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Occurrence of Self-assembled Monolayer J-aggregate of Pseudoisocyanine on Ag (111) Surface

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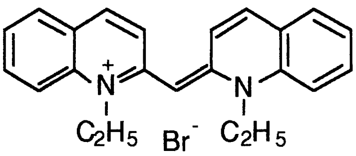
By bathing a smooth and highly [111]-oriented Ag film in a monomeric solution of pseudoisocyanine (1,1'-diethyl-2,2'-cyanine) bromide, we have found a uniform monolayer adsorption of self-assembled two-dimensional J-aggregate. A specific interaction of bromide ions with the Ag (111) surface seemed to be the major driving force for the dye adsorption. The system allows combined conventional spectroscopy and scanning tunneling microscopy studies of adsorbed J-aggregates of cyanine dyes.

Cyanine dyes are important spectral sensitizers in silver-halide photo-imaging systems. In many cases, they adsorb on silver halide surfaces as a J-aggregate, which is characterized by an unusually sharp and fluorescent electronic transition that red-shifted from the molecular band. Pseudoisocyanine (1,1'-diethyl-2,2'-cyanine) bromide (**1**) or chloride is the dye with which such a J-band was first identified by Jelly$^{1)}$ and Scheibe,$^{2)}$ and one of the best known, strongly J-aggregating dyes. The prominent spectral features of the J-band has generally been associated with close-packed cyanine molecules stacked plane-to-plane at a relatively small slip angle below 30°.$^{3)}$ Recognizing that the scanning tunneling microscopy (STM) may potentially be a powerful means to more directly establish such correlations between the spectral and structural properties of cyanine dye aggregates, we have searched for a suitable system that allows both conventional spectroscopy and STM studies of adsorbed J-aggregates. As a result, we have recently found that dye **1** forms a self-assembled monolayer J-aggregate on Ag (111) surfaces by specific adsorption from a monomeric dye solution, with a single spectrally well-defined aggregate structure. The spectral data obtained by using the conventional spectroscopy methods are the average information from the corresponding probing area far greater than the molecular dimensions, whereas STM probes an outstandingly small local area with an atomic scale resolution. The uniform surface coverage of the dye on a highly smooth Ag (111) surface prepared in this work is of significant help in this regard. Also important is the fact that the adsorption of the monolayer J-aggregate on the Ag (111) surface shares a certain close similarity with that on silver halides, because our results suggest that the dye adsorption actually occurs on a halide-ion-modified Ag (111) surface.



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The Ag (111) substrate was prepared by using an Ar-ion sputter deposition technique. A sputter-coating apparatus (Nippon Denshi, JFC-1100) was operated in the dc glow discharge mode in an Ar atmosphere (ca. 30 Pa) with the cathode (gold or silver target) voltage set at -1.2 kV. An Au film approximately 250 nm thick was first sputter-coated on a freshly cleaved natural mica at substrate temperature approximately 300 °C. An Ag film was then sputter-deposited thereupon for approximately 150 nm thick at substrate temperature slightly above 100 °C. Direct deposition of Ag on the cleaved mica did not result in desirable film qualities, often ending up in a whitish cloudy film surface. The thus prepared Ag substrate is a highly [111] oriented crystalline film, as the X-ray diffraction patterns revealed only the (111) reflection with no concomitant (200) and (220) signals. In addition, the film surface is so smooth that a typical root-mean-square roughness per 100×100 nm^2 area is only about 0.2 nm, as estimated from the STM images.

Dye **1** was dissolved in a mixed water and ethanol solvent of 1:1 volume ratio, at various concentrations ranging from 2×10^{-7} to 10^{-3} M. The Ag substrate was bathed in each dye solution at 20 °C, for several minutes to hours. After removal from the dye solution, the sample was quickly rinsed in pure water for several seconds and dried (visible water droplets attached to the surface were blown off with an air jet).

Because of the relatively thick and highly reflecting metal substrate, the reflection spectroscopy is almost the only practical means for spectral analysis of the adsorbed dye aggregate. Such reflection spectra in the visible range were taken by using a microscopic reflection spectrometer (Ohtsuka Denshi, MCPD-100), where the sampling spot diameter was typically 25 μm. The measurement was repeated for a number of randomly selected sampling spots to infer the uniformity of the dye coverage. The spectral analysis was made in terms of the reflection absorbance, defined by $-\log R/R_0$, where R and R_0 represent the reflectances measured with and without adsorbed dyes.

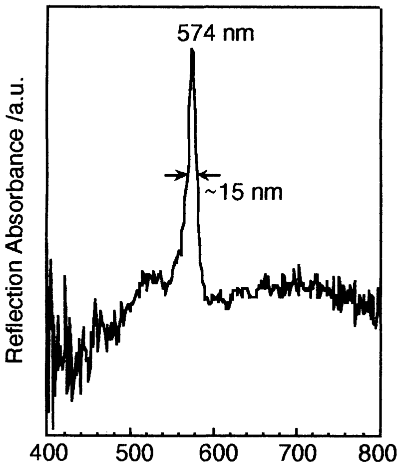

Fig. 1. Typical reflection spectrum of dye **1** adsorbed on the Ag (111) surface.

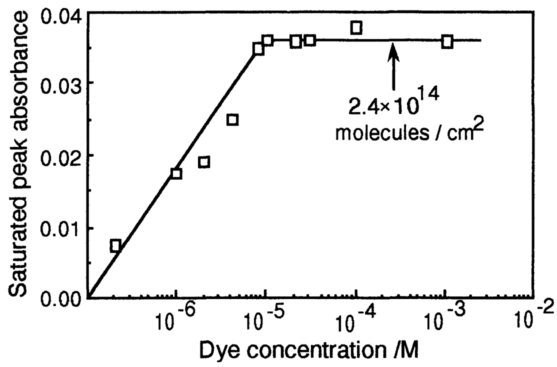

Fig. 2. Relationship between the saturated reflection absorbance (peak intensity) of the J-band and the dye concentration in the solution, showing an equivalent adsorption isotherm.

Figure 1 shows a typical example of such reflection spectra. Above a convex background, a sharp J-band, characteristic of this dye, appears at 574 nm with a band width (FWHM) approximately 15 nm (450 cm^{-1}), along with a weak subsidiary vibronic band at around 520 nm. It may be worth noting that these features closely resemble those of a crystalline spectrum, taken with a polarized light so as to reveal most distinctly the crystalline J-band.4) In addition, both the spectral feature and the band intensity depended so little on the sampling spots that the entire substrate surface seemed to be uniformly covered by the adsorbed J-aggregate.

Throughout the broad dye concentration range, 10^{-7} to 10^{-3} M, the intensity of the J-band, measured as a function of bathing time, was maximized at around 20 min and saturated thereafter. Figure 2 shows an equivalent adsorption isotherm, in which the saturated reflection absorbance of the J-band is plotted as a function of dye concentration. Figure 2 exhibits a single plateau extending over more than two orders of dye concentration above 10^{-5} M, thus strongly indicating the occurrence of a monolayer adsorption. By extracting the adsorbed dyes into a pure ethanol solvent, the total number of dye molecules on the substrate was quantitatively estimated to be $2.4 \times 10^{14}/cm^2$, which is transformed to the corresponding molecular area of 0.42 nm^2. Although we simply used the projective area of the substrate (typically 1×1 cm^2) in this calculation, the molecular area estimated in this way turns out to be comparable to the literature value of 0.57 nm^2, as associated with the edge-on configuration.5) This in turn affirms the excellent planarity of the sputter-deposited Ag (111) substrate.

The Ag film is apparently unique in that we could observe neither the formation of such a monolayer J-aggregate nor even noticeable dye adsorption on other substrates such as Au (111), cleaved mica, and glass. X-ray photoelectron spectroscopy analyses of the sample surface, before and after bathing in the dye solution or in a reference solution containing KBr instead of dye, indicated that the oxygen originally bonded to the surface (the corresponding O_{1s} signal was located at a binding energy ~531 eV) was substitutionally replaced by Br^- ions. We conclude therefore that the dye adsorption occurred on this bromide-ion-modified Ag (111) surface that may simulate the silver halide surface. This is, however, not necessarily a novel concept, because a similar idea was already proposed by Herz, Danner, and Janusonis in respect to dye adsorptions in a colloidal silver dispersion.5) Our XPS data present a more convincing proof for this scheme.

The STM images were taken by using Nanoscope-1 (Digital Instrument) with a tungsten tip prepared in this laboratory. The system was operated under the constant current (0.5-2 nA) mode. Successful STM imaging rests primarily upon the tip condition. With such tips that sustain stable tunneling currents, images that can reasonably be associated with a regular two-dimensional packing of dye monomers were reproducibly obtained under the negative sample biasing (10 - 100 mV) with respect to the tip, where the tunneling electrons flow from the sample to the tip. We tentatively interpret this biasing effect as suggesting that the highest occupied electronic levels of the adsorbed dyes may be involved. An example of the STM images taken in this way is shown in Fig. 3. Although individual atoms are difficult to resolve, each of the bright spots in this gray-scale image is considered to represent one of the two quinoline rings bridged by a monomethin link. As a result, this image does not necessarily single out the real packing pattern of dye molecules. Nevertheless, provided that the occurrence of a small slip angle is the essential need in accounting for the large bathchromic (red) shift of the J-band (~1700 cm^{-1}), and that the ethyl groups are all on the same side of the dye monolayer, either up or down, then the only structure that can match the

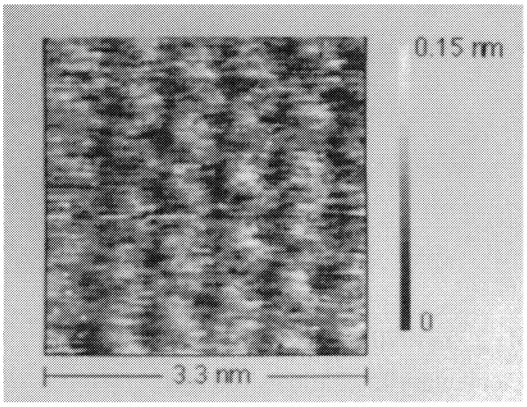

Fig. 3. An example of gray-scale STM image taken for the monolayer J-aggregate of dye **1** adsorbed on the Ag (111) surface. Obtained under the negative biasing (-100 mV) of the sample with respect to the tip.

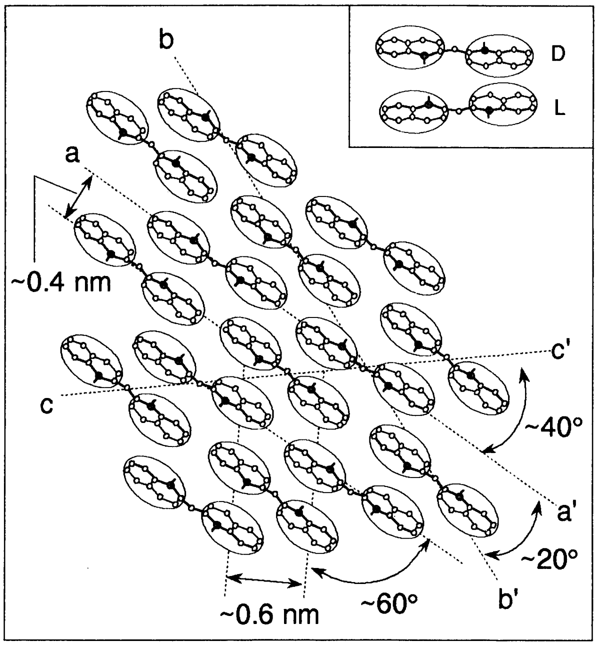

Fig. 4. Illustration of two-dimensional close-packing model for the monolayer J-aggregate of dye **1**, consistent with the STM image (cf. Fig. 3). The top views of two antipodes (D and L) of dye **1**, adsorbed with the edge-on configuration, are shown in the corner. The D and L antipodes are stacked alternately along, e.g., the line b-b', which makes a small slip angle of around 20° with the molecular long axis (e.g., line a-a').

STM image is the one schematically illustrated in Fig. 4. Because of the inherent disymmetry of dye **1**, as related to its twisted nonplaner molecular structure,[6] the two antipodes (denoted by D and L) can occur with equal probabilities. The structure shown in Fig. 4 is obtained by stacking alternately the D and L antipodes so as to allow an adequately small slip angle of around 20°, as shown, along with several other packing parameters, in Fig. 4. Note that this arrangement does not coincide with the symmetric brickstone structure[7] often associated with two-dimensional J-aggregates. Rather, the model (occurrence of an angle ~60°) may even suggest an epitaxial-like relationship of the adsorbed J-aggregate to the Ag (111) surface having a six-fold symmetry.

We expect that such unique systems of self-assembled monolayer J-aggregate adsorbed on the Ag (111) surface may also be prepared with a variety of other cyanine dyes or, more interestingly, with mixed cyanine dyes co-adsorbed. These systems would be useful and interesting not only from the structural point of view, but also in regard to the exciton dynamics involving J-aggregates adsorbed on conducting substrates.

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