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Aggregation-Dependent Excited-State Dynamics of an Organic Dye Targeted for Photovoltaics

Áine R. Hoban[1,*], Zachary S. Walbrun[1], Cathy Y. Wong[1,2]
[1]*Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon, USA*
[2]*Oregon Center for Optical, Molecular, and Quantum Science, and Material Science Institute, University of Oregon, Eugene, Oregon, USA*
**ahoban@uoregon.edu*

Abstract: A highly NIR-absorptive organic dye forms monomers when kinetically trapped in a polymer matrix, but upon thermal annealing, aggregation causes changes in excited-state processes, which are assayed via in situ transient absorption.

1. Introduction

Squaraines (SQs) are a class of donor-acceptor-donor small molecules that absorb efficiently in the near-infrared solar emission range and have increased intermolecular charge transfer character, making them excellent candidates for organic photovoltaics (OPVs) [1]. The SQ molecule, DBSQ(OH)$_2$, primarily forms pi-pi stacks in a thin film, which can be disrupted by co-depositing SQ molecules with an inert and optically transparent polymer, such as PMMA, resulting in a population of primarily monomers. A thin film of primarily monomers can be thermally annealed to induce rearrangement into electronically coupled aggregates. Understanding the degree of aggregation and the interaction between species with different electronic coupling in SQ:PMMA films during thermal annealing is critical for optimization of OPVs, which currently incomplete. We employ in situ UV-Vis and single-shot transient absorption (SSTA) measurements to understand how morphological changes during annealing impact the electronic structure and excited-state dynamics of SQ:PMMA films.

2. Methods and Results

Solutions of varying weight ratios of 2,4-bis(4-dibutylamino-2,6-dihydroxyphenyl)cyclobutane-1,3-dione (DBSQ(OH)$_2$) in a polymethyl methacrylate (PMMA) matrix were spincast onto glass slides. In situ UV-Vis absorbance measurements were taken to quantify the populations of monomer, weakly-coupled species, and pi-pi stacked aggregates. Single-shot transient absorption (SSTA) measurements were concurrently measured with linear absorption and were globally fit using the evolution associated difference spectra (EADS) model with two sequential decays.

Absorption measurements of SQ:PMMA films with increasing weight percent SQ show an increase of the shoulder feature at 600 nm, adjacent to the monomer feature around 650 nm (Fig. 1a). As this feature is associated with weakly-coupled species, it may be understood that increasing the amount of PMMA relative to SQ impedes initial aggregation. The fully annealed films exhibit a double-hump spectrum associated with pi-pi stacks of aggregated SQ [2]. As a function of annealing time, a decline of the monomer feature around 640 nm is observed concurrently with the growth of a blue-shifted feature at 550 nm, indicating a growth of pi-pi stacked aggregates with decrease of monomer population. SSTA data indicate an initial rapid energy transfer process to the weakly-coupled species. Upon full annealing, energy transfer from the monomer is no longer observed, and the aggregated species is directly excited. Our EADS model confirms that energy transfer is occurring from the monomer to more aggregated species.

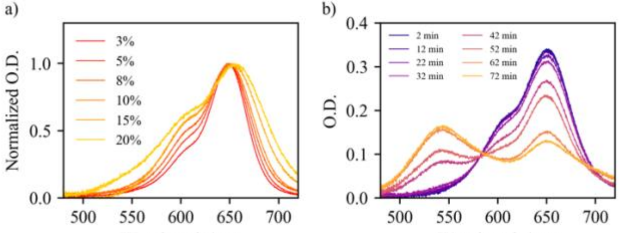

Fig. 1. a) Absorption of the unannealed films as a function of DBSQ(OH)$_2$:PMMA weight ratio, and b) absorption of an 11% DBSQ(OH)$_2$:PMMA as a function of annealing time.

3. Acknowledgements

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4. References

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