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Ultrafast Exciton Relaxation in Microcrystalline Pentacene Films

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The exciton dynamics in microcrystalline pentacene films is investigated by transient absorption measurements with 30 fs time resolution. It is found that the emission from photoexcited Frenkel excitons decays within 70 fs due to the ultrafast formation of an excitonic species with a strongly reduced transition dipole to the ground state and an absorption dipole in the plane of the film. We propose that an excimer exciton is formed and stabilized by changes of the local crystal structure. The subsequent dynamics is dominated by diffusion controlled annihilation and trapping.

The electronic properties of organic materials have been studied intensively to promote their application in electronic devices [1–3]. The research is driven by the expectation of cheap and flexible devices as well as new application areas, particularly in optoelectronics. Microcrystalline pentacene films with a thickness of a few monolayers are used as active layers in many prototype applications, such as organic field effect transistors, because their hole mobility is extraordinarily high for organic materials and can adopt values of more than $1 \, \text{cm}^2/(\text{V s})$ [4,5]. Crystalline pentacene is also intensively studied to investigate basic physical properties of organic crystals [6–8]. The performance of organic devices depends on the internal electronic structure and dynamics of the organic material as well as on its interaction with other device components such as contacts [3]. Femtosecond pump probe experiments allow us to study the internal properties with an unprecedented selectivity because they probe local processes and provide the time resolution necessary to observe the originally generated species, as well as their relaxation and trapping pathways [9,10].

The nature and evolution of the primarily generated excitons in pentacene are not clear at all. The low photoluminescence yield indicates that the photoexcited excitons relax quickly to a nonfluorescing state. It was argued that an ultrafast fission into two triplet excitons can occur in less than 100 fs since the energy of the triplet state is somewhat less than half of the monomeric S_1 energy [7]. On the other hand, terahertz experiments indicate that within their time resolution of 400 fs free charge carriers appear [8]. In this Letter we approach the problem with transient absorption spectroscopy with 30 fs time resolution and provide evidence that within the first 70 fs the photoexcited Frenkel excitons transform to excimer excitons.

Microcrystalline thin film samples are prepared by vacuum deposition of pentacene on a transparent polymer substrate (TOPAS; thermoplastic olefin polymer of amorphous structure). The film consists of closely packed crystalline grains with a diameter of about 1 μm and a height of roughly 30 monolayers [11]. The samples are kept under nitrogen for storage and during the optical experiments. In the pump probe measurements the samples are excited by 30 fs long pulses which are generated with a noncollinearly phase matched optical parametric amplifier (NOPA) [12] pumped by a 1 kHz regenerative Ti:sapphire amplifier system (CPA 2001; Clark MXR). The absorption changes are probed over the whole visible spectral range with a white light continuum generated in a 3 mm thick sapphire substrate. For measurements with a higher time resolution but restricted spectral coverage 25 fs long probe pulses from a second NOPA are used. Pump and probe beam are overlapped and focused to a spot of 260 μm in diameter at the sample, which is oriented normal to the beams or with an angle of incidence of 65°. The recollimated probe beam is dispersed with a SF10 prism after the sample [10] and the transmitted energy is spectrally resolved, measured with a photodiode behind a slit. The cross correlation is measured by sum frequency mixing in a 100 μm thick BBO crystal at the sample position. The pump polarization is adjusted parallel to the probe beam with an achromatic $\lambda/2$-wave plate.

The steady state absorption spectrum of the pentacene films is identical to earlier published ones [see Fig. 1(a)] [8,13]. The center wavelength 670 nm of the pump pulse is at the maximum of the lowest and strongest absorption band. Transient spectra are measured at various time delays after photoexcitation of the films with an angle of incidence of 0° and 65° [see Figs. 1(b) and 1(c)]. They show a strong bleach due to the reduction of the ground state population and excited state absorption (ESA), which is most evident from the positive absorption between 610 and 650 nm and which is attributed to the photogenerated species. The absorption changes show a continuous decay indicating that the excited species returns to the electronic ground state within several hundred picoseconds. To obtain
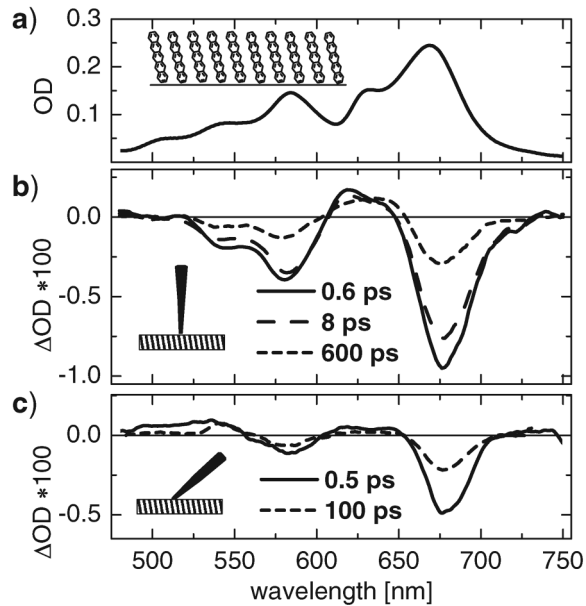
FIG. 1. (a) Steady state absorption spectrum of the micro-crystalline pentacene films, (b) transient absorption spectra 0.6, 8, and 600 ps after photoexcitation at 670 nm measured with laser beams vertical to the substrate and (c) transient spectra at 0.5 and 100 ps with an angle of incidence of 65°. $\Delta OD = -\log(T/T_0)$ is the optical density change, T the sample transmission with photoexcitation, and T_0 without photoexcitation.

the spectrum of the excited species the bleach was subtracted from the transient spectrum measured at a delay of 8 ps and normal incidence (see Fig. 2). The pump pulse excites preferentially grains with transition dipoles enclosing a small angle with the pump polarization, resulting in an anisotropic excitation. The anisotropy of the transient absorption does hardly change with time [14]. Since the steady state spectrum is an average over all polarizations, transient spectra measured with parallel and perpendicular
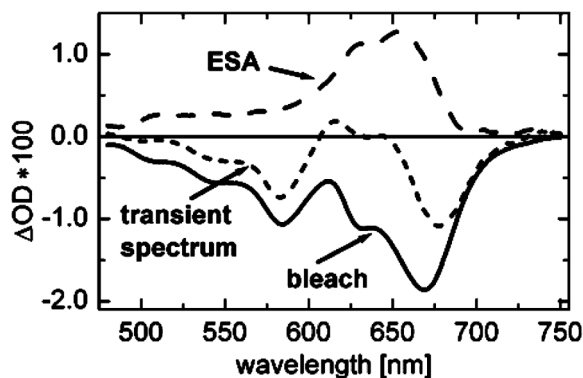

FIG. 2. Decomposition of the polarization averaged transient spectrum (short dashed line) at a delay of 8 ps into ground state bleach (solid line) and the absorption of the excitons (ESA, broken line).

polarizations were averaged prior to subtraction of the bleach.

The resulting ESA is of similar strength as the bleach. There are no indications for stimulated emission which would show up as a negative contribution and which is expected from the optically excited excitons in the red wing of the ground state absorption. Its lack indicates that the primarily excited Frenkel excitons have already transformed into a non fluorescing species. To observe this transformation, spectra with a resolution of 30 fs were measured in the spectral region of the lowest absorption band (see Fig. 3).

They show a strong negative signal between 670 and 710 nm where stimulated emission from Frenkel excitons is expected. This signal decays extremely fast to the transient spectrum measured 600 fs after excitation. To determine the decay time kinetic traces were recorded with 25 fs long probe pulses with pulse spectra centered at 635 and 676 nm [see Fig. 3(b)]. For this purpose the dispersion prism was removed because a spectrally integrating detection avoids artifacts at time zero. The data can be perfectly modeled by a convolution [solid lines in Fig. 3(b)] of an exponential decay with the cross correlation (broken lines). The obtained time constants of 65 and 79 fs are equal within the experimental error. The results show that the emission of the optically excited excitons decays with a time constant of 70 ± 10 fs, reflecting the transformation of the Frenkel excitons into a nonfluorescing species.

This species can neither be attributed to triplet excitons nor to free charge carriers. The lowest absorption band of monomeric pentacene in the triplet state has its origin at 505 nm [15]. It is about 10 times stronger than the $S_0 \rightarrow S_1$ absorption and its transition dipole is oriented along the long molecular axis. Since the pentacene molecules are tilted from a perpendicular orientation with respect to the substrate by only 6° [16] such a transition dipole can hardly interact with laser light polarized parallel to the substrate. To strengthen signatures from potential triplet excitons we tilted the sample to an angle of incidence of 65° and obtained the spectra shown in Fig. 1(c). Taking refraction into account, the laser polarization is now oriented with an angle of about 55° to the long molecular axis. Accordingly, the bleach signal is reduced since it results from transitions polarized along the short molecular axis. The same is obviously true for the ESA. However, a weak additional absorption band is now observed around 525 nm. We assign this band to a small triplet population because its spectral position is as expected moderately redshifted with respect to the triplet absorption of the monomer in solution [15] and its dependence on the angle of incidence shows that it is associated with a transition dipole along the long molecular axis. However, if all excitons would experience fission into triplets this band would be several times stronger than the bleach. We conclude that only a fraction of less then 10% transforms into
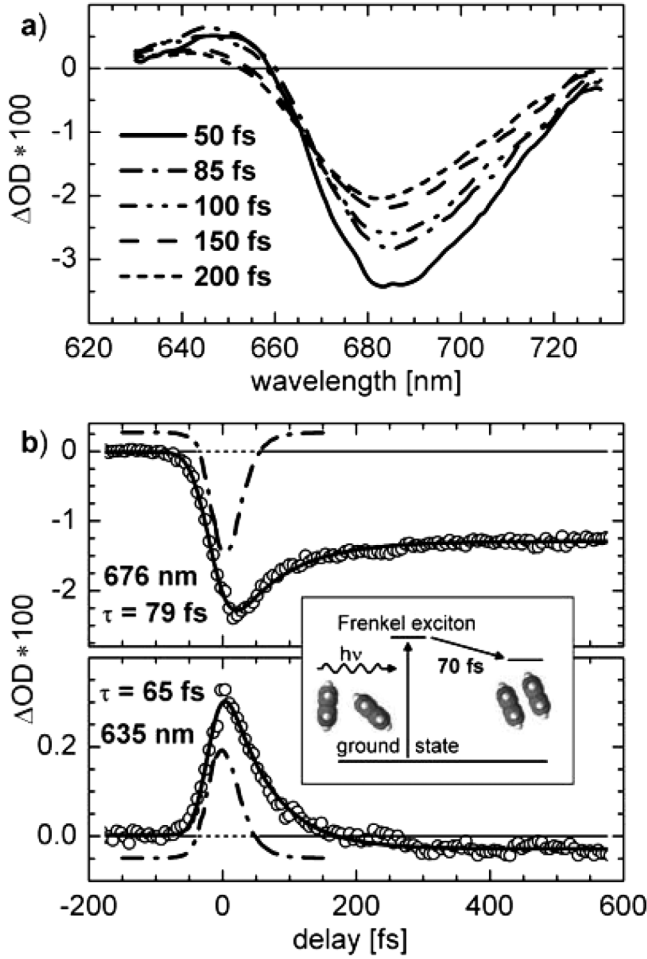
FIG. 3. (a) Transient spectra under normal incidence during the first 200 fs in the region of the first absorption band. (b) Time traces (circles) measured with 25 fs probe pulses centered at 635 and 676 nm. Monoexponential decays (solid lines) are convoluted with the cross correlation (dash-dotted lines, vertically shifted for better visibility) and fitted to the data. The inset shows the corresponding energy diagram.

triplets. The majority adapts a state with an absorption dipole in the plane of the film. Monomeric pentacene cations and anions exhibit no absorption band in the visible spectrum [17] and ionic transitions cannot explain the ESA band even if a strong spectral shift due to the crystalline structure is assumed. This excludes the idea that free charges contribute dominantly to the observed signatures.

We propose that a species very similar to excimers is generated. Two neighboring pentacene molecules form a bound dimer in the electronically excited state [6]. Most probably the two molecules rotate around the long molecular axis to change from the tilted geometry of the original herringbone structure to a parallel geometry and reduce their intermolecular distance to minimize the energy [see inset of Fig. 3(b)]. This electronic configuration corresponds to a symmetric combination of the first excited singlet states of the two molecules but can contain a

significant charge transfer contribution. The transition to this state is electric dipole forbidden as soon as the molecules have adapted a parallel geometry [6]. We think this effect is responsible for the ultrafast decay of the exciton emission. The observed time constant corresponds to the rotation of the molecules. The ESA results from a transition to a doubly excited dimer state.

A detailed analysis of the subsequent picosecond dynamics at several probe wavelengths and excitation intensities will be given in a forthcoming publication [14]. Here we focus on the most important findings and discuss them on the basis of the recovery of the ground state bleach measured at 685 nm and shown in Fig. 4 on a logarithmic time scale. It reflects diffusion controlled annihilation [9] as well as trapping of the excitons. We modeled the exciton decay and the bleach recovery by numerical integration of the rate Eqs. (1) and (2).

$$\frac{dn}{dt} = -\frac{1}{2}8\pi D\bar{a}\left(1 + \frac{\bar{a}}{\sqrt{2\pi Dt}}\right)n^2$$
$$- 4\pi D\bar{a}\left(1 + \frac{\bar{a}}{\sqrt{\pi Dt}}\right)n(n_{T0} - n_T); \qquad (1)$$

$$\frac{dn_T}{dt} = 4\pi D\bar{a}\left(1 + \frac{\bar{a}}{\sqrt{\pi Dt}}\right)n(n_{T0} - n_T) - \frac{1}{\tau}n_T. \qquad (2)$$

n is the time dependent exciton concentration, D the diffusion constant, n_{T0} the concentration of traps, and n_T the concentration of traps that are already occupied. They have a finite lifetime τ till they return to the ground state. $\bar{a}$ describes the distance to which an exciton must approach another exciton or a trap for efficient interaction. It is set to 1 nm, which is in the order of the geometrical average of
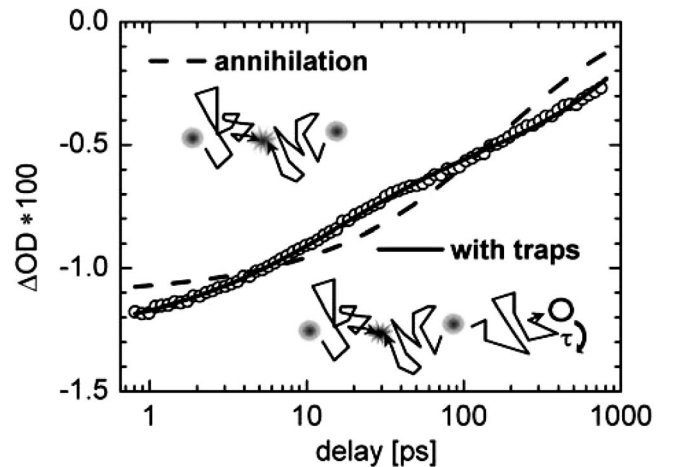

FIG. 4. Bleach recovery probed at 685 nm (circles). Modeling by exciton-exciton-annihilation only (broken line and left sketch) gives poor results, while good agreement is achieved if immobilization of excitons by traps is included (solid line and right sketch).

the lattice constants [9,16]. The exciton concentration $n_0 = 4.8 \times 10^{19}$ cm^3 at $t = 0$ is calculated from the excitation energy of 85 nJ. The time dependent bleach can be very well reproduced with $D = 5 \times 10^4$ cm^2/s, $n_{T0} = 2 \times 10^{19}$ cm^3, and $\tau = 850$ ps (solid line in Fig. 4). These parameters also correctly describe the dependence of the dynamics on the excitation energy (not shown here) [14]. In contrast, neglecting the traps and assigning an intrinsic lifetime to the excitons gives very dissatisfactory results (broken line in Fig. 4).

The observed bleach recovery also provides some evidence against triplet fission as a major relaxation channel. The lifetime τ describing the repopulation of the electronic ground state in the low excitation limit is too short for a triplet state [6,15]. The observed dependence on the excitation intensity is poorly reproduced if it is assumed that each absorbed photon results in two triplet excitons (not shown). Furthermore, triplet excitons in anthracene exhibit two dimensional diffusion [6]. Assuming two dimensional diffusion fails in reproducing the observed kinetics.

If the photoexcited Frenkel excitons would predominantly dissociate into free charge carriers, annihilation would correspond to the recombination of opposite charges. In pentacene highly mobile holes usually determine the mobility. The mobility of a single charged species can be calculated with the Einstein relation $\mu = De_0/(k_B T)$ [18]. From the found diffusion constant a mobility of 0.02 cm^2/(V s) would result. However, the mobility of holes should be higher than 1 cm^2/(V s) [5], indicating that the diffusion of a neutral species instead of holes is observed. Time resolved terahertz [8] and photoconductivity experiments [19] find a significant population of free charge carriers. The observed signals are sensitive to the products' photogeneration yield times mobility or times lifetime [8,19]. With a mobility of 1 cm^2/(V s) and a lifetime of a few hundred ps for the trapped electrons an efficiency of a few percent for the photogeneration of free charges results from these experiments. This is fully compatible with our findings.

In conclusion, transient absorption measurements with 30 fs time resolution show that in microcrystalline pentacene films the stimulated emission of photoexcited Frenkel excitons decays within 70 fs. The decay is attributed to the ultrafast formation of excitons with excimer character. The assignment is supported by the polarization dependence and the diffusion properties as well as the lifetime of the excitons. The time needed for the stabilization of the excimer state reflects changes in the local crystal structure. These deformations should lead to a large effective mass [18] and to small band widths that are comparable to thermal fluctuations [20]. At room temperature a high degree of localization is therefore expected and the propagation of the excitons is better described as a hopping process than as a band-like transport. This conclusion is supported by the small diffusion constant observed in our experiments.

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