

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/282872101>

# Pillar[6]arene Containing Multilayer Films: Reversible Uptake and Release of Guest Molecules with Methyl Viologen Moieties

ARTICLE in ACS APPLIED MATERIALS & INTERFACES · OCTOBER 2015

Impact Factor: 6.72 · DOI: 10.1021/acsami.5b08854

---

READS

21

7 AUTHORS, INCLUDING:



Monika Schönhoff

University of Münster

107 PUBLICATIONS 2,589 CITATIONS

SEE PROFILE



Qing-Zheng Yang

Beijing Normal University

60 PUBLICATIONS 1,578 CITATIONS

SEE PROFILE

# Pillar[6]arene Containing Multilayer Films: Reversible Uptake and Release of Guest Molecules with Methyl Viologen Moieties

Bin Yuan,<sup>†</sup> Jiang-Fei Xu,<sup>†</sup> Cai-Li Sun,<sup>‡</sup> Henning Nicolas,<sup>§</sup> Monika Schönhoff,<sup>§</sup> Qing-Zheng Yang,<sup>‡</sup> and Xi Zhang<sup>\*,†</sup>

<sup>†</sup>Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

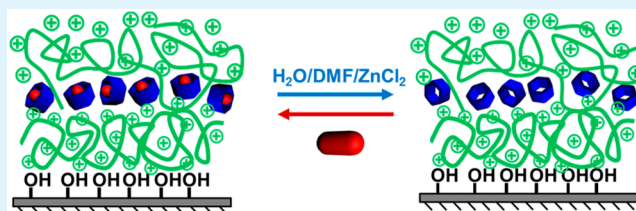
<sup>‡</sup>Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>§</sup>Institute of Physical Chemistry, University of Muenster, Correnstraße 28/30, 48149 Münster, Germany

## S Supporting Information

**ABSTRACT:** Pillar[6]arene-containing multilayer films have been fabricated by alternating deposition of a stoichiometric complex consisting of both pillar[6]arene and methyl viologen with a photoreactive polyelectrolyte, diazoresin (DAR). After photoinduced cross-linking of the multilayer films, the guest molecule, methyl viologen, can be removed. Then, multilayer films with artificial binding sites are fabricated. The films show good properties for molecular uptake and release as well as selectivity for molecules with methyl viologen moieties. It is anticipated that this kind of multilayer films have future applications in the fields of enrichment of molecular dyes and purification of methyl viologen-polluted water.

**KEYWORDS:** layer-by-layer assembly, molecular recognition, pillar[6]arene, methyl viologen, guest uptake and release



## INTRODUCTION

The layer-by-layer (LbL) assembly has been widely used in the area of constructing multilayer films with well-defined compositions and designed functions.<sup>1–5</sup> Rapid progress has been made since it was rediscovered by Decher and co-workers.<sup>6</sup> Different driving forces, such as electrostatic interactions, hydrogen bonds, host–guest interactions, and charge-transfer interactions have been employed to construct LbL films.<sup>7–12</sup> Moreover, to incorporate water-insoluble building blocks or small nonionic molecules into multilayer films, which cannot be realized by conventional LbL assembly, a number of unconventional LbL methods have been developed, including the preassembly of a supramolecular complex in solution that serves as building block for the subsequent LbL deposition at solid–liquid interfaces.<sup>13–17</sup> In this way, a wide range of building blocks could be incorporated into the multilayer thin films, which endows the multilayer films with new structures and functions.

By combining the unconventional LbL assembly with molecular imprinting techniques, surface-imprinted LbL films can be fabricated by introducing template molecules into the multilayer films.<sup>18–22</sup> In general, surface-imprinted LbL films can be built up by the following three steps: first, preassembly of template molecules with a specially designed polymer yield complexes on the basis of covalent bonds or noncovalent interactions. Then, the LbL assembly between the obtained complex and another polyelectrolyte follows. In between the LbL assembly and the removal of the template molecule, chemical or photo-cross-linking is usually conducted to imprint the shape

of the template molecule into the film and to fix the position of the interacting groups. Finally, by removing the template molecules, multilayer films with artificial binding sites for the template are achieved. This method of surface imprinting is considered to be more efficient than the traditional molecular imprinting procedure because imprinted sites at the surface are more easily accessible than sites buried inside a bulk material. However, the size and shape of the imprinted sites in LbL films may change during the loading or release process of the template molecule on account of the flexibility of the polymer matrix.<sup>23</sup> To overcome this problem, in our recent work, a rigid macrocycle, Cucurbit[8]uril (abbreviated as CB[8]), was incorporated into multilayer films as artificial binding site, whose binding sites could be well retained after many loading and release cycles.<sup>23,24</sup> Therefore, rigid macrocycles are an excellent alternative in comparison to the traditionally imprinted binding sites in nanomaterials.

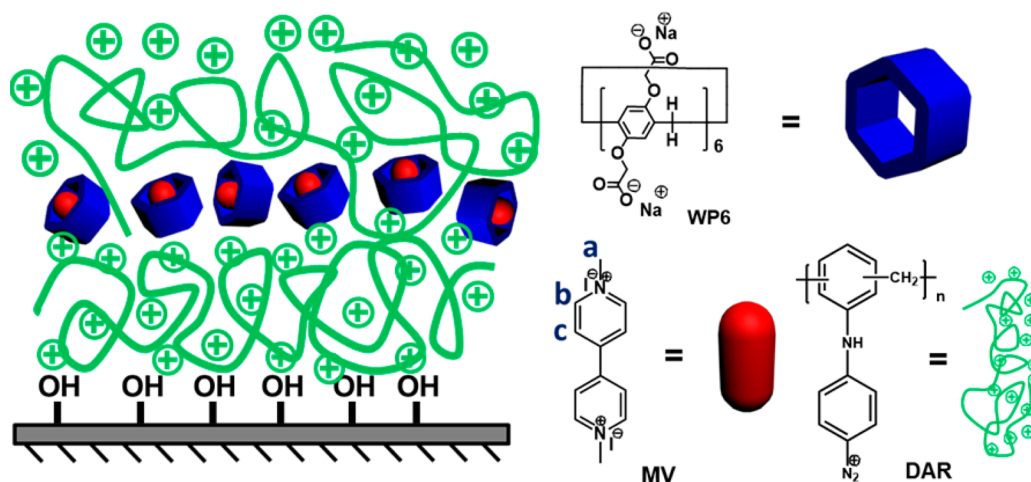
Herein, we attempt to advance the range of host systems in multilayers by assembling pillar[6]arene (abbreviated as WP6) as a novel host into multilayer films, as shown in Scheme 1. The family of pillar[*n*]arenes, named from its shape, represent symmetric macrocycles comprising *n* benzene rings methylene-bridged at the *para*-positions.<sup>25</sup> Once discovered by Ogoshi and

**Special Issue:** Applied Materials and Interfaces in China

**Received:** September 18, 2015

**Accepted:** October 7, 2015

Scheme 1. Schematic Representation of (DAR/WP6-MV)<sub>x</sub>DAR Multilayer Films and the Structures of the Building Blocks for the Layer-by-Layer Assembly



Nakamoto, pillar[*n*]arenes have attracted a lot of attention because of their easy functionalization and their excellent selective binding abilities. A lot of efforts have been made to endow the application of pillar[*n*]arenes in the fields of stimuli-responsive materials, drug delivery systems, and artificial molecular channels.<sup>26–32</sup> In the present paper, pillar[6]arene was first complexed to methyl viologen to form a host–guest complex,<sup>33</sup> then such host–guest complex was employed as anionic building block for the LbL assembly, alternatingly with the cationic photoreactive polyelectrolyte DAR. After UV irradiation, pillar[6]arene was successfully immobilized in multilayer films. By removing methyl viologen, multilayer films with artificial binding sites for molecules with methyl viologen moieties could be obtained. A further novelty of our present approach is the fact the monomeric host containers are assembled as opposed to polymer-bound hosts employed in the previous approach,<sup>23,24</sup> such that a larger surface coverage of the binding sites can be achieved. It is highly anticipated that many other macrocycles may also be assembled into multilayer films in a similar way, which enrich the development of host-containing LbL films.

## EXPERIMENTAL SECTION

**Materials.** 3-Mercaptopropionic acid and 9,10-bis(chloromethyl)-anthracene were purchased from TCI. Electrode polishing materials and gold electrodes were purchased from Shanghai Chenhua instrument co., Ltd. 4,4-Bipyridine was purchased from Alfa Aesar. Methyl viologen was obtained from J&K Chemical Technology. Quartz slides were purchased from Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. The synthesis of WP6 is described in the [Supporting Information, Section 1](#).

**Synthesis of DMVAN.** 9,10-Bis(chloromethyl)anthracene (550 mg) and 4,4-Bipyridine (3.0 g) were dissolved in dimethylformamide. The solution was stirred at 85 °C for 12 h and then filtered to obtain a light yellow solid. The solid was washed thoroughly with diethyl ether to obtain compound 1. The solid was then dried under vacuum at 40 °C (73% yield). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm) δH 8.87 (4H, d), 8.76 (4H, m), 8.42 (4H, m), 8.33 (4H, d), 7.85 (8H, m), 6.97 (4H, s).

Compound 1 (270 mg) and methyl iodide (600 μL) were dissolved in dimethylformamide. The solution was stirred at 60 °C for 2 h to get a dark yellowish solid. The product was obtained by filtration and washed with diethyl ether. DMVAN was dried under vacuum at 40 °C overnight, yielding 65%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm) δH 9.03 (8H, m), 8.46 (12H, m), 7.81 (4H, m), 7.16 (4H, s), 4.47 (6H, s).

**Instruments.** <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-ECA400 spectrometer. UV–vis spectra were obtained using a

HITACHI U-3010 spectrophotometer. Isothermal Titration Calorimetry (ITC) experiments were carried out using a Microcal VP-ITC apparatus. Cyclic voltammograms were carried out on an Autolab PGSTAT12 in a conventional three-electrode electrochemical cell.

### Study of Host–Guest Interactions between WP6 and MV.

Both <sup>1</sup>H NMR spectra and ITC were employed to investigate the interactions between WP6 and MV. ITC was carried out in phosphate buffer solution (10 mM, pH 7.4) at 298.15 K. WP6 (0.1 mM) was in the sample cell (1.43 mL) and MV (1.0 mM) was in the injection syringe (290 μL).

**Substrate Preparation.** Quartz slides were treated in hot piranha solution (98% H<sub>2</sub>SO<sub>4</sub>:30% H<sub>2</sub>O<sub>2</sub> = 7:3, v/v. **CAUTION:** *piranha solution is extremely corrosive, and appropriate safety precautions should be taken.*) for 2 h and then rinsed carefully with distilled water and dried in an oven overnight. Gold electrodes (2 mm diameter) were employed as the working electrode for the electrochemical measurement. The gold electrodes were first mechanically polished with 1, 0.3 μm α-Al<sub>2</sub>O<sub>3</sub> and 0.05 μm γ-Al<sub>2</sub>O<sub>3</sub> followed by washing with distilled water. Then they were electrochemically scanned in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by potential scanning between −0.20 and 1.65 V at a scanning rate of 0.10 V/s until a reproducible cyclic voltammogram was obtained. The electrodes were then rinsed with distilled water and dried with nitrogen, followed by immersion into an ethanol solution of 3-mercaptopropionic acid (5 mM) overnight to obtain electrodes with a negatively charged surface. The electrodes were subjected to ultrasonic agitation in ethanol for a short time to remove the physical adsorbate and then dried with nitrogen before further characterization.

**Preassembly of WP6 and MV.** The host–guest complex WP6-MV was prepared by dissolving an equivalent amount of WP6 into a 500 μM solution of MV in phosphate buffer (10 mM, pH 7.4).

**Multilayer Formation and Photo-Cross-linking.** The treated quartz slides were first immersed in a solution of DAR (1.0 g•L<sup>−1</sup>, pH 7.4) for 10 min, followed by rinsing them with distilled water and drying with nitrogen. The slides were then immersed in a solution of the WP6-MV complex (500 μM, pH 7.4) for 10 min, followed by the same rinsing and drying procedure. By repeating the process above, multilayer films with five bilayers and an extra DAR were prepared. The photo-cross-linking process was carried out by using a 100 W mercury lamp (10 min), and the distance between the lamp and the slides was about 10 cm. Multilayer formation on gold electrodes was performed in the same way.

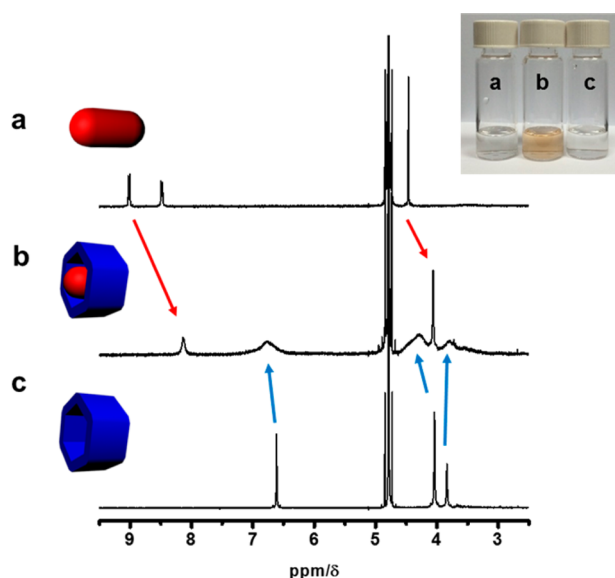
**Electrochemical Measurements.** Electrochemical measurements were performed in a conventional three-electrode electrochemical cell at ambient temperature. The gold electrode modified with (DAR/WP6-MV)<sub>5</sub>DAR multilayer films was used as working electrode, a platinum electrode was used as the auxiliary electrode, and the reference electrode was an Ag/AgCl (3.0 M KCl) electrode. A solution of 2.0 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and 0.1 M KCl was used as the

positive indicator. The electrolyte solutions were purged for 30 min with nitrogen before the measurements.

**Uptake and Release of Guest Molecules with Methyl Viologen Moieties.** After LbL preparation, the release of the respective guest molecule was carried out by ultrasonic agitation of the cross-linked imprinted films for 10 min in a mixed solution of H<sub>2</sub>O/DMF/ZnCl<sub>2</sub> (3:5:2 w/w/w). The uptake of each guest was performed by immersing the imprinted films in a solution of MV or DMVAN, respectively, and then the electrochemical scan was performed in a 2.0 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and 0.1 M KCl solution by potential scanning between −0.40 and 0.15 V at a scanning rate of 0.10 V/s.

## RESULTS AND DISCUSSION

**Preassembly of WP6 and MV.** To investigate the interactions between WP6 and MV, both <sup>1</sup>H NMR and ITC were



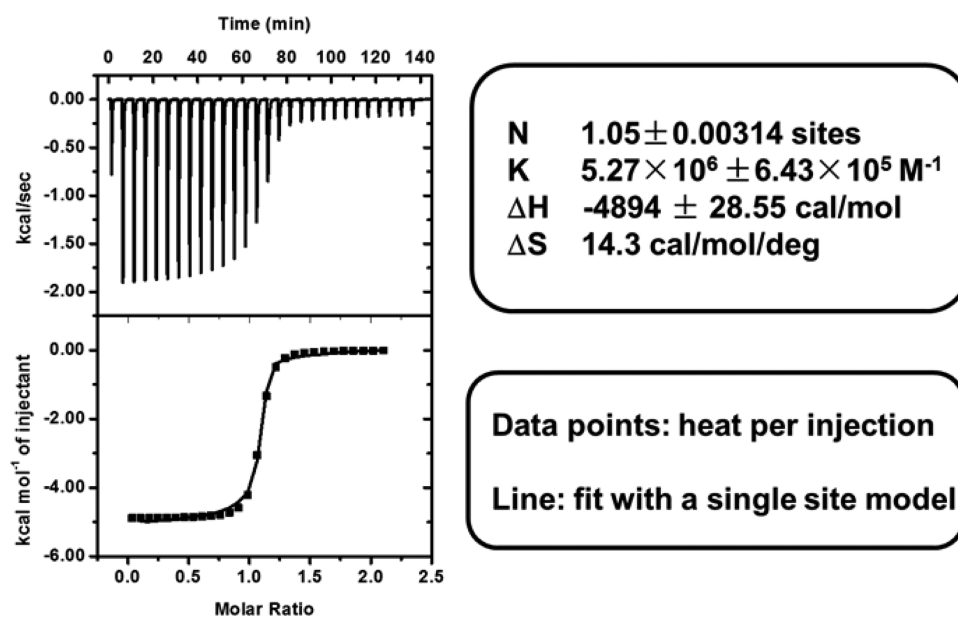
**Figure 1.** <sup>1</sup>H NMR spectra (400 MHz, D<sub>2</sub>O) for (a) MV (1.0 mM); (b) the host–guest complex WP6-MV (1.0 mM); (c) WP6 (1.0 mM). Inset: (a) MV (1.0 mM); (b) the host–guest complex WP6-MV (1.0 mM); (c) WP6 (1.0 mM) in phosphate buffered solution.

employed to elucidate the formation of the host–guest complex. As shown in Figure 1, a transparent red solution formed immediately after equal molar amounts of WP6 and MV were mixed, suggesting the formation of a charge transfer complex of WP6 and MV.

Furthermore, the binding process between WP6 and MV was confirmed by <sup>1</sup>H NMR spectroscopy. As shown in Figure 1, after an equivalent molar ratio of WP6 was added into the solution of MV, the protons attributed to MV shifted significantly upfield. In addition, the resonance peak attributed to protons of MV (proton c as shown in Scheme 1) disappeared after complexation because of a broadening effect. Furthermore, several proton resonances of WP6 also exhibited chemical shift changes due to the formation of host–guest complexes. The binding is further confirmed by a line broadening, which indicates the immobilization of the molecules in the complex. In spectrum b, there is no indication of resonances of free MV or free WP6, such that a complete complex formation in the 1:1 stoichiometry can be concluded.

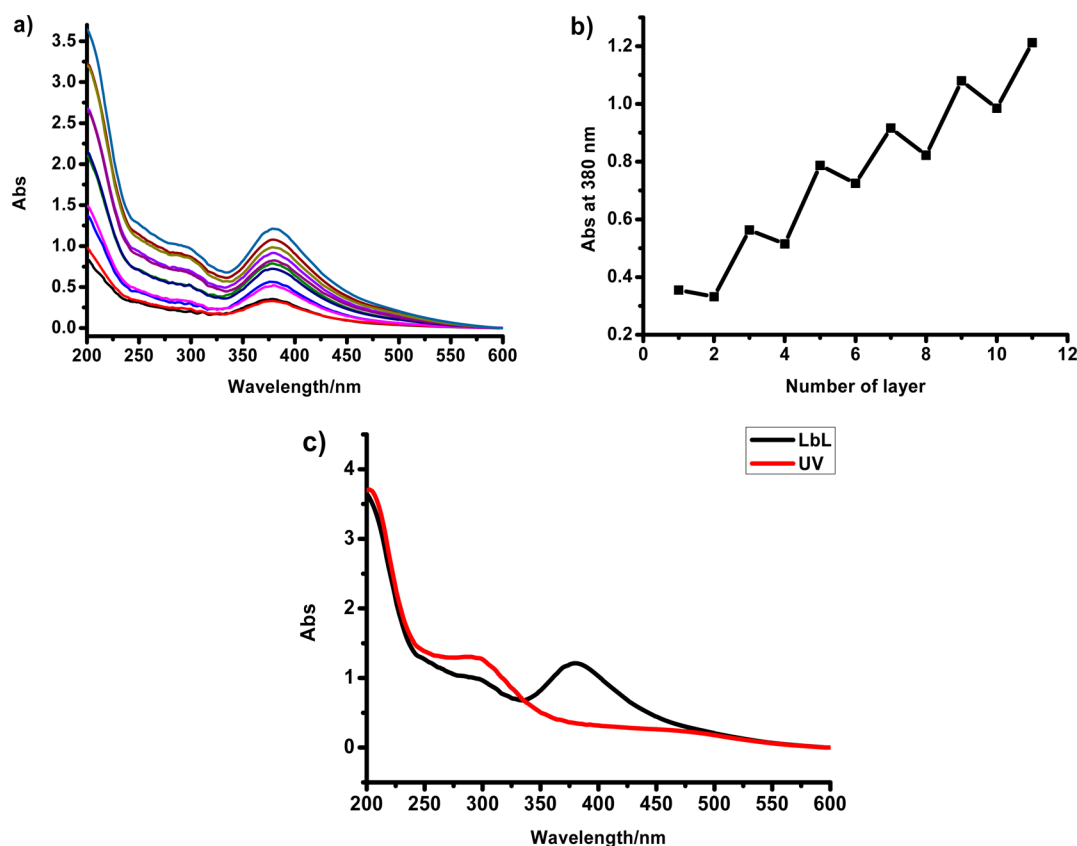
Also in the ITC experiment, the binding stoichiometry between WP6 and MV was found to be 1:1. The fit of the ITC curve (see Figure 2) with a single site binding model resulted in a binding constant of  $5.27 \times 10^5 \text{ M}^{-1}$ . Thus, both ITC and <sup>1</sup>H NMR demonstrate that the host–guest complex between WP6 and MV is formed in the aqueous solution.

**Buildup of Multilayer Films.** The LbL films were fabricated by alternating deposition of the WP6-MV complex and DAR. UV–vis spectroscopy was employed to monitor the assembly process of the multilayer films, as shown in Figure 3a. The absorbance around 380 nm is attributed to the diazonium groups of DAR. For odd layer numbers, there was a significant increase at 380 nm, see Figure 3b. However, a little decrease could be observed for even numbers, because a small amount of the outmost DAR layer exfoliated from the substrate. In general, a continuous growth could be observed by UV–vis spectroscopy (Figure 3b). After deposition, UV irradiation was used for photo cross-linking to stabilize the multilayer films. As shown in Figure 3c, the absorbance of the diazonium groups disappeared after UV irradiation. The disappearance is due to

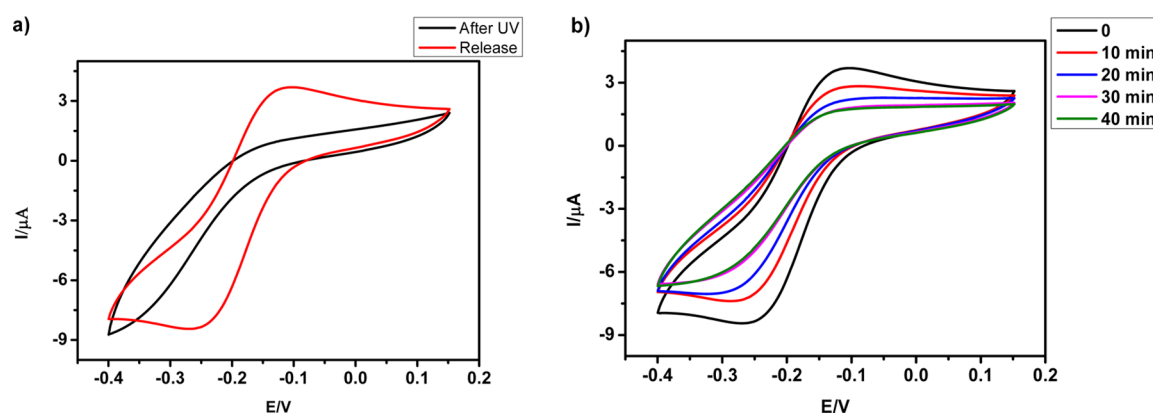


**Figure 2.** ITC data for the titration of MV (1.0 mM) into a solution of WP6 (0.1 mM).





**Figure 3.** (a) UV-vis spectra monitoring the LbL assembly of (DAR/WP6-MV)<sub>5</sub>DAR multilayer films, bottom to top: film of  $n$  layers with  $n = 1$  to 11. (b) Absorbance at 380 nm vs the layer number. (c) UV-vis spectra of the multilayer films before (black) and after (red) UV irradiation.



**Figure 4.** (a) Cyclic voltammograms of gold electrodes modified with (DAR/WP6-MV)<sub>5</sub>DAR multilayer films in the presence of 2.0 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and 0.1 M KCl after UV irradiation (black) and after removal of MV from the film (red). (b) Cyclic voltammograms of the time-dependent loading of MV by immersing (DAR/WP6)<sub>5</sub>DAR multilayer films into a MV (1.0 mM) solution.

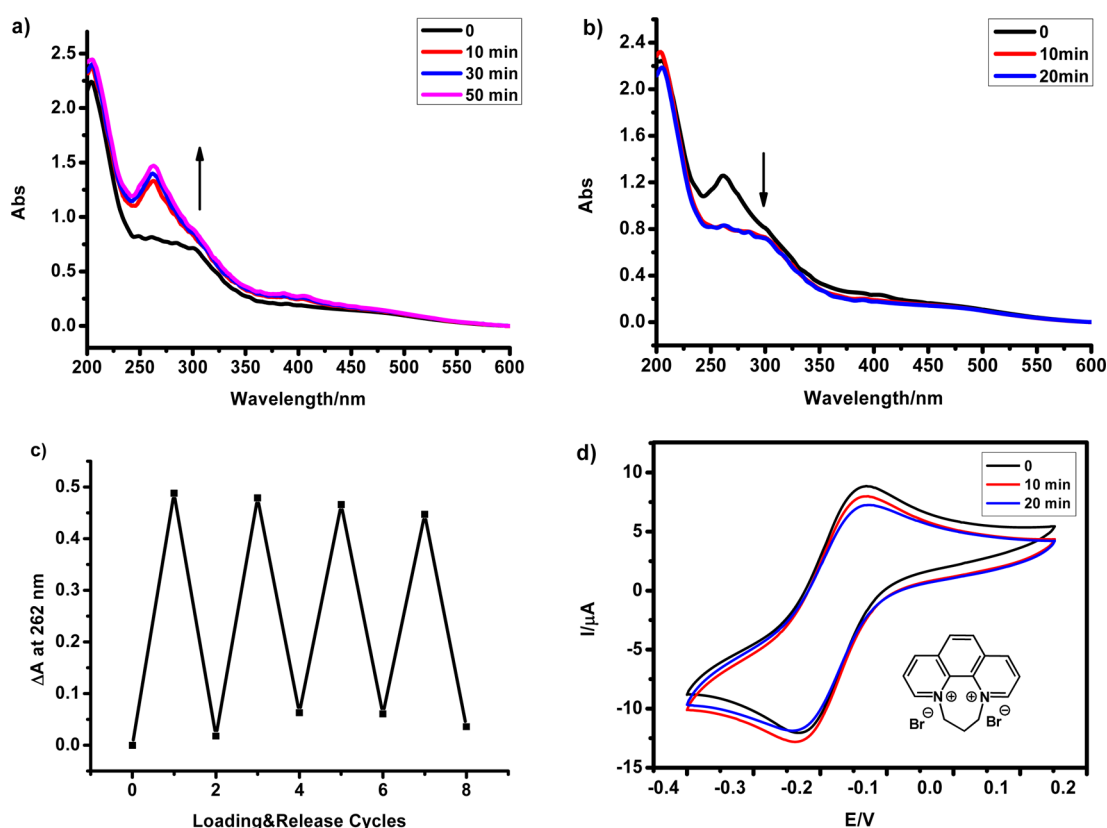
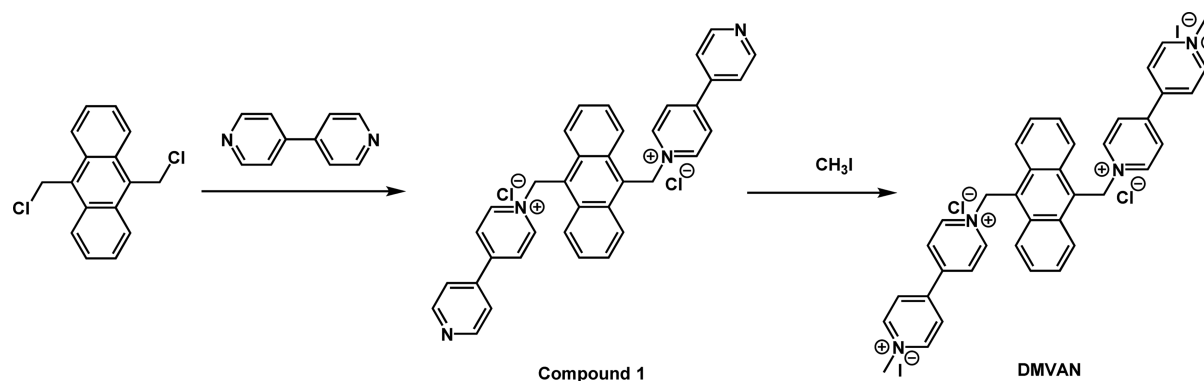
the decomposition of diazonium groups, which tend to form molecular N<sub>2</sub> and ester bonds upon light irradiation. Meanwhile, a new absorption band appeared at about 290 nm, which originated from the contributions of decomposed DAR, WP6 and newly formed ester bonds between both building blocks (Scheme S2). Therefore, the WP6 has been successfully locked in the multilayer thin films by photoinduced chemical cross-linking.

**WP6 as Artificial Binding Site for Reversible Loading and Release.** Cyclic voltammetry was used to study the loading and release of guest molecules. After UV irradiation, no redox response was observed in the CV measurement for the positive probe of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, as shown in Figure 4a (black

curve), indicating that the gold electrode is covered with a compact film, which prevents the penetration of the positive probe to the electrode surface. However, a clear redox signal could be observed after treating the multilayer film with a mixed solvent of H<sub>2</sub>O/DMF/ZnCl<sub>2</sub>, which is an effective solvent for destroying interactions between WP6 and MV,<sup>34</sup> indicating that MV is removed from the LbL films and, consequently, the probe can access the surface of the gold electrode (Figure 4a, red curve). The release process could be finished in 10 min.

After the initial release of MV, we further investigated the reloading process by immersing films into an aqueous solution of such guest (1.0 mM), as shown in Figure 4b. The redox signal gradually disappeared over time because the artificial

Scheme 2. Synthetic Route of DMVAN



**Figure 5.** UV–vis spectra monitoring the time-dependent (a) loading and (b) release of the guest molecule DMVAN; (c) Variation of the UV–vis absorbance at 262 nm during the cyclic loading and release of DMVAN; (d) Cyclic voltammograms of time-dependent loading of R1 by immersing (DAR/WP6)<sub>5</sub>DAR multilayer films into a R1 (1.0 mM) solution.

binding sites were occupied by MV once again and a compact film was rebuilt, impeding the probe to reach the surface of the electrode. The loading process was finished in 30 min, as demonstrated by the vanishing redox signal. In general, the guest molecule MV could be removed from the multilayer films and then be reloaded into the multilayer films.

#### Uptake, Release, and Selectivity of Guest Molecules.

To study the loading kinetics of guest molecules into the WP6-containing multilayer films, a new molecule with two methyl viologen moieties (DMVAN, Scheme 2), which is UV–vis sensitive was employed for the time-dependent loading and release, as shown in Figure 5. After treatment for MV release by the mixed solvent, the quartz slide was immersed into a solution of DMVAN (1.0 mM). The absorption band around 260 nm attributed to the anthracene group of DMVAN increases with

increasing immersion time, therefore indicating that DMVAN is successfully incorporated into the multilayer films. Then, the DMVAN-loaded multilayer films were treated by both the mixed solvent and ultrasonic agitation to perform the release process. The absorption band attributed to the anthracene group totally disappeared within 10 min as observed by UV–vis spectroscopy, indicating that DMVAN can be removed in a fast and complete fashion, see Figure 5b. These loading and releasing processes can be repeated for several cycles (Figure 5c).

The selectivity of the binding sites toward methyl viologen moieties was investigated by CV as well as UV–vis spectroscopy: A phenanthroline derivative bearing a cationic charge but larger structure (R1) was employed as a reference (Figure 5d).<sup>35</sup> When the multilayer films with artificial binding sites were immersed into the solution of R1 (1.0 mM), no significant

changes were observed in both the UV–vis spectrum as well as the cyclic voltammetry curve (Figure Sd and Figure S1). We conclude that R1 cannot be included into the cavity of WP6 due to steric mismatch. In addition, the fact that R1 is not incorporated into the multilayer films confirms that no other interactions than the host–guest interaction are relevant for guest molecule uptake and both MV and DMVAN are therefore exclusively bound by WP6. Thus, WP6-containing multilayer films show good specific and reversible binding and release of methyl viologen bearing derivatives of suitable size, as it was shown for both MV and DMVAN. We conclude that pillar[6]arene host molecules with their rigid structures act as very stable binding sites in a polymer layer environment.

## CONCLUSION

In conclusion, we have successfully fabricated a new kind of functional multilayer thin films by introducing pillar[6]arene as artificial binding sites. Pillar[6]arene host molecules with their rigid structures act as very stable binding sites even in a soft polymer matrix. The as-prepared multilayer films exhibit good loading and release properties toward guest molecules with methyl viologen moieties. Moreover, the uptake and release from the multilayer films works reversibly and is specific for suitable guest molecule geometries. A novelty in contrast to previous approaches with host–guest systems in multilayers is the fact that here the free container was assembled without a precomplexation to a polymeric component, such that larger surface densities can be achieved. It is anticipated that such films could have potential applications in the separation of molecular dyes and purification of methyl viologen-polluted water.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08854.

Experimental details including synthetic route of WP6 and their characterization; photoreaction between DAR and WP6; UV–vis spectroscopy of guest molecules (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: xi@mail.tsinghua.edu.cn.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was financially supported by NSFC-DFG joint grant (TRR61) and NSFC Innovative Group (21421064).

## REFERENCES

- (1) Decher, G.; Schlenoff, J. B. *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*; Wiley–VCH: Weinheim, Germany, 2003.
- (2) Such, G. S.; Johnston, A. P. R.; Caruso, F. Engineered Hydrogen-bonded Polymer Multilayers: From Assembly to Biomedical Applications. *Chem. Soc. Rev.* **2011**, *40*, 19–29.
- (3) Schlenoff, J. B. Retrospective on the Future of Polyelectrolyte Multilayers. *Langmuir* **2009**, *25*, 14007–14010.
- (4) Zhang, X.; Chen, H.; Zhang, H. Layer-by-Layer Assembly: From Conventional to Unconventional Methods. *Chem. Commun.* **2007**, *14*, 1395–1405.
- (5) Li, Y.; Wang, X.; Sun, J. Layer-by-Layer Assembly for Rapid Fabrication of Thick Polymeric Films. *Chem. Soc. Rev.* **2012**, *41*, 5998–6009.
- (6) Decher, G.; Hong, J. D. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: I. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles on Charged Surfaces. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321–327.
- (7) Crespo-Biel, O.; Dordi, B.; Reinhoudt, D. N.; Huskens, J. Supramolecular Layer-by-Layer Assembly: Alternating Adsorptions of Guest- and Host-Functionalized Molecules and Particles Using Multivalent Supramolecular Interactions. *J. Am. Chem. Soc.* **2005**, *127*, 7594–7600.
- (8) Schmitt, J.; Grünwald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Lösche, M. Internal Structure of Layer-by-Layer Adsorbed Polyelectrolyte Films: A Neutron and X-ray Reflectivity Study. *Macromolecules* **1993**, *26*, 7058–7063.
- (9) Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. Preparation of the Layer-by-Layer Deposited Ultrathin Film Based on the Charge-Transfer Interaction. *Langmuir* **1997**, *13*, 1385–1387.
- (10) Stockton, W. B.; Rubner, M. F. Molecular-Level Processing of Conjugated Polymers. 4. Layer-by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions. *Macromolecules* **1997**, *30*, 2717–2725.
- (11) Suzuki, I.; Egawa, Y.; Mizukawa, Y.; Hoshi, T.; Anzai, J. Construction of Positively-Charged Layered Assemblies Assisted by Cyclodextrin Complexation. *Chem. Commun.* **2002**, *2*, 164–165.
- (12) Wang, L.; Wang, Z.; Zhang, X.; Shen, J.; Chi, L.; Fuchs, H. A New Approach for the Fabrication of an Alternating Multilayer Film of Poly(4-Vinylpyridine) and Poly(Acrylic Acid) Based on Hydrogen Bonding. *Macromol. Rapid Commun.* **1997**, *18*, 509–514.
- (13) Artyukhin, A. B.; Bakajin, O.; Stroeve, P.; Noy, A. Layer-by-Layer Electrostatic Self-Assembly of Polyelectrolyte Nanoshells on Individual Carbon Nanotube Templates. *Langmuir* **2004**, *20*, 1442–1448.
- (14) Chen, H.; Zeng, G.; Wang, Z.; Zhang, X.; Peng, M. L.; Wu, L. Z.; Tung, C. H. To Combine Precursor Assembly and Layer-by-Layer Deposition for Incorporation of Single-Charged Species: Nanocontainers with Charge-Selectivity and Nanoreactors. *Chem. Mater.* **2005**, *17*, 6679–6685.
- (15) Fabianowski, W.; Roszko, M.; Brodzińska, W. Optical Sensor with Active Matrix Built from Polyelectrolytes-Smart Molecules Mixture. *Thin Solid Films* **1998**, *327–329*, 743–743.
- (16) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. Efficient Photocurrent Generation in Novel Self-Assembled Multilayers Comprised of [60]Fullerene-Cationic Homooxacalix[3]arene Inclusion Complex and Anionic Porphyrin Polymer. *J. Am. Chem. Soc.* **2001**, *123*, 4855–4856.
- (17) Schütte, M.; Kurth, D. G.; Linford, M. R.; Cölfen, H.; Möhwald, H. Metallosupramolecular Thin Polyelectrolyte Films. *Angew. Chem., Int. Ed.* **1998**, *37*, 2891–2893.
- (18) Chen, H.; Zeng, G.; Wang, Z.; Zhang, X. To Construct “Ion Traps” for Enhancing the Permselectivity and Permeability of Polyelectrolyte Multilayer Films. *Macromolecules* **2007**, *40*, 653–660.
- (19) Niu, J.; Liu, Z.; Fu, L.; Shi, F.; Ma, H.; Ozaki, Y.; Zhang, X. Surface-Imprinted Nanostructured Layer-by-Layer Film for Molecular Recognition of Theophylline Derivatives. *Langmuir* **2008**, *24*, 11988–11994.
- (20) Shi, F.; Liu, Z.; Wu, G.; Zhang, M.; Chen, H.; Wang, Z.; Zhang, X.; Willner, I. Surface Imprinting in Layer-by-Layer Nanostructured Films. *Adv. Funct. Mater.* **2007**, *17*, 1821–1827.
- (21) Zeng, G.; Gao, J.; Chen, S.; Chen, H.; Wang, Z.; Zhang, X. Combining Hydrogen-Bonding Complexation in Solution and Hydrogen-Bonding-Directed Layer-by-Layer Assembly for the Controlled Loading of a Small Organic Molecule into Multilayer Films. *Langmuir* **2007**, *23*, 11631–11636.
- (22) Zhang, J.; Liu, Y.; Wu, G.; Schönhoff, M.; Zhang, X. Bolaform Supramolecular Amphiphiles as a Novel Concept for the Buildup of Surface-Imprinted Films. *Langmuir* **2011**, *27*, 10370–10375.

- (23) Zhang, J.; Liu, Y.; Yuan, B.; Wang, Z.; Schönhoff, M.; Zhang, X. Multilayer Films with Nanocontainers: Redox-Controlled Reversible Encapsulation of Guest Molecules. *Chem. - Eur. J.* **2012**, *18*, 14968–14973.
- (24) Nicolas, H.; Yuan, B.; Zhang, J.; Zhang, X.; Schönhoff, M. Cucurbit[8]uril as Nanocontainer in a Polyelectrolyte Multilayer Film: A Quantitative and Kinetic Study of Guest Uptake. *Langmuir* **2015**, *31*, 10734.
- (25) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T. A.; Nakamoto, Y. para-Bridged Symmetrical Pillar[5]arenes: Their Lewis Acid Catalyzed Synthesis and Host-Guest Property. *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023.
- (26) Cao, D.; Kou, Y.; Liang, J.; Chen, Z.; Wang, L.; Meier, H. A Facile and Efficient Preparation of Pillararenes and a Pillarquinone. *Angew. Chem., Int. Ed.* **2009**, *48*, 9721–9723.
- (27) Hu, X.-B.; Chen, Z.; Tang, G.; Hou, J.-L.; Li, Z.-T. Single-Molecular Artificial Transmembrane Water Channels. *J. Am. Chem. Soc.* **2012**, *134*, 8384–8387.
- (28) Strutt, N. L.; Fairen-Jimenez, D.; Iehl, J.; Lalonde, M. B.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T.; Stoddart, J. F. Incorporation of an A1/A2-Difunctionalized Pillar[5]arene into a Metal-Organic Framework. *J. Am. Chem. Soc.* **2012**, *134*, 17436–17439.
- (29) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F.; Pillararenes, A. New Class of Macrocycles for Supramolecular Chemistry. *Acc. Chem. Res.* **2012**, *45*, 1294–1308.
- (30) Duan, Q.; Cao, Y.; Li, Y.; Hu, X.; Xiao, T.; Lin, C.; Pan, Y.; Wang, L. pH-Responsive Supramolecular Vesicles Based on Water-Soluble Pillar[6]arene and Ferrocene Derivative for Drug Delivery. *J. Am. Chem. Soc.* **2013**, *135*, 10542–10549.
- (31) Yu, G.; Zhou, X.; Zhang, Z.; Han, C.; Mao, Z.; Gao, C.; Huang, F. Pillar[6]arene/Paraquat Molecular Recognition in Water: High Binding Strength, pH-Responsiveness, and Application in Controllable Self-assembly, Controlled Release, and Treatment of Paraquat Poisoning. *J. Am. Chem. Soc.* **2012**, *134*, 19489–19497.
- (32) Xu, J.-F.; Chen, Y.-Z.; Wu, L.-Z.; Tung, C.-H.; Yang, Q.-Z. Dynamic Covalent Bond Based on Reversible Photo [4 + 4] Cycloaddition of Anthracene for Construction of Double-Dynamic Polymers. *Org. Lett.* **2013**, *15*, 6148–6151.
- (33) Ma, Y.; Chi, X.; Yan, X.; Liu, J.; Yao, Y.; Chen, W.; Hou, J.-L.; Huang, F. The per-Hydroxylated Pillar[6]arene: Synthesis, X-ray Crystal Structure and Host-Guest Complexation. *Org. Lett.* **2012**, *14*, 1532–1535.
- (34) Cao, W.-X.; Ye, S.-J.; Cao, S.-G.; Zhao, C. Novel Polyelectrolyte Complexes Based on Diazo-Resins. *Macromol. Rapid Commun.* **1997**, *18*, 983–989.
- (35) Guo, Q.-H.; Zhao, L.; Wang, M.-X. Synthesis and Molecular Recognition of Water-Soluble S<sub>6</sub>-Corona[3]arene[3]pyridazines. *Angew. Chem., Int. Ed.* **2015**, *54*, 8386–8389.