Fabrication of Two-Dimensional J-Aggregates on Au(111) Covered with Self-Assembled Cysteamine Monolayer

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A simple and useful new method to fabricate high-quality 2D J-aggregates of anionic cyanine dyes on a solid surface has been established by using an Au(111) covered with cysteamine self-assembled monolayer. It was also found that this method allows easy control of dye aggregation ranging from a 2D crystalline J-aggregate to a high density of dye monomers without aggregation.

Controlled organization of structurally well-defined functional dye assemblies on solid surfaces has a considerable impact on the future chemical technology. J-aggregate is a particularly interesting form of the organized dye assemblies, because of an unusually sharp absorption, resonance fluorescence, and related non-linear optical properties potentially leading to many useful applications.[1-4] However, it has not been an easy task to prepare a uniform J-aggregate monolayer firmly fixed on the solid surface and freed from any other forms of aggregates and residual monomers. The most popular Langmuir-Blodgett (LB) method [3,5,6] allows a layered J-aggregate to form at the air-water interface and to be translated thereafter to the surface of an arbitrary substrate. Unfortunately, the resultant J-aggregate often lacks sufficient structural uniformity, owing to the difficulty in translating the monolayer to substrates. Recently, Kawasaki and co-workers have worked out an apparently much easier method to prepare a similar J-aggregate monolayer but with a higher level of structural perfection on a halide-covered Ag(111).[7,8] Yet this alternative system has one practical shortcoming in that the dye chromophore makes virtually direct contact with the metal substrate. Under such condition, the excitation energy of the dye is transferred too fast into the metal to be utilized otherwise.

In this letter we introduce a new simple and easy method for fabrication of layered J-aggregates of anionic cyanine dyes, typically 5,5'-dichloro-3,3'-disulfopropyl-9-ethylthiacarbocyanine triethylamine (dye I) on Au(111) precovered with a self-assembled monolayer of cysteamine(CA), a short-chain thiol derivative with a terminal amino group. The formation of ammonium sulfonate salts (a sort of electrostatic interaction [5,9]) helps the dye I to be adsorbed on the monolayer of CA. The method also allows easy control over the extent of dye aggregation, thereby dye molecules can be supported on the solid surface in various forms ranging from a two-dimensional (2D) high-quality crystalline J-aggregate to monomeric adsorbates with high density.

An atomically flat Au(111) film, approximately 250 nm thick, was prepared on freshly cleaved natural mica by using the Ar-ion sputtering method as described in detail elsewhere.[10,11] CA was adsorbed on Au(111) by immersing the gold substrate into 1 μM-10 mM (1 M = 1 mol dm^{-3}) ethanolic solution of CA hydrochloride for 1-20 min at room temperature. The surface coverages of CA on Au(111) were estimated based on the S/Au intensity ratio in the XPS (X-ray photoelectron spectroscopy)

spectra[12] taken by ESCA-750 spectrometer (Shimadzu Co.). Adsorption of dye I onto the CA-covered Au(111) was carried out for typically 5 min in 0.1 mM dye solution in a mixed water and ethanol solvent of 1:1 volume ratio. The dye adsorption temperature was varied from room temperature (~20 °C) up to 60 °C. Longer treatments than 5 min gave no noteworthy effects. The absorption spectra of the adsorbed dyes were measured in the reflection mode by using the Photonic Multi-Channel Analyzer PMA-11 (Hamamatsu Photonics Co.) attached to a Nikon Microscope Optiphot-2. The organized dye assemblies on fully CA-covered Au(111) were also subject to angle-resolved XPS to gain information about the dye-substrate interaction and the vertical orientation of adsorbed dye molecules.

First of all, we evaluated the average coverage of CA on Au(111). We found that almost complete monolayer (1 ML) coverage of CA with 4×10^{14}–5×10^{14} cm^{-2} S atoms[13] (close to that corresponding to the $\sqrt{3} \times \sqrt{3}$ structure [14] on Au(111)) was reached well within a few minutes in 1-10 mM solution. Slower adsorption in 1-100 μM solutions gave various fractional monolayer coverages in the given range of immersion time. The XPS analysis also proved that the terminal amino group of CA adsorbed on Au(111) was uncharged (-NH$_2$) and free from the chloride ion.

The absorption spectrum of dye I adsorbed on the Au(111) precovered completely with the self-assembled CA monolayer is
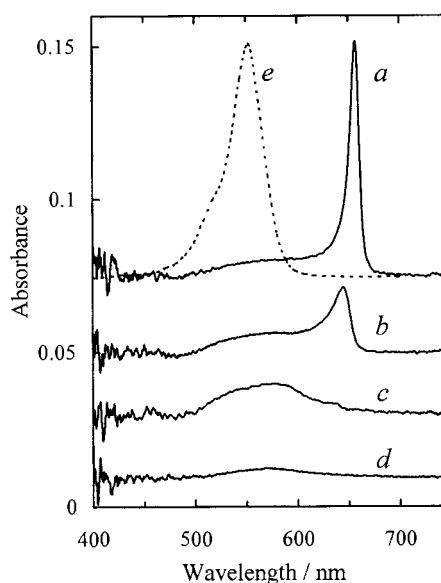

Figure 1. A series of absorption spectra taken for samples with different levels of dye I aggregation. Dye I was adsorbed on the Au(111) completely (*a*) and partially (*b - d*) covered with the self-assembled cysteamine layer. The coverages of cysteamine were 1 ML (*a*), ~0.7 ML (*b*), ~0.6 ML (*c*), ~0.5 ML (*d*). For comparison, absorption spectrum of dye I monomer (0.72 μM) in ethanol is shown as dotted spectrum *e*.

shown as spectrum *a* in Figure 1. An extremely sharp absorption band was observed at 657 nm (FWHM=10 nm). The longer peak wavelength and much smaller FWHM than those of the monomer band (dotted spectrum *e* in Figure 1) as well as 1.3×10^{14} molecules cm^{-2} surface density of adsorbed dye (determined by the ethanolic extraction method) indicate the formation of a high-quality uniform crystalline 2D J-aggregate.[15] Such a perfect J-band as spectrum *a* was dominant only when the dye adsorption was carried out at 50-60 °C onto almost fully CA-covered Au(111). The adsorption at lower temperatures caused a noticeable broadening of the J-band up to 14 nm in FWHM. The dye adsorption temperature was one of the important parameters for the 2D J-aggregation on the CA-covered Au(111).

We also found that the dye aggregation was easily controlled by varying the surface coverage of CA on Au(111). A series of absorption spectra taken for samples with different levels of dye aggregation are also shown in Figure 1. Spectrum *b* was obtained at ~0.7 ML coverage of CA, where a much broader (FWHM=17 nm) J-band overlaps with an extended pseudo-monomer band around 560 nm. At fractional CA coverages below ~0.6 ML, the J-aggregation was almost completely suppressed, leaving only the broad pseudo-monomer band as spectra *c* and *d*. It should be noted that the integrated intensity of those pseudo-monomer bands suggests that a considerably high density of dye molecules, comparable to that making up the crystalline 2D J-aggregate, are supported as monomeric species on the substrate, against the strong tendency of dye I toward J-aggregation. The origin of the pseudo-monomer band is supposed to be non-ordered, random oriented, and semi-isolated monomers that weakly interact with each other.
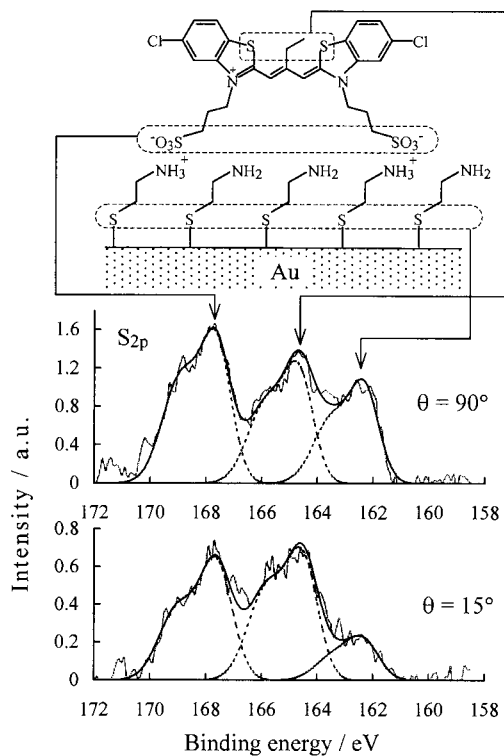
All of the above-noted unique features of the present system can be traced back to the specific interaction between the surface amino groups of the CA adsorbed on Au(111) and the sulfonic acid groups of dye I, leading to the formation of an ammonium sulfonate salt (see the upper part of Figure 2). In fact, a series of N$_{1s}$ XPS spectra indicated that a single peak at 399 eV arising from the uncharged amino groups of the CA adsorbed on Au(111) was largely replaced by a higher binding energy peak at 401 eV after the dye adsorption. The peak at 401 eV partly comes from the charged N atoms in the thiazole rings of dye I but otherwise from the aforementioned surface ammonium sulfonate salts. The resultant vertical orientation of the adsorbed dye molecule, as represented in the upper part of Figure 2, was also supported by the angle-resolved S$_{2p}$ spectra given in the lower part of Figure 2. The three kinds of S atoms were clearly distinguished in binding energy, and the photoemission-angle dependence of their relative intensities unambiguously indicated that the dye chromophore constituting the 2D J-aggregate was located at the outermost position of the layered assembly.[8]

In summary, we have established a simple and useful new method to fabricate high-quality layered J-aggregates of cyanine dyes on a solid surface by using a CA-covered Au(111), a densely amino-group-functionalized surface. The dye aggrega-tion in this system is controlled mainly by the CA coverage, i.e., the density of amino groups anchoring the individual dye molecules. It is also possible to support a high density of dye monomers without aggregation. To clarify the reason why the dye aggregation is controlled by the CA coverage, a more detailed structural characterization of the CA monolayer as well as the overlying dye assembly is currently under way, and will help us to gain better control over the structure and properties of layered molecular assemblies.

Figure 2. Angle-resolved XPS spectra for S$_{2p}$ core levels measured for 2D J-aggregate of dye I, adsorbed on the Au(111) precovered completely with the self-assembled cysteamine monolayer as shown in upper part of Figure, at photoemission angle of 15° and 90° with respect to the sample plane.

References and Notes

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13   S/Au intensity ratio in the XPS spectra was ~6×10^{-3}.
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15   It was also confirmed by the fact that the J-band was scarcely accompanied with the absorption band of any other forms of aggregates and residual monomers.