

Photostability of *J*-aggregates adsorbed on TiO₂ nanoparticles and AFM imaging of *J*-aggregates on a glass surface

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ABSTRACT. Spectral properties and photostability of the 5,5'-6,6'-tetrachloro-1,1'-dioctyl-3,3'-bis-(3-carboxypropyl)-benzimidacarbocyanine (Dye 1) *J*-aggregate was investigated in solution and upon adsorption on TiO₂ nano-particles. Dye 1 was found to photodegrade on the surface of TiO₂. Additionally, the self-assembly of Dye 1 was studied on a glass surface by non-contact atomic force microscopy (NCAFM). The dye molecules form a well-defined fiber like structure that extends for tens of micrometers. The internal structure of the fibers was clearly resolved and showed a number of small tubes wrapped around each other to form a helical structure.

1. INTRODUCTION

In the last decade cyanine dyes have attracted much attention due to their interesting self-assembly which has a strong effect on their spectroscopic properties. It is well known that they form closely packed assemblies in concentrated aqueous solutions, characterized by the appearance of a new and very narrow red-shifted absorption band, with respect to the monomer absorption. This enables light energy migration over tens of molecules in the assembly [1]. Polymethine dyes have a very high π -electron polarizability in the ground state, which is large enough to form ground state π - π complexes [2-10]. Such complexes are well known as dye *J*-aggregates [11]. *J*-aggregates have potential application in solar cells [12-14], photographic processes, charge generation in electrophotography, new laser materials, molecular electronics, displays and nonlinear optical devices and for water splitting in presence of strong electron acceptors.

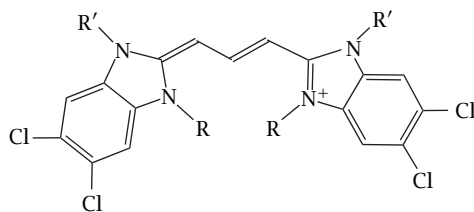


Figure 1. Chemical structure of Dye 1. where R = (CH₂)₃COOH or (CH₂)₃COO⁻ and R' = (CH₂)₈H.

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Recently, derivatives of 5,5'-6,6'-tetrachlorobenzimidacarbocyanine chromophore having 1,1'-dialkyl substituents combined with 3,3'-bis(4-sulfobutyl)-3,3'-bis(4-carboxypropyl) or 3,3'-bis(3-carboxypropyl) substituents have been investigated with a variety of techniques to probe the structure of their *J*-aggregates [15]. A strong dependency on the chemical substitution of the monomer was observed. The superstructures range from monomolecular layers, stacks of bilayer ribbons, to twisted ropelike structures. Surprisingly achiral derivatives of the cyanine dye were found to form chiral *J*-aggregates. This was explained in terms of the packing pattern which enables the most stable hydrogen bonding between the molecules leading to a twist of the molecules in a right or left handed arrangement. Nevertheless, a majority of left-handed aggregates was observed [16]. A similar observation for a system of chemical linked chiral porphyrins has been reported. Nolte et al. has explained this observation through a chirality transfer mechanism: The S-chiral centers in the molecules induce a clockwise orientation of the molecules which aided by strong π - π stacking, leads to the formation of fibers with right-handed helicity. Side-on aggregation of the fibers subsequently yields supercoiled structures with left-handed helicity [17]. The above mentioned observation along with more recent reports [18], indicate that the left handedness of ropelike supramolecular assemblies appears to be a general trend, regardless of the chirality of the monomer units.

In this contribution we report on the spectral properties and the photostability of the *J*-aggregates of the achiral Dye 1 in ethanol and upon adsorption on the surface of TiO₂ nanoparticles. Furthermore, using non-contact atomic force microscopy (NCAFM), topography

images of the *J*-aggregates of Dye 1 adsorbed on a glass surface are presented. NCAFM images clearly indicate the left-handedness of the assemblies on the glass surface. To our knowledge this is the first time direct topography AFM images of the helicity have been reported for such systems.

2. EXPERIMENTAL

The *J*-aggregating 5,5-6,6-tetrachloro-1,1-dioctyl-3,3-bis-(3-carboxy-propyl)-benzimidazole-carbocyanine (Dye 1) was obtained from FEW Chemicals GmbH, Wolfen, Germany and was used as received. An X-DAP spectrometer (polytech, Germany), α -Helios Pye Unicam spectrophotometer and a Shimadzu 5100 spectrofluorophotometer were used to measure the UV-VIS reflectance, absorption and fluorescence spectra, respectively. Dye 1 was adsorbed on TiO₂ nanoparticles suspended in the solution then centrifuged to obtain a dry solid sample for the reflectance spectra. 75 W Xenon arc lamp (PTI-LPS-220 Photon Technology International) was operated at 70 W. The light intensity was measured using a radiometer (IL 1700 International Light) and was found to be 13.2 W/cm²·min. Full light was used for irradiation in the presence of air. Spectroscopic pure ethanol was used. TiO₂ nanoparticles (Degussa P25) were used as received.

Dye 1 was dissolved in an aqueous solution of 10 mM NaOH. A stock solution of 2.8×10^{-4} M of the dye was prepared through stirring at room temperature for at least 24 h. A drop from this solution was spin coated (2500 RPM) at room temperature on a clean glass surface for atomic force microscopy (AFM) measurements. The samples were imaged under ambient conditions with a Discoverer TMX 2010 AFM system (Thermomicroscopes, San Francisco, CA), operating in the non-contact mode. In non-contact AFM (NCAFM), the spacing between the tip and the sample is on the order of tens to hundreds of angstroms. The probe is in the attractive force region, and the cantilever is pulled towards the surface. The total force between the tip and the sample in the non-contact regime is very low, generally about 10^{-12} N. This low force is advantageous for studying soft elastic samples. For the NCAFM measurements, Si-probes (Thermomicroscopes, San Francisco, CA) were used, with a spring constant of 36–49 N/m and a resonance frequency of 182–193 KHz. In all the AFM images shown, bright image intensity corresponds to a relatively high surface region whereas a low intensity corresponds to a relatively low surface region.

3. RESULTS AND DISCUSSION

3.1. Photostability studies. *J*-aggregates have served as an important spectral sensitizer in silver halide photographic materials as the electronically excited *J*-aggregate can effectively inject photoelectrons

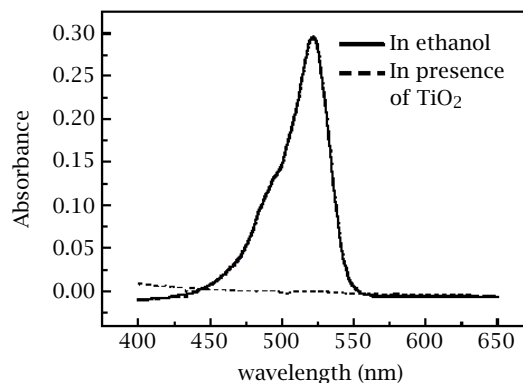


Figure 2. Absorbance spectrum of Dye 1 in ethanol (solid curve), and absorbance of Dye 1 in ethanol in the presence of TiO₂ suspension (dashed curve). Dye 1 is completely adsorbed on the TiO₂ surface.

into the conduction band of AgX. Its sharp absorption band allows easier control over the spectral sensitivity of the photoimaging system. Similarly, a remarkable adsorption of Dye 1 (from 10^{-6} M ethanol or 10 mM NaOH solutions) on TiO₂ nanoparticles was observed and leads to nearly a complete decay of the absorption band, Figure 2 (dashed curve). This prompted us to explore the possibility of Dye 1 for application as a light antenna molecule in dye sensitized solar cells. As a first step in this process, photostability studies of the adsorbed dye molecules were carried out. Figure 3 shows the change of the apparent absorbance (Figure 3(B)) obtained from the reflectance spectrum (Figure 3(A)) of dye 1 on TiO₂ nanoparticles with time of light illumination. Very fast bleaching of the color of Dye 1 was observed ($t_{0.5} = ca$ 15 seconds) compared with the relatively larger value of $t_{0.5} = ca$ 150 seconds obtained for the dye in ethanol, Figure 4. The quantum yield of the photodegradation of Dye 1 in ethanol and adsorbed on TiO₂ nanoparticles was found to be 0.02 and 0.2 respectively. The color bleaching of Dye 1 physisorbed and/or chemisorbed on the TiO₂ surface is due to light absorption induced reactions with e/h^+ pair that might be formed either from the TiO₂ or the *J*-aggregates adsorbed on the surface and/or an active oxidative species generated on the surface of TiO₂.

3.2. Solvent effect. It is well known that the *J*-aggregate of cyanine dyes is a unique molecular assembly characterized by an extraordinary sharp absorption and a resonance fluorescence that is red-shifted from the monomer band. In this work we found that Dye 1 has a remarkable capability to sense the polarity of the environment. The absorption spectrum of a dilute solution of Dye 1 in ethanol is shown in Figure 5. Adding a NaOH solution results in a trifold split of the absorption spectrum, (Figure 5) due to the formation of *J*-aggregates. A negative solvatochromic behavior has been equally (almost to the same extent)

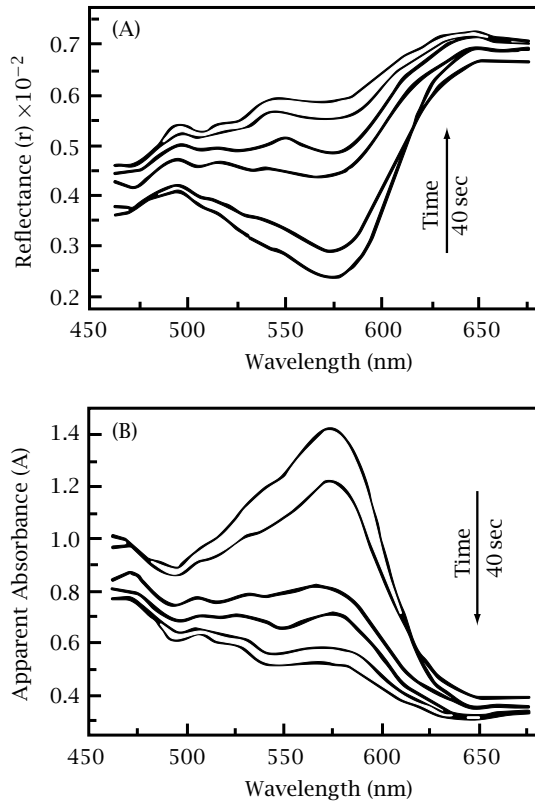


Figure 3. (A) Reflectance spectrum (r) of Dye 1 adsorbed on TiO₂ nanoparticles surfaces. The figure displays the effect of time of illumination on the reflectance of the dye molecules. (B) Apparent absorption spectrum ($A = -\ln(r)$) of Dye 1 molecules adsorbed on the TiO₂ nanoparticles surfaces, calculated from the reflectance spectrum in (A).

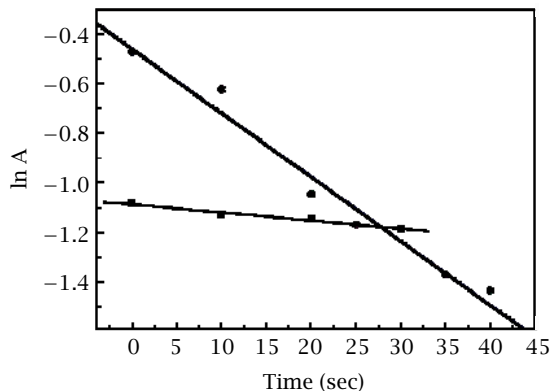


Figure 4. Logarithms of the absorbance of Dye 1 as a function of illumination time in ethanol (■) and in presence of TiO₂ nanoparticles (●). The absorption of the dye molecules rapidly decrease in presence of TiO₂ nanoparticles.

noticed in both ground state absorption and excited state fluorescence spectra. The values of the spectral wavelengths of Dye 1 in different solvents (14 solvents; alcohols, chlorinated solvents, hydrocarbons, HB donor

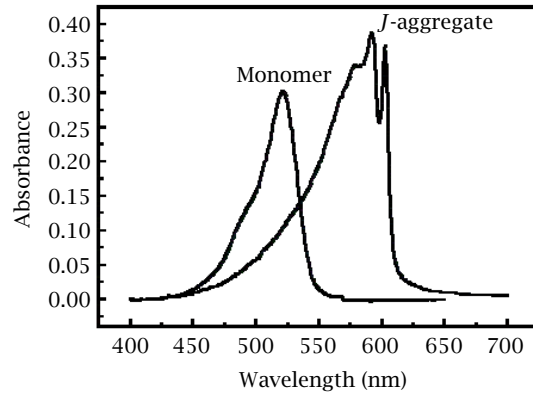


Figure 5. Absorption spectra of Dye 1 in ethanol (monomers) and in presence of NaOH (*J*-aggregates).

and acceptor solvents, polarizable solvents etc.) fit multiparameter equation of Kamlet, Abboud, Abraham and Taft: $Y = Y_0 + a\alpha + b\beta + c\pi^*$, where a is a measure of the susceptibility of the absorption or emission spectra of a probe molecule to solvent hydrogen bond donor (HBD) acidity, b is a measure of the hydrogen bond acceptor (HBA) basicity and c is a measure of solvent polarizability while α , β , and π^* refers to scales used to characterize solvents with respect to these properties [19]. The results show that the absorption spectrum reflects high sensing capability of the Dye for medium basicity (HBA capability of the solvent, β parameter) whereas the fluorescence spectrum shows enhanced sensitivity to the solvent acidity (HBD capability of the solvent, α parameter).

$$\lambda_a = 524.7 - 0.53\alpha - 5.16\beta + 2.71\pi \quad r = 0.9999$$

$$\lambda_f = 541.9 - 3.08\alpha - 4.02\beta + 1.64\pi \quad r = 0.9999$$

3.3. AFM imaging studies. Investigation of a solution of Dye 1 in aqueous NaOH solution revealed the adsorption of *J*-aggregates on the glass surface. Figure 6, shows a NCAFM image with a scanning area of $4 \times 4 \mu\text{m}^2$. In the image two types of *J*-aggregates can be clearly identified, one of which is a well-defined fiber-like structure. This type of aggregates extends for tens of micrometers. Such a structure can be seen extending from the top right corner to the bottom left side of the image. A cloud of less defined structures surrounds the fiber-like structure. The second type of aggregate is comprised of irregular big spots located at the top-left, bottom-left, and bottom-right corners of the image.

Figure 7 shows a zoom in at a section from the fibrous structure in figure 6. In this image, the fibrous structure appears well defined with sharp edges. The middle part of the fiber is 33 nm higher than the glass surface and 93 nm wide, as can be observed from the topography profile taken across the rod. The variation in the height of the cloud around the rod suggests that the cloud consists of two steps; the closest to the center of the fiber is 11.7 nm while the other is 7.4 nm from

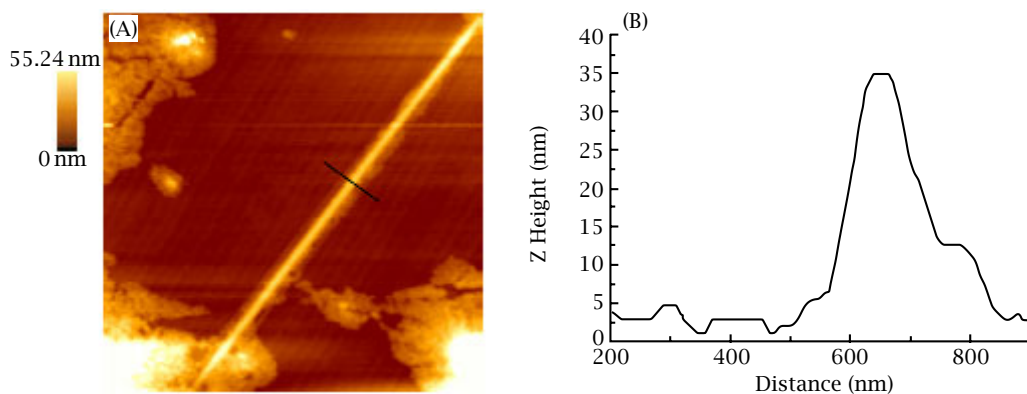


Figure 6. (A) NCAFM image of Dye 1 J-aggregates. Two types of aggregates are clearly evident, well-defined fiber-like structure and less ordered cloud-like structures. A fiber can be easily identified in the image extending from the top-right corner to the bottom-left corner. Image size is $4 \times 4 \mu\text{m}^2$. (B) The topographic profile along the line indicated in the topography image in (A).

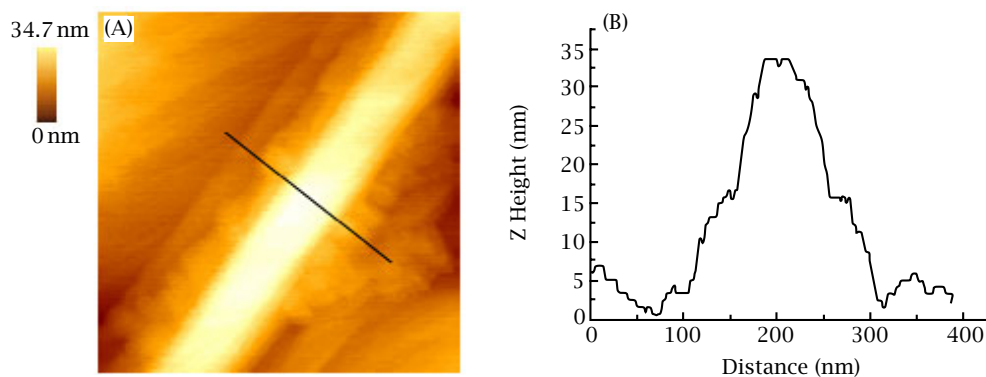


Figure 7. (A) NCAFM image of a zoom in at a section from the fiber structure in Figure 6(A). The fiber structure is well defined, and with height of 33 nm from the glass surface. A less defined cloud-like structure is observed around the fiber. The cloud-like structure appears to consist of two steps with heights 11.7 nm and 7.4 nm. Image size is $0.5 \times 0.5 \mu\text{m}^2$. (B) Topographic profile along the line indicated in (A).

the glass surface. It must be stated that the values for the height of the rod are different from those expected for the fiber in solution, due to the physical adsorption on the glass surface. Line scans at different locations (not shown) across the rod suggest that the rod is not uniform in height.

Figure 8, is a three-dimensional (3D) representation (obtained by image processing) of a section of the fiber. It can be clearly seen that the surface of the fiber is not uniform. The surface appears to be consisting of alternating hill-valley sequences. This structure suggests that the fiber is consisting of a bundle of smaller tubes twisted around each other forming a left-handed helical structure. This is in agreement with the reported cryo-transmission electron microscopy results [16, 17].

4. CONCLUSION

We have investigated the photostability of Dye 1 in solution and adsorbed on the surface of TiO_2 nanoparticles. The results demonstrate the photolability of Dye

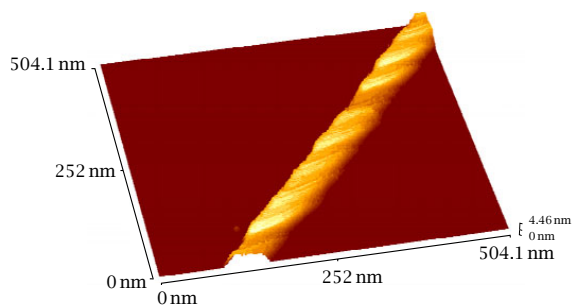


Figure 8. 3D representation of the J-aggregates fiber structure. The image is obtained by image processing of Figure 7(A).

1 adsorbed on the surface of TiO_2 nanoparticles. This is probably due to redox reactions at the surface of TiO_2 . It has been found that Dye 1 has a remarkable capability to sense the polarity of the environment. The absorption spectrum reflects the high sensing capability of the dye for medium basicity (HBA capability of the solvent,

β parameter) whereas the fluorescence spectrum shows enhanced sensitivity to the solvent acidity (HBD capability of the solvent, α parameter). Furthermore, we investigated the self-assembly of Dye 1 *J*-aggregates on glass surfaces using NCAFM. The *J*-aggregates formed well-defined fiber-like structures on the glass surface. The left-handed helicity of the *J*-aggregates was clearly resolved. The fiber was found to consist of a bundle of small tubes twisted around each other to form the left-handed helical structure.

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