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

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Supramolecular hosts offer the ability to template the macroscopic assembly of functional guests like fullerene $C_{60}$ for electronic device applications. Herein, we investigate the effect of triptycene (TPC) addition to polymer/$C_{60}$ blend films. When a transparent polymer matrix is used, we can clearly identify the formation of $C_{60}$–TPC co-crystals via fluorescence microscopy, in which blue-shifted fluorescence spectra are observed, and UV–Vis spectroscopy, in which intermolecular charge-transfer bands are suppressed. When $C_{60}$ and TPC are blended within a fluorescent-conjugated polymer film that undergoes photo-induced electron transfer to $C_{60}$, the composition-dependent evolution of fluorescence quenching shows that TPC organises the nanoscale phase separation of the polymer and fullerene. Our results highlight the potential for supramolecular additives to enhance the properties of organic electronic devices such as solar cells.

Keywords: fullerene; triptycene; polymer film morphology; conjugated polymers; host–guest complex

1. Introduction

Molecular semiconductors such as fullerene $C_{60}$ and its derivatives have become ubiquitous components of organic electronic devices such as thin-film transistors and solar cells owing to their electronic structure and favourable material processing properties (1, 2). Electronic charge conduction in such devices relies on the assembly of $C_{60}$ molecules to provide macroscopic networks of weakly coupled π molecular orbitals. In the case of bulk heterojunction solar cells in which electron-accepting $C_{60}$ derivatives are blended with an electron-donating polymer to separate charges, electron conduction pathways are generally only created with a large excess of $C_{60}$ derivatives in spite of efficient charge transfer (CT) with substantially less $C_{60}$ content (3–5). Devices containing suboptimal amounts of $C_{60}$ result in electrons being trapped in small $C_{60}$ domains or isolated molecules that are not coupled to the electrodes, ultimately suffering charge recombination losses. The need to use excess $C_{60}$ to ensure a percolating network is not ideal because $C_{60}$ contributes little to optical absorption but adds to the thickness of the device, thereby reducing the electric field across the device and increasing the material cost.

Several approaches have been employed to template the macroscopic assembly of $C_{60}$ molecules. One strategy is to covalently tether $C_{60}$ molecules to a polymer chain (6, 7); however, the performance of the devices made by using this strategy has not yet exceeded that of molecular blends. Nanostructured $C_{60}$ domains within polymer films can even be defined more deterministically when $C_{60}$ is tethered to a section of a block copolymer (8). Again, functioning of solar cells has been demonstrated via this approach; however, their relatively low-power conversion efficiencies do not yet justify the large synthetic investment required to make these complex materials.

Supramolecular chemistry offers an alternative approach to template the assembly of molecular semiconductors with minimal synthetic investment. The spheroidal shape and hydrophobicity of $C_{60}$ make it a distinctive guest for recognition by a complementary host of a suitable size, shape and chemical nature. Host–guest complexes of $C_{60}$ are well known for calix-pyrroles (9), calixarenes (10, 11), porphyrins (12), coordination networks (13) and even within block co-polymers (14, 15). Supramolecular assembly has been exploited to anchor $C_{60}$ molecules adjacent to electron-donating chromophores, thus facilitating photo-induced charge separation within biomimetic complexes (16).

Triptycene (TPC) is a simple and readily available molecule whose rigid paddle wheel structure and hydrophobicity present three excellent $C_{60}$ binding cavities, as illustrated in Scheme 1. TPC has been shown to co-crystallise with $C_{60}$ (17–20), inspiring the synthesis of various TPC derivatives to modulate the stability of the TPC-$C_{60}$ complexes in the solid state and in solution (10).

In this study, we use TPC as an additive to polymer/$C_{60}$ blend films in order to manipulate the phase separation of $C_{60}$ within a polymer matrix. We begin our investigations by identifying spectroscopic markers of TPC-$C_{60}$ co-crystallisation and using them we study the formation of...
co-crystals within ternary blend transparent polystyrene (PS) films. UV–Vis absorption spectroscopy and fluorescence microscopy each provide clear evidence that TPC$_z$C$_{60}$ co-crystals form in large concentrations within the polymer film. Finally, we replace the inert PS matrix with the semiconducting polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV), which is often blended with C$_{60}$ derivatives to produce organic solar cells (3). Having accounted for the effect of TPC on the inherent fluorescence of MEH-PPV, we demonstrate via fluorescence quenching measurements that the presence of TPC enhances the phase separation between the polymer and MEH-PPV. Our findings suggest that supramolecular additives like TPC could be used to enhance the morphological properties of organic solar cells.

2. Results and discussion

2.1 TPC$_z$C$_{60}$ co-crystals

Previous investigations of TPC$_z$C$_{60}$ co-crystallisation by Konarev and colleagues and by Feringa and colleagues (17, 18) have revealed the formation of elongated pyramidal crystals via slow evaporation from blend solutions in benzene and plate-like crystals via slow evaporation from blend solutions in O-xylene, respectively (19). Figure 1(a) shows optical micrographs of ~100 μm scale co-crystals and pure C$_{60}$ crystals that we grew using the same method. Consistent with previous studies by Konarev and colleagues, co-crystallisation with TPC from toluene results in large pyramidal crystals, in contrast to the rectangular rod-shaped crystals of pure C$_{60}$. The resulting crystal structure was characterised by a 1:1 ratio of C$_{60}$ to TPC with tetragonal space group $I_4(1)/amd$ symmetry, and
the centre-to-centre spacing between C$_{60}$ molecules increased from 10.02 to 10.17 Å when TPC is present (17).

Optical spectroscopy is a powerful tool to non-destructively identify signatures of the C$_{60}$–TPC interaction when crystals are embedded in films. Figure 1(b) shows the Fourier transform-infrared (FT-IR) absorption spectra measured for the TPC-C$_{60}$ co-crystals shown in Figure 1(a) after they had been ground and pressed into KBr pellets. Since most of the vibrational absorption bands are derived from TPC, the spectrum of ground TPC crystals is also shown for comparison, along with a mixture of separately grown C$_{60}$ and TPC crystals. Evidence of the TPC-C$_{60}$ interaction is seen in several parts of the IR spectrum. The TPC-based C–H out-of-plane bending bands at 741 and 797 cm$^{-1}$, respectively (see Figure 1(b), left inset), undergo a 4 cm$^{-1}$ redshift when C$_{60}$ is present. A pronounced signature of this interaction is observed in the C–H stretching region around 3000 cm$^{-1}$ (see Figure 1(b), right inset). The TPC tertiary C–H stretching bands undergo a 29 cm$^{-1}$ blueshift when C$_{60}$ is bound, consistent with observations by Konarev and colleagues (17), albeit more pronounced in our case. We also find that the C$_{60}$-based vibrational bands around 1182 and 1428 cm$^{-1}$ are little affected by the presence of TPC.

In order to better probe the nature of C$_{60}$ crystals within disordered IR-absorbing polymer films, we turned to fluorescence microscopy. The high symmetry of molecular C$_{60}$ results in dipole-forbidden transitions that suppress its fluorescence compared with most other organic semiconductors. Nevertheless, since TPC has no overlapping visible absorption or emission features, the C$_{60}$ environment can still be easily probed using sensitive fluorescence spectroscopy. Figure 1(c) shows the fluorescence spectra of C$_{60}$ and TPC-C$_{60}$ crystals measured by placing crystals like those shown in Figure 1(a) in a fluorescence microscope. The fluorescence spectra are similar except that the peak shifts from 745 to 725 nm and are sharpened when TPC is present in the crystal. We attribute this spectral shift to increased separation between C$_{60}$ molecules that TPC causes, thereby disrupting the formation of more energetically stabilised delocalised aggregate states that can form in C$_{60}$ crystals. Accordingly, the fluorescence spectra of C$_{60}$ in TPC co-crystals approach that of monomeric C$_{60}$ in dilute solution, which peaks at $\sim$700 nm (21). The previously observed absorption suppression in the intramolecular CT region around 500–600 nm for TPC-C$_{60}$ co-crystals (17) is also consistent with the interpretation that spectroscopic changes result from the increased separation between C$_{60}$ molecules when TPC is present. These UV–Vis spectral shifts are clearly evident in the polymer blend films described in the following section.

2.2 TPC-C$_{60}$ co-crystals in a transparent polymer matrix

Having found clear spectroscopic signatures for the TPC-C$_{60}$ interaction that can be identified in polymer blend films, we spin coated a series of ternary blend films containing C$_{60}$ (42 wt%), TPC (15 wt%, 1:1 molar ratio with C$_{60}$) and PS as a transparent matrix. We also made the corresponding films without TPC in order to discern its effect on C$_{60}$ crystals within the matrix. Chlorobenzene was selected as the casting solvent because it can dissolve each of the three components, and it leads to smooth spin-coated films that are of relevance to thin-film electronic devices.

Figure 2(a) shows fluorescence spectra of PS/C$_{60}$/TPC films as well as PS/C$_{60}$ analogues. While optical microscopy revealed small ($\sim$5 µm) crystallites on the surface of the film which had spectroscopic signatures corresponding to the pure crystals in Figure 1 (not shown), the spatial resolution of fluorescence microscopy (on the order of 1 µm) allowed us to avoid these crystals and focus...
on the bulk film regions. In the case of the ternary blend films, the 725 nm peak matches that found for the pure TPC-C_{60} co-crystal. The only difference is the slightly broader fluorescence spectrum in the case of the polymer blend film, presumably due to disorder and the incomplete formation of crystals within the film. With a peak approaching 750 nm, the fluorescence spectrum of the PS/C_{60} blend film also bears strong resemblance to that of the C_{60} crystal. The main difference is the spectral broadening on the high-energy side in the case of the PS blend film, which is explained by the dispersion of some isolated C_{60} molecules or smaller aggregates within the polymer matrix.

UV–Vis absorption spectroscopy can also be used to clearly illustrate the interaction of TPC and C_{60} within transparent PS films. Figure 2(b) shows the UV–Vis spectra from both ternary and binary blend films at various spin speeds. Normalising to the intramolecular absorption band at \sim 400 nm highlights the pronounced variation in the magnitude of the broad intermolecular CT band centred at \sim 520 nm for these films. This absorption band is strongest for the PS/C_{60} blend film cast with the lowest spin speed (1500 rpm), where relatively slow film drying provides sufficient opportunity for the growth of C_{60} crystals. The relative strength of this peak diminishes as the spin speed is increased to 2000 and 3000 rpm, consistent with the dispersal of C_{60} molecules throughout the film during rapid drying. The effect of TPC is very clear; for each pair of films, there is a pronounced suppression of the CT band when TPC is introduced. Together with the fluorescence microscopy data in Figure 2(a), UV–Vis absorption spectroscopy provides strong evidence that C_{60} co-crystalises with TPC within polymer films.

2.3 Effect of TPC addition in fluorescent polymer/C_{60} blends

Having established the effectiveness of TPC at templating the assembly of C_{60} within transparent polymer films, we turned our attention to electronically functional polymers. This section describes the effect of TPC on the photophysics of MEH-PPV/C_{60} blend films. The strong visible absorption spectroscopy and fluorescence microscopy of MEH-PPV prevent direct probing of the C_{60} environment in the ways described for the PS films above. However, variations in the fluorescence intensity of MEH-PPV offer a probe of nanoscale phase separation because photo-induced electron transfer strongly quenches the polymer fluorescence when the electron acceptor C_{60} is distributed on the \sim 5–10 nm length scale sampled by emissive excitons in the polymer within their nanosecond lifetime (22). Recovery of fluorescence intensity is therefore used to track the evolution of nanoscale phase separation.

Before measuring fluorescence in strongly quenched C_{60} blend films, it was necessary to examine the effect of TPC on the inherent fluorescence spectra of MEH-PPV. Figure 3(a) reveals that the fluorescence efficiency of thin films of MEH-PPV is increased by nearly threefold upon blending TPC (67% by weight) during spin coating, and is markedly increased with less than 20 wt% TPC. The UV–Vis absorption spectra remain virtually invariant across this series of films, both in spectral shape and intensity (not shown). We attribute the observed increase in fluorescence intensity to the suppression of weakly emissive interchain excimer states when TPC molecules are dispersed throughout the polymer film. This phenomenon has been previously demonstrated in polymers where the conjugated backbones are sterically prevented from interacting, for example by incorporating large and rigid pentaptycene units along the backbone (23, 24), or threading the polymer through rotaxanes (25). In our case, the fluorescence enhancement is diminished when the films are subsequently annealed in a solvent vapour atmosphere.
when the fluorescent electron donor MEH-PPV is used as the polymer, reduced fluorescence quenching by \( \text{C}_60 \) when TPC is also present is evidence of induced phase separation on the \( \sim 5-10 \) nm length scale of exciton diffusion. In films lacking the \( \text{C}_60 \) quencher, the TPC additive is also shown to strongly disrupt conjugated polymer interchain interactions, which was necessary to account for in ternary blend films and is an interesting observation in the context of polymer light-emitting devices. The ability to induce controlled polymer/\( \text{C}_60 \) phase separation could be exploited in organic solar cells because it will alleviate the problem of electron trapping at isolated fullerenes and remove the frequent requirement for a large excess of fullerene to provide continuous electron transport phases. Since spectroscopy confirms the expected reduction in electronic coupling between neighbouring \( \text{C}_60 \) molecules when TPC intervenes, future investigations must investigate the effect of TPC on charge photo generation and electronic charge mobility in TPC-\( \text{C}_60 \) co-crystals, and finally overall photovoltaic device efficiencies.

4. Experimental

4.1 Materials

TPC (98%), fullerene-\( \text{C}_{60} \) (99.5%), chlorobenzene and toluene were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as supplied. Poly(styrene) (average \( \text{mw} \) 250,000) and MEH-PPV polymers were purchased from Acros Organics (Geel, Belgium) and American Dye Source Incorporation (Pointe-Claire, Canada), respectively.

4.2 Preparation of crystals and polymer films

4.2.1 TPC-\( \text{C}_{60} \) complex

Crystals of the TPC-\( \text{C}_{60} \) complex were grown by complete evaporation from a 10 ml solution of \( \text{C}_{60} \) (15 mg, \( 2.08 \times 10^{-3} \) mol) and TPC (6.4 mg, \( 2.52 \times 10^{-3} \) mol) 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.

4.2.2 PS and MEH-PPV films

All polymer films were prepared on a Laurell technologies WS-400B-6NPP-Lite spin coater. Poly(styrene) films were prepared from chlorobenzene solutions of PS (5 g/l), \( \text{C}_{60} \) (5 g/l) and TPC (1.8 g/l). PS films were spin coated from 40 \( \mu \)l of the chlorobenzene solutions at 1500, 2000 and 3000 rpm spin speeds for 1 min. MEH-PPV films were prepared from toluene solutions of MEH-PPV (5 g/l), \( \text{C}_{60} \) (1.5 g/l) and TPC (0.18–5.3 g/l). MEH-PPV films were spin coated from 40 \( \mu \)l of the toluene solutions at spin speeds of
2000 rpm for 1 min. Solvent vapour annealing in a toluene atmosphere was achieved by placing the spin-coated films in a 250 ml sealed bottle with 10 ml of toluene for 1 h.

4.3 Spectroscopy

FT-IR spectroscopy of materials ground in KBr pellets was performed on a PerkinElmer spectrum one spectrometer. Absorption spectroscopy (UV–Vis) of polymer films was performed with an Agilent 8453 diode array spectrophotometer over the range of 200–1100 nm on 12 mm diameter FQW-121 quartz substrates purchased from UQG Optics (Cambridge, United Kingdom). Fluorescence microscopy measurements 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 μW to avoid degradation of the C60 material in both the crystals and the polymer films. Fluorescence spectroscopy of polymer films was performed with a Shimadzu RF-5301PC spectrofluorophotometer on 12-mm diameter Spec 2000 WFS-121 quartz substrates purchased from UQG optics (Cambridge, United Kingdom). 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 C60 content were collected at excitation and emission slit widths corresponding to 3-nm spectral resolution. Fluorescence spectra of MEH-PPV/C60 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 of some blend films were also repeated with the same spectrometer configuration as for pristine MEH-PPV films in order to quantify the degree of quenching under identical conditions. Fluorescence spectra were also normalised for the absorption intensity at the excitation wavelength, which was found to vary by less than 10%.

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