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Exciplex−Exciplex Energy Transfer and Annihilation in Solid Films of Porphyrin−Fullerene Dyads

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The excited-state inter-chromophore interactions play an important role in photochemistry of organized molecular systems. In densely packed molecular assembles, the interaction of the most importance are excited-state energy transfer and annihilation, which affects strongly photodynamics of the excitation relaxation. These phenomena were found and studied in a number of natural and artificial systems, such as natural photosynthesis,[1] polymers,[2] dendrimers,[3] and self-assembled and covalently linked molecular arrays.[4]

The energy transfer and annihilation are usually observed for singlet excited states but also known for triplet excited states.[5] Herein we report on the first experimental observation of the exciplex−exciplex annihilation in self-organized films of porphyrin−fullerene dyads. In addition, exciplex−exciplex energy transfer preceding the annihilation is very probable in the films.

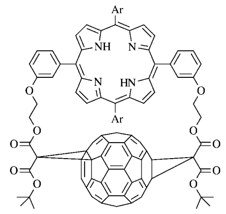
A double-linked porphyrin−fullerene (PF) dyad was used in this study (Chart 1).[6] It is characterized by a short inter-chromophore distance, which enforces a fast formation of the intramolecular exciplex (<0.5 ps in toluene). In relatively nonpolar media, the exciplex has a nanosecond lifetime and can be observed as emitting state in the near-IR region.[6,7] The exciplex is characterized by a gradual shift of the electron density from the porphyrin to fullerene moiety and can be viewed as a partial charge separates state. Noticeably, the exciplex can relax to a complete charge separated (CS) state, yielding porphyrin cation and fullerene anion radicals.

The structure and photochemical properties of the double-linked PF dyads make them attractive candidates for nanochemistry applications. In particular, using Langmuir−Blodgett (LB) technique mono-molecular films with uniform orientation of donor and acceptor moieties can be fabricated.[8] The films perform vectorial CS under light illumination and can be used as, e.g., primary charge separating layers in solar cell applications.

In LB films, the dyads are packed close to each other at distances approaching van der Waals contacts. This enforces intermolecular interactions of the photoexcited species. Femto- to picosecond spectroscopy, such as pump−probe, is a widely used tool to study the fast excited-state interactions. Unfortunately, it cannot be applied to study the dyad monolayers because the absorption of monolayers is too low to achieve an acceptable signal-to-noise ratio. To overcome the problem, multilayer LB films were prepared, but after a few tens of LB layers, the absorption increments for each consecutive layer are smaller than in the beginning of the sample preparation. Therefore, depositions were terminated after transferring 50−60 layers, which gives roughly 0.4 absorption at Soret band maximum (see Supporting Information, Figure S1). Drop casted films were prepared to obtain samples with higher absorption and thus to provide a better signal-to-noise ratio in pump−probe measurements. It was found that the primary photoprocesses were practically the same in LB and drop casted films (as detailed in the Supporting Information).

A well-pronounced exciplex emission in the near-IR wavelength region was detected for drop casted films (see Supporting Information Figure S2).[9] Noticeably, the exciplex emission spectra of the drop casted film and toluene solution are virtually the same. An average lifetime of exciplex measured by time correlated single photon counting method was approximately 1 ns, which is also in agreement with the lifetime in toluene (Supporting Information, Figure 4).

Chart 1. Porphyrin−Fullerene (PF) Dyad[a]



[a] (Ar = 3,5-di-*tert*-butylphenyl).

The pump−probe measurements indicated a fast formation of the intramolecular exciplex (Figure 1). Unlike in liquid phase[6] the porphyrin locally excited singlet state was not time-resolved in films, suggesting that the relaxation of the locally excited-state to the exciplex is faster than the time resolution of the instrument used, i.e., <100 fs.

The transient absorption signal decays gradually during few tens of picoseconds, but the shape of the spectrum remains practically the same at different delay times, as can be seen from Figure 1. The decay time profiles of the exciplex are exampled in Figure 2 at 700 nm (the maximum of the exciplex band). The shapes of the decays have clear fast and slow components and depend strongly on the excitation energy. At higher excitation densities, the decays are faster and relative contribution of the fast component is greater. After fast relaxation (a few picoseconds delay) the remaining signal intensity is virtually independent of the excitation density.

The observed dependence on the excitation density (Figure 2) is typical for exciton−exciton annihilation behavior; also, in this particular case, the excitons are the exciplexes.[10] The nature of the annihilation can be an electrostatic interaction between the exciplexes. A strong dipole moment of exciplex, 13 D,[7] may affect energetics of a neighbor exciplex forcing a faster relaxation.

At least starting from 0.6 mJ/cm^2 excitation density the fast decays (as shown in Figure 2) do not fit to a monoexponential law. In turn, the second-order decay model gives a good approximation of the data at all densities used. The latter can be interpreted in favor of the exciplex−exciplex energy transfer prior to the annihilation, because the energy transfer can be modeled by the second-order kinetic equation with reasonable accuracy,[2a] whereas in a “static” case one would expect faster but exponential decay of two neighbor exciplexes. Formally, the Förster-type exciplex−exciplex energy transfer between dyads is possible because there is an overlap between the emission and ground state absorption spectra of the porphyrin-fullerene complexes.[7] However, its efficiency is expected to be much lower than that of the porphyrin−

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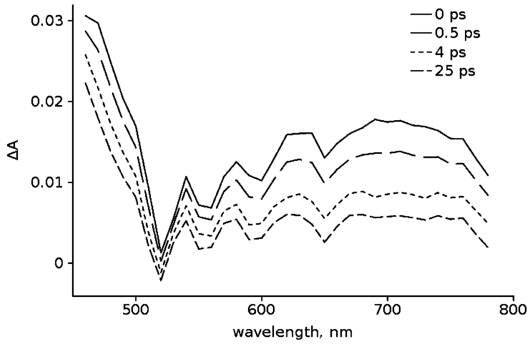

Figure 1. Transient absorption spectra of PF drop casted film at 0, 0.5, 4, and 25 ps delay time. The excitation density was 1.1 mJ cm^{-2} at 420 nm.

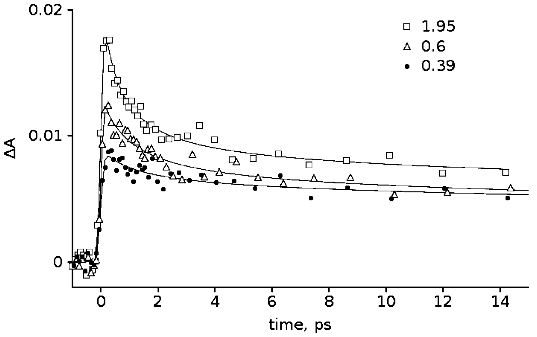

Figure 2. Transient absorption decays at 700 nm. The excitation densities are indicated in the plot in mJ cm^{-2}. Solid lines show data fits with fast second order and slow exponential (140 ps) decay components. Exponential lifetime was kept constant at all excitation densities, and the second-order rate was fitted at each excitation density.

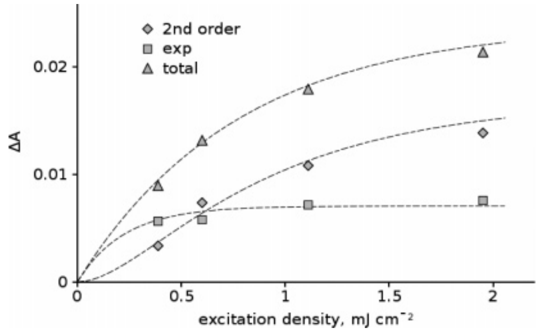

Figure 3. Excitation density dependence of the amplitudes of the second-order and exponential decay components and of the total signal intensity right after excitation. The dependences trend lines were calculated assuming that in average four dyads are participating in excitation energy transfer and annihilation.

porphyrin singlet state energy transfer because the Stokes shift is larger and the absorption and emission intensities are lower.

The dependence of the intensities of the second-order and exponential components of the transient absorption decays on the excitation density is presented in Figure 3. The sum of the components gives the total signal intensity right after the excitation. The total intensity is proportional to the number of excited molecules before the annihilation, and the intensity of the long-lived exponential component is proportional to the number of molecules which have survived the annihilation. The trend lines for the dependences were calculated using a simple exponential excitation dependence model (see Supporting Information for details). The difference between excitation dependences of the responses before and after annihilation suggests that only one of four dyads remains excited at a few picoseconds delay time, e.g., in average four dyads are involved in exciton energy transfer and annihilation process.[11]

In conclusion, the intramolecular exciplexes of porphyrin−fullerene dyads can interact with each other enforcing faster subpicosecond relaxation of the excitation. This behavior is analogous to the exciton−exciton energy transfer and annihilation of the singlet excited states.

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Supporting Information Available: Absorption and emission spectra of LB and drop casted films, emission decays of drop casted films, pump−probe measurements of LB film, and calculation details for trend lines in Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) For LB films, the exciplex emission was sensitive to the type of matrix molecules used, e.g., octadecanoic acid or amine, and relatively less intense. Presumably the differences in local (micro) environment and following complete charge separation are responsible for the difference. A detailed investigation of the cause is on the way at present.

(10) The annihilation is a two-particle reaction, and it strongly depends on the density of the excited states—at higher excitations, the relaxation is faster. Similar type of behavior was reported in refs 1b,1d, 2a, 3b, and 4c for the singlet−singlet annihilation.

(11) In LB films, the proportion is roughly the same despite the fact that the dyads are placed in octadecylamine matrix. This indicates that the dyads are arranged in clusters with structure similar to that in drop casted films.

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