

INTERPLAY OF STRUCTURAL,  
DYNAMICAL, AND ELECTRONIC  
PROPERTIES IN DOPED  
SEMICONDUCTING POLYMER SYSTEMS

SOPHIA ACKLING  
B.Sc. (ADVANCED)

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF  
MASTER OF PHILOSOPHY IN CHEMICAL SCIENCE

FEBRUARY 2017



DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF ADELAIDE  
NORTH TERRACE CAMPUS  
ADELAIDE, SOUTH AUSTRALIA 5005

COPYRIGHT © SOPHIA ACKLING 2017

SUPERVISORS:

DR DAVID M. HUANG

A/PROF. TAK W. KEE

# CONTENTS

<b>Abstract</b>	<b>vii</b>
<b>Declaration</b>	<b>ix</b>
<b>Acknowledgements</b>	<b>xi</b>
<b>Abbreviations</b>	<b>xiii</b>
<b>List of Figures</b>	<b>xv</b>
<b>List of Tables</b>	<b>xvii</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Organic electronics . . . . .	2
1.1.1 Semiconducting polymers . . . . .	2
1.1.2 Molecular doping . . . . .	2
1.1.3 Device fabrication . . . . .	3
1.1.4 Structural control and stability in organic devices . . . . .	5
1.2 Structure dynamics and optoelectronics of donor-acceptor systems . . . . .	5
1.2.1 Aggregation in the P3HT/F4TCNQ system . . . . .	5
1.2.2 Theoretical studies of the P3HT/F4TCNQ system . . . . .	7
1.2.3 Intermolecular interactions in the P3HT/F4TCNQ system . . . . .	8
1.2.4 Stability in the P3HT/F4TCNQ system . . . . .	9
<b>2 Computational methods</b>	<b>11</b>
2.1 Density functional theory . . . . .	11
2.1.1 Technical details . . . . .	11
2.1.2 Density functionals . . . . .	12
2.1.3 Basis sets . . . . .	14
2.1.4 Constrained density functional theory . . . . .	15
2.1.5 Excited states: time-dependent density functional theory . . . . .	16
2.1.6 Solvent models . . . . .	18
2.1.7 Thermodynamic correction . . . . .	19
2.2 Molecular dynamics . . . . .	20
2.2.1 Equilibrium simulations . . . . .	20

---

2.2.2	Steered molecular dynamics . . . . .	23
2.2.3	Alchemical free energy perturbation theory . . . . .	24
<b>3</b>	<b>Ground-state properties of the P3HT/F4TCNQ dimer complex</b>	<b>27</b>
	Abstract . . . . .	28
3.1	Introduction . . . . .	28
3.2	Computational details . . . . .	30
3.2.1	Polymer structure dependence . . . . .	30
3.2.2	Dielectric dependence . . . . .	31
3.2.3	Density functional dependence . . . . .	31
3.3	Results and discussion . . . . .	31
3.3.1	Polymer structure dependence . . . . .	31
3.3.2	Dielectric dependence . . . . .	34
3.3.3	Density functional dependence . . . . .	38
3.4	Conclusions . . . . .	41
<b>4</b>	<b>Photo-induced charge-transfer mechanism</b>	<b>43</b>
	Abstract . . . . .	46
4.1	Introduction . . . . .	46
4.2	Computational details . . . . .	47
4.3	Results and discussion . . . . .	48
4.3.1	Excited-state properties . . . . .	48
4.3.2	Charge-neutral state . . . . .	52
4.4	Conclusions . . . . .	55
<b>5</b>	<b>Molecular mobility of F4TCNQ in P3HT systems</b>	<b>57</b>
	Abstract . . . . .	58
5.1	Introduction . . . . .	58
5.2	Computational details . . . . .	60
5.3	Results and discussion . . . . .	62
5.3.1	Charge transfer . . . . .	62
5.3.2	mF4TCNQ methyl rotation . . . . .	63
5.3.3	Dopant translation . . . . .	64
5.4	Conclusions . . . . .	69
<b>6</b>	<b>Quantifying charge-transfer-induced solubility control</b>	<b>71</b>
	Abstract . . . . .	72
6.1	Introduction . . . . .	72
6.2	Computational details . . . . .	74
6.2.1	Density functional theory calculations . . . . .	74
6.2.2	Molecular dynamics simulations . . . . .	75
6.2.3	Steered molecular dynamics parameters . . . . .	75
6.2.4	Free energy perturbation simulation set-up . . . . .	76

---

6.3	Results and discussion . . . . .	77
6.3.1	Steered molecular dynamics simulations . . . . .	77
6.3.2	Free energy of separation . . . . .	81
6.4	Conclusions . . . . .	84
<b>7</b>	<b>Conclusions and future directions</b>	<b>85</b>
7.1	Conclusions . . . . .	85
7.2	Future directions . . . . .	87
7.2.1	Ground state properties of the P3HT/F4TCNQ dimer complex	87
7.2.2	Diffusion in the P3HT/F4TCNQ system . . . . .	87
7.2.3	Quantifying charge-transfer-induced solubility control . . . . .	89
<b>A</b>	<b>Ground state properties of the P3HT/F4TCNQ dimer complex</b>	<b>91</b>
<b>B</b>	<b>Photo-induced charge-transfer mechanism</b>	<b>97</b>
<b>C</b>	<b>Molecular mobility of F4TCNQ in P3HT systems</b>	<b>99</b>
<b>D</b>	<b>Quantifying charge-transfer-induced solubility control</b>	<b>101</b>
	<b>References</b>	<b>118</b>



# ABSTRACT

High-performing cost-efficient organic electronics will play an important role in shaping the future of flexible electronic devices. Applications for such technology range from smart device screens to sensors and photovoltaics. Precise optical control over polymer structure has recently been reported, with applications in optical film patterning for cost-efficient organic device fabrication. This process was demonstrated within the archetypal poly(3-hexylthiophene) (P3HT) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) polymer/dopant system, wherein optical control over solubility was performed using light at a specific wavelength. However, the underlying mechanism responsible for the solubility change is yet to be fully elucidated. The work presented in this dissertation aims to provide insight into a number of related physical and electronic properties within this polymer/dopant system by means of computational investigation.

Density functional theory is used to investigate how structural and environmental properties of the P3HT/F4TCNQ system affect charge transfer. A simplified oligomer/dopant complex is constructed, and the impacts of oligothiophene chain length and substitution are investigated. An oligomer close to the P3HT conjugation length, with methyl side chains, is found to best replicate experimental results. A dielectric medium is introduced to simulate the effects of the surrounding P3HT chains that are present in the experimental system. The surrounding environment is shown to be intrinsic to realistic charge transfer, as quantitative charge transfer is achieved.

The initial hypothesis for the optical solubility control process suggested a photo-induced charge back-transfer reaction from dopant to polymer, resulting in the latter returning to its neutral, and hence soluble, state. Excited-state density functional theory calculations on the aforementioned optimal model system reveal that the complex does display excitations with charge transfer character near the optical de-doping wavelength. However, constrained density functional theory calculations reveal that the optimised charge-neutral state is unstable, and the charge-separated state is thermodynamically favoured. These calculations illuminate important electronic characteristics of the system, and suggest that a photo-induced charge transfer mechanism is not responsible for the solubility change.

Diffusion processes can dictate physical and electronic properties in doped polymer systems. Density functional theory calculations are used in this work to explain

experimental measurements of atomic motions in P3HT doped with methyl-ester-substituted F4TCNQ. Calculations quantitatively confirm the assignment of experimental measurements of a diffusive process in the system to the methyl rotation on the F4TCNQ analogue. A set of calculations replicating the hopping of the F4TCNQ analogue along the P3HT backbone, a hypothesis for the second experimentally measured process, demonstrates that neither the energy barrier nor the diffusion coefficient for this calculated process are on the order of the experimental results, and hence an alternative process may be responsible for the experimental observations.

Finally, the thermodynamics of the photo-induced solubility change are investigated using classical and quantum techniques. Steered molecular dynamics simulations demonstrate that charge distribution influences the free energy of separation of polymer and dopant. However, these simulations do not account for quantum relaxation or dynamic charge distributions. Density functional theory calculations, which do account for these properties, yield the free energy change for separation using a continuum solvent model. The explicit solvent contribution to the free energy of species separation is extracted from alchemical free energy perturbation simulations. Applying this contribution to the quantum calculations in place of the continuum model contribution yields a free energy change for separation that is in excellent agreement with experimental measurements.



# DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and, where applicable, any partner institution responsible for the joint-award of this degree.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

I acknowledge that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Sophia Ackling  
February 2017



# ACKNOWLEDGEMENTS

There are a number of important people who have contributed to this thesis, to varying degrees and both directly and indirectly. I wish to first acknowledge my supervisor, Dr David Huang, for his considerable contribution. Without your ongoing assistance when the results did not match our expectations, and your continued optimism that just one more calculation would give us the insight we needed, it would have been a far greater challenge to complete this project. Your extensive knowledge, patience and encouragement have made this thesis possible.

I must also thank our American collaborators for including us in their journey towards understanding the interesting chemistry of the doped polymer system. The underlying mechanism turned out to be a little more complicated, but no less exciting, than we originally postulated. I am pleased to have been able to contribute in a small way to the discovery process, and I am grateful for being included in the discussion along the way.

During my time as a Masters student I encountered a number of people who showed interest in my research and helped with the stumbling blocks that I met along the way. Thank you to Leaf Lin for all of your help with the NCI supercomputer and the Q-Chem software that made my project possible, and to Dr Lars Goerigk and Rika Kobayashi for your willingness to share your knowledge of density functional theory. To everyone in the Huang research group: your incredible work ethic does you great credit, and it has helped me to continue to strive towards personal improvement. I have really enjoyed working with you, and appreciate your help along the way. Thanks to Mr Patrick Tapping and Mr Andrew Tarzia, in particular, for your assistance with software.

Successful completion of this research project is also the result of the support of a number of people outside the field of chemistry. Thank you to those at the City Cross General Trader/Minimax store for allowing me to remain a part of the team and covering for me when my studies limited my availability, and in particular thank you to my manager Vicki Gorton for your belief in my ability to complete my studies and your understanding when I had to put my research first. Thank you also to my wonderful friends for the great times we shared over the last two years. These were a welcome break from my studies.

My success as a scientist is owed in large part to my dad, who introduced me to that which underpins science: the wonder of the unknown. Equally importantly,

mum has helped me to stay grounded and focused during the harder times. I am grateful for the continued support from both of my parents and my sister, Chloe, throughout this project. And finally, I wish to express my immense gratitude to my husband, Thomas. Your boundless enthusiasm for everything, including my research, has made the last two years considerably easier. Thank you for believing in me.

# ABBREVIATIONS

<b>B3LYP</b>	Becke three-parameter Lee-Yang-Parr
<b>CDFT</b>	constrained density functional theory
<b>CHELPG</b>	charges from the electrostatic potential on a grid
<b>COM</b>	centre of mass
<b>CPCM</b>	conductor-like polarisable continuum model
<b>DFT</b>	density functional theory
<b>EA</b>	electron affinity
<b>F4TCNQ</b>	2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane
<b>FEP</b>	free energy perturbation
<b>GGA</b>	generalised gradient approximation
<b>HF</b>	Hartree-Fock
<b>HOMO</b>	highest occupied molecular orbital
<b>IEFPCM</b>	integral equation formalised polarisable continuum model
<b>IP</b>	ionization potential
<b>LDA</b>	local density approximation
<b>LJ</b>	Lennard Jones
<b>LRC-<math>\omega</math>PBEh</b>	optimally tuned long-range corrected Perdew-Burke-Ernzerhof
<b>LUMO</b>	lowest unoccupied molecular orbital
<b>M8</b>	eight-unit methyl-substituted oligothiophene
<b>MD</b>	molecular dynamics
<b>mF4TCNQ</b>	methyl-ester substituted 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane
<b>MO</b>	molecular orbital
<b>NMR</b>	nuclear magnetic resonance
<b>NTO</b>	natural transition orbital
<b>OFET</b>	organic field-effect transistor
<b>OLED</b>	organic light emitting diode
<b>OPV</b>	organic photovoltaic
<b>P3HT</b>	poly(3-hexylthiophene)
<b>PCM</b>	polarisable continuum model
<b>PMF</b>	potential of mean force
<b>PPPM</b>	particle-particle particle-mesh
<b>QENS</b>	quasi-elastic neutron scattering
<b>SMD</b>	steered molecular dynamics
<b>TDDFT</b>	time-dependent density functional theory
<b>THF</b>	tetrahydrofuran



# LIST OF FIGURES

1.1	Molecular doping in organic semiconductors . . . . .	3
1.2	Photolithographic process for patterning a silicon wafer . . . . .	4
1.3	Structures of P3HT polymer and F4TCNQ dopant and their respective energy levels . . . . .	6
1.4	Optical patterning of F4TCNQ-doped P3HT . . . . .	7
1.5	Structures of F4TCNQ and modified variants . . . . .	10
2.1	Diagrammatic representation of periodic boundary conditions . . . . .	23
2.2	Non-bonded soft interaction potential . . . . .	26
3.1	Structures of F4TCNQ (left) and the oligothiophenes (right) used in this study. . . . .	31
3.2	Simulated absorption spectra for dimer complexes with increasing oligothiophene length . . . . .	34
3.3	Simulated absorption spectra for different basis sets . . . . .	37
3.4	Molecular orbital energies of the dimer complex in vacuum and solvent . . . . .	37
3.5	Simulated absorption spectra of the dimer complex with various functionals . . . . .	41
4.1	Oligomer and dopant structures and the experimental absorption spectrum of F4TCNQ-doped P3HT . . . . .	47
4.2	Simulated absorption spectra for the B3LYP-D and LRC- $\omega$ PBEh functionals in vacuum and implicit solvent . . . . .	49
4.3	Natural transition orbitals for all excitations with sufficient intensity in the dimer complex . . . . .	51
4.4	Molecular orbital transitions for all excitations with sufficient intensity in the dimer complex . . . . .	53
4.5	Energy profile for increasing charge density on F4TCNQ . . . . .	55
5.1	Structures of the oligomer and dopants studied, and diagrams indicating relevant geometries of the complexes studied . . . . .	62
5.2	Molecular orbital energy diagram for dopants and oligomer . . . . .	63
5.3	Energy profile for dopant translation in the smaller inter-chain separation complex . . . . .	65

---

5.4	Energy profile for dopant translation in the larger inter-chain separation complex . . . . .	66
5.5	Charge transfer profile for dopant translation in the larger inter-chain separation complex . . . . .	66
6.1	Structures of the F4TCNQ dopant and oligothiophene . . . . .	76
6.2	Alchemical free energy perturbation thermodynamic cycle . . . . .	77
6.3	Free energy profiles for both charge distributions . . . . .	80
A.1	Simulated absorption spectra for dimer complexes with increasing methyl-substituted oligothiophene length using B3LYP . . . . .	92
A.2	Simulated absorption spectra for complexes in vacuum and solvent . . . . .	93
A.3	Molecular orbital energies of the complex in vacuum and solvent . . . . .	93
A.4	Simulated absorption spectra in vacuum and solvent using two different basis sets and the B3LYP functional . . . . .	94
A.5	Comparison between simulated absorption spectra from two different continuum solvent models . . . . .	94
A.6	Simulated absorption spectra for various values of optical dielectric constant . . . . .	96
C.1	Rotation energy of the mF4TCNQ ester group for the smaller and larger inter-chain separations. . . . .	99
C.2	Quadratic fit to potential energy data from F4TCNQ, in order to approximate a harmonic fit to the data. . . . .	100
D.1	Atoms, bonds, angles and dihedrals for the F4TCNQ molecule. . . . .	102
D.2	Atoms, bonds, angles and dihedrals for the (3HT) <sub>8</sub> molecule. . . . .	104



# LIST OF TABLES

3.1	Frontier molecular orbital energy levels for all complexes . . . . .	33
3.2	Charge transfer ( $e$ ) in all complexes . . . . .	33
3.3	Dominant excitation energies in hydrogen and methyl substituted oligomers of varying length . . . . .	34
3.4	Ground-state charge transfer (CT) in the M8 dimer with increasing basis set and in dielectric medium . . . . .	36
3.5	Charge transfer, intermolecular separation and molecular orbital energies for the dimer complex obtained using various functionals . . . .	40
4.1	Calculated photo-induced charge-transfer excitations . . . . .	50
4.2	Ground, excited and neutral state properties of the M8 dimer complex	54
5.1	Charge transfer and LUMO energies for the two dopants . . . . .	63
5.2	Calculated model parameters for methyl rotation in mF4TCNQ . . .	64
6.1	Energy decomposition results for the dimer complex . . . . .	81
6.2	Electrostatic contribution to solvation free energy in chloroform . . .	82
6.3	Contributions to the total free energy to separate F4TCNQ from the thiophene oligomer from DFT calculations using a dielectric medium to represent the solvent . . . . .	82
6.4	Solvent contribution to free energies obtained by application of alchemical free energy perturbation in classical MD simulations . . . .	83
A.1	Parameters obtained from tuning the LRC- $\omega$ PBEh functional for the dimer complex in vacuum and in a dielectric medium . . . . .	91
A.2	Molecular orbital energies and charge transfer in the dimer complex for two different continuum solvent models . . . . .	95
A.3	Charge transfer (CT) in the dimer complex for various static dielectric constants . . . . .	95
B.1	Dominant molecular orbital contribution percentage for each excited state with intensity $> 0.1$ a.u. . . . .	97
D.1	Atom parameters for the F4TCNQ molecule . . . . .	101

---

D.2	Bond parameters for the F4TCNQ molecule taken from the charged distribution . . . . .	102
D.3	Angle parameters for the F4TCNQ molecule taken from the charged distribution . . . . .	102
D.4	Dihedral parameters for the F4TCNQ molecule . . . . .	103
D.5	Improper dihedral parameters for the F4TCNQ molecule . . . . .	103
D.6	Atom parameters for the (3HT) <sub>8</sub> molecule . . . . .	103
D.7	Bond parameters for the (3HT) <sub>8</sub> molecule taken from the charged distribution . . . . .	105
D.8	Angle parameters for the (3HT) <sub>8</sub> molecule taken from the charged distribution . . . . .	105
D.9	Dihedral parameters for the (3HT) <sub>8</sub> molecule . . . . .	106
D.10	Improper dihedral parameters for the (3HT) <sub>8</sub> molecule . . . . .	106
D.11	Calculated free energies for the annihilation of neutral F4TCNQ at small and large separation from neutral (3HT) <sub>8</sub> . . . . .	106

# DEDICATION

FOR MY FAMILY