

Ultrafast dynamics of bis (*n*-butylimido) perylene thin films excited by two-photon absorption

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Abstract We report a pump-probe study of the two-photon induced reflectivity changes in bis (*n*-butylimido) perylene thin films. To enhance the two-photon excitation we deposited bis (*n*-butylimido) perylene films on top of gold nanoislands. The observed transient response in the reflectivity spectrum of bis (*n*-butylimido) perylene is due to a depletion of the molecule's ground state and excited state absorption.

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1 Introduction

Perylene tetracarboxylic derivatives (PTCD) are a class of organic molecules that can function as organic semiconductors suitable for device applications [1–4]. The strong absorption and emission of PTCD in the visible region [5], and their thermal and chemical stability [6, 7], make them

prime candidates for optoelectronic devices, such as photoconductors, solar cells [8], and laser materials [9]. It has recently been reported that PTCD possess extremely large two-photon absorption cross sections [10–12] making them ideal for photonic applications, such as upconversion lasing and high-efficiency optical limiting.

A major challenge in developing organic-molecule-based photonic devices is the high intensity threshold required for inducing optical nonlinearities. To increase optical nonlinearities in organic molecules one can use electromagnetic-field enhancement produced by surface plasmons in nanoparticles [13]. Such surface plasmon resonances have been applied to Raman scattering [14, 15] and more recently to two-photon absorption [13, 16, 17]. The enhancement factor depends strongly on the shape, size, and type of metal particles, the incident excitation wavelength, and the permittivity of the material surrounding the organic molecule.

In PTCD, enhancement of the local electromagnetic field induced by surface plasmon resonance has been observed by way of Raman scattering [14, 18, 19], electronic emission [7], and vibrational absorption [20]. Among several different forms of PTCD, the bis (*n*-butylimido) perylene tetracarboxylic derivative (BuPTCD) has attracted special attention not only because of its optoelectronic properties but also because it possesses an absorption band in a conveniently accessible range. The BuPTCD absorption band partially overlaps with the absorption band tail of common metals used for surface-enhancement, including Cu, Ag, and Au. This partial overlap of the band tails allows the enhancement of optical effects, such as two-photon absorption, while maintaining spectrally distinct maxima for both the metal absorption band and the organic absorption band.

Although the structural, electronic, and optical properties of PTCDs have been studied [4, 7, 21–23], the dynam-

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ics resulting from two-photon excitation of these molecules have yet to be determined. In this paper, we report on a femtosecond pump-probe study of BuPTCD films deposited by physical vapor deposition on top of nanometric Au islands on glass substrates. The transient reflectivity of BuPTCD, resulting from two-photon excitation enhanced by surface plasmon resonance, reveals dynamics on the picosecond timescale.

2 Experimental details

The bis (*n*-butylimido) perylene (BuPTCD) used in this work was synthesized by the condensation of appropriate amines with perylene tetracarboxylic dianhydride. The BuPTCD molecular structure is shown in the inset of Fig. 1a.

The data presented here were obtained on two 100-nm-thick BuPTCD films; one was evaporated on top of a glass substrate (BuPTCD thin film) and the other was evaporated on Au nanoislands on top of a glass substrate (Au-BuPTCD thin film). The Au nanoislands were obtained by coating glass slides with a 6-nm-thick Au film, deposited by evaporation at a rate of about 0.05 nm/s. Both the BuPTCD and the metal films were evaporated with the substrates at room temperature, at a pressure of 10^{-8} Pa using an evaporator ma-

chine equipped with quartz crystal oscillator for film thickness determination. We measured the samples' absorbance from 350 to 800 nm with a spectrophotometer.

We performed pump-probe reflectometry experiments on the films using a multipass amplified Ti:sapphire laser system which produces 0.5-mJ, 40-fs pulses at a repetition rate of 1 kHz. The sample is excited by a train of 800-nm *s*-polarized pulses focused into a 100- μ m-diameter spot at the sample, with the pulse energy below the threshold for permanent damage. To measure the time-resolved reflectivity we use a *p*-polarized white-light (350–730 nm) probe, obtained by focusing part of the femtosecond laser output onto a 3-mm-thick piece of CaF₂ [24]. We measured the chirp of the white-light probe separately and corrected the reflectivity data accordingly, as described in Ref. [24].

For the Au-BuPTCD sample we used an excitation energy of 0.44 μ J, about half of the damage threshold, which was determined to be 0.87 μ J. These energies are small compared to the 11.5- μ J damage threshold for the BuPTCD sample indicating that the presence of Au nanoislands significantly increases the absorption of 800-nm laser irradiation.

3 Results

The dashed line in Fig. 1a shows the absorption spectrum for BuPTCD in solution. The spectrum exhibits a π - π^* electronic absorption band around 500 nm (*S*₁ state), with absorption peaks separated by approximately 170 meV corresponding to the vibrational progression of the electronic absorption [7, 21, 25].

The absorption spectrum of the BuPTCD film evaporated on glass (solid line in Fig. 1a) looks different from the spectrum of BuPTCD in solution because the molecules have fewer degrees of freedom in the thin film than when they are suspended. Compared to the solution, the thin film shows a redshifted component with a broad maximum at 572 nm and a blueshifted component centered at 466 nm. The observed band shifts and the double absorption peaks are attributed to the “card pack” (H aggregate \rightarrow blueshift) and “head-to-tail” (J aggregate \rightarrow redshift) arrangement of the chromophores [26].

Figure 1b shows the absorption spectrum for the Au-BuPTCD film (solid line). The reference spectrum used to calibrate this Au-BuPTCD film absorption spectrum was obtained with a glass slide. Compared to the linear absorption spectrum of the BuPTCD film in Fig. 1a, the Au-BuPTCD spectrum in Fig. 1b is blueshifted by about 20 nm, and there is an overall increase in absorbance. The dashed line in Fig. 1b shows the surface-plasmon absorption peaks of the Au nanoislands alone broadened by the wide range of sizes and shapes of the deposited islands on the glass substrate.

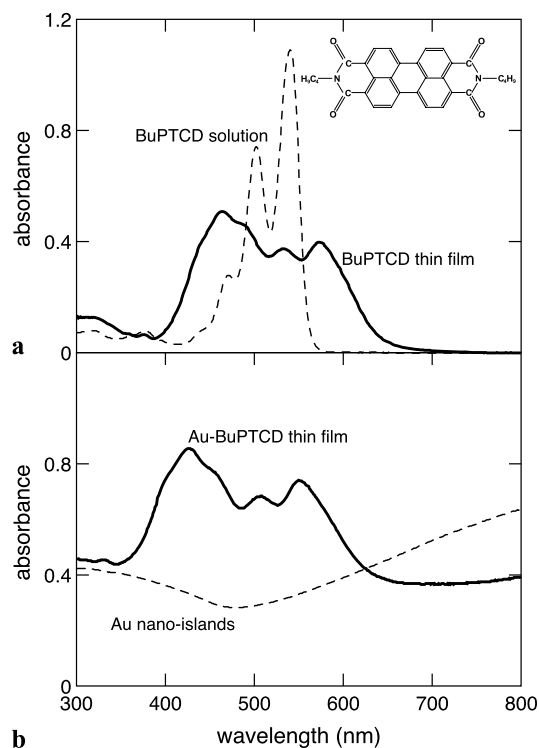


Fig. 1 Absorbance spectra of (a) BuPTCD in solution (dashed line) and a BuPTCD thin film evaporated onto a glass slide (solid line), (b) a BuPTCD thin film evaporated onto Au nanoislands deposited on a glass slide (solid line) and Au nanoislands on a glass slide (dashed line). The inset shows a diagram of the BuPTCD molecule

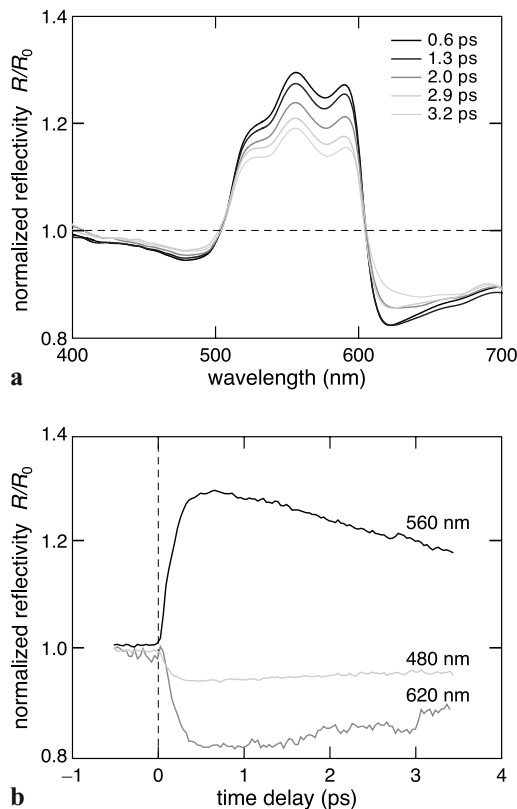


Fig. 2 Normalized reflectivity, R/R_0 , of Au-BuPTCD (**a**) as a function of probe wavelength at various delay times and (**b**) as a function of time delay at three different wavelengths

The BuPTCD spectra in Fig. 1 clearly show that the 800-nm laser excitation wavelength is nonresonant with the electronic absorption spectra, a necessary condition to observe a two-photon induced process. However, the 800-nm laser line is in resonance with the broad surface plasmon absorption of the Au nanoislands. This condition is necessary to activate the surface-plasmon enhancement mechanisms in the organic molecule [27].

Figure 2a shows the transient reflection spectrum of Au-BuPTCD as a function of the probe beam wavelength, at probe delays of 600 fs, 1.3, 2.0, 2.9, and 3.2 ps. Note that as the delay time changes the shape of the Au-BuPTCD reflectivity spectra does not undergo significant changes. Reflectivity data at time delays less than 500 fs are not shown, as they tend to exhibit contributions from coherent artifacts during pulse overlap and from the vibration relaxation of the perylene molecules [4, 21, 22, 28, 29].

Figure 2b show normalized reflectivity, R/R_0 as a function of the time delay between the pump and probe pulses, for three selected probe wavelengths representing the three distinct regions observed in the transient spectrum of Fig. 2a. For these three regions the transient reflectivity of Au-BuPTCD shows: (1) around 550 nm: an increase in reflectivity which reaches a maximum about 500 fs after excitation

and subsequently decays on a 10 ps timescale; (2) around 620 nm: an initial decrease in reflectivity with a characteristic relaxation time of about 10 ps; (3) around 490 nm: a decrease in reflectivity with a slower recovery time of about 30 ps.

4 Discussion

The reflectivity spectra in Fig. 2a present the same profile for different delay times indicating that we are probing the response of a single state of the perylene molecules (the S_1 state) to the excitation. As the reflectivity signal around 550 nm (Fig. 2a) resembles the linear absorption spectrum of the Au-BuPTCD (Fig. 1b solid line), we attribute the increase in reflectivity to depletion of the S_0 ground state. From Fig. 2b, one can see that the ground state is depleted within 500 fs of the excitation and recovers in 300 ps. The other two spectral regions of interest are at wavelengths above 600 nm and below 490 nm, where the decrease in reflectivity can be attributed to excitation of the perylene molecules from S_1 to a higher energy state, in agreement with results presented on transmission pump-probe experiments [4, 21, 22].

Our results also indicate that the two-photon induced reflectivity changes of the Au-BuPTCD films depend strongly on the presence of Au nanoislands. We observed no transient signal in the BuPTCD film on plain glass substrates, even for pulse energies as high as 4.4 μJ , ten times higher than that used for the Au-BuPTCD film. Additionally, we verified that the transient response is due to Au-mediated excitation of BuPTCD organic molecules by performing the same pump-probe reflectivity measurements on a glass substrate covered only with Au nanoislands. Using the same excitation pulse energy of 0.44 μJ , the measured reflectivity change of the Au nanoislands is zero. This indicates that the transient reflectivity response measured in Au-BuPTCD is entirely due to the organic molecular film.

The enhancement factor of the BuPTCD two-photon absorption due to the surface plasmon can be determined by comparing the reflectivity signals obtained from the BuPTCD film and the Au-BuPTCD film at the same excitation energy. However, at an excitation of 4.4 μJ we are unable to distinguish the BuPTCD reflectivity signal from the experimental noise level. We still can obtain a conservative estimate of the enhancement factor by comparing the upper bound of the BuPTCD noise (3%) to the measurements of the Au-BuPTCD reflectivity signal. Compared to the reflectivity change of 30% obtained for the Au-BuPTCD sample at an excitation of 0.44 μJ , the enhancement factor is at least 100. This is comparable to other enhancement factors observed for two-photon absorption processes reported for organic compounds [13, 16, 17].

5 Conclusion

We present pump-probe reflectivity spectra of BuPTCD thin films deposited on Au nanoislands. The observed changes in reflectivity are due to Au-mediated surface plasmon enhancement of two-photon absorption. The reflectivity spectrum reveals depletion of the molecule's ground state and excited state absorption. Our experimental results indicate that the Au nanoislands effectively enhance the two-photon absorption and that they can be used to functionalize organic molecules for device applications.

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