Templated growth of fullerene $C_{60}$ crystals by triptycene in polymer blend films

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Abstract

Molecular semiconductors such as fullerene $C_{60}$ have become ubiquitous components of organic electronic devices, owing to their electronic structure and favourable material processing properties. In most conjugated polymer-fullerene films that form the active layer in bulk heterojunction (BHJ) organic solar cells, organisation of the fullerene phases to the correct nanoscale dimensions for exciton charge separation and transportation to the device electrodes is driven by excess fullerene addition. While this approach can deliver acceptable film morphology for a BHJ solar cell, it is not optimal as the photoactive polymer component of the film becomes diluted by $C_{60}$ thereby reducing device efficiency. This motivates a supramolecular approach as an alternative method to control fullerene assembly and give morphological control of conjugated polymer films. Triptycene (TPC) is a readily available molecule whose rigid paddle wheel structure and hydrophobicity present three excellent $C_{60}$ binding cavities. Triptycene has the potential to template the macroscopic assembly of fullerene molecules within a polymer-fullerene blend film, thereby controlling phase separation without excess fullerene addition.

In this project, the ability of TPC to template the assembly of $C_{60}$ was investigated in single crystals, polymer films, and in functional electronic devices. Blue-shifted fluorescence from TPC-$C_{60}$ co-crystals was used as a spectroscopic signature to probe the molecular environment of $C_{60}$ dispersed through an optically transparent polystyrene polymer film, and confirm that TPC hosts $C_{60}$ molecules within the polymer matrix. Ultraviolet-visible (UV-Vis) spectroscopy of the polystyrene-$C_{60}$:TPC films confirmed a reduction in the orbital overlap between adjacent $C_{60}$ molecules providing further evidence that TPC had spatially separated $C_{60}$ molecules upon templating the macroscopic assembly. When TPC was added to conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and MEH-PPV:$C_{60}$ films as a blend additive, fluorescence spectroscopy identified two unique effects: (1) the suppression of excimer states when TPC spatially separated the conjugated polymer chains, and (2) the assembly of $C_{60}$ into larger domains to drive polymer and $C_{60}$ phase separation, giving morphological control of the polymer film.
The fabrication of polystyrene:C₆₀:TPC sandwich devices showed the electronic conduction of C₆₀ was unaltered by spatial separation and reduction in electronic coupling between neighbouring C₆₀ molecules caused by TPC templation. MEH-PPV:C₆₀ BHJ solar cells suffered a loss in photocurrent when TPC was added to the active layer when compared to fabricated devices that used excess fullerene addition to control film morphology. However, due to time constraints, only one polymer film composition was able to be tested. Since the polymer film morphology was shown to be sensitive to the molar ratios of C₆₀ and TPC, there is immense potential to further investigate TPC as a blend additive in conjugated polymer films and optimise the film composition to obtain desirable morphology for a BHJ solar cell. The functionalisation of TPC could provide a method to further enhance interactions between TPC and C₆₀ and provide greater control over C₆₀ self-assembly within a polymer film.
Publications

The following publication was based upon work carried out during this research project, with the key results discussed in Chapters 2, 3, and 4 of this thesis.

‘Templated growth of fullerene C$_{60}$ crystals by triptycene in polymer blend films’
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<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>CB</td>
<td>chlorobenzene</td>
</tr>
<tr>
<td>CD</td>
<td>cyclodextrin</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
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<tr>
<td>CT</td>
<td>charge transfer</td>
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<tr>
<td>DCB</td>
<td>dichlorobenzene</td>
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<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>eV</td>
<td>electron volt</td>
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<tr>
<td>FT-IR</td>
<td>fourier transform infrared</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>I_{SC}</td>
<td>short curcuit current</td>
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<tr>
<td>KPFM</td>
<td>Kelvin probe force microscopy</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>MDMO-PPV</td>
<td>poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene]</td>
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<tr>
<td>MeCN</td>
<td>acetonitrile</td>
</tr>
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<td>MEH-PPV</td>
<td>poly[2-methoxy-5-(2-ethyhexyloxy)-1,4-phenylene vinylene]</td>
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<tr>
<td>NSPM</td>
<td>near-field scanning photocurrent microscopy</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting diode</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaic</td>
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<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
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<tr>
<td>PCBM</td>
<td>1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61}</td>
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<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
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<td>PCPDTBT</td>
<td>poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']di thiophene)-alt-4,7(2,1,3-benzothiadiazole)]</td>
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<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
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<td>PhCN</td>
<td>benzonitrile</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>rpm</td>
<td>revolutions per minute</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
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<tr>
<td>TPC</td>
<td>triptycene</td>
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<tr>
<td>UV-Vis</td>
<td>ultraviolet visible spectroscopy</td>
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<tr>
<td>$V_{OC}$</td>
<td>open circuit voltage</td>
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Chapter 1

Background

1.1 Introduction

Prior to the mid 1980’s, the two main known allotropic forms of bulk carbon were diamond and graphite. In 1985, motivated by investigating the nature of carbon in interstellar matter, Kroto, Smalley and Curl laser vaporised a graphite target and used mass spectrometry to identify a discrete peak corresponding to the exact mass of 60 carbon atoms.\(^1\) Kroto et al. proposed that the particularly stable cluster of 60 carbon atoms was in fact a close caged structure that adopted icosahedral symmetry which can be described as spherical in shape, much like the shape of a European football. The authors named the cluster of 60 carbon atoms buckminsterfullerene for its resemblance to the geodesic domes designed by the American architect, R. Buckminster Fuller. The \(C_{60}\) cluster, and its family of related clusters (e.g., \(C_{70}\)) became known simply as fullerenes; the name which is most commonly used today. A great stimulus to the research field of fullerenes occurred in 1990 when they became available in gram quantities through the resistive heating of graphite (previously only available in trace quantities in the gas phase).\(^2\) In 1996, Kroto, Smalley and Curl were awarded the Nobel prize in chemistry for their roles in the discovery of this new allotropic form of elemental carbon.

The discovery of \(C_{60}\) generated much excitement within the scientific community due to its interesting properties and array of potential technological applications within the fields of medicine, materials science, electronics, and nanotechnology. \(C_{60}\) is an interesting material because it has unique chemistry, nonlinear optical properties and rich electronic and electrochemical behaviour.\(^3\) It has been investigated as a material in a diverse range of applications such as a superconducting material when
doped with alkali metals, a storage material capable of trapping atoms such as hydrogen inside and outside its molecular cage, and an antiviral compound to complex with HIV-protease based on its biological properties and antioxidant activity. The ability of $C_{60}$ to function as a strong electron acceptor and reversibly accept up to 6 electrons due to its triply degenerate LUMO level has made it a ubiquitous component of organic solar cells, which require an acceptor to help dissociate and transport photoexcited states generated in a conjugated polymer film; the application motivating $C_{60}$ research in this project. Although $C_{60}$ is effective at this process, its ability to do so relies heavily on the distribution and organisation within the polymer film and consequently has a large impact on the operational efficiency of the solar cell device.

In this chapter are reviewed some of the basic structural, electronic, and optical properties of $C_{60}$ that make it well suited as an electron acceptor in organic solar cells as well as some conduction challenges that must be overcome to enhance the performance of photovoltaic devices. The bulk heterojunction (BHJ) solar cell is introduced with an emphasis on the importance of controlling the morphology of the conjugated polymer-$C_{60}$ blend in the active layer. Some methods for organising $C_{60}$ via synthetic modification have been selected from the literature to demonstrate how complex materials can assemble $C_{60}$ macroscopically. Finally, blend additives and supramolecular chemistry are introduced as more simplistic methods for controlling polymer-fullerene morphology for use in organic solar cells.

1.2 Structural properties and electronic conduction of fullerene

The carbon atoms of $C_{60}$ are located at the vertices of a truncated icosahedron where all carbon sites are equivalent. Each carbon atom is trigonally bonded to three other carbon atoms in an $sp^2$ derived bonding configuration and as a first approximation, $C_{60}$ can be considered as a rolled up graphite sheet. $C_{60}$ has a total of 20 hexagonal and 12 pentagonal faces to form a closed shell structure with all the rings fused and all the double bonds conjugated. The incorporation of the pentagonal faces into the molecule introduces some $sp^3$ bonding character to the trigonal carbon bonds which is present in tetrahedrally bonded diamond but absent in planar graphite. The incorporation of these pentagons into the fullerene structure allows for surface curvature into a sphere shaped molecule (see Figure 1.1). $C_{60}$ is highly symmetrical and belongs to the $I_h$ point group with a total of 120 symmetry operations.
Organic semiconductors depend on the presence of $\pi$-orbitals for their electron transport properties. The $\pi$-system provides a direct conducting pathway for extended systems such as conjugated polymers (photoactive component used in organic solar cells) and graphite. The electronic structure of $\pi$-conjugated polymers that allows conduction originates from the $sp^2p_z$ hybridised wavefunctions of the carbon atoms in the repeat unit. Polyacetylene is the most structurally simplistic material in its class and is a good polymer to study the fundamental nature of electric conduction in polymers. The $\sigma$-bonds between adjacent carbon atoms ($sp^2$ wavefunctions) in plane with the macromolecule, form the structural integrity of the polymer and hold it together while the perpendicular $\pi$-bonds (formed by the $p_z$-orbitals) creates the $\pi$-electron system that imparts conductive behaviour. Three of the carbon’s valence electrons occupy $\sigma$-bonds (two carbon and one hydrogen bond) while the fourth valence electron occupies the non-hybridised $p_z$ orbital to form a $\pi$-band through the overlapping $\pi$-electron wavefunctions (Figure 1.2). In graphite, strong in-plane bonds from the hybridised $sp^2$ orbitals of the carbon atoms giving the flat planar structure, while the $p_z$ orbital provides weak interplanar bonding between graphitic layers and imparts semimetallic electronic behaviour.

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**Figure 1.1** Structure of C$_{60}$ fullerene. The 60 carbon atoms located at the vertices of a truncated icosahedron are shown as black spheres. Each carbon atom is trigonally bonded to three other carbon atoms (bonds represented in grey). The closed caged molecular structure is formed from a total of 20 hexagonal and 12 pentagonal faces.  

**Figure 1.2** Schematic band diagram for $\pi$-conjugated polymers (left). The chemical structures of trans-polyacetylene (top right) and cis-polyacetylene (bottom right).
The conduction properties of C$_{60}$ are different to extended organic semiconducting systems because it is a molecular solid that lacks direct conducting pathways. The π-system spans the surface of the polyhedral framework and the transport properties depend heavily on the electronic overlap between adjacent C$_{60}$ molecules. The nature of this overlap is crucial to the properties of the molecular conductor when C$_{60}$ crystallises in the solid state. Therefore, it is necessary to develop efficient methods of macroscopic organisation in order to control the crystallisation of C$_{60}$ and form functional assemblies with good conduction properties.

### 1.3 Fullerene in organic solar cells

#### 1.3.1 Single layer and bilayer devices

The first generation of organic solar cells are based on single layer devices where a light absorbing polymer is sandwiched between two metal electrodes of different work function. In conjugated polymers, intrachain excitations formed upon photoexcitation produces electrons and holes that rapidly relax toward the respective band edges and form excited species known as excitons. Under reverse bias, photogeneration of electrons and holes result in a photocurrent (Figure 1.3).

![Figure 1.3](image.png)

**Figure 1.3** Fundamental operation of an organic solar cell where absorption of a photon generates a neutral exciton that must be charge separated into free electrons and holes in order to extract a photocurrent.

The main disadvantage of organic solar cells built upon this device architecture is related to the Coulombically bound nature of the exciton formed upon photoexcitation. Excitons are neutral species unable to transport charge by themselves unless they can physically separate and generate free charge carriers. The generation of free charge carriers requires the electrostatic interaction of the exciton to be over-
come to separate the bound electron-hole pair. The potential difference in a single layered device, caused by the difference in electrode work functions, has to be high enough to overcome the Coulombic attraction of the exciton otherwise absorbed photons will form excitons that decay (radiatively or non-radiatively) back to the ground state. In most cases, the potential difference is not sufficient to produce a photocurrent through the generation of free charge carriers from bound excitons which results in low efficiency of single layer devices (between $10^{-3}$ and $10^{-2}\%$).

The limitation of photoinduced free charge carrier generation in single layer devices can be overcome through a donor-acceptor approach utilising a heterojunction for charge separation of the exciton. Many organic semiconducting polymers are electron donors upon photoexcitation. The bilayer heterojunction solar cell employs device architecture with a planar heterojunction constructed from two different materials with different electronic band structures (most commonly a $\pi$-conjugated polymer and C$_{60}$ fullerene) sandwiched between high and low work function electrodes. The planar interface between the two materials creates a zone where photoinduced electron transfer is mediated by a potential drop between the donor and the acceptor. Excitons that are able to reach a donor-acceptor interface within their life time can be spatially separated by the two different layers to help overcome the Coulombic binding energy.

A big advantage of the bilayer device over the single layer device is the monomolecular charge transport properties. After excitonic dissociation at a donor-acceptor interface, electrons and holes can travel independently of each other in the n-type and p-type layers, respectively. This is beneficial not only from the consideration of charge pair separation but also for non-symmetric charge carrier mobilities exhibited by most conjugated polymers. The charge transfer (CT) between a donating polymer and accepting C$_{60}$ is driven by the difference in ionisation potential and electron affinity of the two adjacent materials. After a photoexcitation event, the electron promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) level in the donor material ($S_0 \rightarrow S_1$) may be transferred to the LUMO level of an acceptor molecule in close proximity (Figure 1.4). This is energetically favourable when the conditions of Equation 1.1 are met:

$$I_{D^*} - A_A - U_C < 0$$

(1.1)

where $I_{D^*}$ is the ionisation potential of the excited donor, $A_A$ is the electron affinity of the acceptor and $U_C$ is the effective Coulomb interaction. The energy level offset between the donor and acceptor LUMO can be used to separate the exciton
from its Coulombic potential. Experimental and theoretical investigations show that electron transfer occurs provided that the difference in the donor and acceptor LUMO levels are larger than the binding energy of the exciton, which is around 0.4 electron volts (eV). Electron transfer to C\textsubscript{60} results in quenching of the polymer fluorescence (radiative recombination and emission of light), increased photocarrier generation (free charge carriers) and increased photocarrier life times.

![Figure 1.4](image)

Figure 1.4 Energy level diagram of HOMO and LUMO levels between the polymer donor and C\textsubscript{60} acceptor. The donor-acceptor interface spatially separates the Coulombically bound electron and hole to help dissociate the exciton into free charge carriers.

The limitation of planar heterojunction devices are concerned with the effective area capable of efficient charge separation of the exciton. Because charge separation is restricted to only a small region of the device at the planar interface between the donor and the acceptor, only excitons generated within $\sim$10 nm of the interface have a diffusion path to the heterojunction and can contribute to the photocurrent. This limits the power conversion efficiency (PCE) of planar heterojunction solar cells to approximately 1% or less.

### 1.3.2 Bulk heterojunction solar cells

A solution to the small effective area for exciton charge separation in the bilayer device is found in the bulk heterojunction (BHJ) solar cell. The donor and the acceptor are blended together to form an intermixed solid state composite layer. The interpenetrating phase separated donor-acceptor network in the BHJ generates a far greater donor-acceptor interfacial area for exciton separation. Assuming the phase separated domains are of the correct dimensional size, an exciton generated in any area of the BHJ device is in close proximity to a donor-acceptor interface enhancing exciton separation (Figure 1.5). The result is an increase in short circuit current of several orders of magnitude and an increase in device efficiency. Organic
solar cells require an active layer thickness of 100–200 nm to absorb most incident light. The interpenetrating donor-acceptor network in the BHJ solar cell enables active layer thickness of this magnitude while still delivering domain sizes on the nanometre scale.

**Figure 1.5** *Left:* Bulk hetero junction solar cell structure showing the intermixed donor-acceptor active layer. *Right:* photocurrent generation in a solar cell with a heterojunction illustrating the process of exciton generation (1), exciton diffusion to the donor-acceptor interface (2), charge separation (3) and transport of charge carriers to the device electrodes (4).

Bulk heterojunction solar cells, first reported in 1995, were mostly based on composite blends of C\(_{60}\) and poly[2-methoxy-5-(2-ethoxyloxy)-1,4-phenylene vinylene] (MEH-PPV). Because fullerene has limited solubility in most organic solvents, BHJ solar cells today commonly use soluble derivatives of fullerene such as 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C\(_{61}\) (PCBM). Photovoltaic devices are typically fabricated on a laboratory scale by depositing the polymer blend onto a glass substrate with a conductive indium tin oxide (ITO) coating followed by evaporation of a low work function metal such as aluminium as a cathode on top. The most prominent material system used to fabricate organic photovoltaic (OPV) devices today are based on solution cast poly(3-hexylthiophene) (P3HT) and PCBM blends that are capable of reaching power conversion efficiencies greater than 5%.^{21,22}

### 1.3.3 Morphology and organic solar cell efficiency

Efficiency improvement of the BHJ solar cell requires the simultaneous optimisation of a few closely interconnected parameters; molecular structure, device properties, and film morphology. Molecular structure relates to the self-organisation of the materials and how they aggregate in the composite film, while device properties are concerned with molecular energetics and absorption (i.e., matching HOMO-LUMO
levels to electrodes and donor-acceptor molecules and the film thickness available for light absorption). The morphology of the film mostly affects exciton diffusion and subsequent separation as well as the charge transport to the electrodes. Controlling the nanomorphology of the bulk heterojunction and understanding the processing of the active layer, in order to ensure maximum exciton separation and charge extraction, is vital for high performance and continual advancement of device efficiencies.

The current-voltage (I-V) characteristics that determine the power output and efficiency of a solar cell are shown in Figure 1.6. The blue line represents the I-V curve of a solar cell under illumination while the red line is the dark current when there is no light available to the device. The maximum photocurrent flows at the short circuit current ($I_{SC}$) when voltage is equal to 0. The $I_{SC}$ depends on the fraction of photons absorbed and the fraction of separated charges that reach the electrodes. Therefore, absorption properties of the film (e.g., absorption coefficient and active layer thickness) will affect the $I_{SC}$ as well as the ability of the heterojunction to separate excitons and transport them through continuous pathways to the electrodes.

![Figure 1.6](image-url)  
**Figure 1.6** Current-voltage characteristics for a solar cell under illumination (blue line) and in the dark (red line) showing the short circuit current ($I_{SC}$), open circuit voltage ($V_{OC}$), maximum obtainable power ($P_{max}$) and maximum power point (MPP).

The maximum voltage of the device occurs at the open circuit voltage ($V_{OC}$) when current is equal to 0. The $V_{OC}$ is heavily influenced by the energy level difference between the HOMO of the donor material and the LUMO of the acceptor material. While an energy level offset between these levels is required to separate excitons (about 0.4 eV), there is an energetic loss associated with the offset, reflected in the $V_{OC}$. Increasing the energy level offset further may help to separate excitons.
but will also result in lower values of $V_{OC}$ and decrease device efficiency. The maximum power that is theoretically obtainable for a given solar cell is determined from the product of $I_{SC}$ and $V_{OC}$ ($P_{\text{max}}$). The maximum power that can actually be achieved during operation after losses is the maximum power point (MPP) and is the product of $V$ and $I$ which gives the largest power output, as shown by the blue dot in Figure 1.6.

The fill factor (FF) is related to the energy yield of a solar cell and is a key parameter in evaluating the performance of OPV devices. The FF is the ratio of the maximum obtainable power ($I_{MPP}$ and $V_{MPP}$ product) to the theoretical power ($I_{SC}$ and $V_{OC}$ product). Equations 1.2, 1.3 and 1.4 show how the maximum obtainable power ($P_{\text{max}}$), FF and power conversion efficiency (PCE) can be calculated. Another parameter used to evaluate the performance of solar cells is the external quantum efficiency (EQE) which measures the photon to charge carrier generation efficiency (i.e., how many photons induce the formation of free charge carriers).

\[
P_{\text{max}} = V_{MPP} \times I_{MPP} \quad (1.2)
\]
\[
FF = \frac{V_{MPP} \times I_{MPP}}{V_{OC} \times I_{SC}} \quad (1.3)
\]
\[
PCE = \frac{P_{\text{OUT}}}{P_{\text{IN}}} = \frac{V_{MPP} \times I_{MPP}}{V_{IN}} = \frac{FF \times I_{SC} \times V_{OC}}{P_{IN}} \quad (1.4)
\]

In a bulk heterojunction solar cell, the I-V curve is sensitive to the morphology of the donor and acceptor in the active layer. Influence of the nanoscale alters the I-V characteristics of the device. The degree of phase separation between the blended materials determines the nanoscale dimensions of the donor and acceptor domains thereby affecting the process of exciton splitting and photocurrent generation. Inadequate mixing of the donor and acceptor results in domain sizes that are too large for all excitons to be generated within the exciton diffusion length of a donor-acceptor interface resulting in less free charge carriers and a reduced $I_{SC}$. Once excitons are separated into free charge carriers, there must be a path to each electrode so they can be collected. Excessive mixing produces domains that are too fine and lack sufficient interpenetrating networks to form percolation pathways to the electrodes for efficient charge extraction, also reducing the $I_{SC}$.

BHJ solar cells with morphology that is not optimised at the nanoscale also results in decreased fill factor due to the excess field required to compensate for inefficient charge separation and extraction processes. Therefore, the organisation of the $C_{60}$ acceptor within the conjugated polymer is of critical importance to the operation of the BHJ solar cell.
1.4 Controlling the morphology of fullerenes

There is a number of ways the morphology of the BHJ solar cell can be controlled. For solvent processed systems, control of the thin-film morphology in the BHJ active layer can be introduced at the solution level of processing or can be influenced after film deposition through post production annealing. The concentration of C$_{60}$ is often used to drive phase separation in the film but can have negative consequences for device performance. Alternatively, the morphology can be controlled by synthetically modifying or derivatising the film blend components. This can be complex and often not worth the costly synthetic investment. More simplistic methods of organising C$_{60}$ within the polymer film, thereby controlling morphology, include the use of blend additives and supramolecular chemistry. In this section these methods will be reviewed in more detail and some specific examples from the literature will be considered.

1.4.1 Solvent processing

A common solution deposition technique for making conjugated polymer films on a laboratory scale is spin-coating. For a given spin-coating speed and polymer concentration, the time taken for a film to dry is dependent on the solvents vapour pressure or boiling point. Factors that influence the solution processing include the solvent selection and solvent evaporation times, and are therefore important to consider.

A ternary phase diagram for a polymer-fullerene solvent system and the rapid formation of a film as the solvent evaporates is shown in Figure 1.7. Thin polymer films prepared by spin-coating are usually not at a thermodynamic equilibrium due to the fast evaporation rate of the solvent. Therefore, changing the kinetics of the solvent evaporation can have a large influence on the final film morphology. This is often achieved by switching to a solvent with a longer evaporation time or tuning mixtures of low and high boiling point solvents. Longer evaporation times generally result in larger domain sizes of the blend constituents which in turn alters charge separation and transport characteristics of the film in question. As the ternary phase diagram indicates, phase separation of a polymer-C$_{60}$ film is also strongly influenced by the concentration and solubility of each blend component in the solvent system.

The morphological control of P3HT based BHJ solar cells is largely driven by the crystallinity of the polymer. A 1:1 ratio of P3HT to fullerene is generally required to
Figure 1.7  Schematic ternary phase diagram of a polymer-fullerene solvent system at constant temperature and pressure. Rapid evaporation of the initial solvent volume ($C_{s,i}$) from an initial concentration of polymer ($C_{p,i}$) and fullerene ($C_{f,i}$) produces a solid state film (grey line). Figure adapted from Hoppe and Sariciftci.\textsuperscript{30}

give balanced charge transport and optimum film morphology.\textsuperscript{31–33} However, in most conjugated polymer-fullerene films, organisation of the fullerene phases to the correct nanoscale dimensions for exciton charge separation ($\sim 10$ nm), and the creation of electronic conduction pathways to the electrodes for charge extraction, is driven by excess fullerene addition.\textsuperscript{27,34} In Figure 1.8 are transmission electron microscopy (TEM) images of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) polymer films spin-coated from chlorobenzene with different ratios of fullerene.\textsuperscript{27} A 1:4 polymer to fullerene ratio is required to achieve separation of the polymer and fullerene phases.

While this approach can deliver acceptable morphology for a BHJ solar cell it is not optimal, as efficient exciton charge separation can be achieved with much smaller quantities of fullerene and the photoactive polymer component of the film becomes diluted by $C_{60}$.\textsuperscript{16,20} This dilution is not favourable because $C_{60}$ contributes little to the optical absorption, yielding a reduced device efficiency due to fewer photons being absorbed by the active layer. Suboptimal quantities of fullerene on the other hand results in small phase domains and isolated fullerene molecules that are not coupled to the electrodes and act as charge traps. Trapped excitons cannot be extracted from the device to contribute to the photocurrent, and instead undergo recombination which corresponds to a decrease in device performance. The development of new conjugated polymers for more efficient organic solar cells will not necessarily possess the crystalline properties of P3HT which would make methods for controlling morphology through the organisation of $C_{60}$ critically important.
Techniques such as thermal and solvent vapour annealing are often employed in BHJ solar cells to alter the thermodynamic equilibrium state of the blend constituents after film deposition. These post production techniques allow further phase segregation and self-organisation of the blends for optimised film morphology. Thermal annealing at (or above) the glass transition temperature ($T_g$) of a polymer results in higher conformational dynamics that allows other blend components to diffuse around the polymer chains.\cite{chirvase2012effect} Thermal annealing is still possible at temperatures below the $T_g$ but requires longer annealing times as the polymer matrix exists in a more frozen conformational state.

Chirvase et al. investigated the effects of thermal annealing on P3HT:PCBM BHJ solar cells.\cite{chirvase2012effect} Thermal annealing of pristine (i.e., non-annealed) P3HT and PCBM films show practically no change in the absorption spectrum (Figure 1.9). However, the authors observe a bathochromic shift (red-shift to longer wavelengths) in the P3HT:PCBM blend absorption spectrum after annealing, and attribute the shift to molecular diffusion of PCBM out of the P3HT matrix. Red-shifted absorption is indicative of increased $\pi$-$\pi$ stacking between the polymer chains suggesting an increased ordering of the P3HT phases and therefore a change in the film morphology. The authors attribute the improved photocurrents in the annealed devices due to the development of bicontinuous percolation pathways throughout the layer.\cite{chirvase2012effect}

Solvent vapour annealing is a post production technique capable of altering the nanomorphology at non-elevated temperatures. Exposing polymer blends to solvent vapour allows the solvent molecules to penetrate into the film and spatially separate the polymer chains allowing enhanced self-organisation. Zhao et al. demonstrated the technique with P3HT:PCBM films treated by 1,2-dichlorobenzene vapour in a
Figure 1.9  left: Absorption spectra of P3HT and PCBM films, as cast (solid curves) and annealed at 130 °C for 1 hour (dashed curves). right: Absorption spectra of P3HT:PCBM composite blend films, as cast (solid curve) and after four successive thermal annealing steps as indicated by the legend. Figure adapted from Chirvase et al.\textsuperscript{35}

A subsequent thermal annealing process was performed to further investigate the morphological effects on the film blends. In Table 1.1 are given the measured absorption and I-V characteristics of films exposed to the various annealing process combinations. The study revealed solvent vapour annealing in conjunction with thermal annealing increases \( I_{SC} \), \( V_{OC} \), and PCE more than one annealing step in isolation (Figure 1.10). A similar red shifted absorption to that seen in thermal annealing studies by Chirvase et al. was also observed. Zhao et al. accredit the improved PV performance after solvent vapour annealing to both the enhanced absorption and increased hole mobility in the p-type P3HT layer as a result of the enhanced self-organisation.\textsuperscript{36}

Table 1.1 Summary of device performance for P3HT:PCBM films exposed to combinations of thermal annealing (TA) and solvent vapour annealing (SVA).\textsuperscript{36}

<table>
<thead>
<tr>
<th>Film</th>
<th>Treatment method</th>
<th>( I_{SC} ) (mA.cm(^{-2}))</th>
<th>( V_{OC} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>Untreated</td>
<td>2.54</td>
<td>0.58</td>
<td>55</td>
<td>0.80</td>
</tr>
<tr>
<td>No.2</td>
<td>SVA</td>
<td>7.85</td>
<td>0.42</td>
<td>44</td>
<td>1.35</td>
</tr>
<tr>
<td>No.3</td>
<td>TA</td>
<td>8.88</td>
<td>0.63</td>
<td>61</td>
<td>3.43</td>
</tr>
<tr>
<td>No.4</td>
<td>SVA + TA</td>
<td>10.01</td>
<td>0.7</td>
<td>53</td>
<td>3.70</td>
</tr>
</tbody>
</table>
1.4.2 Synthetic methods and complex materials

Several other approaches have been employed to organise the macroscopic assembly of fullerene molecules and control the morphology in a polymer film. One strategy is to synthesise polymeric fullerene by covalently tethering $C_{60}$ molecules to a polymer chain. While this novel approach can be used to cleverly combine the properties of $C_{60}$ with a conjugated polymer, the performance of devices made using this strategy has not yet exceeded that of molecular blends. Nanostructured $C_{60}$ domains within polymer films can be defined even further when $C_{60}$ is tethered to a section of a block copolymer. Heiser et al. grafted $C_{60}$ to a rod-coil block copolymer for use as the active polymer layer in a BHJ solar cell. The rod- and coil-block were constructed from poly[(2,5-di(2'-ethyl)hexyloxy)-1,4-phenylenevinylene]-1,4-phenylenevinylene] and poly(butyl acrylate-stat-chloromethylstyrene), respectively. Fullerene is grafted onto the coil block of the copolymer by chloromethylstyrene (CMS) azidation (Figure 1.11).

The fullerene grafted block copolymer was spin-coated into thin films, and the resulting morphology was investigated to study the influence the grafted $C_{60}$ had on the molecular self-assembly process. Figure 1.12 displays a schematic illustration of the molecular self-assembly along with accompanying AFM phase images. The authors found that the rod section of the copolymer, without the coil section, crystallised into a lamellar phase at room temperature with a monoclinic unit cell (see (a) in Figure 1.12). Introduction of the coil segment was found to destabilise the rod-rod interactions leading to a lamellar phase with the rod section of the copolymer in a liquid crystalline state at room temperature (see (b) in Figure 1.12). Grafting fullerene onto the coil segment of the polymer hindered the formation of the lamellar phase by pinning the coils, and altered the polymer self-assembly through the growth of fullerene nanocrystals (see (c) in Figure 1.12). Heiser et al. reported that although
Figure 1.11  Grafting $C_{60}$ onto a butyl acrylate/PPV based rod-coil block copolymer: (i) NaN$_3$ in DMF for 24 h at 50 °C; (ii) $C_{60}$ in dichlorobenzene at 60 °C for 24 h and 120 °C for 1 h. The red, blue and purple sections highlight the conjugated rod block, coil block and grafted fullerene sections of the copolymer, respectively. Figure adapted from Heiser et al.\textsuperscript{40}

Figure 1.12  Schematic illustration of a homopolymer (a), copolymer (b) and fullerene-grafted copolymer (c). AFM phase images have been included to show the resulting morphology when spin-coated. Figure adapted from Heiser et al.\textsuperscript{40}
the polymer films were strongly quenched in fluorescence studies (indicating \( \text{C}_{60} \) is distributed through the film and is charge separating excitons), the nanostructure remains inappropriate for BHJ solar cells (insufficient charge transport across the disordered copolymer layer) and produced photovoltaic devices with a low power conversion efficiency (PCE).\(^{40}\)

1.4.3 Simple blend additives and host-guest assembly

Simple blend additives and supramolecular chemistry offer an alternative method to control fullerene assembly without large synthetic investment. A blend additive can simply be included in the solvent processed system as a ternary component along with the conjugated polymer and fullerene to help self-assemble the film components. Blend additives have been used to improve the efficiency of BHJ solar cells when added in small quantities.\(^{41}\) An inclusion complex where fullerene interacts with a host molecule is an efficient technique for the construction of functional nanostructures with controlled dimensionality and also offers a simple, yet powerful method of influencing morphology. Host-guest complexes of \( \text{C}_{60} \) are well known for calix-pyrroles,\(^{42}\) calixarenes,\(^{43}\) porphyrins,\(^{44}\) coordination networks,\(^{45}\) and even within block co-polymers.\(^{46}\) Supramolecular assembly has been exploited to anchor \( \text{C}_{60} \) molecules adjacent to electron-donating chromophores, thus facilitating photoinduced charge separation within biomimetic complexes.\(^{47}\)

Heeger et al. found annealing polymer:PCBM solar cells with the low band gap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), did not significantly alter the morphology of the active layer.\(^{41}\) Low band gap polymers that maximize spectral overlap with the solar spectrum are seen as a promising route to highly efficient OPV devices. While most conjugated polymers have an energy band gap (\( E_g \)) around 2 eV (e.g., P3HT \( E_g = 1.9 \) eV) and absorption that does not fully overlap with the solar emission spectrum, PCPDTBT has an \( E_g \) of 1.4 eV, which is nearly ideal for photovoltaics.\(^{41}\) The authors of this study reported a different approach for tailoring the morphology of the PCPDTBT:PCBM heterojunction by addition of alkanedithiols to the chlorobenzene spin-casting solution (i.e., a solvent blend additive). Addition of a few percent (by volume) of alkanedithiols of differing chain lengths red-shifted the film absorption and improved device performance. Figure 1.13 displays the absorption and I-V characteristics produced by the new film morphologies. Addition of 1,8-octanedithiol caused the largest change with a PCE increase from 2.8 to 5.5%.\(^{41}\)

Hasobe et al. investigated supramolecular fullerene self-assemblies to control het-
Figure 1.13  UV-Vis spectra (left) and I-V curves (right) when alkanedithiols are added to PCPDTBT:PCBM films as blend additives to make BHJ solar cells.\textsuperscript{41}

Figure 1.14  Supramolecular organisation of $C_{60}$ between porphyrin rings forming a monolayer on gold nanoparticles. Figure adapted from et al.\textsuperscript{48}
erojunction formation in OPV devices. Organic solar cells are constructed using composite nanoclusters of porphyrin and fullerenes with gold nanoparticles (Figure 1.14). The porphyrin units are functionalised with alkanethiolate chains of variable length (n = 5, 11, 15) and form a monolayer around gold nanoparticles to make a secondary structure. Complexes are formed by hosting C\textsubscript{60} molecules between the porphyrin rings, resulting in supramolecular organisation into a tertiary structure. The nanostructures are assembled as three dimensional arrays onto SnO\textsubscript{2} films using an electrodeposition method. Variation of the alkyl chain length of the porphyrin-alkanethiol had a significant influence on the PCE of the devices. Changing the chain length, n, from 11 to 15 produced a PCE increase from 0.61 to 1.5\%. These literature examples highlight the ability to tune film morphology using solvent blend additives, and organise C\textsubscript{60} via supramolecular chemistry. A particular molecule that has been shown in the literature to supramolecularly organise C\textsubscript{60} is triptycene (TPC). TPC is a rigid paddlewheel shaped molecule that consists of three fused phenyl rings with an angle of 120° between each ring (Figure 1.15). TPC corresponds to the C\textsubscript{60} sphere and has the potential to be used as a non-volatile solvent blend additive in polymer-C\textsubscript{60} films to supramolecularly organise C\textsubscript{60} domains. The ability of TPC to template the macroscopic assembly of C\textsubscript{60} will be discussed in more detail in Chapter 2.

Figure 1.15  The paddlewheel shaped triptycene (TPC) molecule with three fused phenyl rings at an angle of 120° to each other.

1.5 Summary

Fullerene C\textsubscript{60} is an interesting material with good electron accepting properties. This makes it well suited as a component in organic solar cells that use a conjugated polymer for light absorption and require an electron acceptor to charge-separate Coulombically bound excitons. Because fullerene is a molecular conductor, its electronic conduction relies heavily on the \pi-orbital overlap between adjacent C\textsubscript{60} molecules. Therefore, the organisation of C\textsubscript{60} in functional optoelectronic devices is critically important to their efficient operation. The nanoscale organisation
of polymer-C$_{60}$ phases in a BHJ solar cell requires fine tuning to produce optimal morphology capable of both dissociating excitons into free charge carriers and transporting them to electrodes to produce a photocurrent.

The morphology of polymer-C$_{60}$ films is largely influenced by the solvent processing conditions. Most conjugated polymers use excess fullerene addition to drive morphological control and create appropriate sized phase domains (≈10 nm) with a continuous conduction pathway to the electrodes for charge extraction. However, this can dilute the photoactive conjugated polymer responsible for collecting light which impacts negatively on the BHJ solar cell performance. Synthetic methods have been used as an alternative method to control the organisation of C$_{60}$ within a conjugated polymer film. Functioning solar cells have been demonstrated via this approach but their relatively low power conversion efficiencies do not yet justify the large synthetic investment required to make these complex materials.

Simple blend additives and supramolecular chemistry offer another approach for controlling the morphology in polymer-C$_{60}$ films. Blend additives can easily be added to the system as a tertiary component to help organise C$_{60}$ and polymer phases. Supramolecular chemistry can be used to template the assembly of C$_{60}$ molecules by providing a suitable host for self-assembly without having to tether or graft C$_{60}$ to a molecular structure.

### 1.6 Research aims

The aim of this research is to investigate the ability of TPC to control the morphology of polymer-C$_{60}$ films and improve the efficiency of BHJ organic solar cell devices. TPC is a readily available molecule whose rigid paddle wheel structure presents three excellent C$_{60}$ binding cavities and has the potential to be used as a ternary blend additive to supramolecularly organise C$_{60}$ assembly within a conjugated polymer film. This research will investigate the ability of TPC to tune polymer-C$_{60}$ film morphology as an alternative method to using excess fullerene addition (concentration), or making large synthetic investments to give morphological control.

Firstly, TPC-C$_{60}$ co-crystals will be grown to identify spectroscopic signatures of the host-guest complex (Chapter 2). TPC is to be added to transparent polymer films containing C$_{60}$ so any identified spectroscopic signatures can be used to detect templation of C$_{60}$ by TPC (Chapter 3). TPC will then be added to conjugated
polymer-C$_{60}$ films (Chapter 4) and fabricated into laboratory scale BHJ organic solar cell devices (Chapter 5).
Chapter 2

A molecular complex with fullerene and triptycene

2.1 Introduction

The self-organisation of fullerene into various functional nanostructures with controlled dimensionality is required for many end use applications (e.g., organic solar cells and field effect transistors). These end use applications often require C$_{60}$ to be processed from solution which makes the crystallisation dynamics very important to the function and performance of the device. Pristine C$_{60}$ forms crystalline assemblies with different shapes under different preparation procedures. Solvent controlled crystallisation of C$_{60}$ can result in dimensionally regulated nanostructures with different sizes and shapes such as nanorods, nanotubes, nanodisks and nanowiskers. Electrical and optical properties can be retained, modulated or enhanced by the controlled geometries obtained through the different preparation methods.

Park et al. demonstrated that there is a systematic correlation between the geometric shape of the solvent and the final self-assembly of C$_{60}$ crystals via a solution drop drying process. The authors reported that pseudo-three-dimensional (p3D), pseudo-two-dimensional (p2D) and pseudo-one-dimensional (p1D) solvents result in the respective self-assembly of C$_{60}$ into p2D, p1D and pseudo-zero-dimensional (p0D) structures. Dropping target C$_{60}$ solutions onto solid substrates and drying at room temperature formed disk, wire and dot structures of C$_{60}$. Sathish et al. investigated different solvent conditions for the free control of microscopic shapes of pure C$_{60}$. The crystallisation of two-dimensional (2D) fullerene crystals were
transformed into one-dimensional (1D) rods through solvent controlled conditions. Rhombohedron, hexagon, and polygon mixtures were precipitated from different solvent interfaces and transformed into nanorods and nanohexagons. The liquid-liquid interfacial precipitation was achieved from tert-butyl alcohol/toluene, tert-butyl alcohol/benzene and isopropyl alcohol/carbon tetrachloride solvent systems.\textsuperscript{52}

In addition to processing conditions, the organisation of C\textsubscript{60} can be controlled via a supramolecular approach. An important criterion in the bottom up nanofabrication approach for fullerene supramolecular structures is the selection of a component capable of encapsulating (or co-assembling) with fullerene. This typically requires fullerene to reside in the cavities of different hosts, or molecular templates, to assist the organisation of C\textsubscript{60} into favourable architectures. An inclusion complex where fullerene interacts with a host molecule is an efficient technique for the construction of supramolecular assemblies. The advantage of hybrid systems for organisation is that the properties of C\textsubscript{60} can be retained without complicated synthesis. The spontaneous self-assembly at the molecular level can deliver spectacular architectures with correlations between different crystalline ordering and optoelectronic or photoconductive properties.\textsuperscript{56}

Fathalla \textit{et al.} have demonstrated the formation of water soluble unidirectional C\textsubscript{60}−porphyrin nanorods.\textsuperscript{58} Octadentate tetraphenyl-porphyrin with four β-cyclodextrin groups on each porphyrin group were used to form an inclusion complex with pristine C\textsubscript{60}. Transmission electron microscopy (TEM) revealed the presence of unidirectional structures 300–500 nm in length resulting from approximately 150–250 units of the porphyrin-C\textsubscript{60} co-assembly. Triptycene (TPC) is a readily available molecule whose rigid paddle wheel structure and hydrophobicity present three excellent C\textsubscript{60} binding cavities, as illustrated in Scheme 2.1. TPC has been shown to co-crystallise with C\textsubscript{60}\textsuperscript{49–51} inspiring the synthesis of various TPC derivatives to modulate the stability of TPC-C\textsubscript{60} complexes in the solid state and in solution.\textsuperscript{59}

\begin{center}
\textbf{Scheme 2.1} Coordination of a TPC molecule with three fullerenes in the TPC-C\textsubscript{60} molecular complex.
\end{center}
In this chapter, the ability of TPC to template the assembly of C\textsubscript{60} molecules in both solution and solid state crystals is further explored. Dynamic light scattering (DLS) and ultraviolet-visible (UV-Vis) spectroscopy are employed in an attempt to understand the crystallisation of the TPC-C\textsubscript{60} co-crystal at very early stages in solution. The TPC-C\textsubscript{60} co-crystal is grown by a number of crystallisation techniques, visually identified by optical microscopy and characterised by Fourier transform infrared (FT-IR) spectroscopy. Having successfully grown and identified the TPC-C\textsubscript{60} molecular complex, fluorescence microscopy is used to identify a spectroscopic signature that can be used to identify the co-crystal from pristine C\textsubscript{60} crystals.

### 2.2 A spectroscopic signature in fullerene crystals

Before TPC and C\textsubscript{60} were investigated in the solid state, an understanding of early nucleation and crystallisation in solution was desired. Knowledge of the experimental conditions needed to initiate the nucleation of the TPC-C\textsubscript{60} molecular complex in solution would be powerful if a correlation could be made to the nature of the co-crystal in the solid state. Manipulation of experimental parameters such as solvent composition, chemical concentrations, and time could tune the ability of TPC to template the assembly of C\textsubscript{60} molecules in crystals and films giving dimensionally controlled functional nanostructures.

Fullerenes, with their unique cage structures and rigid well defined geometries, interact with solvents in interesting ways. The solubility in a given solvent is determined by two geometrical factors of a fullerene solute: (1) the molecular volume (i.e., volume of the cavity created in the solvent liquid), and (2) the molecular surface area (i.e., surface available for interaction with the solvent). Table 2.1 lists the solubility of C\textsubscript{60} in some common organic solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>[C\textsubscript{60}], mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>0.00</td>
</tr>
<tr>
<td>acetonitrile (MeCN)</td>
<td>0.00</td>
</tr>
<tr>
<td>chloroform</td>
<td>0.16</td>
</tr>
<tr>
<td>benzonitrile (PhCN)</td>
<td>0.41</td>
</tr>
<tr>
<td>benzene</td>
<td>1.7</td>
</tr>
<tr>
<td>toluene</td>
<td>2.8</td>
</tr>
<tr>
<td>chlorobenzene (CB)</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Table 2.1 Solubility of C\textsubscript{60} in various solvents at room temperature. Values obtained from Ruoff et al.\textsuperscript{60}
Dynamic light scattering (DLS) and ultraviolet-visible (UV-Vis) spectroscopy were the techniques chosen to study nanoparticle formation in C$_{60}$ solution, both in the presence and absence of TPC. The initial hypothesis was that if TPC could sufficiently template C$_{60}$ in solution, aggregates of a different size may be detectable. However, the size of the nanoparticles formed in solution were found to be the same regardless of whether TPC is present or not and therefore cannot be used alone to conclusively determine if the nanoparticles formed are pristine C$_{60}$ or TPC·C$_{60}$ co-crystals (results from solution state studies can be found in the appendix).

Since literature methods have been established that grow solid state TPC·C$_{60}$ co-crystals from solution,$^{49,50}$ it is known that the complex will form at some point as saturation is approached in the solution. Therefore, it was concluded that the co-crystal likely forms at super saturated conditions that are difficult to detect via DLS and UV-Vis spectroscopy and directed further experimentation towards solid state interactions between C$_{60}$ and TPC (found in the following section). Although solution experiments were not able to conclusively identify TPC·C$_{60}$ co-crystal formation in solution, DLS experiments were able to successfully simulate the rapid deposition of materials from solution that occurs in polymer film deposition techniques such as spin-coating. If TPC·C$_{60}$ co-crystals are unable to form in such conditions then post production annealing techniques such as thermal annealing or solvent vapour annealing may be required to bring about the conditions necessary for TPC templation of C$_{60}$ in solid state polymer films. Therefore, DLS has provided useful information concerning crystal formation in the solid state and given valuable research direction for sections ahead when C$_{60}$ and TPC are blended with a polymer and rapidly cast from solution via standard film formation techniques.

To better understand the potential of TPC to template C$_{60}$ in polymer films, the TPC·C$_{60}$ complex was grown via a number of crystallisation techniques to be analysed spectroscopically. Toluene was selected as the main solvent from which to grow the co-crystals for several reasons: (1) availability of the solvent, (2) high C$_{60}$ solubility (2.8 mg/mL)$^{60}$ and (3) success growing the TPC·C$_{60}$ complex from structurally similar solvents demonstrated in the literature.$^{49,50}$ The TPC·C$_{60}$ complex was grown by liquid-liquid diffusion, vapour diffusion, and slow solvent evaporation. These three methods are illustrated schematically in Figure 2.1.

In the liquid-liquid diffusion method, a poor solvent is layered on top of a toluene solution containing dissolved C$_{60}$ and TPC (purple solution in Figure 2.1) and allowed to slowly diffuse into the solution till C$_{60}$ becomes insoluble in the mixture and crystallises out. Vapour diffusion works by a similar principle but in this case a vessel of C$_{60}$ and TPC in toluene solution is placed inside a larger sealed vessel
Figure 2.1 TPC-$C_{60}$ co-crystals grown by liquid-liquid diffusion (a), vapour diffusion (b), and slow solvent evaporation (c) crystallisation techniques.

containing a volatile solvent in which $C_{60}$ is poorly soluble (e.g., diethyl ether or methanol). Over time the vapour can slowly diffuse into the toluene solution containing $C_{60}$ and initiate crystallisation. Slow solvent evaporation simply allows the toluene solution to evaporate over time until $C_{60}$ becomes insoluble in the remaining volume of solvent and crystallises from solution.

Previous investigations of TPC-$C_{60}$ co-crystallisation by Konarev et al.\textsuperscript{49} and by Feringa et al.\textsuperscript{50} have revealed the formation of elongated pyramidal crystals via slow evaporation from benzene and plate-like crystals via slow evaporation from o-xylene, respectively. In accordance with these literature reports, slow solvent evaporation was selected as the crystallisation technique to grow crystals from toluene for visual identification and spectroscopic characterisation, due to their large size and quality. A selection of optical microscopy images showing pristine $C_{60}$, TPC and TPC-$C_{60}$ crystals at 10 and 100 × magnification can be found in Figure 2.2. Toluene solutions containing only $C_{60}$ or TPC (i.e., not both) resulted in rod-shaped and needle like crystals, respectively (see (a) and (b) in Figure 2.2). Optical microscopy revealed co-crystallisation of $C_{60}$ with TPC from toluene solution results in large pyramidal shaped crystals (see (c) and (d) in Figure 2.2), consistent with previous studies by Konarev et al. A cluster of pyramidal shaped TPC-$C_{60}$ co-crystals are displayed in Figure 2.2 (e) and (f) at 10 and 100 × magnification, respectively.
Figure 2.2  Optical microscopy images of pristine C$_{60}$, TPC, and TPC-C$_{60}$ crystals grown by slow solvent evaporation. a) Pristine C$_{60}$ crystals at 10 $\times$ magnification. b) TPC crystals at 10 $\times$ magnification. c) Pyramidal shaped TPC-C$_{60}$ crystals at 10 $\times$ magnification. d) A single pyramidal shaped TPC-C$_{60}$ co-crystal at 100 $\times$ magnification. e) An island cluster of TPC-C$_{60}$ co-crystals at 10 $\times$ magnification. f) An island cluster of TPC-C$_{60}$ co-crystals at 100 $\times$ magnification.
Konarev et al. characterised the TPC-C\textsubscript{60} crystal structure as a 1:1 ratio of C\textsubscript{60} to TPC with tetragonal space group I\textsubscript{4}(1)/amd symmetry, with centre-to-centre spacing between C\textsubscript{60} molecules increasing from 10.02 Å to 10.17 Å when TPC is present.\textsuperscript{49} The authors describe the crystal structure as each fullerene molecule having six closest fullerene neighbours in an approximate trigonal prismatic arrangement where each fullerene molecule is also surrounded by three TPC molecules arranged in the vertices of an equilateral triangle. Each TPC molecule has Van der Waals contacts with three fullerene molecules (see Scheme 2.1).\textsuperscript{49}

Since the crystal structure for the TPC-C\textsubscript{60} co-crystal has already been solved, FT-IR spectroscopy was used to confirm the structure of the pyramidal shaped crystals found in this research by co-crystalisation from toluene. In Figure 2.3 shown is the FT-IR absorption spectrum measured for TPC-C\textsubscript{60} co-crystals in KBr pellets. Since most of the vibrational absorption bands are derived from TPC, the spectrum of TPC crystals is also shown for comparison, along with a spectrum of separately grown C\textsubscript{60} and TPC crystals mixed together (i.e., both species are present but not formed as a co-crystal).

Evidence of the TPC-C\textsubscript{60} interaction can be seen in two main parts of the FT-IR spectrum, shown as insets in Figure 2.3. In the TPC-C\textsubscript{60} co-crystal, TPC-based C–H out of plane bending bands at 741 and 797 cm\textsuperscript{-1} shift to lower energy by approximately 4 cm\textsuperscript{-1} (left inset of Figure 2.3) when templating C\textsubscript{60} molecules in the crystal structure. The IR spectrum of mixed C\textsubscript{60}/TPC perfectly overlap with the pristine TPC spectrum at these two characteristic bending frequencies demonstrating the presence of C\textsubscript{60} alone does not shift the C–H out of plane bending bands. A 8 cm\textsuperscript{-1} shift to lower energy in the TPC-based C–H aromatic stretching bands is also seen for the TPC-C\textsubscript{60} co-crystal relative to TPC and the C\textsubscript{60}/TPC mixture (right inset of Figure 2.3).

The most pronounced signature of the interaction between TPC and C\textsubscript{60} in the TPC-C\textsubscript{60} co-crystal is observed in the C–H stretching region around 3000 cm\textsuperscript{-1}, displayed in the right inset of Figure 2.3. The tertiary C–H stretching band of TPC at 2968 cm\textsuperscript{-1} is shifted to higher energy by 29 cm\textsuperscript{-1} when C\textsubscript{60} bound to the cavities of TPC in the co-crystal. The C\textsubscript{60}-based vibrational bands around 1182 and 1428 cm\textsuperscript{-1} showed little change in the presence of TPC. The spectral shifts for the TPC-C\textsubscript{60} co-crystal are in good agreement with Konarev et al. (although the tertiary C–H stretch is more pronounced here), and provides sufficient evidence that the molecular complex has been successfully obtained.
Figure 2.3  FT-IR spectra of TPC-C$_{60}$ crystals, TPC crystals, and a mixture of C$_{60}$/TPC crystals. Spectral regions where co-crystals are distinguished are highlighted in the insets.

Having successfully grown the pyramidal shaped TPC-C$_{60}$ molecular complex, attention was shifted to Raman spectroscopy as a practical technique to potentially differentiate the co-crystal from pristine C$_{60}$ crystals. The initial hypothesis was that Raman spectroscopy could be used later as a sensitive and non-destructive probe of C$_{60}$ morphology in a polymer film if signals could first be assigned to the individual crystals. Coupled to an optical microscope at 100 × magnification, Raman spectra were collected for individual crystals of TPC, C$_{60}$, and TPC-C$_{60}$ at an excitation wavelength of 632 nm (displayed in Figure 2.4). The TPC spectra (black line) runs mostly parallel to the x-axis with Raman lines around 800, 1000 and 1200 cm$^{-1}$.

Raman spectroscopy was serendipitously found to be sensitive enough to detect fluorescence from the crystals containing C$_{60}$, evident by large fluorescent background signals (blue and red lines in Figure 2.4). In most cases, the high symmetry of molecular C$_{60}$ results in dipole-forbidden transitions that suppresses fluorescence compared with most other organic semiconductors, making it weak and difficult to detect. Another interesting observation from the Raman spectra is the disappearance of the polarised $A_g(2)$ “pentagonal pinch mode” at 1469 cm$^{-1}$ in the TPC-C$_{60}$ crystal. The pentagonal pinch mode involves a contraction of the pentagonal rings and an expansion of the hexagonal rings that form the structure of C$_{60}$.$^8$ The disappearance of this mode provides further evidence that TPC has changed the molecular environment of C$_{60}$ in the TPC-C$_{60}$ co-crystal.
Figure 2.4  Raman spectra of TPC, C\textsubscript{60}, and TPC-C\textsubscript{60} crystals. Raman spectroscopy was serendipitously found to be sensitive enough to detect fluorescence from crystals containing C\textsubscript{60}, evident by large fluorescent background signals.

Since TPC has no overlapping visible absorption or emission features with C\textsubscript{60}, the same instrument was used to carry out sensitive fluorescence measurements on C\textsubscript{60} and TPC-C\textsubscript{60} single crystals. In Figure 2.5 are displayed the normalised fluorescence spectra obtained from the single crystals with insets showing the specific crystals the data were collected from. While the fluorescence peaks are similar in shape, the TPC-C\textsubscript{60} co-crystal undergoes a 20 nm hypsochromic shift (blue-shift to shorter wavelengths) from 745 to 725 nm. The fluorescence spectra of C\textsubscript{60} in the co-crystal approaches that of monomeric C\textsubscript{60} in dilute solution which peaks at ∼700 nm, indicating the spectral shift observed could be due to increased separation between neighbouring C\textsubscript{60} molecules caused by TPC templation.

To explain the observed fluorescence blue-shift in TPC-C\textsubscript{60} co-crystals and fully ascribe it to effects from the molecular environment, understanding is drawn from solvatochromism theory. Electronic transitions in a molecule lead to a redistribution of charge and a difference in the dipole moment between the ground state (\(\mu_0\)) and the excited state (\(\mu_1\)). Photoactive species in solution are dependent on the dipole moments of surrounding solvent molecules (polarisable environment) and their ability to influence the relative stability of the dipole moment in the ground and excited state of the solute.\textsuperscript{62} Therefore, as the solvent dipole moment is changed, this ‘solvation effect’ alters the energy difference between the ground and excited states of the solute thus shifting peak absorption and emission wavelengths (i.e., a blue- or red-shift in fluorescence depending on the solvation environment in solution).
Figure 2.5 Fluorescence microscopy spectra of a pristine C$_{60}$ crystal, and a TPC·C$_{60}$ co-crystal.

The solvation effect for a solute in a solution is schematically illustrated in Figure 2.6. For a solute with a greater dipole moment in the excited state than the ground state ($\mu_0 < \mu_1$), increasing solvent polarity (i.e., increasing the solvent molecular dipole moment) preferentially stabilises the excited state, lowering its energy to give a corresponding red-shift in fluorescence. Conversely, for a solute with a greater ground state dipole moment than the excited state ($\mu_0 > \mu_1$), increasing solvent polarity preferentially stabilises the ground state to give a corresponding blue-shift in fluorescence.$^{62}$

Although the solvation effect discussed above describes fluorescence shifts in solution, it is expected that a photoactive species in a solid matrix should experience a similar effect which Farchioni and Grosso refer to as the solid state solvation effect (SSSE).$^{62}$ The SSSE is in fact demonstrated in organic light emitting diodes when polar organic dye molecules are doped into organic molecular thin films to give a fluorescence shift dependent on the average local dipole moment of the host.$^{63,64}$

Figure 2.7 illustrates SSSE applied specifically to C$_{60}$ and TPC·C$_{60}$ crystals. The C$_{60}$ solute dipole moment is depicted as a purple sphere in the case of both the pristine C$_{60}$ (left) and TPC·C$_{60}$ (right) crystals. The ‘solvent’ molecule dipoles (i.e., neighbouring C$_{60}$ molecules) are depicted as blue spheres that organise and align their dipoles with the solute dipole.

In the case of pristine C$_{60}$ crystals, neighbouring C$_{60}$ molecules packed close to the excited state dipole are able to align their dipoles with the excited state dipole to lower the energy of the S$_1$ level and give a red-shift relative to the TPC·C$_{60}$ co-crystal.
Conversely, the relative blue-shift in fluorescence observed in the TPC·C$_{60}$ co-crystal is attributed to a destabilisation of the excited state dipole moment when TPC spatially separates C$_{60}$ molecules, decreasing the extent to which neighbouring C$_{60}$ ‘solvent’ molecules can surround the excited state dipole for stabilisation (unaligned dipoles in S$_1$ excited state). An additional decrease in the energy difference between the ground and excited state is expected for pristine C$_{60}$ crystals upon a radiative fluorescence event that returns C$_{60}$ to the ground state (S$_0$) where ‘solvent’ molecule dipoles that were aligned for the excited state suddenly become un-aligned for the ground state (i.e., destabilises ground state resulting in increased energy) to further contribute to the relative red-shift in fluorescence.

The conclusions made here regarding the reason for the blue-shift in TPC·C$_{60}$ fluorescence are consistent with absorption suppression in the intermolecular charge transfer (CT) region around 500–600 nm for TPC·C$_{60}$ co-crystals reported by Konarev et al., who attribute the spectroscopic changes to result from the increased separation between C$_{60}$ molecules when TPC is present. These UV-Vis spectral shifts are explored in Chapter 3 when TPC and C$_{60}$ are dispersed through a polymer film. The blue-shift in TPC·C$_{60}$ fluorescence can be used to differentiate pristine C$_{60}$ from TPC·C$_{60}$ crystals based on changes in the local molecular environment of C$_{60}$. Therefore, sensitive fluorescence microscopy has identified a powerful spectroscopic
Figure 2.7  Solid state solvation effect as applied to $C_{60}$ (left) and TPC-$C_{60}$ (right) crystals. A relative blue-shift in fluorescence is illustrated in the TPC-$C_{60}$ co-crystal due to a destabilisation of the $S_1$ excited state dipole when TPC spatially separates $C_{60}$ molecules, thereby preventing neighbouring $C_{60}$ ‘solvent’ molecules from aligning their dipoles with the excited state dipole for stabilisation. An additional decrease in the energy difference between the ground and excited state is expected for pristine $C_{60}$ crystals upon a radiative fluorescence event that returns $C_{60}$ to the ground state as ‘solvent’ molecule dipoles become un-aligned, and destabilise the ground state.

signature that can be used to probe the molecular environment of $C_{60}$ and TPC in polymer blend films.

2.3 Summary

In summary, in this chapter was explored the interactions of TPC and $C_{60}$ in both solution and the solid state. UV-Vis spectroscopy and DLS studies showed no conclusive evidence of the TPC-$C_{60}$ molecular complex forming in solution. $C_{60}$ nanoparticles formed in solution in both the presence and absence of TPC but were of similar size raising the question of whether the co-crystal had been formed and was the same size as pristine $C_{60}$ crystals by coincidence, or whether it had not formed under the prescribed experimental conditions. Despite this result, DLS experiments were able to successfully simulate the rapid deposition of materials from solution that occurs in polymer film deposition techniques such as spin-coating. If TPC-$C_{60}$ co-crystals are unable to form in such conditions then post production annealing techniques such as thermal annealing or solvent vapour annealing may be required to bring about the conditions necessary for TPC templation of $C_{60}$ in solid state polymer films. Therefore, DLS has provided useful information concerning crystal formation in the solid state and given valuable research direction for sections ahead when $C_{60}$ and TPC are blended with a polymer and rapidly cast from solution via standard film formation techniques.
Scheme 2.2 Schematic diagram of TPC templating C$_{60}$ in a pyramidal shaped TPC-C$_{60}$ co-crystal (left) to give a relative blue-shift in fluorescence compared to rod shaped pristine C$_{60}$ crystals (right).

TPC-C$_{60}$ co-crystals were successfully grown by liquid-liquid diffusion, vapour diffusion and slow solvent evaporation. Large single crystals of the TPC-C$_{60}$ molecular complex grown by slow solvent evaporation were visually identified as pyramidal shaped crystals by optical microscopy (consistent with previous studies in the literature), in contrast to the rod and needle shaped crystals formed by pristine C$_{60}$ and TPC, respectively. The pyramidal shaped co-crystals obtained were compared to FT-IR signatures reported in the literature to confirm the complex had been formed. A pronounced signature was found in the form of a 29 cm$^{-1}$ shift in the TPC tertiary C–H stretching frequency giving spectroscopic evidence of the modified molecular environment of TPC.

Raman spectroscopy of C$_{60}$ and TPC-C$_{60}$ single crystals gave spectroscopic evidence of the modified molecular environment specific to C$_{60}$ upon templation by TPC. The $A_g(2)$ “pentagonal pinch mode” at 1469 cm$^{-1}$ was absent in the TPC-C$_{60}$ co-crystal. Raman spectroscopy also serendipitously revealed weak fluorescence from the C$_{60}$ crystals that could be further probed by sensitive fluorescence microscopy. As explained by solid state solvation effects and C$_{60}$-to-C$_{60}$ centre-to-centre spacing, the TPC-C$_{60}$ co-crystal fluorescence is blue-shifted 20 nm relative to the fluorescence of pristine C$_{60}$ crystals, thus providing sensitive spectroscopic means of differentiating the two different crystal structures. The significance of this finding is that the fluorescence signature can now be used to non-destructively identify TPC templation of C$_{60}$ in polymer blend films giving valuable information about the molecular environment around C$_{60}$ molecules.
Chapter 3

Fullerene and triptycene in a transparent polymer matrix

3.1 Introduction

Since the development of methods for mass production of fullerenes, there has been great interest in fullerene-containing polymeric materials driven by the ease of processing polymers. The nucleation dynamics of fullerene can change greatly once blended into a polymer film. Optoelectronic materials that contain C$_{60}$ within a polymeric matrix require C$_{60}$ to phase separate from the polymer component on the appropriate size scale dimensions to create optimal morphology for efficient device function. These devices often contain conjugated polymers that produce strong absorption and fluorescence in the visible spectrum that saturate any spectroscopic signatures from C$_{60}$ molecules that could otherwise be used to probe the resulting morphology when C$_{60}$ is cast into a polymer film.

One method to prevent the saturation of spectroscopic signatures from C$_{60}$ while still maintaining a realistic matrix that is comparable to a conjugated polymer, is to disperse C$_{60}$ in a transparent polymer matrix that does not absorb or fluoresce in the same spectroscopic region as C$_{60}$. A transparent polymer can also be used to identify C$_{60}$ crystals within the film by optical microscopy, without interference from an intensely coloured polymer matrix which can make it difficult to visually see small crystals. Wong and Cabral investigated the nucleation of C$_{60}$ within polystyrene (PS) films to study the mechanism and kinetics of fullerene association. Optical microscopy was used to visually identify C$_{60}$ crystals upon thermal annealing treatment while atomic force microscopy (AFM) was used to investigate the surface to-
pography and provide height information about the crystals formed in the C$_{60}$ doped polystyrene films. Photophysical studies have been performed on polystyrene films containing C$_{60}$ to probe triplet states by diffuse reflectance laser flash photolysis and analyse morphology by UV-Vis absorption and fluorescence spectroscopy. Minami et al. made pure C$_{60}$ films by chemical vapour deposition (CVD) and compared the fluorescent behaviour of the CVD C$_{60}$ films to that of C$_{60}$ dispersed through a wide range of transparent polymer matrices including poly(methyl methacrylate), poly(methyl phenyl silane), and poly(phenyl silsesquioxane).

Here, a mixture of C$_{60}$ and TPC were dispersed through a transparent polystyrene matrix in order to study the ability of TPC to organise C$_{60}$ within a polymer film. Optical microscopy was used to visually identify TPC templation of C$_{60}$ as micrometre sized crystals. Crystals formed in the polystyrene films were further investigated using a Dektak profilometer to gather information about the surface topography that supports the results obtained by optical microscopy. UV-Vis absorption spectroscopy was used to analyse the polystyrene-C$_{60}$ films and collect information about the molecular environment that is consistent with co-crystal formation. Finally, the fluorescence signature obtained from single TPC-C$_{60}$ co-crystals (Chapter 2) was used to conclusively determine TPC templation of C$_{60}$ within a polymer film.

### 3.2 Optical microscopy of polystyrene films

Having visually identified the TPC·C$_{60}$ molecular complex as pyramidal shaped crystals (see Chapter 2), TPC and C$_{60}$ were dissolved in solution with polystyrene and spin-coated into polymer films, thereby allowing optical microscopy and spectroscopy techniques to be used to investigate TPC templation of C$_{60}$ within a polymer matrix. Polystyrene is characterised by a hydrocarbon polymer backbone with alternating carbon centres attached to phenyl groups (see Scheme 3.1). The aromatic nature of polystyrene makes it similar to the structure of some common conjugated polymers (e.g., polyparaphenylene vinylenne, which has phenyl groups incorporated into the polymer backbone), but due to its lack of conjugation it is not optically active in the visible spectrum. Therefore, polystyrene is considered optically transparent and can be used to investigate TPC and C$_{60}$ dispersed through a polymer film without the interference of an intensely coloured conjugated polymer matrix capable of strong visible light absorption and fluorescence that would otherwise saturate weaker C$_{60}$ spectroscopic signatures.
Polystyrene Polyphenylene vinylene (PPV)

Scheme 3.1 Structure of polystyrene (left) and polyphenylene vinylene (right). Polystyrene is used to disperse TPC and C\textsubscript{60} through a transparent polymer matrix.

The thickness of a spin-coated polymer film is highly dependent on the concentration of the polymer and the spin-speed selected to deposit the film. Since organic solar cells typically require a conjugated polymer layer around 100–200 nm in thickness, polystyrene was dissolved at different concentrations and spin-coated at various spin-speeds in order to select a combination that would give a similar film thickness for the remaining experiments. Polystyrene concentrations of 5, 10, 15, 20 and 30 mg/mL were spin-coated at speeds between 1000 and 3000 revolutions per minute (rpm) (results displayed in Figure 3.1). A polystyrene concentration of 20 mg/mL gave films that were around 100 nm thick. At this concentration, a spin-speed of 2000 rpm produced uniform films of high quality and was therefore selected to investigate TPC templation of C\textsubscript{60} within a polymer matrix by optical microscopy.

![Figure 3.1](image)

**Figure 3.1** Thickness of polystyrene films spin-coated at different concentrations and spin-speeds, as measured using a Dektak profilometer.
TPC was blended into polystyrene films at different concentrations relative to the molar concentration of C$_{60}$. Ternary blend films (polystyrene, C$_{60}$ and TPC) were made with TPC at 1, 3 and 10 times the molar concentration of C$_{60}$ along with a binary film containing only polystyrene and C$_{60}$ with no TPC to act as a control. In Figure 3.2 are displayed the optical microscopy images of TPC and C$_{60}$ dispersed through polystyrene films with the different concentrations of TPC at 10 and 100 × magnifications. With no TPC in the polystyrene film, C$_{60}$ crystals are very small and difficult to see with optical microscopy, even at 100 × magnification. The result is similar when the molar concentration of TPC is equivalent to that of C$_{60}$ (1:1 molar ratio).

When the concentration of TPC was raised to 3 and 10 times the molar concentration of C$_{60}$, extensive crystallisation was initiated. Image (e) and (f) in Figure 3.2 show that TPC at 3 times the molar concentration of C$_{60}$ caused crystals to increase in size significantly. However, the crystals are still relatively small and difficult to see by optical microscopy, making their exact size and shape hard to determine. When TPC was increased to 10 times that of the C$_{60}$ molar concentration, a very significant change in morphology was observed (image (g) and (h) in Figure 3.2). A much wider distribution of C$_{60}$ crystal sizes within the polystyrene film was observed. The crystals formed are large enough to determine they are pyramidal shaped; consistent with the TPC-C$_{60}$ co-crystals described in Chapter 2.

To further investigate the micrometre sized C$_{60}$ crystals detected by optical microscopy, the surfaces of the polymer films were studied using a Dektak profilometer. The surface profiles for the polymer films containing different concentrations of TPC can be found in Figure 3.3. The polystyrene films that contained no TPC, and a 1:1 molar ratio of TPC to C$_{60}$, were both found to have very smooth surfaces. This result is consistent with the visual investigation by optical microscopy where only very small C$_{60}$ crystals were observed in these polystyrene films.

In contrast, the surface profiles of polystyrene films containing TPC at 3 and 10 times the molar concentration of C$_{60}$ were irregular; indicating TPC has templated C$_{60}$ to produce large crystals that protrude out of the polystyrene film yielding a rough and jagged surface. Dektak showed that TPC concentrations 3 times the molar concentration of C$_{60}$ produced surface irregularities up to 200 nm in size. The effect is even more pronounced when the TPC concentration is increased to 10 times the molar concentration of C$_{60}$ with crystals detected up to 600 nm in height. These results are consistent with the large crystals observed by optical microscopy in the polymer films at these TPC concentrations.
Figure 3.2 Optical microscopy images of $C_{60}$ dispersed though polystyrene films with different concentrations of TPC. Images (a), (c), (e) and (g) show films at 10 × magnification with TPC concentrations of 0, 1, 3 and 10 times the molar concentration of $C_{60}$, respectively. Images (b), (d), (f) and (h) show films at 100 × magnification with TPC concentrations of 0, 1, 3 and 10 times the molar concentration of $C_{60}$, respectively.
Figure 3.3 Dektak profiles of C\textsubscript{60} dispersed in polystyrene films with different concentrations of TPC. The profiles have been staggered so each profile can be clearly seen without overlapping on top of other profiles. Films with TPC concentrations of 0 and 1 times the molar concentration of C\textsubscript{60} have smooth surfaces, showing TPC has not induced micrometre sized crystals within the polymer film. Films with TPC concentrations of 3 and 10 times the molar concentration of C\textsubscript{60} have irregular surfaces with peaks up to 200 and 600 nm in height, respectively.

The results here are significant as they demonstrate that TPC is able to template the assembly of C\textsubscript{60} within a polymer film deposited rapidly by spin-coating. Post film production annealing was not required to bring about morphological changes to the polymer films as initially expected and was instead controlled by increasing the TPC concentration in the polystyrene films. However, the high TPC concentrations required here to show visual evidence of the co-assembly would be impractical for organic solar cells. TPC would dilute the electrically conducting species in the polymer film and give coarse morphology on the micrometre length scale, preventing excitation charge separation thus lowering device performance. Nanoscale phase separation of the polymer and C\textsubscript{60} components (∼10 nm) give optimal device performance in organic solar cells.\textsuperscript{16} Therefore, smaller concentrations of TPC to control the nanoscale assembly (i.e., not the microscale) would be more relevant to this research.
3.3 Spectroscopy of polystyrene films

UV-Vis and fluorescence spectroscopy was used to probe the molecular environment of C$_{60}$ within a polymer matrix upon the addition of TPC, and elucidate information about the nanoscale morphology of the polystyrene films. Konarev et al. performed UV-Vis absorption spectroscopy on C$_{60}$ and TPC·C$_{60}$ single crystals and found predominant absorption bands at 265 nm and 345 nm, along with a broad absorption band at $\sim$420–500 nm. Absorption at $\sim$500 nm in C$_{60}$ is attributed to dipole-forbidden HOMO-LUMO transitions in one C$_{60}$ molecule (intramolecular)$^{74}$ or HOMO-LUMO transitions between adjacent C$_{60}$ molecules (intermolecular).$^{75}$ The authors found the broad absorption band in the TPC·C$_{60}$ co-crystal diminished when compared to pure C$_{60}$ crystals, which they attribute to increased spacing between C$_{60}$ molecules, thereby weakening the overlap of HOMO-LUMO orbitals between adjacent C$_{60}$ molecules.$^{49}$ This observation indicates that the absorption in this broad region is predominantly from intermolecular charge transfer (CT) rather than intramolecular phenomena.

A broad intermolecular CT band is also seen here in polystyrene:C$_{60}$ (binary) and polystyrene:C$_{60}$:TPC (ternary) blend films centered at $\sim$520 nm (Figure 3.4). Normalising to the intramolecular absorption band at $\sim$400 nm highlights the pronounced effect in the intermolecular CT band when film processing conditions are changed and TPC is introduced into the films at an equimolar concentration with C$_{60}$ (1:1 molar ratio). The intermolecular CT band is greatest in the binary film spin-coated at the slowest speed of 1500 rpm (solid black line) where slower drying of the polymer film allows larger C$_{60}$ crystals to form and greater overlap between HOMO-LUMO orbitals to develop. Increasing the spin-speed to 2000 and 3000 rpm (solid red and blue lines respectively) showed the intermolecular CT band diminished, consistent with a greater dispersion of C$_{60}$ molecules throughout the polymer film during a more rapid drying process, thus suppressing larger crystal growth and preventing orbital overlap from developing. The effect of TPC addition to the polystyrene blend films is clear. A change in the spin-coating speed of ternary blend films (dashed lines) shows an identical trend to the binary blend films. Additionally, a comparison of the intermolecular CT band of binary and ternary films deposited at the same spin-coating speed shows that TPC further diminishes the absorption in this region.

The results obtained here in polymer blend films is consistent with observations by Konarev et al. who saw the intermolecular CT band diminish in single crystals of the TPC·C$_{60}$ complex based on increased separation distances between C$_{60}$ centres when TPC is incorporated in the crystal. This provides evidence that TPC has modified
the molecular environment of C\textsubscript{60} and templated its assembly within a polymer matrix. The results presented here show UV-Vis spectroscopy has the ability to be used to look at more subtle bulk film effects using lower concentrations of TPC (i.e., 1:1 TPC:C\textsubscript{60} molar ratios instead of 10:1) which are more realistic for practical device fabrication.

**Figure 3.4** UV-Vis spectra of binary and ternary polystyrene films deposited at different spin-coating speeds showing the intermolecular CT band of C\textsubscript{60} \(\sim\)500 nm. The ternary polystyrene films contain C\textsubscript{60} and TPC at equimolar concentrations (1:1 molar ratio).

To further investigate the molecular environment of C\textsubscript{60} within a polymer film and study the morphology on the nanometre scale, fluorescence microscopy was used as a spectroscopic technique as it was for the pure C\textsubscript{60} and TPC:C\textsubscript{60} single crystals (Chapter 2). The spectroscopic signature identified from the pure TPC-C\textsubscript{60} co-crystals can be used to identify any TPC templation of C\textsubscript{60} occurring in the ternary polystyrene films. As shown in the previous section, optical microscopy of polystyrene films containing C\textsubscript{60} and TPC at equimolar concentrations showed small crystallites of C\textsubscript{60} throughout the film (image (c) and (d) in Figure 3.2). The spatial resolution of fluorescence microscopy (\(\sim\)1 \(\mu\text{m}\)) enabled the crystallites to be avoided so that fluorescence spectra could be collected from the bulk regions of the polystyrene films and therefore directly probe the molecular environment of C\textsubscript{60} molecules dispersed throughout the polymer matrix. In Figure 3.5 are the fluorescence spectra collected from binary and ternary polystyrene films (solid red and blue lines respectively) along with the spectra of pure C\textsubscript{60} and TPC-C\textsubscript{60} single crystals for direct comparison (dashed red and blue lines respectively).
Figure 3.5  Fluorescence microscopy of binary and ternary polystyrene (PS) films collected from the bulk regions of the polymer matrix. Fluorescence spectra of pure C\textsubscript{60} and TPC·C\textsubscript{60} crystals have been included for direct comparison.

Fluorescence microscopy of the binary film produced a peak with a similar spectroscopic signature to pure C\textsubscript{60} single crystals. The peak reaches a maxima around 740–745 nm and is similar in shape; albeit slightly broader on the side closest to the blue end of the visible spectrum, explained by dispersion of some isolated C\textsubscript{60} molecules or smaller aggregates in the polymer film. In comparison, the fluorescence signature from the ternary film very closely resembles the signature obtained from the pure TPC·C\textsubscript{60} co-crystals and is blue-shifted relative to the binary film fluorescence. The ternary film fluorescence peaks at the identical point to the TPC·C\textsubscript{60} co-crystal (725 nm) but is slightly broader, presumably due to disorder and incomplete formation of crystals within the polymer film. The similarity between the fluorescence from the TPC·C\textsubscript{60} co-crystal and the ternary blend film suggests C\textsubscript{60} is in a similar molecular environment in both cases and therefore provides strong evidence that C\textsubscript{60} is templated by TPC in the bulk regions of the polystyrene film.

### 3.4 Summary

TPC and C\textsubscript{60} were spin-coated into polystyrene films to investigate the ability of TPC to template C\textsubscript{60} within a polymer matrix. Binary (polystyrene and C\textsubscript{60}) and ternary (polystyrene, C\textsubscript{60}, and TPC) polystyrene blend films were made with a
range of TPC concentrations. Optical microscopy images showed that larger C\textsubscript{60} crystals form when TPC reaches 3 times the molar concentration of C\textsubscript{60}. When TPC reaches 10 times the molar concentration of C\textsubscript{60}, pyramidal shaped crystals can be clearly seen, confirming TPC has templated C\textsubscript{60} within the polystyrene film. A Dektak Profilometer was used to further investigate the polystyrene films with different TPC concentrations. Dektak showed films with no TPC or a 1:1 molar ratio of TPC to C\textsubscript{60} produced smooth polymer films. In contrast, films with TPC at 3 and 10 times the molar concentration of C\textsubscript{60} produced rough films with large features (200 and 600 nm respectively) that protruded from the films surface. The Dektak experimental data are consistent with increased crystal growth observed by optical microscopy when TPC reaches higher molar concentrations than C\textsubscript{60}.

![Scheme 3.2 Schematic diagram showing TPC templating C\textsubscript{60} in a polystyrene matrix which gives characteristic spectroscopic signatures. For polystyrene films with TPC, the intermolecular CT absorption band diminishes and a relative blue-shift in fluorescence is observed (blue lines). Polystyrene-C\textsubscript{60} films without TPC are represented as red lines.](image)

Although optical microscopy and Dektak analysis provide clear evidence that TPC templates C\textsubscript{60} within a polymer matrix, the high concentrations of TPC and the micrometre scale organisation of C\textsubscript{60} is not optimal for organic solar cells which require nanometre sized C\textsubscript{60} domains for efficient excitation separation. Films with a 1:1 molar ratio of TPC to C\textsubscript{60} were analysed by UV-Vis absorption and fluorescence spectroscopy to investigate the ability of TPC to organise C\textsubscript{60} on the nanoscale and probe subtle bulk film effects. UV-Vis absorption spectroscopy revealed the intermolecular CT band at \(\sim 500\) nm is suppressed upon the addition of TPC which spatially separates C\textsubscript{60} and prevents HOMO-LUMO orbital overlap between adjacent C\textsubscript{60} molecules. Fluorescence microscopy on the bulk regions of ternary polystyrene
films produced a spectroscopic signature that very closely resembles the signature found in pure TPC-C₆₀ co-crystals. The fluorescence signature therefore indicates that the molecular environment of C₆₀ within the polystyrene film is similar to that of the co-crystal providing strong evidence that TPC has the ability to template the assembly of C₆₀ within a polymer matrix.
Chapter 4

Addition of triptycene to conjugated polymer blend films

4.1 Introduction

Upon photoexcitation, conjugated polymers can form two different types of excitation species; excitons and excimers (Figure 4.1). An exciton is an intrachain excitation formed when an electron and hole rapidly relax toward their respective band edges on the same polymer chain.\textsuperscript{11} The electron-hole pair is bound by its mutual Coulomb attraction and will radiatively recombine if it cannot physically separate and generate unbound charge carriers; a recombination process that lowers the performance of organic solar cells.\textsuperscript{76–78} Once an exciton is formed, the wavefunction of the resulting excited state can spread onto neighbouring chains and form a multi-chain excitation known as an excimer (excitation formed between two like chromophores) or an exciplex (excitation formed between two distinctly different chromophores).\textsuperscript{11} Jenekhe and Osahemi describe this process as the interaction of an excited chromophore with an unexcited chromophore (Equation 4.1). The excited state is stable as a result of resonance from exciton and charge-transfer configurations (Equation 4.2).\textsuperscript{79}

\[
\begin{align*}
\text{1A}^* + \text{1A} & \rightarrow \text{1(AA)}^* \quad (4.1) \\
\text{1(A*A)} & \rightarrow \text{1(AA*)} \rightarrow \text{1(A^-A^+)} \rightarrow \text{1(A^+A^-)} \quad (4.2)
\end{align*}
\]

Excimers lead to excited states of lower energy which are only weakly coupled to the ground state. Such states are generally considered to be detrimental to devices that require high luminescence efficiencies such as fluorescent sensors and organic
light emitting diode (OLED) devices.\textsuperscript{80–82} Furthermore, lower energy excited states of the excimer reduces the polymer band gap and alters light emission. This is undesirable for the fabrication of blue light emitting diodes and therefore full colour displays.\textsuperscript{83} Since the formation of excimer species is detrimental to the performance of OLEDs, fine control and understanding of the interchain effects are required in order to achieve high electroluminescence efficiency.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{The formation of an exciton (left) and an excimer (right) on conjugated polymer chains. Upon photoexcitation, electrons and holes relax to the band edges to form a Coulombically bound neutral exciton. Excimers can form between two conjugated polymer chains that are in close proximity to each other when an exciton extends over both of the chains.}
\end{figure}

An effective method of reducing interchain excimer states is to spatially control the solid state packing of the polymer. This can be achieved by introducing additional side group substituents to the conjugated polymer. Anderson \textit{et al.} demonstrated a novel method for reducing interchain interactions in OLED devices by threading conjugated polymers through cyclodextrin (CD) rings.\textsuperscript{83} The CD units spatially separate the polymer chains, thereby reducing solid state packing effects and excimer formation, which is responsible for partially quenching luminescence (Figure 4.2). The construction of the polyrotaxane architectures preserved fundamental semiconducting properties of the polymers while increasing luminescence efficiency and blue shifting the emission of the conjugated cores.\textsuperscript{83}

Yang and Swager constructed fluorescent sensor devices that use a similar principle to disrupt interchain interactions in conjugated polymers.\textsuperscript{84} Incorporating rigid three-dimensional pentiptycene moieties (similar structure to TPC) into the polymer backbones prevents π–stacking between the polymer chains and maintains high fluorescence quantum yields (Figure 4.3). While these methods effectively reduce intermolecular interactions and increase luminescence efficiencies by suppressing excimer formation, they are chemically challenging to fabricate and require large synthetic investments.
Figure 4.2 Chemical structure of a cyclodextrin-threaded conjugated polyrotaxane with poly(para-phenylene) cores (β-CD-PPP). The polymer is threaded through the cyclodextrin (CD) rings to reduce interchain excimers from forming and prevent luminescence quenching. Figure adapted from Anderson et al.$^{83}$

Figure 4.3 Rigid three-dimensional pentiptycene groups incorporated into the backbone of conjugated polymers to prevent excimer formation and create cavities large enough for analyte molecules to diffuse through. Figure adapted from Yang and Swager.$^{84}$
The other conjugated polymer excitation species introduced here is the exciton. Excitons must be generated within a diffusion length (~10 nm) of a conjugated polymer-C$_{60}$ donor-acceptor (D-A) interface if they are to separate into charge carriers.\textsuperscript{85,86} Excitons that successfully reach a D-A interface avoid potential radiative recombination and hence quench the polymer films fluorescence. Therefore, the fluorescent properties of a conjugated polymer-C$_{60}$ blend film is sensitive to the organisation of the donor/acceptor and can be used to probe the morphological structure of the film. Yang \textit{et al.} fabricated P3HT bulk heterojunction (BHJ) solar cells and studied the effect of increasing the alkyl chain length of C$_{60}$ derivatives.\textsuperscript{87} The authors find that certain alkyl chain lengths resulted in reduced fluorescence quenching, which is an indication of phase separation between P3HT and C$_{60}$.

MEH-PPV is a conjugated polymer that has been commonly used in organic solar cells (see Figure 4.4 for structure).\textsuperscript{88–90} It lacks the crystallisation properties of P3HT and therefore requires methods such as excess fullerene addition to form a desired morphology in the MEH-PPV:C$_{60}$ blend film. In the first section of this chapter is reported the investigation of the addition of TPC to MEH-PPV films as a simple blending additive to prevent excimer formation and increase fluorescence efficiency without synthetically modifying the polymer. In the second section studies a separate effect, when TPC is added to MEH-PPV:C$_{60}$ blend films. Fluorescence spectroscopy was used to probe the nanoscale morphology of the film and further investigate the ability of TPC to template C$_{60}$ within a polymer matrix (see Chapter 3 for templation in polystyrene films). Fluorescence quenching studies are able to effectively demonstrate that TPC can template C$_{60}$ in a conjugated polymer film without synthesising complicated materials or using excess fullerene addition for morphological control.

\textbf{Figure 4.4} Structure of poly[2-methoxy-5-(2-ethyhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) used in this study to investigate excimer suppression and TPC templation of C$_{60}$ within a conjugated polymer film.
4.2 Excimer suppresion in MEH-PPV films

The effect of blending TPC into MEH-PPV films in the absence of C$_{60}$ was examined using spectroscopy. TPC has the potential to modulate excimer formation in conjugated polymer blend films without synthetically modifying the polymer. Binary blend films containing MEH-PPV and different concentrations of TPC (MEH-PPV:TPC films) were fabricated by spin-coating and examined using fluorescence spectroscopy to determine the fluorescence efficiency. Additionally, it is important to determine the effect TPC itself has on the spectroscopic characteristics of MEH-PPV before C$_{60}$ is introduced into the film. Therefore, the results here also act as a control to the experiments that are presented in the following section which involve MEH-PPV:C$_{60}$ and MEH-PPV:C$_{60}$:TPC blend films.

When TPC was blended with MEH-PPV in a toluene solution and cast into solid state films, a pronounced increase in fluorescence was observed at 570 nm, consistent with the suppression of excimer interchain states (Figure 4.5). The fluorescence efficiency of the films increases by nearly threefold upon blending TPC into the films (67% by weight). The UV-Vis spectra of the films (Figure 4.5 inset) remain virtually invariant across the series, both in spectral shape and intensity.

The fluorescence efficiency enhancement is assigned to the disruption of interchain excimer states when TPC molecules are dispersed throughout the MEH-PPV film preventing polymer interchain interactions from occurring. It is noteworthy that while the formation of excimers can result in red-shifted fluorescence, it is not observed here likely due to weak intensity, which is completely saturated by the strong residual fluorescence from MEH-PPV.

Having established that the fluorescence efficiency of MEH-PPV films could effectively be enhanced through the addition of TPC, the polymer films were subsequently annealed in a toluene vapour atmosphere for 1 hour to give film components additional time to organise at the molecular level. In Figure 4.6 the peak fluorescence intensities of pristine and annealed MEH-PPV polymer films as a function of TPC (as a weight percentage (wt%)) are given. The fluorescence of pristine MEH-PPV steadily increases as TPC is introduced into the polymer film (red line). However, the fluorescence enhancement diminishes when the films are annealed in a solvent vapour atmosphere (blue line). The diminished fluorescence is attributed to the reformation of polymer interchain excimer states when MEH-PPV and TPC are allowed to phase separate during annealing.
Figure 4.5  Fluorescence spectra of pristine spin-coated MEH-PPV:TPC blend films as a function of TPC content. The inset shows UV-Vis absorption spectra for the films which all remain virtually invariant across the series, both in spectral shape and intensity.

Figure 4.6  Variation of peak fluorescence intensities for pristine MEH-PPV:TPC films compared with those solvent vapour annealed in a toluene atmosphere for 1 hour.
The results presented here highlight a simple method of controlling polymer interchain interactions. By simply blending TPC into pristine conjugated polymer films, excimer states are suppressed without modifying the polymer backbone or making other large synthetic investments. The results also show that after solvent vapour annealing, fluorescence of MEH-PPV films are not modified significantly by TPC addition. Therefore, any changes in fluorescence intensity observed in MEH-PPV:C$_{60}$:TPC films (see next section) after solvent vapour annealing is likely to result from interactions between MEH-PPV and C$_{60}$ rather than interactions between TPC and MEH-PPV.

4.3 Fullerene morphology in MEH-PPV films

In Chapter 3, sensitive fluorescence spectroscopy was used to measure C$_{60}$ fluorescence in polystyrene films and probe the molecular environment of C$_{60}$ molecules. Here, C$_{60}$ is distributed through the conjugated polymer MEH-PPV which has strong visible absorption and fluorescence that completely overwhelms the weak spectroscopic signals of C$_{60}$, and therefore prevents direct measurement of fluorescence from C$_{60}$ molecules.

However, the fluorescence intensity of MEH-PPV offers a method to indirectly probe the molecular environment of C$_{60}$ because of its ability to strongly quench polymer fluorescence.$^{17}$ The ability of C$_{60}$ to quench the polymer fluorescence will depend on how many emissive excitons are within a diffusion length ($\sim$10 nm) of a C$_{60}$ interface, which is determined by the distribution and size of the C$_{60}$ domains within the polymer film. In Figure 4.7 is shown a diagram of the fluorescence quenching of an exciton at a polymer-C$_{60}$ interface and the formation of charge carriers. If C$_{60}$ forms small phases $\sim$10 nm that are well distributed throughout the film, an exciton generated anywhere in the polymer will be able to diffuse to a C$_{60}$ interface during its lifetime and the fluorescence will be heavily quenched. In contrast, if C$_{60}$ forms large phases bigger than the diffusion length of an exciton, not all the generated excitons will be within a diffusion length of a C$_{60}$ interface and the exciton will most likely relax by a radiative process. Therefore, after the films have been initially quenched by dispersing C$_{60}$ through the film, the fluorescence intensity of MEH-PPV can be used to indirectly probe C$_{60}$ phase domain sizes. As the domains develop in size (e.g., during annealing), the recovery of the fluorescence intensity can be used to monitor the evolution of nanoscale phase separation. This can be used to indicate how well TPC can template C$_{60}$ into larger phase domains within a conjugated polymer film.
After dispersing TPC through MEH-PPV:C$_{60}$ films at an equimolar ratio to C$_{60}$ (8 wt%), fluorescence spectroscopy was used to measure the fluorescence intensity of the polymer films after different periods of solvent vapour annealing (Figure 4.8). The spectra in Figure 4.8 are colour coded to indicate how long the film was solvent vapour annealed and plotted as a solid or dashed line (TPC present) to indicate the presence of TPC in the film. Pristine films, both with and without TPC, that have not been solvent vapour annealed (red spectra) produce very similar fluorescence intensities indicating that TPC has done little to template C$_{60}$ into larger domain sizes and recover fluorescence as initially casted into the film.

As expected, annealing the MEH-PPV:C$_{60}$ films with no TPC steadily increases the fluorescence with longer annealing times as the solvent vapour allows C$_{60}$ to diffuse through the polymer matrix and form larger domain sizes. Less excitons are now able to reach an MEH-PPV:C$_{60}$ donor-acceptor interface to charge separate within their lifetime and instead radiatively decay producing greater fluorescence intensity. Interestingly, the fluorescence intensity of films that contained TPC was even further enhanced when annealed for identical periods of time to the series of films that did not contain TPC.

The fluorescence intensities from both series of films are plotted against the solvent vapour annealing time in Figure 4.9 to more clearly demonstrate the effect of annealing and TPC addition. The fluorescence intensity sharply increases for both series of films after annealing for 2 hours, reaching approximately 90% of the total fluorescence intensity obtained after 5 hours of annealing. After 2 hours of solvent vapour annealing, the fluorescence intensity of MEH-PPV:C$_{60}$ films increases approximately 4- and 2-fold with and without TPC, respectively.
Figure 4.8 Fluorescence spectra of spin-coated MEH-PPV:C\textsubscript{60} films with and without TPC, all solvent vapour annealed for different time periods. Dashed and solid lines represent the films with and without TPC, respectively.

Figure 4.9 Peak fluorescence intensity of MEH-PPV:C\textsubscript{60} films both with and without TPC plotted against solvent vapour annealing time to clearly show the effect of annealing and TPC addition.
An analysis of the quenching behaviour was carried out for the ternary (MEH-PPV:C\textsubscript{60}:TPC), binary (MEH-PPV:C\textsubscript{60}) and control (MEH-PPV:TPC) blend films. To calculate the degree of quenching, the fluorescence intensity measured for each film series at 570 nm (I) was divided by the fluorescence intensity of the appropriate denominator in the absence of the C\textsubscript{60} quencher (I\textsubscript{0}) to give the fractional quenching (see Table 4.1 for each denominator used). The quenching results are shown in Figure 4.10. When no TPC is present in the film (red line), the presence of 21 wt\% C\textsubscript{60} quenches the emission of the MEH-PPV film by 98\% as initially cast by spin-coating (i.e., $I_{(PPV-C_{60})}/I_{0(PPV)} = 0.02$). This result is consistent with the strong quenching observed in MEH-PPV:C\textsubscript{60} blend films used to make organic solar cells and confirms that C\textsubscript{60} has been dispersed through the conjugated polymer film on the nanoscale.\textsuperscript{20} Solvent vapour annealing for 2 hours leads to a partial recovery of fluorescence ($I_{(PPV-C_{60})}/I_{0(PPV)} = 0.04$) consistent with the evolution of slightly larger C\textsubscript{60} domains. The quenching data shows that the fluorescence recovery is further enhanced when 8 wt\% TPC is added to the film in combination with solvent vapour annealing (blue line).

<table>
<thead>
<tr>
<th>Film series</th>
<th>$I_{(PPV-C_{60}-TPC)}$</th>
<th>$I_{0(PPV)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV-C\textsubscript{60}-TPC</td>
<td>$I_{(PPV-C_{60})}$</td>
<td>$I_{0(PPV)}$</td>
</tr>
<tr>
<td>PPV-C\textsubscript{60}</td>
<td>$I_{(PPV-C_{60})}$</td>
<td>$I_{0(PPV)}$</td>
</tr>
<tr>
<td>PPV-TPC</td>
<td>$I_{(PPV-TPC)}$</td>
<td>$I_{0(PPV)}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The fractional quenching is determined by dividing the fluorescence intensity, I, by the fluorescence intensity in the absence of the C\textsubscript{60} quencher, I\textsubscript{0}. The quenching percentage is calculated as $1 - \frac{I}{I_0} \times 100$.

The enhanced fluorescence of quenched MEH-PPV:C\textsubscript{60}:TPC blend films cannot be attributed to the suppression of intermolecular excimer states when TPC spatially separates the conjugated polymer chains. The fluorescence intensity of MEH-PPV films that lack C\textsubscript{60} as a quencher but retain the same quantity of TPC (grey line) has been used as the I\textsubscript{0} denominator and therefore already accounts for the fluorescence enhancement caused by TPC/polymer interactions. Additionally, the fluorescence behaviour of MEH-PPV:C\textsubscript{60}:TPC and MEH-PPV:TPC films after solvent vapour annealing provides further evidence that enhanced fluorescence cannot be attributed to the suppression of excimers. In the ternary blend films, fluorescence intensity increases with solvent vapour annealing time, whereas the opposite trend is seen for MEH-PPV:TPC. These results indicate that TPC has successfully templated C\textsubscript{60} within the conjugated polymer to grow larger domain sizes, thereby producing enhanced phase separation between C\textsubscript{60} and MEH-PPV.
Figure 4.10  Fluorescence quenching of MEH-PPV blend films by C$_{60}$ (21 wt%) with and without TPC (TPC 8 wt%, equimolar with C$_{60}$ content) as a function of solvent vapour annealing time. The effect of solvent vapour annealing for MEH-PPV:TPC films that lack C$_{60}$ is also shown to account for the effect of TPC on the inherent polymer fluorescence. Arrows show which graph axis each line corresponds to.

4.4 Summary

Blending TPC into MEH-PPV films leads to a large increase in fluorescence efficiency, consistent with the suppression of excimer states when TPC spatially separates the conjugated polymer chains. Fluorescence intensities were also used to track the evolution of nanoscale phase separation in MEH-PPV:C$_{60}$ films upon the addition of TPC via the recovery of fluorescence. TPC addition leads to markedly increased fluorescence values that cannot be attributed to excimer suppression because: (1) quenching studies show the fluorescence increases even when the interaction between TPC and the polymer (suppressing excimers) are accounted for in the I$_0$ denominator, and (2) the fluorescence diminishes in MEH-PPV:TPC films upon solvent vapour annealing while it increases for MEH-PPV:C$_{60}$:TPC films. These results indicate that TPC has successfully templated C$_{60}$ within the conjugated polymer to grow larger domain sizes and remove isolated fullerene molecules within the polymer film producing enhanced phase separation between C$_{60}$ and MEH-PPV.
Scheme 4.1 Schematic diagram showing fluorescence of MEH-PPV conjugated polymer films with no C$_{60}$ or TPC (a), with TPC (b), with C$_{60}$ (c), and with both C$_{60}$ and TPC. When TPC was added to MEH-PPV films with and without C$_{60}$, fluorescence intensity was enhanced due to the suppression of excimer formation when TPC spatially separated polymer chains, and due to templation of C$_{60}$ to drive phase separation (i.e., control film morphology), respectively.
Chapter 5

Triptycene as a blend additive in functional electronic devices

5.1 Introduction

The bulk heterojunction (BHJ) solar cell offers an elegant solution to increase the effective conjugated polymer-C$_{60}$ donor-accepter interfacial area for exciton charge separation. The morphology of this randomly deposited intermixed layer is critical to the efficiency of BHJ solar cells and therefore requires effective methods of inducing morphological control. TPC has the potential to be used as a simple blend additive in BHJ organic solar cells and organise the macroscopic assembly of C$_{60}$ thus altering morphology and alleviating the requirement of excess fullerene addition (see Chapter 1 for more detail). However, since spectroscopy confirms spatial separation and a reduction in electronic coupling between neighbouring C$_{60}$ molecules upon TPC templation (Chapters 3), electronic conduction in the presence of TPC needs to be determined in functional electronic devices. External quantum efficiency (EQE) measures the percentage of photons that interact with the photoactive layer of a device to produce charge carriers when exposed to different wavelengths of light (i.e., how many photons induce the formation of free charge carriers). EQE can therefore be used to measure the photocurrent of a solar cell and evaluate its performance when exposed to solar irradiance.$^{94-97}$

The electronic conduction of C$_{60}$ in devices when C$_{60}$ is sandwiched between two metal electrodes has been measured by several authors.$^{98-101}$ There is a debate in the literature whether the I-V characteristics of C$_{60}$ films are ohmic or non-ohmic (i.e., diode or linear metallic I-V curve). Yonehara and Pac reported that Al/C$_{60}$/Al
devices are ohmic under vacuum but become non-ohmic once exposed to air, and an aluminium oxide (Al$_2$O$_3$) layer is allowed to form at the electrodes in the presence of oxygen.\textsuperscript{98} Huang \textit{et al.} more recently reported that ITO/C$_{60}$/Al devices are non-ohmic but the authors removed their devices from being under vacuum and tested their behaviour in air so the formation of an Al$_2$O$_3$ layer during testing cannot be ruled out.\textsuperscript{100} Hou \textit{et al.} also fabricated ITO/C$_{60}$/Al sandwich devices to re-evaluate the I-V characteristics of C$_{60}$.\textsuperscript{101} Under vacuum, both ohmic and non-ohmic devices are found which suggests non-ohmic behaviour is not a result of air exposure and aluminium oxide formation (Figure 5.1). The authors then exposed the devices to oxygen to find the ohmic device becomes non-ohmic over a period of two days. After further analysis, they concluded that the ohmic device has short circuit spots which act as the sites for Al$_2$O$_3$ formation thereby restoring non-ohmic I-V characteristics to the C$_{60}$ film.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{i-v_curves.png}
\caption{I-V curves for ITO/C$_{60}$/Al sandwich devices under vacuum showing ohmic and non-ohmic behaviour. Ohmic devices are found to be a result of device short circuiting in the literature which proves normal C$_{60}$ electronic conduction is non-ohmic.\textsuperscript{101} Figure adapted from Hou \textit{et al.}\textsuperscript{101}}
\end{figure}

Khlyabich \textit{et al.} studied ternary blend BHJ solar cells and used EQE to investigate the photocurrent.\textsuperscript{97} Two different analogues of P3HT polymer (high and low band gap) are blended with PCBM as an acceptor at different ratios. As the ratios are varied and the amount of high band gap P3HT becomes greater, the authors found that the open circuit voltage (V\textsubscript{OC}) increases. The polymer composition for the ternary blend has a large impact on short circuit current (I\textsubscript{SC}) densities. Ternary blend devices were found to have greater I\textsubscript{SC} densities than binary blends due to complementary polymer absorption, as verified using EQE measurements.\textsuperscript{97}
Here, TPC is added to the active layer in polystyrene:C\textsubscript{60} sandwich devices to test the effect of TPC on electronic conduction. TPC is also added to the BHJ active layer in organic solar cells as a simple method to help assemble C\textsubscript{60} phases and offer an alternative method for driving morphological control besides using excess fullerene addition or synthesising complex materials. MEH-PPV:C\textsubscript{60}:TPC ternary blend films were deposited from chlorobenzene (CB) and dichlorobenzene (DCB) solvents to make the active layer of the solar cells, and the EQE was measured to evaluate the performance of each device. The EQE of the solar cells was remeasured after solvent vapour annealing to provide additional time for film components to organise at the molecular level and bring about further morphological changes.

5.2 Electronic conduction in sandwich devices

Spectroscopy results detailed in Chapter 3 and 4 show that TPC can successfully template the assembly of C\textsubscript{60} within a polymer film. However, the results also confirm spatial separation and a reduction in electronic coupling between neighbouring C\textsubscript{60} molecules when TPC templation occurs. Because C\textsubscript{60} is a molecular solid which requires sufficient $\pi$-orbital overlap between adjacent molecules for electronic conduction,\textsuperscript{14} TPC templation could potentially interfere with conduction and inhibit charge transport in the film.

To investigate the electronic conduction of devices containing C\textsubscript{60} and TPC in the active layer, a series of sandwich devices were fabricated. Most electronic devices with C\textsubscript{60} as the conduction medium are deposited as films by CVD\textsuperscript{101} but since this research is concerned with organisation of C\textsubscript{60} within a polymer film, polystyrene was selected as a non-conducting polymer (i.e., not to interfere with C\textsubscript{60} conduction) to deposit C\textsubscript{60} as a film blend. Polystyrene:C\textsubscript{60} and polystyrene:C\textsubscript{60}:TPC films (TPC concentration equimolar with C\textsubscript{60}) were spin-coated on 1 cm\textsuperscript{2} ITO coated glass substrates with Al evaporated on top to sandwich the polymer layer between the ITO and Al electrodes (see Figure 5.2 for device structure). Note that the Al electrode is capped with Ag to increase the thickness of the electrode and prevent Al\textsubscript{2}O\textsubscript{3} formation at the point of contact for device testing.

Devices with thin C\textsubscript{60} active layers (<100 nm) have been shown to short circuit when hot Al vapour punctures through the film (particularly during initial deposition) and creates a direct conduction pathway between the Al and ITO electrodes.\textsuperscript{101} Therefore, an important design consideration was to select a polystyrene concentration and spin-coating speed to deliver a film thickness >100 nm without excessively diluting
C\textsubscript{60} in the film, which would inhibit electronic conduction. A polystyrene concentration and spin-coating speed of 20 mg/mL and 1500 rpm respectively (from CB solution), were selected to give films \(\sim\)100 nm thick (see Figure 3.1 for polystyrene spin-coating parameters and film thickness).

Despite optimising the device architecture (described above) and depositing the Al electrode at slow initial rates (0.1–0.3 Å), a significant proportion of devices in the series short circuited. Most of the sandwich devices that showed some form of conduction performed poorly and displayed unusual electrical characteristics (results not shown), presumably due to the presence of polystyrene and the disordered nature of the film which likely interfered with C\textsubscript{60} conduction. However, there were a select number of devices that showed electronic conduction behaviour comparable to C\textsubscript{60} sandwich devices (based on very similar architectures) reported in the literature.\(^{101}\) The I-V characteristics of these polystyrene:C\textsubscript{60} and polystyrene:C\textsubscript{60}:TPC sandwich devices are displayed in Figure 5.3. The two curves are very similar and therefore suggest that the addition of TPC to polystyrene:C\textsubscript{60} films had little effect on the electronic conduction of C\textsubscript{60}. Considering the templation of C\textsubscript{60} by TPC increases centre-to-centre spacing between C\textsubscript{60} molecules in the crystal from 10.02 Å to only 10.17 Å,\(^{49}\) it is plausible that TPC would have little effect on charge transport properties through the n-type material.

This result can be justified by looking at molecular packing in similar fullerene assemblies. PCBM is a soluble derivative of C\textsubscript{60} and is reported to crystallise from CB (the same solvent used here) with C\textsubscript{60}-to-C\textsubscript{60} centre-to-centre distances of \(\sim\)10 Å forming a three-dimensional network of closely packed fullerene moieties.\(^{102}\) This packing distance is very similar to packing distances observed in pristine C\textsubscript{60} crystals.\(^{49}\) Cheng \textit{et al.} synthesised diphenylmethano-C\textsubscript{60} bis-adduct (DPCBA) where phenyl rings are attached to the surface of C\textsubscript{60} molecules (see Figure 5.4), thus spac-
Figure 5.3  I-V curves of polystyrene:C$_{60}$ and polystyrene:C$_{60}$:TPC sandwich devices. The addition of TPC to the polystyrene:C$_{60}$ sandwich device did not significantly alter the I-V characteristics suggesting C$_{60}$ conduction was little effected by templation with TPC.

The authors fabricated P3HT:PCBM and P3HT:DPCBA organic solar cells and reported electron mobilities of $1.3 \times 10^{-4}$ for both materials (i.e., the presence of the phenyl groups between C$_{60}$ moieties does not alter the electron mobility). Since PCBM and C$_{60}$ both crystallise with centre-to-centre distances of $\sim 10$ Å and DPCBA spatially separates C$_{60}$ molecules with phenyl groups like triptycene, this system is roughly analogous to the templation found in this research. Therefore, based on reports in the literature, the observation of similar electronic conduction behaviour between polystyrene:C$_{60}$ and polystyrene:C$_{60}$:TPC sandwich devices is a plausible result.

Figure 5.4  Structure of diphenylmethano-C$_{60}$ bis-adduct (DPCBA). Phenyl groups bound to the fullerene’s surface are highlighted in red. Figure adapted from Cheng et al.\textsuperscript{103}
5.3 Triptycene and BHJ organic solar cells

After spectroscopically investigating TPC templation of C\textsubscript{60} in single crystals (Chapter 2), transparent polymers films (Chapter 3), and conjugated polymer films (Chapter 4), in addition to studying C\textsubscript{60} conduction in sandwich devices (previous section), the next phase in this research project was to fabricate functional organic solar cells with TPC as a blend additive and evaluate the resulting performance. A BHJ layer consisting of MEH-PPV, C\textsubscript{60}, and TPC were sandwiched between Al and ITO electrodes on 1 cm\textsuperscript{2} glass substrates to construct laboratory scale organic solar cells (Figure 5.5). A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer was spin-coated onto the ITO substrate before the BHJ layer to improve hole conduction to the ITO anode.

![Device architecture of laboratory scale organic solar cells used evaluate TPC as a blend additive for the purpose of organising C\textsubscript{60} domains and controlling morphology in the BHJ active layer.](image)

Organic solar cells were first fabricated with excess fullerene addition (1:4 weight ratio of MEH-PPV to C\textsubscript{60}) to drive morphological control; a technique commonly used to drive morphological change in most non-P3HT conjugated polymers (see Chapter 1 for more detail).\textsuperscript{27,34} These cells were made to provide a bench mark for the performance of MEH-PPV devices with the specific materials and laboratory conditions available. Organic solar cells typically require a BHJ active layer ∼100–200 nm in thickness to capture incident light,\textsuperscript{16} which generally requires an MEH-PPV concentration of 4–5 mg/mL when spin-coating.\textsuperscript{34} This therefore requires C\textsubscript{60} concentrations up to 16–20 mg/mL which is not achievable in chlorobenzene (CB); the solvent most commonly used in this research to cast polymer films via spin-coating. However, dichlorobenzene (DCB) can dissolve C\textsubscript{60} at such concentrations (see Table 2.1) and was consequently selected as the casting solvent for the devices.
in this series. In Figure 5.6 is displayed the external quantum efficiency (EQE) of the devices with 1:1–1:4 weight ratios of MEH-PPV to C\textsubscript{60}, cast from DCB. As the C\textsubscript{60} concentration increases in the BHJ active layer, the EQE also increases reaching a value of 30% at the highest C\textsubscript{60} concentration. This trend is consistent with other MEH-PPV:C\textsubscript{60} devices reported in the literature, which also use a 1:4 weight ratio of MEH-PPV to C\textsubscript{60} to drive morphological changes in the film.\textsuperscript{27,34}

**Figure 5.6** EQE of MEH-PPV:C\textsubscript{60} devices with different weight ratios of C\textsubscript{60} to induce morphological control and improve device performance.

Having established EQE values for devices with a morphology driven by excess fullerene addition, a series of devices were fabricated from CB and DCB solvents with a 1:1 weight ratio of MEH-PPV to C\textsubscript{60} (CB can be used as a casting solvent here due to lower C\textsubscript{60} concentration requirements). Devices were made with and without TPC in the BHJ active layer to change morphology of the film in place of excess fullerene addition (TPC equimolar with C\textsubscript{60}). EQE values of the devices are displayed in Figure 5.7, with error bars to indicate the standard deviation in the data set. In the devices casted from CB, TPC addition lowers the EQE from 16.0 ± 0.7 to 11.6 ± 1.2%. A similar trend is seen for devices casted from DCB where TPC lowers EQE from 10.3 ± 0.2 to 4.4 ± 0.3%. The initial addition of TPC to the devices without solvent vapour annealing was not expected to template C\textsubscript{60} and improve EQE as results presented in Chapter 4 show it is not until pristine films are annealed that TPC is able to effectively template C\textsubscript{60} allowing larger phase domains to develop; indicated by increased fluorescence when excitons cannot reach donor-acceptor interfaces to charge separate and instead recombine radiatively.
Figure 5.7  EQE of pristine MEH-PPV:C$_{60}$ and MEH-PPV:C$_{60}$:TPC devices cast from CB and DCB solvents.

Figure 5.8  EQE of BHJ organic solar cells with a MEH-PPV:C$_{60}$ weight ratio of 1:1, cast from CB and annealed in toluene vapour to give TPC longer to co-assemble with C$_{60}$ in the active layer.
A new batch of devices cast from CB was fabricated and solvent vapour annealed to give TPC longer to co-assemble with C\textsubscript{60} in the active layer. Devices both with and without TPC were annealed for up to 120 minutes in a toluene vapour atmosphere and the EQE measured (Figure 5.8). The EQE of MEH-PPV:C\textsubscript{60}:TPC devices reaches a maximum of 19.2% after 60 minutes of annealing. Further annealing lowered the EQE to \(\sim 17.8\%\). MEH-PPV:C\textsubscript{60} devices used as an experimental control (i.e., no TPC in the active layer) showed a near identical trend. However, the MEH-PPV:C\textsubscript{60} devices showed EQE values approximately 20% higher at each solvent vapour annealing time.

The data presented in Chapters 2, 3, and 4 provide good evidence that TPC can successfully template the macroscopic assembly of C\textsubscript{60}, and early results given in the previous section indicate that TPC addition to polymer films does not disrupt electronic conduction of C\textsubscript{60}. It is likely that the reason TPC did not enhance BHJ solar cell performance is because the device preparation method was not correctly optimised. Studies of TPC addition to polystyrene:C\textsubscript{60} films (Chapter 3) showed the films were sensitive to different ratios of C\textsubscript{60} and TPC. There was not sufficient time to explore different film compositions for the MEH-PPV:C\textsubscript{60}:TPC devices, but this could be explored in future work. Another reason device efficiency was not enhanced by TPC could be because some type of loss mechanism occurs whereby the photocurrent is reduced. A number of explanations for the reduction in photocurrent can be offered based on observations from the literature.

A reduced photocurrent is observed in MEH-PPV:C\textsubscript{60} organic solar cells when the BHJ active layer is cast from toluene instead of CB\textsuperscript{104}. The same effect was also observed in MDMO-PPV:PCBM organic solar cells (MDMO-PPV is structurally similar to MEH-PPV) when cast from these solvents\textsuperscript{26,27,30}. In Figure 5.9 are displayed tapping mode AFM images of the resulting morphology when cast from toluene and CB. Both C\textsubscript{60} and PCBM are less soluble in toluene and segregate into larger clusters when the blend evaporates, resulting in a morphology that is un-optimised for exciton charge separation and transportation (see Chapter 1 for an in-depth discussion on morphology and photocurrent generation). It is possible that the addition of TPC to the BHJ active layer in the devices presented in this research causes a similar effect. Although the device active layers are cast from CB, TPC may be too efficient at templating C\textsubscript{60} and results in a morphology analogous to that of MEH-PPV:C\textsubscript{60} or MDMO-PPV:PCBM blends cast from toluene. AFM could be used to investigate MEH-PPV:C\textsubscript{60}:TPC films to prove this hypothesis, but could not be completed during the allocated time for practical research in this project and is instead suggested as future work.
Figure 5.9  Tapping mode AFM topography scans of MDMO-PPV:PCBM blended films, spin-cast from (a) chlorobenzene and (b) toluene solution. The toluene cast film exhibits large clusters a few 100 nm in width while those on chlorobenzene cast films are around 50 nm. Figure from Martens et al.\textsuperscript{27}

Figure 5.10  Height and local photocurrent signal obtained by near-field scanning photocurrent measurements of MDMO-PPV:PCBM blended films, spin-cast from toluene. Figure adapted from McNeill et al.\textsuperscript{105}
McNeill et al. offer an alternative explanation for the observed reduction in photocurrent when MDMO-PPV:PCBM organic solar cells are cast from toluene instead of CB. The authors use near-field scanning photocurrent microscopy (NSPM) to examine large PCBM elevations and find they contribute significantly less to the overall current than the surrounding regions (Figure 5.10). In contrast, CB cast active layers show a stable photocurrent from all regions of the device. The authors propose that the loss mechanism results from an electron insulating polymer shell that forms around the large PCBM clusters. Hoppe et al. investigated the proposed polymer shell using high resolution scanning electron microscopy (SEM) and found a 10–30 nm thick ‘skin’ structure which envelopes the large PCBM clusters. The authors used Kelvin probe force microscopy (KPFM) to detect increased work function on top of the embedded clusters (Figure 5.11). The large work function detected at the film surface on PCBM elevations is a clear signature for increased hole density and indicates the presence of a hole conducting polymer.

The presence of a hole rich region encapsulating the PCBM domains represents a severe photocurrent loss mechanism for two reasons: (1) electrons have to penetrate the hole rich layer where the probability of encountering a hole and recombining is high, and (2) holes in the polymer skin have to travel a greater distance to get around the large PCBM clusters before they can be collected at the PEDOT:PSS/ITO electrode. MEH-PPV:C₆₀:TPC films in this research could suffer photocurrent losses for an identical reasons if TPC templates C₆₀ into a morphology where MEH-PPV

**Figure 5.11** Topography (a) and work function (b) of a toluene cast MDMO-PPV:PCBM blend film measured by Kelvin probe force microscopy (KPFM). A clear correlation between the topographic hills caused by the PCBM clusters in (a) and the locally highest work functions in (b) is observed. The high work function regions can be understood as locally hole enriched areas, thus referring to the polymer-skin on top of most of the PCBM clusters. Figure adapted from Hoppe et al.

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forms a skin around TPC-$C_{60}$ co-crystals in the film, or otherwise interferes with the formation of percolation pathways to the electrodes. Alternatively, TPC itself could be forming an insulating layer around $C_{60}$ phases. Another possible loss mechanism could arise if residual TPC, that does not co-crystallise with $C_{60}$, forms phases on its own within the polymer film and provides further obstacles for charge carriers as they travel to the device electrodes, thus reducing the photocurrent and EQE. If this is occurring in the organic solar cell devices, a lower concentration of TPC could solve this problem by allowing enough TPC for $C_{60}$ templation and morphological control, yet eliminating excess TPC that could potentially be lowering device performance. Again, these proposed loss mechanisms could not be investigated during the allocated time for practical research in this project and are suggested as future work.

5.4 Summary

In summary, the electronic conduction of polystyrene:$C_{60}$ sandwich devices and the EQE of MEH-PPV:$C_{60}$ organic solar cells upon the addition of TPC to the active layers were investigated. Sandwich devices, both with and without TPC, produced very similar I-V curves indicating that the presence of TPC does not interfere with electronic conduction. However, EQE measurements of MEH-PPV:$C_{60}$ organic solar cells cast from both CB and DCB solvents showed a reduction in photocurrent when TPC was incorporated in the BHJ active layer. Assuming TPC had insufficient time to organise with $C_{60}$ in the film (based on observations presented in Chapter 4), the BHJ solar cells were annealed in a solvent vapour atmosphere. While the EQE increased for devices with TPC in the active layer, control devices without TPC also increased and were higher at each solvent annealing time.

The data reported in Chapters 3 and 4 provide good evidence that TPC templates $C_{60}$ within polymer films, and $C_{60}$ conduction is un-affected by the presence of TPC. It is likely that the reduction in photocurrent is simply due to un-optimised device preparation and could be corrected by modifying the film composition (suggested as future work). Another reason TPC did not enhance BHJ solar cell performance could be due to recombination loss mechanisms related to non-optimal morphology or interference with the formation of percolation pathways to the electrodes for efficient charge carrier extraction. TPC could template $C_{60}$ phases into domains that are either too large or that adopt an unfavorable morphology where $C_{60}$ is insulated from the electrodes, consequently causing recombination losses to occur.
Chapter 6

Conclusions

In conclusion, TPC was used to template C$_{60}$ crystallisation in single crystals, polymer films, and in functional electronic devices. Dynamic light scattering (DLS) experiments did not provide any conclusive evidence that TPC was able to assemble C$_{60}$ in solution. However, slow solvent evaporation of toluene containing dissolved C$_{60}$ and TPC afforded the TPC·C$_{60}$ molecular complex previously demonstrated in the literature. Blue-shifted fluorescence from single TPC·C$_{60}$ co-crystals was identified as a spectroscopic signature of TPC templation to probe the molecular environment of C$_{60}$ in polymer films. When C$_{60}$ and TPC were dispersed through the optically transparent polystyrene polymer, blue-shifted fluorescence was also observed; confirming spatial separation and a reduction in electronic coupling between neighbouring C$_{60}$ molecules when TPC templates the macroscopic assembly. UV-Vis absorption spectroscopy showed a reduction in orbital overlap between adjacent C$_{60}$ molecules in the polystyrene films providing further evidence of TPC templation within the polymer matrix.

The addition of TPC to conjugated polymer MEH-PPV and MEH-PPV:C$_{60}$ blend films produced two unique effects: (1) the suppression of excimer states when TPC spatially separated polymer chains, and (2) the assembly of C$_{60}$ into larger domains to drive polymer and C$_{60}$ phase separation. Adding TPC as a blend additive to conjugated polymer films to suppress excimer states highlights a simple method of enhancing fluorescence efficiency that does not require any synthetic investment of the polymer; an application that could be useful for devices that require high luminescence efficiencies such as fluorescent sensors and organic light emitting diodes. The ability of TPC to drive phase separation between a conjugated polymer and C$_{60}$ demonstrates how a blend additive can be used to give morphological control of the polymer film instead of using excess fullerene addition.
Polystyrene:C\textsubscript{60} and polystyrene:C\textsubscript{60}:TPC blend films sandwiched between ITO and Al electrodes demonstrated similar I-V characteristics indicating that the electronic conduction of C\textsubscript{60} was not impaired by TPC when it templates its crystalline structure. To confirm a well established technique in the literature and provide a benchmark for performance, excess fullerene addition was used to control morphology of MEH-PPV:C\textsubscript{60} devices. In an attempt to avoid detrimental effects caused by this method, and to avoid synthesising complex materials, the research goal of controlling polymer film morphology by alternative means was addressed by using TPC as a simple blend additive to supramolecularly host C\textsubscript{60} molecules and drive phase separation from the polymer in BHJ solar cells.

However, the EQE of MEH-PPV:C\textsubscript{60}:TPC BHJ organic solar cells was found to decrease when compared to control devices that lacked the TPC blend additive. Since TPC was shown to successfully template C\textsubscript{60} assembly in polymer films, and because film composition was found to be sensitive to different ratios of C\textsubscript{60} and TPC, a likely explanation for the reduction in photocurrent is because the polymer film composition requires further tuning. Another reason for the loss in photocurrent could be due to recombination loss mechanisms related to exciton charge separation and transportation to the device electrodes. TPC has immense potential as a blend additive to give desirable morphology in a BHJ solar cell but requires further investigation and optimisation.
Chapter 7

Future Work

The EQE results collected for MEH-PPV:C$_{60}$:TPC BHJ solar cells creates a number of opportunities to be further explored in future work. Due to time constraints, only one particular film composition was tested in BHJ organic solar cell devices. Since the film composition was shown to be sensitive to different molar ratios of C$_{60}$ and TPC (see Chapter 3), there is a lot of potential for optimisation of the film morphology. The potential recombination loss mechanisms could also be explored to obtain a greater understanding of the device photophysics and how TPC is effecting the photocurrent generation. One lead suggested here is to analyse MEH-PPV:C$_{60}$:TPC blend films by atomic force microscopy (AFM) and resolve the morphology to gain better insight on how film composition needs to be adjusted to improve the efficiency of the BHJ solar cell devices.

Although it is convenient to use TPC as purchased, the molecule could be synthetically modified to enhance the ability to host C$_{60}$ molecules between phenyl rings. Feringa et al. envisaged enhancing interactions in the host-guest system by incorporating a nitrogen atom at the bridge head position of TPC (carbon position 4 in Figure 1.15) to give azatriptycene.$^{50}$ The functionalisation of TPC could provide a method to enhance interactions between TPC and C$_{60}$ and provide greater control over C$_{60}$ self-assembly. The surface of C$_{60}$ could also be derivatised with a suitable functional group that would favourably interact with the functional group at the TPC bridge head position (e.g., co-operational functionalisation to produce favourable electrostatic or hydrogen bonding interactions). An additional benefit of functionalising C$_{60}$ is that by selecting the correct functional groups, HOMO-LUMO levels (i.e., the band gap, E$_g$) could be tuned to match those of a specific conjugated polymer; a method considered to be a very promising route to high performance organic solar cells.$^{18}$
Another interesting avenue to explore in future work is the TPC templation of 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C$_{61}$ (PCBM). The soluble derivative of C$_{60}$ is routinely used in organic solar cells because of its enhanced solubility and favourable E$_g$ that is well matched to many conjugated polymers. The solubilising tail of the methanofullerene may complicate the supramolecular host-guest assembly with TPC and would need to be thoroughly investigated. In addition to investigating other C$_{60}$ derivatives for templation with TPC, other conjugated polymers could also be explored to evaluate the ability of TPC to drive phase separation in different polymer matrices.
Chapter 8

Experimental

Materials

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received, unless otherwise stated. Polystyrene (average MW 250,000) and poly[2-methoxy-5-(2-ethyhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) polymers were purchased from Acros Organics (Geel, Belgium) and American Dye Source Incorporation (Pointe-Claire, Canada), respectively. 12 mm diameter FQW-121 and Spec 2000 WFS-121 quartz substrates were purchased from UQG Optics (Cambridge, United Kingdom). F3-3x.205W tunstun coils purchased from R.D.Mathis (Long Beach, CA, USA) were used to evapourate Al device electrodes.

Dynamic light scattering in solution

Dynamic light scattering (DLS) measurements were performed on a Nano-ZS ZEN3600 zetasizer from Malvern Instruments. Samples were measured in a four polished side quartz cell with a 1 cm path length at 25 °C. $\text{C}_60$ solutions in toluene at a range of different concentrations up to the point of saturation (0.5–2.8 mg/mL, $6.94 \times 10^{-3}–3.89 \times 10^{-3}$ mol/L), were prepared with and without triptycene (TPC) (equimolar with $\text{C}_60$ at all concentrations). Samples for DLS studies in toluene and acetonitrile (MeCN) mixtures were prepared by the addition of 50 µL of a toluene solution containing dissolved $\text{C}_60$ (1.5 mg/mL, $2.08 \times 10^{-3}$ mol/L) and TPC (0.53 mg/mL, $2.08 \times 10^{-3}$ mol/L) to 1 mL of MeCN. Samples for DLS studies in benzonitrile (PhCN) were prepared by dissolving $\text{C}_60$ (0.41 mg/mL, $5.69 \times 10^{-4}$ mol/L) and
TPC (0.145 mg/mL, 5.69×10⁻⁴ mol/L) in PhCN.

**Ultraviolet-visible absorption spectroscopy in solution**

Solutions used to investigate the binding strength between C₆₀ and TPC were prepared as saturated C₆₀ solutions in chloroform (0.16 mg/mL, 2.22×10⁻⁴ mol/L) with TPC additions between 1 and 100 times the molar concentration of C₆₀ (0.056–5.65 mg/mL, 2.22×10⁻⁴–2.22×10⁻² mol/L). Ultraviolet-visible (UV-Vis) absorption spectroscopy measurements were collected using an Agilent 8453 UV-Visible spectrophotometer over the range 200-1100 nm using a quartz cuvette with a 1 cm path length.

**Preparation of crystals**

All crystals were grown from toluene solutions containing dissolved C₆₀ (1.5 mg/mL, 2.08×10⁻³ mol/L), with and without dissolved TPC (0.64 mg, 2.52×10⁻³ mol/L). Crystals grown by liquid-liquid diffusion were prepared by layering 1 mL of C₆₀ solution on top of 6 mL of chloroform in a 10 mL vial. The solutions were allowed to mix by gradual diffusion overnight. Crystals grown by vapour diffusion were prepared by placing 2 mL of C₆₀ solution in a small vial inside a sealed chamber with 3 mL of diethyl ether or methanol. The diethyl ether and methanol were allowed to slowly evaporate and diffuse into the C₆₀ solution to induce crystallisation over a period of 3 days. Crystals of the TPC·C₆₀ complex used to collect Fourier transform infrared (FT-IR) and fluorescence spectroscopy data were grown by complete evaporation from a 10 mL solution of C₆₀ and TPC in toluene over a period of 4 weeks. The resulting pyramidal shaped crystals were transferred to quartz substrates for examination under an optical microscope at 10 and 100 × magnifications.

**Preparation of polymer films**

All polymer films were prepared by spin-coating 40 µL of a polymer solution on a substrate using a Laurell technologies WS-400B-6NPP-Lite spin-coater. Polymer films investigated by UV-Vis absorption and fluorescence spectroscopy were
deposited on 12 mm diameter FQW-121 and Spec 2000 WFS-121 quartz substrates, respectively. Details beyond the experimental section that are relevant to particular samples are given throughout the thesis. All MEH-PPV polymer films prepared for fluorescence spectroscopy and quenching studies were spin-coated from 5 mg/mL MEH-PPV solutions in toluene at 2000 rpm for 1 minute (1.5 mg/mL C<sub>60</sub> and 0.53 mg/mL TPC). All polystyrene films were spin-coated from chlorobenzene (CB) at polystyrene concentrations between 5 and 30 mg/mL with spin-speeds between 1000 and 3000 rpm (C<sub>60</sub> 5 mg/mL and TPC 1.76 mg/mL). Solvent vapour annealing in a toluene atmosphere was achieved by placing the spin-coated films in a 250 mL sealed bottle with 20 mL of toluene for 30–120 minutes. Optical microscopy was performed on a Nikon optical microscope fitted with a Sitek camera. Polymer film thickness was determined using a Veeco 150 Dektak profilometer.

**Spectroscopy**

FT-IR spectroscopy of materials ground in KBr pellets was performed on a PerkinElmer spectrum one spectrometer. Absorption spectroscopy of polymer films was performed with an Agilent 8453 diode array spectrophotometer over the range of 200-1100 on 12 mm diameter FQW-121 quartz substrates, held in the spectrometer with a custom build optics holder. Fluorescence microscopy measurements of C<sub>60</sub> and TPC-C<sub>60</sub> crystals were performed on a LabRAM Jobin Yvon-Horiba instrument with a 632.81 nm laser, a 600 groove/mm grating and a 100 × objective lens, which results in spatial resolution on the order of 1 µm. A filter was applied to reduce the laser power to 300 mW to avoid degradation of the C<sub>60</sub> material in both the crystals and the polymer films.

Fluorescence spectroscopy of MEH-PPV polymer films was performed with a Shimadzu RF-5301PC spectrofluorophotometer on 12 mm diameter Spec 2000 WFS-121 quartz substrates, held in the spectrometer with a custom build optics holder. All fluorescence spectroscopy emission spectra were collected at an excitation wavelength of 500 nm over the range of 530-800 nm. Fluorescence spectra of MEH-PPV films without C<sub>60</sub> content were collected at excitation and emission slit widths corresponding to 3 nm spectral resolution. Fluorescence spectra of MEH-PPV/C<sub>60</sub> blend films were collected at excitation and emission slit widths corresponding to 10 nm spectral resolution in order to collect more photoluminescence in the strongly quenched films. Fluorescence spectra were normalised for the absorption intensity at the excitation wavelength, which was found to vary by less than 10%.
Device fabrication

Polystyrene sandwich devices

Polystyrene sandwich devices were fabricated by spin-coating polystyrene:C$_{60}$ and polystyrene:C$_{60}$:TPC blend films (polystyrene, C$_{60}$, and TPC at 20 mg/mL, 5 mg/mL, and 1.76 mg/mL concentrations respectively) onto indium tin oxide (ITO) coated glass substrates. A 50 nm thick Al electrode was evaporated on top of the active layer by thermal evaporation and capped with 50 nm of Ag (to prevent oxidation of the Al surface) using an Ångstrom Engineering Nexdep evaporator. The conduction of C$_{60}$ in the polystyrene sandwich devices was measured using Agilent 4156 semiconductor probe station analyser.

MEH-PPV BHJ organic solar cell devices

MEH-PPV BHJ solar cells were fabricated by spin-coating PEDOT:PSS (3000 rpm for 1 minute) onto indium tin oxide (ITO) coated glass substrates, and were thermally annealed at 120 °C for 20 minutes to remove residual water from the film. MEH-PPV:C$_{60}$ and MEH-PPV:C$_{60}$:TPC blend films were then spin-coated on top of the PEDOT:PSS layer (MEH-PPV concentration 5 mg/mL for all devices). Devices cast from dichlorobenzene (DCB) to determine external quantum efficiency (EQE) by using excess fullerene addition, prepared with 1:1, 1:2, 1:3 and 1:4 MEH-PPV:C$_{60}$ ratios, had C$_{60}$ concentrations of 5, 10, 15 and 20 mg/mL respectively. Devices cast from CB and DCB to test the effect of TPC addition were prepared with C$_{60}$ and TPC concentrations of 5 and 1.76 mg/mL respectively. A 50 nm thick Al electrode was thermally evaporated on top of the active layer and capped with 50 nm of Ag (to prevent oxidation of the Al surface) using an Ångstrom Engineering Nexdep evaporator.

Spectrally resolved EQEs were measured by illuminating the devices with a Xenon arc lamp coupled to a monochrometer that scanned over the range of 400–800 nm. The photocurrent at each wavelength was measured under short circuit conditions with a Stanford Research Systems SR830 DSP lock-in amplifier that was synchronised with an optical chopper in the excitation beam path. The EQE was calculated by comparing the measured photocurrent from the BHJ device at each wavelength with the photon flux measured by a calibrated reference silicon photodiode.
Appendix

This appendix contains dynamic light scattering (DLS) and ultraviolet-visible (UV-Vis) spectroscopy results of \( C_{60} \) and TPC in solution.

*DLS results*

\( C_{60} \) solutions with and without TPC were prepared in toluene at a range of different concentrations up to the point of saturation (2.8 mg/mL, \( 3.89 \times 10^{-3} \) mol/L). Analysing by light intensity scattered showed that \( C_{60} \) solutions in toluene had a significant amount of polydispersity (a range of different particle sizes in solution), and gave poor data quality reports. Since the particles scatter light via Rayleigh scattering which scales to the 6th power of particle size, the DLS intensity signal has strong bias for larger particles in solution (including dust) even though the actual quantity of those particles may be insignificant relative to the number of smaller particles present. Analysing instead by number distribution (i.e., number of particles of a given size taking into consideration the strong bias for light scattering by larger particles) showed there was no significant quantity of \( C_{60} \) nanoparticles in solution (data not shown) leading to the conclusion that \( C_{60} \) is well solubilised in toluene and the correct conditions for crystallisation had not been established.

Polar solvents, such as acetonitrile (MeCN) are considered poor solvents for \( C_{60} \) because of unfavorable interactions that prevent the molecule from dissolving. A study by Alargova *et al.* reports the detection of different sized \( C_{60} \) nanoparticles by DLS when small volumes of \( C_{60} \) dissolved in toluene (5–50 µL, \( [C_{60}] \) 1.7 mg/mL) are added to larger volumes (5–20 mL) of a poor organic solvent such as ethanol, acetone or MeCN.\(^{108}\) In the case of MeCN, nanoparticles 210 ± 30 nm in size were reported. Adopting a similar methodology to that in the literature, 50 µL of a toluene solution with a 1.5 mg/mL and 0.53 mg/mL concentration of \( C_{60} \) and TPC respectively, was added to 1 mL of MeCN (TPC equimolar with \( C_{60} \)). A \( C_{60} \) control sample with no TPC present in solution was prepared and analysed in an identical manner. The DLS results are tabulated in Table 8.1 and displayed in Figure 8.1.
While the size of the nanoparticles formed are consistent with those reported in the literature, within experimental uncertainty, there is no difference in particle size when TPC is present in the toluene solution.

Alargova et al. explain the formation of $C_{60}$ nanoparticles in solution by the formation of instantaneous toluene emulsion droplets upon addition to MeCN. Since toluene is miscible with MeCN it can diffuse into the medium causing $C_{60}$ within the toluene droplet to reach saturation where crystallisation quickly takes place and fullerene crystals are formed.\textsuperscript{108} TPC is sparingly soluble in MeCN, meaning there is a possibility that it could transfer from the toluene emulsion droplet into MeCN solution, thereby allowing pristine $C_{60}$ crystals to form. However, this is considered unlikely given the non-polar nature of TPC and the effort required to dissolve TPC in polar MeCN (30–60 minutes of vigorous stirring). Therefore, the instantaneous formation of emulsion droplets will likely trap TPC where it is available for co-crystalisation with $C_{60}$.

**Table 8.1** Size of nanoparticles when 50 $\mu$L of a $C_{60}$ solution in toluene (1.5 mg/mL) was added to MeCN (1 mL) with and without TPC present in solution, as determined by DLS.

<table>
<thead>
<tr>
<th></th>
<th>$C_{60}$ particle size (nm)</th>
<th>$C_{60}$ + TPC particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$ particle</td>
<td>264.7</td>
<td>279.5</td>
</tr>
<tr>
<td>$C_{60}$ + TPC</td>
<td>244.2</td>
<td>205.8</td>
</tr>
<tr>
<td></td>
<td>264.5</td>
<td>234.0</td>
</tr>
<tr>
<td></td>
<td>247.1</td>
<td>211.0</td>
</tr>
<tr>
<td>Average</td>
<td>255.1</td>
<td>232.6</td>
</tr>
</tbody>
</table>

The size of the nanoparticles formed in solution were found to be the same regardless of whether TPC is present or not and therefore cannot be used alone to conclusively determine if the nanoparticles formed are pristine $C_{60}$ or TPC-$C_{60}$ co-crystals. The TPC-$C_{60}$ co-crystals may have formed and just happen to be of identical size to those of pristine $C_{60}$. However, it is possible that this method of crystallisation is too quick to allow TPC-$C_{60}$ co-crystals to form, causing $C_{60}$ and TPC to crystallise separately. Despite this, the experiment is useful as a comparison to polymer film formation techniques where dissolved species in solution are forced to crystallise quickly. For example, spin-coating takes a small volume of solution (~50 $\mu$L) on a substrate (usually glass or quartz) and spins it to rapidly evaporate the solvent, thereby driving the dissolved species to their saturation points very suddenly where they can crystallise and aggregate in the solid state (a technique used to crystallise $C_{60}$ and TPC in polymer films in Chapters 3, 4, and 5). While the results from this DLS experiment did not produce conclusive evidence of the TPC-$C_{60}$ molecular complex in solution, it has provided a strong indication that $C_{60}$ and TPC quickly
cast from solution into a polymer film may require post production annealing techniques (e.g., thermal annealing or solvent vapour annealing) to allow enough time for TPC templation of $C_{60}$ to occur, thus giving valuable research direction.

In a study investigating $C_{60}$ nanoparticles in benzonitrile (PhCN) DLS was successfully used to identify $C_{60}$ aggregates in solution.\textsuperscript{109} Nanoparticles $\sim$250 nm in size were found in solutions containing $0.29 \text{ mg/mL } C_{60}$ ($4 \times 10^{-4} \text{ mol/L}$). Since large $C_{60}$ nanoparticles where easily detected by DLS in this study, PhCN was selected to further investigate nanoparticle formation with and without TPC in an attempt to identify any TPC templation of $C_{60}$ in solution. In Figure 8.1 is displayed the number distribution of $C_{60}$ nanoparticles found in PhCN solution in both the presence and absence of TPC, as determined by DLS. Particle sizes of 218 nm and 238 nm were found for solutions with and without TPC, respectively. Again, while the results are consistent with the literature, there is no significant difference in nanoparticle size within the limits of experimental uncertainty that can be used to distinguish between pristine $C_{60}$ crystals and TPC-$C_{60}$ co-crystals.

**UV-Vis results**

In light of all DLS results collected, the technique was deemed unsuitable to investigate TPC templation of $C_{60}$ in solution. Subsequent research efforts were redirected to UV-Vis spectroscopy as an alternative method of analysis. This was motivated by a recent study, which used substituted dianthracene (similar structure to TPC with
2 potential C₆₀ binding cavities) as a host for C₆₀ and C₇₀ molecules to form supramolecular fullerene assemblies as gels.¹¹⁰ A solvent extraction method was used to determine the association constant for the binding of C₆₀ and C₇₀ with dianthracene by dispersing the fullerenes in a poor solvent with and without the host. The authors of this study demonstrated the use of UV-Vis spectroscopy to measure the amount of fullerene the host pulls into solution by calculating the concentration from the peak absorbance at 579 nm. A similar method was adopted from this study to see if UV-Vis spectroscopy could be used to detect TPC pulling C₆₀ into solution. A series of saturated C₆₀ solutions (in chloroform) were made with a range of TPC concentrations up to 100 times the molar quantity of C₆₀. The association constant of C₆₀ with a host molecule can be calculated from the following equations:

\[
C_{60} + \text{Host} \rightleftharpoons K_{\text{assoc}} \text{Host} \cdot C_{60}
\]  

\[
K_{\text{assoc}} = \frac{[\text{Host} \cdot C_{60}]}{[C_{60}(\text{solution})][\text{Host}_{\text{free}}]} = \frac{[\text{Host} \cdot C_{60}]}{[C_{60}(\text{solution})].([\text{Host}_{\text{total}}] - [\text{Host} \cdot C_{60}])}
\]

where [Host \cdot C₆₀] is the concentration of the host-guest complex, [C₆₀(solution)] is the concentration of dissolved C₆₀ and [Host_total] is the initial concentration of the host before complexation. In Figure 8.2 is displayed the UV-Vis spectra of C₆₀ with and without TPC at 100 times the molar quantity of C₆₀. Both spectra almost perfectly overlap indicating that TPC was unable to extract more C₆₀ into the chloroform solution, making equation 8.1 and 8.2 unusable in this situation.

![Figure 8.2](image)

**Figure 8.2** UV-Vis spectra of C₆₀ in chloroform with and without TPC at 100 times the molar quantity of C₆₀.
References


