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In Situ Transient Absorption During Thermal Annealing of a Polymer: Fullerene Blend

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Abstract: In situ linear absorption and single-shot transient absorption are employed to understand how morphological changes during thermal annealing impact the electronic structure and excited-state dynamics of a polymer: fullerene blend.

1. Introduction

Understanding the influence of film morphology on excited-state dynamics is critical for improving efficiency of organic photovoltaics (OPVs). The active layer of an OPV consists of organic semiconducting materials that have either electron donating or accepting character. When these materials absorb a photon, an excited electron-hole pair, or exciton, is generated. A charge transfer (CT) state is formed once the electron and hole reside in the electron acceptor and donor materials, respectively. If these charges can overcome Coulomb attraction, they can separate and form a charge separated (CS) state. Controlling the donor-acceptor interfacial area and domain size can change the likelihood of charge transfer, leading to greater charge separation, and greater device efficiency. Poly(3-hexylthiophene-2,5-diyl)(P3HT): phenyl-C61-butyric acid methyl ester (PCBM), an electron donor-acceptor system, is a perfect model system as it has been characterized before and after annealing, showing an increase in P3HT crystallinity [1], but the picture is incomplete for what occurs during annealing. Here we report the first in situ single-shot transient absorption measurements during thermal annealing of P3HT and P3HT:PCBM.

2. Methods and Results

Linear absorption and single-shot transient absorption (SSTA) [2] were concurrently measured on a homebuilt electric heating stage. Samples were heated to 140°C before they were allowed to passively cool. The SSTA data were modeled using evolution associated decay spectra (EADS) with two sequential decays.

UV-Vis measurements of neat P3HT during thermal annealing and cooling show a reversible spectral blueshift that has been previously characterized as a reversible decrease in the polymer conjugation length [3]. EADS fits to SSTA data of neat P3HT indicate that there are two species that have less and more interchain order. As annealing proceeds, the 0-0:0-1 ratio of the species with less interchain order decreases significantly, likely due to torsion from thermal energy, which reverts upon cooling.

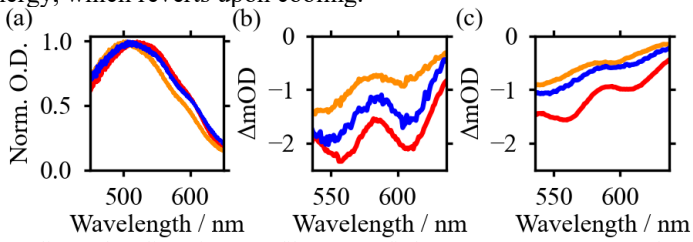

Fig. 1. (a) Absorbance during annealing and cooling of a P3HT film. EADS fit from SSTA measurements of a P3HT film with less (b) and more interchain order (c). Slices at 30°C during heating (red), 140°C during heating (orange), and 30°C during cooling (blue). 0-0 and 0-1 peaks are shown at ~560 nm and ~610 nm.

3. Conclusions

SSTA measurements show that the energy landscape for excitons changes during thermal annealing and cooling and can inform on how energy transfer and charge separation can be optimized in organic semiconducting materials for use in OPVs.

4. Acknowledgements

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5. References

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