Photophysics and Photochemistry of Conjugated Polymer Nanoparticles

Scott N. Clafton

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

November, 2014

Department of Chemistry
School of Chemistry and Physics
The University of Adelaide

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma 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.

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.

The author acknowledges that copyright of published works within this thesis (as listed below) resides with the copyright holder(s) of these 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 catalogue, the Australian Digital Theses Program (ADTP) and also through search engines, unless permission has been granted by the University to restrict access for a period of time.

_____

Scott N. Clafton

Abstract

Nanoparticles prepared by the reprecipitation of conjugated polymers are an exciting development in the field of biological imaging and fluorescence sensing. The colloidal stability of these hydrophobic polymers in aqueous suspension was found to originate from the surface charge density of ~15 mC/m^2, which is in part attributed to negatively charged functional groups produced by polymer oxidation.

The suitability of these nanoparticles in traditional conjugated polymer applications, such as polymer photovoltaics, was also investigated using femtosecond fluorescence upconversion and transient absorption spectroscopies. Polarisation resolved studies of energy transfer in highly compact nanoparticles and extended polymer conformations showed the nanoparticles exclusively undergo intermolecular energy transfer. These observations were supported by energy transfer simulations on polymer structures obtained from coarse-grained molecular dynamics simulations.

Next, the recombination of polarons in composite rr-P3HT/PCBM nanoparticles, dominated by geminate recombination below 10 wt% PCBM, was demonstrated using a one dimensional diffusion model. This model also yielded the P3HT domain size of ~5 nm, which confirms these nanoparticles can serve as a model system for probing charge generation and recombination processes in device-like environments.

Finally, the power dependent exciton decay in highly ordered nanowires yielded an exciton diffusion length of 11 ± 3 nm, which is toward the upper limit of diffusion lengths reported for annealed P3HT films. This data indicates the gentle solution based crystallisation of nanowires is a promising route for enhancing the performance of bulk heterojunction devices.

Acknowledgements

I would firstly like to extend my sincere gratitude to my supervisor Dr Tak Kee for allowing me to undertake my PhD studies in his group. His guidance, expertise and persistence have been crucial to my development. Although, in retrospect I wish I had followed some of his advice immediately and with greater enthusiasm to make this an even greater educational experience.

Dr David Beattie, my secondary supervisor, and his group at the Ian Wark Institute of the University of South Australia were extremely valuable, especially during the early studies of these nanoparticles. In particular, Dr Agnieszka Mierczynska-Vasilev and Dr Robert Acres for the AFM and XPS work, respectively.

Dr David Huang has been a great help with modelling and computational studies relating to this work. Thanks must also go to the members of his group, Ming Chiu, Kyra Schwarz and Patrick Tapping for their collective work on modelling exciton migration in MEH-PPV.

My fellow labmates past and present, Alex Gentleman, Mandy Leung, Taka Harada *et al.*, are all fantastic scientists and regardless of whether research is part of my future I look forward to learning more from you guys.

I am hugely thankful for the opportunity to visit the research group of Professor David Vanden Bout at the University of Texas at Austin supported by the D R Stranks Travelling Fellowship and the Research Abroad Scholarship. It was an incredible experience and I wholeheartedly encourage any graduate students reading this thesis to strongly consider undertaking research in an overseas laboratory. Also, it was here I learnt the value of having a postdoc like Dr Zhongjian Hu in the lab, who was able teach me so much in such a short period of time.

Finally and most importantly, I would like to thank my parents, Steve and Christine, my brother Andrew and my wonderful fiancée Rebecca for their encouragement and support throughout this ordeal. Your patience and understanding, especially during the final months of my studies, will not be forgotten.

List of Publications

Publications based on work presented in this thesis:

Chemical Defects in the Highly Fluorescent Conjugated Polymer Dots

Scott N. Clafton, David A. Beattie, Agnieszka Mierczynska-Vasilev, Robert G. Acres, Alan C. Morgan and Tak W. Kee, *Langmuir* **2010**, *26*, 17785-17789.

Femtosecond Dynamics of Excitons and Hole-Polarons in Composite P3HT/PCBM Nanoparticles

Scott N. Clafton, David M. Huang, William R. Massey and Tak W. Kee, *Journal of Physical Chemistry B* **2013**, *117*, 4626-4633

Femtosecond Fluorescence Upconversion and Molecular Dynamics Simulations of Energy Transfer in MEH-PPV Nanoparticles

Scott N. Clafton, Patrick Tapping, Ming Chiu, Kyra Schwarz, David M. Huang, and Tak W. Kee, *In Preparation*

Other publications:

Aggregation and Host-Guest Interactions in Dansyl Substituted Poly(acrylate)s in the Presence of β-Cyclodextrin and a β-Cyclodextrin Dimer in Aqueous Solution: A UV-Visible, Fluorescence, 1H NMR and Rheological Study

Jie Wang, Duc-Truc Pham, Tak W. Kee, Scott N. Clafton, Xuhong Guo*, Philip Clements, Stephen F. Lincoln*, Robert K. Prud'homme, and Christopher J. Easton, *Macromolecules* **2011**, *44*, 9782–9791.

Table of Contents

Abbreviations

BBO	β-barium borate
BEH-PPV	poly[2,5-(2′-ethylhexyloxy)]-1,4-phenylenevinylene
CCD	Charge-coupled Device
DLS	Dynamic Light Scattering
EET	Excitation Energy Transfer
FT-IR	Fourier Transform Infrared
GVD	Group Velocity Dispersion
LEGS	Local Exciton Ground State
MEH-PPV	poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene]
P3HT	poly(3-hexylthiophene-2,5-diyl)
PCBM	phenyl-C_{61}-butyric acid methyl ester
PDHF	poly(9,9-dihexylfluoreneyl-2,7-diyl)
PDOF	poly(9,9-dioctylfluoreneyl-2,7-diyl)
PFBT	poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-(2,1’,3)-thiadiazole)]
PFPV	poly[{9,9-dioctyl-2,7-divinylenefluorenylene}-*alt*-*co*-{2-metoxy-5-(2-ethylhexyloxy)-1,4-phenylene}]
PLED	Polymer Light Emitting Diode
PMANa	poly(sodium methacrylate)
PPE	poly(2,5-di(3',7'-dimethyloctyl)phenylene-1,4-ethynylene)
PPV	poly(phenylene vinylene)
PSBTBT	poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-dsilole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl]
PSS	poly(styrene sulphonate)
PTFE	polytetrafluoroethylene
rr	regioregular
rra	regiorandom
TFP	Thin Film Polarisor
THF	tetrahydrofuran
TOPAS	Travelling-Wave Optical Parametric Amplifier of Superfluorescence
VRS	Vibrationally Relaxed State
WLG	White Light Generation

List of Figures

List of Tables