Macromolecules **2007,** *40,* 653−660

To Construct “Ion Traps” for Enhancing the Permselectivity and Permeability of Polyelectrolyte Multilayer Films

Huan Chen,[†,‡] Guanghong Zeng,[†] Zhiqiang Wang,[†] and Xi Zhang*,[†]

Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, People’s Republic of China, and Key Lab for Supramolecular Structure and Materials, Jilin University, Changchun, 130012, People’s Republic of China

Received June 23, 2006; Revised Manuscript Received September 5, 2006

ABSTRACT: We introduced single-charged molecules into layer-by-layer film of polymers by mixing polyelectrolyte and single-charged molecules with an appropriate ratio to form polymer complex and then deposition in alternation with counter-polyelectrolyte. By immersing the layer-by-layer film into aqueous solution of electrolytes, the single-charged molecules could be released from the layer-by-layer film. An interesting finding is the releasing of the single-charged molecules gave the multilayer film the permselectivity. For example, cations would be trapped and anions be repelled if positive-charged molecules were used. Multilayer films able to trap either cations or anions could be fabricated, depending on the nature of single-charged template molecules used. Thus, the ion permselectivity of multilayer film was enhanced. Moreover, the permeability of the film was also dramatically increased, suggesting the potential application of layer-by-layer films as highly efficient ion-permselective membranes.

Introduction

Ion permselectivity in membranes has received considerable attention recently due to its potential applications in filtration systems, membrane-based separations, bioseparations, and sensors. An ideal separation membrane contains actively selective sites which can be easily controlled to enable selectivity for a wide range of separations, while simultaneously maintaining high transport rates of desired molecules. A number of novel ion-permselective membranes have been studied, such as gold nanotubule membranes[1] prepared via the template method,[2] sol−gel films prepared from organosilanes containing acidic/basic permselective sites and ion-exchange coatings,[3] and redox polyelectrolyte thin films that were assembled by layer-by-layer deposition for Donnan permselectivity.[4] Very recently, White and Zharov et al.[5] reported on using chemically modified opal films as thin permselective nanoporous membranes with high molecular throughput.

The layer-by-layer (LbL) self-assembly technique[6] has proven to be a suitable, versatile, and inexpensive means for the preparation of nanostructured films.[7,8] It permits the sequential assembly of multiple layers of oppositely charged materials on planar substrates[9,10] and spherical supports[11,12] using polyelectrolytes as electrostatic binders. Numerous substances have been assembled successfully into the films via the LbL procedure, including oligo-charged dyes,[13] inorganic compounds,[14] polyelectrolytes,[15] photoreactive species,[16] thermoresponsive materials,[17] colloids,[10,18] and biomacromolecules.[19] By using LbL assemblies for material separation, a lot of work has been done on gas separation,[20,21] ethanol−water pervaporation,[22] and selective ion transport.[23] Advincula et al.[24] prepared pH-sensitive bipolar ion-permselective films of polyelectrolyte multilayers and photo-cross-linking of benzophenone-modified poly(acrylic acid) and poly(allylamine hydrochloride). The number of un-ionized −COOH or $-NH_2$ groups could be tuned by changing the pH to yield switchable ion permselectivity. However, for many polyelectrolyte multilayer films, charges on polycations are almost fully compensated by charges of polyanions and vice versa. Thus, net charge resides only at the surface of the membrane.[25] To overcome this limitation, Bruening and co-workers[26] developed a method of inserting net charge into multilayer polyelectrolyte films by photolysis of nitrobenzyl ester groups on derivate poly(acrylic acid) (PAA) through an intramolecular reaction. Cl^-/SO_4^{2-} selectivity was greatly enhanced due to net charge produced inside the film. Recently, Caruso et al.[27] reported the use of removable polyelectrolytes in LbL assembled polyelectrolyte multilayer thin films as a versatile approach to the production of nanoporous polymer films via polyelectrolyte templating. Inspired by the concept of molecular imprinting,[28,29] we introduced single-charged species into the LbL films of polymers as molecular templates to induce permselectivity. Single-charged species were mixed at an appropriate ratio with polyelectrolytes in solution and then deposited alternately with counter-polyelectrolytes. Removal of the single-charged species may form “ion traps”, which enables the film with strong permselectivity for cations or anions as well as high permeability. In this paper, we have demonstrated that both organic anions and organic cations can be used as molecular templates for constructing either “anion traps” or “cation traps”. We have also tried different cations and anions in attempt to provide an answer what kind of organic species are better candidates for assembly in this way. Furthermore, we have investigated whether these “ion traps” could be tuned by changing the initial concentration of the molecular templates in polyelectrolyte complex solution.

Experimental Section

Chemicals and Materials. The polyelectrolytes used for the preparation of the polyelectrolyte multilayers were poly(diallyldimethylammonium chloride) (PDDA), $M_w = 400\,000$, and poly(4-styrenesulfonate) (PSS), $M_w = 70\,000$. Both were obtained from Aldrich Chemical Co. and used as received. The single-charged molecules, sodium 9-anthracenepropionate (SANP), and anthracen-9-ylmethyltrimethylammonium bromide (ATAB), were kindly

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* Corresponding author. E-mail: xi@mail.tsinghua.edu.cn.

[†] Tsinghua University.

[‡] Jilin University.

10.1021/ma061406k CCC: $37.00 © 2007 American Chemical Society
Published on Web 01/06/2007

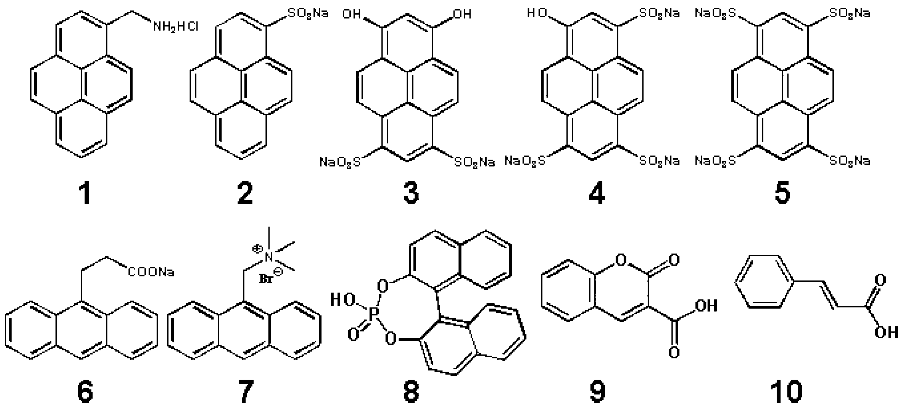

Figure 1. Template molecules tried for constructing ion "traps" in the layer-by-layer films. Compound number **1**: 1-pyrenemethylamine hydrochloride (PMAH); **2**: 1-pyrenesulfonic acid sodium salt (PSAH); **3**: 6,8-dihydroxypyrene-1,3-disulfonic acid disodium salt (P-2S); **4**: 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (P-3S); **5**: 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (P-4S); **6**: sodium 9-anthracenepropionate (SANP); **7**: anthracen-9-ylmethyltrimethylammonium bromide (ATAB); **8**: 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (BNDHP); **9**: coumarin-3-carboxylic acid (coumarin-3); and **10**: cinnamic acid.

provided by Prof. Li-Zhu Wu, Technical Institute of Physics and Chemistry, Chinese Academy of Science. 1-Pyrenemethylamine hydrochloride (PMAH), 1-pyrenesulfonic acid hydrate (PSAH), and coumarin-3-carboxylic acid (coumarin-3) were obtained from Aldrich Chemical Co. 6,8-Dihydroxypyrene-1,3-disulfonic acid disodium salt (P-2S) was purchased from Fluka Chemical Co. 8-Hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (P-3S) and 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (P-4S) were obtained from ACROS Chemical Co. 1,1′-Binaphthyl-2,2′-diyl hydrogen phosphate (BNDHP) was purchased form Alfa Aesar Chemical Co. Cinnamic acid was obtained from Beijing Chemical Reagent Co. All the above chemicals, as shown in Figure 1, were used as received. Dendrimer G_2-Por (with carboxylic acid groups as peripheries and porphyrin as core) was kindly provided by Prof. Liyan Wang, College of Chemistry, Jilin University ($M_w = 4066$). Sodium sulfate was purchased 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, 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. *(1) Film with "Canion Traps"*: 6.5×10^{-3} mmol of PMAH was added to 6 mL of PSS aqueous solution (1 mg/mL) at pH = 2, forming a polyanion−cation complex. Cation:polyanion monomer = 1:4.5 (molar ratio). Multilayer films were fabricated on clean quartz substrates by sequential deposition of polycation (1 mg/mL PDDA aqueous solution) and such polyanion−cation complex. The substrates were first immersed in PDDA aqueous solution for 10 min, followed by rinse with a continuous flow of deionized water for 10 s, and dried with nitrogen stream for 1 min. In our experiment, 10 s is enough to remove the uncomplexed single-charged molecules. The substrates were then immersed in PSS−PMAH aqueous solution for 10 min, followed by the same rinse cycle. The entire process was repeated with PSS−PMAH as the outmost layer. *(2) Film with "Anion Traps"*: 8×10^{-3} mmol SANP or PSAH was added to 6 mL of PDDA aqueous solution (1 mg/mL) at pH = 12, forming the polycation−anion complex. Anion:polycation monomer = 1:4.5 (molar ratio). Multilayer films were fabricated on clean quartz substrates by sequential deposition of such PDDA−SANP or PDDA−PSAH and PSS. The entire process was repeated with PDDA−SANP or PDDA−PSAH as the outmost layer.

Ion permselectivity was studied on preformed multilayer films with the structure (PDDA-anion/PSS)$_9$PDDA-anion or (PDDA/PSS-cation)$_{10}$, from which anions or cations were removed by Na_2SO_4 aqueous solution previously. Unless otherwise noted, the concentration of Na_2SO_4 was 6.2×10^{-2} mol/L. The concentrations of single-charged molecules used for permeability study of the films were the same as the ones used for multilayer assembly.

Electrodes and Electrochemical Setup. Gold electrodes (2 mm diameter) were used as the working electrodes for all modifications and measurements. The electrodes were polished sequentially with 1.0, 0.3, and 0.05 μm α-Al_2O_3 powders and extensively washed with deionized water. A cyclic voltammogram recorded in 2 mM $K_3Fe(CN)_6$ solution was used to determine the state of the electrode surface just before modification. Finally, the electrode was dried with high-purity nitrogen stream immediately before use. For the fabrication of LbL assemblies, gold electrodes were modified with $HSCH_2CH_2COOH$ in advance.

Cyclic voltammetry was performed with an Autolab PGSTAT 12 in a conventional three-electrode electrochemical cell using multilayer-modified gold electrode as the working electrode, platinum wire as the auxiliary electrode, and Ag/AgCl/KCl(sat.) as the reference electrode in aqueous media. All electrochemical measurements were performed in 0.1 M KCl as supporting electrolyte at room temperature, ca. 25 °C.

UV−vis spectra were recorded with a Hitachi UV−vis 3010 spectrophotometer.

Results and Discussion

Fast Loading and Releasing of PMAH during Multilayer Fabrication of PDDA and PSS−PMAH. LbL multilayer films containing single-charged molecules were fabricated as shown in Figure 2. The fabrication of PDDA/PSS−PMAH multilayer films was monitored by UV−vis absorption spectroscopy in Figure 3a. The incorporated PMAH is clearly identified by the characteristic strong absorption bands around 244, 268, 279, 331, and 347 nm. The absorption band around 225 nm is mainly attributed to PSS. An interesting finding is that there exists a fluctuation of fast loading and releasing during the multilayer fabrication of PDDA/PSS−PMAH. As clearly shown in Figure 3b, after each deposition of PDDA layer, the PMAH absorbance at 347 nm is almost completely lost. However, after further deposition of an additional PSS−PMAH layer, the characteristic PMAH absorbance appears again. This phenomenon becomes clearer as the number of layers increases.

Releasing of small molecules during film fabrication was widely observed by many other groups. However, when the absorbance at 347 nm is plotted against the number of PDDA/PSS−PMAH layers, we can see clearly that the absorbance at 347 nm increases linearly with the even number of layers after

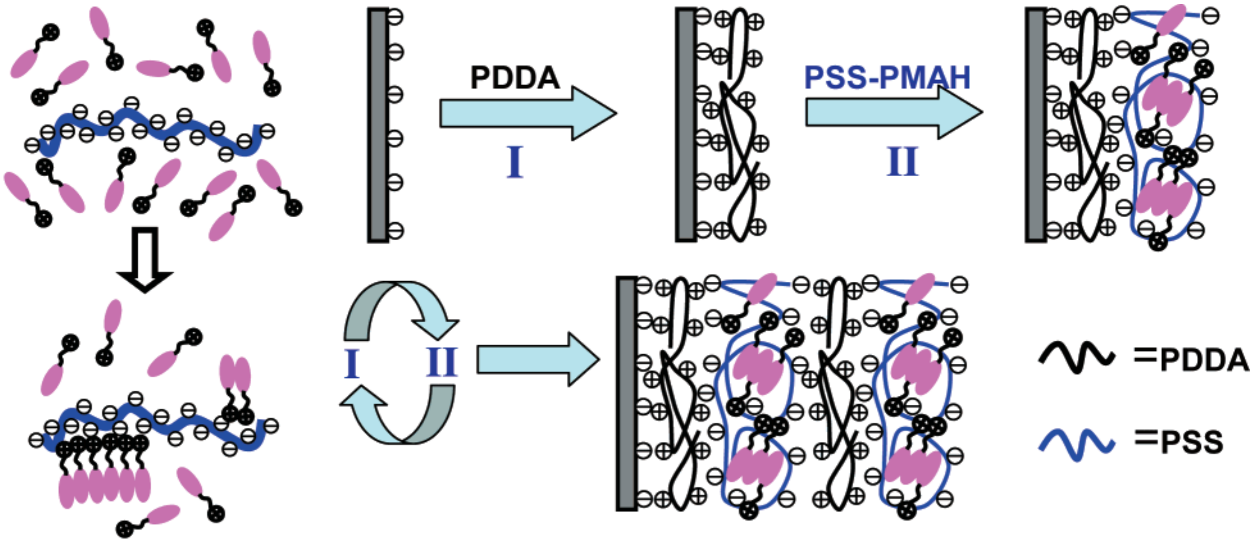

Figure 2. Schematic illustration of the fabrication of LbL film incorporated with single-charged molecules. First, we mixed PSS and PMAH in aqueous solution to form the PSS−PMAH complex; second, we alternately deposited PDDA and the PSS−PMAH complex on a quartz plate to fabricate the LbL assemblies.

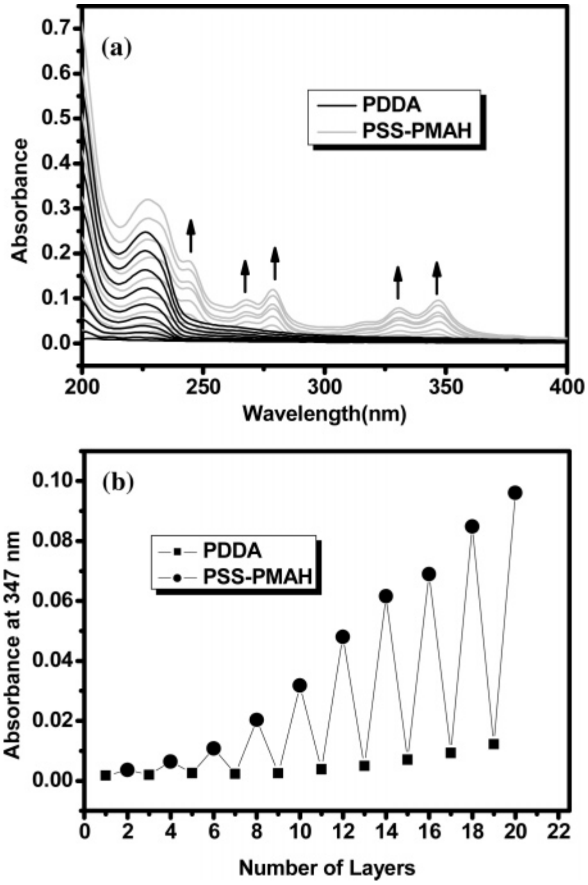

Figure 3. (a) Absorption spectra of 20 PDDA/PSS−PMAH layers, measured after each deposition cycle. The gray spectra are recorded after PSS−PMAH adsorption, and the black spectra are recorded after PDDA adsorption. The arrow indicates the characteristic absorption of PMAH increases with the number of the deposited layers. (b) Absorbance at 347 nm vs the number of PDDA/PSS−PMAH layers, extracted from the data set shown in (a). The solid line is an outline of the stepwise dye adsorption/desorption process.

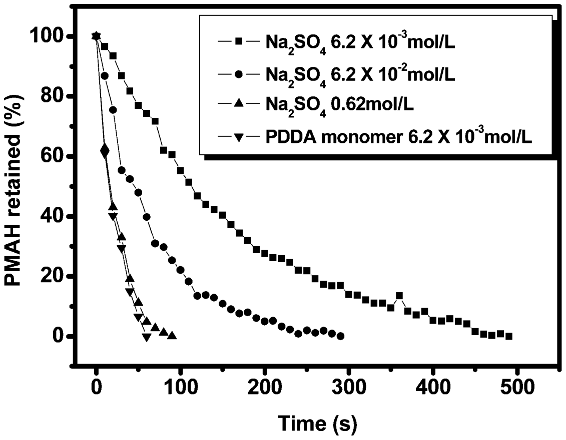

Figure 4. Releasing procedure of PMAH from the (PDDA/PSS−PMAH)$_{10}$ multilayer film in PDDA aqueous solution and Na_2SO_4 aqueous solution of varying concentration.

the nonlinear initial buildup. (It is reasonable because nonlinear initial buildup is usually observed before linear buildup during the LbL deposition.[30]) The linear increase of PMAH during the multilayer fabrication indicates that the small molecules undergo a controlled assembly into the multilayer film, which means that the loading capacity of PMAH can also be easily tuned by the number of layers deposited. Moreover, the linear growth of PMAH implies that PMAH probably permeates into the interior of the film after nearly total released during deposition of the previous layer, instead of readsorbing only at the surface.

Possible Mechanism of Fast Release of PMAH from the LbL Film. It was reported that both the adsorption of polyelectrolytes[31] and the ionic strength[32] in aqueous solution can cause the release of the small dyes from LbL films. In our previous study,[33] we used a diluted polyelectrolyte aqueous solution for film fabrication and found that at the very beginning little polyelectrolyte adsorbed on the film; meanwhile, the dyes in the film were still released in a high rate. We thus concluded that the adsorption of polyelectrolytes was not the main reason for the release of dyes from the LbL multilayer film. In the present work, we fabricated a (PDDA/PSS−PMAH)$_{10}$ LbL film and immersed it into PDDA aqueous solution or Na_2SO_4 aqueous solution of varying concentration, as shown in Figure 4. The releasing rate of PMAH greatly depends on the concentration of Na_2SO_4 solution. In a high Na_2SO_4 concentration (0.62 mol/L), PMAH can be released completely in about 90 s. The releasing rate becomes lower as the concentration of Na_2SO_4 is decreased. At the lowest concentration (6.2×10^{-3} mol/L), it takes nearly 500 s for the complete release of PMAH.

However, PMAH is released in about 50 s in a PDDA solution of the same monomer concentration. This leads to the conclusion that both the ionic strength and the adsorption of polyelectrolyte are important factors that influence the releasing behavior of the small dyes.

Mechanism of Fast Reloading of PMAH into the LbL Film. Since the PMAH was released almost completely from the multilayer film during the deposition of the odd number of layers, how could the amount of PMAH loaded into the film still increase linearly with the number of layers deposited? A possible explanation could be that the negative charged binding sites on PSS, previously occupied by PMAH, which are denoted as "ion traps" by us, remained in the PSS layers within the multilayer film when PMAH were released, and these "ion traps" could "trap" positively charged PMAH in PSS−PMAH solution during the next deposition cycle.

This explanation was confirmed by the study of loading capacity of the films with "ion traps". We fabricated a (PDDA/PSS−PMAH)$_{10}$ multilayer film and then removed PMAH from the multilayer by immersing it in Na_2SO_4 solution. After the treatment, there should be many "ion traps" within the layers. When the film was then immersed in PMAH solution, we found that both the velocity of diffusion and the amount of PMAH diffused into the multilayer increased dramatically compared to when a normal PDDA/PSS multilayer was used. Moreover, we found interestingly that the film showed dramatically different trapping abilities for positively charged species, such as PMAH, and negatively charged species, such as PSAH, as shown in Figure 5a. The trapping ability of the PMAH of negatively charged "ion traps" in the film reaches nearly 1.9×10^{-9} mol/cm^2; however, we hardly observed any PSAH trapped into the film. (The trapping ability of the PSAH is below zero, which is due to the removal of residual PMAH in the film.) This fact is due mainly to the electrostatic repulsion of the negatively charged "ion traps" to negatively charged PSAH, as illustrated in Figure 6. In order to confirm the existence of the "ion traps", we examined the trapping ability of other positively charged moieties, such as ATAB. Indeed, the film can trap positively charged ATAB (Figure 5a), and moreover, the trapping ability of ATAB is even higher than that of PMAH. This fact is probably due to the smaller molecular size of ATAB, which results in a higher content of ATAB in the negatively charged "ion traps" film. The figure also shows that the trapping rate for the cations is very high, with the saturation time less than 4 s.

For a normal LbL film of (PDDA/PSS)$_{10}$, as shown in Figure 5b, the trapping ability is as low as 5×10^{-10} mol/cm^2 (for PMAH) or 2.4×10^{-10} mol/cm^2 (for PSAH). The rate of permeation is also very low, with a saturation time as long as nearly 50 min. However, we can enhance the ion permselectivity in LbL film by the construction of "ion traps". The total amount of PMAH diffused into the (PDDA/PSS−PMAH)$_{10}$ film is much greater than the (PDDA/PSS)$_{10}$ film. No PSAH is observed to diffuse into the negatively charged "ion traps" film of (PDDA/PSS−PMAH)$_{10}$ while PSAH can diffuse into the normal LbL film of (PDDA/PSS)$_{10}$ despite the small amount. Therefore, the films with "ion traps" fabricated by LbL deposition have shown great advantage over normal LbL films in terms of enhanced permselectivity, greater trapping ability, and much higher diffusing rate.

After desorption caused by PDDA aqueous solution, PMAH could readsorb onto/into the multilayer film in two possible ways: adsorption of PSS−PMAH complex at the outmost layer and diffusion of uncomplexed PMAH into the multilayer film.

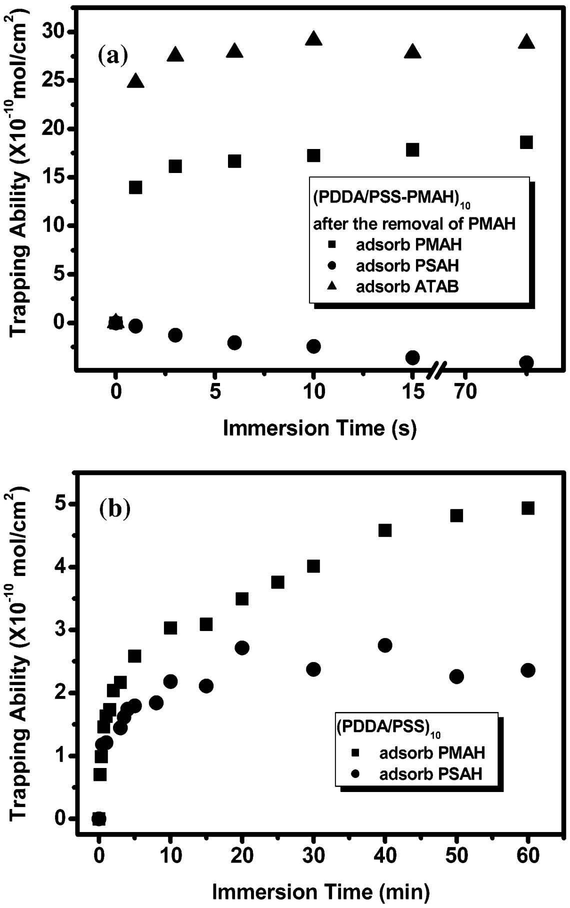

Figure 5. (a) Trapping abilities for PMAH (square, 1.1 mM), PSAH (circle, 1.3 mM), and ATAB (triangle, 1.1 mM) within (PDDA/PSS−PMAH)$_{10}$ films as functions of immersion time in their aqueous solutions. **(b)** Trapping abilities for PMAH (square, 1.1 mM) and PSAH (circle, 1.3 mM) within (PDDA/PSS)$_{10}$ films as functions of immersion time in their aqueous solutions.

As discussed above, it is important to notice that the "linear increase" suggests that PMAH molecules not only adsorb on the top layer of the LbL assemblies but also can diffuse into the multilayer films. In order to further demonstrate the "linear increase" of loading capacities, we fabricated five (PDDA/PSS−PMAH)$_n$ films with different layers. Each film was dipped into Na_2SO_4 aqueous solution to remove PMAH in advance and then immersed in PMAH aqueous solution for 10 min. Figure 7 shows the absorbance of (PDDA/PSS−PMAH)$_n$ multilayer film at 347 nm as a function of the number of layers. The absorbance shows a good linear increase of PAMH vs the number of layers, indicating that PMAH can diffuse into the LbL assemblies uniformly. These results confirm that PMAH molecules not only adsorb on the surface of the LbL multilayer film but also diffuse into the inner film.

As we all know, it is quite hard to introduce single-charged molecules into LbL assemblies besides the postdiffusion method[32a] due to the lack of binding sites to the film compared to multicharged molecules. It is believed that strong interaction between small molecule and polyelectrolyte might be helpful for its retention in the LbL assemblies after the adsorption of the next layer.[34] PMAH is a single-charged molecule, which may result in abundant free PMAH in the solution due to the binding and unbinding interactions between PMAH and PSS. We consider that it is an important factor for the successful incorporation of single-charged molecules into the LbL film.

Construction of "Anion Traps" in the LbL Multilayer Film. A similar concept can also be applied to fabricate thin

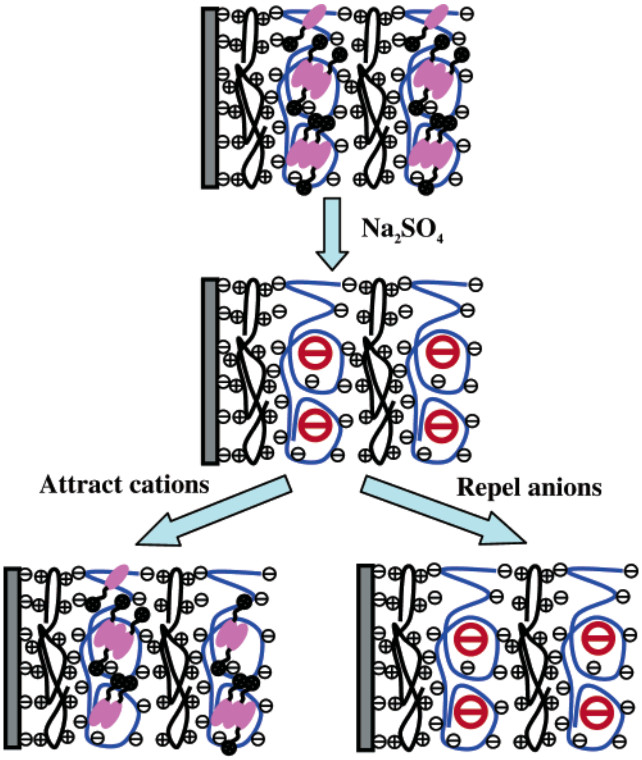

Figure 6. Schematic illustration of the formation of negatively charged ion “traps” in the LbL assemblies. The release of cations from the LbL assemblies renders the LbL film with imprinting sites of negative charge. Then the LbL film fabricated in this way can trap cations while repelling anions in aqueous solution.

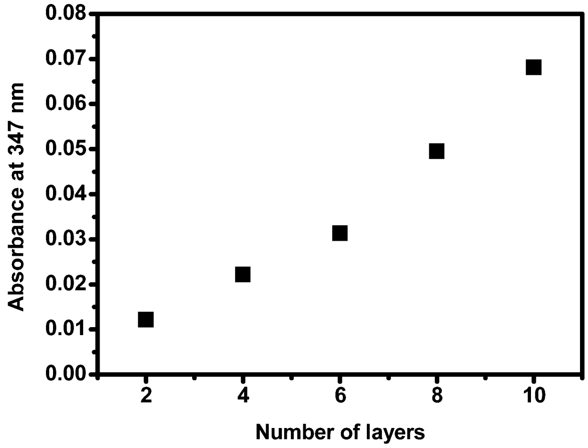

Figure 7. Absorbance at 347 nm for five films of (PDDA/PSS−PMAH)$_n$ (with $n = 2$, 4, 6, 8, and 10, respectively) after immersion in PMAH (1.1 mM) aqueous solution. The films were immersed in Na_2SO_4 aqueous solution in advance.

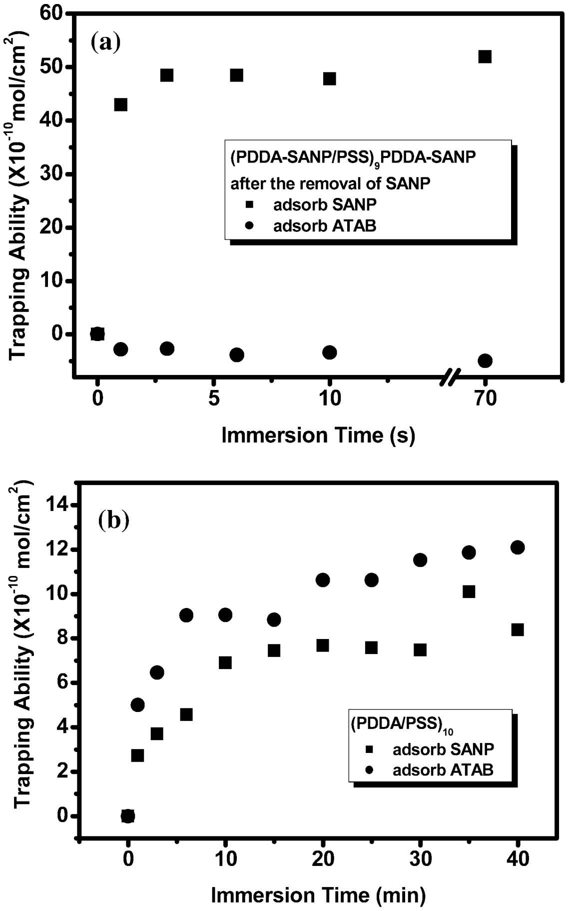

Figure 8. (a) Trapping abilities for SANP (square, 1.3 mM) and ATAB (circle, 1.3 mM) within (PDDA−SANP/PSS)$_9$PDDA−SANP films as functions of immersion time in their aqueous solutions. (b) Trapping abilities for SANP (square, 1.3 mM) and ATAB (circle, 1.3 mM) within (PDDA/PSS)$_{10}$ films as functions of immersion time in their aqueous solutions.

films with positively charged “ion traps” when a template of anionic dye is used. The ion permselectivity in the film can be greatly enhanced with the existence of positively charged “traps”. The positively charged “traps” of the film can trap anions such as SANP, PSAH, P-2S, P-3S, and P-4S, etc., while repelling cations. Taking SANP as a template, for example, we mixed PDDA and SANP in aqueous solution to form the PDDA−SANP complex and then alternately deposited the PDDA−SANP complex and PSS on a quartz plate to fabricate the LbL assemblies; finally, we removed the template from the assemblies. Figure 8a shows the trapping ability of the (PDDA−SANP/PSS)$_9$PDDA−SANP LbL film for cations and anions. From the figure we can see that the trapping ability of SANP of positively charged “ion traps” in the film reaches nearly 5×10^{-9} mol/cm^2 while positively charged moieties, ATAB, cannot enter such a film with positively charged “traps”. However, for normal LbL film of (PDDA/PSS)$_{10}$ as shown in Figure 8b, the trapping abilities of SANP and ATAB are comparable, both of which are much lower than that of SANP in positively charged “ion traps” film while much higher than that of ATAB in positively charged “ion traps” film. The above facts indicate that we can promote the permeability into the film of cations while reducing that of the anions (and vice versa) through constructing of either “cation traps” or “anion traps”. Thus, the ion permselectivity is enhanced by the “ion traps” in the film.

Trapping Big Molecules through “Ion Traps” in the LbL Multilayer Films. Not only small organic molecules could be trapped into such a film but also larger molecules, such as dendrimer G_2-Por, could be trapped, and the trapping ability of G_2-Por increased when we increased the initial concentration of SANP in PDDA−SANP complex, as shown in Figure 9a. This result indicates that more templating molecules leave more ion “traps” in the film when they are expelled. In order to confirm it, we used potassium ferricyanide as an anionic probe to test the ion “traps” in the films which were fabricated with different ratio of SANP in the PDDA−SANP complex. (PDDA−SANP/PSS)$_9$PDDA−SANP multilayer films were fabricated on a gold electrode, with SANP removed from the film by Na_2SO_4 aqueous solution. While keeping the concentration of PDDA at 1 mg/mL, concentrations of SANP varied from 0.333 to 0.167 and 0.033 mg/mL. A higher concentration of SANP in the PDDA−SANP complex solution might result in more

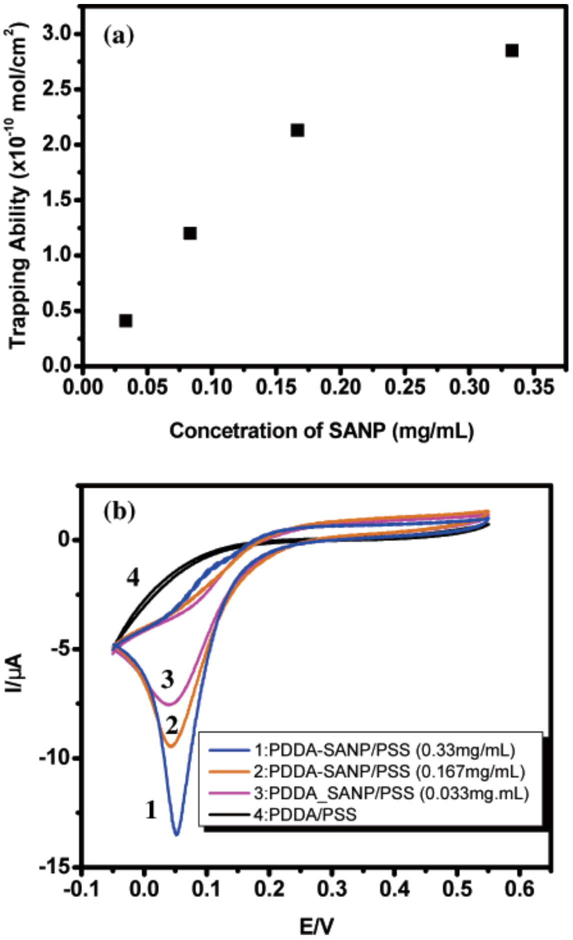

Figure 9. (**a**) Trapping abilities for G2-Por (0.412 mg/mL) within (PDDA−SANP/PSS)$_9$PDDA−SANP films as functions of initial concentrations of SANP in PDDA−SANP complex solution. (**b**) Cyclic voltammograms of gold electrodes modified with [(PDDA−SANP/PSS)$_9$(PDDA−SANP)] (SANP has been removed by Na_2SO_4 aqueous solution) in the presence of potassium ferricyanide. The concentration of SANP in the PDDA−SANP complex solution: 1, 0.33 mg/mL; 2, 0.167 mg/mL; and 3, 0.033 mg/mL. Curve 4 corresponds to the cyclic voltammogram of a normal LbL film.

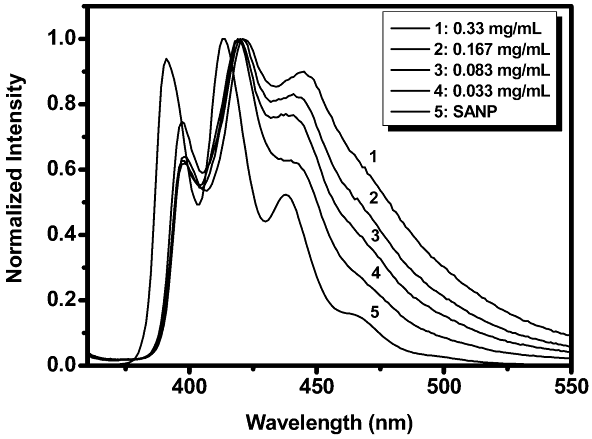

Figure 10. Fluorescence spectra (λ_{ex} = 350 nm) of (PDDA−SANP/PSS)$_5$PDDA−SANP multilayer film fabricated from different initial concentrations of SANP in PDDA−SANP complex solutions: 0.33 mg/mL (line 1), 0.167 mg/mL (line 2), 0.083 mg/mL (line 3), and 0.033 mg/mL (line 4). Line 5 is the fluorescence spectrum of diluted SANP aqueous solution.

positively charged “ion traps” when SANP is released. Thus, the negatively charged potassium ferricyanide probe can be loaded into the multilayer film more effectively. This is confirmed by performing cyclic voltammetry measurements to examine the different loading ability of (PDDA−SANP/PSS)$_9$PDDA−SANP films fabricated under different ratios of SANP, as shown in Figure 9b. At a lower concentration of SANP, potassium ferricyanide probe still can be loaded into the film in spite of the lower cathodic current. But in the condition of normal LbL film, we hardly observed any obvious cathodic current. The above results indicate that the “ion traps” are important for LbL films to trap charged molecules, whatever small or big, and the trapping ability is closely related to the initial concentration of SANP in the PDDA−SANP complex solution.

The fact that big molecules such as dendrimer G2-Por can enter the film demonstrates that even in a lowest concentration of SANP in PDDA−SANP complex solution in our experiment, SANP molecules may still form aggregates in the film. As shown in Figure 10, in the emission spectra, there appear new emission bands at longer wavelength in (PDDA−SANP/PSS)$_5$PDDA−SANP LbL assemblies as compared with monomer emission of SANP aqueous solution,[35] 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. The aggregates affect the trapping behavior both in amount and in size. As the concentration of SANP in PDDA−SANP complex solution increased, the number of aggregates also increased. Thus, the number of “ion traps” increased. This fact is the reason for the increase of the amount of “trapped” dendrimer G$_2$-Por in the film vs the initial concentration of SANP, as shown in Figure 9a. When we increased the initial concentration of SANP to 0.33 mg/mL, not only the amount of SANP aggregates increased, but the size of aggregates also increased. However, the “ion traps”, which were formed after the removal of the aggregates from the film, trapped molecules less than we expected (last point as shown in Figure 9a). This fact is mainly because that the increase of the size of aggregates results in the decrease of the specific surface area of aggregates and thus causes that the increase of the charge density of “ion traps” deviates from the linearity.

Permselectivity of “Ion Traps” in the LbL Multilayer Films. To further demonstrate the ion permselectivity of the “ion traps”, we fabricated a (PDDA−PSAH/PSS)$_{10}$PDDA−PSAH film (positively charged “ion traps”) by electrostatic complexing and then LbL alternating deposition. The templating PSAH was removed from the thin film afterward in order to construct “ion traps”. The film was then immersed into two kinds of mixed aqueous solutions of anions and cations to test the ion permselectivity. As shown in Figure 11a, in the mixed aqueous solution of ATAB and PSAH, only the characteristic absorption of negatively charged PSAH is observed between 250 and 370 nm, while the characteristic absorption of positively charged ATAB at 261 nm does not appear. In the other mixed aqueous solution of SANP and PMAH, similarly, only the characteristic absorption of negatively charged SANP at 261 nm is observed. Therefore, in the mixed aqueous solution, only anions can be “trapped” in the film and cations are repulsed by the positively charged “ion traps” in the film. The same experiment was done on a negatively charged “ion traps” film by using PMAH as the template, which has also shown similar results (not shown here).

Permselective behavior was also apparent when we immersed different ion “traps” films in the same mixed aqueous solution. Figure 11b shows the subtraction spectra of a negatively charged “ion traps” film and a positively charged “ion traps” film in an aqueous solution of SANP/PMAH. When we immersed the

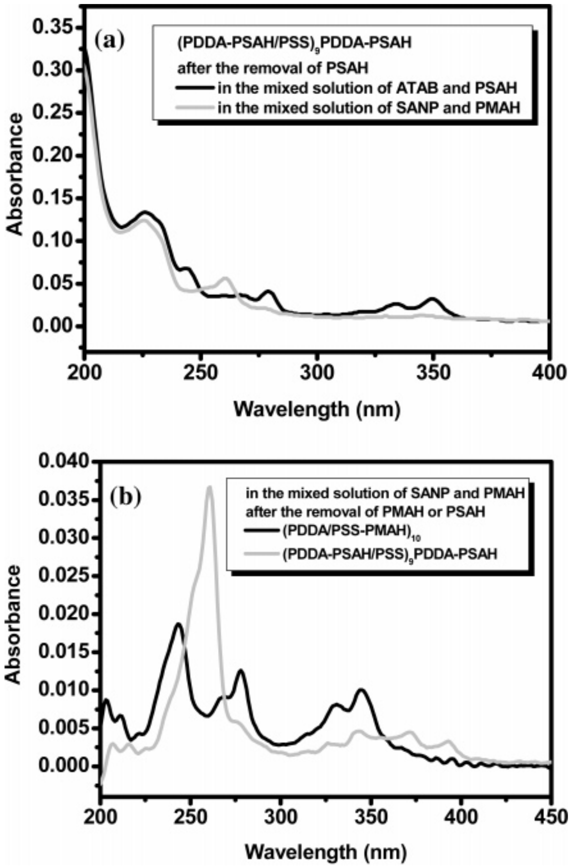

Figure 11. (a) Absorption spectra of (PDDA−PSAH/PSS)$_9$PDDA−PSAH LbL film after immersion in different mixed aqueous solutions, the black spectrum for ATAB and PSAH, and the gray spectrum for SANP and PMAH. (b) The subtraction spectra of (PDDA−PSAH/PSS)$_9$PDDA−PSAH and (PDDA/PSS−PMAH)$_{10}$ LbL films after the immersion in the mixed aqueous solutions of SANP and PMAH. The black line is the subtraction spectrum of the absorption of (PDDA/PSS−PMAH)$_{10}$ LbL film before and after immersion in the mixed aqueous solution of SANP and PMAH, and the gray line is the subtraction spectrum of the absorption of (PDDA−PSAH/PSS)$_9$PDDA−PSAH before and after immersion in the mixed aqueous solution of SANP and PMAH.

(PDDA−PSAH/PSS)$_{10}$PDDA−PSAH LbL film (a positively charged "ion trap" film) in the mixed aqueous solution, only the characteristic peak of SANP at 261 nm along with the finger peaks from 320 to 410 nm can be observed. By contrast, the characteristic peaks of PMAH from 250 to 370 nm do not appear. However, if we immerse the (PDDA/PSS−PMAH)$_{10}$ LbL film in the above solution, we observe only the absorption of PMAH instead of the absorption of SANP. These results indicate that these "ion traps" in the films can recognize ions of one charge from the other.

Small Molecules Suitable for the Construction of "Ion Traps" in the LbL Multilayer Films. Not all small molecules are suitable templates for fabrication of ion "traps" films. We have tried many kinds of molecules which are shown in Figure 1. Usually, polyelectrolyte can form complex with small molecules with countercharge,[36] and this can be comfirmed easily by mixing excessive small molecules with polyelectrolyte: if the aqueous solution becomes turbid, we consider the polyelectrolyte complex forms. As shown in Table 1, for compound **1**, it can be dissolved well in PSS aqueous solution in an appropriate ratio to form the PSS−**1** complex. For compounds **3**, **4**, and **5**, they can also be dissolved well in polyelectrolyte such as PDDA aqueous solution to form PDDA−**3**, **4**, or **5** complexes, but we failed when they were used as molecular templates to construct ion "traps". Compounds **7** and **10** cannot be used as molecular templates, either. From this systematic study, we realize that single-charged molecules bearing condensed aromatic structures are good candidates for the construction of ion "traps" in LbL assemblies because of the following reasons: (1) Single-charged molecules can form complexes with polyelectrolytes and also unbind easily, which is an important factor for successful incorporation into LbL films as we have mentioned above. Molecules with two or more charges can hardly unbind from the polyelectrolytes. For compounds **3**−**5**, once polyelectrolyte complexes are formed, uncomplexed compounds **3**−**5** are little in aqueous solution. The lack of uncomplexed compounds **3**−**5** makes it impossible for the linear increase when fabricating LbL assemblies, as we mentioned before. There is one more possibility that the polyelectrolyte−dye complexes may not be in the single chain form, which prevents the LbL buildup and an effective unbinding of the charged compounds. (2) The small molecules we used in our experiment, e.g., compound **1**, have a hydrophilic group ($-NH_3^+$) and a hydrophobic group (pyrene). When forming a PSS−**1** complex in aqueous solution, the hydrophobic groups might get together due to hydrophobic interaction. Furthermore, the pyrene groups can aggregate in the LbL assemblies to some extent due to the strong $\pi-\pi$ stacking interaction.[33] Thus, once removed in the aqueous solution of electrolyte, compound **1** could leave many charged binding sites within the LbL assemblies, as mentioned before. Interestingly, for compound **7**, we do not observe the formation of ion "traps" in the LbL multilayer film, which may be due mainly to the steric hindrance of quaternized group which may hinder the $\pi-\pi$ stacking between two anthracene moieties.

Table 1. Small Molecules That Can Be Used for Construction of Ion "Traps"

compd no.	PDDA complex	PSS complex	ion "traps"
1	no	yes	yes
2	yes	no	yes
3	yes	no	no
4	yes	no	no
5	yes	no	no
6	yes	no	yes
7	no	yes	no
8	yes	no	yes
9	yes	no	yes
10	no	no	no

Conclusions

We have used single-charged molecules as templates to fabricate "ion trap" in the films that can trap ions of one sign of charge while repelling the opposite. The film shows enhanced ion permselectivity as well as increased permeability compared with a normal LbL film. It is anticipated that this line of research may open a new direction of LbL surface molecularly imprinting if it endows the film with ability not only permselectivity but also other selective properties.

Acknowledgment. We thank the National Natural Science Foundation of China (20334010, 20473045, 50573042, 20574040) and National Basic Research Program (2005CB724400, 2007CB808000) for financial support. The authors thank Prof. Adi Eisenberg, McGill University, for helpful discussions as well as for polishing the English and thank Mr. Jia Niu for his kind help.

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MA061406K