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

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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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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.; Clafton, 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-C_{61}-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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