

Layer-by-Layer Self-Assembling of a Low Molecular Weight Organic Material by Different Electrostatic Adsorption Processes

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Received July 9, 2001. In Final Form: October 23, 2001

A novel method has been reported to deposit low molecular weight organic materials by a layer-by-layer self-assembled film deposition method. A different electrostatic adsorption process has been followed to show its advantage over the conventional method. When an organic material, namely, alizarin violet, with fewer ionic groups was used as the anion for electrostatic self-assembly, the dye was found to come off the film during the subsequent polycation deposition. As an alternative approach, the dye has been anchored to the polycation via a physioadsorption process prior to deposition. By controlling the concentration ratio of the two, the combination of low molecular weight material and the polycation as a whole has been used as the polycation. The absorption spectra after each deposition showed that there was no material loss during layer depositions. The results showed that the method of anchoring low molecular weight molecules to polyions could effectively be used to deposit homogeneous layer-by-layer self-assembled films of small organic molecules in general.

Introduction

In recent years, studies on ultrathin organic films are receiving technological importance due to their applications in electronic and optical devices.¹ Over the years, molecular assemblies of supramolecules in the nanometer scale were achieved mostly by Langmuir–Blodgett (LB) film deposition and self-assembled monolayer (SAM) techniques. The most recent method along this direction is thin film depositions based on layer-by-layer self-adsorption of positively and negatively charged polyions. Although some singular studies were reported earlier,^{2,3} a focused route for layer-by-layer self-assembly was developed in the early 1990s.⁴ Soon, deposition of heterostructures⁵ and subsequently use of layer-by-layer self-assembled films in devices^{6,7} were reported. In recent years, in-depth studies have been carried out on deposition procedures⁸ and applications^{9–12} of such films.

Since the layer-by-layer self-assembly method relies on the electrostatic interaction of complementary anion and

cation pairs in successive adsorption steps, polyions are generally used for film deposition. To extend the choice of materials in the new deposition method, efforts have also been made to incorporate low molecular weight organic molecules, which offer many interesting properties for electronic and optical applications. Most of the small dye molecules cannot usually be manipulated into molecular layers due to their nature to form aggregates and microcrystals. There are few reports on the formation of layer-by-layer self-assembled films of organic dye molecules.^{13–15} Either the molecules had alkyl chains,¹⁴ or a correct combination of polyion had been used.¹⁵ Due to the small number of charged groups in organic dyes, physioadsorption of such molecules in films is not straightforward. Material loss by washing is substantial in many cases. In this article, we present a novel technique to deposit layer-by-layer self-assembled films of a small organic dye molecule, namely, alizarin violet. The simplicity of the deposition mode suggests that the layer-by-layer film deposition technique can now be applicable to any dye molecule with only one or a few charged groups in combination with any polyanion or polycation, without any material loss or release during the subsequent layer's physioadsorption.

Experimental Section

The dye used in this work was alizarin violet, whose chemical structure is shown in Figure 1. Poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) have been used as the polycation and the polyanion, respectively (Figure 1). PAH (molecular weight = 70 000) and the dye have been purchased from Aldrich Chemical Co. PAA (molecular weight = 90 000) was obtained from Polyscience as a 25% aqueous solution. The electrolyte deposition baths were prepared with 10^{-2} M (based on the repeat units for the polyions) aqueous solutions using 18.2 M Ω Millipore water. The pH of each solution was adjusted

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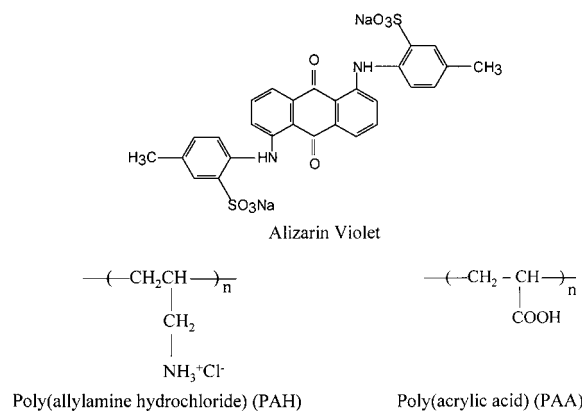


Figure 1. Molecular structure of alizarin violet and the polyelectrolytes.

with either HCl or NaOH. We have deposited two basic types of self-assembled films. While using alizarin violet as the anion (pH = 3.5), PAH was used as the polycation (henceforth referred to as PAH/alizarin film). To deposit the other type of film, the solution of alizarin violet was first mixed with PAH in a controlled manner so that the SO_3^- ions of alizarin violet get attached to the NH_3^+ ions of PAH. Alizarin violet molecules were therefore physisorbed to PAH polymer. The low molar ratio of alizarin in PAH left about 80% of the NH_3^+ ions of PAH free to take part in the adsorption process during layer-by-layer deposition. The pH of the PAH–alizarin mixture, which acts as the polycation, was kept at 7.5. The pH of PAA (as the polyanion) was varied as 3.0, 3.5, and 4.0 to control the free charge density of the polyanion solution and hence to vary the morphology of the physisorbed films.¹⁶ The layer-by-layer films with PAH–alizarin and PAA will be referred to as PAH–alizarin/PAA in this article.

To deposit layer-by-layer self-assembled films, thoroughly cleaned quartz substrates were immersed in a polycation solution for 15 min followed by rinsing in three water baths for 2, 1, and 1 min. The rinsing washes off the surplus cations attached to the surface. The substrates were then immersed in anion solution for 15 min followed by the same rinsing protocol. After each depositing and rinsing procedure, the film was blown dry and the UV–vis absorption spectrum was recorded to monitor film growth. Depositions of anion and cation layers resulted in one bilayer of self-assembled film, and the whole sequence was repeated for a desired number of times to get a desired number of bilayer films. UV–vis absorption spectroscopy and atomic force microscopy (AFM) were carried out by a Shimadzu UV-2101 PC absorption spectrophotometer and an AutoProbe CP from ThermoMicroscopes (former Park Scientific Instruments), respectively.

Results and Discussion

We have recorded absorption spectra of layer-by-layer self-assembled films of alizarin violet deposited via different routes. Figure 2 shows such spectra for the PAH/alizarin and PAH–alizarin/PAA (three different pHs) cases along with the alizarin solution absorption spectrum. The spectra enabled us to study any interaction of alizarin with PAH and formation of aggregates in the self-assembled films. The solution spectrum showed the presence of a J-aggregate band at around 543 nm along with three monomeric bands in the 240–330 nm region. All the bands appeared in the absorption spectra of self-assembled films showing the presence of alizarin in such films. The aggregate absorption band was red-shifted by 9 and 13 nm in the cases of PAH–alizarin/PAA and PAH/alizarin films, respectively. In the absorption spectra of alizarin violet solution, the J-aggregate band appeared in

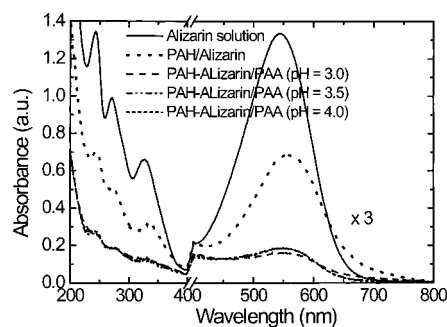


Figure 2. Absorption spectra of the alizarin violet aqueous solution and layer-by-layer self-assembled films deposited at different conditions.

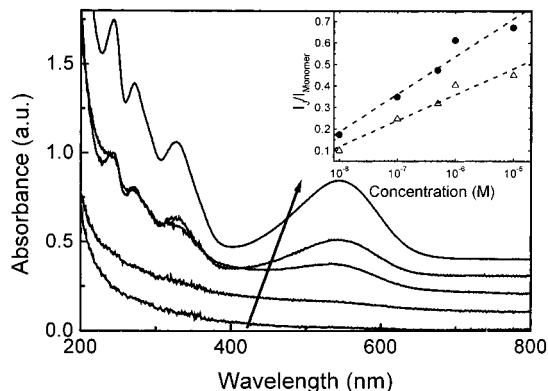


Figure 3. Absorption spectra of alizarin violet 10^{-8} – 10^{-5} M aqueous solutions. The arrow indicates the direction of increase in alizarin concentration. The inset shows the concentration variation of the ratio between the intensities of the aggregated and the monomeric absorption bands. The circles and the triangles represent the ratio with respect to the monomeric band at 326 and 271 nm, respectively.

the range of 537–545 nm at different concentrations of alizarin violet. The band maximum increased in wavelength with an increase in concentration of alizarin in the solution. This shows that the red-shift in the absorption maximum of PAH–alizarin/PAA or PAH/alizarin self-assembled films to 552 or 556 nm, respectively, cannot be solely due to aggregation of alizarin violet molecules. Some electrostatic interaction between alizarin and PAH might enhance the shift in the absorption maximum. In fact, the shift was higher in the case of PAH/alizarin film as compared to PAH–alizarin/PAA cases. This could be due to twofold interaction between alizarin and PAH from both sides of the alizarin layer in the former case (PAH/alizarin/PAH/alizarin/...). In the PAH–alizarin/PAA films, any interaction between alizarin and PAA is unlikely due to the anionic nature of both the materials.

Figure 3 represents absorption spectra of aqueous solutions of alizarin violet in the concentration range of 10^{-8} – 10^{-5} M. The inset of the figure shows that as the concentration of alizarin in the solution increases, the intensity of the J-aggregate band with respect to the monomer band increases. The intensities of the monomer bands at 326 and 271 nm have been taken to calculate the ratios separately. This shows that with an increase in alizarin concentration in the solution, the absorption band due to the aggregated sites starts to dominate as compared to the monomeric bands.

To exclude any possibility of intramolecular charge-transfer bands and also to study the effect of pH of the solution on aggregation, we have recorded absorption spectra of alizarin solutions at different pHs (Figure 4).

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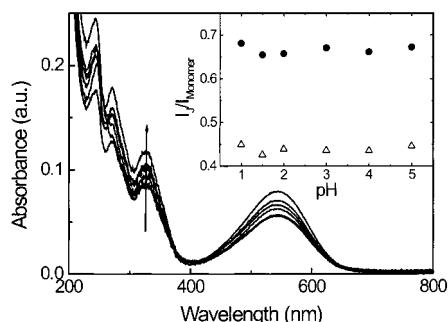


Figure 4. Absorption spectra of alizarin violet aqueous solutions in the pH range of 1.0–5.0. The arrow indicates the direction of increase in pH. The inset shows the pH variation of the ratio between the intensities of the aggregated and monomeric absorption bands. The symbols have the same meaning as in Figure 3.

As the pH of the solution was lowered, the intensities of the absorption bands decreased, which could be due to the ionic nature of the molecules at low pHs. The ratio of the intensities of the aggregated band and the monomeric bands however remained the same (inset of Figure 4). This shows that the band at 543 nm cannot be due to any kind of intramolecular charge transfer. The wavelength at the band maximum did not change with pH, which suggests that the nature and size of the aggregated sites do not depend on the pH of the alizarin solution.

We have deposited layer-by-layer self-assembled films using PAH and alizarin as the polycation and the anion, respectively. To vary the electrostatic adsorption process, we have also used the PAH–alizarin combination (as the polycation) and PAA (as the polyanion) for film deposition. Here, alizarin molecules are anchored to the PAH chain. The molar concentrations of alizarin and PAH were chosen in such a way that the PAH–alizarin combination as a whole acts as the polycation. In this case, we have varied the pH of the polyanion (PAA), which could create different morphologies in the self-assembled films.¹⁶ To monitor the growth of films with increase in the number of dipping layers, we have recorded absorption spectra after deposition of every layer. Parts a and b of Figure 5 show the intensity of absorption maximum for the monomeric (at 271 nm) and aggregate bands, respectively, as a function of number of deposited layers. As the deposition was both started and completed with the polycation, the 21-layer film shown in the figure represents $10\frac{1}{2}$ bilayers of self-assembled films. The cases of PAH/alizarin and PAH–alizarin/PAA (three pHs) are shown in the figure. In the former case, where alizarin was used as the anion, the absorption intensity did not rise monotonically with the number of deposited layers. In fact, the intensity followed a regular zigzag pattern. A closer look at the figure reveals that the intensity of the absorption maximum decreased when the polycation layer (PAH in this case) was deposited. In other words, the intensity of the absorption maximum was lower after PAH deposition as compared to that after the deposition of previous alizarin (anion) layer. Some alizarin molecules must therefore have come out of the film during PAH deposition, which was also evidenced by a slight coloration of the PAH bath as the deposition continued. The removal of alizarin molecules from the films could be due to fewer numbers of ionic groups in the molecule. The alizarin molecules were therefore attached loosely to the NH_3^+ ions of PAH of the previous layer.

The case of the PAH–alizarin/PAA self-assembled film was however different. The intensity of the absorption

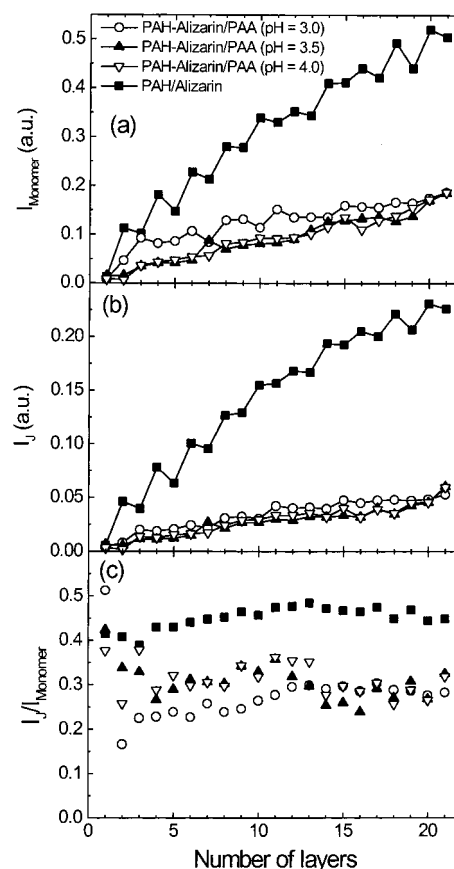


Figure 5. Intensity of (a) monomeric absorption band, (b) aggregated absorption band, and (c) the ratio between the intensities of the aggregate and monomeric bands, as a function of the number of deposited layers during different layer-by-layer self-assembled film depositions.

maximum for both the monomeric and the aggregate bands increased monotonically with the number of deposited layers [Figure 5a,b]. In this configuration, the absorption intensity after either polyanion or polycation deposition did not show any decrease at regular intervals. This shows that the alizarin molecules did not come out of the films during any layer deposition. The results therefore show that the method of anchoring small molecules to polyions prior to layer-by-layer film deposition has an advantage over the regular deposition method, where only small molecules themselves are used in the deposition baths.

To know if the nature of aggregation has changed as deposition progressed, we have plotted the ratio between the intensities of aggregate and monomeric bands as a function of number of deposited layers in Figure 5c. The figure shows that the ratio remained independent of the layer number for both types of film deposition. The decrease in absorption intensity after PAH deposition therefore occurred without any change in the nature of aggregation in the films. In other words, although the absorption intensity of the monomeric and aggregate bands decreased due to a loss of alizarin molecules during PAH deposition, their ratio did not show any change. The loss of alizarin molecules from the film was therefore uniform for the monomeric sites and aggregated clusters.

We have taken AFM images of different self-assembled films to know the homogeneity of the surface of the films. The root mean square roughness of both types of films was less than 5 nm.

Conclusions

We have presented a novel method for deposition of low molecular weight organic molecules via electrostatic self-assembly. The small molecules, alizarin violet with only two anionic groups, when acting as the anion, tend to come out of the films during subsequent polycation deposition. The intensities of the absorption band maxima of alizarin therefore decreased due to the next polycation deposition. Absorption spectra revealed the presence of monomeric and aggregated sites in the films. The material loss from the films was found to be uniform for both the sites. As an alternative approach, the alizarin molecules have been electrostatically anchored to a polycation prior

to deposition. When the polycation–alizarin combination as a whole was used as the polycation for film deposition, the absorption spectra did not show any evidence of material loss during the layer depositions. The alternative approach to deposit small organic molecules has revealed its advantage over the conventional method.

Acknowledgment. The authors thank Dr. K.-M. Källman and Professor H. Stubb of Åbo Akademi University, Finland, for the AFM images. This work was supported by the Department of Science & Technology, Government of India (Project No. SP/S2/M-11/94).

LA011043B