

Supramolecular Organisation Of Spectral Sensitizers On Atomically Flat Bromide-Modified Ag(111). A combined STM and DRS Study.

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Abstract

The relation between optical properties and aggregate structure of spectral sensitizers was studied by a combination of Diffuse Reflectance Spectroscopy (DRS) and Scanning Tunneling Microscopy (STM). For this purpose highly planar Ag films with a (111) crystallographic orientation were deposited on mica. After immersing the Ag films in a diluted KBr solution, X-ray Photoelectron Spectroscopy (XPS) showed that the surface was converted into a AgBr layer. STM images of this bromide-modified surface revealed a quasi-hexagonal atomic configuration with a lattice spacing of 3.9 Å which is slightly less than for AgBr microcrystals. Substrates are also bathed in separate or mixed KBr and dye solutions and the adsorbed dye aggregates are spectrally analysed using DRS. The reflectance spectra obtained for the Ag/AgBr model system are similar to those of AgBr microcrystals. An easy-to-handle, home-built STM operating under ambient conditions was used to image the molecular structure of the aggregates. Although image interpretation is not straightforward, two pairs of cyanine dyes, forming different aggregate types, are observed. For J-aggregating dyes, STM images reveal a "network"-like structure with a slip angle of ~22°. For the other dyes STM images display a "column"-like structure with a plane-to-plane distance of 3.5 to 4 Å.

Introduction

The typical absorption characteristics of photographic emulsions result from the organisation of dye molecules into aggregates on the AgX (X=Cl, Br, I) crystal surface. The molecular structure of the dyes together with many experimental parameters determine the final structure and the corresponding optical behaviour of these self-assembled

layers. A distinction is made between aggregates whose spectrum show a hypsochromic shift (H-aggregate) or a bathochromic shift (J-aggregate) compared to the monomer spectrum. Proposals for the aggregate structure are usually based on extended dipole model calculations [1] and molecular modelling [2]. During the last years a number of analytical techniques such as color fluorescence electron microscopy [3] and high-resolution scanning electron microscopy [4] have been applied to study aggregate structures, all lacking however the ability to deliver information on a molecular scale. Suzuki and Nozoye [5] and Kawasaki and Ishii [6] used respectively atomic force microscopy (AFM) and a commercial scanning tunneling microscope (STM) to study aggregation of PseudoIsoCyanine with molecular resolution.

For this work a combination of Diffuse Reflectance Spectroscopy and Scanning Tunneling Microscopy was used to study the relation between optical properties and aggregate structure of spectral sensitizers on AgBr. Because of the insufficient conductivity of AgBr microcrystals for STM analysis, it was necessary to prepare a model system that fulfils the requirements of STM and both chemically and structurally represents the AgBr crystal surface [7]. For this purpose silver films with a bromide-modified surface were used. Aggregates were formed after immersing the film in a dye solution. Aggregation behaviour on the AgBr model surface and on the AgBr microcrystals was compared on the basis of diffuse reflectance spectra. Molecularly resolved STM images of the adsorbed dye aggregates were acquired using a home-built STM. Molecular modelling was used to support interpretation of the complex STM images, which are built up by a combination of topographical and electronic effects. In this way a correlation can be made between the optical properties and the aggregate structure of a dye. A number of cyanine dyes, forming different aggregate types, have been studied.

Experimental

A Perkin-Elmer Ultek Rapid Cycle System, equipped with an electron gun for evaporation, was used to deposit Ag films on freshly cleaved mica at a substrate temperature of 200 °C to obtain atomically flat terraces[8]. Sample temperature was measured with a thermocouple connected to the clamps holding the mica. A deposition rate of 10 Å/s was chosen to prepare films of 2400 Å thickness. The pressure during evaporation was $\sim 5 \cdot 10^{-7}$ Torr. After deposition the Ag films were annealed at 200 °C for 60 to 100 minutes. X-ray diffraction (XRD) indicated a (111) orientation.

The prepared Ag films were bathed consecutively in a 10^{-3} M KBr solution (10 min.) and a 10^{-3} M dye solution (35 min.) or in a mixed KBr/dye solution (35 min.). Afterwards the films were rinsed with cooled water and the remaining droplets were blown off with nitrogen. Solutions consisted of a 1:1 water to ethanol volume ratio.

XPS analysis of prepared substrates was performed by a Perkin-Elmer PHI 1257 spectrometer with a hemispherical energy analyser. The samples were irradiated with monochromatic Mg $K\alpha$ X-rays of 1253.6 eV. The electron take-off angle was 90° with respect to the sample surface.

A SHIMADZU 2101 diffuse reflectance spectrometer, equipped with a halogen lamp (360 to 800 nm) and a deuterium lamp (240 to 360 nm), was used for spectral analysis of dye aggregates adsorbed on the films. The dye spectra were obtained by subtracting the absorbances of the film with and without dye. The slowest scan speed was chosen to reduce noise in the spectrum. By using a variable energy slit width the energy reaching the detector is approximately constant.

STM images were acquired with a home-built, easy-to-handle high-resolution microscope operating under ambient conditions [9]. A vibration isolated optical workbench, together with a very low vibration level of the floor, reduces the influence of vibrations on the STM. Furthermore, it is shielded from acoustic noise by a metal box. The hardware consists of a simple analogue feedback system and an analogue I-O board in a personal computer. To avoid noise problems with D-A converter we control the lateral tip position in an indirect way by integrating a voltage to obtain the required velocity of the STM tip. In this way we get a more accurate control of the tip position as well as more time to acquire and average the incoming data. Special care is needed to minimize the intrinsic drift of these integrators. To reduce this drift we designed special software which accomplishes the reduction without the need of additional hardware. For this work the STM was operated in the constant current mode. All images shown below were acquired with a Pt/Ir tip. The tunneling current (I_t) was varied from 5 to 50 pA for bias voltages (V_b) of 50 to 500 mV.

Results and discussion

Figure 1 shows a STM image of a highly planar Ag(111) film deposited on mica (10 Å/s, 2400 Å, 200 °C). Atomically flat terraces several tens of square nanometer in size are present. Average surface roughness is within 1 nm over several hundreds of nanometer which is sufficiently flat for STM measurements of adsorbed dye aggregates. The (111) crystallographic directions can clearly be seen.

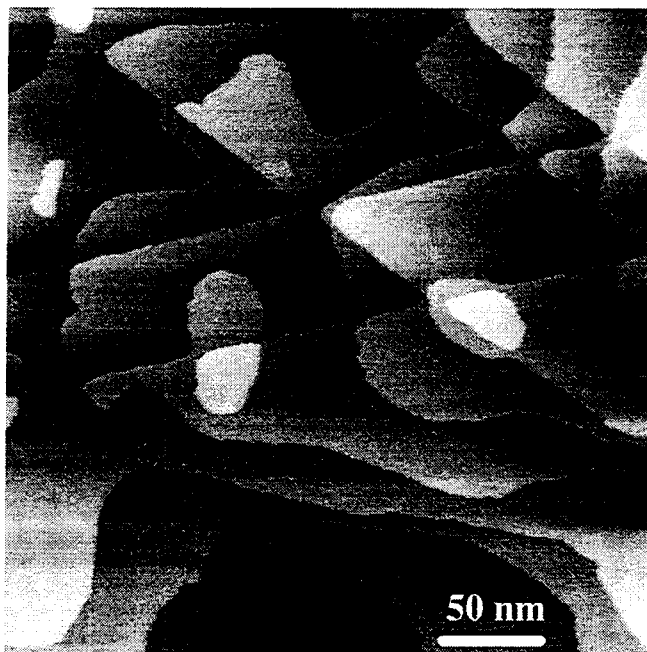


Figure 1. STM image ($300 \times 300 \text{ nm}^2$, 30 pA, 100 mV) of a Ag(111) film with atomically flat terraces deposited on mica (10 Å/s, 2400 Å, 200 °C).

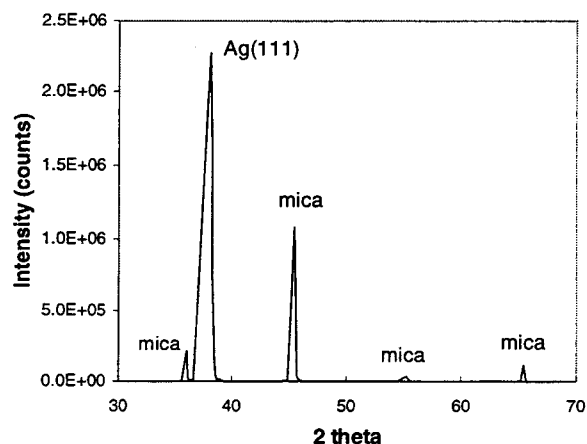


Figure 2. XRD spectrum of an Ag(111) film deposited on mica.

The crystallographic orientation of the Ag film was confirmed to be (111) by XRD (Fig.2). An interplanar

distance of 2.36 Å was found in agreement with the expected value (2.359 Å).

After bathing a Ag film in a KBr solution small Br peaks appear in the XPS spectrum indicating that a very thin AgBr layer has been formed on the surface (Fig. 3).

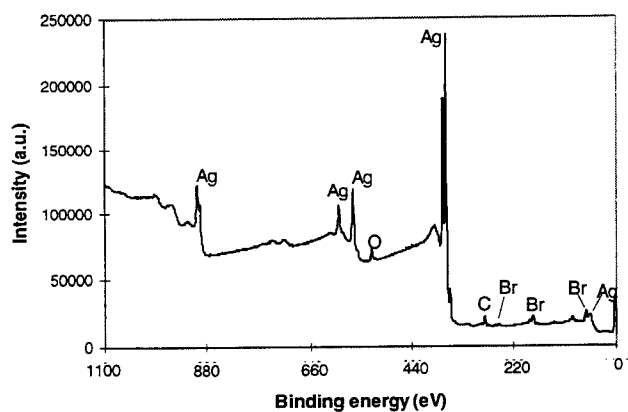


Figure 3. XPS spectrum of the bromide-modified Ag(111) surface.

The AgBr surface layer was studied by STM. A high-resolution STM image is shown in figure 4. A quasi-hexagonal atomic configuration is found with a lattice parameter of ca. 3.9 Å which is slightly smaller than for a (111) surface of octahedral AgBr crystals (4.08 Å). However, for all dyes we have studied, similar spectral behaviour has been found on the AgBr model surface and on octahedral AgBr crystals.

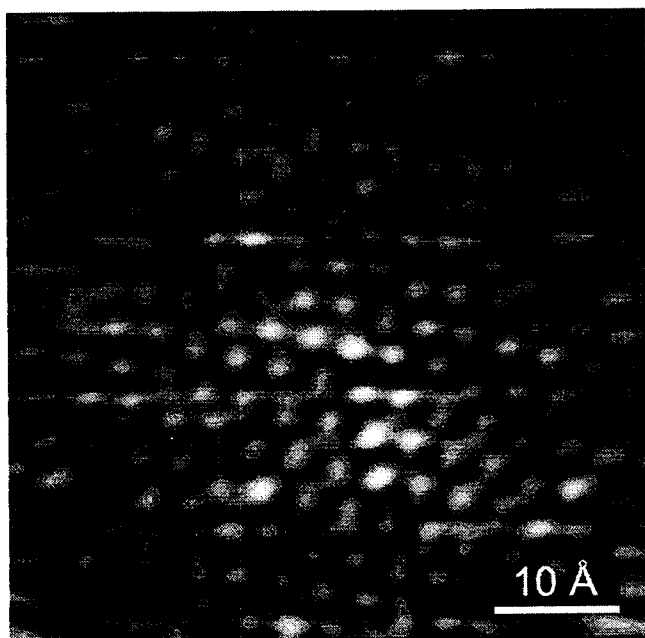


Figure 4. STM image of the bromide-modified Ag(111) surface (50 x 50 Å², 220 pA, 200 mV).

The chemical structure of the four cyanine dyes studied in this work is shown on top of figures 5 to 8. The reflection absorbance of dye I on a AgBr model film was measured as a function of concentration (10^{-7} to 10^{-2} M). Saturation of the intensity was found for a concentration of $\sim 5 \cdot 10^{-4}$ M. For this concentration the intensity was monitored as a function of time. After a bathing time of 30 to 40 minutes (at room temperature) the intensity remained constant. In order to obtain complete surface coverage of the substrate all experiments described below were carried out with 10^{-3} M dye solutions and a bathing time of ~ 35 min.

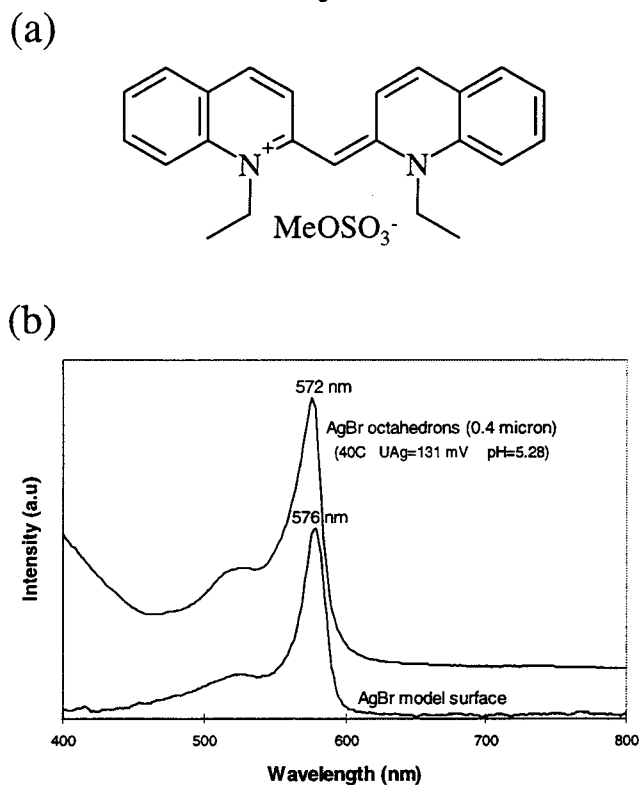
Diffuse reflectance spectra of the four dyes studied are given for an emulsion of AgBr octahedral microcrystals and for the AgBr model surface. For the emulsions absolute spectra are plotted. Surface coverage is 80 %.

Dye I (Fig. 5a) (PseudoIsoCyanine, PIC) and dye II (Fig. 6a) have been studied with STM by Kawasaki [6]. For both spectra of dye I a red-shifted J-band (compared to the monomer spectrum) is observed with its maximum respectively at 572 and 576 nm (Fig. 5b). Both spectra of dye II show a broad profile ranging from 500 to 700 nm, with maxima at 550, 600 and 645 nm for the model substrate (Fig. 6b). The STM image of dye I shows a structure with a "ring-like" pattern between the molecules (Fig. 5c). A slip angle of ~ 22 degrees is found. The STM image of dye II (Fig. 6c) displays a "column-like" structure with molecules stacked plane-to-plane and separated by 3.5 to 4 Å. In some images domains are visible with columns rotated over 120 degrees, corresponding to the (111) crystallographic orientation of the underlying AgBr surface. It is clear that from the STM images that a distinction can be made between the aggregate structure of both dyes. Results agree with those reported by Kawasaki [6].

The second pair of dyes studied are of the thiacyanine type (Fig. 7a and 8a). Both dyes are identical except for the mesomethine substituent. The spectra of dye III, which has a meso-methyl group, have a hypsochromic band (compared to the monomer spectrum) at respectively 525 nm and 535 nm (Fig. 7b). The spectra of dye IV, which has a meso-ethyl group, show a bathochromic band at respectively 637 nm and 621 nm (Fig. 8b). The shift of the absorption maxima of emulsion and model substrate is possibly due to slightly different absorption interactions of dye molecules on the Br-modified layer and the AgBr crystal surface. The STM image of dye III (Fig. 7c) reveals a column-like structure while the image of dye IV displays a 2D-network structure with a slip angle of ~ 22 degrees (Fig. 8c). Again, one can conclude that also for this pair of thiacyanine dyes a clear distinction can be made between aggregate types.

Because STM images are built up by a combination of topographical and electronic effects image interpretation can be rather difficult. Further interpretation of the STM images, based on molecular modelling results, will be presented at the conference.

Dye I



Dye II

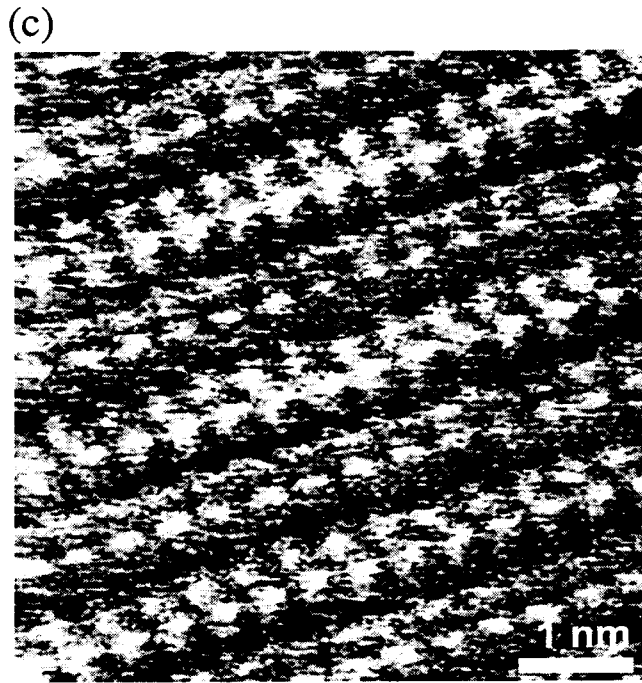
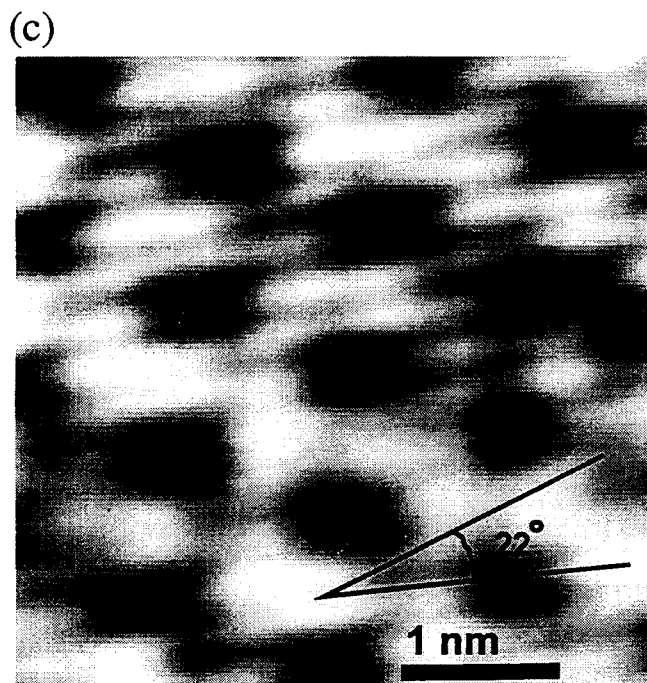
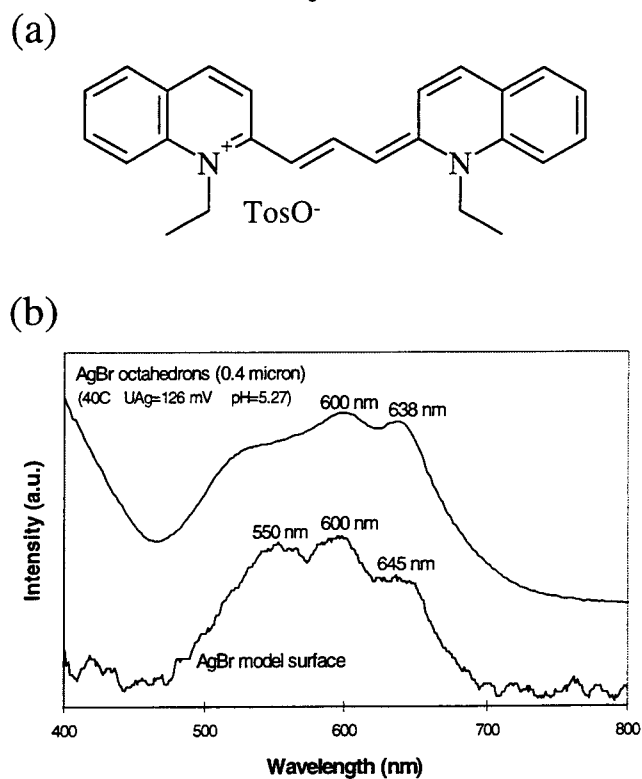
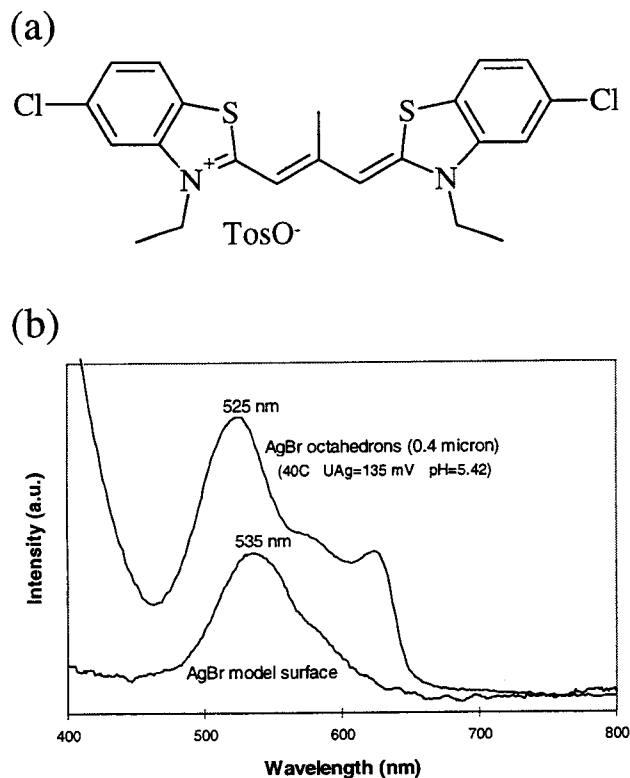


Figure 5. (a) structure of dye I, (b) DRS spectrum of dye I on AgBr octahedral microcrystals and on the AgBr model surface, (c) STM image ($4 \times 4 \text{ nm}^2$, 12 pA, 102 mV).

Figure 6. (a) structure of dye II, (b) DRS spectrum of dye II on AgBr octahedral microcrystals and on the AgBr model surface, (c) STM image ($6 \times 6 \text{ nm}^2$, 25 pA, 200 mV).

Dye III



Dye IV

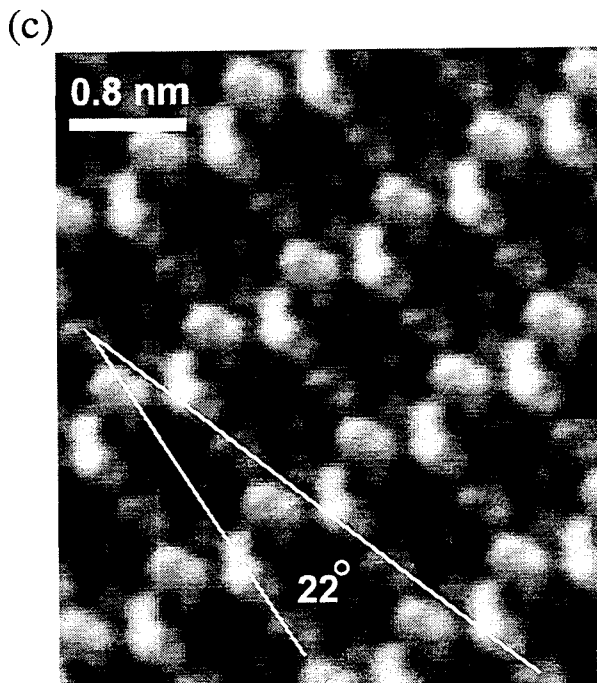
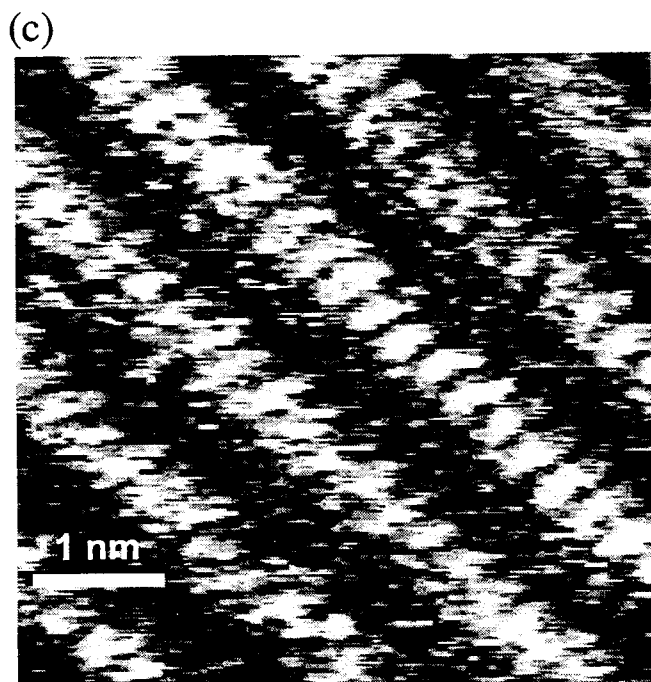
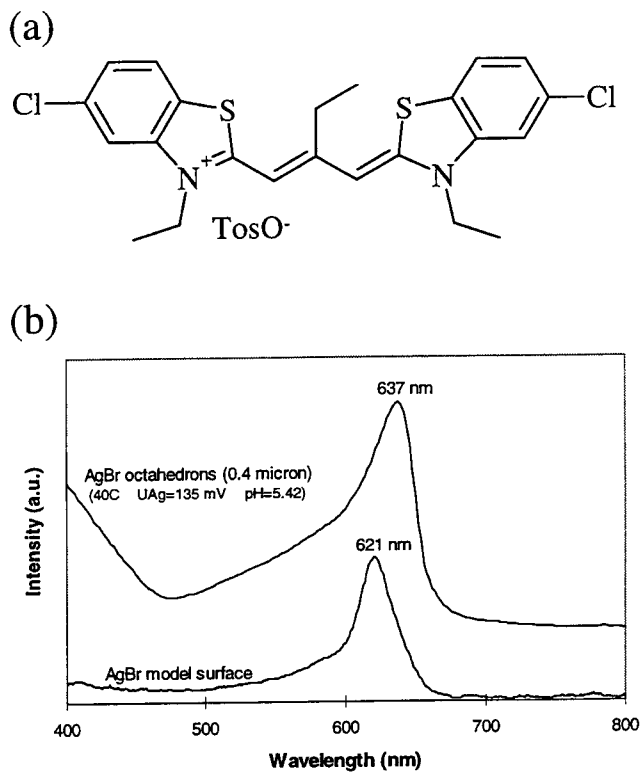


Figure 7. (a) structure of dye III, (b) DRS spectrum of dye III on AgBr octahedral microcrystals and on the AgBr model surface, (c) STM image ($5 \times 5 \text{ nm}^2$, 28 pA, 120 mV).

Figure 8. (a) structure of dye IV, (b) DRS spectrum of dye IV on AgBr octahedral microcrystals and on the AgBr model surface, (c) STM image ($3.6 \times 4.2 \text{ nm}^2$) obtained from cross correlation calculations.

Post-processing of STM images

For post-processing of measured STM images we have a large library of noise reduction and image manipulation routines which are available to the users. One such technique we use to improve our STM images is correlation averaging [10,11].

A STM image ($12.5 \times 12.5 \text{ nm}^2$) of an aggregate of dye IV is shown in figure 9a. A reference cell ($3.6 \times 4.2 \text{ nm}^2$) is taken from this raw image. Then a correlation matrix is calculated by moving the reference cell pixel by pixel across the image. A threshold value is set to select local maxima in the correlation matrix. Figure 9b shows that 70 spots with high correlation are detected, i.e. positions in the image that matches the reference cell (given a certain threshold value). All cells corresponding to the positions with high correlation are then averaged. In this way an image is produced with the size of the reference cell and containing the pattern found in the original image but with reduced noise (Fig. 8c).

Conclusion

By heating a mica substrate a highly planar Ag(111) film could be deposited whose surface was modified by bathing in a diluted KBr solution. In this way a model system was developed which on one hand is representative for the surface of octahedral AgBr microcrystals both chemically as well as structurally and on the other hand is conducting and flat enough for STM measurements. After immersing a silver film in separate or mixed KBr/dye solutions DRS showed similar aggregation behaviour as on spectrally sensitized AgBr crystals. Results of four dyes are presented. A clear distinction can be made between STM images of different aggregating dyes. For some dye aggregates a plane-to-plane stacking is found while others are built up of a molecular network with a slip angle of ~ 22 degrees.

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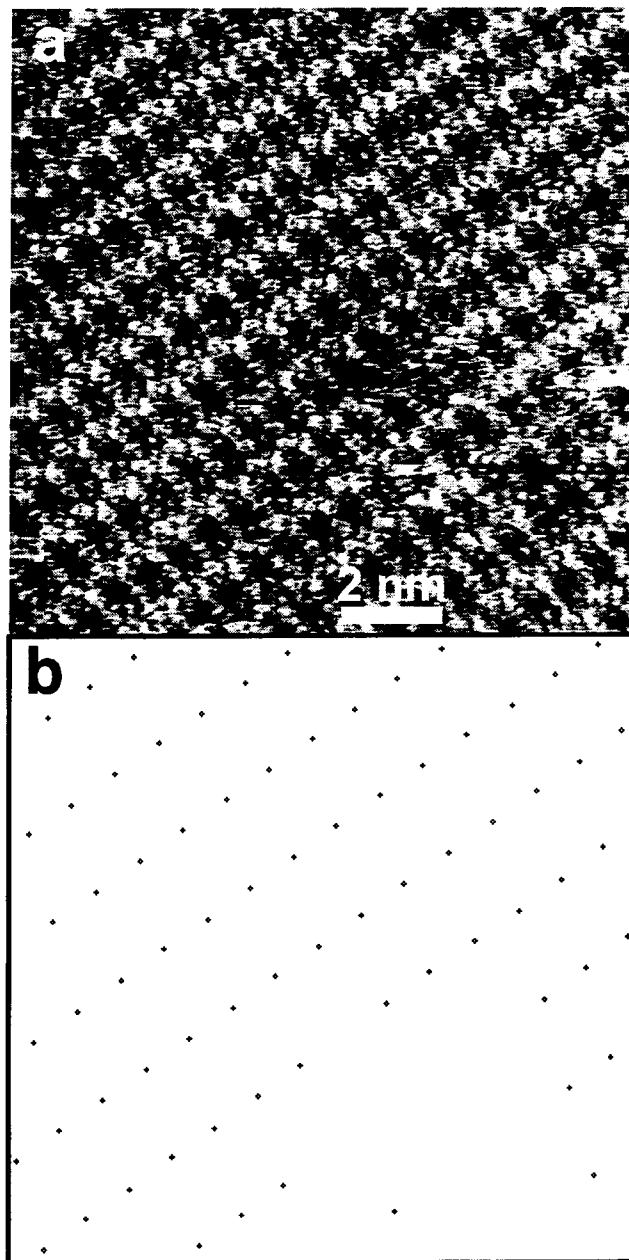


Figure 9. (a) raw STM image of dye IV ($12.5 \times 12.5 \text{ nm}^2$, 45 pA, 300 mV), (b) 72 spots detected with very high correlation.

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