

# Structural Characterization of 2-D Cyanine Dye Aggregates on Model AgX Surfaces by Combined Physical and Chemical Methods

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## Abstract

Atomically-flat Ag(111) films covered with a halide monolayer or Au/Ag(111) films covered with an AgX monolayer provide a useful model of AgX surface on which large-area, well-ordered 2-D cyanine dye aggregates can be easily self-assembled with a specific J- or H-type structure. The excellent planarity of the sample makes angle-resolved XPS, in addition to STM, a powerful method to illuminate the molecular orientation and arrangement with which dye molecules are incorporated into the 2-D aggregate. Kinetic analysis of solvent extraction of dye molecules from the 2-D dye islands also gives indirect support for the proposed aggregate structures and key physical parameters that control the 2-D packing geometry of dye molecules.

## Introduction

Spectral sensitization of silver halide emulsion involves a variety of dye aggregates adsorbed on AgX grain surfaces. However, the environmental complexity associated with the emulsion system does not easily allow direct structural characterization of dye aggregates relevant to the sensitizing process. Large-area model AgX surfaces, which are simple to prepare, both chemically and structurally resemble the real AgX surface, and allow construction of well-ordered stable 2-D dye aggregates adsorbed thereupon in a gelatin-free environment, are thus of significant use in gaining better insight into the structural as well as spectroscopic properties of sensitizing dye aggregates on AgX surfaces. Atomically-flat Ag(111) films covered with a halide monolayer<sup>1]</sup> or Au/Ag(111) films covered with an AgX monolayer<sup>2</sup> are particularly suited for such model AgX surfaces with respect to the sensitizing dye adsorption. Unlike real AgX crystals, these model surfaces do not deteriorate by extended irradiation of UV light or even X ray. Along with the excellent surface planarity and the gelatin-free sample condition, this expands the range of physical and chemical methods or combinations of thereof from which we can choose for detailed structural analysis of the dye/pseudo-AgX interface. As an example, this paper introduces a successful

application of angle-resolved XPS to illuminate the molecular arrangement and orientation in 2-D dye aggregates of some typical cyanine dyes. The results suggest an important role of the long-range Coulomb interactions between dye molecules in determining the 2-D dye aggregate structure. The importance of this structural parameter is also supported indirectly by kinetic analysis of solvent-induced desorption of dye molecules from the 2-D dye islands, thereby each island is proved to consist of so large number of dye molecules that removal of the majority of dyes initially adsorbed still leaves a sharp enough J-band.

## Experimental

2-D dye aggregates were self-assembled from a dilute solution of sample dyes on an atomically flat Ag(111) film covered with a halide monolayer according to the method described elsewhere.<sup>3</sup> Among a variety of cyanine dyes, those in which the counter anion is fixed by an alkyl chain to the conjugated dye cation with a delocalized positive charge are particularly suited for this work. An example is the thiocarbocyanine dye (Dye 1) shown in Figure 1. This dye, which is known to exhibit a strong tendency of J aggregation, has an additional merit in that the two S atoms, one at the anion (sulfonic) site and the other in the cationic dye chromophore, are clearly distinguishable by XPS in terms of core-level binding energy. This fact plays an important role in interpreting the XPS data taken for the corresponding 2-D J aggregate. All XPS data were taken with an ESCA-750 spectrometer (Shimazu Corp.) with Mg K $\alpha$  radiation of 1253.6 eV. The absorption spectra of 2-D dye aggregates, adsorbed on the non-transparent Ag(111) substrate, were obtained by reflection spectroscopy at normal incidence. The solvent-induced desorption study was made by using three different kinds of common solvents— water, ethanol, and mixed water and ethanol with 1:1 volume ratio, where desorption-induced decrease in absorbance at each aggregate band was monitored as a function of extraction time and temperature.

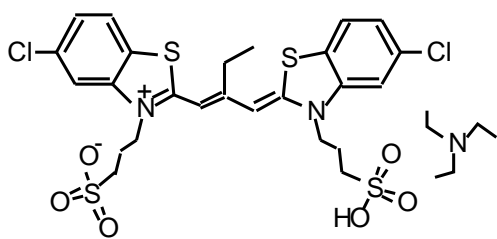


Figure 1. Structure of typical cyanine dye used in this work.

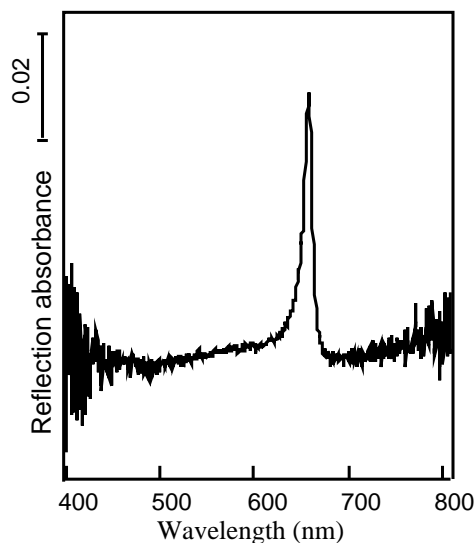


Figure 2. Absorption spectrum of 2-D J-aggregate of Dye 1 formed on a bromide-covered Ag(111).

## Results and Discussion

A sharp J band obtained for the 2-D aggregate of Dye-1 on the halide(bromide)-covered Ag(111) film is shown in Figure 2. The absorption spectrum exhibits no other side bands, indicating that Dye 1 has been self-assembled into some well-defined J-aggregate structure. Of a series of angle-resolved XPS spectra obtained for the same sample, one that concerns the  $S_{2p}$  core level signal is shown in Figure 3, where the intensity is given relative to that arising from the Br monolayer underlying the 2-D dye aggregate to eliminate the angle-dependent instrumental factors. It can be seen that the lower binding energy peak associated with the S atom in the heterocyclic ring of dye chromophore shows little angle dependence, while the intensity of the higher binding energy peak associated with the sulfonic site exhibits marked increase with decreasing photoemission angle. A similar angle dependence was observed also for the  $O_{1s}$  signal, which arises from the same functional group. It thus immediately follows that each dye molecule in the 2-D J-aggregate is adsorbed with the edge-on configuration where the cationic dye chromophore is in direct contact with the Br monolayer, locating the sulfonic groups outside the dye cation layer at a distance determined by the length of the propyl chain.

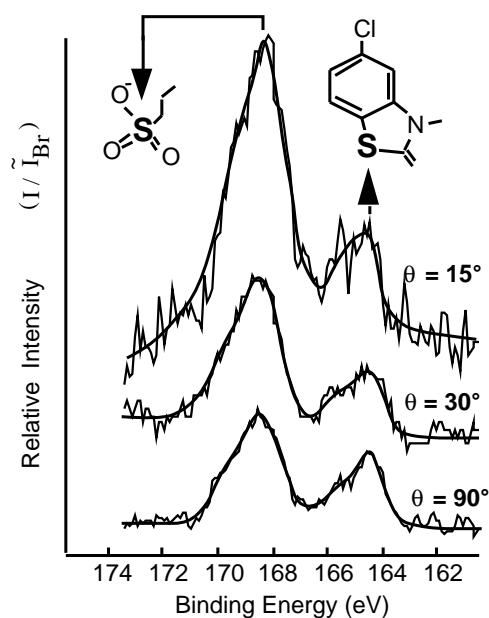


Figure 3. Angle-resolved  $S_{2p}$  spectra taken for the 2-D J-aggregate of Dye 1.

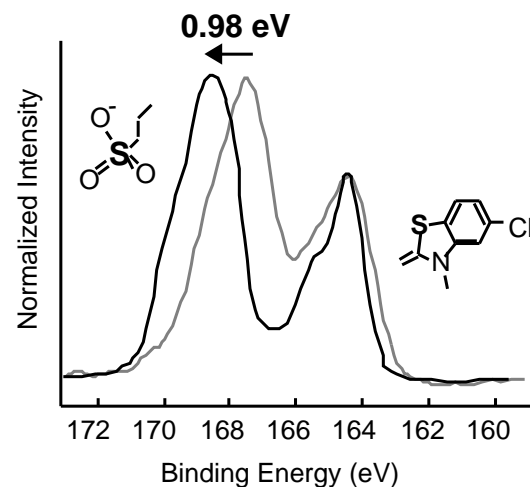


Figure 4. Comparison between  $S_{2p}$  spectra obtained for 2-D J-aggregate (solid line) and for cast film (dotted line).

The lateral arrangement of dye molecules in the 2-D J-aggregate can also be assessed from XPS data, based on unusual core-level binding energy shifts between atoms in the dye chromophore and those in the sulfonic group. Figure 4 shows a comparison between  $S_{2p}$  spectra taken for the 2-D J-aggregate (solid line spectrum) and for a cast film or powder sample of Dye 1 (broken line spectrum) in which the dye molecules probably construct some 3-D structure. Here the binding energy refers to that of the  $N_{1s}$  signal, arising from the heterocyclic ring of dye chromophore, fixed at the standard position of 401 eV for both samples. Then the  $S_{2p}$  signal associated with the sulfonic group in the 2-D

aggregate undergoes a significant ( $\sim 1$  eV) shift to higher binding energy. Again, the  $O_{1s}$  signal associated with the same sulfonic group responded in parallel to this change and exhibited an approximately equal shift to higher binding energy. These systematic shifts can be best explained in terms of the Madelung potential associated with the ordered 2-D array of dye molecules possessing an intramolecular charge separation between the dye chromophore and the sulfonic group. In fact a simple numerical calculation by point charge approximation predicts that a Madelung potential comparable to the observed binding energy shift can indeed occur for the 2-D J-aggregate. The same calculation also suggests that the contribution of this long-range Coulomb interaction to the cohesive energy is so sharply maximized at a slip angle of  $\sim 20^\circ$  as to essentially rule out all the other possible geometries except for the J-type aggregation. It seems that, at least for 2-D cyanine dye aggregates as a whole, the role of this long-range Coulomb interaction seems to play more important role than short-range van der Waal interaction in determining their stability.

When the 2-D J-aggregate of Dye 1 formed on the bromide-covered Ag(111) is subject to extraction by the series of more or less polar solvents, the absorption spectrum changed with extraction time typically as shown in Figure 5(a). Here even after more than 90% of initially adsorbed dye molecules have been removed into the solvent, desorption-induced spectral changes of the J band are hardly noticeable. Besides, as shown in Figure 5(b), the square root of the residual J-band intensity shows good linearity as a function of extraction time. These facts support that Dye-1 indeed forms a 2-D J-aggregate and, upon solvent extraction, the dye molecules are dissolved preferentially along the edges of each 2-D dye island. According to this mechanism, if the physical size of the original 2-D island is sufficiently large, even removal of the majority of dye molecules from the substrate may leave discrete patches of 2-D dye islands, each of which still contains a sufficient number of dye molecules to keep the spectral sharpness in the J-band. Figure 5(a) proves that this is really the case.

Thus the linear relationship shown in Figure 5(b) can be used to determine the apparent rate constant for the corresponding desorption process. The temperature dependence of this quantity is shown in Figure 6 in the form of Arrhenius plot for the three different kinds of solvents. It can be seen that all the plots can be fit by straight lines with equal slopes, so as to give an invariant apparent activation energy of  $\sim 0.8$  eV. The difference in the net desorption rate among these solvents is thus attributed to the difference in activation entropy, which may be altered significantly by the degree of hydrophobic interaction between dye molecules and each solvent; stronger for solvent with higher ratio of ethanol. It should be also noted that, according to the dissolution mechanism involving the edges of the 2-D dye island, the apparent activation energy for the dissolution,  $\sim 0.8$  eV, reflects only half of the molar cohesive energy in

the interior of the 2-D dye island. Though the contribution of dye-substrate interaction to the apparent activation energy has not been known yet, the result seems to suggest a relatively large cohesive energy for the 2-D aggregate not rationally accounted for just in terms of van der Waals interaction. What comes up here again is the long-range Coulomb interaction as suggested already based on the XPS data. Indeed, the predicted Madelung potential can be large enough to account for cohesive energies of the order of 1 eV.

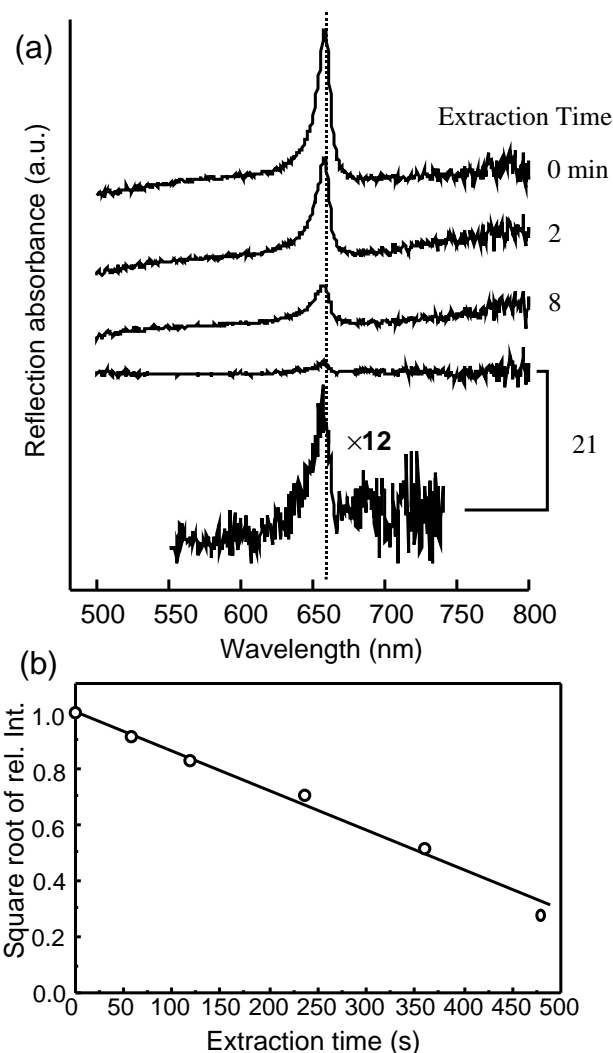


Figure 5 Typical changes of J-band (a) and the square root of its relative intensity (b) with extraction time in mixed water and ethanol solvent.

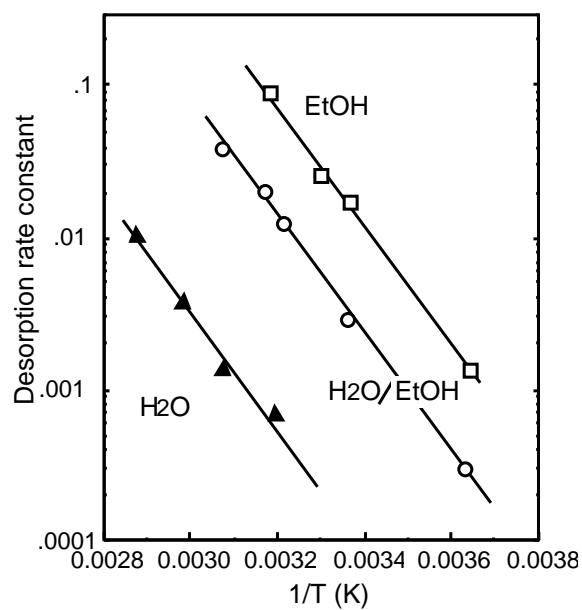


Figure 6 Typical changes of J-band (a) and the square root of its relative intensity (b) with extraction time in mixed water and ethanol solvent.

Similar XPS and solvent-induced desorption studies for a variety of cyanine dyes forming different aggregate structures are necessary to establish the proposed correlations, and a part of such comparative studies will also be reported.

### References

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