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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 (≤1 ps) excited-state dynamics. Exciton decay was found to be dominated by exciton–exciton annihilation with a r−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 fact that no transient absorption signal attributable to the monomer is detected within the detection limit of ΔA ≥ 5 × 10−4 OD results in an upper limit of residual monomer concentration of 0.2%. The colloids remained stable more than a month after preparation, and it was light stable up to a 10 mL/cm2 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 DU spectrophotometer (Model UV 5200). 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 range. 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 divided by a factor of 5). The concentration of ClAlPc was $3 \times 10^{-5}$ 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 $2 \times 10^{-5}$ 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 ($\Delta A$) 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-$\Delta A$ 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 (~2–3 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.
the absorption coefficient of a colloid depends on nanometers. Nevertheless, the fact that the shape of the absorption spectrum of the colloid 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. 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.

Transient Difference Absorption Spectra. We will divide the discussion of the excited-state dynamics into 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 into 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. Excitation with a 30-ps laser pulse is not adequate for probed the spectral properties.

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 (so-called phase II). However, the optical density at the absorption maxima of the colloidal 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 implies 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.

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 (so-called phase II). However, the optical density at the absorption maxima of the colloidal 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 implies 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.

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Similar fast relaxation processes have previously been observed in various dye molecules and porphyrin molecules and attributed to vibrational energy relaxation and dissipation.

Another possibility to interpret the time evolution of the $\Delta \lambda$ 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 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. 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 $\Delta \lambda$ 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 $\Delta \lambda$ spectra of CIAIpc 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 $\Delta \lambda_1$ into $\Delta \lambda_2$, or when both transition and transformation take place simultaneously, this method gives only approximate information about the initial spectrum. The presence or absence of isosbestic points in difference spectra usually serves 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 CIAIpc 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, but quantitatively they exhibit some differences. Thus, in addition to the long-wavelength bleaching band at 800 nm, which is also observed in FAIpc, CIInPc, and VOPc films, 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 FAIpc film Williams et al. observed subpicosecond spectral shifts similar to those described above for the CIAIpc 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 excitation relaxation dynamics in the CIAIpc 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:

$$\frac{dn^*}{dt} = [(N - n^*) \sigma_0 - n^* \sigma_{em}] I(t) - \frac{n^*}{r} - \frac{1}{2} \gamma (n^*)^2$$

where $\sigma_0$ is the ground-state absorption cross section, $\sigma_{em}$ the excited-state stimulated emission cross section, $N$ the density of molecules, $I(t)$ the excitation pulse intensity, $r$ the intrinsic lifetime of excitations, and $\gamma$ the annihilation rate constant. If $r$ is long compared 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 $\Delta \lambda$ temporal dependence ($dn/dt = 0$). 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 CIAIpc 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-nm 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 $\gamma = \gamma_0 e^{-h/\lambda}$, where $h$ may attain values between $1/e$ and $1/2$, the exact value depending on the dimensionality of the exciton motion. Then, if the linear relaxation is slow, $r/h$ is small, the solution of eq 1 gives the temporal dependence of the exciton density as

$$n^* = \left(1/n^*\|_{\tau = 0} + 2 \gamma_0 \tau^2 e^{h/\lambda}\right)^{-1}$$

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

Decay curves calculated from eq 2 were fitted to the experimental $\Delta \lambda$ kinetics at different wavelengths to find the parameter $h$. The best agreement was found for $h = 1/2$, which
different wavelengths and excitation intensities was found to be equal to 0.2-1 ps. Due to uncertainty in the determination of several parameters, these values are approximate.

As the diffusion coefficient determined from the absorption decays at times $t > 1$ ps is unknown, but there are some indications (good agreement in the reduced 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.

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, 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 CIAIPc 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 $r^{-1/2}$, 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 CIAIPc, 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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References and Notes

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