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Molecular Recognition with Microporous Multilayer Films Prepared by Layer-by-Layer Assembly of Pillar[5]arenes

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Supporting Information

ABSTRACT: Pillar[5]arene-based multilayer films are constructed by layer-by-layer assembly with consecutive adsorption of cationic and anionic pillar[5]arenes. The films have active pores that allow shape-selective uptake of dinitrobenzene isomers: the film adsorbs *para*-dinitrobenzene, but not *ortho*- and *meta*-dinitrobenzene. The ability of the film to adsorb *para*-dinitrobenzene is result of the surface electrostatic potential: *para*-dinitrobenzene adsorbs on films with a positive surface, but not on films with a negative surface. The adsorbed amount of *para*-dinitrobenzene exponentially increases with increasing number of deposited layers.

The growth of thin films with controlled micropores (<2 nm) on substrates is highly desirable for surface reformation, adhesive improvement, and gas and molecular separation.[1] Thin films with two- and three-dimensional mesoporous structures are mainly synthesized using reactive precursor solutions, which have been used to construct of ordered two- and three-dimensional porous structures, such as mesoporous silica,[2] metal−organic frameworks, or porous coordination polymers[3] and covalent organic frameworks.[4] However, precise control of the porosity and thickness of the films and functionalization of pores are challenging topics.

In this study, thin multilayer films with controlled pore sizes at the angstrom level were constructed using layer-by-layer (LbL) assembly of pillar-shaped macrocyclic compounds, pillar[5]arenes, which were first introduced by our group in 2008.[5−8] LbL assembly is generally used to synthesize of polymer-based thin films by consecutive adsorption of oppositely charged polyelectrolytes on a solid substrate[9] because multiple interaction points, which are observed in polymer systems, are necessary to construct thin films by LbL assembly. Application of LbL assembly to molecules with low molecular weight is generally difficult and comparatively rare because of the lack of multiple interaction points.[10] However, in this study, we successfully synthesized multilayer films by LbL assembly of macrocyclic building block pillar[5]arenes. Unique pillar-shaped structure[5] and the presence of functional groups at both rims of pillar[5]arenes[6e,f] enable formation of multilayer thin films by LbL assembly. Furthermore, LbL assembly allows control of the thickness of the building blocks in the vertical direction of the films. Thus, the thickness of the pillar[5]arene layers with controlled micropores can be tuned by the number of deposited layers. The pillar[5]arene-based multilayer films have intrinsic pores from the pillar[5]arene cavities and can thus show their original guest-shape selective molecular recognition. Furthermore, the ability of the films to adsorb guest molecules depends on the surface electrostatic potential and is amplified as the number of deposited layers increases.

Pillar[5]arene multilayers were constructed by LbL assembly with consecutive adsorption of cationic (Figure 1a, **P+**) and anionic (Figure 1a, **P−**) pillar[5]arenes[7,8] on quartz substrates. To generate anionic silanol moieties on the surface, the substrates were sonicated in concentrated nitric acid for 30 min, washed with methanol three times, and dried for 12 h at 100 °C. First, the substrate was immersed in an aqueous solution of **P+** for 2 h to introduce **P+** molecules onto the anionic

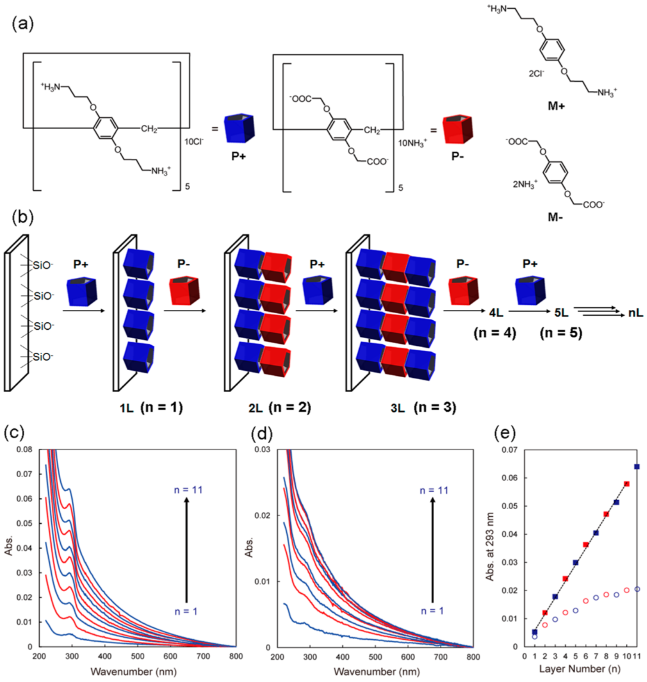

Figure 1. (a) Chemical structures of cationic (**P+**) and anionic (**P−**) pillar[5]arenes and cationic (**M+**) and anionic unit (**M−**) models. (b) LbL assembly by consecutive adsorption of **P+** and **P−**. UV−vis absorption spectra of LbL-assembled multilayer films using (c) ionic pillar[5]arenes (**P+** and **P−**) and (d) ionic unit models (**M+** and **M−**) with layer number n = 1−11 on a quartz substrate. (e) Plots of the absorbance at 293 nm as a function of the layer number using ionic pillar[5]arenes (solid squares) and ionic unit models (open circles).

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substrate surface, washed with a large amount of water to remove excessive unmodified **P+** molecules, and dried for 2 h at 25 °C under reduced pressure to obtain the cationic monolayer (Figure 1b, **1L**). Then, **1L** was immersed in an aqueous solution of **P−** for 2 h to introduce **P−** molecules onto **1L**, washed with a large amount of water, and dried in a vacuum to give the bilayer with an anionic surface (**2L**). Multilayer films (***n*L**, *n* is the number of deposited layers) were obtained by repeating the alternating immersion steps in **P+** and **P−** solutions. The buildup of the multilayers was monitored at each immersion step with a UV−vis spectrometer (Figure 1c). The absorption at 293 nm, which corresponds to the absorption of phenyl moieties of pillar[5]arenes, linearly increases with increasing number of deposited layers (Figure 1e, solid squares), which is evidence for the consecutive adsorption of oppositely charged pillar[5]arenes. In contrast, when we used unit models (Figure 1a, **M+** and **M−**), the absorption did not linearly increase with increasing number of deposited layers (Figure 1d,e, open circles), indicating that multilayer formation using these unit models is difficult. Therefore, successful formation of multilayer films using pillar[5]arenes is because of the unique pillar-shaped structures and the presence of functional groups at both rims of pillar[5]arenes.

The surface morphology of the pillar[5]arene multilayer films was investigated by atomic force microscopy (AFM) measurements. The cationic and anionic surfaces have a very smooth morphology (Figure S2), with RMS values for the 2 × 2 μm^2 area of only 0.90 and 1.25 nm, respectively.

The ability of pillar[5]arene multilayer to adsorb guest molecules was investigated by UV−vis measurements. Pillar[5]arenes have an electron-rich cavity and can thus capture electron-deficient guests.[5,6] In this work, the dinitrobenzene isomers, *ortho*- (*o*-**DNB**), *meta*- (*m*-**DNB**) and *para*-dinitrobenzene (*p*-**DNB**, Figure 2d) were used as guest molecules because these dinitrobenzenes are electron-deficient molecules.[11] The **5L** multilayer film with a cationic surface was immersed in *o*-, *m*-, or *p*-**DNB** (40 mM) in chloroform for 48 h and then washed with a large amount of chloroform to remove the **DNB** on the surface of the film. The film was dried in a vacuum before UV−vis measurement. When *p*-**DNB** was used as a guest, the intensity of the absorption at 293 nm increased (Figure 2a, black solid line). The adsorption band is assigned to *p*-**DNB**. Therefore, the result indicates inclusion of *p*-**DNB** in **5L**. In contrast, an increase in absorption was not observed for *o*-**DNB** and *m*-**DNB** (Figure S8), indicating no complexation with *o*-**DNB** and *m*-**DNB**. The cavity size of pillar[5]arene is ca. 5 Å, which is larger than the size of *p*-**DNB** (ca. 4.3 Å), but smaller than *o*-**DNB** (ca. 5.9 Å) and *m*-**DNB** (ca. 5.9 Å). Therefore, micropores from the pillar[5]arene cavities in **5L** can take up *p*-**DNB**, but not *o*-**DNB** and *m*-**DNB**. Thus, **5L** can selectively adsorb *p*-**DNB** in a solution containing the three dinitrobenzene isomers (Figure 2d). As a reference experiment, we also investigated the ability of a multilayer consisting of monomer units (**M+** and **M−**) to adsorb *p*-**DNB**. In a multilayer film prepared by alternate deposition of five layers of **M+** and **M−**, the absorption intensity from *p*-**DNB** did not increase after immersing the film in *p*-**DNB** (Figure 2, dash lines), indicating no complexation and that cavities of pillar[5]arenes in **5L** act as adsorption sites for *p*-**DNB**.

The effect of the charge on the multilayer surface was also investigated. The **5L** multilayer film with a cationic surface can adsorb *p*-**DNB** (Figure 2a). In contrast, when the **6L** multilayer film with an anionic surface was used, the absorption hardly changed after immersing in *p*-**DNB** (Figure S9), indicating no complexation. This would be because of electrostatic repulsion between the anionic surface of **6L** and *p*-**DNB**. Electrostatic effects play an important role in molecular recognition. Figure 2d shows the calculated electrostatic potential profiles of *p*-**DNB**. The electrostatic potential of nitro groups at the *para*-position is significantly negative because the nitro moiety is an electron-withdrawing group. The **6L** multilayer film has an anionic surface. Thus, electrostatic repulsion between the anionic surface of **6L** and *p*-**DNB** would inhibit formation of the complex. In contrast, attractive electrostatic interactions between the cationic surface of **5L** and *p*-**DNB** would promote complexation.

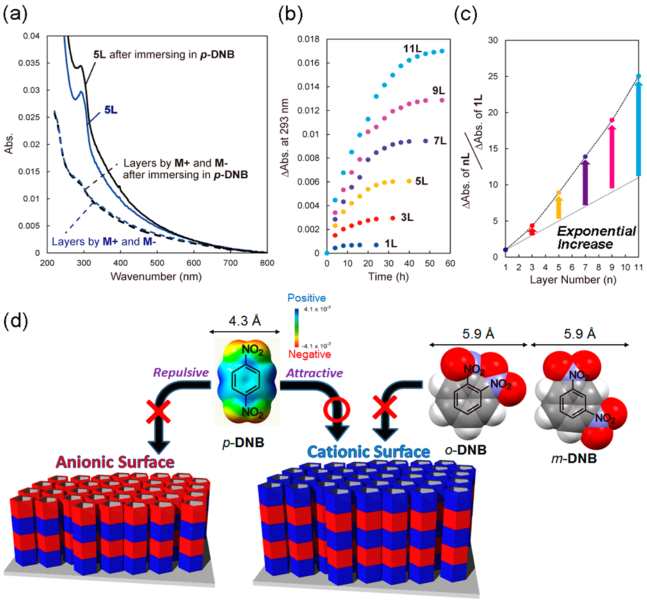

Figure 2. (a) UV−vis absorption spectra of LbL-assembled five-layer films by repeating the alternating immersion steps in **P+** and **P−** (solid blue line) and **M+** and **M−** solutions (dash blue line) and after immersing in *p*-**DNB** (solid lines). (b) Absorbance at 293 nm versus immersion time for the multilayer films. (c) Ratio of ***n*L** to **1L** at the equilibrium state versus layer number. (d) Size-selective and surface potential-dependent molecular recognition of multilayer films.

The effect of the number of deposited cationic layers on the host−guest property was investigated. Inclusion of *p*-**DNB** was monitored by the increase of the absorption band at 293 nm from *p*-**DNB** (Figure 2b). As the number of deposited layers increased, the time to reach an equilibrium state increased: it took 20 h for **5L**, but 40 h for **11L**. However, at the equilibrium state, the maximum adsorbed amount of *p*-**DNB** molecules exponentially increased as the number of deposited layers increased. The absorbed amounts of *p*-**DNB** in **5L** and **11L** were ca. 9 and 25 times larger than that in **1L** (Figure 2c), respectively. This indicates that *p*-**DNB** molecules were included in not only the top surface layer but also in the pillar[5]arene cavities of lower layers. The exponential increase of the absorbed amount of *p*-**DNB** would indicate formation of continuous micropores by intermolecular connecting pillar[5]-arene molecules. *p*-**DNB** molecules would be also included into the space between pillar[5]arene molecules.

In conclusion, we successfully synthesized thin films with controlled micropores by LbL assembly of simple macrocyclic hosts, pillar[5]arenes. The films showed the original guest-shape selectivity and the ability of the films to adsorb guest

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molecules depended on the surface electrostatic potential. Thus, host−guest ability of pillar[5]arenes in solution state can translate into the film state. Furthermore, host−guest property of pillar[5]arene can be enhanced by increasing the number of deposited layers. LbL assembly has been used to create thin films with new structures and additional functions, including reaction media for stereoregular organic polymer synthesis,[9b] tunable plasmonic properties,[9c] inkjet printing,[9d] gas sensing,[9e] and controlled release of drugs.[9f] However, to the best of our knowledge, this is the first example of the creation of thin films with micropores using LbL assembly. The thin films have controlled pores at the angstrom level from the cavity size of pillar[5]arene. The pore volume can be controlled by the number of deposited layers, which cannot be accomplished in thin films with porous structure. Therefore, the present study provides a new powerful method to construct controlled microporous thin films, which have potential applications in molecular separation and storage.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07415.

> Experimental section, ^{1}H NMR, UV−vis spectra, Job plot, AFM images and ^{1}H NMR titrations (PDF)

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Notes

The authors declare no competing financial interest.

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(11) Selective inclusion of *p*-**DNB** by pillar[5]arene among dinitrobenzene isomers was also observed in solution state (Figure S5). The stoichiometry of the complex was 1:1, and the association constant was found to be $K = (2.2 \pm 0.5) \times 10^2$ M^{-1} (Figures S6 and S7).