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Ultrafast Excitation Relaxation in Colloidal Particles of Chloroaluminum Phthalocyanine: One-Dimensional Exciton–Exciton Annihilation

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The excited-state dynamics of crystalline ClAl phthalocyanine colloidal particles have been studied by means of picosecond and femtosecond absorption spectroscopy. In the measured relaxation dynamics, the initial excited-state evolution, taking place during the first picosecond after excitation, was distinguished from the overall exciton decay. Excitation transfer between different molecular species is suggested to be the most probable reason to the initial ($\leq$1 ps) excited-state dynamics. Exciton decay was found to be dominated by exciton–exciton annihilation with a $t^{-1/2}$ time dependence of the excited-state population, suggesting a one-dimensional exciton diffusion. A 0.2–1 ps intermolecular exciton hopping time was determined from the annihilation dynamics.

Introduction

Micromization of electronic and optoelectronic devices and the possible use for their fabrication of new molecular materials stimulate interest in space-limited molecular structures. Thin molecular films, Langmuir–Blodgett films, molecular aggregates, etc., are currently under intense investigation. Due to limited freedom of motion, migration and relaxation of excitons and charge carriers in space-limited structures are different than in bulk materials. Numerous theoretical works describe the properties of excitons restricted in a one-dimensional space.[1] Experimentally, such excitons have been observed in polymers,[2,3] J-aggregates,[4,5] columnar phases of phthalocyanines,[6,7] and some other materials consisting of linear chains, where probabilities of intra- and interchain hopping are very different.

Colloidal solutions are easily prepared and convenient to use for investigation of space-restricted molecular structures. In addition, colloids are in themselves of interest as materials filling the gap between the solid state and single molecules. Investigations of excitation energy relaxation in colloidal solutions of chloroaluminum phthalocyanine (ClAlPc) are presented in this work. Phthalocyanines are promising materials to be used in sensors, photoelements, or devices of molecular electronics. The relaxation mechanism of the light-induced excitations is one of the most important factors determining the optical and optoelectrical properties of such materials. Despite numerous investigations, this mechanism is not well characterized and understood in phthalocyanines up to now. The difficulties in the investigation of phthalocyanines by means of time-resolved spectroscopy are caused in part by the fast exciton–exciton annihilation and related to it local heating.[8,9] Abrupt local heating induces thermal expansion and generates acoustic waves.[10] All these processes occur simultaneously and make the relaxation process very complex. Colloidal solutions are materials composed from ultrasmall particles, which can efficiently transfer their heat energy to the surrounding solvent. Local heating and related effects are therefore expected to be reduced, leading to simpler relaxation processes.

Experimental Section

A 10^{-4} mol/L ClAlPc solution in ethanol was prepared and this solution was gradually diluted 5 times by distilled water. The solubility of ClAlPc in water is very low; therefore colloidal particles formed as a result of dilution. The residual free ClAlPc molecules in the solution were estimated from the difference absorption spectra. Since the monomer is efficiently excited at the chosen excitation wavelength of 590 nm, a long-lived bleaching of the monomer absorption band should be observable in the difference absorption spectrum of colloid if monomer were present. The fact that no transient absorption signal attributable to the monomer is detected within the detection limit of $\Delta A \geq 5 \times 10^{-4}$ OD results in an upper limit of residual monomer concentration of 0.2%. The colloid remained stable more than a month after preparation, and it was light stable up to a 10 mJ/cm^2 energy density of picosecond pulses. A further increase of energy density led to the appearance of monomer molecules, which disappeared again 5–10 min after the irradiation was switched off. The absorption spectra of the sample solutions were recorded on a Beckman spectrophotometer (Model UV 5240). A femtosecond spectrometer, based on a Spectra-Physics laser system generating ~200-fs pulses, was used to measure transient absorption kinetics and time-resolved difference absorption (ΔA) spectra. The 70-ps infrared pulses generated with a CW mode-locked Nd YAG laser were compressed in a fiber-grating compressor to ~3 ps (FWHM), frequency doubled and used to pump a R6G dye laser. The subpicosecond (~300–400 fs) light pulses at 590 nm generated in this dye laser were further compressed in a fiber-prism compressor and amplified in a two-stage dye amplifier pumped by a regenerative YAG amplifier. The amplified 590-nm pulses of 10–40 μJ energy, 200 fs duration, and 1 kHz repetition rate were used for excitation of samples and for continuum generation. The continuum used as a probe light enabled us to carry out investigations in the 400–900-nm spectral region. Some measurements of time-resolved ΔA spectra were also performed with the 790-nm and 300-fs excitation pulses of a mode-locked and amplified titanium:Sapphire laser. The same detection system and methods of data analysis were used in the two types of measurements.

Measurements of the excitation intensity dependence of ground-state bleaching and excitation wavelength dependence of transient spectra were performed by means of a picosecond spectrometer based on a passively mode-locked Nd YAG:laser, having low repetition rate and high energy excitation pulses. The samples

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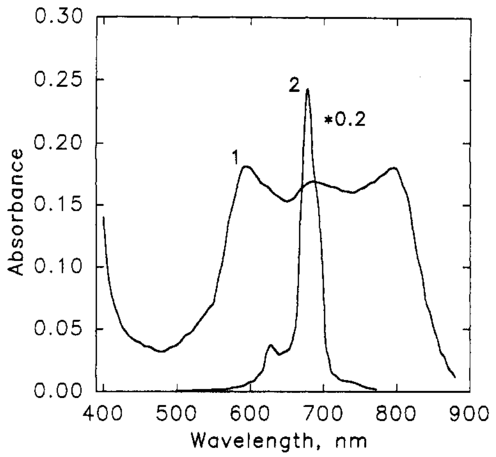

Figure 1. Absorption spectrum of ClAlPc colloid (1) and ClAlPc solution in ethanol (2) measured in a 2-mm-thick cuvette (solution spectrum is devided by a factor of 5). The concentration of ClAlPc was 3 × 10^{-5} mol/L in both samples.

were excited by the pulses of an optical parametric generator tunable in the 400–1700-nm range. Continuum probe pulses were generated in a heavy water cell. The time resolution in this case was 30 ps.

Experimental Results

Figure 1 shows the absorption spectra of 2 × 10^{-5} M ClAlPc colloid and ClAlPc solution in ethanol. The visible absorption spectrum (Q band) of the colloid has three maxima of almost equal intensity and is much wider than that of the solution. The maximal absorption coefficient of the colloid is about 7 times lower than that of the solution. The transient difference absorption (ΔA) spectra of ClAlPc colloid recorded at different delay times after excitation by the 200-fs pulses at 590 nm (1 mJ/cm^2 energy density) are presented in Figure 2A. The spectra show bleaching in the region of the shortest (~600 nm) and longest (~800 nm) components of the visible absorption spectrum and induced absorption between the Soret and visible absorption bands (400–550 nm). A weak induced absorption is observed in the region of the central visible absorption component (~700 nm). The transient difference spectra evolve in time; in addition to a proportional decay of the entire spectrum, a blue shift of the long wavelength edge of the ~400–570-nm induced absorption band and relaxation of the bleaching in the 700–760-nm region take place during the first few picoseconds after excitation. These spectral shifts are most clearly observed as a blue shift of the isosbestic point at ~570 nm, a red shift of the isosbestic point at ~700 nm, and a small red shift of the bleaching band maximum at ~800 nm (see Figure 2A). The changes are even more apparent in the computed early and late time–ΔA spectra of Figure 6. Kinetics measured at 570 and 715 nm (Figure 3) show that both the band-shift and the fast relaxation of the bleaching are complete within ~1 ps after excitation. Kinetics measured at other wavelengths (at low excitation energy <0.1 mJ/cm^2 where exciton annihilation is avoided) within the interval 400–900 nm exhibit very similar characteristics with a very fast (~1 ps) initial relaxation, only the amplitude of this component is wavelength dependent. The dynamics at later times (≥1 ps) is nonexponential and independent of probing wavelength but dependent on excitation intensity (Figure 4); the relaxation becomes faster when excitation intensity increases.

Transient difference absorption spectra measured with 25-ps duration pulses and with variable excitation wavelength were similar to those obtained with femtosecond pulses at longer delays. The shape of the spectra was independent both of delay time (on the picosecond time scale) and of excitation wavelength in the region 550–900 nm. Figure 5 shows the dependence on excitation energy density of the induced absorption at 500 nm measured with high energy picosecond pulses at 0 and 1 ns delay times. The induced absorption at zero delay time increases proportionally to the square root of the intensity, while at 1 ns delay time it saturates at a low level, when excitation energy density exceeds 0.1 mJ/cm^2 and starts to increase again from 2–3 mJ/cm^2. Further increase of excitation energy results in decomposition of the colloidal particles and appearance of individual molecules, revealed by a long-lived bleaching in the 650–700-nm region.

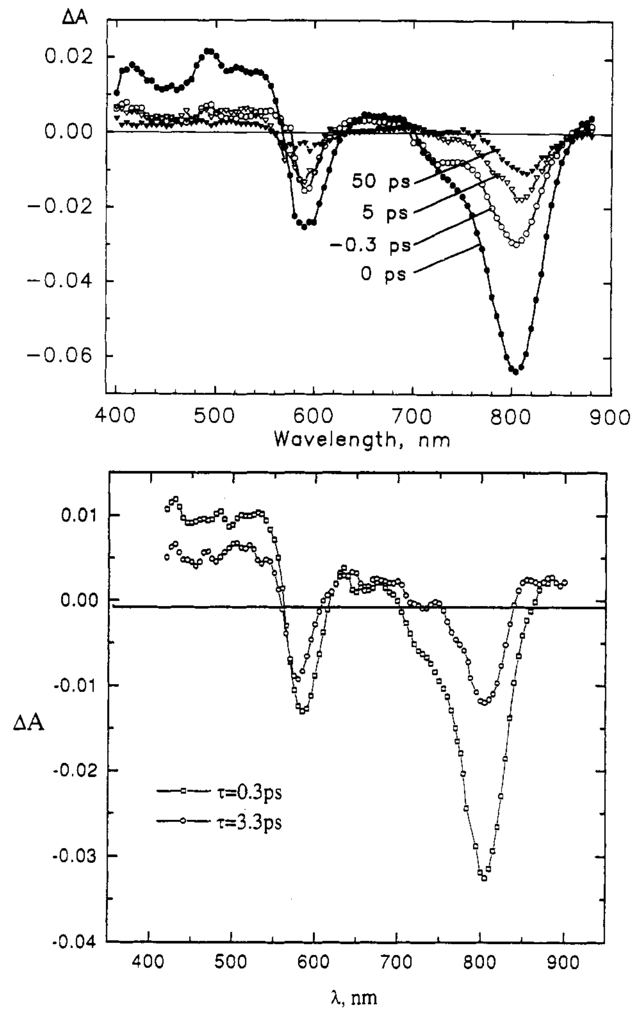

Figure 2. (A, top) Differential absorption spectra of ClAlPc colloid at various delay times after excitation by the 200-fs light pulses at 590 nm and 1 mJ/cm^2 energy density. (B, bottom) ΔA spectrum at 0.3 and 3.3 ps measured with 300-fs excitation pulses at 790 nm.

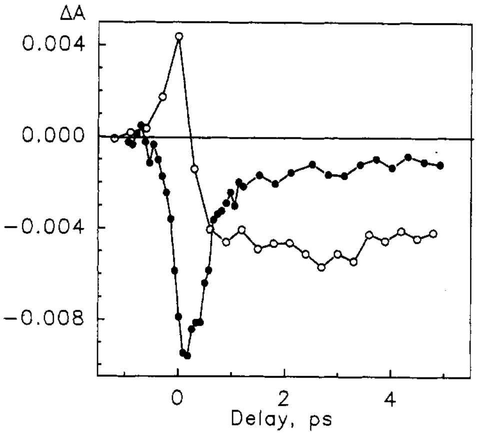

Figure 3. Absorption kinetics of ClAlPc colloid at 570 nm (open circles) and 715 nm (filled circles).

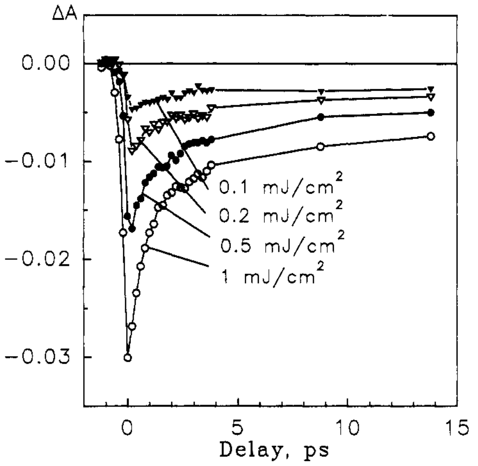

Figure 4. Absorption kinetics of ClAlPc colloid at 810 nm excited by various intensity light pulses.

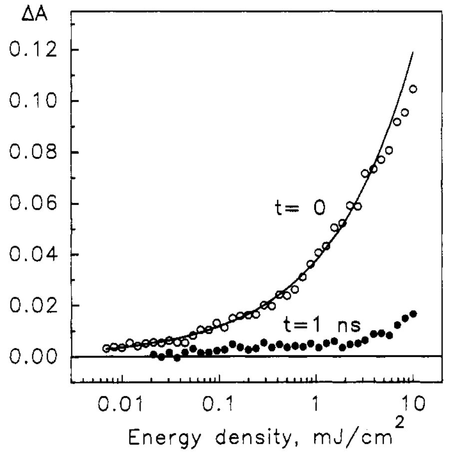

Figure 5. Dependence on excitation energy density of the induced absorption of ClAlPc colloid at 500 nm measured with 30-ps duration pulses at 0 (open circles) and 1 ns (filled circles) delay times. Excitation wavelength 630 nm. Solid line is square-root function.

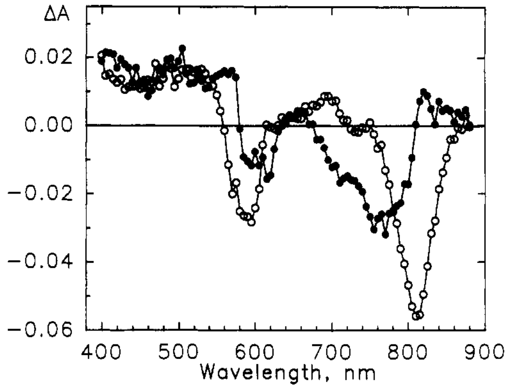

Figure 6. Calculated short-lived (ΔA_1) (filled circles) and long-lived (ΔA_2) (open circles) components of the differential absorption spectrum of ClAlPc colloid.

Discussion

Steady State Absorption Spectra. The absorption spectrum of ClAlPc colloid has a Soret band in the ultraviolet region and a broad band with three distinguishable maxima in the visible (Figure 1). Qualitatively the spectrum is similar to the spectra of phthalocyanine-doped polymer films or vapor-deposited films being in a crystalline phase (socalled phase II).[11,12] However, the optical density at the absorption maxima of the colloid layer is about 2–3 times lower than that of a vapor-deposited ClAlPc film, having the same number of molecules per unit volume. The similarity of the absorption spectra imply that the absorption cross sections of molecules in the colloidal particle and in the films are similar. The higher transmission of light in the colloid (at a given ClAlPc concentration) could be a result of high optical density for light going through large colloidal particles. Molecules being in a shadowed part of the particles give little contribution to the light absorption and a relative transmission enhancement is caused by the free space between the particles. For this reason the absorption coefficient of a colloid depends on the size of the particles; it decreases when the size of particles increases. An estimation based on a calculation of the dependence of absorbed light on the size of particles shows that the optical density of a colloid decreases by a factor of 2–3 if the optical density of the particles is approximately equal to 0.5–1.5, and a smoothing of spectral features is expected. Such an optical density corresponds to an average size of the phthalocyanine particles of several tens of nanometers. Nevertheless, the fact that the shape of the absorption spectrum of the colloid is similar to that of the solid thin films shows that, if present, these shadowing and smoothing effects do not cause major changes of the absorption spectrum, which in its turn shows that the light penetrates deep enough into the colloidal particles to probe its spectral properties.

Transient Difference Absorption Spectra. We will divide the discussion of the excited-state dynamics in two parts. First we will discuss the initial spectral evolution taking place during the first few picoseconds and then the slower decay of the entire excited-state population. A simple way to analyze the time-dependent spectral evolution of the transient absorption spectra of Figure 2 is to decompose the measured spectrum in two component spectra, corresponding to two different species or states whose concentrations vary in time. The transition to a second state (species) from the state (species) created by photon absorption occurs within approximately 1 ps (see Figure 3) and is most clearly observed at approximately 570 and 720 nm (Figure 3). With this interpretation of the spectral evolution, the measured difference absorption spectrum can be expressed as a sum of ΔA spectra related to the first (ΔA_1) and the second (ΔA_2) excited states (species): $\Delta A(\lambda,t) = N_1(t)\Delta A_1(\lambda) + N_2(t)\Delta A_2(\lambda)$, where N_1 and N_2 are occupation numbers of the respective excited states (species). The spectral component ΔA_2 corresponds to the ΔA spectrum, which settles a few picoseconds after excitation (when $N_1 \approx 0$). Due to the finite duration of the laser pulses, the pure spectral component ΔA_1 is not observed even at negative delays; it contains some fraction of the ΔA_2 spectrum. In order to obtain the true ΔA_1 spectrum, the intensities of the ΔA spectra at different delays were normalized to equal intensity at the long-wavelength bleaching band. We assumed that the intensity of the spectral component ΔA_1 in the region of this band is negligible, because the shape of this band is independent of time and there is no fast component in its decay kinetics. The spectrum ΔA_1 was calculated by subtracting the normalized long time difference spectrum from the normalized difference spectrum received at zero and negative delay times. Both calculated spectral components are presented in Figure 6. The ΔA_1 spectrum exhibits bleaching bands that matches the ~600- and ~700-nm features of the ground-state absorption spectrum (Figure 1). At wavelengths shorter than 500 nm there is a strong excited-state absorption, and the lack of bleaching at wavelengths corresponding to the ~800-nm ground-state absorption band could also be a result of excited-state absorption at these wavelengths. In the relaxed ΔA_2 spectrum the 800-nm ground-state absorption is visible as an intense bleaching, whereas the 700-nm band has been replaced by a weak induced absorption and the 600-nm bleaching is somewhat blue-shifted. This spectral evolution could essentially be described by a blue shift of excited-state absorption from ~800 to ~700 nm, occurring with a ~1-ps relaxation time. This blue shift could be associated with vibrational relaxation and internal conversion processes following the excitation of the short-wavelength component of the absorption spectrum Q-band.

Similar fast relaxation processes have previously been observed in various dye molecules[18] and porphyrin molecules[19,20] and attributed to vibrational energy relaxation and dissipation.

Another possibility to interpret the time evolution of the ΔA spectrum is that it corresponds to excitation energy transfer between phthalocyanine crystal forms or molecular species having different spectral properties. It was proposed by Huang and Sharp[16] that in VOPc in a polymeric matrix only the absorption bands with maxima at 635 and 840 nm belong to the crystalline phase II, while the absorption between those bands is related to the residual of the crystalline phase I. From X-ray diffraction investigations Yamashita et al. assigned the absorption band near 700 nm in VOPc and TiOPc molecular beam deposited films to the amorphous phase.[17] The one-dimensional nature of exciton diffusion in the colloidal particles (see below) suggests that different crystalline and amorphous phases are unlikely to form together in the colloidal particles. However, the middle absorption component at ~700 nm may be caused by the dislocations in the crystalline structure or by the edges of the crystallites. Then, the transient spectrum at long delays may be interpreted as a bleaching of the crystalline phase II absorption only, while the early time spectrum could correspond to a molecular species similar to the amorphous phase or crystalline phase I. The temporal evolution of the ΔA spectrum during the first picosecond would then be a consequence of energy transfer from this species to the crystalline phase II. In an attempt to distinguish between these two possibilities, time-resolved ΔA spectra of ClAlPc colloid were measured with the 790-nm to ~300-fs excitation pulses of a mode-locked Ti:Sa laser. The fact that very similar spectra and similar temporal characteristics were observed for both excitation wavelengths (see Figure 2A and B) suggests that vibrational relaxation only plays a minor role in the observed spectral relaxation. Work is in progress using excitation wavelengths tunable over the interval 540 to 750 nm in order to obtain further details about this process. In the experiments with 30-ps pulses, fast energy transfer could explain the absence of bleaching in the 650–750-nm region even when the excitation wavelength was within this region; if molecules of the phase corresponding to the 700-nm absorption occupy the excited state only less than 1 ps, it is obvious that the absorption bleaching of those molecules could not be observed with the 30-ps time resolution.

The applied procedure to determine the initial spectrum is valid only in the case of a transition between two states with spectra independent of time. In the case of a gradual transformation of ΔA_1 into ΔA_2, or when both transition and transformation takes place simultaneously, this method gives only approximate information about the initial spectrum. The presence or absence of isosbestic points in difference spectra usually serve as a criterion to distinguish between the two mechanisms. In order to determine isosbestic points in the case of variable density of excitations, the difference spectra should be normalized to the excitation density. Unfortunately, limited accuracy of measurement of transient spectra and of determination of excitation density prevented us from doing this.

The steady-state spectrum of ClAlPc colloid is qualitatively similar to the spectra of phthalocyanine solids and the transient difference spectrum at long times (>1 ps) of the colloid is qualitatively similar to the corresponding spectra of phthalocyanine films,[13-15] but quantitatively they exhibit some differences. Thus, in addition to the long-wavelength bleaching band at 800 nm, which is also observed in FAlPc, ClInPc, and VOPc films,[13-15] there is a relatively strong bleaching at approximately 600 nm. The latter bleaching band is more intense in the colloid than what is normally observed in the films. In the wavelength region 630–700 nm between the two bleaching bands, there is a broad structureless induced absorption of low intensity in the colloid, whereas in the film there is a weak bleaching. From the low intensity bands of either sign in the colloid and films, it appears likely that the spectrum in this region is dominated by strong excited-state absorption, and the sign of the observed spectrum (bleaching or absorption) is simply determined by the relative magnitude of the involved extinction coefficients. In a FAlPc film Williams et al.[13] observed subpicosecond spectral shifts similar to those described above for the ClAlPc colloid. During the first few hundred femtoseconds after 615-nm excitation, the ~800-nm bleaching band underwent an apparent red shift which was accompanied by a blue shift of the induced absorption around 500 nm. These spectral transients were interpreted as formation of a subgap (two-photon) state from which induced excited-state absorption was suggested to occur. However, it should be noticed that the absorption bleaching signal, which is due to bleached ground-state molecules, is not sensitive to excited-state relaxation processes unless there is excited-state absorption or stimulated emission gain at the probe wavelength. The energy transfer processes discussed above (or possibly vibrational relaxation) could be an alternative explanation to these observations.

Exciton Relaxation Dynamics. The strong dependence of the exciton relaxation dynamics in the ClAlPc colloidal particles on the excitation intensity (Figure 4) implies that interaction between the excitons is essential. Migration of excitons via the dipole–dipole mechanism and annihilation of the excitons is usually considered to be the consequence of the interaction, resulting in the increase of the exciton relaxation rate, when excitation intensity is increased. When annihilation takes place, the dynamics of exciton density n^* may be expressed by the equation:

$$\frac{\mathrm{d}n^*}{\mathrm{d}t} = [(N-n^*)\sigma_0 - n^*\sigma_{\mathrm{em}}]I(t) - \frac{n^*}{\tau} - \frac{1}{2}\gamma(n^*)^2 \qquad (1)$$

where σ_0 is the ground-state absorption cross section, σ_{em} the excited-state stimulated emission cross section, N the density of molecules, $I(t)$ the excitation pulse intensity, τ the intrinsic lifetime of excitations, and γ the annihilation rate constant. If τ is long in comparison with the inverse of the exciton relaxation rate caused by the annihilation, it follows from eq 1 that the density of excitons under the conditions of stationary excitation is proportional to the square root of the light intensity. In the case of pulsed excitation, when light pulses are not very short, i.e. longer than the average lifetime of the excitons, this relationship should be approximately valid for the maximum of the ΔA temporal dependence ($\mathrm{d}n/\mathrm{d}t = 0$). Some deviation from a square-root dependence could exist at low excitation intensity when the annihilation is slow and the lifetime of the excitons is long. The experimentally measured energy dependence of ClAlPc colloid bleaching at zero delay (Figure 5) is close to a square-root function, which confirms that annihilation plays a crucial role in the exciton relaxation process. The deviation of the experimental data from a square-root dependence observed at very high excitation intensities is probably caused by saturation of excitations. The saturation of bleaching at 1-ns delay is in agreement with annihilation theory and follows from eq 1.

Equation 1 is obtained from classical binary collision theory, but the motion-limited diffusion theory as well as annihilation via Förster long range dipole–dipole interactions leads to a time-dependent annihilation constant, which can approximately be expressed as $\gamma = \gamma_0 t^{-h}$,[21,22] where h may attain values between $^1/_6$ and $^1/_2$, the exact value depending on the dimensionality of the exciton motion. Then, if the linear relaxation is slow, n/τ is small, the solution of eq 1 gives the temporal dependence of the exciton density as

$$n^* = (1/n^*_{t=0} + 2\gamma_0 t^{1-h})^{-1} \qquad (2)$$

where $n^*_{t=0}$ is the exciton density at time zero.

Decay curves calculated from eq 2 were fitted to the experimental ΔA kinetics at different wavelengths to find the parameter h. The best agreement was found for $h = {}^1/_2$, which

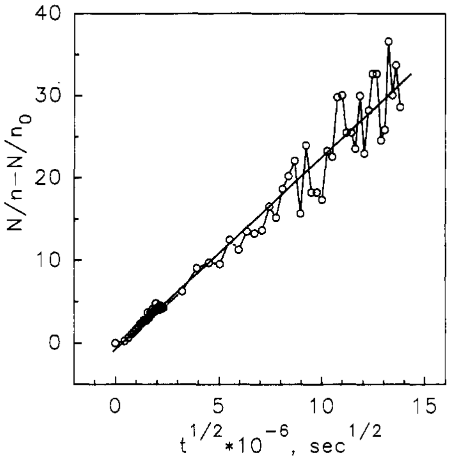

Figure 7. Plot of $N/n - N/n_0$ versus $t^{1/2}$. Exciton densities n and n_0 were calculated from the absorption decay kinetics at 480 nm.

corresponds to the case of one-dimensional diffusion-limited annihilation, or static annihilation via Förster interactions. The static annihilation hardly can be dominating because the exciton hopping probability decreases with distance as r^{-6}; therefore stochastic motion of singlet excitons via hopping between neighboring molecules should be much more probable than the long distance energy transfer between nonneighbor excited molecules. A low-dimensional diffusion is expected because phthalocyanine crystals have a columnar-like stacked structure with different closest-neighbor distances within a plane of molecules and between such planes, the interplane distance being the smallest. Exciton hoping can therefore have preferred directions due to the different distances and/or orientations between neighboring molecules. Exact solution of the one-dimensional diffusion-limited Smoluchowski-type equation[6,23] gives an expression for γ_0:

$$\gamma_0 = \frac{(32D/\pi)^{1/2}}{2dN} \tag{3}$$

were D is the exciton diffusion coefficient and N is the density of molecules. Now eq 2 can be rewritten to yield the fraction of excited molecules:

$$\frac{n^*}{N} = \left(\frac{N}{n^*_{t=0}} + \frac{(32D/\pi)^{1/2}}{d}t^{1/2}\right)^{-1} \tag{4}$$

The fraction of excited molecules is related to ΔA via $n^*/N = \Delta A/A \times [\epsilon_0/(\epsilon_0 - \epsilon_1)]$, where ϵ_0 and ϵ_1 are extinction coefficients of molecules in the ground and excited states. Unfortunately ϵ_1 is unknown, but there are some indications (good agreement in the long wavelength edge of absorption and bleaching spectra and the absence of induced absorption in the 850–870-nm region, at times > 1 ps) that ϵ_1 at 800 nm is much smaller than ϵ_0, while at 600 nm $\epsilon_1 \approx 0.7\epsilon_0$.

In Figure 7 the time dependence of the excitation density is plotted as $N/n^* - N/n^*_0$ versus $t^{1/2}$. The linear dependence confirms one-dimensional exciton annihilation and the diffusion coefficient of excitons could be determined from the slope of the linear plot. Assuming that the distances between molecules in the colloidal particles are similar as in solids ($d \approx 4.5$ Å), the diffusion coefficient determined from the absorption decays at different wavelengths and excitation intensities was found to be in the interval (1–5) × 10^3 cm^2 s^{-1}. The exciton hopping time can be calculated from the relation $\tau = d^2/2D$, and it was found to be equal to 0.2–1 ps. Due to uncertainty in the determination of several parameters, these values are approximate.

Heating of the Material. Through the discussion thus far we have ignored the heating of the colloidal particles, although the local heating was found to play a significant role in ultrafast spectroscopy of phthalocyanine films.[8,10] We observed no manifestations of temperature increase of the material on spectral and dynamical properties of the excited colloid. Only the energy dependence of bleaching measured at 1-ns delay with picosecond pulses shows that a certain temperature increase takes place. The increase of the bleaching when excitation energy is higher than 3 mJ/cm^2 we relate to the heating of the material. It is reasonable to expect the manifestation of heating at long delay times, when the degree of electronic excitation is low and its energy is converted into heat. Due to saturation of electronic excitation and due to the linear dependence of temperature increase on excitation energy, at long delay times and at high excitation intensity the absorption change caused by heating becomes comparable and even bigger than that caused by electronic excitation. Nevertheless, the temperature influence on transient absorption is much weaker in the colloid than what was observed in films; in a VOPc film under similar experimental conditions, heating-induced absorbance changes were of similar magnitude as absorbance changes of electronic excitation origin, also at short delay times.[10] This difference is probably a result of efficient heat energy transfer from the colloidal particle to the solvent. Heat transfer from a single large molecule to the solvent takes several picoseconds,[18] but in a colloidal particle having a size of tens or hundreds of nanometers this process is determined by the heat diffusion rate and should occur on a nanosecond time scale. Phthalocyanines in the crystalline solid state have a columnar structure; therefore it is likely that colloidal particles have a needle-like shape or are composed from many such needles. Heat transfer from colloidal particles in this case could be almost as fast as from a single molecule.

Conclusions

In conclusion, a ClAlPc colloid was made, which, judging by the absorption spectrum, has colloidal particles with crystalline phase II structure. The excited-state dynamics of the colloidal particles have some features in common with that of phthalocyanine films: absorption bleaching only in part of the wide complex Q-band, femtosecond initial excitation energy redistribution, and exciton annihilation as a main excited-state decay channel. Two different explanations of the observed transient absorption spectral shape and time evolution were discussed: (i) fast (≤1 ps) relaxation between two different excited states (vibrational relaxation), both having strong excited-state absorption in the 700–800-nm spectral region, and (ii) that the absorption spectrum is a result of two different molecular species, and fast (≤1 ps) electronic energy transfer occurs between the two species. By using two excitation wavelengths on the blue and red side of the absorption spectrum, respectively, it was concluded that vibrational relaxation probably is of minor importance for the observed ~1-ps spectral relaxation. The reduced heating of the colloidal particles in comparison to phthalocyanine films enabled us to carry out a detailed investigation of the exciton decay dynamics. Exciton–exciton annihilation with a time-dependent annihilation "constant" was found to be the main relaxation channel. The annihilation "constant" varies as $t^{-1/2}$, which is characteristic of a one-dimensional exciton diffusion. A 0.2–1-ps exciton hopping time was determined from the excitation decay kinetics. The results of this work show that colloids of ClAlPc, offering experimental conditions which minimize the interference from temperature-induced spectral changes, are useful systems for the study of excited-state dynamics of space-limited structures.

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