To Combine Precursor Assembly and Layer-by-layer Deposition for Incorporation of Single-charged Species: Nanocontainers with Charge-selectivity and Nanoreactors

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We describe a method to fabricate single-charged functional species of sodium 9-anthracenepropionate (SANP) into poly(diallyldimethylammonium chloride) (PDDA)/poly(4-styrenesulfonate) (PSS) multilayer film by precursor assembly in bulk and then layer-by-layer (LbL) deposition at interface. By formation of PDDA−SANP complex in aqueous solution and then deposition in alternation with PSS, SANP was successfully introduced into PDDA/PSS multilayer assemblies. Our detailed experiment revealed that the release rate of SANP from the film was related to the concentration of electrolyte in aqueous solution, and the fast adsorption of SANP onto the film was related to the positively charged binding sites in the film. These binding sites, which were formed by desorption of SANP, can attract negatively charged molecules and repulse positively charged molecules in aqueous solution. In addition, photocycloaddition reaction of SANP can take place with a quantum yield 4 times higher than that in solution, suggesting that LbL assemblies are good candidates as nanoreactors.

Introduction

Layer-by-layer (LbL) assembly[1] has been well established as a simple and versatile method to construct ultrathin organic films with controlled thickness in the nanometer range through sequential adsorption of polycations and polyanions from dilute solutions.[2] The electrostatic nature of the interaction allows a variety of polyelectrolytes to be deposited, thereby forming polyelectrolyte multilayers. This approach has been extended to various other materials, including inorganic nanoparticles,[3−5] dyes,[6,7] and biological macromolecules such as DNA[8,9] and proteins.[10,11] Very recently, Crespo-Biel et al.[12] have built up a novel kind of self-assembled organic/inorganic multilayer based on multivalent supramolecular interactions between guest-functionalized dendrimers and host-modified gold nanoparticles. For the attractive feature of this technique, that is, thoroughly controlled assembly, a few model systems have demonstrated a controlled desorption of functional species from the multilayer assemblies, such as use of degradable polymers and thermoresponsive materials as building blocks,[13−15] release triggered by adsorption of polyelectrolyte,[16,17] and pH-dependent loading and release.[18] The ability to control film properties at a nanoscale level has led to studies of LbL assemblies for applications such as biosensors, microcapsules, membranes, and coatings to improve biocompatibility.[19−25]

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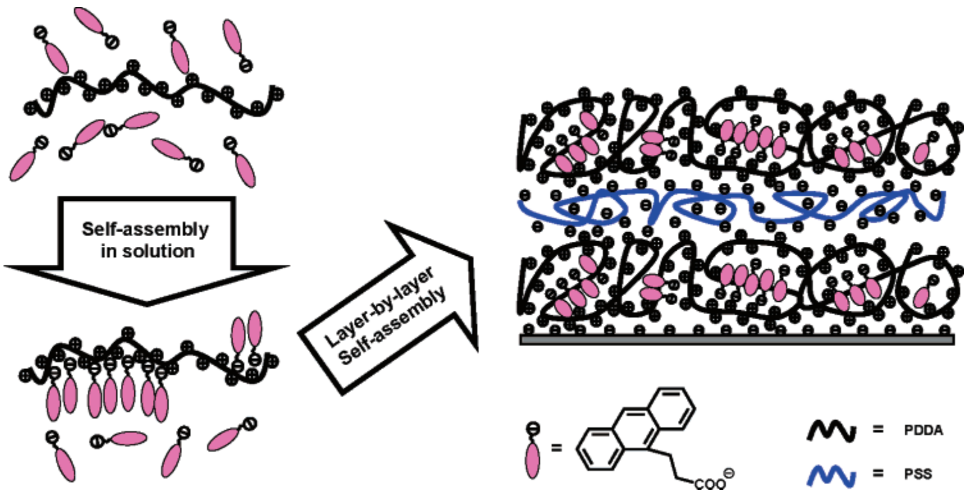

Figure 1. Illustration of hierarchical self-assembly: step 1, sodium 9-anthracenepropionate tethered to PDDA in solution; step 2, layer-by-layer self-assembly of PDDA−SANP/PSS.

One of the methods to realize the functionalization of LbL assemblies is incorporation of small functional molecules into the LbL assemblies. There are several ways to incorporate small functional molecules into the LbL assemblies, for example, the grafting of polyelectrolytes by functional moieties,[26,27] the alternate deposition of polyelectrolytes and multicharged functional molecules,[6,28,29] the postdiffusion of the functional molecules into the multilayers,[30,31] and the introduction of functional molecules into LbL assemblies by post-chemical reaction.[32] However, the challenge still remains to incorporate single-charged molecules into LbL assemblies due to their easy extraction from the film.

In this paper, we investigate the incorporation of a single-charged dye molecule into the polyelectrolyte films using a model dye that exhibits a chromophore moiety, which is sensitive to the local environment and can undergo photocycloaddition reaction, namely, sodium 9-anthracenepropionate (SANP). Herein we attempt to use the concept of hierarchical self-assembly to fabricate multilayer assemblies of SANP, involving precursor assembly in bulk and LbL deposition at interface, and we wondered whether the LbL assemblies could be used as microreactors for the photocycloaddition reaction under UV irradiation.[33,34] For this purpose, as shown in Figure 1, we mixed cationic polyelectrolyte of poly(diallyldimethylammonium chloride) (PDDA) with anionic dye of SANP in appropriate concentrations, forming a PDDA−SANP complex by interpolyelectrolyte complexation,[35] and then fabricated multilayer assemblies by alternate deposition of PDDA−SANP complex and poly(4-styrenesulfonate) (PSS). This research is different from the previous publications in the following points: (1) Because unique dyes of SANP can aggregate after being complexed into the film and many positive binding sites may be formed after release of SANP, this interesting property makes the next adsorption of SANP occur not only on the surface but also inside the films. Thus our systems can show linear growth of the thin film fabrication. (2) We have found, interestingly, that the dye molecules of SANP incorporated in the film can function as molecular templates. The release of these molecules can lead to formation of cavities, somewhat like surface molecularly imprinting, which allows for binding charged species with good selectivity. (3) The unique molecular template we choose here is photoreactive SANP. So we can carry out photochemical reaction in a restricted space, suggesting that layer-by-layer assemblies may be used as nanoreactors.

Experimental Section

Materials. The polyelectrolytes used for preparation of the polyelectrolyte multilayers were poly(diallyldimethylammonium chloride) (PDDA), M_w 400 000, and poly(4-styrenesulfonate) (PSS), M_w 70 000. All were obtained from Aldrich Chemical Co. and used as received. The single-charged dyes sodium 9-anthracenepropionate (SANP) and 9-anthracenetrimethyammonium bromide (ATAB) were synthesized according to literature.[36] Sodium 1-pyrenesulfonate (SPS) was obtained from Aldrich Chemical Co., and L-tryptophan was obtained from Beijing Dingguo Biotechnology Co., Ltd. Na_2SO_4 was from Beijing Chemical Reagent Co. (purity >99%). Quartz slides were purchased from Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences.

Substrate Preparation. Quartz substrates were cleaned by 3:7 (vol %) H_2O_2/H_2SO_4 (piranha solution) at 100 °C for ca. 40 min,

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followed by sonication in deionized water for 1 h, and then extensive rinsed with deionized water. (CAUTION: Piranha solutions are very aggressive, corrosive solutions, and appropriate safety precautions should be utilized, including the use of acid-resistant gloves and adequate shielding.) After these cleaning procedures, the slides were completely hydrophilic.

Assembly of Multilayer Films. SANP (2 mg) was added to 6 mL of PDDA aqueous solution (1 mg/mL), forming PDDA−SANP complex (molar ratio of SANP:PDDA monomer = 1:4.65). Multilayer films were fabricated on the clean quartz substrates by sequential deposition of such PDDA−SANP complexes and PSS or of PDDA and PSS. The concentrations of PDDA and PSS aqueous solution were both 1 mg/mL. The substrates were first immersed in PDDA−SANP or PDDA for 10 min, followed by rinsing with a continuous flow of deionized water for 10 s (in our experiment, 10 s is enough for removing the physisorbed SANP molecules), and dried in a nitrogen stream for 1 min. The substrates were then immersed in PSS for 10 min, followed by the same rinse cycle. The entire process was repeated with PDDA−SANP as the outermost layer, unless otherwise noted.

All investigations on PDDA−SANP/PSS multilayer films were performed on films with the structure [(PDDA−SANP/PSS)$_n$-(PDDA−SANP)] or on such films with SANP removed by Na_2SO_4 aqueous solution in advance.

Dye penetration was studied on preformed multilayer films with the structure [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)], from which SANP was removed by Na_2SO_4 aqueous solution in advance. Unless otherwise noted, the concentration of Na_2SO_4 was 4.7×10^{-3} mol/L. The concentrations of dyes used for penetration into the films were the same as the concentration of SANP in PDDA aqueous solution used for multilayer assembly.

Absorption and Fluorescence Measurements. UV−vis spectra were recorded with a Hitachi UV−vis 3010 spectrophotometer. Steady-state fluorescence measurements were performed with a Perkin-Elmer LS-50B luminescence spectrophotometer. The excitation wavelength used throughout the experiments was 350 nm. The irradiation light source for photocycloaddition was a UV optical fiber (RW−UVA φ05−100, purchased from Shenzhen Runwing Mechanical & Electrical Co., Ltd). The main wavelength is 365 nm and the intensity is 100 mW. The relative quantum yield of LbL film was measured by UV−vis spectroscopy referenced to the aqueous solution.

Atomic Force Microscopy Measurements. For the AFM measurements a commercial microscope (Multimode Nanoscope IV, Digital Instruments) was used. Imaging was performed in tapping mode in air employing commercially available cantilevers. Tapping amplitude and especially the damping factor were carefully chosen to allow imaging of the polyelectrolyte surface structure without inducing alterations by the imaging process.

Results and Discussion

Fast Loading and Release of SANP during the Multilayer Buildup of PDDA−SANP and PSS. The PDDA−SANP/PSS multilayer films were fabricated by alternate deposition of PDDA−SANP complex and PSS as monitored by UV−vis absorption spectroscopy in Figure 2a. The incorporated SANP is clearly identified by the characteristic strong peak at around 263 nm and the fingerprinting absorption bands between 325 and 425 nm. The absorption band around 225 nm is mainly attributed to PSS. Herein, we take the first to fifth layer deposition as examples to show the multilayer buildup. The first layer of PDDA−SANP was deposited on a quartz slide, and then the slide was immersed into the solution of PSS for deposition of the second layer. The third layer of PDDA−SANP can be well deposited on the PSS layer, however, the SANP absorbance at 263 nm is lost when the fourth layer of PSS is adsorbed. For further deposition of the fifth layer of PDDA−SANP, the characteristic SANP absorbance appears, suggesting that PDDA−SANP is deposited onto the PSS layer again. So there exists a fluctuation of fast loading and release during the multilayer buildup of PDDA−SANP/PSS.

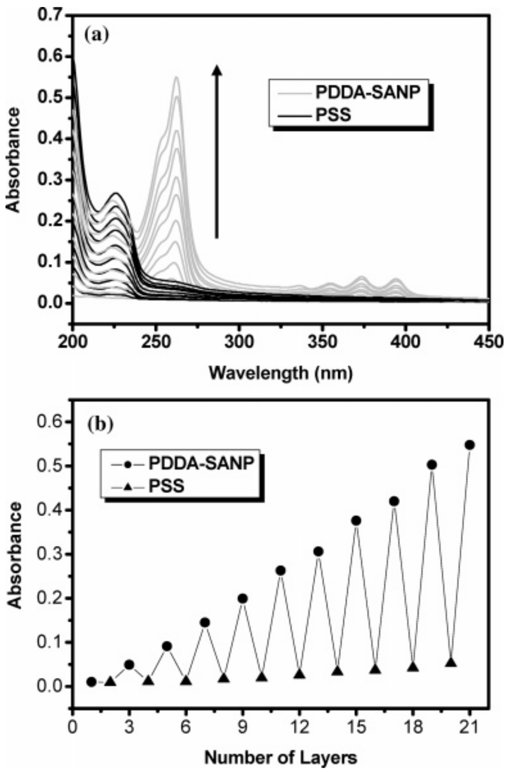

Figure 2. (a) Absorption spectra of 21 PDDA−SANP/PSS layers, measured after each deposition cycle. The gray spectra are recorded after PDDA−SANP adsorption, and the black spectra, after PSS adsorption. The arrow indicates the absorption of SANP at 263 nm increases with the number of the deposited layers. (b) Absorbance at 263 nm vs the number of PDDA−SANP/PSS layers, extracted from the data set shown in panel a. The solid line is a guide to the eye to outline the stepwise dye adsorption/desorption process.

The fast loading and release process is obvious, when the absorbance at 263 nm is plotted against the number of PDDA−SANP/PSS layers. As shown in Figure 2b, we can see clearly that the absorbance at 263 nm increases linearly with the odd number of layers, which suggests that the small molecules undergo a controlled assembly into the multilayer film through hierarchical self-assembly that involves precursor assembly in bulk and LbL deposition at the interface. The loading capacity of SANP also can be easily tuned by changing the SANP concentration when the PDDA−SANP complex is formed. Interestingly, almost all the SANP incorporated in the multilayer desorbs during the deposition of the PSS layers. This suggests that, in the desorption process, not only dye molecules adsorbed at the surface layer but also those trapped more deeply in the multilayer are released.

Plausible Mechanism of Fast Release of SANP from the LbL Film: Electrolyte Effect. It was found that release of SANP became slower when the concentration of PSS was

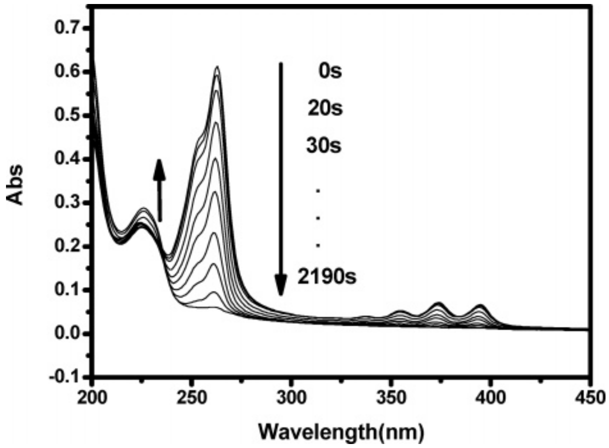

Figure 3. Absorption spectra of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film in dilute PSS aqueous solution (0.01 mg/mL). The left arrow indicates the increase in absorbance of PSS with the immersion time. The right arrow indicates the decrease in absorbance of SANP with the immersion time. The film was washed with pure water and dried with pure nitrogen gas after each immersion.

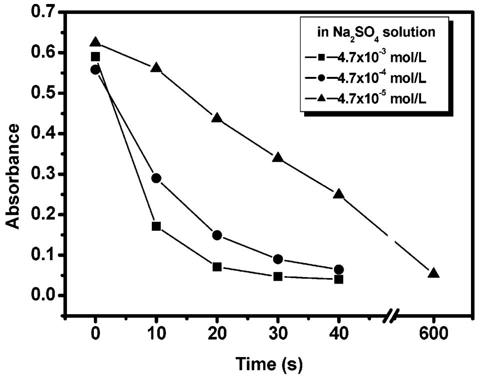

Figure 4. Absorbance at 263 nm vs immersion time of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film in Na_2SO_4 aqueous solution of varying concentration.

decreased. Some groups have reported that the release of low molecular weight molecules from the film was related to the ionic strength of the solution,[30,37] and other groups reported that the release process was related to the adsorption of polyelectrolyte.[16] In our experiment, we immersed a [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film in a dilute PSS aqueous solution (0.01 mg/mL). As shown in Figure 3, at the very beginning of immersion only a little PSS adsorbed on the film, which we can see from the characteristic absorbance of PSS at 225 nm; simultaneously, the release rate of SANP from the film was still high (absorbance at 263 nm). Moreover, when we did a systematic study of the release process, we found that not only PSS but also PDDA and other polyelectrolytes were able to cause the release of SANP, no matter whether the polyelectrolytes were polyanions or polycations. Therefore, the release of SANP seems to be related to ionic strength of the solution instead of adsorption of the polyelectrolytes. To confirm this speculation, we fabricated a [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film and exposed it to Na_2SO_4 aqueous solution of varying concentrations. As shown in Figure 4, the release rate of SANP from the multilayer film is indeed correlated with the concentration of Na_2SO_4 solution. In a high Na_2SO_4 concentration (4.7×10^{-3} mol/L), SANP can be released completely in about 40 s. The release rate becomes lower when the concentration of Na_2SO_4 is decreased. At the lowest concentration (4.7×10^{-5} mol/L), it takes 10 min for the complete release of SANP. All these data suggest the release of SANP is influenced by the ionic strength in the solution and the release rate is much higher in an environment of higher ionic strength. A possible explanation for the mechanism of the release of SANP from the film is that the small ions in the electrolyte aqueous solution are easy to exchange with SANP in the film, and then SANP can diffuse out of the film into the aqueous solution.

Positively Charged Binding Sites and Charge Selectivity of the Multilayer Film Responsible for the Linear Deposition and Fast Loading of SANP. Since the SANP is released almost completely from the multilayer film during the deposition of the even number of layers, we are curious why there is still a linear increase of the absorbance at around 263 nm during the adsorption of PDDA−SANP as the odd number of layers. A possible explanation could be that the binding sites for SANP still remain in the PDDA layers within the multilayer film when the previously adsorbed SANP are released, and these binding sites are refilled with free SANP in PDDA−SANP solution during the next deposition cycle.

To test the above assumption, we fabricated a [(PDDA−SANP/ PSS)$_9$(PDDA−SANP)] multilayer film and then tried to remove SANP from the multilayer by washing in Na_2SO_4 solution. After the treatment, there should be many binding sites within the layers. When the film was then immersed in SANP solution, we found that both the velocity of diffusion and the amount of SANP diffused into the multilayer increased dramatically as compared to when a normal PDDA/PSS multilayer was used. An interesting property for the film prepared in this way is that it shows dramatically different adsorption capabilities for negatively charged species, such as SANP, and positively charged species, such as 9-anthracenetrimethylammonium bromide (ATAB). Figure 5a shows the change of absorbance at 263 nm at different immersion times in SANP and ATAB solution. We can see that SANP diffuses easily into the film; however, ATAB is barely adsorbed into the film even after a long immersion time. The low amount of adsorption of ATAB is obviously due to a charge effect. Release of SANP should leave many positively charged binding sites in the multilayer matrix. Therefore it is hard for ATAB to diffuse into such a film due to its positive charge. We performed a similar experiment with another negatively charged molecule, sodium 1-pyrenesulfonate (SPS). Not surprisingly, SPS could diffuse into the multilayer film as efficiently as SANP (the result is not shown here). In contrary, for a normal multilayer of PDDA/PSS, SANP and ATAB showed similar diffusion abilities.

To further demonstrate the charge effect, we chose a probe that would bear different charges under different conditions. As we knew, amino acids could be made to switch their charge in aqueous solution by simply changing the pH of

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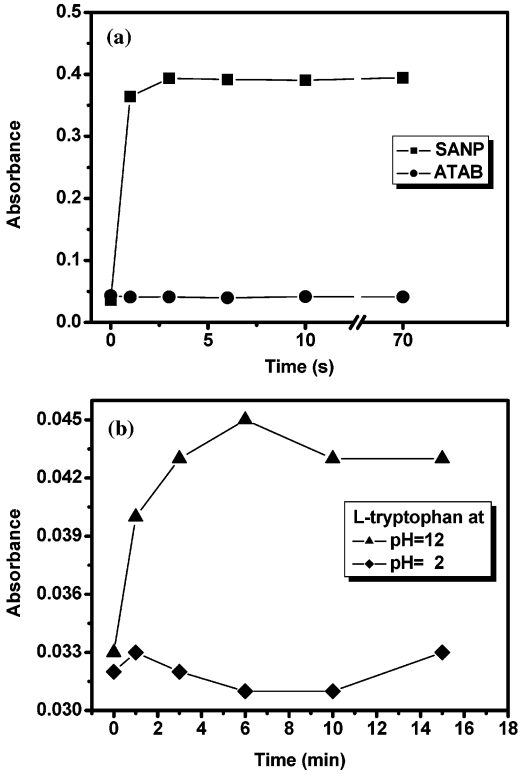

Figure 5. (a) Absorbance at 263 nm vs immersion time of [(PDDA−SANP/PSS)$_9$(PDDA−SANP)] multilayer film in aqueous solutions of different anthracene derivatives, SANP and ATAB. The films were immersed in Na_2SO_4 aqueous solution to remove SANP in advance. (b) Absorbance at 278 nm vs immersion time of [(PDDA−SANP/PSS)$_9$(PDDA−SANP)] multilayer film in L-tryptophan aqueous solution at pH = 12 and pH = 2. The films were immersed in Na_2SO_4 aqueous solution to remove SANP in advance.

the solution. So we decided to use L-tryptophan as a probe to see the difference of diffusion into [(PDDA−SANP/PSS)$_9$(PDDA−SANP)] multilayer film, after SANP was removed, under conditions where it bears opposite charge. Figure 5b shows the absorbance at 278 nm of a [(PDDA−SANP/PSS)$_9$(PDDA−SANP)] multilayer film (SANP removed in advance) as a function of the time of immersion in L-tryptophan aqueous solution at pH = 12 and pH = 2. The absorbance at 278 nm is ascribed to the characteristic absorption band of L-tryptophan. L-Tryptophan is negatively charged at pH = 12 in aqueous solution and positively charged at pH = 2. From the figure we see that L-tryptophan can diffuse into the multilayer freely at pH = 12 but hardly diffuses into the same multilayer film at pH = 2. This difference of diffusion between positively and negatively charged molecules strongly suggests that there are positively charged binding sites in the multilayer film after removal of SANP.

It should be noted that the “linear increase” suggests that SANP molecules not only are adsorbed on the top layer of the LbL assemblies but also can diffuse into the multilayer films. As we all know, it is quite hard to introduce single-charged molecules into LbL assemblies due to their easier extraction than multicharged molecules. A traditional viewpoint is that strong interaction between a single-charged molecule and a polyelectrolyte might be helpful for its retention in the LbL assemblies after the adsorption of the next layer. Unlike rhodamine B and other strong electrolytes,[28] the SANP we chose in our experiment is a weak electrolyte, which results in abundant uncomplexed SANP in the solution due to the weak interaction between SANP and PDDA after being added in the PDDA aqueous solution to form PDDA−SANP complex. A greater loading was observed at higher pH than lower pH, and in this experiment the pH was fixed at 12. After desorption caused by PSS aqueous solution, SANP could readsorb into the multilayer film in two ways: adsorption of PDDA−SANP complex at the outermost layer, and diffusion of uncomplexed SANP into the multilayer film. For rhodamine B, there do not exist many uncomplexed dye molecules in the solution because most of dye molecules form polyelectrolyte−rhodamine B complexes due to the strong interaction between them. As a result, after desorption from the multilayer film, rhodamine B can only readsorb on the top of the multilayer film as part of the complex but cannot diffuse into the layers.

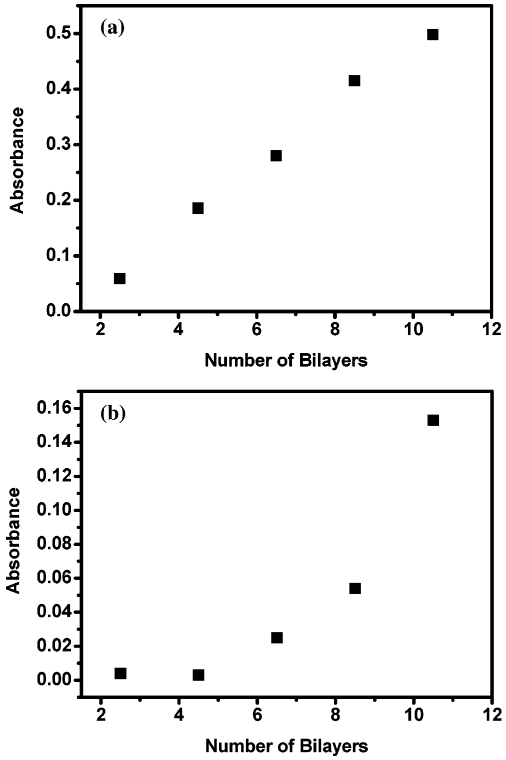

Figure 6. Absorbance at 262 nm for [(PDDA−SANP/PSS)$_n$(PDDA−SANP)] (a) and 261 nm for [(PDDA−SANP/PSS)$_n$(PDDA)] (b) after immersion in SANP aqueous solution where n = 2, 4, 6, 8, or 10. The films were immersed in Na_2SO_4 aqueous solution in advance.

Figure 6a shows the absorbance of [(PDDA−SANP/PSS)$_n$(PDDA−SANP)] multilayer film at 262 nm as a function of the number of layers. Each film was dipped into Na_2SO_4 aqueous solution to remove SANP in advance and then immersed in SANP aqueous solution for 10 min. The absorbance shows a good linear increase of SANP versus the number of layers, indicating that SANP could diffuse into the LbL assemblies uniformly. We found that, in order to get a linear increase, the outermost layer must be PDDA−SANP. When PDDA is deposited as the outermost layer instead of PDDA−SANP, we could not observe a linear increase of the amount of SANP versus the number of layers, as shown in Figure 6b. A similar result is found when PSS is the outermost layer. A reasonable explanation is that the different conformations of PDDA−SANP and PDDA result in different surface structures of the films, and thus different

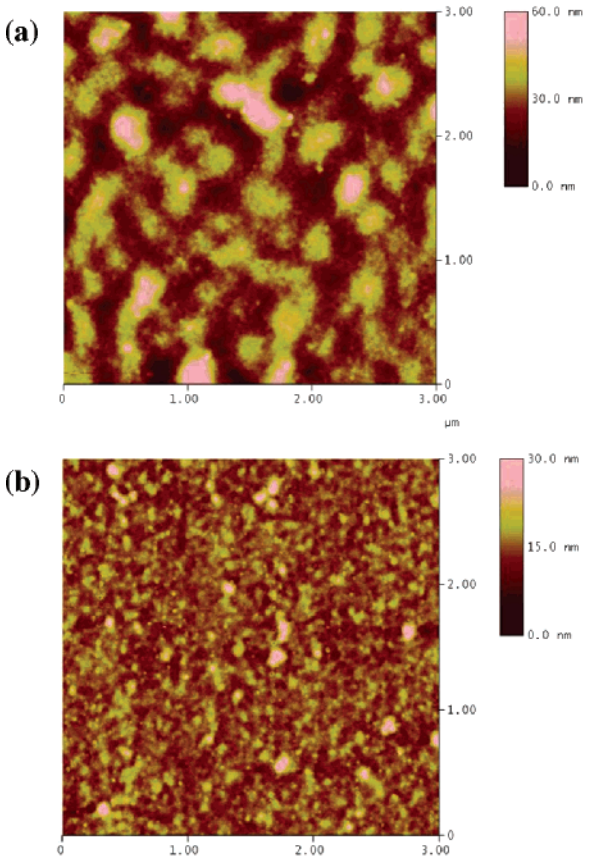

Figure 7. AFM images (3 μm × 3 μm) of multilayer films of (a) [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] and (b) [(PDDA−SANP/PSS)$_{10}$(PDDA)].

permeabilities of the films. There is also a possibility that the low binding capacity of the film terminated with PDDA could be due to the reduced access to underlying ion exchange. We used AFM to observe the surface morphology of the film with different outermost layers. As shown in Figure 7, the surface roughness of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film is higher than that of [(PDDA−SANP/PSS)$_{10}$PDDA] multilayer film, indicating that the surface of the film is more compact when PDDA is the outermost layer rather than PDDA−SANP. This probably means it is easier for SANP to diffuse into the LbL assemblies with PDDA−SANP as the outermost layer.

Moreover, the small molecule we used in our experiment, SANP, has a hydrophilic group (-COO$^-$) and a hydrophobic group (anthracene). When a PDDA−SANP complex is formed in aqueous solution, the hydrophobic groups might get together due to the hydrophobic interaction. Furthermore, the fact that anthracene groups could form strong $\pi-\pi$ stacking suggests SANP could aggregate in the LbL assemblies to some extent. In other words, once removed by electrolyte, SANP could leave many binding sites within the LbL assemblies as mentioned before. These binding sites are accessible to SANP when the film is immersed in SANP solution again. As the number of layers increases, the capacity of the film to bind SANP molecules also increases.

Advantage of This Hierarchical Self-Assembly That Involves Preassembly and LbL Deposition. There are several advantages of this hierarchical self-assembly approach over normal methods in introducing single-charged functional molecules into the LbL assemblies, in terms of efficiency and loading capacity. Thus far, we have fabricated normal [(PDDA/PSS)$_{10}$(PDDA)] LbL assemblies and then exposed them to SANP aqueous solution with a concentration of 1.3 × 10^{-3} mol/L to let SANP diffuse into the LbL assemblies. As shown in Figure 8, the saturation time of adsorption is about 80 min in this case, much longer than that with hierarchical self-assembly. A slow diffusion process of SANP into PDDA/PSS would be expected if we consider that the polycation PDDA and the polyanion PSS are densely packed and interpenetrated in the LbL film. In addition, the total amount of SANP diffused and adsorbed in [(PDDA/PSS)$_{10}$(PDDA)] LbL film is also much less than that in [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] LbL film. This could be due to the lack of positively charged binding sites that can bind negatively charged molecules in the PDDA/PSS system, because most of the charges neutralize each other in the formation of LbL assemblies. When we decreased the concentration of SANP aqueous solution from 1.3 × 10^{-3} to 1.3 × 10^{-4} mol/L, SANP molecules hardly diffused into [(PDDA/PSS)$_{10}$(PDDA)] LbL film even if the film was exposed to the solution for 2 days. At the same time, by keeping a low concentration of SANP at 1.3 × 10^{-4} mol/L in PDDA aqueous solution and using hierarchical self-assembly, we found that the total amount of SANP in the LbL film still increased linearly with the number of layers though with a lower loading capacity than when a high concentration of SANP was used.

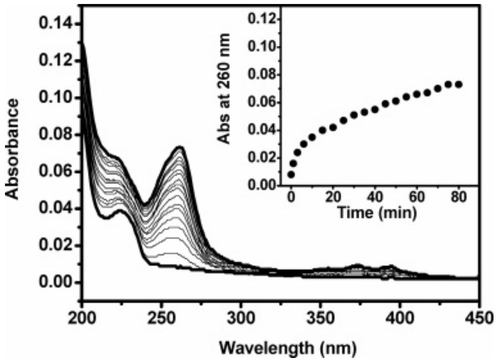

Figure 8. Absorption spectra of [(PDDA/PSS)$_{10}$(PDDA)] exposed to SANP aqueous solution (1.3 × 10^{-3} mol/L) for different times. (Inset) Absorbance at 260 nm vs adsorption time.

Photocycloaddition of SANP in Multilayer Film. It is well-known that anthracene moiety can undergo photocycloaddition under UV irradiation.[38] Using anthracene moiety as a probe, we wondered whether the multilayer could act as a nanoreactor. Figure 9a shows the absorbance change of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] LbL film before and after UV irradiation. As shown in this figure, the decrease of characteristic absorbance of anthracene between 250 and 425 nm as well as the increase of characteristic absorbance of benzene around 205 nm with increasing time of UV irradiation indicate that SANP moieties incorporated in the LbL film do undergo photocycloaddition to produce a photocyclomer. The quantum yield of photocycloaddition is about 4 times higher than that in the solution. The reason such photocycloaddition occurred with an enhanced quantum yield should correlate with the aggregation of SANP in the

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(38) Bradshaw, A. W.; Chapman, O. L. *J. Am. Chem. Soc.* **1967**, *89*, 2372.

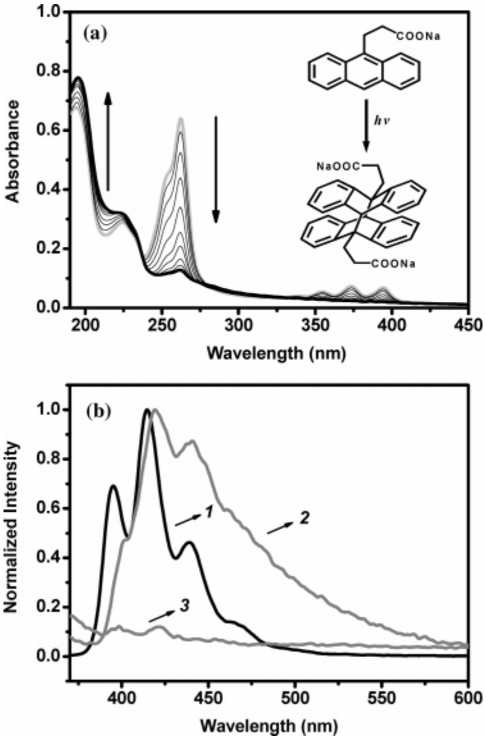

Figure 9. (a) Absorption spectra of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film under UV irradiation for different times. (Inset) Chemical structures of SANP and its photocyclomer. Arrows indicate the transformation of the spectrum with increasing irradiation time. (b) Fluorescence spectra ($\lambda_{ex} = 350$ nm) of SANP aqueous solution (line 1) and of [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] multilayer film before UV irradiation (line 2) and after UV irradiation for 10 min (line 3). The concentration of SANP aqueous solution is 2.86×10^{-5} mol/L.

LbL assemblies. Fluorescence spectroscopy was used to confirm our hypothesis. As seen from Figure 9b, there appears a new emission band at longer wavelength in [(PDDA−SANP/PSS)$_{10}$(PDDA−SANP)] LbL assemblies as compared with monomer emission of SANP aqueous solution,[39] and the feature of the excitation spectrum for excimer in LbL assemblies is significantly different from that for monomer in solution, suggesting that SANP aggregates and forms intermolecular excimers upon excitation, thus speeding up the reaction. As the photocycloaddition proceeds, the SANP forms photocyclomer, which is evidenced by the decreasing fluorescence.

Conclusions

We have proposed a method of hierarchical self-assembly for the controlled assembly and release of single-charged functional species by combining the precursor assembly and the LbL deposition technique. By formation of PDDA−SANP complex in aqueous solution and then deposition in alternation with PSS, SANP was successfully introduced into PDDA/PSS multilayer assemblies. At each PSS adsorption step, nearly the total SANP in the multilayer assemblies was released, and the rate of SANP released depended on the ionic strength in the solution. The diffusion abilities into PDDA−SANP/PSS multilayer films (SANP removed in advance) were quite different for positively and negatively charged dyes. This should be attributed to the positively charged binding sites that contained SANP originally in the multilayer film. In addition, photocycloaddition reaction of SANP can take place with a higher quantum yield than that in solution, suggesting that LbL assemblies are good candidates as nanoreactors. We expect that this similar concept could be applied to introduce different functional molecules into the LbL assemblies and then open a new avenue for fabricating functional nanoassemblies.

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