# Exciton fission and electronic delocalization in organic semiconductors

Jon Burdett[1], Astrid Mueller[1], Wolfgang Schoeller[1], Yuri Avlasevich[2], Klaus Muellen[2], David Gosztola[3], Gary Wiederrecht[3] and Chris Bardeen[1*]

*[1]Department of Chemistry, University of California, Riverside, CA 92521, USA*
*[2]Max Planck Institute for Polymer Research, Ackermannweg 10, D55128 Mainz, Germany*
*[3]Center for Nanoscale Materials, Argonne National Lab, Argonne, IL 60439, USA*
**e-mail: chrisopher.bardeen@ucr.edu*

The ability to generate two or more excitons after absorption of a single photon can lead to significant increases in solar cell efficiency, with the theoretical value rising from 31% to 43% in a single junction cell.[1] Recent results demonstrating multiple exciton generation (MEG) in inorganic nanocrystals have focused attention on this phenomenon as a possible method for accomplishing the 1→2 photon to exciton conversion. A similar phenomenon, exciton fission, has long been known in organic semiconductors. In exciton fission, the initially created singlet state spontaneously splits into a pair of triplets via a spin-allowed process. One requirement for efficient exciton fission is that the energy of the relaxed singlet state must be twice that of the triplet state.[2] Tetracene is a relatively simple conjugated molecule that fulfills this requirement. In this talk, we describe our recent studies on exciton fission in both covalent tetracene dimmers and in crystalline tetracene.

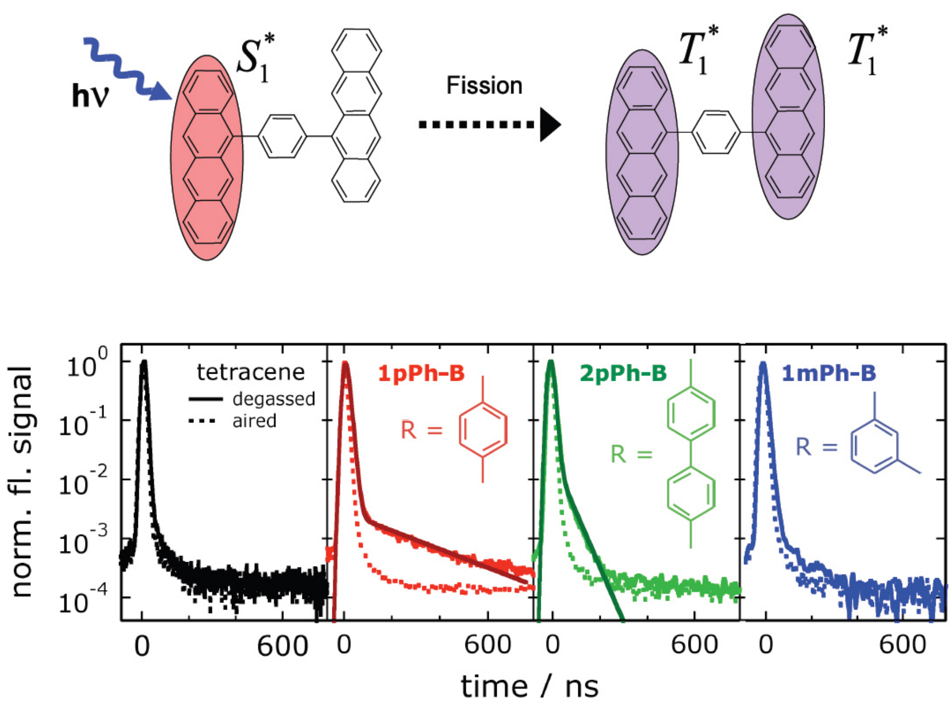


**Figure 1.** Top: Schematic of exciton fission process. Bottom: Prompt and delayed fluorescence decay data from phenylene bridged tetracene dimers. Also shown are data from oxygenated solutions, demonstrating that the presence of $O_2$ quenches the delayed fluorescence, and kinetic fits to the data.

The top panel of Figure 1 shows a phenylene-bridged tetracene dimer that we have studied.[3-4] If a pair of triplet states are created on this dimer, they can either decay nonradiatively or recombine back into the singlet state and generate delayed fluorescence. This recombination process provides a way to their formation and decay dynamics. We study three different bridging groups: para-phenylene, para-biphenylene, and meta-phenylene, whose prompt and delaye fluorescence decays are shown in the bottom panel of Figure 1. Also shown in Figure 1 are the decays measured when the solution is supplied with oxygen, a triplet quencher that suppresses the delayed fluorescence. We find that measurable exciton fission occurs in the first two molecules, but at relatively low yields of 2-3%. The low yields result from fission rates that are 100-1000 times lower than those reported for crystalline tetracene.[5]

In order to understand the reasons for the large difference between the exciton fission rates in the tetracene dimers and crystalline tetracene, we have studied excited state dynamics in polycrystalline tetracene thin films.[6] Picosecond fluorescence measurements confirm the presence of a delocalized, superradiant J-type exciton in the crystal that decays on the 100 picosecond timescale, along with a longer-lived component that corresponds to the delayed fluorescence lifetime due to triplet-triplet recombination. The delayed fluorescence lifetime reflects the triplet decay process, which is much more rapid in the polycrystalline films than in the single crystal, as shown in Figure 2. Comparison of femtosecond transient absorption experiments on monomeric tetracene in solution and the solid film reveal the existence of an even more delocalized exciton that decays on the more rapid timescale of approximately 10 ps, which was the time resolution of the fluorescence measurements. This rapid decay is shown in Figure 3. The triplet excited state absorption is obscured both by the enhanced $S_0 \rightarrow S_1$ transition and by the residual orientation of the tetracene microcrystallites on the surface. Our data is consistent with the traditional picture that exciton fission is the dominant relaxation channel for singlet excitons in crystalline tetracene. But our results also show that in order to quantitatively analyze this process, the delocalized nature of the initial singlet state should be taken into account. The stronger electronic coupling between tetracene molecules in the crystal appears to facilitate exciton fission, and may provide a criterion for the design of exciton fission materials.

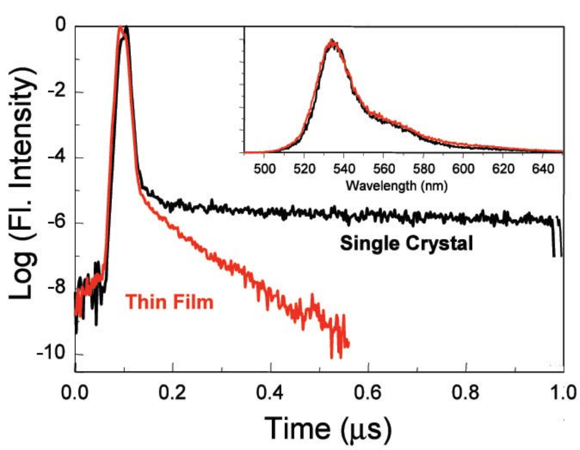


**Figure 2.** Fluorescence decay in polycrystalline film and single crystal, showing that triplet lifetime is much longer in the single crystal. Inset: early and late time fluorescence spectra, showing that the same singlet species is responsible for both time regimes.

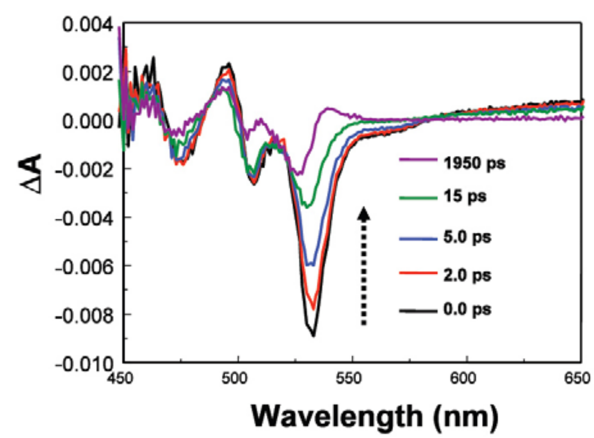


**Figure 3.** Transient absorption data for polycrystalline tetracene showing rapid decay of stimulated emission due to decay of initially excited superradiant exciton.

<u>References:</u>

1. Hanna, M. C.; Nozik, A. J., Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. J. Appl. Phys. 2006, 100, 074510/1-074510/8.
2. Paci, I.; Johnson, J. C.; Chen, X.; Rana, G.; Popovic, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J., Singlet fission for dye-sensitized solar cells: can a suitable sensitizer be found? J. Am. Chem. Soc. 2006, 128, 16546-16553.
3. Muller, A. M.; Avlasevich, Y. S.; Mullen, K.; Bardeen, C. J., Evidence for exciton fission and fusion in a covalently linked tetracene dimer. Chem. Phys. Lett. 2006, 421, 518-522.
4. Muller, A. M.; Avlasevich, Y. S.; Schoeller, W. W.; Mullen, K.; Bardeen, C. J., Exciton fission and fusion in bis(tetracene) molecules with different covalent linker structures. J. Am. Chem. Soc. 2007, 129, 14240-14250.
5. Swenberg, C. E.; Stacy, W. T., Bimolecular radiationless transitions in crystalline tetracene. Chem. Phys. Lett. 1968, 2, 327-328.
6. Burdett, J. J.; Mueller, A. M.; Gosztola, D.; Wiederrecht, G.; Bardeen, C. J., to be submitted.