# A dynamic Monte Carlo and experimental study of organic solar cells

By


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# Declaration

**Statement of Originality** This thesis 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.

**Acknowledgement of Collaboration** I hereby certify that the work embodied in this thesis has been done in collaboration with other researchers, or carried out in other institutions. I have included as part of each chapter in this thesis a statement clearly outlining the extent of collaboration, with whom and under what auspices.

**Acknowledgement of Authorship** I hereby certify that the work embodied in this thesis contains substantative components of published papers of which I am a joint author. I have included as part of each relevant chapter in this thesis a written statement attesting to my contribution to the joint publications.

Krishna Feron

# Acknowledgements

A research project is never a one-man show and my PhD project is no exception. For this reason, I dedicate this section to thanking everyone who had a significant contribution to my development as a researcher or directly to my PhD project.

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# List of Publications

- K. Feron, X. Zhou, W. J. Belcher and P. C. Dastoor, *Exciton transport in organic semiconductors: Förster resonance energy transfer compared with a simple random walk.* Journal of Applied Physics **111**, 044510 (2012)
- K. Feron, C. J. Fell, L. J. Rozanski, B. B. Gong, N. Nicolaidis, W. J. Belcher, X. Zhou, E. Sesa, B. V. King and P. C. Dastoor *Towards the development of a virtual organic solar cell: An experimental and dynamic Monte Carlo study of the role of charge blocking layers and active layer thickness.* Applied Physics Letters **111**, 193306 (2012)
- K. Feron, T. J. Nagle, L. J. Rozanski, B. B. Gong and C. J. Fell *Spatially-resolved photocurrent measurements of organic solar cells: Tracking water ingress at edges and pinholes.* Solar Energy Materials and Solar Cells **109**, 169-177 (2013)
- K. Feron, W. J. Belcher, C. J. Fell and P. C. Dastoor *Organic solar cells: Understanding the role of Förster Resonance Energy Transfer.* International Journal of Molecular Sciences **13**, 17019-17047 (2012)

# Contents

# Abstract

The main focus of this thesis was to develop a dynamic Monte Carlo (DMC) model that could act as a virtual organic solar cell, which would then be used to analyse and predict OPV performance.

The photoconversion process in organic solar cells consists of several molecular processes: light absorption, exciton transport, exciton dissociation, charge transport and extraction. The optical field and thus exciton generation profile is determined using transfer matrix techniques. Exciton transport is modelled using Förster resonance energy transfer (FRET) theory. Charge transport is described using Marcus theory and charge injection is known to follow Miller-Abrahams expressions. The DMC approach provides a platform where these various theories can be combined to model the entire photoconversion process.

Exciton transport can be modelled using a simple random walk or using a more rigorous and computationally more intensive theory such as FRET theory. The DMC model was used to investigate the consequence of either theories on exciton dissociation and charge transfer state separation. A random walk is computationally more efficient than FRET and is the preferred approach when modelling single component systems as found in photoluminescence experiments. However, neglecting energy relaxation and non-nearest neighbour hops leads to an underestimation of geminate recombination and an overestimation of photocurrent up to 2 % in organic solar cells.

Experimental validation of the DMC model was provided by modelling and experimentally measuring external quantum efficiency and short-circuit current as a function of active layer thickness. Excellent agreement was found and the model was further used to analyse charge selectivity at the electrodes, interface recombination and bulk recombination. It was found that interface recombination is dominant for thin active layers and that a substantial gain in performance is expected by improving charge selectivity at the electrodes, in particular the anode.

Full I-V curves can be calculated using the DMC model. This capability was used to investigate s-shaped I-V curves. Electron traps were only found to induce s-shaped I-V behaviour when the traps are located at the electrode interfaces. Injected charge carriers do not induce s-shaped I-V curves; photogenerated charge carriers are necessary to observe this behaviour. Simulations suggest that OPV material systems that exhibit less charge recombination are more likely to exhibit s-shaped I-V curves. The open-circuit voltage does not always coincide with the centre of the 's' and could be changed by tuning charge recombination. DMC modelling was further used to investigate why thermal annealing removes s-shaped behaviour. Results suggest that vertical phase composition at the electrodes is not the cause of inflected I-V curves, rather charge traps is the cause of this anomalous behaviour. Energy traps were also found to affect exciton transport as they reduce the exciton diffusion length.

DMC models take into consideration the three dimensional nanostructure of the photoactive layer. This capability was used to investigate core-shell nanoparticle morphologies. Annealing was found to improve the efficiency of nanoparticle devices and modelling suggests that different annealing conditions to what is commonly used for BHJ devices are needed the increase the efficiency further. In addition, simulations indicate that annealing conditions should be re-optimised when changing the nanoparticle size. The performance of core-shell nanoparticles approaches that of the BHJ morphology, when optimised for both feature size and nanoparticle size. Hence, the core-shell morphology does not necessarily severely limit charge extraction and, in theory, optimised nanoparticle devices should yield similar efficiencies as optimised BHJ devices.

A high resolution light beam induced current (LBIC) setup was developed and used to investigate lateral non-uniformities that are the result of imperfect fabrication

techniques or degradation.

The primary degradation mechanism in standard organic solar cells is water diffusion limited oxidation of the aluminium cathode. A diffusion model was applied, which allowed for the determination of the diffusion rate and also the diffusivity of water in PEDOT:PSS. Diffusion through pinholes is quantified to be significantly slower than diffusion at the cathode edge. Lateral device design was shown to substantially influence the degradation rate and pattern.