Multilayer films of single-component and charged tetraaminocalix[4]arenes based on hydrogen bonding†

Shuiying Gao,[a] Daqiang Yuan,[a] Jian Lü,[ab] Taohai Li[ab] and Rong Cao*[a]

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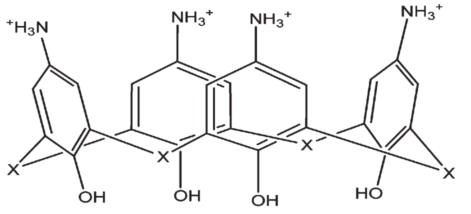
Multilayer films composed of single-component and positively-charged tetraaminocalix[4]arenes are formed through hydrogen bonding.

The molecular self-assembled films are of great interest due to their potential applications in nonlinear optics and molecular electronics.[1–3] Moreover, molecular self-assembly can control the composition, ordering, and structure of thin films on a molecular level. Hydrogen bonding as weak interaction of self-assembly plays an important role in understanding life sciences and organizing multicomponent supramolecular assemblies. Layer-by-layer self-assembly based on the alternate adsorption of polycations and polyanions through electrostatic attraction is simple, powerful and versatile.[4,5] In general, two components are required in the multilayer films *via* LbL assembly due to the alternating adsorption of oppositely charged compounds. Besides electrostatic force, the layer-by-layer self-assembly includes hydrogen bonding,[6] charge-transfer interaction,[7] host–guest interaction,[8] among which hydrogen bonding is one of the most important interactions. The LbL multilayer films constructed by uncharged components *via* hydrogen bonding were first reported in 1997.[6a,6b] For example, polyacrylamide (PAAm)/polyaniline (PAni), poly(ethylene oxide) (PEO)/polyaniline (PAni) and poly(vinyl alcohol) (PVA)/polyaniline (PAni) multilayer films were fabricated through hydrogen bonding.[6b] Compared to electrostatic interaction, hydrogen bonding is weaker. Thus, it is difficult to construct multilayer films through layer-by-layer self-assembly method with low-molecular-weight organic molecules through hydrogen bonding due to their easy desorption. To the best of our knowledge, low-molecular-weight organic molecule multilayer films based on hydrogen bonding have not been reported until now, especially for the same positively-charged molecule.

Herein, we report the fabrication of multilayer films by small molecular components *via* hydrogen bonding. Calix[4]arene derivatives are among the most used macrocyclic frameworks, because they have bowl-shaped molecular cavities composed of four benzene rings.[9] The top and bottom rims of calix[4]arenes can be modified with a variety of functional groups, which make them wide application such as host–guest chemistry,[10] inclusion compounds,[11] and analytical chemistry.[12] In this report, we chose two functional calix[4]arenes, *p*-tetraamino-tetrathiacalix[4]arene (*p*ATC4) and *p*-tetraamino-calix[4]arene (*p*AC4), derived from calix[4]arenes by modifying the upper rims with amino groups.[13] The two calix[4]arenes are unstable in air, therefore, their amino groups are protonized with hydrochloric acid, and the positively charged calix[4]arenes, $[H_4pATC4]^{4+}$ (**1**) and $[H_4pAC4]^{4+}$ (**2**) (Fig. 1), are used for fabrication of multilayer films. The protonized amino groups of the two calix[4]arenes are used as hydrogen bonding donor, whereas the hydroxyl groups are used as hydrogen bonding acceptor. Hydrogen bonding donor and acceptor groups are introduced at the upper and lower rims of calix[4]arenes, which have profoundly affected their self-assembly properties.

The multilayer films were prepared *via* layer-by-layer self-assembly method (See ESI†). The schematic assembly process is showed in Scheme 1. Between each adsorption step, the films were washed with water and allowed to dry in a nitrogen stream. When the substrate pre-coated with a positively-charged PEI (PEI = poly(ethylenimine)) layer was dipped into the solution of **1**, it was found by UV-vis spectrum that **1** was not absorbed due to electrostatic repulsion between **1** and PEI. This shows **1** was protonated and it was positively-charged. Therefore, the PEI-coated substrate was immersed in the anionic polyoxometalate BW_{12} ($BW_{12} = BW_{12}O_{40}^{5-}$) solution in order to adsorb the positively-charged calix[4]arenes through the electrostatic interaction. UV-Vis spectroscopy is used to monitor the LbL assembly. Fig. 2 shows the UV-vis spectra of the multilayer films. For PEI-BW_{12}-$(\mathbf{1})_n$ films, the absorbance at 325 nm is assigned to **1**, in agreement with the aqueous solution of **1**. When the PEI-BW_{12}-**1** film again absorbed one subsequent layer of **1**, hydrogen bonding (N–H···O) between one layer of calix[4]arene and one subsequent layer of calix[4]arene was formed through protonated amino groups and hydroxy groups. Interestingly, the absorbance increases with the number of the layer of **1**, indicating that **1** is successfully incorporated into the films. In the case of PEI-BW_{12}-$(\mathbf{2})_n$ films, the absorbance peak from **2** occurs at 275 nm. The



1 X = S
2 X = CH_2

Fig. 1 Chemical structures of $[H_4pATC4]^{4+}$ (**1**) and $[H_4pAC4]^{4+}$ (**2**).

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[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, 350002, China. E-mail: rcao@fjirsm.ac.cn; Fax: +86 59183796710; Tel: +86 59183796710*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China*

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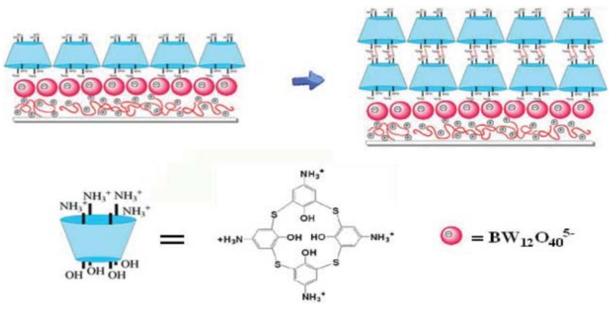

Scheme 1 The self-assembly process of the films.

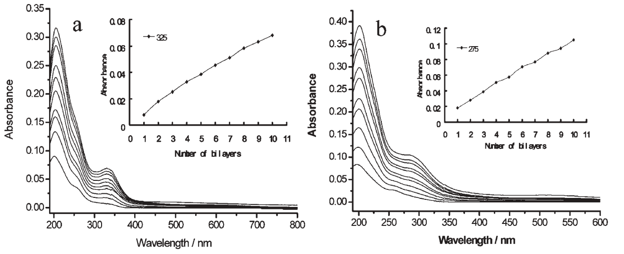

Fig. 2 UV-Vis spectra of the multilayer films. a: PEI-BW_{12}-(**1**)$_n$; b: PEI-BW_{12}-(**2**)$_n$.

absorbance at 275 nm also increases with the number of the layer of **2**, indicating that **2** is incorporated into the films. The above-mentioned multilayer films are composed of a single calix[4]arene with identically charged molecules based on hydrogen bonding (N–H···O) between amino groups and hydroxy groups. According to the general perception proposed by Decher,[4] it is difficult to adsorb layers of identically charged polyions onto each other due to the repulsion of equally charged molecules. However, Laschewsky reported the successful adsorption of up to four subsequent polycation layers with two different polycations containing azo chromophore *via* alternating layer-by-layer assembly.[14] The result indicated that the formation of the films overcomes the electrostatic repulsion between two different polycations through a secondary interaction. Our films are different from that reported by Laschewsky, because our films are composed of the same component with a positively-charged calix[4]arene and the number of the layer reaches up to ten, probably the protonized amino groups increases the strength of hydrogen bonding.[15] Although the strength of hydrogen bonding is weaker than electrostatic attraction, the cooperative interaction of multiple hydrogen bonding overcomes the electrostatic repulsion between the positively-charged calix[4]arenes. However, the calix[4]arene adsorbed on solid surfaces from solution is not infinite. When the adsorption time was prolonged, the continuous adsorption of **1** and **2** was not observed from the absorbance analyses. Therefore, the self-assembly process reaches equilibrium and it is self-limiting. This demonstrates that washing and drying between each adsorption step play an important role on the growth of the multilayer films. During the rinsing and drying process, some rearrangements occur in the adsorbed layer and generally adopt the lowest energy state.[4] In case of calix[4]arenes, due to bowl-shaped molecular cavities, they favorably adopt the stabilized cone conformation instrumental in forming hydrogen bonding in this process. The film morphology and film roughness with different layer numbers are characterized by the AFM images (See ESI†). The root-mean-square (RMS) roughness increases with the number of layer. As seen from AFM images, van der Waals interaction between adjacent calix[4]arene structures in the in-plane structure of the films is responsible for film growth and stability.

The formation of hydrogen bonds between the same calix[4]arene was confirmed by FTIR spectra (Fig. 3). Fig. 3 shows the FTIR spectra of different layers. For the PEI-BW_{12} layer, the broad absorption band around 3510 cm^{-1} is assigned to the O–H stretching vibrations of water molecule. When the PEI-BW_{12} layer absorbed the layer of **1**, a shoulder peak at 3364 cm^{-1} attributed to N–H stretching vibration of **1** was observed. For PEI-BW_{12}-(**1**)$_5$, the peak of N–H is shifted to the lower frequency region at 3343 cm^{-1} and becomes more pronounced, suggesting that the amino group is in an associated state. This demonstrates that the formation of the multilayer films of **1** is through hydrogen bonding (N–H···O) between protonated amino groups and hydroxy groups. The frequency at 1345 cm^{-1} is attributed to O–H bending vibration. For PEI-BW_{12}-(**1**)$_{10}$, no significant changes are observed in the band positions. However, the peak intensity is increased, indicating that the growth of **1** increases with the number of layer. It was reported that calix[4]arene derivatives formed dimeric capsules, host–guest complexes and nanotubes through intermolecular hydrogen bonding.[15] For example, Shuker and co-worker reported the tetraalaninecalix[4]arenes dimer in the solid state through intermolecular hydrogen bonding between the terminal amine and the carbonyl group.[15a] However, the multilayer films of the single-component calix[4]arene on a solid substrate have not been yet reported based on hydrogen bonding.

We investigated the stability of the multilayer films after the substrate with the top layer of calix[4]arene was immersed into the $CuCl_2$ solution for 25 min. It was found that the absorbance from the calix[4]arenes increases with the number of layer (Fig. 4). After the substrate with the top layer of calix[4]arene was immersed into the $CuCl_2$ solution for 25 min, the UV absorbances at characteristic peaks of calix[4]arenes increased linearly with number of layers of calix[4]arene/Cu^{2+}. The IR spectra of PEI-BW_{12}-(**1**/Cu^{2+})$_5$ film is slightly different from that in PEI-BW_{12}-(**1**)$_5$ film due to the influence from Cu^{2+} ions (Fig. 5). IR spectra indicate that the peak at 1345 cm^{-1} from the O–H bending vibration is unobvious. This is possibly because Cu^{2+} ions are

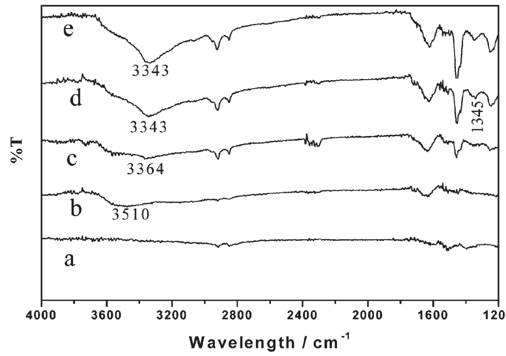

Fig. 3 FTIR spectra of the films with the different layer on a CaF_2 substrate. a: PEI; b: PEI-BW_{12}; c: PEI-BW_{12}-(**1**)$_1$; d: PEI-BW_{12}-(**1**)$_5$; e: PEI-BW_{12}-(**1**)$_{10}$.

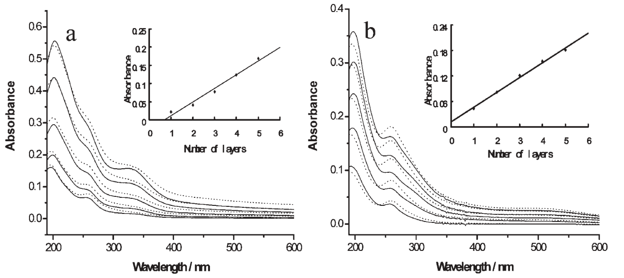

Fig. 4 UV-Vis spectra of the multilayer films. a: PEI-BW$_{12}$-(**1**/Cu^{2+})$_n$; b: PEI-BW$_{12}$-(**2**/Cu^{2+})$_n$. The solid lines represent the spectra after the addition of calix[4]arenes layers. The dotted lines represent the spectra after addition of Cu^{2+} ion layers. From bottom to top: 1, 2, 3, 4, 5, respectively. Inset: Increase in the absorbance at 325 nm (a) and 260 nm (b) as a function of the number of layers of calix[4]arene/Cu^{2+}.

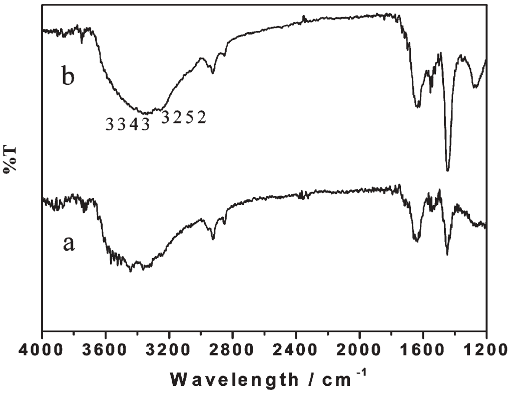

Fig. 5 FTIR spectra of the films with the different layer on a CaF$_2$ substrate. a: PEI-BW$_{12}$-(**1**/Cu^{2+})$_1$; b: PEI-BW$_{12}$-(**1**/Cu^{2+})$_5$.

weakly coordinated to O–H of calix[4]arenes. In the range of 3200–3600 cm^{-1} region, the N–H stretching vibration peak for PEI-BW$_{12}$-(**1**/Cu^{2+})$_5$ still occurs at the lower frequency region of 3343 cm^{-1}, suggesting that there is hydrogen bonding in the multilayer film. However, the shoulder peak occurs at 3252 cm^{-1}, indicating that there is weak coordinated interaction between Cu^{2+} ions and calix[4]arenes. UV-Vis and IR spectra demonstrate that after the films with the top layer of calix[4]arene was dipped into the Cu^{2+} ions solution, it was not desorbed. The influence of pH on the stability of the films was also investigated. The results show that the films are stable in low pH value but dissociated in high pH value (see ESI†).

In order to demonstrate that Cu^{2+} ions are also absorbed in the films, the electrochemical behavior of the GCE modified with the PEI-BW$_{12}$-(**1**/Cu^{2+}) film was performed in sodium chloride solution (See ESI†). The voltammogram exhibits one sharp oxidation peak at +0.420 V (E_{pa}) owing to the incorporation of Cu^{2+} ions at the scan rate of 50 mV s^{-1} in the first cycle. From the above results, many different interactions such as hydrogen bonding interaction and metal ion–ligand coordination interaction contribute to molecular binding. Thus, it is difficult to delineate the contribution from a specific interaction. However, hydrogen bonding is responsible for the uniform and reproducible growth of the multilayers and plays an important role in the formation of the above multilayers.

In summary, we have presented the first example of the multilayer films depositing the single and small molecule tetraaminocalix[4]arenes based on hydrogen bonding. The report will provide strong evidence for hydrogen-bonded self-assembled capsules of calix[4]arenes. In addition, it will exploit the potential applications of calix[4]arenes as metal ion sensor.

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