Energy Migration in Hierarchic Structures of Polymer Microdomes Containing Two Cyanine Dyes

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Dewetting of a polymer solution was used to prepare micrometer-sized 'domes' of polymers. Co-casting two different cyanine dyes led to the incorporation of the dyes into the microdomes. Fluorescence microscopy and micro-spectroscopy was used to determine the aggregation state of the dyes within the microdomes. Bleaching experiments revealed that the dyes form hierarchic structures: dye molecules form sub-micrometer J-aggregates, which in turn align at the edge of micrometer-sized domes that form 2-dimensional arrays. Furthermore, it was found that energy migration occurs between different aggregates. [DOI: 10.1380/ejssnt.2005.165]

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I. INTRODUCTION

Nano-to-micro-sized arrangement of dyes and dye aggregates is important to study energy migration properties. One important example of the effect of nanoscale arrangement of porphyrin dyes in nature are the so-called antenna protein complexes surrounding the photosynthetic reaction center in algae and green plants [1, 2]. Mimicking this process is one of the most ambitious goals in chemistry and physics. It would allow the harvesting of sunlight and converting it into chemical forms of energy. Several approaches have been made to reach the precise arrangement of dyes and sensitizers: linking organic dyes covalently [3], or via coordination bonds [4], and synthesis of colloidal nanocrystal heterostructures of cadmium tellurides, sulfides or selenides [5]. Both, organic as well as inorganic, approaches control the dye arrangement on the scale of one to a few nanometers.

Here we describe the formation of controlled arrangements of organic cyanine dye J-aggregates in polymer 'microdomes' on the scale of tens of nanometers to micrometers.

Cyanine dyes are an important class of organic dyes. They have an ionic structure and an extended pi-system. Cyanine dyes readily aggregate into so-called J-aggregates, because of their large dipole moment and the extended and flat pi-system. The J-aggregates are characterized by red-shifted and narrow absorption and fluorescence spectra [9] and are used for sensitizers and energy transfer in photographic films [10].

Microdomes are fabricated by a dewetting process in which a dilute polymer solution is cast on a substrate. Solvent evaporation leads to a fingering instability at the edge of the solution and the precipitation of micron sized spherical polymer aggregates, the so-called microdomes [6]. By mixing two different dyes, it was possible to observe energy migration upon photo-excitation from one species to the other.

II. EXPERIMENTAL

The cyanine dyes, 3-ethyl-2-[3-(3-ethyl-2(3H)-benzothiazolylidene)-2-methyl-1-propenyl] benzothiazolium iodide (1) and 5,6-dichloro-2-[3-(5,6-dichloro-1,3-diethyl-2(3H)-benzimidazolylidene)-1-propenyl]-1,3-diethylbenz-imidazolium iodide (2) were purchased from Aldrich, Inc and used without further purification. Polystyrene had a Mw of 280,000 g/mol and was purchased from Aldrich Inc. Chloroform was spectroscopic grade from Merck.

Mica was cut into 2 × 5 cm² sheets and cleaved prior to casting. Casting was performed by placing a polystyrene solution (1 mg in 1 ml CHCl₃) close to the short edge of the mica substrate. A glass rod of 1 cm diameter was placed on top of the solution. Teflon spacers around the glass rod resulted in a 0.5 mm thick liquid film between rod and substrate. The rod was rolled over the substrate at constant speed of a few mm/min. This procedure ensures that a straight edge of the solution recedes at a constant speed over the substrate, which is a prerequisite for dewetting and ordered pattern formation of micrometer-sized polymer domes [7].

Concentration gradients of two dyes were achieved by placing a small droplet of a solution of 1 on the center of FIG. 1: Chemical structure of the used cyanine dyes.
FIG. 2: Schematic of the roller apparatus and the dewetting procedure to produce microdome arrays with concentration gradients of cyanine dyes.

of the mica substrate, prior to dewetting. The solvent evaporated and dye crystals were left on a spot with ca. 100 µm diameter. A solution of 2 in polystyrene/CHCl₃ was placed close to the edge of the mica substrate, as described above, and the solution passed over the spot where 1 was placed. This led to a slow solution of the dye crystals, and a concentration gradient of 1 and 2 in the 2-D array of polystyrene microdomes was produced.

An Olympus BX-51 microscope was used for optical and fluorescence microscopy. In situ bleaching experiments were carried out by irradiation through the microscope. A home built microspectrometer was used to measure the fluorescence spectra of single microdomes [8].

III. RESULTS AND DISCUSSION

We already have reported about the formation of J-aggregates of cyanine dyes of 1 in polystyrene microdomes [11]. It was found that the J-aggregates show dome-size dependent fluorescence spectra. The larger the dome, the more red-shifted the fluorescence [12]. This can be explained by the formation of larger J-aggregates in larger domes.

Figure 3 shows the fluorescence spectra of polymer microdomes that contain 5 wt% of 1 or 2. Both spectra are narrow, with a full width at half maximum (FWHM) of around 10 to 15 nm, and shifted as compared to the solution spectra of molecularly dispersed dyes in methanol. Compound 1 has a fluorescence maximum at 611 nm, 2 has a maximum at 596 nm. The spectra in methanol solution show several maxima, which can be expected for a dye that is molecularly dispersed. Compound 1 shows maxima at 564, 632, and 666 nm, and compound 2 at 529, 566, and 628 nm. This indicates that both compounds form J-aggregates in polystyrene microdomes when cast separately.

In the present study we are especially interested in energy migration between J-aggregates. Energy migration depends crucially on the average distance between energy donor and energy acceptor. Thus for finding the optimum reaction conditions, a series of samples, each with different concentrations and donor/acceptor ratios have to be prepared. By imposing a concentration gradient of one dye, we were able to circumvent the necessity for a large number of samples, since a variety of concentrations and donor/acceptor ratios can be prepared simultaneously.

Figure 4 shows the optical micrograph of a mixture of both dyes in the same sample. The dye concentration is 5 wt% for each dye and no macroscopic phase separation can be seen – the domes are transparent and have a regular 2-dimensional array. Fluorescence microscopy reveals that the cyanine dyes are located in the microdomes, as expected from previous experiments with single dyes. Since both dyes emit fluorescence at around 600 nm, they have similar red color and optical microscopy cannot be used to discriminate between both dyes.

Fluorescence microspectroscopy showed some unexpected results. Instead of having two sharp fluorescence peaks, as it would be expected for J-aggregates of both dyes co-existing in the same microdome, two broad fluorescence peaks were observed, as can be seen in Fig. 6. The peaks of the fluorescence are at around 590 and 620 nm. A weak peak at 613 nm is barely visible. That would indicate that 2 does not form J-aggregates and that 1 forms very little, if at all, J-aggregates. It has been known that mixing J-aggregate-forming cyanine dyes with structural analogues can disrupt J-aggregate formation [13]. This might be the case here, since both dyes have a similar structure and might form mixed aggregates, or other undefined species. The small peak at 613 nm indicates that some J-aggregates of 1 are formed nevertheless. The broad peaks can come from to monomer, dimer or aggregates other than J-aggregates.

Drastic changes occur in the fluorescence spectrum when the sample is irradiated in the fluorescence microspectrometer with 532 nm laser light. Both broad peaks decrease in intensity and, surprisingly, the J-
aggregate peak at 613 nm increases in turn. Photoinduced generation of J-aggregates is rare and only observed for photochromic systems [14], so this can be ruled out in the present case. Thus we conclude that the drastic increase in J-aggregate intensity can be attributed to energy transfer, based on the following model.

J-aggregates of 1 are produced during the casting of the solution, but the energy is transferred to lower lying energy states of undefined species (monomer, dimer, excimer of 1, 2 or mixtures of both). These low-energy states then emit light at wavelength longer than 613 nm. These undefined species also are responsible for the broad emission at 590 nm. J-aggregates are more stable against photobleaching than these undefined species and thus these species bleach faster, leading to a decrease in fluorescence intensity at 590 and 620 nm. Now, the excitation energy cannot be transferred to the lower-lying states anymore, and the J-aggregates start to emit fluorescence at 613 nm. This model implies several notable features:

(1) J-aggregates are intimately mixed with other fluorescent species of cyanine dyes. For Förster energy transfer to occur, the distance between energy donor and acceptor must be smaller than 10 nm.

(2) Photobleaching does not produce non-fluorescent trap sites, to which the excitation energy of the J-aggregate could migrate.

In order to gain an insight into the spatial distribution of the dyes, fluorescence microscopy was performed. One can clearly see that the fluorescence intensity is nonhomogeneous from the very start of the experiment (Fig. 7). Upon photobleaching, the center of the microdome darkens, whereas the bright spots at the rim are stable. We have already reported the preferential formation of J-aggregates along the rim of a polymer microdome [15] and conclude that the rim is made of J-aggregates of 1. The center, and also parts of the rim are occupied by other aggregate states of both dyes.
FIG. 7: Fluorescence microscope images of a single microdome containing 5 wt% of 1 and 2 during photobleaching. The diameter of the dome is 7 µm.

IV. CONCLUSIONS

By a simple dewetting process ordered arrays of dye-containing polymer microdomes could be prepared. Mixing two cyanine dyes in these domes leads to the formation of J-aggregates of one dye and other, yet undefined aggregates of the second dye. Multi-step excitation-energy transfer from high energy states of the undefined species to J-aggregates and to further to low-lying energy states of the undefined species was observed. Photobleaching revealed the spatial segregation of J-aggregates from the undefined species on the (sub)micrometer scale.

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