Application for a TSM-DTC funded PhD studentship

Please complete this form electronically
and submit to Lilian Wanjohi (l.wanjohi@imperial.ac.uk)
by Friday January 8, 2010

1st supervisor
Name: Jenny Nelson
CID (IC only):
Institution, Department, Address: Physics, Imperial College London
Email: jenny.nelson@ic.ac.uk
Phone: x47581

2nd supervisor
Name: James Kirkpatrick
CID (IC only):
Institution, Department, Address: Physics, Imperial College London
Email: james.kirkpatrick@ic.ac.uk
Phone: x43316

3rd supervisor
Name: Andrew Horsfield
CID (IC only): 00523934
Institution, Department, Address: Imperial College, Materials, South Kensington Campus
Email: a.horsfield@imperial.ac.uk
Phone: 020 7594 6753

Please complete the following:

1. Project title

Exciton band formation in conjugated polymers: the role of order.

2. Project abstract (≤ 200 words please and please add 1 or 2 key references)

For crystalline polymer such as polythiophene, the appearance of a red shoulder in absorption is strongly correlated with improved external quantum efficiencies and better photovoltaic performance [1]. The conclusion from that work is that annealing leads a more crystalline microstructure which is the cause of all the observed changes. In this project we want to investigate the following question: is crystalline order necessary to induce changes in spectroscopic properties or are subtle changes in packing density sufficient? This question is important because it helps explain whether the diagnostic tool of spectroscopy is sufficient to probe the conjugated polymer's microstructure.

At the moment the best model for the photophysics of polythiophene is the model of Spano where H aggregate form leading to exciton bands [2]. In this model exciton transfer integrals have a fixed value and the polymer chains are simply modeled as sites with a distribution in energies: disorder

is simply an energetic parameter uncorrelated to the microstructure of the polymer. The aim of this project is to compute exciton transfer integrals [3] for realistic morphologies of conjugated polymer generated by molecular dynamics. This will allow to greatly clarify the relationship between microstructure and spectroscopic properties.

[1] Y. Kim *et al.*, Nature Materials **5**, 197 (2006)
[2] F. Spano J Chem Phys **122**, 234701 (2005)
[3] D. Beljonenne *et al.* J Chem Phys **112**, 4749 (2000)

3. What is the multi-scale nature of the project? (≤ 100 words please)

The shortest length scale in the project is given by the fact that exciton transfer integrals peak for small distances. Even though they are related to Coulomb integrals and are therefore rather long ranged – at short range the accurate description of Coulomb interactions between molecular orbitals requires accurate electrostatic models. The longest length and time scales involved come from the morphology of polymers. Relaxation times in polymers are very long indeed and – since conjugated polymers tend to have a rigid backbone – so are conjugation lengths. A significant challenge in the project is the MD simulation of conjugated polymers. It is likely that the best approach will be to prepare extreme cases of morphology from the least order (melts) to the most ordered (crystals extracted from X-ray data).

4. How do the expertises of the supervisors complement each other? (≤ 100 words please)

James Kirkpatrick has considerable experience in a similar project whose aim was to compute charge transfer integrals in conjugated polymers with the aim of studying their charge mobility. He has existing collaborations with groups at the Max Planck Institute who are experts in molecular dynamics simulation of polymers. Jenny Nelson has considerable experience in organic photovoltaics and in both the experimental and modeling sides of probing polymer microstructures.

5. Is there a self-contained 12-week MSc project that would usefully initiate this PhD project? (If the answer is no the project will not be offered as an MSc project)

Testing and refining models for exciton transfer integrals would be a good short term MSc project. Development of force fields would also be very useful if polymers other than polythiophene were to be looked at.