INTERPLAY OF STRUCTURAL, DYNAMICAL, AND ELECTRONIC PROPERTIES IN DOPED SEMICONDUCTING POLYMER SYSTEMS

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ABSTRACT

High-performing cost-efficient organic electronics will play an important role in shaping the future of flexible electronic devices. Applications for such technology range from smart device screens to sensors and photovoltaics. Precise optical control over polymer structure has recently been reported, with applications in optical film patterning for cost-efficient organic device fabrication. This process was demonstrated within the archetypal poly(3-hexylthiophene) (P3HT) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) polymer/dopant system, wherein optical control over solubility was performed using light at a specific wavelength. However, the underlying mechanism responsible for the solubility change is yet to be fully elucidated. The work presented in this dissertation aims to provide insight into a number of related physical and electronic properties within this polymer/dopant system by means of computational investigation.

Density functional theory is used to investigate how structural and environmental properties of the P3HT/F4TCNQ system affect charge transfer. A simplified oligomer/dopant complex is constructed, and the impacts of oligothiophene chain length and substitution are investigated. An oligomer close to the P3HT conjugation length, with methyl side chains, is found to best replicate experimental results. A dielectric medium is introduced to simulate the effects of the surrounding P3HT chains that are present in the experimental system. The surrounding environment is shown to be intrinsic to realistic charge transfer, as quantitative charge transfer is achieved.

The initial hypothesis for the optical solubility control process suggested a photo-induced charge back-transfer reaction from dopant to polymer, resulting in the latter returning to its neutral, and hence soluble, state. Excited-state density functional theory calculations on the aforementioned optimal model system reveal that the complex does display excitations with charge transfer character near the optical de-doping wavelength. However, constrained density functional theory calculations reveal that the optimised charge-neutral state is unstable, and the charge-separated state is thermodynamically favoured. These calculations illuminate important electronic characteristics of the system, and suggest that a photo-induced charge transfer mechanism is not responsible for the solubility change.

Diffusion processes can dictate physical and electronic properties in doped polymer systems. Density functional theory calculations are used in this work to explain experimental measurements of atomic motions in P3HT doped with methyl-ester-substituted F4TCNQ. Calculations quantitatively confirm the assignment of experimental measurements of a diffusive process in the system to the methyl rotation on the F4TCNQ analogue. A set of calculations replicating the hopping of the F4TCNQ analogue along the P3HT backbone, a hypothesis for the second experimentally measured process, demonstrates that neither the energy barrier nor the diffusion coefficient for this calculated process are on the order of the experimental results, and hence an alternative process may be responsible for the experimental observations.

Finally, the thermodynamics of the photo-induced solubility change are investigated using classical and quantum techniques. Steered molecular dynamics simulations demonstrate that charge distribution influences the free energy of separation of polymer and dopant. However, these simulations do not account for quantum relaxation or dynamic charge distributions. Density functional theory calculations, which do account for these properties, yield the free energy change for separation using a continuum solvent model. The explicit solvent contribution to the free energy of species separation is extracted from alchemical free energy perturbation simulations. Applying this contribution to the quantum calculations in place of the continuum model contribution yields a free energy change for separation that is in excellent agreement with experimental measurements.

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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Sophia Ackling
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I must also thank our American collaborators for including us in their journey towards understanding the interesting chemistry of the doped polymer system. The underlying mechanism turned out to be a little more complicated, but no less exciting, than we originally postulated. I am pleased to have been able to contribute in a small way to the discovery process, and I am grateful for being included in the discussion along the way.

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ABBREVIATIONS

B3LYP	Becke three-parameter Lee-Yang-Parr
CDFT	constrained density functional theory
CHELPG	charges from the electrostatic potential on a grid
COM	centre of mass
CPCM	conductor-like polarisable continuum model
DFT	density functional theory
EA	electron affinity
F4TCNQ	2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane
FEP	free energy perturbation
GGA	generalised gradient approximation
HF	Hartree-Fock
HOMO	highest occupied molecular orbital
IEFPCM	integral equation formalised polarisable continuum model
IP	ionization potential
LDA	local density approximation
LJ	Lennard Jones
LRC-ωPBEh	optimally tuned long-range corrected Perdew-Burke-Ernzerhof
LUMO	lowest unoccupied molecular orbital
M8	eight-unit methyl-substituted oligothiophene
MD	molecular dynamics
mF4TCNQ	methyl-ester substituted 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane
MO	molecular orbital
NMR	nuclear magnetic resonance
NTO	natural transition orbital
OFET	organic field-effect transistor
OLED	organic light emitting diode
OPV	organic photovoltaic
P3HT	poly(3-hexylthiophene)
PCM	polarisable continuum model
PMF	potential of mean force
PPPM	particle-particle particle-mesh
QENS	quasi-elastic neutron scattering
SMD	steered molecular dynamics
TDDFT	time-dependent density functional theory
THF	tetrahydrofuran

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DEDICATION

FOR MY FAMILY