

PHOTOPHYSICS OF THIOPHENE BASED LIGHT HARVESTERS

Adam Huss, Nathan Wells, and David Blank

Department of Chemistry
University of Minnesota
Minneapolis, MN 55455

Ultrafast time resolved spectroscopy, including fluorescence upconversion and pump probe spectroscopy, was used to investigate the excitation and excited state relaxation dynamics of a series of thiophene light harvesters. The molecules studied include phenyl cored thiophene dendrimers and substituted terthiophene derivatives. These molecules were chosen due to their promise as light harvesters and hole conductors in dye-sensitized and organic photovoltaics. We have focused on the dynamics of the initial events following light absorption by these molecules in solution phase, including structural and energetic relaxation as well as intersystem crossing.

Time resolved fluorescence decays were measured for the thiophene dendrimers and used to determine spectral diffusion and fluorescence anisotropy decay time constants. A representative fluorescence anisotropy decay is given in figure 1 for one of the dendrimers (4G1-3S) compared to a linear analog, sexithiophene, following excitation at 470 and 400 nm respectively. It was found that, for the dendrimer, the anisotropy decay and spectral diffusion dynamics occurred in multiple steps with a significant fraction taking place within the first 100 fs followed by slower processes on the order of picoseconds. This is consistent with fast nuclear relaxation followed by energy migration between dendrimer arms, very different from the linear molecule whose anisotropy decays with a single exponential, consistent with rotational diffusion. The dendrimer dynamics are similar to those seen in conjugated polymers used in organic photovoltaics.

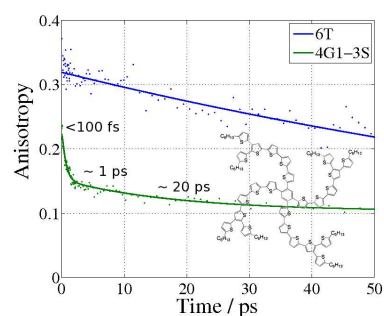


Figure 1: Dendrimer Anisotropy Decay

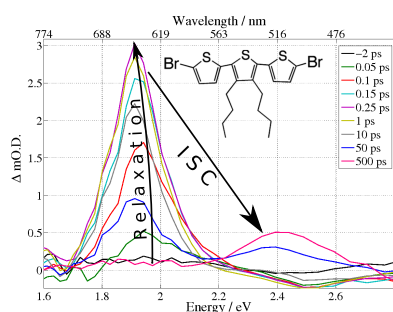


Figure 2: ISC in terthiophene derivative

Figure 2 shows spectrally-resolved pump probe spectroscopy of 3',4'-dibutyl-5,5''-dibromo-2,2':5',2''-terthiophene following excitation at 400 nm. Transient absorption from the excited singlet state appears within the first 100 fs near 650 nm. On longer time scales the singlet absorption at 650 nm retreats and is replaced by another feature at 520 nm, triplet state absorption. Comparing the two time scales gives the intersystem crossing (ISC) rate (50 ps). This rate is highly dependent on substituents and varying them allows us to compare ISC rates with the relative energies of the singlet and triplet states as computed using CIS and TDDFT methods. This data, combined with time resolved fluorescence and quantum yield measurements, offers a reasonably complete picture of the excited state dynamics of these molecules.