third, a positive charge is delocalized to the one position of the fluorenone. The electron withdrawing character at the one position of the charge separated cyanine state, results in a downfield shift of the proton at this position.

The NMR of DAA-Fl-PI varies significantly from the other dyes. A comparison of DAA-Fl-60 and DAA-Fl-PI can be seen in Figure 3.11. The $^1$H NMR suggests that the molecular structure of this dye is not symmetrical. Additionally, the $J$ values help us to identify which peaks correspond to the fluorenone peaks. It can be seen that each of the six protons that correspond to the fluorenone are magnetically inequivalent. These peaks are also vastly different in chemical shift. This suggests
Figure 3.11: Comparison of 1H NMR of DAA-Fl-6O and DAA-Fl-PI.

that DAA-Fl-PI demonstrates a partial benzenoid and partial quinoid state, shown in Figure 3.12. The benzenoid portion of the fluorenone has protons that are upfield shifted due to the lack of aromatic ring current. The partial quinoid form of DAA-Fl-PI most likely results from the acceptor gaining aromaticity resulting in enhanced stabilization of the cyanine dye.

Figure 3.12: Chemical structure of the charge separated state of DAA-Fl-PI.

In order to further support these results, the dyes were investigated by DFT using Gaussian 09\textsuperscript{38} with a B3LYP level of theory and 6-311g(d,p) basis set. The surfaces calculated for the HOMO energy levels of DAA-Fl-6O and DAA-Fl-PI can be
seen in Figure 3.13. It can be seen that in the case of DAA-Fl-6O, the HOMO energy level is evenly distributed throughout the backbone. This further suggests that the structure is symmetric and that there is delocalization throughout the molecule. The HOMO of DAA-Fl-PI is preferentially localized onto half of the backbone suggesting an asymmetric structure. This is most likely a result of DAA-Fl-PI existing in the charge separated state.

3.2.4 Field Effect Transistor Measurements

The field effect transistor (FET) mobilities of thin films of the ketocyanine dyes were measured using bottom contact devices with various channel lengths both before and after annealing. All of the dyes were found to be hole transporting except for DAA-Fl-PI, which is ambipolar. The maximum mobility of each material, before and after annealing, is reported in Table 3.3. It can be seen that in all cases except DAA-Fl-PI, the mobility is lowest in the case of DAA-Fl and highest in the cases of the stronger two acceptors, DAA-Fl-6O and DAA-Fl-6S. The mobility of
DAA-FI is on the order of $10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is approximately the mobility of small molecule triarylamine molecules. The dyes with strong acceptors are conjugated throughout the molecule and therefore the mobility increases. This also suggests that the dyes with strong acceptors have increases cyanine character. The mobility of DAA-FI-PI is approximately the same as DAA-FI. This could be a result of the charge separated state resulting in charge trapping.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Charge Carrier</th>
<th>As Is $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Annealed$^a$ $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAA-FI</td>
<td>hole</td>
<td>$7.25 \times 10^{-8}$</td>
<td>$2.74 \times 10^{-7}$</td>
</tr>
<tr>
<td>DAA-FI-CN</td>
<td>hole</td>
<td>$1.14 \times 10^{-5}$</td>
<td>$1.94 \times 10^{-5}$</td>
</tr>
<tr>
<td>DAA-FI-In</td>
<td>hole</td>
<td>$3.94 \times 10^{-7}$</td>
<td>$4.16 \times 10^{-7}$</td>
</tr>
<tr>
<td>DAA-FI-60</td>
<td>hole</td>
<td>$1.12 \times 10^{-5}$</td>
<td>$8.54 \times 10^{-6}$</td>
</tr>
<tr>
<td>DAA-FI-65</td>
<td>Hole</td>
<td></td>
<td>$1.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>DAA-FI-PI</td>
<td>Hole</td>
<td>$3.19 \times 10^{-8}$</td>
<td>$1.59 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Electron</td>
<td>$1.56 \times 10^{-8}$</td>
<td>$3.40 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

$^a$ Annealed at 80 °C for 30 mins.

Table 3.3: Maximum mobility of each dye determined using bottom contact FET configuration. All dyes show hole mobility, while DAA-FI-PI shows ambipolar charge transport.

### 3.3 Summary

Cyanine dyes have shown promise for applications in OPVs due to their enhanced light harvesting abilities. Ketocyanine dyes show tunable absorbance characteristics through modification of the chemical structure. Installing stronger electron acceptors onto the fluorenone core results in a significant red shift in the absorbance spectra. The chemical shifts in the $^1\text{H}$ NMR of DAA-FI-PI suggest that
this dye exists solely in the partial quinoid form resulting from enhanced stabilization of the negative charge due to the gain in aromaticity of the acceptor moiety. The light harvesting and hole transport properties of these dyes suggest that they might be useful as donor materials for OPVs.

3.4 Experimental

3.4.1 Synthesis of 3,6-dibromophenanthrene-9,10-dione

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]  

3,6-dibromophenanthrene-9,10-dione was synthesized according to a published procedure\textsuperscript{37}. Phenanthrene-9,10-dione (5.56 g, 26.7 mmol) and benzoyl peroxide (214 mg, 0.89 mmol) were suspended in 25 mL nitrobenzene. Bromine (3 mL, 57.7 mmol) was dissolved in 5 mL nitrobenzene and added dropwise. The reaction was allowed to heat at 120 °C overnight. Ethanol was poured into the reaction and the precipitate was collected and washed with ethanol. The product was used without further purification (89 %). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): δ 8.12 (s, 2H, a), 8.07 (d, 2H, J = 8 Hz, b), 7.67 (d, 2H, J = 8 Hz, c).

3.4.2 Synthesis of 3,6-dibromo-9H-fluorene-9-one

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\]  

3,6-dibromo-9H-fluoren-9-one was synthesized according to a published procedure\textsuperscript{33}. KOH (6.52 g, 119 mmol) was suspended in 15 mL water and heated to 130 °C. 3,6-dibromophenanthrene-9,10-dione (4.0 g, 11.9 mmol) was added. Once the solution turned black, KMnO\textsubscript{4} (9.14 g, 52.8 mmol) was added in parts over several minutes and reacted for 1 hour. The reaction was neutralized with 4 mL sulfuric acid. Sodium bisulfite was added until the reaction tuned yellow. The precipitate was collected and washed with water. The product was used without further purification (58 %). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): \textit{δ} 7.67 (s, 2H, a), 7.55 (d, 2H, J = 8 Hz, b), 7.49 (d, 2H, J = 8 Hz, c).

**3.4.3 Synthesis of 3,6-bis(diphenylamino)-9H-fluoren-9-one (DAA-FI)**

![Chemical Structure](image)

Pd\textsubscript{2}(dba)\textsubscript{3} (0.27 g, 0.3 mmol), P(tBu)\textsubscript{3}HBF\textsubscript{4} (0.17 g, 0.6 mmol), and NaOtBu (1.7 g, 17.7 mmol) was suspended in 25 mL degassed toluene and stirred at room temperature for 10 mins. Diphenylamine (2.3 g, 13.6 mmol) and 3,6-dibromo-9H-fluoren-9-one (2.0 g, 5.9 mmol) was added and the reaction was refluxed overnight. The toluene was removed under vacuum and the crude product was purified on CombiFlash (22%). \textsuperscript{1}H NMR (400MHz, acetone-d6): \textit{δ} 7.43 (d, 2H, J = 8 Hz, a), 7.35 (t, 8H, J = 8 Hz, b), 7.15 (m, 12H, J = 8 Hz, c/d), 7.12 (d, 2H, J = 2 Hz, e), 6.75 (dd, 2H, J = 8 Hz, f). \textsuperscript{13}C NMR (100MHz, CDCl\textsubscript{3}): \textit{δ} 191.0, 162.0, 153.5, 146.8, 145.3, 129.8,
129.7, 128.6, 126.1125.7, 125.2, 124.8, 124.5, 122.4, 121.4, 115.2, 113.4, 29.1. m/z calculated for C_{37}H_{26}N_{2}O: 514.2 found by FAB: 515.4.

3.4.4 Synthesis of 2-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)malononitrile (DAA-Fl-CN)

DAA-Fl (100 mg, 0.2 mmol) and malononitrile (39 mg, 0.59 mmol) were dissolved in 15 mL chloroform. Piperidine (0.12 mL, 1.17 mmol) was added and the reaction was refluxed overnight. The solvents were removed under vacuum and the crude mixture was purified by Combiflash (10%). ADP_3.190 \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 8.14 (d, 2H, \(J = 8\) Hz, a), 7.31 (t, 8H, \(J = 8\) Hz, b), 7.14 (m, 12H, c/d), 6.96 (d, 2H, \(J = 4\) Hz, e), 6.73 (dd, 2H, \(J = 8\) Hz, f). \(^13\)C NMR (100MHz, CDCl\(_3\)): \(\delta\) 153.3, 146.2, 143.5, 129.9, 128.0, 127.7, 126.2, 125.3, 120.2, 115.3, 112.6, 1.2. m/z calculated for C_{49}H_{26}N_{4}: 562.2 found by FAB: 562.4.

3.4.5 Synthesis of 5-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (DAA-Fl-6O)
DAA-Fl (50 mg, 0.1 mmol) and 1,3-dimethylbarbituric acid (47 mg, 0.3 mmol) were dissolved in 2 mL acetic acid and 2 mL acetic anhydride and refluxed overnight. The acetic acid and acetic anhydride were removed under vacuum and the crude mixture was dissolved in DCM and washed twice with water and once with saturated sodium bicarbonate. The product was purified by Combiflash (51%).

**SRB_1_34** ¹H NMR (400MHz, acetone-d6): δ 8.04 (d, 2H, J = 8 Hz, a), 7.34 (t, 8H, J = 8 Hz, b), 7.14 (m, 12H, c/d), 6.86 (d, 2H, J = 4 Hz, e), 6.45 (dd, 2H, J = 8 Hz, f), 3.26 (s, 6H, g). ¹³C NMR (100MHz, CDCl₃): δ 162.1, 153.5, 151.8, 146.3, 146.0, 133.9, 132.5, 129.7, 126.4, 125.7, 125.3, 119.2, 111.6, 106.8. 28.7. m/z calculated for C₄₃H₃₂N₄O₃: 652.3 found by FAB: 653.5.

### 3.4.6 Synthesis of 5-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (DAA-Fl-6S)

![Chemical Structure](image)

DAA-Fl (50 mg, 0.1 mmol) and 1,3-diethyl-2-thiobarbituric acid (160 mg, 0.8 mmol) were dissolved in 2 mL acetic acid and 2 mL acetic anhydride and refluxed overnight. The acetic acid and acetic anhydride were removed under vacuum and the crude mixture was dissolved in DCM and washed twice with water and once with saturated sodium bicarbonate. The product was purified by Combiflash (86%).

**SRB_1_41** ¹H NMR (400MHz, acetone-d6): δ 8.01 (d, 2H, J = 8 Hz, a), 7.36 (t, 8H, J = 8 Hz, b), 7.08 (m, 12H, c/d), 6.83 (d, 2H, J = 4 Hz, e), 6.37 (dd, 2H, J = 8 Hz, f), 3.24 (s, 6H, g).
Hz, b), 7.17 (m, 12H, J = 8 Hz, c/d), 6.83 (d, 2H, J = 4 Hz, e), 6.43 (dd, 2H, J = 8 Hz, f).

$^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 198.3, 177.5, 167.8, 160.1, 159.0, 153.5, 146.8, 146.4, 145.8, 145.3, 134.3, 132.7, 129.7, 129.7, 128.6, 126.5, 125.7, 125.6, 125.3, 124.5, 121.4, 119.0, 113.4, 111.7, 97.5, 43.4, 43.1, 25.6, 12.8, 12.5, 12.4, 12.1. m/z calculated for C$_{45}$H$_{36}$N$_4$O$_2$: 696.3 found by FAB: 697.6.

### 3.4.7 Synthesis of 2-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-1H-indene-1,3(2H)-dione (DAA-Fl-In)

![Diagram of the compound](image)

DAA-Fl (25 mg, 0.05 mmol) and 1,3-indandione (2 mg, 0.15 mmol) were dissolved in 2 mL acetic acid and 2 mL acetic anhydride and refluxed overnight. The acetic acid and acetic anhydride were removed under vacuum and the crude mixture was dissolved in DCM and washed twice with water and once with saturated sodium bicarbonate. The product was purified by Combiflash (45%).

$^{1}$H NMR (400MHz, acetone-d6): $\delta$ 8.60 (d, 2H, J = 8 Hz, a), 7.88 (m, 4H, b/c), 7.37 (t, 8H, J = 8 Hz, d), 7.17 (m, 12H, e/f), 6.99 (d, 2H, J = 4 Hz, g), 6.64 (dd, 2H, J = 8 Hz, h). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 190.7, 152.5, 146.5, 145.6, 141.6, 134.3, 133.6, 131.2, 129.7, 126.4, 126.1, 124.8, 122.5, 120.1, 112.5. m/z calculated for C$_{46}$H$_{30}$N$_2$O$_2$: 642.2 found by FAB: 643.5.
3.4.8 Synthesis of 4-(3,6-bis(diphenylamino)-9H-fluoren-9-ylidene)-3-phenylisoxazol-5(4H)-one (DAA-Fl-PI)

DAA-Fl (110 mg, 0.2 mmol) and 3-phenyl-5-isoxazolone (192 mg, 1.2 mmol) were dissolved in 2 mL acetic acid and 2 mL acetic anhydride and refluxed overnight. The acetic acid and acetic anhydride were removed under vacuum and the crude mixture was dissolved in DCM and washed twice with water and once with saturated sodium bicarbonate. The product was purified by Combiflash (18%).

SRB_1_59 $^1$H NMR (400MHz, acetone-d$_6$): $\delta$ 8.72 (d, 1H, J = 8 Hz, a), 7.52 (dd, 2H, J = 8 Hz, b), 7.46-7.31 (m, 11H, c-f), 7.22-7.14 (m, 8H, g-i), 7.07 (dd, 4H, J = 8 Hz, j), 7.01 (d, 1H, J = 4 Hz, k), 6.91 (d, 1H, J = 4 Hz, l), 6.65 (dd, 1H, J = 8 Hz, m), 6.35 (d, 1H, J = 8 Hz, n), 5.98 (dd, 1H, J = 8 Hz, o). $^{13}$C NMR (100MHz, acetone-d$_6$): $\delta$ 171.6, 163.8, 159.6, 154.4, 153.5, 146.9, 146.7, 146.0, 145.9, 133.7, 133.0, 132.3, 130.9, 130.7, 130.6, 129.7, 129.3, 127.3, 127.1, 126.3, 126.3, 119.4, 118.2, 112.7, 112.4, 107.3. m/z calculated for C$_{46}$H$_{31}$N$_{5}$O$_{2}$: 657.2 found by FAB: 658.4.

3.4.9 Solution Absorbance

Solution absorbance spectra were recorded on a Cary 100 spectrophotometer in DCM. All extinction coefficients were determined from a linear fit of five data points.
3.4.10 Thin Film Transistor Fabrication and Measurements

All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer. The field effect transistors were constructed using pre-patterned substrates made of heavily n-doped silicon substrate with a 230 nm silicon dioxide layer and a capacitance of 14.9 nF/cm². The gold source and drain electrodes were deposited on the gate oxide layer resulting in bottom contact FETs. Before the films were spin coated onto the surface, the substrates were cleaned with acetone and dried with an argon stream. Solutions of 10mg/mL in chloroform were spin coated onto the surface (1500 rpm for 45 seconds). The devices were measured both before and after annealing at 80 °C for 30 mins. The channel width of all transistors was 10 mm and channel lengths were 2.5 μm, 5 μm, 10 μm, and 20 μm. Mobilities were determined from the saturated regime and maximum mobility are reported.
$^1$H and $^{13}$C NMR of DAA-Fl-CN
$^1$H and $^{13}$C NMR of DAA-F1-60
$^1$H and $^{13}$C NMR of DAA-Fl-6S
$^1$H and $^{13}$C NMR of DAA-Fl-In
$^1$H and $^{13}$C NMR of DAA-Fl-PI
3.5 References


CHAPTER 4
DONOR ACCEPTOR SYSTEMS AS SENSITIZERS FOR BLOCK COPOLYMER PHOTOVOLTAICS

4.1 Introduction

The most successful OPVs to date are fabricated from a conjugated polymer donor and a modified fullerene acceptor in a bulk heterojunction configuration\textsuperscript{1,2}. The absorption of the active layer relies predominantly on the conjugated polymer. Therefore, significant attention has been paid to the design and synthesis of donor-acceptor (D-A) polymers with low bandgaps for enhanced light harvesting\textsuperscript{3-6}. Orbital mixing of the donor and acceptor moieties in the backbone of the polymer result in a decrease of the bandgap which can be manipulated by varying the individual components\textsuperscript{7-13}.

The morphology of the active layer is also critical for realizing high efficiency devices. Efficient charge separation, charge transport, and charge collection all depend significantly on the morphology of the active layer\textsuperscript{14-16}. It is therefore necessary that the active layer of the devices have a well-ordered and controlled morphology. Unfortunately, the morphologies resulting from the phase separation of conjugated polymers are irregular and difficult to control\textsuperscript{17-19}. Significant focus has been placed on manipulating solvent systems\textsuperscript{20,21}, annealing conditions\textsuperscript{22-24}, and the use of solvent additives\textsuperscript{25-27} in order to gain control over the length scale and continuity of the active layer domains.

Block copolymers are a specific type of copolymer that consists of two different homopolymers that are covalently attached. Significant attention has been
paid to the study of block copolymers due to their superior morphological control\textsuperscript{28-30}. Block copolymers are capable of generating a variety of nanostructured morphologies in thin films. The morphology of a block copolymer is dictated by two parameters: \( N \), the molecular weight of each block, and \( \chi \), the Flory-Huggins interaction parameter, a measure of the incompatibility of the two blocks\textsuperscript{28,29}.

Block copolymers have many desirable characteristics for OPVs. Firstly, flexible polymers with insulating backbones are significantly more soluble than conjugated polymers, which require significant solubilizing groups for solution processing. Secondly, in a block copolymer, the donor and acceptor domains are covalently attached to each other, increasing the interfacial area and guaranteeing an interface for exciton dissociation within the exciton diffusion length\textsuperscript{31-37}. Lastly, the morphology control of block copolymers allows access to “ideal” domains for OPVs. Small, continuous, and well-ordered domains result in efficient exciton dissociation due to increased interfacial area\textsuperscript{29,38,39}. Additionally, such domains produce unobstructed pathways for the charges to travel throughout the film. This greatly improves the efficiency at which charges migrate towards and are collected by the electrodes\textsuperscript{40}.

Despite all of the benefits of block copolymers, OPVs based on such active layers have shown disappointing efficiencies. Unfortunately, block copolymers suffer from one major disadvantage limiting their success. Coil-coil block copolymers, which consist of charge transporting functional groups attached through an insulating backbone, do not offer the extended conjugation and thus the low bandgap that conjugated polymers do. Therefore, block copolymers are
typically not good light harvesters. Improving the light harvesting properties of block copolymers may result in high efficiency OPVs. Some efforts have focused on the design of rod-coil block copolymers, in which the rod portion consists of a conjugated polymer with efficient light harvesting\textsuperscript{41-43}. Although such polymers do offer improved absorbance, changing the rigidity of the block perturbs the system, making the morphology unpredictable\textsuperscript{42,44-47}. Installing low bandgap moieties, while maintaining traditional coil-coil block copolymer architecture, could result in a system with improved light harvesting and efficient charge separation and mobility.

### 4.2 Results and Discussion

#### 4.2.1 Molecular Design

Block copolymers are excellent candidates for OPVs because of their predictable control over film morphology\textsuperscript{30,48-50}, which leads to good charge separation and mobility. To date, the efficiencies of block copolymer OPVs are disappointing, most likely due to poor light harvesting as a result of limited conjugation. Installing a sensitizer between the two blocks of the copolymer should improve the absorbance of the system. In order to minimize the perturbation of the system, a small molecule, rather than a conjugated block, should be used to maintain the predictable morphology. Small molecule D-A systems show significant reduction of bandgap without the need to extended conjugation. Therefore, D-A systems will be utilized for the purpose of sensitizing the block copolymers.
In addition to low bandgap, the sensitizer must also have energy levels that align appropriately with the donor and acceptor polymers to allow for facile charge transfer. In order to maintain appropriate energy level alignment, the same donor and acceptor moieties utilized for the sensitizer will be used as the functional groups of the polymers. When a donor is conjugated to an acceptor, the resulting molecule will have a stabilized HOMO energy level. Therefore, the HOMO of the D-A molecule should necessarily be below that of the donor itself. Likewise, when an acceptor is conjugated to a donor, the resulting molecule will be more difficult to reduce. Therefore the LUMO of the D-A molecule should be above that of the acceptor itself. A schematic representation of such a block copolymer, with appropriate energy alignment, can be seen in Figure 4.1. Appropriate energy level alignment is achieved when either the HOMO of the donor is at least 0.3 eV above that of the D-A molecule, or the LUMO of the D-A molecule is at least 0.3 eV above that of the acceptor, or both.

Figure 4.1: Schematic representation of a donor-acceptor block copolymer linked through a D-A sensitizer for improved light harvesting. The system requires specific energy level alignment to achieve efficient exciton dissociation.
In order to determine the design criteria for such a D-A system, a few donors, (dithienopyrrole (DTP), 3,4-ethylenedioxythiophene (EDOT), and carbazole (CBZ)), and acceptors (perylenediimide (PDI), naphtalenediimide (NDI), and naphtalamicide (NI)) were chosen. Additionally, both directly-linked and acetylene-linked molecules were investigated. A series of D-A systems were designed and the structures are shown in Figure 4.2.

![Molecular designs of small molecule D-A systems as sensitizers for block copolymers.](image)

Figure 4.2: Molecular designs of small molecule D-A systems as sensitizers for block copolymers.

The synthesis of 2,9-bis(2-ethylhexyl)-5-(4-hexyl-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (DTP-PDI), seen in Scheme 4.1, started with the synthesis of the DTP donor and the PDI acceptor. To synthesize the DTP, 2,2'-bithiophene was brominated using Br₂ and acetic acid, followed by selective debromination using zinc and hydrochloric acid. A palladium catalyzed ring-closing Buchwald coupling with hexylamine resulted in DTP. Reaction of DTP with butyllithium followed by 2-
(tributylstannyl)thiophene, resulted in 4-hexyl-2-(tributylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole\textsuperscript{51}. The synthesis of 5-bromo-2,9-bis(2-ethylhexyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone began with the reaction of perylenedianhydride with ethylhexylamine, followed by monobromination with Br\textsubscript{2}\textsuperscript{52}. The final product, DTP-PDI, was synthesized by a Stille coupling between the stannylDTP and monobromoPDI.

![Image]

Scheme 4.1: Scheme for the synthesis of DTP-PDI.

The synthesis of 2-butyl-6-(9H-carbazol-9-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-NI), shown in Scheme 4.2, started with the reaction of 4-bromo-1,8-naphthalic anhydride with butylamine, resulting in NI\textsuperscript{53}. A Buchwald coupling with CBZ resulted in the desired product, CBZ-NI.

![Image]

Scheme 4.2: Scheme for the synthesis of CBZ-NI.
The synthesis of 2-butyl-6-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (EDOT-NI), Scheme 4.3, began by reacting EDOT with butyllithium followed by 2-(tributylstannyl)thiophene, to give stannylEDOT. Stille coupling with NI (described above) resulted in EDOT-NI.

Scheme 4.3: Scheme for the synthesis of EDOT-NI.

The synthesis of 2-butyl-6-(4-(4-hexylphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (DTP-NI), Scheme 4.4, began with the synthesis of DTP similar to that described above. Dibromobithiophene was subjected to Buchwald coupling with hexylaniline followed by butyllithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to yield boronate ester DTP. NI was synthesized as described above. Finally, a Suzuki coupling between NI and boronate ester DTP resulted in the desired product, DTP-NI.

Scheme 4.4: Scheme for the synthesis of DTP-NI.
The synthesis of 2-butyl-6-((9-hexyl-9H-carbazol-3-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-a-NI), Scheme 4.5, began with the synthesis of acetylene functionalized carbazole. Carbazole was monobrominated using NBS and alkylated with hexylamine. Sonogashira coupling with TMS-acetylene and subsequent deprotection with K$_2$CO$_3$, resulted in CBZ-acetylene$^{54}$. Sonogashira coupling with NI, described above, resulted in the desired product CBZ-a-NI.

Scheme 4.5: Scheme for the synthesis of CBZ-a-NI.

The synthesis of 2,7-bis(2-ethylhexyl)-4,9-bis((9-hexyl-9H-carbazol-3-yl)ethynyl)benzo[1mn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (CBZ-a-NDI-a-CBZ), Scheme 4.6, began with the synthesis of dibromoNDI. Naphthalicdianhydride was brominated with dibromoisoocyanuric acid under acidic conditions, followed by reaction with ethylhexylamine to yield dibromoNDI$^{55}$. Sonogashira coupling with CBZ acetylene resulted in CBZ-a-NDI-a-CBZ.
4.2.2 Absorbance Properties

The absorbance properties of these D-A systems in comparison to their individual moieties were investigated and the results are reported in Table 4.1. It can be seen that in most cases, the absorbance of the D-A molecule is red shifted when compared to the parent donor and acceptor molecules. In the case of DTP-PDI, the absorbance is nearly the same as in PDI itself. Similarly, the optical bandgap of all the D-A molecules are smaller than the parent compounds. Again, the bandgap of DTP-PDI is similar to that of PDI itself. This is most likely due to the sterics of the molecule resulting in a break in the conjugation. It can also be seen that all of the D-A systems show significant absorbance with extinction coefficients ranging from $5.97 \times 10^3$ M$^{-1}$ cm$^{-1} - 1.40 \times 10^4$ M$^{-1}$ cm$^{-1}$. 

Scheme 4.6: Scheme for the synthesis of CBZ-a-NDI-a-CBZ.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{g}^{\text{opt}}$ (eV) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTP</td>
<td>304</td>
<td>355</td>
<td>3.49</td>
</tr>
<tr>
<td>EDOT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBZ</td>
<td>341</td>
<td>354</td>
<td>3.50</td>
</tr>
<tr>
<td>PDI</td>
<td>528</td>
<td>565</td>
<td>2.19</td>
</tr>
<tr>
<td>NDH</td>
<td>341</td>
<td>380</td>
<td>3.26</td>
</tr>
<tr>
<td>Ni</td>
<td>325</td>
<td>378</td>
<td>3.28</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon$ ($10^4$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{g}^{\text{opt}}$ (eV) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTP-PDI</td>
<td>7.04</td>
<td>525</td>
<td>583</td>
<td>2.33</td>
</tr>
<tr>
<td>CBZ-Ni</td>
<td>5.97</td>
<td>421</td>
<td>484</td>
<td>2.56</td>
</tr>
<tr>
<td>EDOT-Ni</td>
<td>8.27</td>
<td>381</td>
<td>463</td>
<td>2.68</td>
</tr>
<tr>
<td>DTP-Ni</td>
<td>8.26</td>
<td>464</td>
<td>584</td>
<td>2.12</td>
</tr>
<tr>
<td>CBZ-a-Ni</td>
<td>7.73</td>
<td>438</td>
<td>507</td>
<td>2.45</td>
</tr>
<tr>
<td>CR7-a,Ni</td>
<td>14.8</td>
<td>449</td>
<td>467</td>
<td>1.96</td>
</tr>
</tbody>
</table>

$^a$Charge transfer band.  $^b$ $\Delta \lambda_{\text{onset}} = \lambda_{\text{max}}^{\text{ICT}} - \lambda_{\text{max}}^{\text{e-e}}$

Table 4.1: Summary of the absorbance properties of the D-A systems and their parent donor and acceptor moieties.

4.2.3 Electrochemical Properties

As mentioned previously, in addition to low bandgap, the D-A systems must also have well aligned HOMO and LUMO energy levels with the parent donors and acceptors. In order to determine the values of the HOMO and the LUMO, cyclic voltammetry of the D-A molecules were taken. All of the D-A molecules exhibit both oxidation and reduction allowing for the direct determination of HOMO, LUMO, and electrochemical bandgap ($E_{g}^{\text{elec}}$). The donor molecules exhibit only oxidation, allowing for the direct calculation of HOMO. The LUMO is determined by using the optical bandgap. Alternatively, the acceptor molecules exhibit only reduction, allowing for the direct determination of the LUMO energy level only. For the acceptor molecules, the HOMO is estimated from the optical bandgap.
The energy levels for the DTP-PDI system can be seen in Figure 4.3. It can be seen that the bandgap of DTP-PDI is significantly lower than that of DTP and PDI, and that the HOMO of DTP is well above that of DTP-PDI. The LUMO of DTP-PDI, however, is not aligned appropriately, as it lies below that of PDI. This will not allow for electron transfer from the LUMO of the excited state of DTP-PDI to the LUMO of PDI. PDI is a large molecule and therefore is most likely twisted with respect to DTP. This leads to break in conjugation between the two moieties, preventing communication between the donor and the acceptor.

The energy levels of the CBZ-NI system can be seen in Figure 4.4. Similar to the DTP-PDI system, the bandgap of CBZ-NI is lower than that of CBZ and NI, and the HOMO of CBZ is properly aligned with the HOMO of CBZ-NI. The CBZ-NI system is also most likely twisted, and it can be seen that the LUMO of CBZ-NI lies below that of NI. These results suggest that, in order for appropriate alignment, the D-A system should be a small molecule that is not sterically hindered.
Figure 4.4: Energy levels of CBZ, CBZ-NI, and NI. CBZ-NI has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-NI is lower than NI.

The energy levels for the EDOT-NI system can be seen in Figure 4.5. It can be seen that the bandgap of EDOT-NI is significantly larger than that of PEDOT. It is therefore necessary that the polymers used should be pendent polymers rather than conjugated polymers. The linkage of the molecule is between a five membered and a six membered ring. This demonstrates minimal twisting and therefore both the HOMO and the LUMO energy levels are aligned correctly. The energy levels of the DTP-NI system can be seen in Figure 4.6. Similar to the EDOT-NI system, the HOMO and LUMO energy levels are aligned appropriately despite the fact that the bandgap
of DTP-NI is similar to that of DTP. Minimizing the steric twisting in D-A systems seems to favor appropriate energy levels. However, these strict requirements exclude many of the available donors and acceptors.

Figure 4.6: Energy levels of DTP, DTP-NI, and NI. DTP-NI has bandgap similar to DTP. The HOMO levels align appropriately.

Minimizing sterics can also be achieved through the utilization of linkers, such as acetylene. Due to the nature of the acetylene linker, conjugation is maintained while forcing planarity between the donor and acceptor, regardless of the size of the molecule. The energy levels for the CBZ-a-NI and CBZ-a-NDI-a-CBZ systems can be seen in Figure 4.7 and Figure 4.8, respectively. In both cases, it can

Figure 4.7: Energy levels of CBZ, CBZ-a-NI, and NI. CBZ-a-NI has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-a-PNI is lower than NI.
be seen that the D-A systems have lower bandgaps than their parent donor and acceptor moieties. Both systems also show improper alignment of both HOMO and LUMO energy levels. Recently, it has been reported that when acetylene linkers are utilized in D-A systems, the communication between the donor and the acceptor is interrupted because the acetylene itself acts as an acceptor\textsuperscript{56,57}. This disrupts the push pull nature of both the CBZ-a-NI and CBZ-a-NDI-a-CBZ systems.

![Energy Levels Diagram](image)

Figure 4.8: Energy levels of CBZ, CBZ-a-NDI-a-CBZ, and NDI. CBZ-a-NDI-a-CBZ has a lower bandgap than either of the parent molecules. The HOMO energy levels align appropriately but the LUMO of CBZ-a-NDI-a-CBZ is lower than NDI.

### 4.2.4 Design Rules

Developing the sensitizer unit for a block copolymer has been a significant challenge in realizing such a system. All of the following criteria must be met in a successful system: i) the bandgap of the sensitizer must be smaller than that of the donor and acceptor polymers; ii) the energy levels must align appropriately to allow for efficient charge transfer; iii) the polymers in the system should not be conjugated, but rather flexible polymers with pendent groups that show efficient charge transfer; iv) the sensitizer should be a small molecule to prevent significant
perturbation of the system; v) the sterics of the system should be minimized to prevent twists and bends which break conjugation; vi) acetylene linkers should not be utilized as they tend to act as acceptors. This is a significant list of requirements, which will be hard to satisfy with such a system.

4.3 Summary

Installing a sensitizer into a block copolymer can greatly increase the light harvesting of the system. This improved light harvesting, in addition to the benefits of block copolymers, i.e. efficient exciton diffusion, charge mobility, and desired morphology, results in a system that satisfies all the requirements for efficient OPVs. D-A systems were investigated as possible sensitizers for these systems. The donor acceptor systems show desirable red shifted absorbance but often exhibit inappropriate energy level alignment. The systems studied in this chapter have resulted in an understanding of the design rules for such a system. This extensive list of requirements limits the realization of such a system.

4.4 Experimental

Several of the intermediate targets for the synthesis of the donor-acceptor systems were published according to previously published procedures: 4-hexyl-2-(tributylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole; 5-bromo-2,9-bis(2-ethylhexyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone; 6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione; 3-ethynyl-9-hexyl-9H-carbazole; 4,9-dibromo-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone.
4.4.1 Synthesis of 2,9-bis(2-ethylhexyl)-5-(4-hexyl-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (DTP-PDI)

5-bromo-2,9-bis(2-ethylhexyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (260 mg, 0.37 mmol), 4-hexyl-2-(tributylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (243 mg, 0.44 mmol), and Pd(PPh₃)₂Cl₂ (3 mg, 0.004 mmol) were dissolved in DMF and heated to 70 °C overnight. The reaction mixture was washed with water and extracted into ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under vacuum. The product was purified on Combiflash (33%). ADP_1_176 ¹H NMR (400MHz, CDCl₃): δ 9.68 (d, 1H, J = 8 Hz, a), 8.79 (s, 1H, b), 8.58 (t, 5H, J = 8 Hz, c), 8.44 (dd, 3H, d/e), 4.10 (m, 6H, f), 1.93 (m, 2H, g), 1.32 (m, 24H, h), 0.94 (m, 15H, i). ¹³C NMR (100MHz, CDCl₃): δ 164.0, 163.6, 163.6, 162.7, 139.3, 137.8, 137.0, 135.0, 134.0, 133.6, 131.2, 130.7, 129.6, 128.8, 128.7, 128.2, 128.0, 127.9, 127.1, 125.0, 124.9, 124.2, 123.9, 123.7, 123.5, 123.1, 122.8, 121.1, 44.6, 44.5, 38.1, 38.1, 30.9, 28.8, 24.2, 23.3, 23.2, 14.3, 10.8, 10.8. m/z calculated for C₅₄H₅₇N₃O₄S₂: 876.2 found by FAB: 875.1.
4.4.2 Synthesis of 2-butyl-6-(9H-carbazol-9-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-NI)

Pd₂(dba)₃ (6.7 mg, 0.03 mmol), P(tBu)₃HBF₄ (43.5 mg, 0.15 mmol), and NaOtBu (433 mg, 4.5 mmol) were suspended in degassed toluene and stirred under argon to 10 mins. 6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (500 mg, 1.5 mmol) was added and the reaction was heated to 60 °C for 10 minutes. Carbazole (300 mg, 1.8 mmol) was added and the reaction was refluxed overnight. The toluene was removed under vacuum and the product was purified on Combiflash (67%). \(^{1}H\) NMR (400MHz, CDCl₃): \(\delta\) 8.80 (d, 1H, J = 8 Hz, a), 8.67 (dd, 1H, J = 8 Hz, b), 8.61 (dd, 1H, J = 8 Hz, c), 8.21 (dd, 2H, J = 8 Hz, d), 7.91 (d, 1H, J = 8 Hz, e), 7.78 (t, 1H, J = 8 Hz, f), 7.62 (t, 1H, J = 8 Hz, g), 7.36 (m, 3H, h), 7.02 (dd, 2H, J = 8 Hz, i), 4.26 (t, 2H, J = 8 Hz, j), 1.78 (m, 2H, k), 1.49 (m, 2H, l), 1.02 (t, 3H, m). \(^{13}C\) NMR (100MHz, CDCl₃): \(\delta\) 164.1, 163.9, 163.5, 141.7, 140.2, 133.8, 131.9, 131.6, 131.1, 130.1, 129.7, 129.0, 128.1, 127.6, 127.4, 126.9, 126.4, 123.8, 123.5, 122.8, 122.7, 120.7, 120.6, 110.0, 40.4, 40.3, 30.3, 30.3, 20.5, 13.9. m/z calculated for C₂₉H₂₂N₂O₂: 418.2 found by FAB: 419.2.
4.4.3 Synthesis of 2-butyl-6-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (EDOT-NI)

3,4-ethylenedioxythiophene (0.149 mL, 1.4 mmol) was dissolved in dry THF and cooled in a dry ice-acetone bath. nBuLi (0.9 mL of 1.6M in hexane, 1.4 mmol) was added slowly and allowed to react for one hour. Bu$_3$SnCl (0.4 mL, 1.54 mmol) was added and the reaction was allowed to come to room temperature overnight. Pd(PPh$_3$)$_2$Cl$_2$ (9.8 mg, 0.014 mmol) and 6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (558 mg, 1.68 mmol) were added and the reaction was refluxed overnight. The reaction was washed with water and extracted into ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under vacuum. The product was purified on Combiflash (18%). $ADP_{2,39}$ $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.63 (dd, 1H, $J$ = 8 Hz, a), 8.60 (d, 1H, $J$ = 8 Hz, b), 8.46 (dd, 1H, $J$ = 8 Hz, c), 7.80 (d, 1H, $J$ = 8 Hz, d), 7.75 (t, 1H, $J$ = 8 Hz, e), 6.60 (s, 1H, f), 4.30 (m, 2H, g), 4.25 (m, 2H, g), 4.20 (t, 2H, $J$ = 8 Hz, h), 1.72 (m, 2H, i), 1.45, (m, 2H, j), 0.98 (t, 3H, $J$ = 8 Hz, k). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 164.5, 164.2, 143.0, 141.9, 139.3, 137.2, 133.3, 132.7, 131.5, 130.8, 130.1, 129.6, 129.5, 128.9, 126.9, 123.1, 122.7, 122.1, 121.7, 113.7, 101.5, 77.4, 65.0, 64.7, 64.2, 40.4, 30.4, 20.6, 14.0. m/z calculated for C$_{22}$H$_{19}$NO$_4$S: 393.1 found by FAB: 394.1.
4.4.4 Synthesis of 2-butyl-6-(4-(4-hexylphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (DTP-NI)

6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (325 mg, 1 mmol) and 4-(4-hexylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (512 mg, 1.1 mmol) were dissolved in 15 mL dry THF. K₂ CO₃ (2.8 g/10 mL, aq) was added and the reaction was stirred under argon. Pd(PH₃)₄ (96 mg, 0.1 mmol) was added and the reaction was refluxed overnight. The reaction was washed with water and extracted into ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under vacuum. The product was purified on CombiFlash (21%). *ADP_2_10* ¹H NMR (400 MHz, CDCl₃): δ 8.75 (d, 1H, J = 8 Hz, a), 8.63 (d, 1H, J = 8 Hz, b), 8.59 (d, 1H, J = 8 Hz, c), 7.86 (d, 1H, J = 8 Hz, d), 7.74 (t, 1H, J = 8 Hz, e), 7.53 (d, 2H, J = 8 Hz, f), 7.43 (s, 1H, g), 7.35 (d, 2H, J = 8 Hz, h), 7.26 (d, 1H, J = 8 Hz, i), 7.18 (d, 1H, J = 4 Hz, j), 4.17 (t, 2H, J = 8 Hz, k), 2.68 (t, 2H, J = 8 Hz, l), 1.79 (m, 2H, m), 1.67 (m, 2H, n), 1.33 (m, 8H, o), 1.03 (t, 3H, J = 8 Hz, p), 0.90 (t, 3H, J = 8 Hz, q). ¹³C NMR (100 MHz, CDCl₃): δ 164.4, 164.1, 144.6, 144.3, 141.6, 140.1, 137.3, 137.2, 132.6, 131.4, 130.8, 130.0, 129.1, 128.7, 127.3, 127.0, 125.1, 123.1, 122.8, 121.6, 118.6, 116.7, 114.2, 112.4, 42.1, 35.7, 31.8, 31.6, 29.2, 22.7, 21.5, 14.2, 11.7. m/z calculated for C₃₅H₃₂N₂O₂S₂: 576.2 found by FAB: 577.2.
4.4.5 Synthesis of 2-butyl-6-((9-hexyl-9H-carbazol-3-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CBZ-a-NI)

3-ethynyl-9-hexyl-9H-carbazole (50 mg, 0.18 mmol), 6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (60 mg, 0.18 mmol), Pd(PPh₃)₂Cl₂ (13 mg, 0.018 mmol), and Cul (7 mg, 0.036 mmol) were dissolved in triethylamine and heated to 70 °C overnight. The triethylamine was removed under vacuum and the product was purified by Combiflash (32%). ADP.4.29 ¹H NMR (400MHz, CDCl₃): δ 8.84 (dd, 1H, J = 8 Hz, a), 8.65 (dd, 1H, J = 8 Hz, b), 8.56 (d, 1H, J = 8 Hz, c), 8.43 (s, 1H, d), 8.14 (d, 1H, J = 8 Hz, e), 7.97 (d, 1H, J = 8 Hz, f), 7.86 (t, 1H, J = 8 Hz, g), 7.77 (dd, 1H, J = 8 Hz, h), 7.52 (t, 1H, J = 8 Hz, i), 7.44 (d, 2H, J = 8 Hz, j), 7.30 (t, 1H, J = 8 Hz, k), 4.33 (t, 2H, J = 8 Hz, l), 4.20 (t, 2H, J = 8 Hz, m), 1.90 (t, 2H, J = 8 Hz, n), 1.76-1.72 (m, 2H, o), 1.50-1.25 (m, 8H, p), 0.99 (t, 3H, J = 8 Hz, q), 0.88 (t, 3H, J = 8 Hz, r).

¹³C NMR (100MHz, CDCl₃): δ 164.3, 164.1, 141.0, 132.8, 131.7, 131.7, 130.7, 130.4, 129.6, 127.4, 126.6, 124.7, 120.7, 119.8, 109.3, 109.2, 101.6, 101.6, 85.3, 43.5, 40.5, 31.7, 30.4, 29.1, 27.1, 22.7, 20.6, 14.2, 14.0. m/z calculated for C₃₆H₃₄N₂O₂: 526.3 found by FAB: 527.3.
4.4.6 Synthesis of 2,7-bis(2-ethylhexyl)-4,9-bis((9-hexyl-9H-carbazol-3-yl)ethyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (CBZ-a-NDI-a-CBZ)

3-ethyl-9-hexyl-9H-carbazole (100 mg, 0.36 mmol), 4,9-dibromo-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (232 mg, 0.36 mmol), Pd(PPh3)2Cl2 (25 mg, 0.036 mmol), and CuI (14 mg, 0.072 mmol) were dissolved in dry THF with 1 mL triethylamine. The reaction was stirred for 1 minute. The solvents were removed under vacuum and the product was purified on CombiFlash (57%). \textit{ADP}_2 \textit{118}^1 \text{H NMR} (400MHz, CDCl$_3$): \( \delta \) 8.88 (s, 2H, a), 8.49 (s, 2H, b), 8.15 (d, 2H, J = 8 Hz, c), 7.84 (dd, 2H, J = 8 Hz, d), 7.50 (t, 2H, J = 8 Hz, e), 7.43 (dd, 4H, J = 8 Hz, f), 7.31 (t, 2H, J = 8 Hz, g), 4.32 (t, 4H, J = 8 Hz, h), 4.23 (t, 4H, J = 8 Hz, i), 2.06 (m, 2H, j), 1.89 (m, 4H, k), 1.39 (m, 28H, l), 1.01 (t, 6H, J = 8 Hz, m), 0.96-0.85 (m, 12H, n). \textit{13}C NMR (100MHz, CDCl$_3$): \( \delta \) 162.8, 162.0, 141.1, 140.9, 137.1, 130.5, 127.2, 126.5, 126.2, 125.7, 124.6, 124.2, 123.1, 122.5, 120.7, 119.9, 112.7, 109.3, 109.0, 105.6, 90.0, 44.6, 43.4, 38.0, 31.7, 30.9, 29.1, 28.8, 27.1, 24.3, 23.3, 22.7, 14.4, 14.1, 10.8. m/z calculated for C$_{70}$H$_{76}$N$_4$O$_4$: 1036.6 found by FAB: 1037.2.

4.4.17 Absorbance Measurements

Solution absorbance spectra were recorded on a Cary 100
spectrophotometer. All extinction coefficients were determined from a linear fit of five data points.

4.4.18 Cyclic Voltammetry and Energy Level Estimation

Cyclic voltammetry experiments were carried out using a BASi C3 cell stand fitted with three electrodes: a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag⁺ reference electrode. The voltammograms were recorded in dry DCM using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the standard. HOMO and LUMO energy levels were calculated using the peak onsets using the equations:

HOMO = -(4.8 + E_{ox onset})

LUMO = -(4.8 + E_{red onset})
$^1$H and $^{13}$C NMR of DTP-PDI.
$^1$H and $^{13}$C NMR of CBZ-NI.
$^1$H and $^{13}$C NMR of EDOT-NI.
$^1$H and $^{13}$C NMR of DTP-Ni.
$^1$H and $^{13}$C NMR of CBZ-a-NI.
$^1$H and $^{13}$C NMR of CBZ-a-NDI-a-CBZ.
4.5 References


CHAPTER 5
SUMMARY AND FUTURE DIRECTIONS

5.1 Summary

All organic photovoltaics (OPVs) undergo four interrelated processes to convert sunlight into electrical energy: light absorbance, exciton dissociation, charge migration, and charge collection\(^1\). Optimization of the active layer through molecular design and processing conditions has resulted in a steady increase in the efficiencies of OPVs\(^2-5\). Significant efforts have focused on improving the light absorbance of the donor material through three methods: utilizing polymers with extended conjugation\(^6-8\), designing polymers with stabilized quinoid forms\(^9,10\), and developing polymers with backbones consisting of alternating donor and acceptor moieties\(^5,11\). More recently, small molecule dyes capable of absorbing a significant portion of the solar spectrum have been demonstrated to result in high efficiency OPVs\(^12-19\). Chapter 1 focuses on introducing the processes and parameters of OPVs as well as current successful designs in both polymer and small molecule OPVs.

In Chapter 2, small molecule squaraine dyes were investigated for their use in OPVs. Squaraine dyes with triarylamine functional groups are promising candidate for OPVs\(^20-26\). All of the squaraine dyes show significant absorbance at long wavelengths. Functionalizing the triarylamine with electron donating and electron withdrawing groups results in a tuning of the HOMO energy level. Strategically tuning the bandgap and HOMO energy level placement allows for the optimization of the light harvesting and the \(V_{oc}\) of the system. Sq-TAA-OH, Sq-TAA-
$C_6H_{13}$, and Sq-TAA-H show strictly hole mobility in thin film transistor configuration. The fluorinated molecules demonstrate a change in the charge carrier, with Sq-TAA-F being ambipolar and Sq-TAA-CF$_3$ being strictly electron transporting. Preliminary PV devices show that these molecules are promising candidates for small molecule OPVs.

In Chapter 3, the acceptor strength of ketocyanine dyes are tuned to manipulate the absorbance properties of the dyes. Ketocyanine dyes have been investigated for OPVs due to their enhanced light absorbance$^{27-31}$. All of the ketocyanine dyes investigated show significant absorbance and long wavelengths with both a $\pi$$\pi^*$ transition as well as a charge transfer band. It was found that as the acceptor strength is increased, both the $\pi$$\pi^*$ and CT peaks are red shifted. The changes in the chemical structure also affect the shifts in the $^1H$ NMR of the dyes, as well as their charge transport properties.

In Chapter 4, D-A systems are investigated for sensitizing block copolymers. Block copolymers show desirable morphological control, resulting in films with small, well-ordered, and continuous domains$^{32-35}$. Unfortunately, block copolymers often suffer from poor light harvesting due to flexible, rather than conjugated, backbones. The design rules for D-A small molecule sensitizers are investigated. Small molecule sensitizers are desired due to minimal perturbation to the polymer system. Small molecules with connections that minimize steric are needed. Bulky molecules result in twists and bends in the D-A system, causing breaks in conjugation. This prevents appropriate communication between the donor and acceptor, and thus improper alignment of the energy levels. Acetylene linkers
should also be avoided, as they act as acceptors and disrupt the communication between donor and acceptor.

5.2 Future Directions

5.2.1 Squaraine Dyes for Organic Photovoltaics

Squaraine dyes have shown significant promise as donor materials in organic photovoltaics. Interestingly, both Sq-TAA-F and Sq-TAA-CF$_3$ show significant electron mobility. It has been shown previously that installing fluorine atoms results in a change in charge carrier$^{36-41}$. It is not clear what causes this change. Squaraine dyes can easily be synthesized with various fluorine-containing triarylamines to determine what affect fluorine is having on the dyes. Both the location and number of fluorines should be tuned to gain insight. Additionally, electron transporting squaraine dyes could potentially act as acceptors for OPVs. This could offer a significant advantage over fullerene acceptors due to the enhanced light absorbance.

Croconium dyes have been explored extensively in the field of sensing$^{42-44}$. Croconic acid is a stronger acceptor than squaric acid and therefore could potentially offer materials with even lower bandgaps. Small molecule croconium dyes have absorbances that extend to nearly 900 nm. Some polymers based on croconic acid condensed with various electron donating moieties have been investigated, and are shown along with their absorbance spectra in Figure 5.1. It can be seen that these dyes have significantly low bandgaps, making them efficient
light harvesters. Unfortunately, materials with very small bandgaps often suffer low V\textsubscript{OC} or exciton dissociation due to improperly placed energy levels.

![Croconium dye polymers with pyrrole and dithienopyrrole acceptors. The absorbance of these dyes are significantly broadened and red shifted with absorbances reaching into the NIR.](image)

**5.2.2 Ketocyanine Dyes for Organic Photovoltaics**

Cyanine dyes have been explored for several applications including bioimaging, polarity and pH sensors of microenvironments, and organic photovoltaics. These specific dyes were designed with photovoltaic applications in mind. Both fluorenone and triarylamines have been extensively studied in photovoltaics. Some of the dyes with stronger acceptors show significant hole mobility, and therefore future studies will include making and measuring OPVs from these dyes.

Further variation of the molecular structure can lead to a greater degree of absorbance and energy level tuning. Throughout the series of dyes reported in this chapter, the acceptor strength was varied but the donor remained consistent throughout the study. Tuning the donor strength can result in the tuning of the
energy levels of the dyes, allowing for optimization of light harvesting and OPV parameters, such as exciton dissociation and $V_{OC}$.

5.2.3 Sensitized Block Copolymers for Organic Photovoltaics

The design criteria for D-A small molecules as sensitizers for block copolymers are outlined in Chapter 4. These criteria are extensive and require significant compromises to the molecular design in order to achieve appropriate energy level alignment. Dye molecules may offer a significant improvement over D-A systems. Dyes, such as BODIPY, show intense absorbances at long wavelengths and exhibit bandgaps lower than most donor and acceptor polymers with non-conjugated backbones. Significant work has been done in the Thayumanavan group with BODIPY based polymers as well as small molecules$^{45,46}$. BODIPY dyes can be functionalized in both the beta- and meso-positions. The beta-positions can be used as a synthetic handle for attaching the donor and acceptor polymers to the BODIPY. The meso-position of the BODIPY can be used for tuning the energy levels of the BODIPY dye. Therefore, donor and acceptor polymers can be chosen and the dye to can be manipulated synthetically to result in energy levels that align with the chosen polymers. An example of such a system can be seen in Figure 5.2.
5.3 References


APPENDIX

EFFECT OF TITANIUM OXIDE–POLYSTYRENE NANOCOMPOSITE DIELECTRICS ON MORPHOLOGY AND THIN FILM TRANSISTOR PERFORMANCE FOR ORGANIC AND POLYMERIC SEMICONDUCTORS

A.1 Introduction

Organic thin film transistors (OTFTs) have received much attention over the past two decades due to their potential for the fabrication of low cost and large area devices\(^1\)-\(^4\). Perhaps one of the more exciting applications of OTFTs is in the achievement of flexible devices. Designing flexible OTFTs is not trivial as these devices contain many components, which must be made flexible and optimized to function with the other parts of the device.

Significant advances have been made in the field of semiconductors with high charge carrier mobilities\(^1\),\(^3\). One of the bottlenecks for the realization of flexible devices is the lack of options for flexible gate dielectrics. In addition to flexibility, it is also critical that the dielectric material have high capacitance to permit greater charge injection into the semiconductor layer\(^5\). This will allow the device to operate at lower gate voltages, which is advantageous if the device is to be fabricated onto a plastic substrate. The most commonly used dielectrics are inorganic oxides, such as titanium dioxide (TiO\(_2\)) and silicon dioxide (SiO\(_2\)). Although these dielectrics have a high capacitance, they often require difficult processing techniques that prevent their utility in flexible devices\(^6\). Easily processable polymer dielectrics suffer from low dielectric constants\(^5\),\(^7\). Several techniques have been utilized in order to increase the capacitance of polymer dielectrics, often resulting in a lack of flexibility of the resulting film\(^8\)-\(^10\).
The core-shell approach allows for the combined benefits of inorganic and organic dielectrics. The inorganic oxide nanoparticle core imparts a high dielectric constant to the material and the polymer shell allows for flexibility and solution processability. As seen in Figure A.1, the TiO$_2$ nanorod is covalently attached to polystyrene (PS) chains resulting in the TiO$_2$-PS nanocomposite$^{11}$. These nanoparticles are monodisperse anatase rods with a length of 20 nm and a diameter of 4 nm. The monodisperse polystyrene shell, with a molecular weight of 8-10 kDa, is attached to the nanorod preventing unwanted aggregation and phase separation. The effective dielectric constant of the nanocomposite is 8.2. The nanocomposite can be blended in varying ratios with a PS matrix, resulting in films with dielectric constants between 2.5 and 8.2$^{12}$, shown in Figure A.2.

Recent studies have sought to explore the roll that dielectric strength has on the mobility of the semiconductor in thin film transistors. Some studies have shown that the mobility of the transistor decreased with increasing dielectric constant$^{5,13,14}$. However, surface roughness and surface tension were not controlled
Figure A.2: a) Schematic representation of the blending of the TiO$_2$-PS nanocomposite with the PS matrix resulting in the tuning of the dielectric constant of the resulting film; b) the dielectric constant of the resulting films increases with increasing concentration of the TiO$_2$-PS nanocomposite.

resulting in several variations to the device other than dielectric constant. Another study sought to control surface energy and found that the mobility of a semiconductor increases with increasing dielectric strength, but only over a small range of dielectric constants$^{15}$.

A.2 Results and Discussion

A.2.1 Effect of Dielectric Strength on Crystalline Small Molecule Semiconductors

Unlike the previously reported studies, Table A.1 shows that the surface roughness and contact angle remain constant over the whole range of dielectric constants. This allows for a unique opportunity in which the effect of dielectric constant on semiconductor mobility can be studied independent of surface
roughness or surface tension. It was previously reported that pentacene films evaporated onto the surface of these nanocomposite dielectrics demonstrated increased mobility with increased dielectric constant\cite{1,2}, as seen in Figure A.3. It was also observed that the grain size of the pentacene films decreased with

<table>
<thead>
<tr>
<th>% TiO$_2$-PS in PS matrix</th>
<th>Roughness (Å)$^*$</th>
<th>Contact angle (°)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>3</td>
<td>91</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>25%</td>
<td>6</td>
<td>94</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>50%</td>
<td>7</td>
<td>94</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>75%</td>
<td>16</td>
<td>94</td>
<td>6.2 ± 0.7</td>
</tr>
<tr>
<td>100%</td>
<td>21</td>
<td>95</td>
<td>8.2 ± 0.3</td>
</tr>
</tbody>
</table>

*rms roughness for 1×1 μm area

Table A.1: The surface roughness and contact angle of the nanocomposite films remains constant across the entire range of blends studied.

Figure A.3: a) Chemical structure of pentacene, a crystalline small molecule semiconductor; b) the mobility of the pentacene devices increases with increasing dielectric constant.
increasing dielectric constants, as seen in Figure A.4. It has previously been shown in literature that smaller grains in pentacene films results in higher mobilities$^{16-18}$.

![AFM images of the pentacene films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite.](image)

Sexithiophene (α-6T), another crystalline small molecule semiconductor, offers a greater degree of flexibility over pentacene due to the single bonds between thiophene rings. Devices were fabricated using a top contact bottom gate configuration onto an indium tin oxide (ITO) coated glass substrate. The device architecture and chemical structure of α-6T can be seen in Figure A.5. The TiO$_2$-PS nanocomposite blends are spin coated onto the ITO-glass, followed by evaporation of the α-6T layer and subsequent evaporation of gold electrodes.

![Chemical structure of sexithiophene (α-6T); device architecture of the thin film transistor.](image)
As seen in Figure A.6, the mobility of $\alpha$-6T increases with increasing dielectric strength. These devices have a charge mobility that is comparable with conventional $\alpha$-6T devices supporting the validity of this nanocomposite blend dielectric$^{19-21}$. These results are consistent with those of the pentacene devices. The morphology of the $\alpha$-6T layer was determined using atomic force microscopy (AFM). As seen in Figure A.7, the grain size of the $\alpha$-6T decreases with increasing concentrations of the nanocomposite in the polystyrene matrix. This is the same

Figure A.6: The mobility of the $\alpha$-6T devices increases with increasing dielectric constant.

Figure A.7: AFM images of the $\alpha$-6T films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite.
trend that was seen for the pentacene morphology although it seems to be more pronounced in the case of \(\alpha\)-6T.

It appears that the TiO\(_2\)-PS nanocomposite increases the nucleation rate of the semiconductor while the film is forming\(^{22,23}\). This results in a larger number of grains, which are smaller in size. In addition to smaller grain sizes, well-oriented grain boundaries allow for a larger number of low angle pathways for charge transport resulting in higher effective mobilities\(^{16-18,24,25}\).

### A.2.2 Effect of Dielectric Strength on Semicrystalline Polymer Semiconductors

To explore the generality of this mobility enhancement effect, devices with semicrystalline polymer, poly(3-hexylthiophene) (P3HT), were fabricated. Small molecule semiconductors can be thermally evaporated allowing for easy evaporation onto a polymeric dielectric. Polymers, such as P3HT, cannot be thermally evaporated. Additionally, because the P3HT layer is being deposited onto a polymeric dielectric, traditional solution casting techniques, such as spin coating, are not feasible. Attempting to spin coat the P3HT film would result in a compromised dielectric layer and a poor interface with the semiconductor. It has been shown that the interface between the dielectric and the semiconductor is very important to device performance\(^4,5,7\). To circumvent the solvent compatibility issue\(^{26,27}\), a film transfer technique was employed\(^{28}\). As seen in Figure A.8, the
Figure A.8: Film transfer method for the fabrication of P3HT thin film transistors. The film transfer method allows for the solvent free deposition of the P3HT film onto the nanocomposite dielectric.

dielectric film was spin coated onto the ITO-glass substrate. A sacrificial layer, polystyrenesulfonate sodium salt (PSSNa), was spin coated onto a glass slide. This layer was spun from an aqueous solution and is unaffected by organic solvents. A solution of P3HT in chlorobenzene was then spun onto the sacrificial layer and annealed to remove the residual organic solvent. The two substrates were then sandwiched together and water was added to selectively dissolve the sacrificial layer allowing the P3HT film to release and be transferred onto the dielectric film. Aluminum electrodes were then deposited on the surface to complete the fabrication of the transistors.

As seen in Figure A.9, the mobility of the semiconductor was unaffected by the composition of the dielectric layer. Additionally, the mobility did not improve upon annealing of the devices. Due to the annealing of the P3HT film prior to transfer, the morphology has been set preventing the dielectric material from imparting changes in the morphology to the semiconductor film. As seen in Figure A.10, the P3HT film shows typically grainy features prior to transfer. After transfer, the films appear to be significantly smoother. This is most likely because after transfer, the top of the film is the face that was in contact with the sacrificial layer.
Figure A.9: The mobility of the P3HT devices on dielectric films with increasing concentrations of TiO$_2$-PS nanocomposite show no consistent trend in mobility both a) before and b) after annealing.

After annealing, there are very slight changes to the morphology of the film but they do not appear to be significant enough to affect the mobility of the P3HT film.

Figure A.10: AFM images of the P3HT films on different dielectric films with various concentration of TiO$_2$-PS nanocomposite both before and after annealing.
A.3 Summary

TiO$_2$-PS nanocomposite dielectrics offer a novel platform for studying the effect of dielectric strength on semiconductor mobility independent of surface roughness and surface energy. The mobilities of pentacene, α-6T, and P3HT were measured using top-contact bottom-gate thin film transistors. For the crystalline small molecules, the mobility increases with increasing concentrations of the TiO$_2$-PS nanocomposite. In the case of pentacene, the mobility is 11 times greater on a film of 100% TiO$_2$-PS than for 100% PS. In the case of α-6T, the mobility increased by 115 times from 100% PS to 75% TiO$_2$-PS. This increase in mobility is attributed to the smaller grain sizes found in the semiconductor films when they are formed on dielectrics with higher concentrations of TiO$_2$-PS nanocomposites.

A.4 Experimental

A.4.1 Preparation of TiO$_2$-PS/PS Blend Dielectrics

TiO$_2$–PS/PS blended dielectrics were prepared as previously reported$^{11}$. 

A.4.2 Preparation of Pentacene and α-6T Devices on TiO$_2$-PS/PS Blend Dielectrics

Pentacene devices were prepared as previously reported$^{12}$. α-6T was deposited in a method similar to that used for pentacene. The substrate was heated to 40 °C, and α-6T was thermally evaporated using an Edwards Auto 306 thermal evaporator. 60 nm of α-6T was deposited at ∼ 0.1 nm/s as measured by a quartz crystal deposition monitor. Subsequent to the deposition of α-6T, gold electrodes (50 nm) were deposited at a deposition rate below 1 Å/s.
A.4.3 Preparation of P3HT Devices on TiO2-PS/PS Blend Dielectrics

P3HT films were prepared on a PSSNa sacrificial release film on a glass substrate. First, a 20\% PSSNa water solution was spin coated onto a glass substrate at 400 rpm for 30 s followed by 1000 rpm for 30 s. Immediately following the deposition of PSSNa, a 15 wt.\%/vol P3HT solution in chlorobenzene was spun onto the PSSNa film at 1000 rpm for 60 s. The bilayer film on glass is annealed for 30 min at 100 °C. In order to transfer the P3HT film to the blended dielectrics, the glass-PSSNa-P3HT film is placed on top of the blended TiO2–PS/PS dielectrics/ITO–glass substrate. A few drops of water are placed around the edges of the films to dissolve the sacrificial PSSNa film. After 1 h, the transfer is complete. The films were washed with water and the residual water was removed by an argon stream. The “as transferred” devices are brought into the glove box for device fabrication by evaporation of 200 nm thick aluminum source/drain electrode bars. A second set of devices was annealed in a vacuum oven for 30 min at 110 °C and then brought into glove box for device fabrication.

A.4.4 TFT Measurements

The source-drain current ($I_{SD}$) in the saturation region was measured using an Agilent 4156C precision semiconductor parameter analyzer and saturation mobility was calculated using the following equation:

$$I_{SD} = \frac{Z}{2L} C \mu (V_G - V_T)^2$$

In this equation, $Z$ is the channel width, $L$ is the channel length, $C$ is the capacitance per unit area, $\mu$ is the mobility, $V_G$ is the gate voltage, and $V_T$ is the threshold voltage.
Capacitance values were obtained from prior measurements of the effective dielectric constant ($\varepsilon_{\text{eff}}$) for the blended dielectric films\textsuperscript{12}, film thickness measurements using a Dektak surface profiler, and the equation below (where $C$ is the capacitance per unit area, $\varepsilon_0$ is the permittivity of free space, and $d$ is the measured film thickness).

\[
C = \frac{\varepsilon_0 \varepsilon_{\text{eff}}}{d}
\]

### A.4.5 AFM Characterization

AFM characterization of the thin films was performed using an Innova scanning force microscope (Veeco) in the tapping mode. The cantilever (Budget Sensors, Tap190-G) characteristics are as follows: force constant 48 N/m, resonant frequency 190 kHz, and tip radius ca. 10 nm. Analysis of the AFM images (flattening, rms measurements) was performed with WSxM software (Nanotec Electronica)\textsuperscript{29}.

### A.5 References


(17) Shstein, M.; Mapel, J.; Benziger, J. B.; Forrest, S. R. Effects of Film Morphology and Gate Dielectric Surface Preparation on the Electrical Characteristics...


BIBLIOGRAPHY


Guo, S.; Sun, J.; Ma, L.; You, W.; Yang, P.; Zhao, J. Visible Light-Harvesting Naphthalenediimide (NDI)-C60 Dyads as Heavy-Atom-Free Organic Triplet


Photovoltaics, N. N. C. f.: Best Research-Cell Efficiencies.


