STM Imaging of Cyanine Dye J-Aggregates Formed on Carboxyl-Terminated Self-Assembled Monolayers

Robert W. Owens and D. Alastair Smith*

Department of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, United Kingdom

We report on the preparation and STM imaging of J-aggregates of 1,1′-diethyl-2,2′-cyanine (PIC) dye formed on a self-assembled monolayer of 11-mercaptoundecanoic acid (HS−$(CH_2)_{10}$−COOH). The formation of J-aggregates on the COOH surface was verified by reflection absorption measurements; however, the molecular assemblies were not bound strongly enough to the SAM to withstand the lateral forces applied during STM imaging. We found that pretreating the COOH surface with a solution of 1 mM $AgNO_3$ before application of the PIC dye solution greatly improved the stability of the J-aggregates. We suggest that the reason for this is the formation of a silver chelate with the carboxyl head groups of the SAM which permits the subsequent adsorption of bromide counterions from the dye solution. The formation of a counterion monolayer has been shown to be important in the formation of stable J-aggregates. STM images of these samples revealed long, essentially linear aggregates (with a packing structure similar to the proposed "staircase structure") extending over hundreds of nanometers with an interaggregate spacing of 30 Å. We compare these structures with those formed by the same dye applied directly on silver (111). In addition to the reported brickwork packing structure of the dye monolayer which is in direct contact with the metal substrate,[1] we also observed a previously unreported bilayer structure. The second layer of dye molecules comprises linear aggregates with a similar packing arrangement to those formed on the pretreated COOH SAM.

Introduction

The self-association of dyes in solution and at interfaces due to strongly attractive van der Waals forces is a well-known phenomenon. The aggregation leads to a strong coupling of the molecular transition dipole moments, resulting in a narrow excitonic absorption band which is considerably shifted in wavelength from the absorption of the monomeric species.[2] Aggregates which exhibit a red shift are termed J-aggregates, and those which have a blue shift are referred to as H-aggregates. J-aggregating dyes, such as the well-known cyanines, have found wide application for many years in photographic materials, since they will strongly absorb to silver halide surfaces, forming planar aggregates which act as the spectral sensitizers.[3] The photophysical and photochemical properties of J-aggregates have also attracted attention recently because of their potential as new laser materials, in molecular electronics, and in displays and nonlinear optical devices and because of their analogous characteristics to aggregates important in biology, such as those in photosynthetic systems.

Many theoretical models[4] have been proposed to describe the relationship between physical properties and the molecular packing within aggregates both in solution and at surfaces though an exact description is still a matter of debate. It is known that the molecular orientations in the unit cell affect the excitonic transitions, which suggests

that some degree of control might be exerted over the optical properties of J-aggregate thin films if the molecular packing could be manipulated. Consequently, there is considerable interest in high-resolution imaging of these molecular assemblies; however, there have been only a few such studies reported, probably because bulk silver halide crystals are essentially nonconducting and are therefore unsuitable as substrates for imaging with the scanning tunneling microscope (STM). Since the STM is an ideal tool for high-resolution imaging of the electronic structure in J-aggregates, alternative sample preparations are required. The STM has been used to characterize the formation of halide monolayers on silver,[5] and Kawasaki and Ishii[1] have recently used such surfaces to obtain images of both H- and J-aggregates. No other surface that was studied by this group (gold, mica, glass) permitted the formation of J-aggregates. Other groups have reported molecular resolution atomic force microscope (AFM) images of J-aggregates,[6] and Barbara and co-workers have used scanning near-field optical microscopy (SNOM) to study exciton dynamics and the environment-dependent photophysics of polymer-bound aggregates.[7]

There is also growing interest in the behavior of molecular excited states in the tip−sample junction of an STM from the point of view of developing an improved understanding of the electron tunneling process which provides the contrast in STM images, but also because of potential applications in molecular electronic devices. We are particularly interested in the possibility of STM

* To whom correspondence should be addressed.

(1) Kawasaki, M.; Ishii, H. *J. Imaging Sci. Technol.* **1995,** *39* (3), 213.

(2) Jelly, E. E. *Nature* **1937,** *139,* 631. Scheibe, G. *Angew. Chem.* **1936,** *49,* 563. Norland, K.; Ames, A.; Taylor, R. *Photogr. Sci. Eng.* **1970,** *14,* 295.

(3) West, W.; Gilman, P. *The Theory of Photographic Processes,* 4th ed.; Macmillan: New York, 1977.

(4) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958,** *28,* 721. Czikkely, V.; Forsterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970,** *6* (1), 11. Kato, T.; Sasaki, S.; Abe, S.; Kobayashi, S. *Chem. Phys.* **1998,** *230,* 209. Scherer, P. O. J.; Fisher, S. F. *Chem. Phys.* **1984,** *86,* 269. Fidder, H.; Terpstra, J.; Wiersma, D. A. *J. Chem. Phys.* **1991,** 6895. Spano, F. C.; Kuklinski, J. R.; Mukamel, S. *J. Chem. Phys.* **1991,** *94,* 211.

(5) Haefke, H.; Meyer, E.; Guntherodt, H.-J.; Gerth, G.; Krohn, M. *J. Imaging Sci.* **1991,** *35* (5), 290. Schott, J. H.; White, H. S. *Langmuir* **1994,** *10,* 486. Schott, J. H.; White, H. S. *J. Phys. Chem.,* **1994,** *94,* 291. Schott, J. H.; White, H. S. *J. Phys. Chem.* **1994,** *94,* 297.

(6) Wolthaus, L.; Schaper, A.; Mobius, D. *Chem. Phys. Lett.* **1994,** *225,* 322. Saijo, M.; Shiojiri, M. *J. Cryst. Growth* **1996,** *166* (1−4), 930. Daehne, L.; Tao, J.; Mao, G. *Langmuir* **1998,** *14,* 565.

(7) Higgins, D. A.; Barbara, P. F. *J. Phys. Chem.* **1995,** *99,* 3. Reid, P. J.; Higgins, D. A.; Barbara, P. F. *J. Phys. Chem.* **1996,** *100,* 3892. Higgins, D. A.; Reid, P. J.; Barbara, P. F. *J. Phys. Chem.* **1996,** *100,* 1174.

imaging of laser-induced molecular excited states, since the combination of resonant laser excitation and STM imaging has the potential to be a useful high-spatial-resolution, chemically specific analytical technique.[8,9] One aspect of this work has been to develop methods for reducing the nonradiative relaxation rates of molecular systems when they are in close proximity to a metal substrate which is essential for STM imaging. Our approach has been to use a self-assembled monolayer (SAM) to space the chromophore of interest away from the underlying metal substrate. The thickness of this spacer layer is a compromise between the reduction in nonradiative decay rate and the preservation of electron tunneling for STM imaging. To do this, we have developed two systems: self-assembled monolayers (SAMs) with covalently attached chromophoric head groups (we have recently reported STM images of the self-organization of triphenylene head groups tethered to a gold substrate[10]) and the use of alkanethiol SAMs as spacers onto which organic dyes can be adsorbed. J-aggregating dyes are ideal for our purposes, since they exhibit strong, narrow absorptions in the visible region of the spectrum.

We report here on the novel use of a chemically modified SAM as a substrate which promotes the formation and stable binding of J-aggregates and present STM images of the structures formed. We have found that J-aggregates of 1,1′-diethyl-2,2′-cyanine (PIC) extending over several hundred nanometers can be imaged by STM when prepared on a carboxyl-terminated SAM which has been pretreated with a silver nitrate solution, but without this pretreatment the aggregates were not bound well enough to the SAM to withstand the forces exerted by the tip during imaging.

Experimental Methods

Flat silver and gold substrates were prepared by the template-stripping method.[11] Approximately 1000 Å of metal was evaporated onto a silicon wafer at ambient temperature which had been cleaned by ultrasonicating several times in water and methanol. The metal surface was then glued to a float glass microscope slide using EPO-Tek 377 adhesive (Promatech, U.K.) and cured at 140 °C for 1 h. The silicon wafer was then peeled off the sandwich structure immediately before use, exposing large (111) terraces, typically 100×100 nm², with a mean roughness of a few Angstroms.

The dye (1,1′-diethyl-2,2′-cyanine), commonly referred to as pseudoisocyanine or PIC, was used with a bromide counterion (NK-1046, Nippon Kankoh Shikiso Kenkyusho, Japan). J-aggregates were formed directly on silver or on SAMs by adsorption from droplets of a 10^{-4} M solution of the dye in a 1:1, water/ethanol mixture. The droplets were left on the substrate for about 20 min at room temperature before they were washed away gently with distilled water and the substrate was blown dry with nitrogen.

The carboxylic acid-terminated SAM material, 11-mercaptoundecanoic acid, $(HS-(CH_2)_{10}-COOH)$, was obtained from Aldrich, U.K. SAMs were prepared by immersing a metal-coated slide into a 1 mM ethanol solution of the compound, and upon removal from solution the substrates were rinsed extensively with absolute ethanol and distilled water (pH = 7). The silver nitrate

pretreatment of the carboxyl-terminated SAM involved incubation in a 1 mM aqueous solution of $AgNO_3$ at room temperature for 1 h. It was not possible to treat SAMs prepared on *silver* substrates with $AgNO_3$ because the silver substrate was damaged by the procedure, but gold substrates were unaffected.

STM imaging was performed in ambient using a Molecular Imaging picoSPM controlled by Digital Instruments Nanoscope IIIa electronics with the scanning conditions reported in the figure captions. Reflection absorption measurements were made using a Shimadzu UV2101PC scanning UV−Vis spectrometer. The reflection absorption spectrum of the metal substrate (or the substrate/SAM where relevant) was subtracted from the raw data to yield the absorption spectrum of the dye.

Results and Discussion

Formation of Aggregate Multilayers on Silver (111). Kawasaki and Ishii[1] reported STM images of J- and H-aggregates formed on silver (111) substrates in the presence of halide counterions. In contrast to their report of only a single monolayer of J-aggregates under all imaging conditions, we have observed a second layer of dye aggregates on top of the first which shows a very different molecular packing structure. The J-aggregates are believed to form on silver via the initial adsorption of a halide counterion monolayer which interacts electrostatically with the positively charged nitrogens in the quinoline rings of PIC. Figure 1a shows a constant-current image of the bromide counterion monolayer on silver (111) imaged beneath the J-aggregates (Figure 1b) by careful control of the current set point. The packing arrangement of the bromide ions (a quasi $\sqrt{3} \times \sqrt{3}$ structure with a spacing of 4.9 ± 0.5 Å) agrees well with the results reported by Kawasaki and Ishii[1] (4.6 ± 0.4 Å) and reasonably well with those reported by Haefke et al.[5] (4.1 Å) and Schott and White et al.[5] (4.1, 5.1, and 5.3 Å nearest neighbor distances). When the current set point is reduced from 2.4 to 2.0 nA, the first layer of PIC molecules can be resolved (Figure 1b). As far as we can ascertain, these molecules are lying directly on top of the bromide counterion monolayer. A schematic representation of the proposed packing structure is shown in Figure 1c. The nearest neighbor distances (labeled a and c in Figure 1c) were measured to be 8.9 and 8.3 Å, respectively, which corresponds roughly with the nearest neighbor distances reported by Kawasaki and Ishii[1] in what they refer to as a "ring-like" structure observed using a tungsten tip and very similar imaging conditions. The distance d (16 Å) in Figure 1c may be compared with the molecular length of approximately 10 Å, suggesting that the molecules are not very tightly packed end-to-end and that the observed features correspond in size with the molecular length. We observe a slightly larger slip angle (defined as the angle between the long molecular axis and the row direction) of about 30° in comparison with 20° in their images. Despite these slight differences, we believe that the brickwork packing of dye molecules observed in our experiments corresponds to the ring-like structure reported by Kawasaki and Ishii.[1] The brickwork packing structure appears to form rings when the individual dye molecules are not quite as well resolved. This type of structure, originally proposed by Kuhn and co-workers[4] was also observed by Wolthaus et al.[6] in AFM images of J-aggregates of a mercocyanine dye.

The tunneling mechanism in our images appears to be quite straightforward. A simple model in which the electrons of the highest occupied molecular orbital (HOMO)
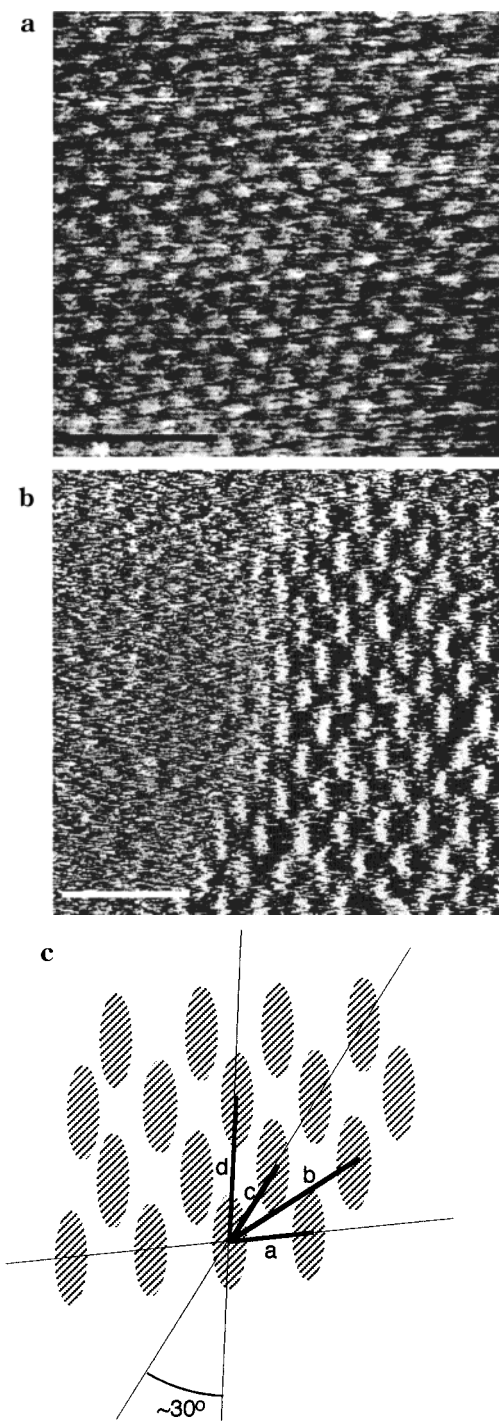
(8) Grafstrom, S.; Schuller, P.; Kowalski, J.; Neumann, R. *Appl. Phys. A* **1998**, *66* (2), S1237−S1240.

(9) Maeda, Y.; Matsumoto, T.; Kawai, T. *Surf. Sci.* **1997**, *384* (1−3), L896−L903.

(10) Boden, N.; Bushby, R. J.; Martin, P.; Owens, R. W.; Smith, D. A. *Mol. Cryst. Liq. Cryst.*, in press.

(11) Hegner, M.; Wagner, P.; Semenza, G. *Surf. Sci.* **1993**, *291*, 39.

Figure 1. (a) Constant-current STM height image of the bromide adlayer on a template-stripped silver (111) substrate imaged beneath an adsorbed PIC J-aggregate layer shown in part b. (PtIr tip, i_t = 2.403 nA, v_b = −500 mV, D_z = 0.35 nm; scale bar 25 Å). The atomic arrangement is a quasi $\sqrt{3} \times \sqrt{3}$ structure with an estimated spacing of 4.9 ± 0.5 Å. (b) Constant-height image of a J-aggregate monolayer on top of the halide adlayer in part a. The image was obtained by lowering the current set point from 2.403 nA in part a to withdraw the tip from the substrate. The expected "brickwork" packing arrangement of the PIC molecules can be seen clearly (PtIr tip, i_t = 2.075 nA, v_b = −500 mV, D_z = 379 pA; scale bar 25 Å). (c) Schematic representation of the molecular arrangement in the PIC monolayer shown in part b: nearest and next-nearest neighbor distances of a = 8.9 Å, b = 16.0 Å, c = 8.3 Å, and d = 16.0 Å; slip angle of about 30°.

of the PIC tunnel into the tip is qualitatively supported by the biasing conditions required. The STM images of

adsorbed dye aggregates could only be acquired at quite large negative sample biases (∼ −500 mV). The work function of silver is 4.6 eV,[12] and the HOMO of PIC lies about 0.8 eV below the Fermi level of silver.[13] If we assume an average work function for PtIr of 5 eV (about 0.4 eV above the dye HOMO), then negative sample biases of the order we are observing would support the simple model of electrons from the dye HOMO tunneling into the tip.

Upon further reduction of the current set point by 2 orders of magnitude to 20−100 pA, we observed a second layer of molecular aggregates with a different molecular packing arrangement from that of the first layer (Figure 2a and b). The dye molecules in the second layer form aggregates in rows, which appear to correspond to the "staircase" arrangement proposed by Kuhn et al.,[4] rather than the brickwork pattern. In the structures shown in Figure 2, the molecules are tilted by about 30° to the row axis and there is a perpendicular distance of 12 Å between rows (compared with 7 Å between rows in the first layer (Figure 1c). It is more difficult to resolve the individual molecules in the second layer; however, on the basis of the STM data in Figure 2a and b, the packing arrangement in Figure 2c is proposed. The nearest neighbor distances are approximately 9.0, 12.0, and 14.3 Å. This "staircase" packing arrangement is similar to the structures reported by Kawasaki and Ishii[1] for 1,1′-diethyl-2,2′-carbocyanine bromide, an H-aggregate-forming dye. This dye differs from PIC because (i) the distance between the two quinoline rings is doubled and (ii) the quinoline rings are coplanar, whereas in PIC they adopt a twisted structure.[14] However, the reflection absorption spectrum of the PIC samples we prepared (Figure 3) shows only the narrow absorption (peak 575 nm, fwhm ∼ 18 nm), red-shifted from the monomer absorption at 521 nm typical of J-aggregates.

It is clear that a well-ordered bromide monolayer forms on the Ag(111) surface, and this layer appears to play a key role in the formation of stable monolayers of dye through an interaction of the bromide with the dye cations. The plane to plane stacking of the aromatic rings in the dye is presumably driving the formation of molecular aggregates, and it seems reasonable, therefore, to assume that the aromatic rings lie roughly perpendicular to the substrate and that the nitrogen substituents face the bromide counterion monolayer. It is not possible to develop an unequivocal model for the packing relationship between the two J-aggregate layers from our STM data alone or to determine whether there is a second counterion layer involved in the bilayer formation. Further work is necessary to address these questions.

Dye Aggregates Formed on Self-Assembled Monolayers. As described above, the principle of our approach to reducing the nonradiative relaxation rate for J-aggregates on metal surfaces, while maintaining our ability to use the STM to image the structures, is based on spacing the dye molecules away from the metal substrate using self-assembled monolayers (SAMs). A schematic of the system is shown in Figure 4. We experienced no success in forming dye assemblies on SAMs with methyl head groups, but reflection absorption measurements of a COOH-terminated SAM that had been incubated with the PIC bromide dye solution indicated that J-aggregates had been formed on the surface. However, it was not possible to find any conditions under

(12) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: London.
(13) Misawa, K.; Ono, H.; Minoshima, K.; Kobayashi, T. *J. Luminesc.* **1994**, *60–1*, 812.
(14) Smith, D. L. *Photogr. Sci. Eng.* **1974**, *18*, 309.
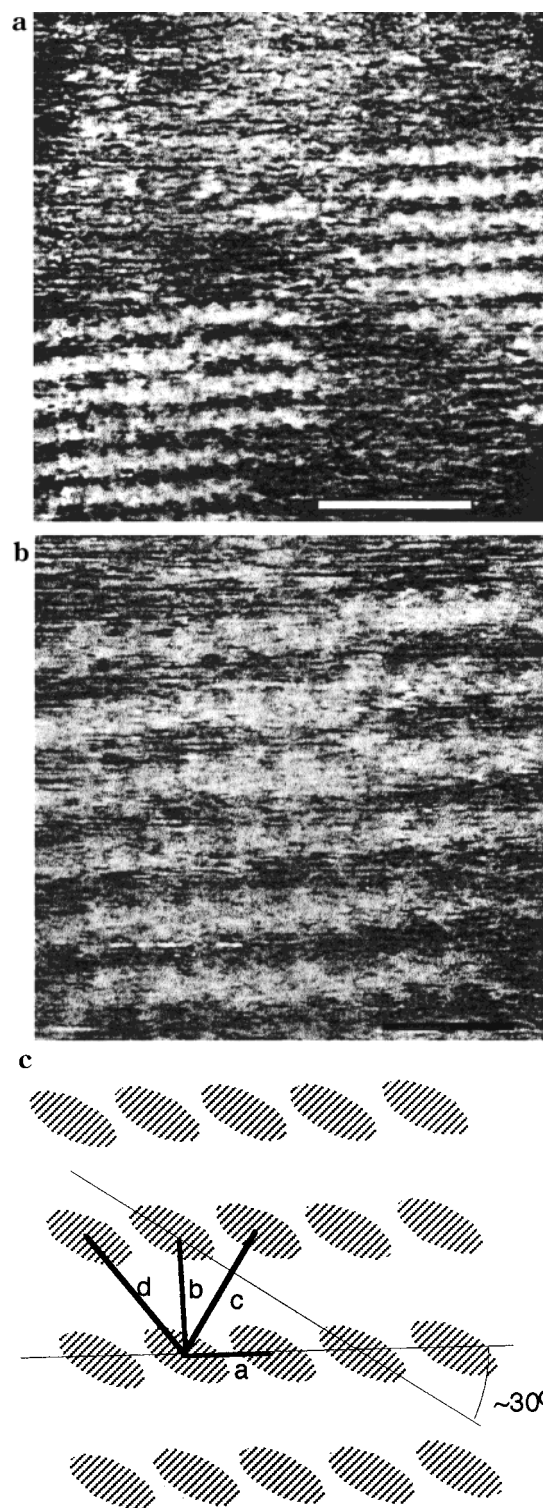
Figure 2. (a) Constant-current STM height image of a second layer of adsorbed PIC dye molecules on top of the first shown in Figure 1b. The dye molecules in the second layer are seen to form linear assemblies or rows rather than the brickwork structure of the first layer. The PIC molecules have a tilt of about 30°to the row axis and a row spacing of 12 Å (PtIr tip, $i_t = 19.7$ pA, $v_b = -598$ mV, $D_z = 9.2$ Å; scale bar 50 Å). (b) Higher resolution image of the *J*-aggregate second adlayer (same imaging conditions as in part a; scale bar 20 Å). (c) Proposed molecular packing arrangement of the PIC molecules in the linear aggregates shown in parts a and b. The row separation is approximately 12 Å, and the dye molecules appear to lie at a tilt angle of about 30° with respect to the row axis. The nearest neighbor distances are $a = 9.0$ Å, $b = 12.0$ Å, $c = 14.5$ Å, and $d = 14.3$ Å.
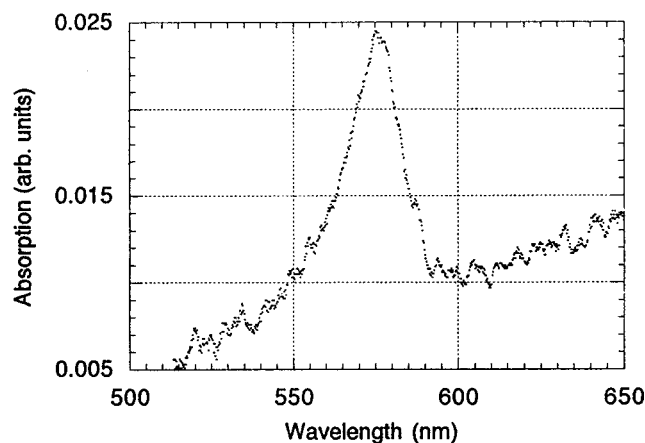
Figure 3. Reflection absorption spectrum of the dye layer(s) imaged in Figures 1 and 2. The spectrum exhibits the typical absorption feature of a J-aggregate—a narrow (fwhm ~18 nm) peak, red-shifted (center ~ 575 nm) from the monomer absorption (~521 nm). The absorption spectrum acquired for a bare silver substrate has been subtracted from the raw data.
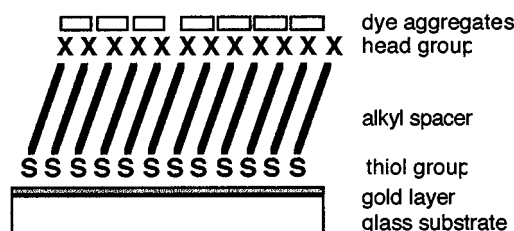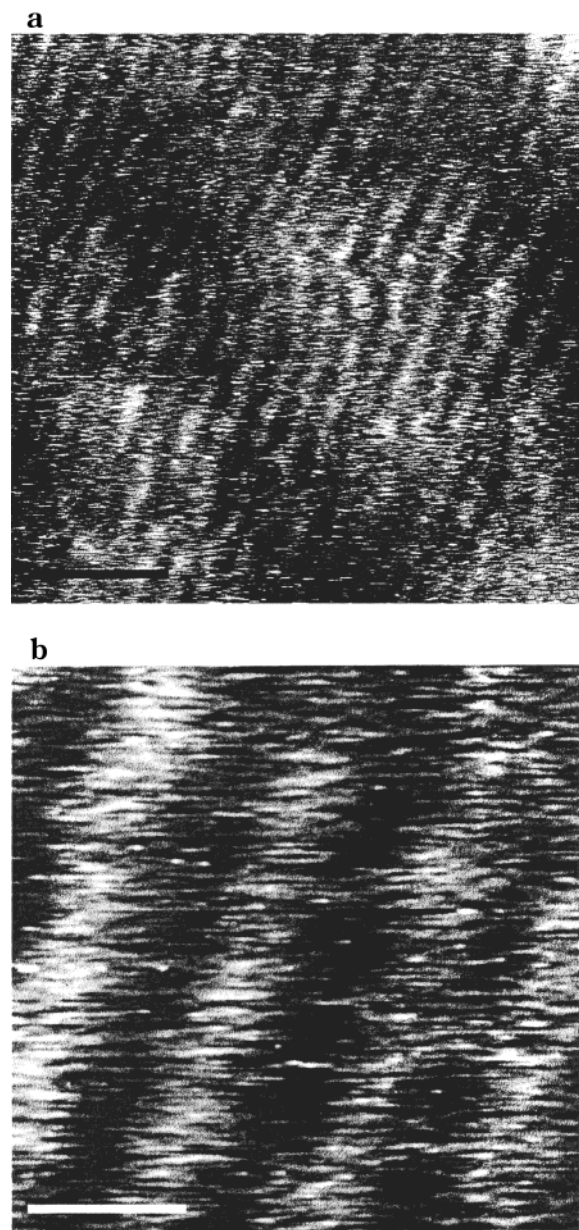

Figure 4. Schematic representation of the SAM/J-aggregate system.

which these aggregates could be imaged with the STM, suggesting that although aggregates were formed, they were not bound strongly enough to the carboxylic acid surface to withstand the forces exerted by the tip during imaging. This further supports the hypothesis that the negative halide counterion plays a key role in the stable adsorption of PIC to surfaces. Pretreatment of the COOH SAM with 1 mM AgNO$_3$ solution prior to exposure to the dye solution did, however, yield large stable J-aggregates (Figure 5a). The linear aggregates, which typically measured many tens of nanometers in length, completely covered the SAM surface, and in some areas we observed very large aggregates of many hundreds of nanometers. The higher resolution image of the aggregates shown in Figure 5b does not reveal any information about the molecular packing within the aggregates but provides an accurate row spacing of 30 Å. This lack of resolution is presumably due to the increased distance between the organic dye and the metal substrate (the spacing from the surface produced by an 11 carbon spacer SAM is about 15 Å and depends to some extent on how well ordered a monolayer has been formed) but may also be an indication of increased dye mobility on the SAM in comparison with that of the aggregates formed directly on silver. No such linear structures were observed on the AgNO$_3$-pretreated SAMs without the application of the PIC bromide solution (images not shown). The only observable effect of the AgNO$_3$ pretreatment was to increase slightly the roughness of the SAM surface.

It is known that silver forms complexes with the carboxyl group of acids which mostly have centrosymmetric dimeric structures.[15] Known examples are silver(I) benzoate[16] and

(15) Ulku, A.; Nawaz Tahir, M.; Movsumov, E. M. *Acta Crystallogr.* **1996**, *C52*, 2678.

a

b

Figure 6. Reflection absorption spectrum of the PIC sample prepared on the AgNO$_3$-pretreated COOH SAM. The absorption spectrum of the gold/SAM substrate has been subtracted from the raw data. The peak absorption wavelength is ~581 nm; fwhm = 10 nm.
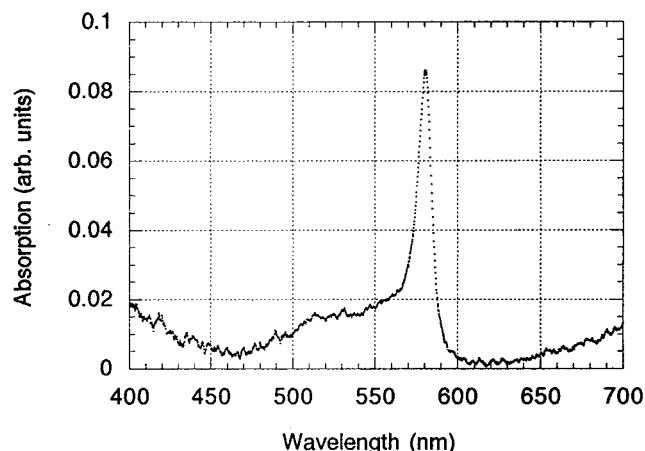
Figure 5. (a) Constant-current STM height image of PIC J-aggregates formed on a AgNO$_3$-pretreated COOH-terminated SAM. The dye molecules appear to form linear assemblies over large distances with a row spacing of approximately 30 Å (PtIr tip, i_t = 550 pA, v_b = −500 mV, D_z = 25 Å; scale bar 125 Å). (b) High-resolution height image of the same area as that in Figure 4a. The detailed molecular arrangement within the aggregates cannot be resolved (PtIr tip, i_t = 285 pA, v_b = −500 mV, D_z = 3 Å; scale bar 25 Å).

silver(I) 4-hydroxybenzoate.[16] Silver is also known to form polymeric structures via cross-linking between Ag−OH groups, for example, poly[bis(*p*-nitrosalicylato-O:O′)-disilver(I)-O^3:Ag′:Ag:O^3].[17] This propensity to form dimeric and polymeric structures with acids suggests that the AgNO$_3$ pretreatment of the SAM is likely to result in chelation of silver atoms between the carboxyl head groups of the monolayer. The presence of silver in the SAM and its polycoordinate chemistry would then permit bromide counterions to adsorb from the PIC solution to assist in the formation of the stable aggregates which we observe.

(16) Ushbaliev, G. J.; Movsumov, E. M.; Amiraslanov, I. R.; Akhmedor, A. I.; Musaev, A.; Mamedov, K. S. *J. Struct. Chem.* **1981**, *22*, 73.
(17) Tahir, M. N.; Ulku, D.; Movsumov, E. M. *Acta Crystallogr.* **1996**, *C52*, 593.

Unfortunately, we have not been able to image the silver/SAM complex or the postulated bromide adlayer with our current instrumentation. However, the formation of large, stable J-aggregates strongly implies that bromide counterions are playing a role.

The reflection absorption spectrum of the J-aggregate on the pretreated SAM exhibits the typically narrow (fwhm 10 nm), red-shifted J-aggregate peak at ~581 nm (Figure 6). The band is stronger, narrower (10 nm cf. 15 nm), and more red shifted (581 nm cf. 575 nm) than that in the case of the J-aggregate formed directly on Ag(111). A peak absorption of 575 nm for a brickwork structure of PIC has been reported several times, and it appears from our data that a linear aggregate or staircase structure has a greater red shift, presumably due to an increased electron delocalization.

In the case of the samples prepared directly on silver and discussed above, where linear aggregates formed on top of a monolayer with a brickwork structure, the difference in red shift of the two structures might be expected to lead to a broadened absorption peak or a shoulder appearing on the red edge of the absorption band. The spectrum in Figure 3 is indeed broader than that in Figure 6, where only a monolayer was observed by STM, and there is some evidence of a shoulder at 581 nm. However, these monolayer absorption spectra are difficult to obtain and the data presented in Figure 3 are too noisy to reliably identify such features. Further work is necessary to determine whether the second adsorbed layer has different optical properties from the first.

Conclusions

The long-term goal of our research is to develop methodologies for STM imaging of molecular excited states pumped by laser excitation. J-aggregate dyes are ideal systems for such studies, since they have strong, narrow absorptions at convenient wavelengths accessible by tuneable dye lasers. However, to reduce the quenching of the excited state by energy transfer to the metal substrate, the dye molecules must be spaced away from the metal, but not too far to prevent STM imaging. We have achieved this by preparing J-aggregates of 1,1′-diethyl-2,2′-cyanine (PIC) dye on top of self-assembled monolayers of 11-mercaptoundecanoic acid (HS−(CH$_2$)$_{10}$−COOH). J-aggregates were formed on this carboxylic acid surface (confirmed by reflection absorption spectroscopy); how-

ever, it was not possible to image them with the STM. We have attributed this to the weak binding of the dye assemblies to the COOH surface and subsequent destruction of the aggregates under the forces exerted by the tip during scanning. We further suggest that this instability is due to the fact that bromide counterions from the PIC solution cannot adsorb on the COOH surface, which appears to be an essential step in the formation of stable aggregates on surfaces. By pretreating the SAM with a solution of 1 mM $AgNO_3$ before the application of the PIC dye solution, we have been able to detect the formation of J-aggregates both by spectroscopy and by STM imaging. We believe that silver atoms form a chelate with the carboxyl head groups of the SAM, permitting the subsequent adsorption of the bromide counterions from the dye solution and the formation of stable aggregates. In contrast with the brickwork structure of the J-aggregates formed directly on Ag(111) surfaces reported by Kawasaki and Ishii,[1] those formed on the $AgNO_3$-pretreated SAM are linear assemblies similar to the "staircase" structure proposed by Kuhn[4] with a row spacing of 30 Å.

J-aggregate monolayers formed on silver (111) with a bromide counterion have also been imaged with a STM for comparison with the structures formed on SAMs. In these samples we observed the previously unreported formation of a second layer of dye molecules at quite low coverage on top of the first "brickwork" layer. This second adsorbed aggregate layer comprises linear aggregates similar to those observed on the pretreated COOH SAM surface with a row spacing of 12 Å. From the data presented here it has not been possible to determine the spatial relationship between these two layers of J-aggregates, and further work is necessary to elucidate the exact packing arrangement.

LA9905214