

Architecture and Surface Properties of Monomolecular Films of a Cyanine Dye and Their Light-Induced Modification

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Monolayers of a water-insoluble cyanine dye are deposited on negatively charged substrates such as glass, mica, or a thin film of a poly(acrylic acid) (PA) by adsorption from a solvent in which the dye is scarcely soluble. The choice of the substrate has a strong influence on the architecture of the dye layers. A submonolayer coverage of the monomeric dye is formed on PA, whereas a complex layer structure of J-aggregated dye molecules is formed on mica. The dye layers on mica have different affinities for the adsorption of charged colloidal particles and macromolecules. Photooxidation of the dye yields a water-soluble product. This photochemical reaction is the basis for forming surface structures of different reactivity by photopatterning of the dye layers. After photopatterning the bleached dye is dissolved in water. Conditions were found where macromolecules or colloidal particles adsorb preferentially either to exposed or to unexposed areas of photopatterns on a mica substrate.

Introduction

This work was motivated by the aim to develop monomolecular layers of a dye as photosensitive layers (photolayers) for photopatterning by near-field optical methods. Near-field optical methods can, by use of visible light, be used to generate interfacial nanostructures with structural details well below the diffraction limit of conventional light microscopy. Contact imaging by energy transfer was used as a near-field optical method to make copies of metal nanostructures onto monomolecular dye layers at a resolution of 70 nm,¹ and scanning near-field optical lithography (SNOL) using aperture type near-field probes was used to write structures into a conventional photoresist at a resolution of 80 nm.^{2–4} The resolution that was achieved so far in photopatterning using these near-field optical techniques can probably be improved considerably. The resolution of contact imaging by energy transfer is limited by the grain size of the light-sensitive medium and by the distance between the light-sensitive medium and the mask¹ and thus ultimately by the size of the dye molecules on the order of 1 nm. In scanning near-field optical microscopy, by use of light-emitting near-field probes, a resolution in the 1–10 nm range was obtained recently,⁵ and there is a possibility that a resolution in the 1–10 nm range can be achieved also in SNOL by applying similar methods. To make use of the full resolution potential of near-field photopatterning, the photosensitive layers should be as thin as possible, since the aspect ratio d/l between depth of exposure d and the lateral extension l of a small structural detail is significantly less than 1.⁴ Therefore, monolayers of a dye are suitable as photosensitive layers for photopatterning by near-field optical methods.

Instead of using a photoresist as a mask to etch structures into the underlying substrate, we intend to use monomolecular dye layers as photolayers to create surface patterns of different chemical reactivity by photopatterning. The photopatterns may serve to build up nanostructures by selective adsorption of

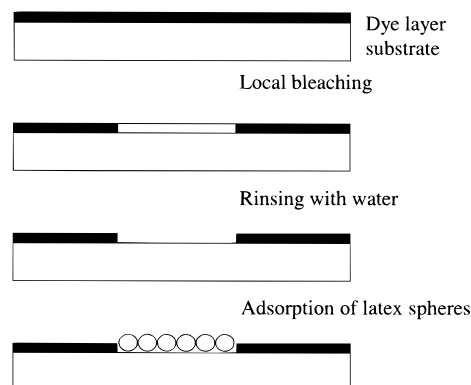


Figure 1. Concept of monomolecular dye layer as a photolayer. The dye layer is bleached locally by exposure of a pattern. The water-soluble bleached dye is removed by rinsing with water. Colloidal particles are selectively adsorbed to exposed areas because of the different affinities of the unbleached regions and the substrate toward binding of the colloidal particles.

macromolecules or colloidal particles to either the exposed or unexposed areas.

The concept of a photolayer as elaborated here is summarized in Figure 1. The photolayer consists of a monomolecular film of a water-insoluble dye. The photoproduct of the dye is water-soluble and can therefore be removed by rinsing with water. This concept accidentally is similar to the one of conventional photoresists where a differential solubility of unexposed and exposed regions is made use of for the development process. Other concepts of a photolayer are conceivable, where a development process such as rinsing with water is not necessary. Owing to the different adsorption properties of the substrate and of the photolayer, colloidal particles may be adsorbed selectively either to the exposed or to the unexposed regions of the pattern. In our case we investigate the adsorption of colloidal particles and charged macromolecules to the photopatterns, which is dominated by electrostatic interactions.

The concept of building up nanostructures on the basis of lithographically defined surface structures in monomolecular

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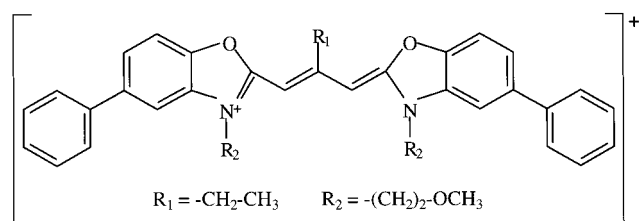


Figure 2. Structure of the cyanine dye molecule

films was previously demonstrated by Zingsheim⁶ using a focused electron beam and by Calvert⁷ using UV radiation or an STM for exposure of the monomolecular layers. The advantage of photopatterning resides in the specificity of the photoreactions in the visible spectral range. By use of schemes similar to the ones described here, the concept of combinatorial chemistry that is made use of, for example, in spatially addressable photodirected synthesis,⁸ might eventually be scaled down to molecular dimensions.

In this communication we report a method to deposit water-insoluble monomolecular layers of a cyanine dye (Figure 2) onto different substrates. The substrate has a strong influence on the absorption spectra of the dye and on the structure of the films as investigated by atomic force microscopy. The kinetics of the photooxidation of the dye molecules and the affinity of the dye layers toward the binding of polyelectrolytes and of colloidal particles yield additional information on the structure of the dye layers. On the other hand, photooxidation of the dye layers is the basis for their use as a photolayer to generate photopatterns. Differences in the affinity of bleached and unbleached regions toward binding of charged particles serve to demonstrate the selective adsorption of colloidal particles and macromolecules to the photopatterns.

Thin films of the cyanine dye are not only of interest with respect to their use for photopatterning but they are also interesting objects for investigating the interaction of the dye molecules within these films. Under certain preparation conditions, the chosen dye readily forms so-called J-aggregates on various substrates.^{9,10} This dye serves as a sensitizer for the photographic process in color films. Energy-transfer processes within aggregates of the dye serve a light-harvesting function that increases the sensitivity of the photographic film. In this context monomolecular films of cyanine dyes of variable architecture seem to be a promising model system for a further locally resolved investigation of energy-transfer processes by near-field optical methods as already attempted previously.^{1,11}

Materials and Methods

(1) Preparation of Monomolecular Dye Layers. The cyanine dye as shown in Figure 2 was used in these investigations. The purity of the substance was checked by thin film chromatography where it appeared as a single spot.¹² Dye layers are reproducibly formed simply through immersing a substrate in a saturated dye solution of a solvent where the dye is only scarcely soluble. The positively charged dye molecule is deposited onto the substrate by adsorption from the solvent. The choice of the substrate has a strong influence on the architecture of the deposited film. The techniques described here are closely related to the molecular deposition (MD) technique of thin film formation by successive adsorption of oppositely charged polyelectrolytes as described by Decher¹³ and the extension of this MD technique to the monolayer formation of smaller charged dye molecules to oppositely charged surfaces as described by Xi Zhang et al.¹⁴ and by Katsuhilo Ariga et al.¹⁵

Substrates for the Dye Layers. Glass, mica, and a thin layer of polyacrylate (PA) serve as negatively charged substrates for

the deposition of monomolecular layers of the cationic dye. Microscope cover glasses are cleaned by sonication for 15 min in a hot detergent (70 °C 0.5% Hellmanex, Hellma GmbH, Germany) and then washed extensively in doubly distilled water. Mica is freshly cleaved before being used. The thin layer of the negatively charged PA is formed by first depositing a thin layer of the positively charged polyelectrolyte polyethyleneimine (PEI) on a negatively charged glass surface and then a thin layer of PA on PEI. The adsorption process is performed by dipping a freshly cleaned cover glass first for 25 min into a 10^{-4} M solution of PEI and then after rinsing with water for another 25 min into a 10^{-4} M solution of PA. Finally, the film is again rinsed with water. The branched PEI of an average molecular weight of 1800 u was purchased from Polysciences, and the sodium salt of polyacrylate 2100 was purchased from Fluka.

Preparation of the Solution. A saturated solution of the dye in 2-propanol with a 2-fold excess of precipitated dye is formed by stirring 30 mg of the dye in 100 mL of solvent for 30 min and then leaving the solution to equilibrate for 12 h. The diluted solution, from which generally dye layers are adsorbed, consists of 15 parts of the saturated solution and 85 parts of doubly distilled water.

Formation of Dye Layers. The standard procedure for forming thin dye films on all substrates except mica consists of immersing the substrates for 90 min in the diluted solution and then withdrawing the plate and rinsing it with water. Mica is immersed in the solution for 24 h.

(2) Absorption Spectroscopy. Absorption spectra were recorded with an absorption spectrophotometer (14 R Cary Instruments, Monrovia, CA) in single-beam mode. Data were recorded on a computer using homemade software (A. Naber). In a well-equilibrated state of the instrument variations above 4×10^{-4} in optical density could be reproducibly detected in the spectra of the dye layers on the PA substrate after subtraction of the reference spectra of the substrate. The remaining offset in spectra of different dye layers (dye layers on PA after different adsorption times or different times of bleaching) was corrected by linear subtraction on the basis of the residual values at 400 and 600 nm, where the absorption of the dye can be neglected. To increase the accuracy of the data, the mean value of two to five spectra was formed for monolayers of dye layers having an OD of less than 0.05. In the case of mica as a substrate, the subtraction of a reference was less accurate because of unavoidable differences in the optical properties of different mica samples and because the absorption spectrum of mica shows some structure in the visible wavelength range. The reproducibility in these spectra was not better than $\pm 2 \times 10^{-3}$ in optical density.

(3) Adsorption of Latex Spheres. For adsorption of the latex spheres, the mica plate bearing the dye layers was immersed for 15 s into a 5% v/v (volume/volume) of cationically stabilized 0.22 μ m latex spheres as obtained from the BASF company without further specification, suspended in 0.1 M NaOH. The plate was then removed and rinsed for 30 s with water. By use of this procedure for pure mica, a nearly statistically close-packed monolayer of adsorbed latex spheres can be recognized using a light microscope. For these conditions latex spheres bind irreversibly onto mica. The packing increases if the concentration of NaOH increases to 1 M. The high concentration of NaOH, however, affects the dye layers, so the lower concentration of 0.1 M is used.

(4) Exposure of a Pattern. A pattern is exposed onto a dye layer by a 5-fold demagnified projection of a copper grid onto the sample by means of a light microscope. The width of the

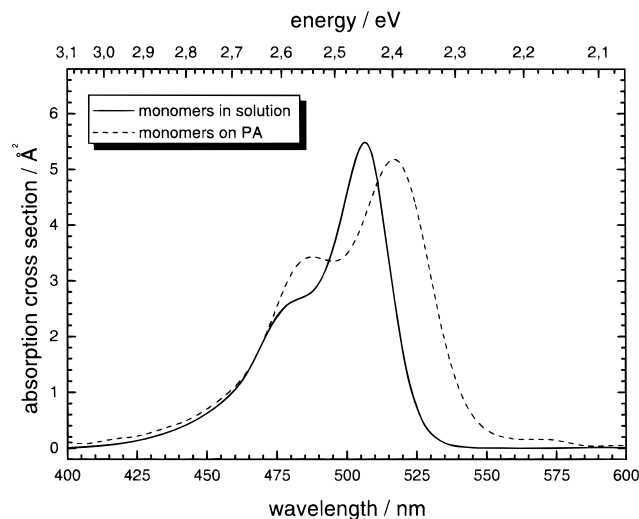


Figure 3. Absorption cross sections of the dye dissolved in a solution of 2-propanol and of the dye when it is adsorbed on a film of polyacrylate.

grid bars is 50 μm . Dye layers on mica were used as a sample. The film was exposed using the filtered light of a xenon arc lamp in the wavelength range above 450 nm. After exposure, the dye film was developed by rinsing with water for 25 s. Latex spheres were adsorbed to the developed film as described above.

Experimental Results

The experimental results are reported in the sequence of the different methods that have been applied.

(1) By absorption spectroscopy, specific information about the coverage of the substrate with dye molecules and about the interaction between dye molecules is obtained.

(2) Atomic force microscopy (AFM) yields information about thickness and surface properties of the layers.

(3) The surface charge of the dye layers is investigated by adsorption of charged latex spheres.

(4) The kinetics of photobleaching of the dye is strongly influenced by the structure of the dye layers, and therefore, the investigation of photobleaching yields additional structural information.

(5) A photopattern was exposed to dye layers, and adsorption of latex spheres to the photopatterns is investigated to demonstrate the potential of the dye layers for generating interface patterns of different chemical reactivity.

(1) Absorption Spectroscopy. Dye Layers on a PA Substrate. The most simple behavior of dye adsorption is observed for the PA substrate. Figure 3 shows the absorption cross section of the dye for different conditions. The absorption maximum is shifted from 507 nm in solution to 515 nm for the dye layer on PA. The absorption cross section of the adsorbed dye was determined from the absorption spectrum of the dye layer and the density of adsorbed dye molecules in the dye film. This density was determined by measuring the optical density of a solution that was prepared by redissolving the adsorbed dye from a known nominal area of the substrate in a known amount of 2-propanol. The density of the dye in the adsorbed layer was found to be 0.25 nm^{-2} corresponding to an average area of 4 nm^2 occupied by a dye molecule. This value should be compared to an area of the molecule of 1.57 nm^2 as calculated by semiempirical Dreiding structure calculations according to Mayo et al.¹⁶ and semiempirical MOPAC structure calculations according to Stewart, J. J. P. *OCPE* No. 455) (private communication by R. Ellerbrake). It is concluded that dye

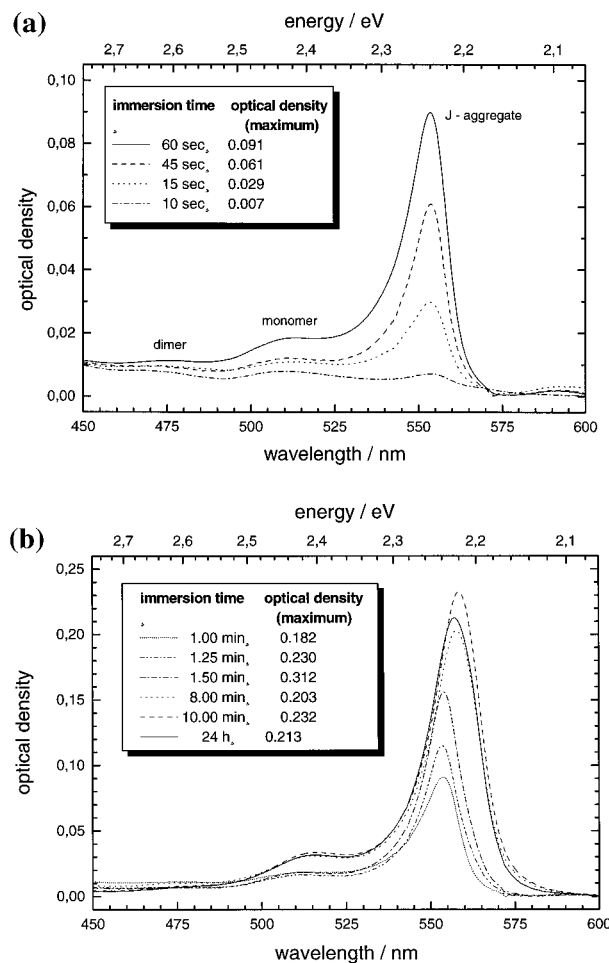


Figure 4. Absorption spectra of film formation on mica: (a) immersion times up to 1 min; (b) immersion times from 10 min to 24 h. Note that a maximal absorption is obtained for an immersion time of 10 min.

adsorption stops at a density significantly lower than a complete monolayer coverage. The absorption cross section of $(5.2 \pm 1) \times 10^{-2} \text{ nm}^2$ of the adsorbed dye at its absorption maximum is, within errors, the same as the one of $(5.5 \pm 0.2) \times 10^{-2} \text{ nm}^2$ of the dye in solution. The width of the absorption spectrum of the adsorbed dye appears to be larger than the one of the dye in solution, indicating a stronger inhomogeneous broadening of the spectrum of the adsorbed dye. The integral absorption of the dye over the whole spectrum was determined by integrating the extinction coefficient as a function of light energy over the whole absorption spectrum. This integral absorption is by about 12.6% larger for the adsorbed dye. Since the orientation of the dye was neglected in these derivations, this result may be explained by a preferential 2-D orientation of the dye within the plane of the adsorbed layer. In solution the dye is statistically oriented in three dimensions, and in an absorption measurement, a dye molecule is not detected when it is oriented perpendicularly to the incident beam.

Dye Layers on a Mica Substrate. A completely different and much more complex behavior of the formation of the dye layer is observed by using mica as the substrate. The formation of the dye layers as a function of the immersion time can be monitored by following the evolution of the absorption spectra as shown in Figure 4. Within the first 10 s an absorption around 510 nm develops and a slight increase at 555 nm occurs. In the subsequently recorded spectra mainly this red-shifted absorption maximum develops with a gradual further red shift of the absorption maximum from 554 to 559 nm up to an immersion

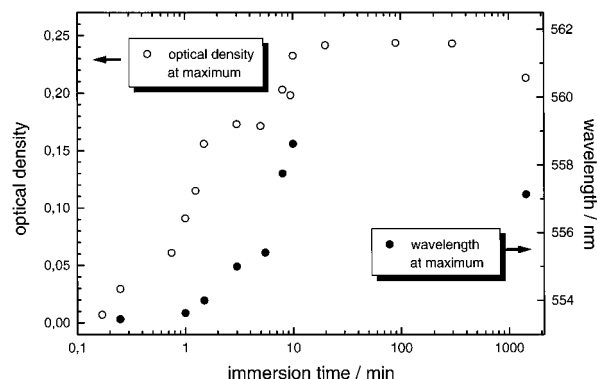


Figure 5. Overview of absorption properties of dye films during film growth on a mica substrate. The optical density of the dye layer at the wavelength of the maximal absorption in the red-shifted part of the spectrum is shown as a function of the immersion time. The absorption rises up to an immersion time of 10 min. Then the absorption decreases slightly because of a degradation of an incomplete fourth layer of J-aggregates. Furthermore, the wavelength of the red-shifted absorption maximum as a function of the immersion time is shown.

time of 300 min. Longer immersion times lead to a slight decrease of the absorption and to a slight blue shift of the absorption maximum. These results are summarized in Figure 5. The red-shifted absorption maximum is a clear indication of the formation of so-called J-aggregates⁹ of the dye molecules, as can be deduced from previous investigations of the same dye on other interfaces.¹⁰ A gradual further red shift for longer times of adsorption was also observed and was attributed to the formation of multilayers of J-aggregates. Up to an immersion time of 10 s, mainly an increase of absorption at 510 nm is observed, indicating that the formation of J-aggregates is preceded by the formation of a monolayer of dye in its monomeric form. This interpretation is further substantiated by AFM investigations described below. A close packed monolayer of J-aggregates of the dye is known to have an optical density (OD) of about 0.07.¹⁰ An OD of 0.21 of the dye films after saturation indicates that an equivalent of three monolayers of the J-aggregated dye is formed. Images taken with a polarization microscope reveal close-packed interlocked domains of differently oriented J-aggregates of a typical size of several micrometers, as is shown in Figure 6. The transient increase in the absorption above an OD of 0.21 for immersion times between 10 and 1400 min (Figure 5) indicates a beginning formation of a fourth layer of aggregates that, however, decays again.

Dye Layers on a Glass Substrate. A behavior between that of PA and the one of mica is observed for glass as a substrate. The behavior is similar to the case of mica, but the adsorption of the dye saturates at a lower absorption (OD = 0.07) corresponding to the formation of only one completed layer of J-aggregates. Furthermore, the red shift of the absorption maximum to 545 nm (data not shown) is less pronounced than on mica where the maximum shifts to 558 nm (Figure 5). Furthermore, the red shift occurs gradually and no distinct formation of a first monolayer of the dye in its monomeric form can be identified (data not shown). No large domains of polarized J-aggregates are observed on glass in the polarization microscope. Therefore, we conclude that the domains must be smaller than 0.5 μm , the resolution limit of our light microscope.

(2) Atomic Force Microscopy. The formation of the dye layers on mica is also proven by using an atomic force microscope (AFM). After an immersion time of 10 s an AFM image as shown in Figure 7a was obtained. Only few domains are visible in this image, and the surface properties apart from the domains are distinct from the ones usually observed for the

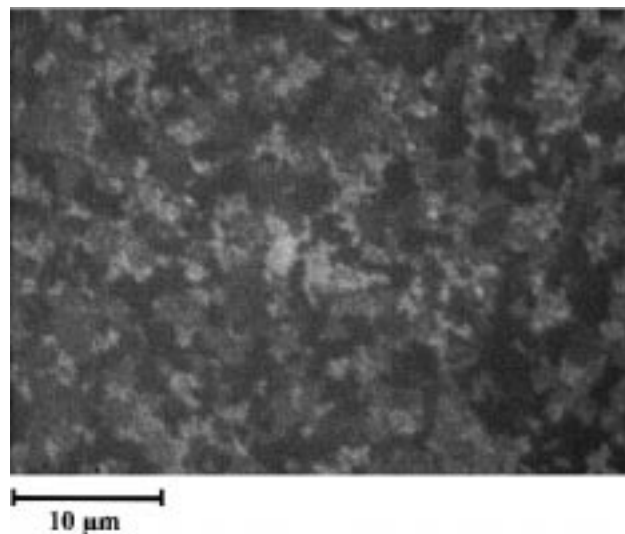


Figure 6. Polarization micrograph of completed dye film on mica.

mica substrate. There is a significant increase of surface roughness, and there are characteristic holes with a depth of 0.5 nm. In conjunction with the absorption measurements we assign the changed surface properties to the formation of a first monolayer of disordered dye molecules. The domains in the AFM image are assigned to J-aggregated dye molecules. It is conceivable that the formation of J-aggregates starts by a rearrangement of dyes within the first monolayer, leading to domains of closer-packed dye molecules that are thicker than the monolayer and are therefore visible in the topographic AFM image. Alternatively, the formation of J-aggregates may start with the adsorption of dye molecules on top of the first monolayer. We cannot distinguish between these two possibilities by our AFM investigations. In the AFM image an irregularity of the surface within the domain is observed, possibly indicating that the domains have a further inner structure consisting of an assembly of much smaller aggregates. A hierarchical structure of an oriented assembly of small aggregates consisting of about 100 molecules into large domains was indeed suggested by Misawa and Kobayashi.⁹ A first nearly completely closed monolayer of domains is then formed. Subsequently, two more monolayers are formed on top of the first one. The formation of the third layer on a completed second layer is shown in the AFM image of Figure 7b. Figure 7c shows an AFM image of the nearly completed third layer of J-aggregates. The form and size of the domains in the third layer appear in AFM images similar to the one observed in the polarization microscope (Figure 6). The layers have a thickness of about 0.5 nm. This is consistent with a monolayer of J-aggregated dye molecules. J-aggregates of similar cyanine dye molecules adsorbed on AgBr single crystals have a thickness of 0.8 ± 0.15 nm as determined by ellipsometry.¹⁷ The subsequent monolayers can be distinguished by their different appearance in the phase contrast in AFM images taken in the dynamic mode as shown in Figure 8. These AFM images were taken under similar conditions as the one shown in Figure 7. But in this case the second layer of J-aggregates happens to be incomplete, as indicated by dark areas in the topographic image of the second layer, which we attribute to the exposed first layer. The first layer of aggregates appearing as a depression in the topographic image of Figure 8a shows the same contrast as the third layer in the phase contrast image of Figure 8b. Phase-contrast imaging is very sensitive to differences in surface properties of thin films.¹⁸ Although a correlation of the phase

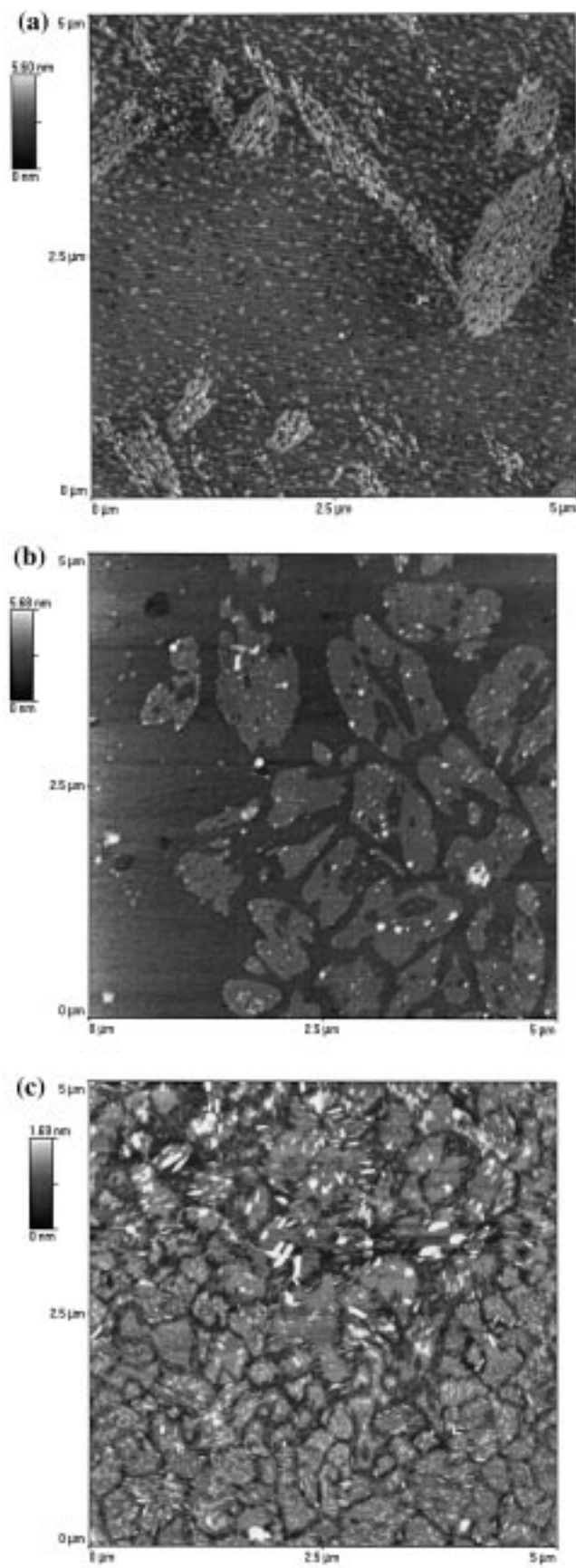


Figure 7. Topographic AFM images of dye films on mica: (a) after an immersion time of 40 s²²; (b) during formation of the third layer of aggregates on top of the completed second layer; (c) AFM image of third layer of J-aggregates.

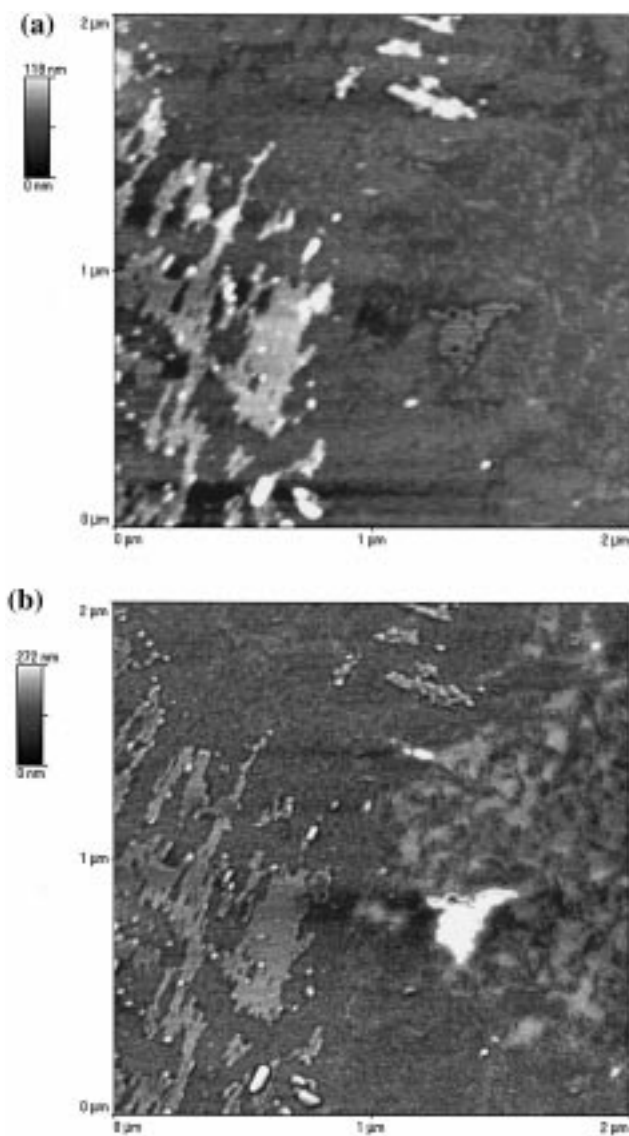


Figure 8. (a) Topographic AFM image of dye film during formation of the third layer of J-aggregates on the second layer at a place where the underlying second layer was not completed; (b) phase-contrast image of the same area.

contrast to surface properties is not easily possible, the alternating contrast in successive layers of J-aggregates clearly shows that the surface properties of successive films are different.

(3) Adsorption of Latex Spheres. Further strong evidence for the assumption of a subsequent formation of a disordered monolayer and three monolayers of J-aggregates of alternating surface properties on mica is obtained from an investigation of the adsorption of cationically stabilized latex spheres to the respective dye layers. The binding of small particles from an aqueous solution to a solid substrate is strongly influenced by the surface charge of both the particles and the substrate. When the particles and the substrate have the same polarity, usually no binding occurs, and the binding of charged molecules can thus be used as a qualitative indicator of the surface charge of a substrate.^{19,20} The positively charged latex spheres bind to the mica substrate and to the first disordered monolayer of dye molecules. For preparations of dye layers of different immersion times corresponding to the completion of the four successive dye layers, adsorption of latex spheres was tested as described above for the mica plate. The result of this test is summarized in Figure 9. The latex spheres do not bind to the first and third

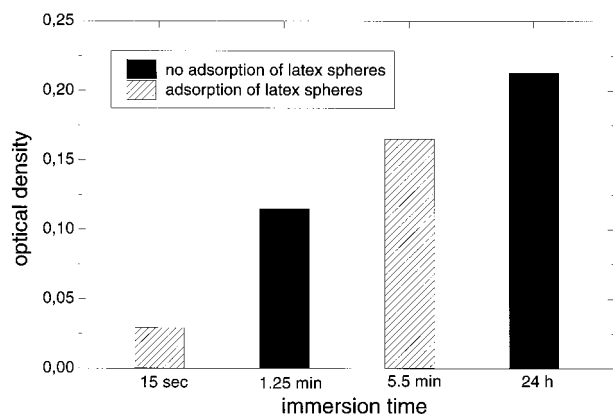


Figure 9. Schematic bar chart showing the adsorption of latex spheres to dye layers in different stages during dye film formation.

layer of J-aggregates. In contrast, the latex spheres bind to the second layer of J aggregates. For a tentative model of the structure of the dye layers based on these observations, we assume that the dye molecule consists of a positively charged part and an uncharged one. The first layer of disordered dye molecules compensates only incompletely the negative surface charges of the mica surface. Therefore, the positively charged latex spheres are adsorbed to this layer in a similar way as to the mica substrate. In the first and third layer of J-aggregates the molecules are rather densely packed with the positively charged part of the molecule pointing to the outside such that a positive surface charge is formed that repels the positively charged latex spheres, which therefore are not adsorbed to these layers. The second layer of J-aggregates is adsorbed with opposite polarity such that the uncharged part of the molecule is exposed to the surface and the positively charged latex spheres are adsorbed to this surface. We have no experimental results about whether negatively charged counterions are being incorporated into the layer structure.

(4) Photochemistry of the Dye Layers. The adsorbed dye can be bleached by irradiation with light. The bleaching is the basis for the intended photopatterning processes; therefore, the bleaching process was characterized in some detail. Several aspects of the photochemistry were investigated.

Photoproducts. The photoproducts of the bleaching process were investigated by time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Dye layers were prepared on an oxidized silicon wafer as a substrate in the same way as on glass. The native layer (a), a partially bleached layer (b), an extensively bleached layer (c), and the bleached layer after rinsing with water were investigated. Spectra a–c are shown in Figure 10. In the native layer a peak of 573 u appears, which corresponds to the molecular weight of the cationic dye. After partial bleaching two peaks of 589 and 605 u arise. After extensive bleaching, the peak at 573 u nearly disappears whereas the peak at 605 u now dominates. The size of the peaks relative to the peak at 573 u is shown for the different conditions in Figure 11. The peaks at 589 and 605 u correspond to the molecular weight of the once- and twice-oxidized dye molecules, respectively. After the bleached sample is rinsed with water, both peaks are absent, indicating that the photoproduct is washed away. The change in solubility has to be due to an oxidation of the dye molecule. The reason for the change in solubility was not further explored.

Kinetics of Bleaching. The dye layers were bleached using the 546 nm line of a 100 W mercury arc lamp, which is close to the absorption maximum of the dye in its J-aggregated form. The bleaching behavior of the dye layers on mica is rather

complex. An overview of the time dependence of spectral changes for bleaching times up to 20 min is shown in Figure 12. With progressive bleaching, the bleaching process slows down substantially. Qualitatively, the bleaching process occurs quite fast from an optical density of 0.21 to 0.14. It is significantly slower for the decay from 0.14 to 0.07 and becomes extremely slow for optical densities below 0.07. The J-aggregates bleach much more quickly than the monomeric form as shown in Figure 13 showing a time sequence of absorption spectra during the bleaching process. The slow bleaching of the monomeric form is certainly partly due to the choice of the mercury arc lamp.

In the first 60 s a preferential bleaching of the J-aggregates with a concomitant decrease in OD from 0.21 to 0.14 corresponding to the bleaching of one layer of J-aggregates is observed (Figure 13a). It seems that the quantum yield of bleaching is different for the three dye layers, implying that the bleaching occurs layer by layer. This interpretation is further substantiated by the change in surface properties of the dye film with a progressive extent of bleaching as manifested by the changes in the affinity toward the binding of colloidal latex beads. We observed that the adsorption of latex spheres during bleaching of a dye film on mica follows the same pattern as shown in Figure 9 if it is assumed that a bleaching by a decrement in OD of 0.07 corresponds to the bleaching of one layer of aggregates.

A reason for a bleaching process layer by layer could be that the lower dye layers are protected from bleaching by the upper ones. To test this assumption, experiments were performed, where one sample is bleached continuously, whereas a second sample is partially bleached to an OD of 0.14. At this stage, the film is rinsed with water in order to remove the bleached molecules, then the bleaching is continued. In Figure 14 the two cases are compared. After a rinse with water, the half time of bleaching decreases by a factor of about 4. A reason for the protective property of the top layers could be that they inhibit access of oxygen. We therefore compared bleaching rates in the presence and absence of oxygen. The bleaching rate in a nitrogenous environment is indeed by a factor of 20 smaller than in ambient air as shown in Figure 15.

The complex bleaching behavior and the coarse domain structure of the dye layers as described above is not favorable for their use as a photolayer because one has to expect that the bleaching behavior is rather inhomogeneous in time and space. It would therefore be difficult to write homogeneous structures onto such a film. Spatially homogeneous films with a homogeneous bleaching behavior are preferred. A successive improvement of these conditions is observed when switching from mica to glass and to PA as a substrate. As described above, the spectrum of a dye layer on glass is a characteristic mixture of the dye in its monomeric and J-aggregated forms whereas on PA the dye adsorbs exclusively in the monomeric and possibly the dimeric form. The bleaching of dye monolayers was investigated by monitoring the decay of their absorption as well as of their fluorescence. Details of the bleaching characteristics will be described in a forthcoming publication that deals with near-field optical lithography on monomolecular layers of this dye.²¹ Whereas on glass a complex bleaching behavior is observed, the bleaching of the dye layer on PA occurs to about 65% in an exponential decay with a quantum yield of 1×10^{-4} at a wavelength of 488 nm.

(5) Adsorption of Colloids and Macromolecules to Unexposed and Developed Regions of the Resist. We intend to use lithographically written structures to build up nanostructures

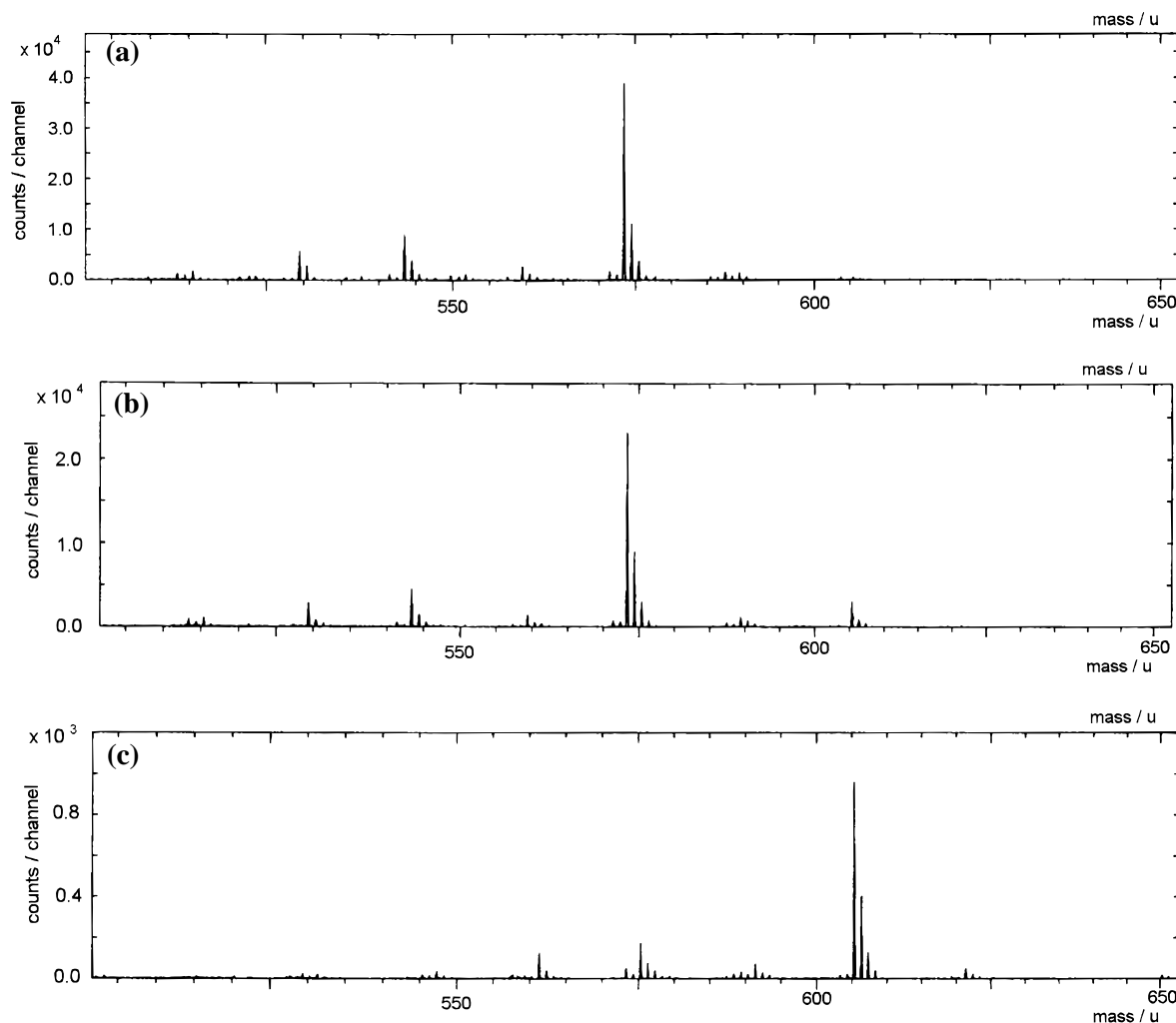


Figure 10. TOF-SIMS spectra of (a) dye layer on an oxidized silicon wafer and (b) dye layer irradiated with a low dose and (c) with a high dose. The molecular weight of the dye is 573 u, and the one of the once- and twice-oxidized photoproducts is 589 and 605 u, respectively.

	Peak height relatively to peak at 573 u (native dye)	
	589 u (once oxidized)	605 u (twice oxidized)
Spectrum a (native dye layer)	0.03	0.02
Spectrum b (low dose)	0.05	0.13
Spectrum 3 (high dose)	0.67	20.00

Figure 11. Peak height of fragments corresponding to once- and twice-oxidized photoproducts relative to the native dye. The absolute peak heights are no quantitative measure of the concentration of the respective components at the surface. Relative changes should be seen as a qualitative indicator of the photooxidation processes.

by selective adsorption of molecules or colloidal particles to these structures. To test its feasibility, we first conducted experiments to bind latex spheres of a diameter of 0.22 μm to photopatterns on the basis of the different affinities of the latex spheres to the different dye layers on mica as described above. The photopatterns were generated by projection of a grid as described in Materials and Methods.

The observed adsorption patterns are shown in Figure 16 for three different times of exposure.

(a) 2.5 min. Under these conditions, the J-aggregates are completely bleached in the exposed areas whereas the monomers (or dimers) are presumably not bleached because the bleaching

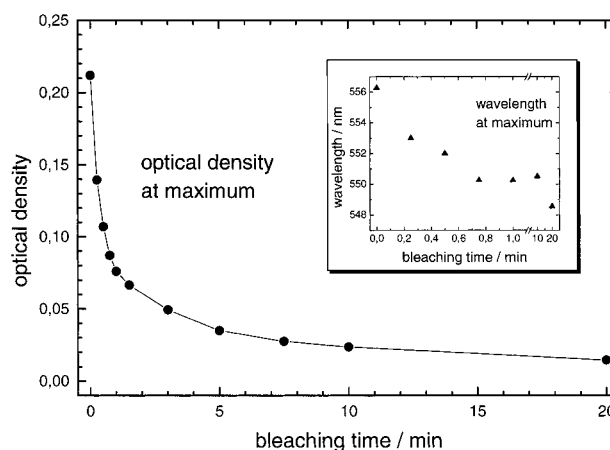


Figure 12. Time course of spectral changes of a dye layer on mica during the first 20 min of bleaching as expressed by the optical density at the absorption maximum of the red-shifted component and the wavelength at the maximum absorption of this component (inset).

of the monomers is much slower. Regions in the shadow of the bars remain nearly unexposed. After a rinse with water, the pattern should therefore consist of areas of the dye in its monomeric or dimeric form in the exposed regions and of areas with triple layers of J-aggregates in the shadow of the bars. Latex spheres are almost exclusively adsorbed to the exposed areas. This pattern thus is consistent with the model for the

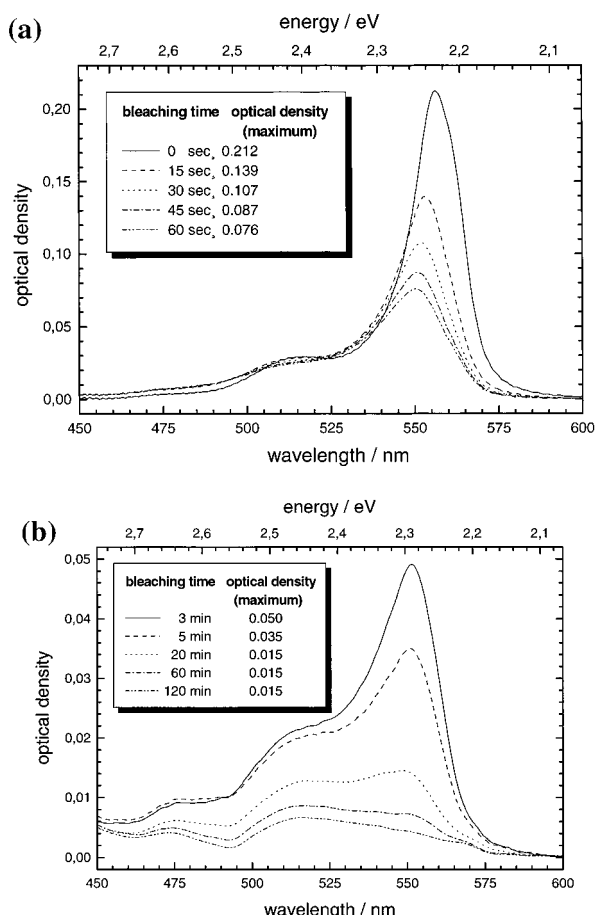


Figure 13. Time evolution of absorption spectra during bleaching of a dye layer on mica: (a) 0–1 min bleaching time; (b) 1–120 min bleaching time.

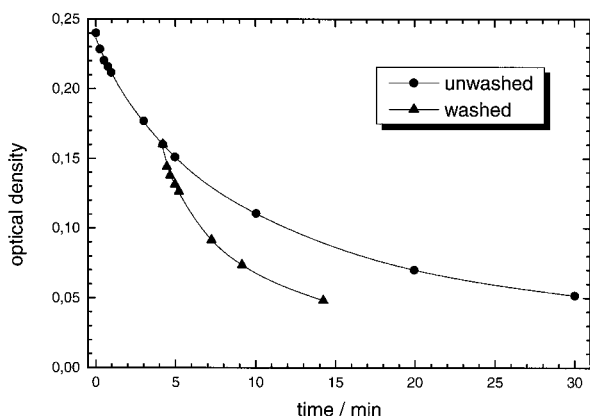


Figure 14. Influence of a cover layer on bleaching.²³ The time course of the OD as a function of time is recorded. In a second experiment the dye layer was bleached partially until an optical density close to 0.14 was reached. The film was then washed with water. Afterward, the time course of the OD during bleaching of this partially bleached washed layer was recorded.

structure of the film where positively charged latex spheres adsorb to the first layer of monomers or dimers but not to the third layer of J-aggregates.

(b) 5–30 min. When the exposure time is increased, the areas in the shadow of the bars also become exposed to some extent. Latex spheres are now preferentially adsorbed to the areas in the shadow of the bars. This adsorption is likely to be due to a bleaching of the uppermost layer of aggregates in the shadow of the bars such that the second layer of aggregates is exposed

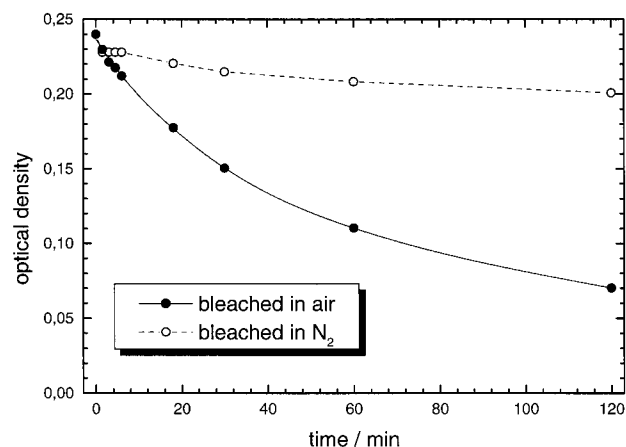


Figure 15. Influence of oxygen on bleaching.²³ The time course of the OD of a layer of a dye was monitored during bleaching in ambient air and in an atmosphere of nitrogen.

to the surface where latex spheres adsorb. We would, however, expect that the adsorption occurs more or less to the same extent in the exposed areas. An adsorption to the same extent in these areas is, however, only observed in a narrow window of exposure times between 3 and 5 min. To explain this discrepancy of our qualitative model for the adsorption of latex spheres to the different dye layers, one would have to take into account quantitative differences in the affinity of latex spheres, which were not investigated.

(3) 1 h. For these conditions nearly the same adsorption pattern is observed as for the short exposure time of 2.5 min. The bleaching may have progressed in the shadow regions such that the first aggregate layer is exposed to the surface, which again has a low affinity for the latex spheres.

To test whether it is possible to bind selectively molecules instead of latex particles to photopatterns, the same type of experiments was performed using the cationic polyelectrolyte PEI instead of the cationically stabilized latex spheres as an adsorbant. To find out whether PEI was bound or not, the binding of negatively charged latex spheres was used as an indicator for the presence of the positively charged PEI because they readily are adsorbed to the positively charged surface of an adsorbed layer of PEI. In these experiments a very similar pattern of adsorbed latex spheres was observed as in the three cases above, indicating that the adsorption of PEI is determined by similar factors as the one of the cationically charged latex spheres.

Conclusions

Monomolecular layers of the cationic dye are formed on different substrates. The architecture of the monolayers and the spectral properties of the dye depend strongly on the substrate. On PA a rather homogeneous but not completely close-packed layer of dye molecules is formed. This kind of a monolayer seems to be especially suited for photopatterning at a high resolution because of the homogeneous structure and the homogeneous bleaching properties. These films were used for writing structures by SNOL.²¹ On other substrates such as glass or mica the architecture of the films is more complex. Interactions of the dye with the substrate have a strong influence on spectral properties of the dye and the formation of J-aggregates. The controlled variability of film structure and spectral properties of the dye molecules on various substrates is a basis for the potential use of these films as objects for near-field optical investigations of locally resolved energy-transfer processes and

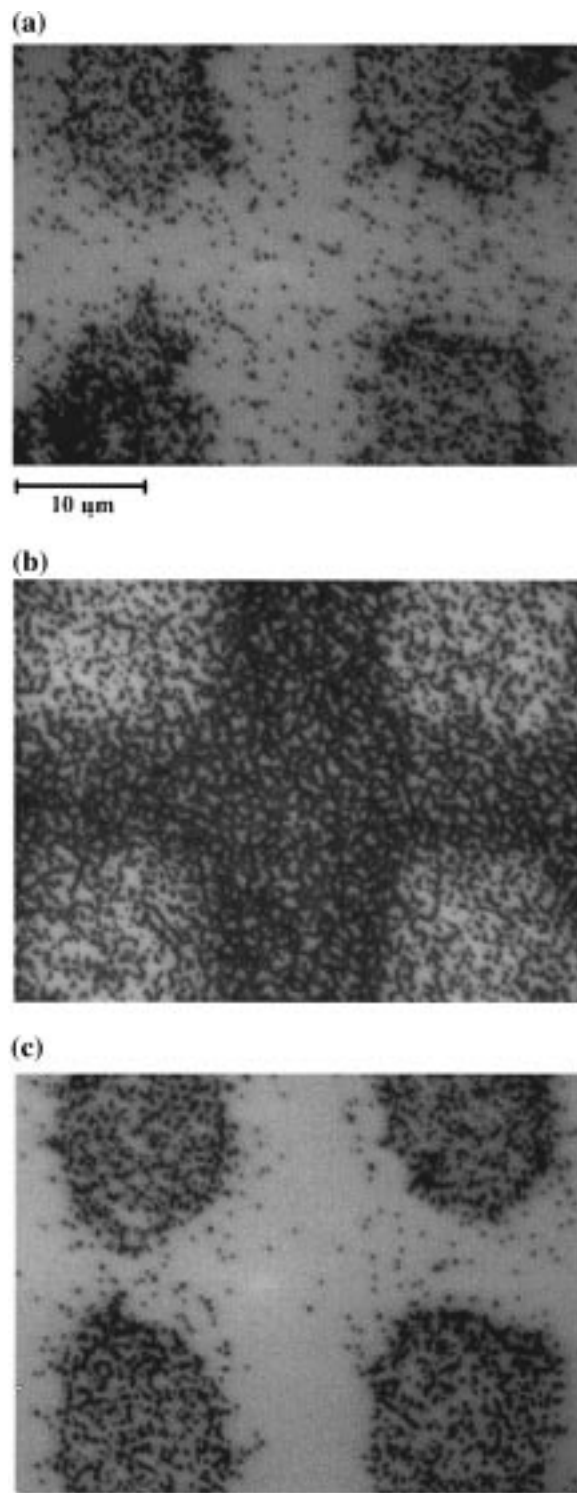


Figure 16. Light micrograph of the adsorption of cationically stabilized latex spheres to a patterned dye layer after exposure of the dye layer through a grid (a) for 2.5 min, (b) for 10 min, and (c) for 1 h. Single latex spheres appear as diffraction-limited spots in the micrograph.

of influences of the local environment on spectral properties of dye molecules. The bleaching behavior of the dye molecules determines the use of the dye films for photopatterning. Irradiation of the dye leads to a photooxidation of the dye. A relatively simple nearly single-exponential bleaching is only observed on PA as a substrate. On glass and mica the bleaching behavior is much more complex. This complex behavior is shown to be due to the different spectroscopically distinguishable

forms of the dye molecules and also to differences in the accessibility of the dye molecules to oxygen, which has a strong influence on the rate of photobleaching. Whereas the dye molecule is insoluble in water, the photooxidized product is soluble. An example on a microscopic scale demonstrates how the difference in the solubility of bleached and unbleached dye can be used to generate surface patterns of different adsorption properties by photopatterning of the dye layers on mica. It is not clear at the moment whether these processes can be scaled down to the submicrometer and nanometer regime, but even if it turns out that this is not possible, the general concept of photopatterning of monomolecular films of a dye may well be a useful one for producing surface structures in the nanometer regime.

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