Ultrafast reflectivity dynamics in bis (n-butylimido) perylene thin films

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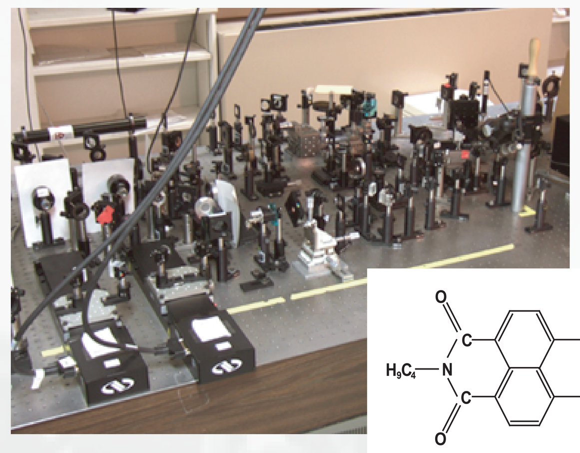
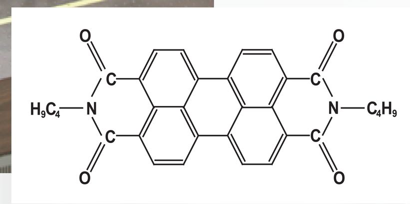
Abstract

Using pump-probe reflectometry, we study the ultrafast excited-state dynamics in thin films of BuPTCD, an organic semiconductor, deposited on gold nanoparticles. We observe depletion of the ground state and excited state absorption after photo-excitation.





Perylene Derivatives

Perylene tetracarboxylic derivatives (PTCD) are organic molecules of interest because of their electrical and optical properties. In particular, the strong absorption and emission of PTCD in the visible region make them prime candidates for applications such as photoconductors, solar cells, and laser materials [1-4]. Additionally, PTCD are thermally stable and chemically inert, favoring device applications based on organic compounds. It has recently been reported that perylene derivatives possess extremely large two-photon absorption cross sections, making this class of molecules ideal candidates for photonic applications such as upconversion lasing and high-efficiency optical limiting [2, 5-7].

Although several studies on the structural, electronic, and optical properties of perylene derivatives have been performed in the past [4, 5, 8], the relaxation processes following photo-excitation of these molecules, especially on the ultrafast time scale, are still not well understood. However, such information is of paramount importance for the understanding of the excited-state dynamics in PTCDs, which can lead to new applications for this class of materials.

Pump-Probe Reflectivity Measurements

In this work, we report a pump-probe study of bis (n-butylimido) perylene tetracarboxylic derivative (BuPTCD) films (100 nm thick) deposited by physical vapor deposition on top of Au nanometric islands (~6 nm) on glass substrates. Figure 1 shows the pump-probe reflectometry setup we used to obtain data on the BuPTCD films.

Our femtosecond laser source is a multipass amplified Ti:sapphire laser system which produces 0.5-mJ, 40-fs pulses at a repetition rate of 1 kHz. The pump beam consists of a train of 800-nm s-polarized pulses focused onto a 100-µm diameter spot on the sample, with spot on the sample, with enetry below the threshold for permanent damage. The transient reflectivity is measured using a p-polarized white-light (350–830 nm) probe, obtained by focusing part of the femtosecond laser output onto a 3-mm thick piece of CaF2. We measured the chirp of the broadband probe separately and time-shifted the data accordingly [9].

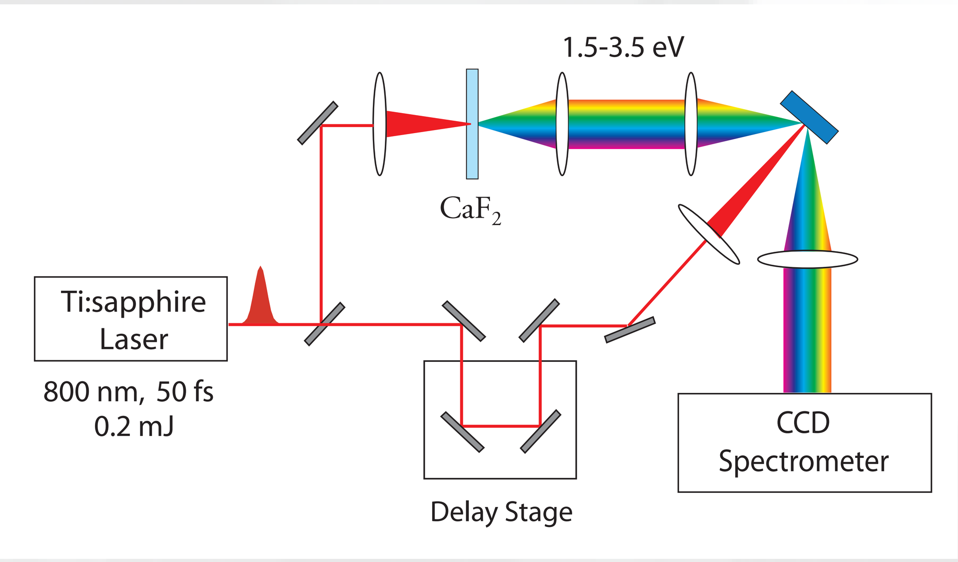


Fig. 1. Femtosecond Broadband pump-probe reflectivity measurement setup.

Results

Our results in Fig. 2 show two distinct features in the transient reflectivity of BuPTCD for two different spectral regions: i) an increase in the reflectivity around 550 nm, which reaches a maximum after approximately 500 fs and subsequently decays on a 10 ps time scale, and ii) a decrease in the reflectivity for wavelengths above 620 nm, and below 500 nm, with a characteristic relaxation time in the picosecond regime. We did not observe significant changes on the profile of the spectrum with time, implying that the excitation does not cross over multiple states, i.e., we are observing a single state. We verified that the transient response is solely due to the BuPTCD by performing experiments on a glass substrate covered only with Au islands, in which no signal was observed.

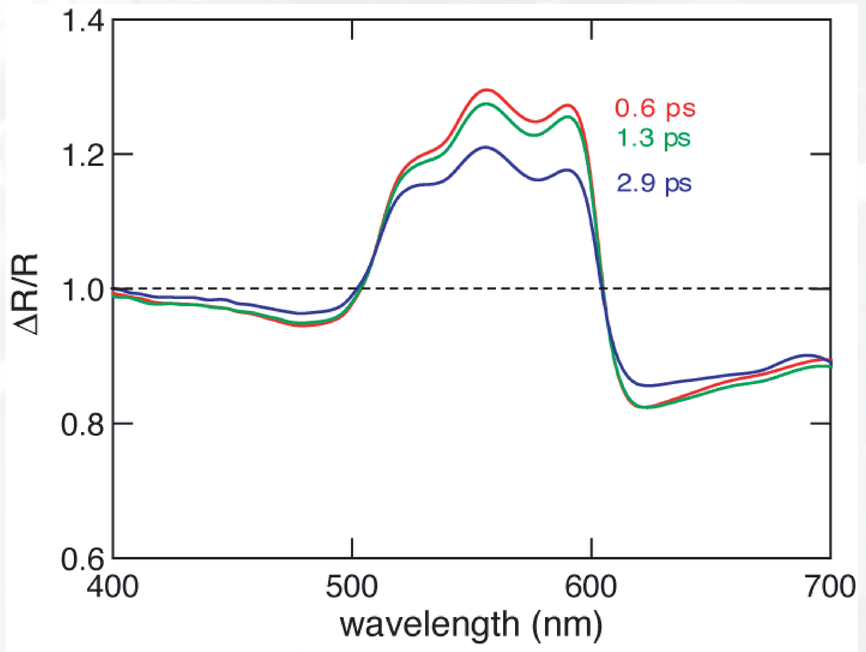
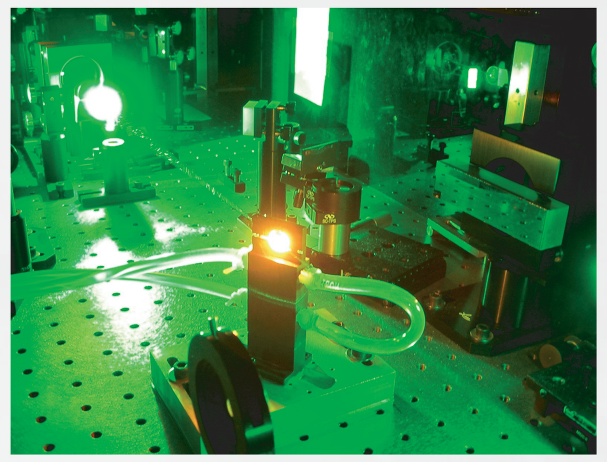


Fig. 2. Observed changes in reflectivity spectra of photo-excited Au-BuPTCD in time.

Because the measured spectrum around 550 nm resembles the profile of the linear absorption curve in the same region for BuPTCD, we attribute the increase of the reflectivity to the depletion of the ground state S0. For wavelengths above 600 nm and below 500 nm, the decrease in reflectivity is related to an excited state absorption of the perylene molecules from S1 to a higher energy state. Our results indicate that the observed changes of the reflectivity are due to a modulation of the BuPTCD films transmission, induced by the excitation beam, which consequently modulates the reflectivity of the Au islands. This explanation was confirmed when no transient signal was observed in BuPTCD films on plain glass substrates, without Au nanoparticles.

Conclusions

In summary, the pump-probe reflectometry technique enabled us to understand the ultrafast excited-state dynamics in BuPTCD thin films, a very promising material for applications in photonics.



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