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

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Materials and instruments

Poly(ethylenimine) (PEI, 50 wt% aqueous solution) was purchased from Aldrich Chemical Co. $K_5BW_{12}O_{40}$ (BW_{12}) was prepared by published method.[1] *p*-tetraamino-tetrathiacalix[4]arene (*p*ATC4) and *p*-tetraamino-calix[4]arene (*p*AC4) were prepared according to the references.[2, 3] The amino groups of *p*ATC4 and *p*AC4 are protonized with hydrochloric acid, abbreviated as $[H_4pATC4]Cl_4$ (**1**) and $[H_4pAC4]Cl_4$ (**2**).

UV-vis absorption spectra were recorded on a quartz slide using a Lambda35 spectrophotometer (Perkin-Elmer, USA). AFM images were taken on a single-crystal silicon slide using a Nanoscope Ⅲa (Digital Instruments Inc., Veeco, USA) operating in the tapping mode with silicon tips. All measurements were performed in air. IR spectra were taken on films on CaF_2 plates, using a Spectrum One FTIR (Perkin-Elmer, USA). Electrochemical experiments were carried out on an Epsilon Analyzer (BAS Inc., USA) in a three-electrode cell: glassy carbon electrode (GCE, diameter 3 mm) as working electrode, platinum wire as counter electrode, and Ag/AgCl/KCl (3 M) as reference electrode. The solutions were deaerated with prepurified nitrogen for at least 15 min.

The preparation of the multilayer films

The quartz slides (or single-crystal silicon slides) were cleaned with a “piranha solution” at 80 ℃ for 40 min, and thoroughtly rinsed with distilled water. Further purification was carried out by immersion in a $H_2O/H_2O_2/NH_3OH$ (5:1:1) (V/V/V) bath for 30 min at 70℃.

*PEI-BW$_{12}$-(**1**)$_n$ and PEI-BW$_{12}$-(**2**)$_n$ multilayer films* The clean quartz slides or single-crystal silicon slides (or CaF_2 plates) were immersed in aqueous solution of PEI for 20 min, washing with water and drying with nitrogen stream. The pre-coated substrates were then immersed in BW_{12} solution for 20 min, washing with water and drying with nitrogen stream. Thus, the surface of the substrates is negatively charged. Then, the PEI-BW_{12} substrates were cyclically dipped into **1** or **2** (1.8 mM) aqueous solution (pH 3.2) for 20 min, washing with water and drying with nitrogen stream. Cyclic repetition of the last adsorption step leads to the formation of the multilayer films.

*PEI-BW$_{12}$-(**1**/Cu^{2+})$_n$ and PEI-BW$_{12}$-(**2**//Cu^{2+})$_n$ multilayer films* The quartz slides (or CaF_2 plates) pre-coated with PEI-BW_{12} were immersed in **1** or **2** (1.8 mM) aqueous solution for 20 min. Then, the substrates were dipped into $CuCl_2$ solution (pH 4.6) for 25 min. Between each immersion step, the substrates were washed with water and dried with nitrogen stream. By repeating the two steps, the multilayer films were obtained.

The AFM characterization of the films

The AFM images of the films are indicated in Fig.S**1**. The surface of the films is uniform and smooth. For the first four layers, the surface of the films shows no features due to the soft surface. When the number of layer reaches to six and the film shows the rigidity, the surface of the films exhibits nanometer-sized features similar to the nanotube-shaped structure. A large number of nanotube-shaped particles are located in the surface. Moreover, the nanotube-shaped particles of $(\mathbf{1})_6$ and $(\mathbf{1})_8$ are uniform and compact. It indicates that the vertical structure of the film is formed through hydrogen bonding between calix structures, whereas the in-plane structure of the film is formed through van der Waals interactions between neighboring calix structures. If the in-plane structure of the film is not through van der Waals interactions, the surface of the film shows an incompact surface and fewer particles due to the absence of the interaction confinement. However, as seen from AFM images, the nanotube-shaped nanostructure surface of the film is rather compact. Therefore, it demonstrates that the array of calix's in plane is attributed to van der Waals interactions between calix structures.

The root-mean-square (RMS) roughness of the films increases with the number of layers (Table S**1**).

Table S**1** The RMS roughness of the film of different layer number

Layer numbers	PEI-BW_{12}-$(\mathbf{1})_1$	PEI-BW_{12}-$(\mathbf{1})_2$	PEI-BW_{12}-$(\mathbf{1})_4$	PEI-BW_{12}-$(\mathbf{1})_6$	PEI-BW_{12}-$(\mathbf{1})_8$
Root-Mean-Square (RMS) Roughness	0.3 nm	0.4 nm	0.5 nm	0.8 nm	1.1 nm

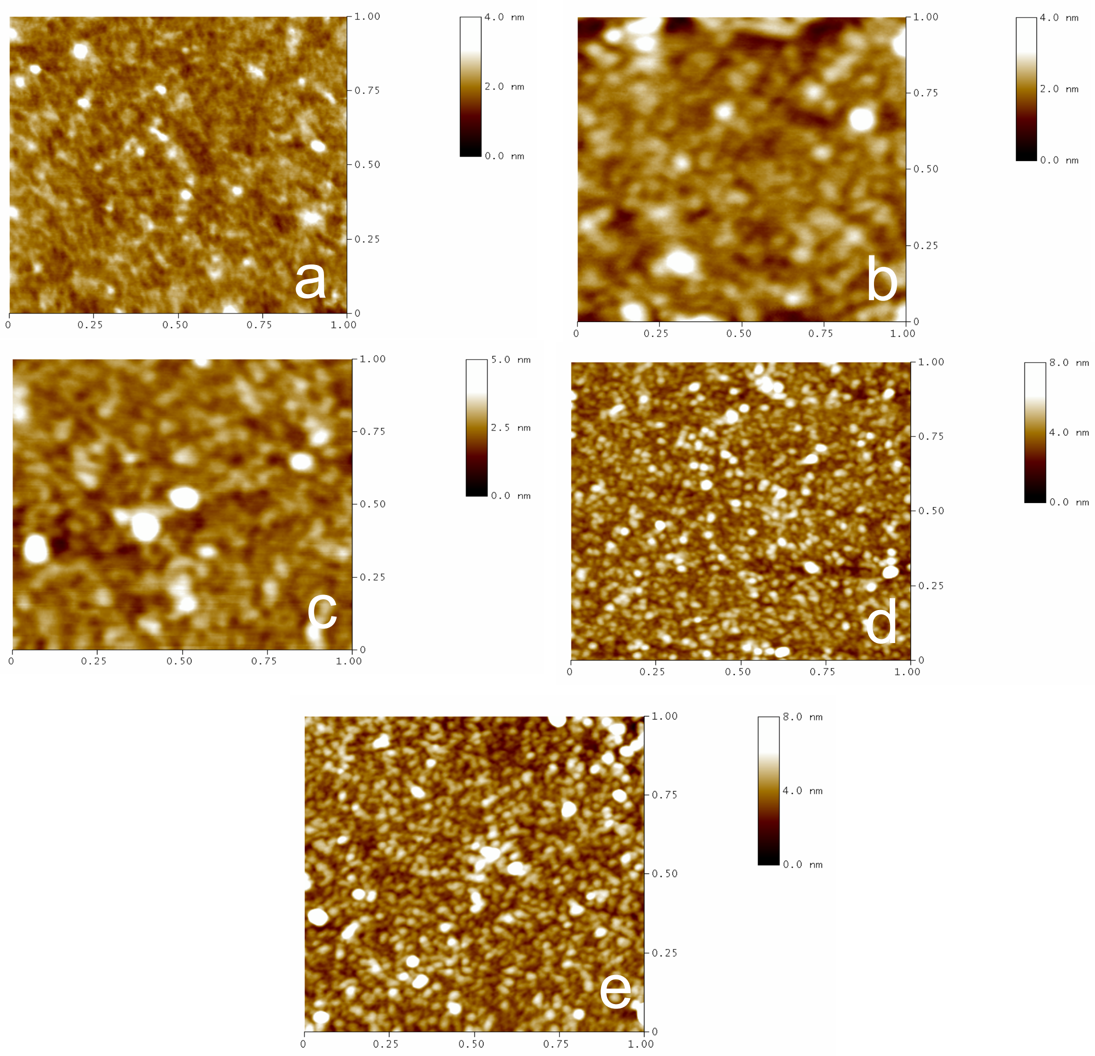

Fig. S1. AFM images of the films with different layer numbers on a single-crystal silicon slide (1.0 ×1.0 μm^2). a: PEI-BW$_{12}$-($\mathbf{1}$)$_1$**;** b: PEI-BW$_{12}$-($\mathbf{1}$)$_2$; c: PEI-BW$_{12}$-($\mathbf{1}$)$_4$; d: PEI-BW$_{12}$-($\mathbf{1}$)$_6$; e: PEI-BW$_{12}$-($\mathbf{1}$)$_8$

The influence of pH on the stability of the film

The pH value of the calix[4]arene solution is around 3.0, whereas the pH value of the $CuCl_2$ solution is 4.6. This indicates that the films are stable at pH 3.0 and 4.6. In addition, after we immersed the films into hydrochloric acid solution (pH 2.0) for 10 min, it was found that the absorbance did not decrease, as monitored with UV-Vis spectroscopy. After the films were immersed into sodium hydroxide solution (pH 11.0) for 10 min, the absorbance of the films obviously decreased. Therefore, the films are stable at pH from 2.0 to 4.6. In higher pH, OH^- ions can act to dissociate hydrogen bonds.

The IR characterization of the films

The IR spectra of PEI-BW_{12}-(**1**/Cu^{2+})$_5$ film is slightly different from that in PEI-BW_{12}-(**1**)$_5$ film. The comparison of IR spectra is represented on Figure S2.

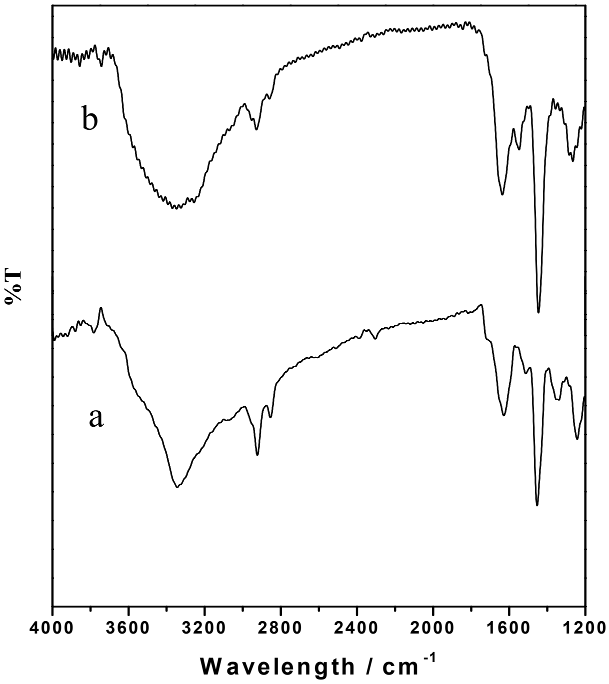

Fig. S**2** FTIR spectra of the films on a CaF_2 substrate. a: PEI-BW_{12}-(**1**)$_5$; b: PEI-BW_{12}-(**1**/Cu^{2+})$_5$

The characterization of electrochemical behavior

The electrochemical behaviors of the GCE modified with PEI-BW_{12}-**1**/Cu^{2+} and

PEI-BW$_{12}$-**2**/Cu^{2+} films are represented on Figure **2**. In NaCl solution, the electrochemical behaviors of **1** and **2** exhibit no peak in the positive potential region at the scan rate of 50 mV s^{-1}. The oxidized peak at + 0.420 V is ascribed to the incorporation of Cu^{2+} ions (Fig. S3a). In the negative potential region, the electrochemical response is from the BW$_{12}$ polyoxoanion.

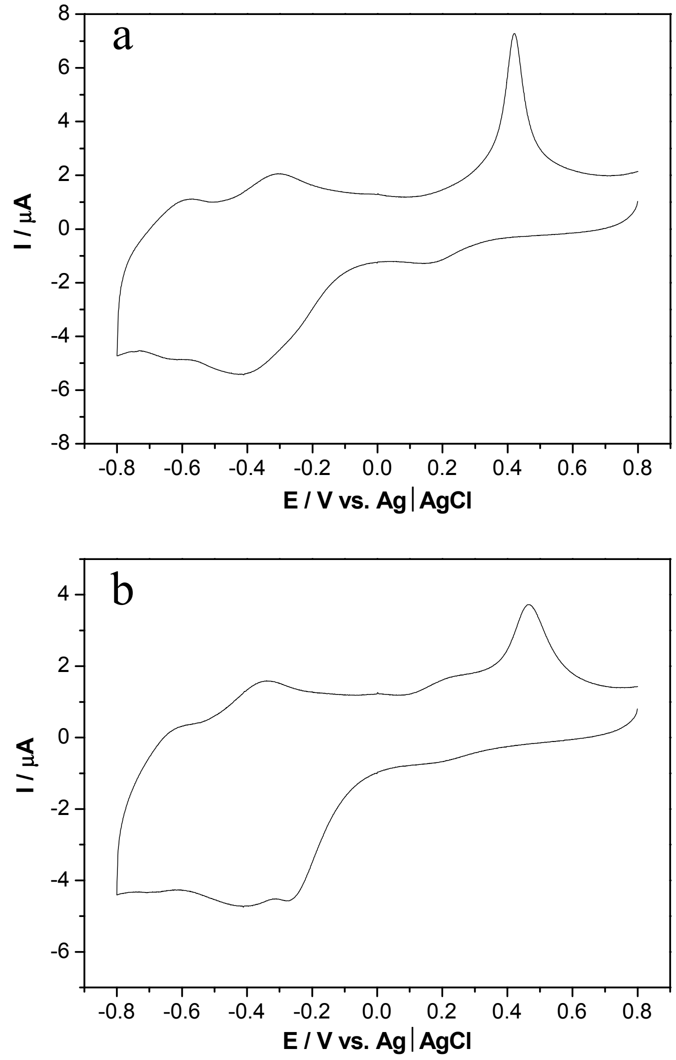

Fig. S**3** Cyclic voltammograms of the films in 0.1 M NaCl solution. a: PEI-BW$_{12}$-(**1**/Cu^{2+})$_1$, b: PEI-BW$_{12}$-(**2**/Cu^{2+})$_1$. Scan rate: 50 mV s^{-1}.

References

1 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.,* 1983, **22,** 207-216.

2 Y. Morita, T. Agawa, E. Nomura and H. Taniguchi, *J. Org. Chem.,* 1992, **57,** 3658-3662.

3 P. Lhoták, J. Morávek and I. Stibor, *Tetrahedron Lett.,* 2002, **43,** 3665-3668.