

A Supramolecular Chiroptical Switch Based on Chitosan and Anionic Porphyrin Complex Film

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ABSTRACT: A supramolecular chiroptical switch based on chitosan and tetrakis (4-sulfonatophenyl) porphine (TPPS) complex films was prepared. The reversible changes of the chirality of the complex films were studied by UV-vis and circular dichroism (CD) spectra. It was found that the chirality of the complex films can be wiped off by being exposed to NH₃ gas and subsequently recovered by being exposed to moist HCl gas. The complex film is stable and can stand at least 20 cycles of the switching to NH₃ and HCl gases. There is no change in the above properties after the complex films were stored in the air at room temperature. [doi:10.1295/polymj.PJ2007036]

KEY WORDS Supramolecular Chirality / Chitosan / Chiroptical Switch / Porphyrin /

Chirality is an attractive issue in chemistry, biology, material science etc. and has been studied extensively.^{1–4} The chiral switch, which shows the reversible change in chirality with an external stimulation, is particularly attractive due to the potential applications in data storage and sensor systems.^{5–9} Many chiral optical switches have been proposed, which are based on photochemically induced interconversions,^{10,11} photochemically induced changes in liquid crystals,^{12,13} stereoisomers of chiral photoresponsive molecules and chiral supramolecular systems,^{14,15} etc. The most attractive one in this field is the chiral optical supramolecular switch because it is easily controlled.^{16–19} Tetrakis(4-sulfonatophenyl)porphine (TPPS, Figure 1) is a well investigated dye. It has two negative charges and forms stable J- and H-aggregates depending on the pH and ionic strength in the system. The TPPS J- and H-aggregates shows the property of induced chirality in many systems, such as multilayer and Langmuir-Schaefer (L-S) films prepared from chiral and achiral molecules,^{20–23} the solutions containing polyglutamic acid, polylysine, cationic porphyrin etc.,^{24–30} and even by mechanical stirring in solutions.³¹ However, there is no report about the reversible chirality of TPPS aggregates in film.

Chitosan, a chiral biopolymer, is used widely in many fields, e.g. biomedical^{32–34} and chemical materials,³⁵ textiles,³⁶ pharmaceuticals,^{37,38} etc. Chitosan is a cationic polyelectrolyte and can interact with the anionic TPPS. More recently, Synytsya *et al.*³⁹ studied the interaction of TPPS with chitosan in aqueous solutions at different pH value. The results confirmed that

the formation of optically active species of TPPS in the presence of chitosan and the J- and H-aggregates depended on pH value and chitosan concentration. However, no work had been reported on the interactions between TPPS and chitosan on chitosan film.

In this paper, the reversible change in chirality of chitosan/TPPS complex films when they are alternatively exposed in moist HCl and NH₃ gases was studied. The morphology of the complex films and the interaction between chitosan and TPPS were discussed.

EXPERIMENTAL

Water-soluble anionic porphyrin TPPS was purchased from Dojindo Laboratories. Chitosan ($M_n = 100$ Kda, the degree of deacetylation was 91 mol %) was received from Professor Yanming Dong's laboratory, Xiamen University.

TPPS was dissolved in deionized water and then the pH value of the solution was adjusted to 6.6 by adding NaOH. The concentration of TPPS in the final solution was 20 μ M. Chitosan was dissolved in 0.5% acetic acid solution with a concentration of 10 mg/mL.

Chitosan film was prepared with the chitosan solution by spin-coating and air dried on clean quartz. The film was neutralized by exposed in NH₃ gas and then immersed in the TPPS stock solution. Chitosan/TPPS complex film was obtained after the film was removed from the TPPS solution and dried. A red complex film about 1 μ m in thickness was obtained. The TPPS film

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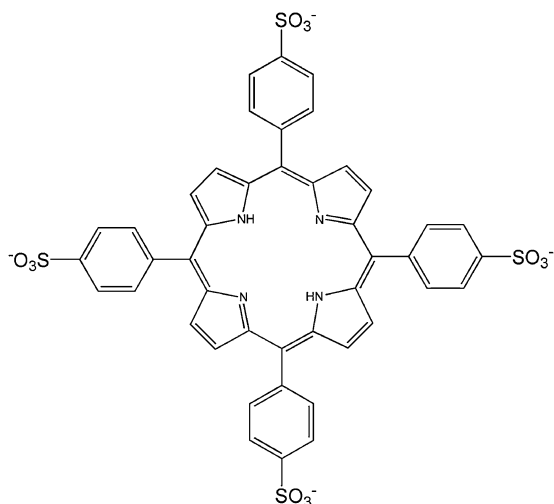


Figure 1. Chemical structure of non-protonated TPPS.

was prepared by dropping with 50 μL TPPS solution on a piece of clean quartz ($C_{\text{TPPS}} = 0.2 \text{ mM}$, $\text{pH} = 4.0$) and air dried. The chirality switch was achieved by a sequence exposing the chitosan/TPPS complex films in moist HCl and NH_3 gas for 15 seconds and 10 seconds, respectively. The moist HCl gas is composed of water vapor from 50 $^\circ\text{C}$ water and HCl gas.

UV-vis spectra of the complex film were recorded on a Vrian model UV-530 spectrophotometer and circular dichroism (CD) spectra were recorded by a CD spectrophotometer (JASCO, model J-810), the recording range is 200 nm–800 nm. During CD spectral recording, the complex film was placed perpendicular to the light path and rotated within the film plane, by which the polarization-dependent reflection was avoided and the possible angle dependence of the CD signals was also eliminated.

Atomic force microscopy (AFM) images were collected with a Nanoscope III multimode atomic force microscope (Veeco Metrology Group) in the tapping mode. FT/IR spectra of the films deposited on CaF_2 were recorded by a Bruker-Equinox 55 FT/IR spectrometer.

RESULTS AND DISCUSSION

Figure 2a shows the UV-vis spectrum of the aqueous TPPS solution at $\text{pH} = 6.6$. The strong absorption at 414 nm and several weak absorptions come from the B-band and Q-bands of the non-protonated TPPS monomer. In this work, the complex films of chitosan/TPPS were prepared by dipping the chitosan film in TPPS solution, in which the anionic porphyrin TPPS absorbed to polycationic chitosan film by electrostatic force. The absorption process was monitored by using UV-vis spectroscopy and the results are shown in Figure 2b as a function of the immersing time. The results show that there are two absorption bands at 410 nm and 422 nm, which are attributed to the non-protonated TPPS monomer and the B-bands of the TPPS H-aggregate, respectively. However, when a piece of clean quartz without chitosan was immersed the TPPS solution for enough time, there was no any UV-vis absorption signal in the TPPS absorption region after it was removed from the TPPS solution, which indicates that the TPPS can not be absorbed by the clean quartz without chitosan. All of the results indicate that TPPS is absorbed just by the chitosan film on the quartz and the H-aggregates are formed when TPPS is absorbed on to the chitosan film. Moreover, the relative intensity of the peaks at 410 nm and 422 nm change with the time that the chitosan immersed in the TPPS solution. In details, the intensity of the absorption peak of TPPS H-aggregate at 422 nm is much higher than that of 410 nm firstly, while the intensity of the absorption peak at 410 nm increases much faster than that of 422 nm. Both of the absorption bands saturated at about 60 min. At pH value of 6.6, part of chitosan amino groups are protonated and the anionic sulphonato groups are shielded by the counter ions,³⁹ which leads the aggregation of the non-protonated TPPS monomers to H-aggregates. With the increasing of the loading time, the non-protonated TPPS monomer in the film increases, while the chitosan amino groups in the proto-

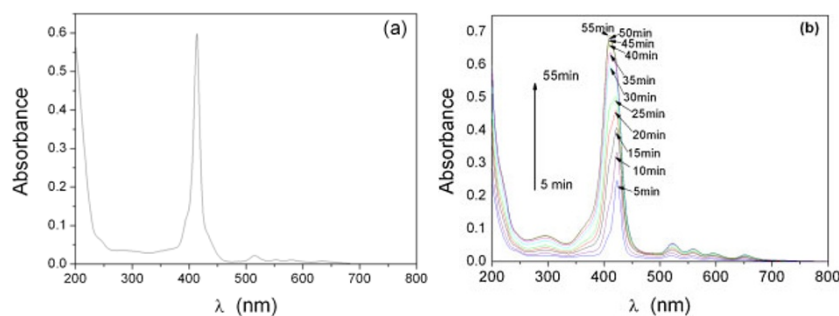


Figure 2. The UV-vis absorbance spectra of (a) TPPS solution and (b) the chitosan complex film after being immersed in the TPPS solution for different time.

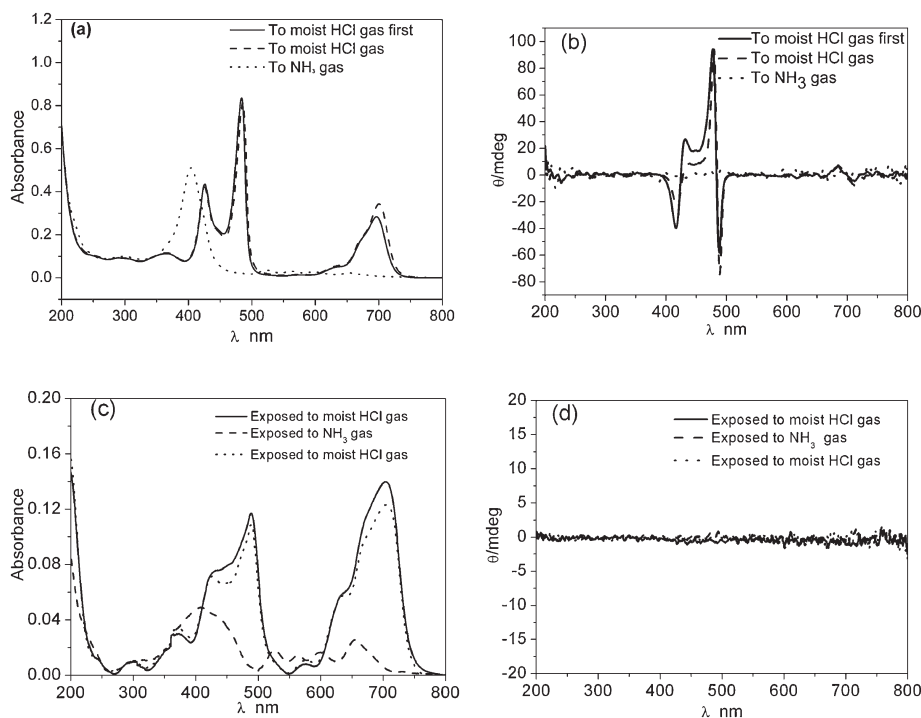


Figure 3. UV-vis (a) and CD (b) spectra of the chitosan/TPPS complex film, and UV-vis (c) and CD (d) spectra of TPPS film on clean quartz without chitosan, when being exposed to NH_3 gas and to moist HCl gas.

nated form are not changed, which results in the absorbance of the non-protonated monomers is stronger than that of the H-aggregates in the film in the end. The saturated film is dark red in color and no CD signal can be observed, which indicates that there is no induced chirality in the prepared complex film. Similar results were observed in the chitosan/TPPS solutions in the pH range from 5.6 to 6.8.³⁹

When the non-induced chirality as-prepared complex film is exposed in moist HCl gas for 15 s, the color of complex film is changed into green, and the absorption bands for TPPS B-band of H-aggregates and B-band and Q-band of J-aggregates, at 424, 491 and 707 nm, respectively, appear on the UV-vis spectra (Figure 3a). Simultaneously, the absorption band of TPPS monomers at 410 disappears. CD spectra shows some splitting CD signals at these absorption bands (Figure 3b). When the film is exposed in NH_3 gas, the color of the film is changed from green to rosiness immediately. Meanwhile, the absorption bands at 424, 488, and 704 nm disappear and a new absorption band at 404 nm, which is attributed to the non-protonated TPPS single molecules, appears simultaneously (Figure 3a, dash line). The results indicate that the H- and J-aggregates of the TPPS are disaggregated and turned into non-protonated molecules when the film is exposed in NH_3 gas. When the complex film is subsequently exposed in the moist HCl gas, its color is recovered from rosiness to green immediately and the absorption band of the non-protonated TPPS mole-

cules disappears in the UV-vis spectra and the absorption bands of the H- and J-aggregates are recovered in the UV-vis spectra (Figure 3a, dotted line). The results indicate that the non-protonated TPPS single molecules are re-assembled into H- and J-aggregates when the complex film is exposed in the moist HCl gas. Figure 3b shows the CD spectra of the complex film at different stages. There are three CD bands in the CD spectrum of the original complex film (solid line in Figure 3b). The one centered at 421 nm with splittig attributes to the TPPS H-aggregates.²⁰ The others centered at 484 and 700 nm come from the J-aggregates.²⁰ The results suggest that H- and J-aggregates show induced chirality on the chitosan film in the presence of the acid atmosphere. Moreover, the H- and J-aggregates show D-type and L-type induced chirality respectively.³⁹ After the complex film is exposed in NH_3 gas, no CD signals can be observed in the range of TPPS absorption (Figure 3b, dash line). While when the film is subsequently exposed in moist HCl gas, the CD signals in the range of H- and J-aggregates absorption of the TPPS reappear and are similar to those of the original film (Figure 3b, dotted line). In the same way, the UV-vis and CD spectra changes of TPPS film on the clean quartz without chitosan when it is exposed to the moist HCl or NH_3 gas were investigated. Though TPPS can be assembled into H- and J-aggregates when it is exposed to the moist HCl gas (as shown in Figure 3c), no any CD signals can be observed in the absorption re-

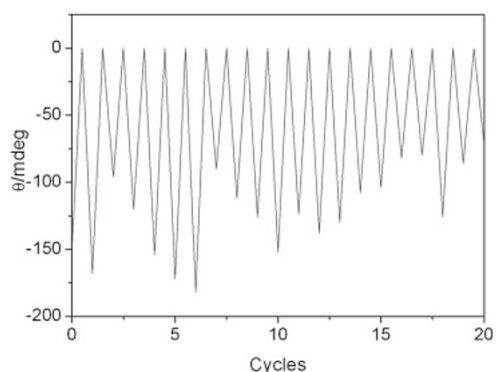


Figure 4. The CD couplet amplitude of TPPS J-aggregates at the Soret band changes with cycles.

gion of TPPS (as shown in Figure 3d). All of the results indicate that the chirality of TPPS aggregates in the complex film should come from the inducement of chitosan. At the same time, it is found that the reversibility of the CD signal changes of the complex film can be repeated for many times, and it is clarified by the CD couplet amplitude of the TPPS J-aggregates at the B-band as a function of cycles in Figure 4. It is showed in Figure 4 that the complex film stands at least 20 cycles of the change between chirality and achirality mentioned above without obviously decay in the CD intensity. Moreover, after being stored in air at room temperature for more than one month, the CD signals of the complex film can still be observed without obvious change in the UV-vis spectra and CD signals. Meanwhile, the chirality of the complex film is still sensitive to NH_3 gas and moist HCl gas as the original one, and the reversible change between chirality and achirality can be still repeated many cycles. It should be noted that NH_4Cl produced in the experimental process, which is increased with the increment of the cycles. However, no obvious weakening of the CD signals was observed during the 20 cycles as shown in Figure 4. Therefore, it is reasonable to consider that the production of NH_4Cl has no or only a trivial influence on CD signals.

It is known that the CD signal can be affected by the linear dichroism (LD) during CD measurement.^{40–42} In this work, the influence of the LD was eliminated by averaging at different angles with the similar procedure reported in literatures.^{23,41,42} It has been found that the average of the CD spectra at eight angles (0° , 45° , 90° , 135° , 180° , 225° , 270° , 315° , and 360°) results in similar CD spectra as those in a rotating manner (Figure 5). The CD spectra reported in this paper are measured by rotating the film during the measurement.

The above discussions indicate that the complex film shows chirality when it is exposed to moist HCl gas and TPPS is in its H- and J-aggregates states.

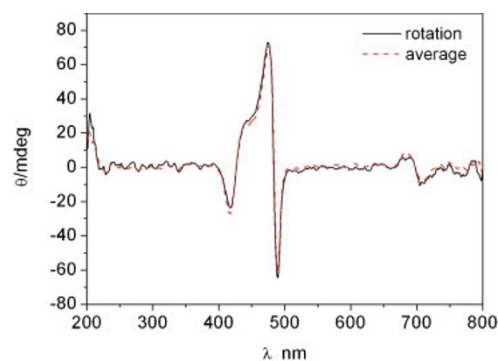


Figure 5. Comparison between the CD spectra of chitosan/TPPS complex films obtained by averaging the CD spectrum in eight different rotation angles (0° , 45° , 90° , 135° , 180° , 225° , 270° , 315° , and 360°) and that obtained by continuous rotation.

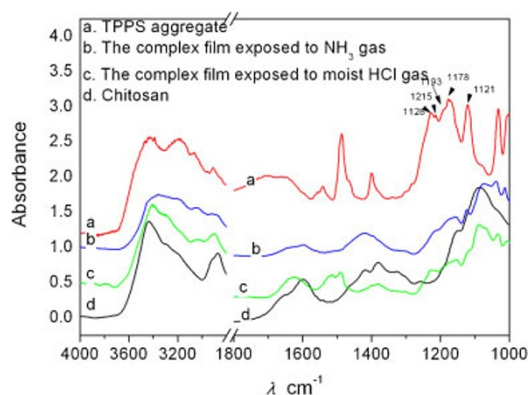


Figure 6. FT/IR spectra of TPPS aggregate, the chitosan, the chitosan/TPPS complex film exposed to moist HCl and subsequently NH_3 gas, respectively.

In this case, both chitosan and TPPS molecules are protonated. Therefore, it is reasonable that the chirality of the complex comes from the interaction between TPPS and chitosan, which can be confirmed by FT/IR (Figure 6). In the FT/IR spectrum of the TPPS aggregates, the bands at 1230, 1215, 1193, 1178 and 1121 cm^{-1} are all attributed to $-\text{SO}_3^-$ groups stretching vibration.^{43,44} In the FT/IR spectrum of the TPPS/chitosan complex film that is exposed to moist HCl gas, the characteristic band of chitosan corresponding to the NH_2 scissoring vibration of primary amino group at 1600 cm^{-1} is absent. At the same time, the band at 3600–2800 cm^{-1} , which is attributed to stretching vibration of primary amino group, shifts to the lower wavelength. Simultaneously, the intensity of the absorption bands of the $-\text{SO}_3^-$ groups stretching of the TPPS aggregates at 1215 and 1193 cm^{-1} decrease and the absorption bands of the $-\text{SO}_3^-$ groups of TPPS aggregates in the chitosan/TPPS complex film at 1178 cm^{-1} , 1121 cm^{-1} shift to 1171 cm^{-1} and 1116 cm^{-1} , respectively. The results indicate there are interactions between $-\text{SO}_3^-$ groups of the TPPS aggregates and amino groups of chitosan. After the complex

film is exposed to the NH_3 gas, the typical absorption peak of the chitosan amino group at 1600 cm^{-1} reappears and the absorption band of the $-\text{SO}_3^-$ groups of the TPPS at 1230 cm^{-1} disappears, the band at 1121 cm^{-1} shift to 1125 cm^{-1} , which suggests that the TPPS molecules and the chitosan are deprotonated and the ionic interaction between the TPPS and the chitosan disappears.

The TPPS aggregates in the chitosan complex film show splitting CD signals in the absorption regions. The split CD signals come from excited coupling and suggest that the TPPS aggregates are CD activity. It is well known that TPPS aggregates are easily induced to show CD activity by achiral molecules or even by mechanical stirring.³¹ The chirality of TPPS aggregates is normally attributed to the helical formation of the TPPS aggregates due to the broken of the mirror-symmetry of the diprotonated porphyrins in the TPPS aggregates or the formation of a 90° fold of the TPPS aggregates.³¹ It has been reported that in tryptophan chiral L- or D-isomers solutions, the chirality of the TPPS aggregates always follows the chiral molecules and the TPPS aggregates form L- or D-helix respectively.⁴⁵ Moreover, the chirality of the TPPS J-aggregates in the complex L- or D-Trp multiplayer films formed *via ex situ* also follows the chirality of films.²² All the reported results indicate that the presence of the chiral molecules promotes the broken of the mirror-symmetry of diprotonated porphyrins in the TPPS aggregates, which results in the induced chirality of the TPPS aggregates. More recently, the chirality of the TPPS aggregates in chitosan solutions has been studied.³⁹ It has been found that the distance of the neighbored amino groups in chitosan is similar to that of the neighbor non-bonded sulphonato groups in the TPPS aggregates if the porphyrin molecules are in half-overlapped. Therefore, the optically active twisted structure of the TPPS aggregates comes from the helical distortion of the TPPS aggregates induced by the chiral chitosan molecules.³⁹ The splitting CD signals of TPPS aggregates may come from either the adjacent aggregates that are arranged along the chitosan helix or the helix of the aggregate itself. It has been reported that L- and D-helix structure of TPPS aggregates can be formed in chitosan solution.³⁹ In this work, the CD activity of the TPPS aggregates in the complex film should be similar to that in the solution of chitosan and comes from the helix of the TPPS aggregate itself.³⁹ When the complex film is exposed to the moist HCl gas, the amine groups on the backbone of the chitosan molecules and TPPS molecules are protonated and the TPPS molecules self-assemble into H- and J-aggregates simultaneously with helix due to the promoting of the chiral chitosan (as illustrated in Figure 7a).

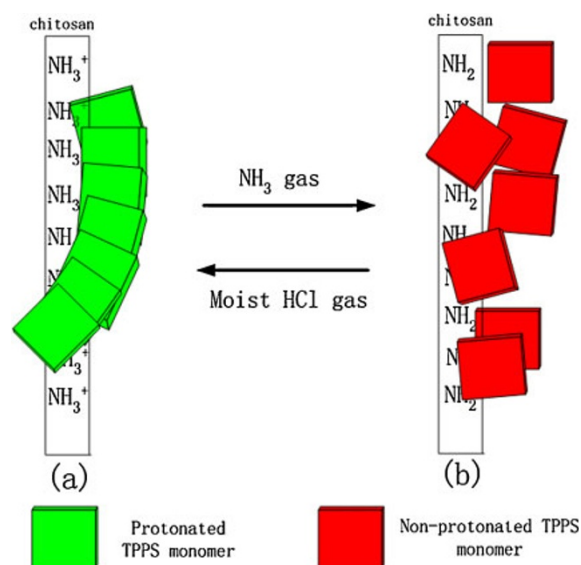


Figure 7. Illustration of aggregation (a) and disaggregation (b) of TPPS in the chitosan complex film.

When the complex film is exposed to the NH_3 gas, the amine groups on the backbone of the chitosan chains and TPPS molecules are deprotonated and the TPPS molecules are disaggregated, which results in the loss of the chirality of the TPPS aggregates (as illustrated in Figure 7b).

The morphology of the complex films was investigated by AFM and the results are shown in Figure 8. The results show that the as prepared chitosan film is smooth and without any special structures (Figure 8a). After the chitosan film is exposed to moist HCl gas, the chitosan molecules aggregate to a worm-like morphology (Figure 8b). When the chitosan/TPPS complex film is exposed to the moist HCl gas, a granular structure tightly packed on the surface of the film can be observed (Figure 8c), which suggests that the TPPS molecules are aggregated in the chitosan film and form short-range ordered aggregates. When the complex film is exposed to the NH_3 gas, it can be found that the granular structure disappeared (Figure 8d), which indicates the disaggregation of the TPPS aggregates occurs at this time. Therefore, it can be concluded that the CD activity should come from the granular structure in the chitosan/TPPS complex film. However, it is a pity that more details of the morphology, such as the helix structure, of the TPPS aggregates can not be observed by AFM.

The chiral switches based on dye-intercalated DNA film⁵ and L-S film⁸ have also been reported by liu's group. In the dye-intercalated DNA film, the chirality can be wiped off by the HCl gas and be recovered by the NH_3 gas and water vapor due to the protonation and deprotonation of the dye TMPyP respectively. But the intensity of the CD signals may be reduced after 10 cycles. In our case, the reversible change be-

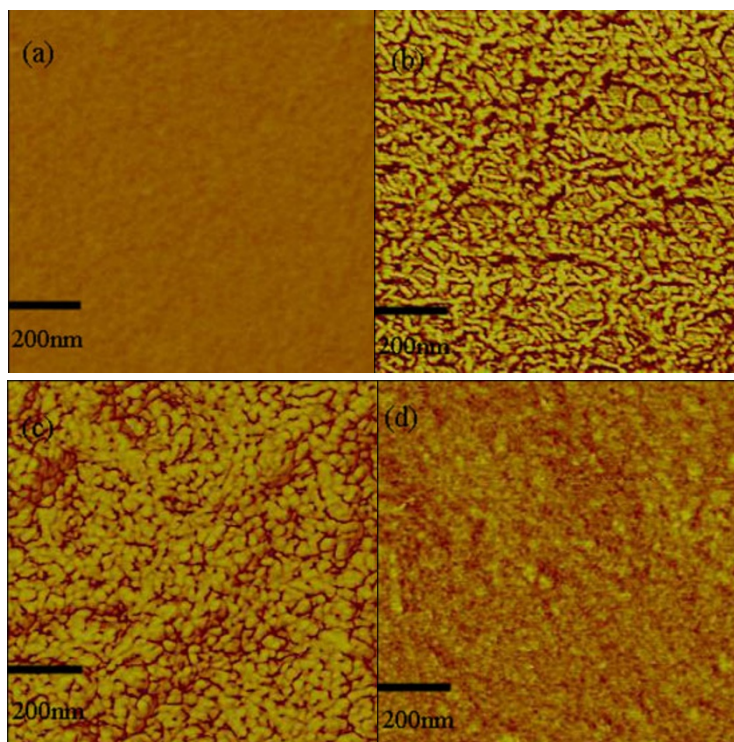


Figure 8. AFM images of (a) the chitosan film, (b) the chitosan film exposed to moist HCl gas, (c) chitosan/TPPS complex film exposed to the moist HCl gas, (d) chitosan/TPPS complex film exposed to the NH_3 gas. Images size: $1\ \mu\text{m} \times 1\ \mu\text{m}$.

tween the chirality and achirality in the chitosan/TPPS complex films can be repeated many cycles even after the complex film is stored in air for more than one month, which indicates that the obtained chitosan/TPPS complex film is stable the reversible change of the chirality and can be practical used as a chiroptical switch.

CONCLUSIONS

Chitosan/TPPS complex films are prepared and the film shows supramolecular chirality induced by chitosan to the TPPS aggregates. The supramolecular chirality of the complex films is sensitive to the NH_3 and moist HCl gases and is reversible when it is alternatively exposed in the NH_3 and the moist HCl gases. The complex film is stable and can stand at least 20 cycles of the changes between the chirality and achirality in the NH_3 and the HCl gases. The storage of complex film at room temperature in the air for more than month has no obvious influence on its chiroptical switch properties.

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