

Photophysics and Photochemistry of Conjugated Polymer Nanoparticles

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Declaration

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Scott N. Clifton

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 $\sim 15 \text{ mC/m}^2$, 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 $\sim 5 \text{ nm}$, 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 $11 \pm 3 \text{ nm}$, 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.

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List of Publications

Publications based on work presented in this thesis:

Chemical Defects in the Highly Fluorescent Conjugated Polymer Dots

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

Scott N. Clifton, 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. Clifton, 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. Clifton, Xuhong Guo*, Philip Clements, Stephen F. Lincoln*, Robert K. Prud'homme, and Christopher J. Easton, *Macromolecules* **2011**, *44*, 9782–9791.

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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-dihexylfluorenyl-2,7-diyl)
PDOF	poly(9,9-dioctylfluorenyl-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-divinylene-fluorenylene}- <i>alt-co</i> -{2-methoxy-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- <i>alt</i> -(2,1,3-benzothiadiazole)-4,7-diyl]
PSS	poly(styrene sulphonate)
PTFE	polytetrafluoroethylene
rr	regioregular
rra	regiorandom
TFP	Thin Film Polariser
THF	tetrahydrofuran
TOPAS	Travelling-Wave Optical Parametric Amplifier of Superfluorescence
VRS	Vibrationally Relaxed State
WLG	White Light Generation

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