Self-Standing Polyelectrolyte Multilayer Films Based on Light-Triggered Disassembly of a Sacrificial Layer

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ABSTRACT In the present article, we present a new and convenient optical method for the preparation of self-standing polyelectrolyte multilayer films. This method employs the disassembly of a sacrificial layer stratum composed of five poly(acrylate, merocyanine) PMC/poly(diallyldimethylammonium chloride) PDADMAC bilayers, which is triggered by the irradiation with visible light. This leads to the conversion of the zwitterionic PMC to its neutral isomer poly(acrylate, spiropyran) PSP, whereby the attractive ionic interactions between the neighboring bilayers vanish. The disassembly of the sacrificial layers in deionized water was completed within 47 s, when in-situ monitored at the maximum absorbance of PSP ($\lambda = 360$ nm), employing UV/visible spectrometry. Surprisingly, the disassembly duration of the sacrificial layers increased very little with an upper target film composed of 75 PDADMAC/PSS bilayers. The quick release of a thick target film ($d \sim 232$ nm) composed of 100 (PDADMAC)/(PSS) bilayers in a large scale (7×18 mm^2) could be ascribed not only to the vanished electrostatic attractive interaction between the layer pairs but also to increased hydrophobicity of the sacrificial layer element due to the photoisomerization of zwitterionic ionic PMC to neutral PSP. The unique advantages of this method as compared to the conventional approaches are demonstrated with the fast release ($\sim$2 min) of self-standing film combined with a well-defined, thin sacrificial layer ($d \sim 30$ nm). Moreover, harsh release conditions are also avoided, which significantly broadens the choice of materials that can be incorporated into the free-standing film.

KEYWORDS: free-standing film · photoionization · spin-coating electrostatic self-assembly · polyelectrolyte multilayer film · photodetachment

Polyelectrolyte multilayer (PEM) thin films with a well-defined architecture at the nanometer scale have great potential for the multifunctionalization, miniaturization, and integration of devices in a broad range of applications, such as separation membranes, sensors, catalytic films, micromechanical devices, wound dressing, or even artificial organs.[1] Techniques allowing the release of thin PEM films from a solid substrate to a "free-standing" state have opened the door for advanced exploitation of these materials as well as providing new experimental challenges.[2−6] In general, existing techniques for the freely suspended 2D (or quasi-2D) polymer or polymer composite films are based on the use of stimuli-responsive materials as a "sacrificial layer," which is usually disassembled in the pH,[1,3−5] salt concentration,[3] solvent,[6−8] or temperature.[9,10] In most cases (>90%), the release of a thin polymer film from a substrate surface is achieved *via* the disassembly of a pH-responsive sacrificial layer composed of polyelectrolytes bearing amino or carboxylic groups. The sacrificial layer disassembles near neutral pH due to the loss of electrostatic attractive interactions between the oppositely charged layers. These conventional approaches include slow (from hours to days), multistep process and have limited applications. They are particularly limited for the integration of pH-sensitive materials into layer-by-layer (LBL) assembled films.

In the article, we describe a novel and convenient method to prepare ultrathin "free-standing" PEM films. This method is based on the use of a light-responsive sacrificial stratum,[11] which disassembles in water, when exposed to visible light. The principle of the method is depicted with a schematic illustration in Figure 1.

First, a multilayer film composed of oppositely charged polyelectrolyte pairs is deposited onto a solid substrate, which is precoated with the light-responsive sacrificial layer by means of the spin self-assembly method.[12−14] The spin self-assembly method allows fast and efficient layer deposition under shear forces, resulting in well-ordered, multilayered structures with modest nonuniformity in the resulting films. The spin-assembled multilayer film is then irradiated with visible light ($\lambda > 460$ nm) (Figure 1B), whereby a zwitterionic layer component of the sacrificial stratum is photoisomerized to a neutral form, leading to the loss of attractive interactions between the layer pairs. As a result, the target film is released from the substrate surface, with the sacrificial layer disassembling during the rinse in Milli-Q water (pH 6.0−7.5) (Figure 1C). Figure 1D shows a photograph of a vacuum-dried target film composed

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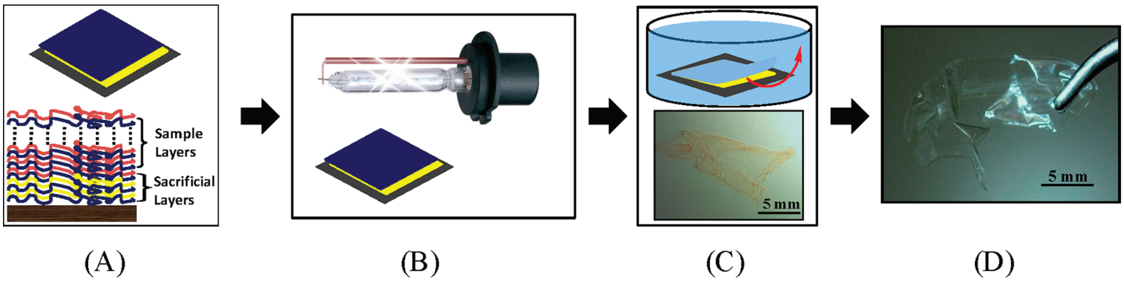
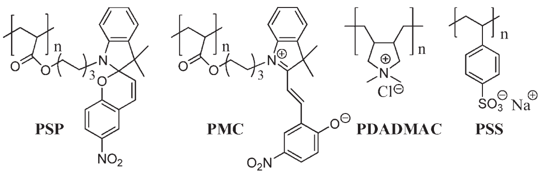


Figure 1. Route and steps for the preparation of a free-standing target (PEM) film. (A) Schematic view with a multilayer architecture of SiO_2/sacrificial layer/target film. (B) Irradiation of the multilayer film with visible light. (C) Rinse in deionized water. (D) The target film dried in vacuum.

of 100 poly(diallyldimethylammonium chloride) (PDADMAC)/poly(styrenesulfonate sodium salt) (PSS) bilayers. The film was obtained using a light-responsive sacrificial stratum composed of five poly(acrylate, merocyanine) PMC/PDADMAC bilayers (chemical structures shown in Scheme 1).



Scheme 1. Chemical structures of polyelectrolytes used for spin assembly.

RESULTS AND DISCUSSION

The photochromic properties of spiropyran have been extensively studied and well-described in the literature.[15−23] Upon irradiation with UV light (λ = 360 nm), the neutral spiropyran (SP) ring opens *via* the bond cleavage between the oxygen of the pyran ring and the spiro-carbon, resulting in the zwitterionic and intensely colored merocyanine (MC) form (Scheme 2). The MC reverts to SP due to the electrocyclization that takes place at the pyran ring upon irradiation with visible light ($\lambda > 460$ nm). The UV/visible spectroscopic method was exploited to monitor the regular LBL deposition of PMC and PDADMAC onto a fused silica, which was performed by means of the spin self-assembly method described previously,[12−14] as shown in Figure 2A. It is necessary to point out that, prior to LBL spin-deposition, poly(acrylate, spiropyran) (PSP) solution needs to be irradiated with UV light (λ = 360 nm, P = 2 mW/cm^2) for 2 min to achieve the conversion to zwitterionic PMC. The regular deposition of PMC/PDADMAC bilayers was confirmed from a plot of the characteristic absorption bands of PMC at 360 and 560 nm *versus* the layer number (Figure 2A, inset). The presence of the zwitterionic PMC layers between the oppositely charged PDADMAC layers was confirmed again in the UV/visible absorbance of the hybrid multilayer film. The mean absorbance per PDADMAC/PMC bilayer at 360 nm was determined to be $(8.38 \pm 1.10) \times 10^{-3}$. It is necessary to mention that it is not possible to spin-deposite PMC on a negatively charged polyelectrolyte PSS, probably due to the strong repulsion produced by the anionic nitrophenolate group of MC. The deposition of the PDADMAC/PMC bilayers on silicon was also examined with optical ellipsometry. The thickness of the PDADMAC/PSP bilayers grew linearly with the number of adsorption cycles (Figure S1 in the Supporting Information). The average thickness of the PDADMAC/PMC bilayers was determined to be 6.92 ± 0.51 nm. On the basis of the thickness of a PDADMAC monolayer (∼0.81 nm), PMC monolayers were estimated to be ∼6.11 nm thick, which is considerably thicker than typical spin-assembled monolayers of common polyelectrolytes, *i.e.*, PSS, poly(allylamine hydrochloride), *etc.*, which have a thickness of ∼1−2 nm.[12−14] This is probably due to the bulky pendant zwitterionic MC groups, which lead to the formation of a thick PMC layer. The back isomerization of zwitterionic PMC to neutral PSP in a multilayer film with a $SiO_2/(PDADMAC/PMC)_5/(PDADMAC/PSS)_{10}$ structure was achieved within 3 min by irradiation with visible light (λ = 460 nm, P = 100 mW/cm^2). This was confirmed by the spectral changes (a → b) in the UV/visible spectra (Figure 2B). Figure S2 (Supporting Information) shows the isomerization kinetics of PSP ↔ PMC in solution and in the spin-assembled multilayer films.

Because of the extensive interpenetration of neighboring polyelectrolyte layers,[24,25] each stratum must be at least several layers thick. Sukhishvili *et al.*[21] reported on systematic release kinetics of hydrogen-bonded multilayer films composed of polyvinylpyrrolidone (PVPON)/poly(methacrylic acid) (PMAA) bilayers on a sacrificial layer composed of temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAM)/PMAA bilayers. The optimal conditions for the target film release (∼25 min) were achieved with a sacrificial stratum composed of 17 PNIPAM/PMAA bilayers (∼114 nm), revealing the significant interpenetration between the hybrid multilayer stacks. For multilayer stacks with an architecture of $SiO_2/(PDADMAC/PMC)_n/(PDADMAC/PSS)_{10}$ with n from 1 to 5, the dependency of the target film release on the number of

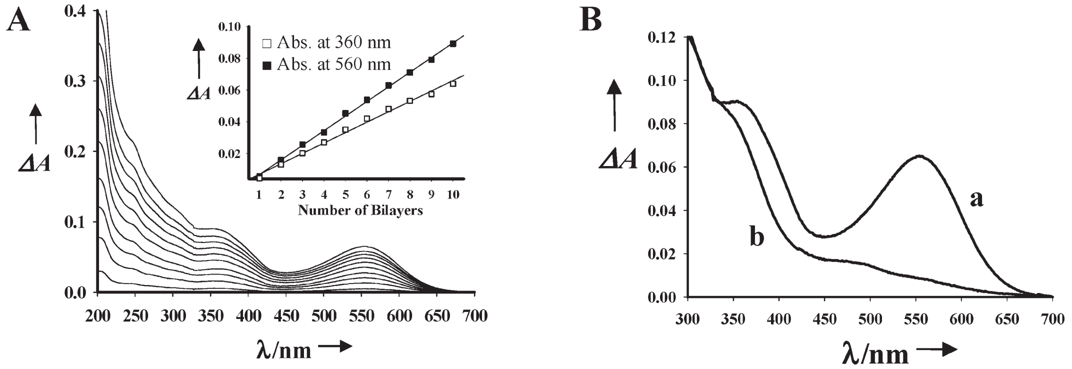
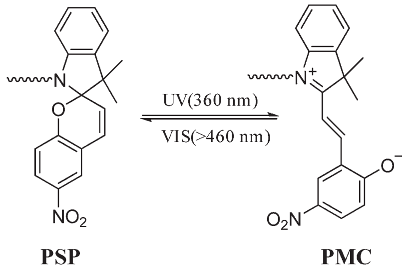


Figure 2. Layer-by-layer deposition of PDADMAC and PMC on a fused silica substrate by the spin self-assembly method. (A) UV−visible spectra of PDADMAC/PMC bilayers, LBL spin-deposited on a fused silica, and a plot of absorbance at 360 and 560 nm of PMC *vs* the bilayer numbers in the inset. (B) UV−visible spectra of the light-responsive sacrificial stratum composed of either 10 PDADMAC/PMC bilayers (a) or 10 PDADMAC/PSP (b). The spectral change (a → b) was completed in 3 min by vis irradiation (λ = 460 nm, P = 100 mW/cm^2). The inverse change was completed in 2 min by UV irradiation (λ = 360 nm, P = 2 mW/cm^2).



Scheme 2. Light-induced reversible switching between PSP and PMC.

TABLE 1. Release Property of Upper Layers Depending on the Thickness of the Light-Responsive Layer[a]

n	thickness of sacrificial layer (nm)	rinse time (min)	released or not
1	6.48 ± 0.25	60	no
2	14.63 ± 0.85	60	no
3	21.42 ± 1.28	60	no
4	29.61 ± 1.01	3	released
5	34.38 ± 1.28	2	released

[a] The original architecture of the hybrid film is $SiO_2/(PDADMAC/PMC)_n/(PDADMAC/PSS)_{10}$.

sacrificial layers was investigated by measuring the thickness change of the multilayer film using optical ellipsometry, before and after a rinse in Milli-Q water. The results are summarized in Table 1. Note that the PEM stacks, prior to the dip into water, were irradiated for 3 min with visible light.

The total thickness of the multilayer films with one or two sacrificial bilayers was hardly changed after 7 days immersion in water, indicating strong interpenetration between the (PDADMAC/PMC) and (PDADMAC/PSS) layers. In the case of a sacrificial stratum composed of three (PDADMAC/PMC) bilayers, the total thickness of the film stacks on silicon slightly decreased after 7 days immersion in water, indicating the partial release of the target film. The target film supported on the four or five sacrificial bilayers was completely released after a 2 min immersion in water, leaving only a PDADMAC monolayer (0.81 ± 0.18 nm) on silicon, whose thickness is in good agreement with independent ellipsometry measurements on a PDADMAC/PSS multilayer. From these results, the interpenetration thickness between the target film and the sacrificial layer is estimated to be approximately 21 nm, which is much lower than that (~114 nm) of the hydrogen-bonding multilayer system reported by Sukhishvili, *et al.*[10] The critical thickness of the sacrificial layer for smooth release of the target film is around 30 nm.

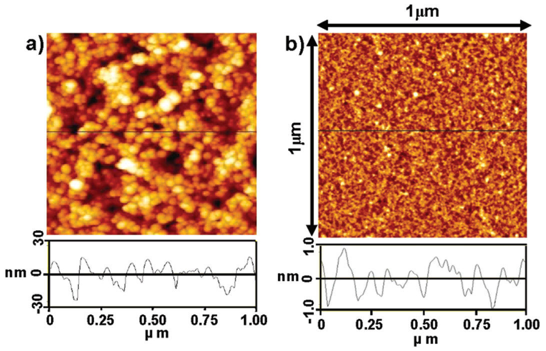
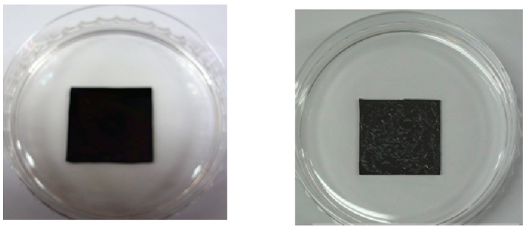
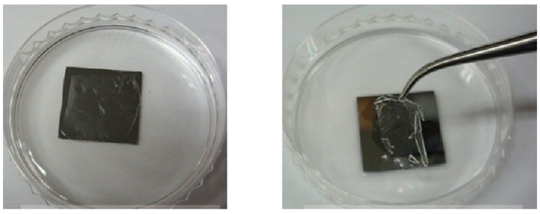


Figure 3. Topographical AFM images of the sacrificial layer composed of (PDADMAC/PMC) bilayers on a silicon substrate (a). The substrate after the detachment of the sacrificial layer through irradiation with visible light and dipping in deionized water for 2 min (b). Note that the AFM images recorded in a tapping mode are given in a top-view presentation with lighter areas indicating higher regions and the darker areas denoting lower regions.

Atomic force microscopy (AFM) was employed to confirm the disassembly of the sacrificial layer with a $SiO_2/(PDADMAC/PMC)_5$ architecture during a rinse in deionized water. As mentioned earlier, the sacrificial layer was irradiated with visible light prior to the dip in water. The surface morphology of the sacrificial stratum (Figure 3) exhibits a granular structure, which is almost identical to the structures observed in typical images of PEM comprising chromophore-containing polyelectrolytes on a silicon substrate, as reported previously.[26−28] The root-mean-square (rms) surface roughness of the sacrificial stratum was determined to be 6.73 nm. The substrate surface became much smoother after exposure to visible light for 3 min and a 2 min rinse of the sacrificial layer in water, as shown in the reduction of the rms roughness from 6.71 to 0.19 nm. This demonstrates the complete disassembly of the sacrificial layers.



(a) 0 min (b) 1.0 min



(c) 1.5 min (d) 2.0 min

Figure 4. Photographs of the target film (composed of 100 PDADMAC/PSS bilayers) releasing from a silicon substrate precoated with five PDADMAC/PMC bilayers in a time sequence during the rinse in deionized water, after 3 min irradiation with visible light: (a) 0, (b) 1.0, (c) 1.5, and (d) 2.0 min.

Figure 4 displays macroscopic pictures of a free-standing hybrid multilayer film with an architecture of $SiO_2/(PDADMAC/PMC)_5/(PDADMAC/PSS)_{100}$ (size = 18 × 7 mm^2). The pictures are taken in a time series over 2 min, showing the release of the film from the substrate surface during the rinse in deionized water (after irradiation with visible light). The releasing spots scattered over the entire film surface were apparent after only 1 min immersion in water (Figure 4b). After 1.5 min, the released areas were larger and broader over the whole film surface (Figure 4c). After 2 min, the multilayer film had completely self-released from the substrate surface (Figure 4d). Note that the hybrid multilayer film is stable under water at least for 7 days without any damage to the surface, unless it is irradiated by visible light.

The free-standing target film composed of 100 PDADMAC/PSS bilayers was carefully transferred from water onto a clean silicon surface using tweezers and dried in vacuum. A topographical AFM image of the intersection between the film and the substrate is shown in Figure 5. The "self-standing" film surface was smooth and flat. Furthermore, the thickness of the thin film was estimated to be ∼240 nm from the cross-sectional analysis of the thin film edge (Figure 5a), which is in good agreement with the ellipsometric thickness (∼232 nm), demonstrating the complete release of the thin film from the substrate without any

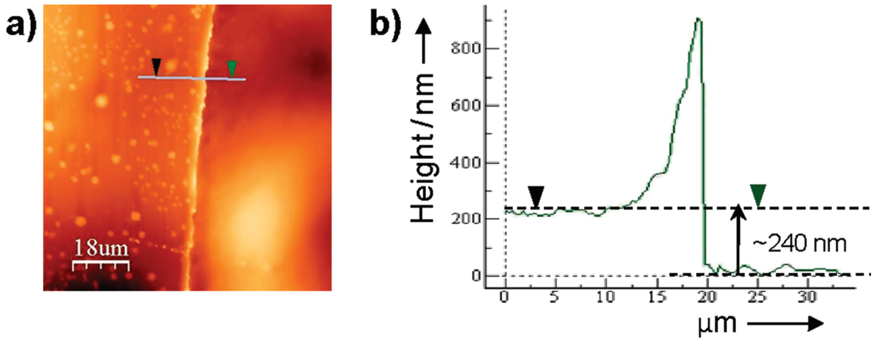


Figure 5. AFM image (a) and surface profile diagram (b) of the intersection area of the self-standing film transferred onto a silicon substrate after thorough washing and vacuum drying.

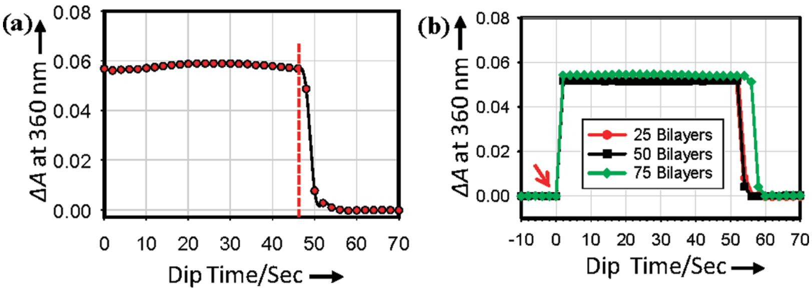


Figure 6. Disassembly kinetics of the sacrificial film composed of five (PDADMAC/PSP) bilayers: (a) without or (b) with a target film ranging the layer number from 25 to 50 and 75 PDADMAC/PSS bilayers (a red arrow indicates the dipping point).

significant damage. Note that the sharp increase in the thickness across the film edge is due to folding of the film.

The disassembly of the sacrificial layers with or without a target film on a fused silica in deionized water was *in situ* monitored at the maximum absorbance of PSP ($\lambda = 360$ nm) using the time drive mode of the UV/visible spectrometer, as shown in Figure 6. The sacrificial stratum composed of five PDADMAC/PSP bilayers was shown to disassemble very rapidly from the substrate after ~47 s rinse in deionized water that was tenderly circulated with a weak N_2 gas stream (Figure 6a). Interestingly, the disassembly duration of the sacrificial layers increased very little with an upper target film on it, of which layer numbers were varied to 25, 50, and 75 PDADMAC/PSS bilayers (Figure 6b). The quick disassembly of the sacrificial layers, even coated with the thick target film, could be ascribed not only to the vanished electrostatic attraction between the layer pairs but also to the increased hydrophobicity of the light-responding layer in the photoisomerization of zwitterionic PMC to neutral PSP. It is necessary to note that the water contact angle of the PMC and PSP surface was determined to 14.6° and 53.2°, respectively.

In conclusion, we present a new and convenient method for the preparation of self-standing PEM films. This method employs a sacrificial layer that, upon the irradiation with visible light, disassembles in water. The disassembly of the sacrificial layers is triggered by the irradiation with visible light, which leads to the conversion of the zwitterionic MC to its neutral isomer SP, whereby the attractive ionic interactions between the neighboring bilayers vanish. The unique advantages of this method as compared to the conventional approaches are the fast release (~2 min) combined with a well-defined, thin sacrificial layer ($d \sim 30$ nm). The fact that this method is based on a light-responsive sacrificial layer means that harsh release conditions are avoided, which significantly broadens the choice of materials that can be incorporated into the free-standing film. The authors strongly believe that the preparation of self-standing PEM films based on optical tools would have great potential to make a significant and wide-ranging impact in application areas, such as future biomedical nanodevices, drug delivery, and tissue engineering.

EXPERIMENTAL SECTION

Materials. Poly(styrenesulfonate, sodium salt) (PSS, M_w = 70 000), poly(diallyldimethylammonium chloride) (PDADMAC, M_w = 100 000, 35 wt % in water), and acrylic acid were purchased from Sigma-Aldrich and used as received. Deionized water (Milli-Q > 18.2 $M\Omega\cdot cm^{-1}$) was employed for the preparation of polyelectrolyte solutions, spin self-assembled multilayer films, and disassembly studies. The synthesis and structural analysis of PSP (M_w = 8 745 g/mol, PDI = 1.07) is described in the Supporting Information. Surprisingly, the PSP is rather uniform despite the synthesis employing the radical polymerization. The uniformity of the PSP could be ascribed to the exclusion of the combination mode of the termination reaction of two propagating polymer radicals due to the strong steric effect of their voluminous side chains. The steric effect on the combination could be evidenced by the formation of PSP with the relatively low molecular weight ($X_n \sim 18$).

Methods. Layer-by-layer deposition of polyelectrolytes was performed on a substrate (silicon wafer or fused silica slide) that was cleaned in piranha solution (H_2SO_4/H_2O_2 = 7:3) and subsequently with a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1), at 80 °C for 1 h, in each solution. The LBL spin-assembly was carried out by a cyclic repetition of the following operations: (1) the slide was spin-coated (3000 rpm, 20 s) with a few drops of an aqueous PDADMAC solution (5 unit mM, pH 6.4); (2) spin-assisted washing was performed three times with deionized water; (3) spin-assisted deposition (3000 rpm, 20 s) with either 2 vol % DMSO/H_2O solution of zwitterionic PMC (4 unit mM, pH 6.4) or an aqueous PSS solution (5 unit mM, pH 6.5) was performed; and (4) spin-assisted washing three times with deionized water was performed. The quantity of material deposited at each step was determined by absorbance on a PerkinElmer UV–vis spectrophotometer (Lambda 40) and optical ellipsometry.

The thickness of the multilayer film deposited on silicon was measured using a real-time spectroscopic ellipsometer (Ellipso Technology, Elli-SE-F) with a Xe arc lamp (350–820 nm) equipped with a rotating polarizer, a liquid cell with optical access at an incidence angle of 60°, an analyzer, and a multichannel detection system. These experimental values were used to calculate the corresponding film thickness, which was obtained from the average of five sampling points.

AFM measurements were performed on a Si wafer in air at room temperature using a Nanoscope IV multimode microscope (Veeco). Using a 125 μm long Si cantilever, a tip radius of below 10 nm, and a resonance frequency of 320 kHz (Nanoworld) with a force constant of 42 N/m, topographic images were recorded in tapping mode (1 μm × 1 μm size) at a scan rate of 0.854 Hz. Data were manipulated using Nanoscope IV software.

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Supporting Information Available: Experimental details. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Ono, S. S.; Decher, G. Preparation of Ultrathin Self-Standing Polyelectrolyte Multilayer Membranes at Physiological Conditions Using pH-Responsive Film Segments as Sacrificial Layers. *Nano Lett.* **2006**, *6*, 592–598.
2. Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B. Multiple Membranes from "True" Polyelectrolyte Multilayers. *J. Am. Chem. Soc.* **2001**, *123*, 5368–5369.
3. Lim, M. H.; Ast, D. G. Free-Standing Thin Films Containing Hexagonally Organized Silver Nanocrystals in a Polymer Matrix. *Adv. Mater.* **2001**, *13*, 718–721.
4. Sukhishvili, A. S.; Granick, S. Layered, Erasable, Ultrathin Polymer Films. *J. Am. Chem. Soc.* **2000**, *122*, 9550–9551.
5. Sukhishvili, A. S.; Granick, S. Layered, Erasable Polymer Multilayers Formed by Hydrogen-Bonded Sequential Self-Assembly. *Macromolecules* **2002**, *35*, 301–310.
6. Mamedov, A. A.; Kotov, N. A. Free-Standing Layer-by-Layer Assembled Films of Magnetite Nanoparticles. *Langmuir* **2000**, *16*, 5530–5533.

7. Fujie, T.; Okamura, Y.; Takeoka, S. Ubiquitous Transference of a Free-Standing Polysaccharide Nanosheet with the Development of a Nano-Adhesive Plaster. *Adv. Mater.* **2007**, *19*, 3549–3553.
8. Strook, A. D.; Kane, R. S.; Weck, M.; Metallo, S. J.; Whitesides, G. M. Synthesis of Free-Standing Quasi-Two-Dimensional Polymers. *Langmuir* **2003**, *19*, 2466–2477.
9. Okano, T.; Yamada, N.; Okuhara, M.; Sakai, H.; Sakurai, Y. Mechanism of Cell Detachment from Temperature-Modulated, Hydrophilic-Hydrophobic Polymer Surfaces. *Biomaterials* **1995**, *16*, 297–303.
10. Zhuk, A.; Pavlukhina, S.; Sukhisvhili, S. A. Hydrogen-Bonded Layer-by-Layer Temperature-Triggered Release Films. *Langmuir* **2009**, *25*, 14025–12029.
11. A stratum is defined as a sequence of multiple “layer pairs” of two complementary-charged polyelectrolytes, such as PSS and PDADMAC.
12. Cho, J.; Char, K.; Hong, J.-D.; Lee, K.-B. Fabrication of Highly Ordered Multilayer Films Using a Spin Self-Assembly Method. *Adv. Mater*. **2001**, *13*, 1076.
13. Lee, S.-S.; Hong, J.-D.; Kim, C. H.; Kim, K.; Koo, J. P.; Lee, K.-B. Layer-by-Layer Deposited Multilayer Assemblies of Ionene-Type Polyelectrolytes Based on the Spin-Coating Method. *Macromolecules* **2001**, *34*, 5358–5360.
14. Lee, S.-S.; Lee, K.-B.; Hong, J.-D. Evidence for Spin-Coating Electrostatic Self-Assembly of Polyelectrolytes. *Langmuir* **2003**, *19*, 7592–7596.
15. Fischer, E.; Hirshberg, Y. Formation of Colored Forms of Spiropyrans by Low-Temperature-Irradiation. *J. Chem. Soc.* **1952**, 4522–4524.
16. Hirshberg, Y. Reversible Formation and Eradication of Colors by Irradiation at Low Temperatures. A Photochemical Memory Model. *J. Am. Chem. Soc.* **1956**, *78*, 2304–2301.
17. Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyrans and Spirooxazines for Memories and Switches. *Chem. Rev.* **2000**, *100*, 1741–1754.
18. Bertelson, R. C. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R., Eds.; Plenum Press: New York, 1999; pp 11−83.
19. Pimiennta, V.; Lavabre, D.; Levy, G.; Samat, A.; Guglielmetti, R.; Micheau, J. C. Kinetic Analysis of Photochromic Systems under Continuous Irradiation. Application to Spiropyrans. *J. Phys. Chem*. **1996**, *100*, 4485–4490.
20. Such, G. K.; Evans, R. A.; Davis, T. P. Control of Photochromism through Local Environment Effects Using Living Radical Polymerization (ATRP). *Macromolecules* **2004**, *37*, 9664–9666.
21. Giordani, S.; Reymo, F. M. A Switch in a Cage with a Memory. *Org. Lett.* **2003**, *5*, 3559–3562.
22. Inouye, M.; Ueno, M.; Tsuchiya, K.; Nakayama, N.; Konishi, T.; Kitao, T. Alkali-Metal Cation Recognition Induced Isomerization of Spirobenzopyrans and Spironaphthoxazins Possessing a Crown Ring as a Recognition Site: Multifunctional Artificial Receptors. *J. Org. Chem.* **1992**, *57*, 5377–5383.
23. Reymo, F. M.; Giordani, S. P. Supramolecular Chemistry and Self-assembly Special Feature: All-Optical Processing with Molecular Switches. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941–4944.
24. Kellogg, G. J.; Mayes, A. M.; Stockton, W. B.; Ferreira, M.; Rubner, M. F. Neutron Reflectivity Investigations of Self-Assembled Conjugated Polyion Multilayers. *Langmuir* **1996**, *12*, 5109–5113.
25. Schlenoff, J. B.; Dubas, S. T. Mechanism of Polyelectrolyte Multilayer Growth: Charge Overcompensation and Distribution. *Macromolecules* **2001**, *34*, 592–598.
26. Hong, J.-D.; Jung, B.-D.; Kim, C. H.; Kim, K. Effects of Spacer Chain Lengths on Layered Nanostructures Assembled with Main-Chain Azobenzene Ionenes and Polyelectrolytes. *Macromolecules* **2000**, *33*, 7905–7911.
27. Advincula, R.; Park, M.-K.; Baba, A.; Kaneko, F. Photoalignment in Ultrathin Films of a Layer-by-Layer Deposited Water-Soluble Azobenzene Dye. *Langmuir* **2003**, *19*, 654–665.
28. Kumar, S. K.; Hong, J.-D. Synthesis and Photoisomerization Characteristics of a 2,4,4′-Substituted Azobenzene Tethered to the Side Chains of Polymethacrylamide. *Langmuir* **2008**, *24*, 4190–4193.