
Theoretical and Spectroscopic Studies of Energy and Charge Transport in Organic Semiconductors

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B.Sc. (Hons), MRACI

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

January 2017



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Abstract

The performance of organic semiconductor devices is heavily dependent on the precise molecular-level arrangement and overall morphology of the functional layers. In organic photovoltaic applications, exciton mobility, fission/fusion or dissociation, as well as charge transport and separation are some of the morphology-dependent processes that are of interest for efficient device design. In this work a combination of experimental and computational techniques are used to elucidate the behaviour of excitons in conjugated polymer and small-molecule semiconductor systems. While there is an emphasis on photovoltaic applications, many concepts are generally applicable to other organic electronic applications such organic light emitting diodes and photodetectors.

In Chapter 3, a pump-push-probe transient absorption technique is used to observe high-energy “hot” excitons formed by photoexcitation of the conjugated polymer poly(3-hexylthiophene) (P3HT). The work demonstrates the ability to clearly isolate the transient signal of the hot exciton decay processes from the thermalised exciton population, where picosecond and sub-picosecond relaxation of hot excitons through torsional motion in the disordered polymer chain is observed. In addition, the push-induced dissociation of high-energy excitons into free charge carriers is able to be quantified and an upper bound on the exciton binding energy determined.

Spectroscopic experiments on P3HT are accompanied by a hybrid quantum-classical exciton hopping model in Chapter 4. Coarse-grained molecular dynamics are used to obtain realistic structures of P3HT free chains and nanofibre aggregates, to which a Frenkel–Holstein exciton model and Monte Carlo hopping simulation is applied. This novel approach captures exciton transport properties of polymer systems with a monomer-level of detail unachievable with continuum or lattice style models, but at a large scale infeasible with fully quantum calculations. Reasonable quantitative agreement with experimental observables is obtained, offering insight into the morphology-dependence of exciton transport in conjugated polymers. In particular, the observed tendency for exciton migration to the core of the polymer aggregate can explain the relatively poor performance of highly crystalline or nanofibre-based polymer solar cells, as well as the unusually high fluorescence yield of aqueous P3HT nanoparticles.

The effect of disorder in small molecule semiconductor films is investigated in Chapter 5 in the context of singlet exciton fission and triplet fusion under the influence of applied magnetic fields. A model is presented that extends the historical theory of molecular spin interactions in crystalline materials and corrects the current understanding in the literature regarding such disordered solid-phase systems. The possibility of using the fluorescence response to magnetic fields to probe the morphology and degree disorder in the films is demonstrated. Extending the model to solution-phase behaviour is then discussed in Chapter 6, where the potential of improving the light-harvesting ability of solar cells through a molecular triplet–triplet annihilation upconversion process is considered. Molecular dynamics simulations are used to obtain physical parameters and collision geometry of the emitter molecules in solution. The complications of applying a static model of triplet fusion to the dynamic solution-phase behaviour are elucidated and the potential of synthesising an ideal upconversion emitter molecule is discussed.

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.

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Patrick Charles Tapping
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Acknowledgements

Firstly, this work would not be possible without the assistance of my supervisors Assoc. Prof. Tak W. Kee and Dr David M. Huang. I am incredibly grateful for their time, support and advice as well as the many opportunities they have given me to travel and expand my experience and knowledge.

Many past and current members of the Kee and Huang research groups also deserve thanks. Scott Clifton, Mandy Hei Man Lueng and Takaaki Harada in particular helped introduce me to life in research. Many other deserving people will invariably be left out of any list, so a general thanks goes to everyone who has provided me with advice or assistance over the last few years.

To the other co-author on my publications, Kyra Schwarz, it has been a pleasure to work with you.

The technical staff members at the University of Adelaide, Peter Apoeffis and Matthew Bull have been invaluable when it comes to building, testing or repairing all sorts of mechanical and electronic equipment and generally deserve more recognition than these few words.

Much of the work performed during research never makes it into a finished product. My time studying for this degree and this thesis is no exception, but I do not consider that work wasted. Thanks goes to those who I have worked with on all the projects that did not make it into this document, Drew Evans and Rick Fabretto to name just a few. Particular thanks to Bernd Fischer and Korbinian Kalternecker for hosting me in their lab during my time in Germany and introducing me to terahertz spectroscopy.

Finally, my parents Jeffrey and Carmel have been great inspiration and have encouraged scientific endeavour for literally as long as I can remember. Thanks to you both for your eternal support and encouragement.

Publications

This thesis is based on the following publications that detail some of the research undertaken during the period of candidature:

1. Tapping, P. C.; Kee, T. W. Optical Pumping of Poly(3-hexylthiophene) Singlet Excitons Induces Charge Carrier Generation. *J. Phys. Chem. Lett.* **2014**, *5*, 1040–1047
2. Tapping, P. C.; Clifton, S. N.; Schwarz, K. N.; Kee, T. W.; Huang, D. M. Molecular-Level Details of Morphology-Dependent Exciton Migration in Poly(3-hexylthiophene) Nanostructures. *J. Phys. Chem. C* **2015**, *119*, 7047–7059
3. Tapping, P. C.; Huang, D. M. Comment on “Magnetic Field Effects on Singlet Fission and Fluorescence Decay Dynamics in Amorphous Rubrene”. *J. Phys. Chem. C* **2016**, *120*, 25151–25157.
4. Tapping, P. C.; Blacket, S.; Ackling, S.; Huang, D. M. Molecular Understanding of Photochemical Upconversion for Efficient Solar Cells. **2016**. Manuscript in preparation.

Additionally, contributions have been made to the following publications:

5. Yang, J.; Wen, X.; Xia, H.; Sheng, R.; Ma, Q.; Kim, J.; Tapping, P. C.; Harada, T.; Kee, T. W.; Huang, F.; Cheng, Y.-B.; Green, M.; Ho-Baillie, A.; Huang, S.; Shrestha, S.; Patterson, R.; Conibeer, G. Exploring Hot Carrier Thermalization in Perovskites by Ultrafast Optical Characterization. *Nat. Commun.* **2017**. Accepted for publication. DOI: 10.1038/ncomms14120
6. Cao, W.; Lin, Y.; Patterson, R.; Wen, X.; Tapping, P. C.; Kee, T. W.; Veetil, B. P.; Zhang, P.; Zhang, Z.; Zhang, Q.; Reece, P.; Bremner, S.; Shrestha, S.; Conibeer, G. Difference in Hot Carrier Cooling Rate between Langmuir-Blodgett and Drop Cast PbS QDs Films Due to Strong Electron-Phonon Coupling. **2017**. Manuscript submitted for publication.

Abbreviations

BBO	β -barium borate
DET	Dexter excitation transfer
DoS	density of states
EET	excitonic energy transfer
ESA	excited-state absorption
FET	field effect transistor
FRET	Förster resonance energy transfer
FWHM	full width half maximum
GSB	ground-state bleach
HOMO	highest occupied molecular orbital
IC	internal conversion
ISC	inter-system crossing
LCD	liquid crystal display
LED	light emitting diode
LEES	local exciton excited state
LEGS	localised exciton ground state
LJ	Lennard-Jones
LUMO	lowest unoccupied molecular orbital
MD	molecular dynamics
MEH-PPV	poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
MSD	mean-squared displacement
NIR	near infra-red
OD	optical density
OLED	organic light emitting diode
OPA	optical parametric amplifier
OPLS	optimised potentials for liquid simulations

- OPLS-AA** optimised potentials for liquid simulations – all atoms
- P3HT** poly(3-hexylthiophene)
- P3MT** poly(3-methylthiophene)
- PCBM** phenyl-C₆₁-butyric acid methyl ester
- PEDOT** poly(3,4-ethylenedioxythiophene)
- PPV** poly(phenylenevinylene)
- PSS** poly(4-vinylbenzenesulfonic acid)
- QEES** quasi-extended exciton state
- RDF** radial distribution function
- SE** stimulated emission
- SFG** sum frequency generation
- TCSPC** time correlated single photon counting
- TDC** transition density cube
- TDM** transition dipole moment
- THF** tetrahydrofuran
- TTA** triplet–triplet annihilation
- TTA-UC** triplet–triplet annihilation upconversion
- ZINDO/S** Zerner’s intermediate neglect of differential overlap - spectra

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