

Irreversible transformation of the porphyrin supramolecular structures under a water vapor environment

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Abstract Supramolecular structures formed by $H_4TPPS_4^{2-}$ have been widely used for different applications. In this paper, the stability of $H_4TPPS_4^{2-}$ nanorods on mica substrate is investigated by atom force microscopy (AFM) observation. An irreversible transformation of $H_4TPPS_4^{2-}$ from nanorods (3.8 ± 0.4 nm in height) to a lower film structure (1.9 ± 0.4 nm in height) was found with the samples incubated at various relative humidities (RH). The transformation rate depends strongly on the RH and environment temperature.

Key words Supramolecular structures, $H_4TPPS_4^{2-}$, Stability, AFM

1 Introduction

Recently, the formation of functional self-assembled nanomaterials with well-defined shapes has attracted considerable research interests^[1], such as porphyrins and other tetrapyrrole macrocycles that possess unique aromatic structures, excellent photochemical and photophysical properties^[2-6]. It has been shown that many porphyrin derivatives are good candidates as building blocks for sensors, electronic devices, and light-energy conversion systems^[7-10]. Porphyrin-based nanostructures, i.e. nanorods, nanotubes and nanofiber bundles, were formed *via* self-assembly processes, and showed encouraging performances^[11].

The self-assembled $H_4TPPS_4^{2-}$ supramolecular structures have shown good photoconductivity^[12-19]. With a rapid turning on/off dependence of the current on the light, they can be used for fabrication of nanometer-sized photoelectronic devices^[20]. It has also been shown that $H_4TPPS_4^{2-}$ supramolecular structures are sensitive to water vapor in the atmosphere, and this makes it possible to use them as humidity and gas sensors^[21].

The $H_4TPPS_4^{2-}$ can self-assemble into nanorod structure on substrate surfaces, and the balance between the three porphyrin states of free-base, diacid and J-aggregate can be adjusted by adding either acid or salts into the solution^[13]. Conformational changes of the supramolecular porphyrin systems are important when using them in devices or sensors, because this may strongly affect the device performances. A small variation of the supramolecular structures would give rise to a strong fluctuation of the functions and efficiency. It has been found that, in the porphyrin self-assembled structures, the distance between the pigments and the space arrangement are key factors for optimizing energy transfer^[13,22]. On the other hand, supramolecular structures formed by the porphyrin monomers are mainly maintained by weak non-covalent interactions like π - π interaction, electrostatic interaction, etc. This would mean an easy performance degradation of porphyrin structures caused by environmental fluctuations. In this regard, the long term stability of the nanoscaled $H_4TPPS_4^{2-}$ under different environment conditions should be well testified^[23-25].

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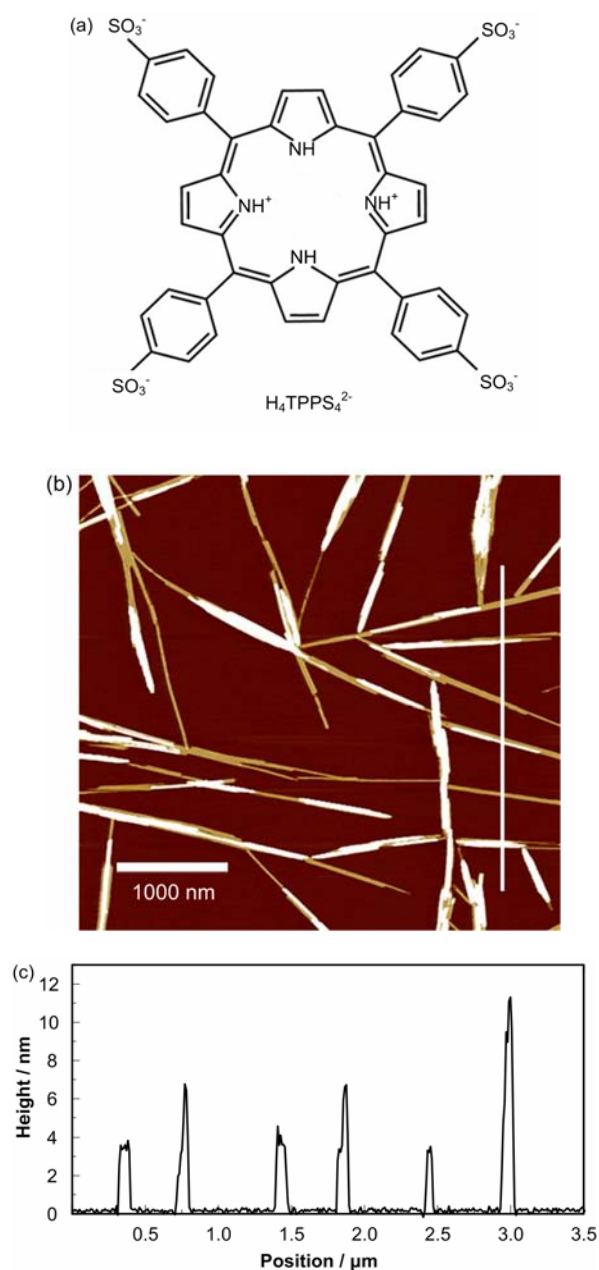


Fig.1 Structural illustration of tetrakis (4-sulfonatophenyl) porphine ($H_4TPPS_4^{2-}$) (a), AFM image of the self-assembled $H_4TPPS_4^{2-}$ nanorods (b) and their bundles on the mica substrate, and profile of the white line in Fig.1b (c).

In this paper, we investigate influence of water vapor, a common environmental factor, on stability of $H_4TPPS_4^{2-}$ nanorod structure (Fig.1a) adsorbed on a hydrophilic mica substrate. At room temperature, an irreversible transformation of the nanorods into a much lower film-like structure was found under high relative humidity (RH). The alteration of ionic environment on the substrate under high RH condition may be the main cause of the reduction of the stability of $H_4TPPS_4^{2-}$ nanorods.

2 Experimental

2.1 Preparation of $H_4TPPS_4^{2-}$ nanorod

The $H_4TPPS_4^{2-}$ nanorod structure was prepared from the chloride salt of $H_4TPPS_4^{4-}$, which was purchased from Sigma-Aldrich Co., USA and used as received. A concentrated stock solution containing $1.6 \text{ g}\cdot\text{L}^{-1}$ $H_4TPPS_4^{4-}$ were prepared by dissolving the chloride salt of $H_4TPPS_4^{4-}$ into a $0.1 \text{ mol}\cdot\text{L}^{-1}$ phosphate buffer solution (PBS, pH 6.8). Then, $10 \mu\text{L}$ stock solution was sufficiently diluted to a solution containing $10 \mu\text{mol}\cdot\text{L}^{-1}$ [$H_2TPPS_4^{4-}$] using the PBS buffer. An acid-induced aggregate solution was made by mixing equal volume of $0.6 \text{ mol}\cdot\text{L}^{-1}$ HCl with $10 \mu\text{mol}\cdot\text{L}^{-1}$ [$H_2TPPS_4^{4-}$] solution, and the solution of $0.3 \text{ mol}\cdot\text{L}^{-1}$ HCl and $5 \mu\text{mol}\cdot\text{L}^{-1}$ $H_2TPPS_4^{2-}$ was obtained. For each experiment, a fresh solution was prepared. The acid-induced solution was heated to 90°C which was kept for 5 min, and aged in a 60°C water bath for 2 h to generate $H_2TPPS_4^{2-}$ with supramolecular structures. The as-prepared $H_2TPPS_4^{2-}$ supramolecules were deposited onto freshly-cleaved mica substrate by dropping $20\text{-}\mu\text{L}$ of the aged solution onto the surface.

2.2 Incubation of samples

The samples with adsorbed $H_4TPPS_4^{2-}$ supramolecular structures were incubated in a chamber (SDH-01N, Shanghai Jianheng Instrument Co.) for a certain time. In the sample chamber, the RH and temperature were controlled with an accuracy of 5% and 0.1°C , respectively. All the RH and temperature data were calibrated and recorded by a SHT-15 digital humidity sensor (accuracy: $\pm 0.3^\circ\text{C}$ in temperature and $\pm 2\%$ in RH, Sensirion Inc. USA).

2.3 Atomic force microscope (AFM) observation

An atomic force microscope (multi-mode Nanoscope IIIa, Veeco/Digital Instruments, Santa Barbara, CA) equipped with a J scanner ($100 \mu\text{m} \times 100 \mu\text{m}$) and an E scanner ($15 \mu\text{m} \times 15 \mu\text{m}$) was employed to reveal the self-assembled $H_4TPPS_4^{2-}$ supramolecular structures. Silicon cantilevers with a nominated force constant of $\sim 48 \text{ N/m}$ and resonant frequency of $\sim 330 \text{ kHz}$ (NSC11, MikroMasch Co., USA) were used. All AFM operations were carried out in air at room temperature and relative humidity of $<40\%$.

3 Results and discussion

Fig.1b revealed the self-assembled morphologies of $H_4TPPS_4^{2-}$, including individual rods and their bundles. The individual $H_4TPPS_4^{2-}$ rods were of a uniform height of 3.8 nm (Fig.1c). They appeared to be basic building blocks for larger, bundled aggregates with heights of multiple of 3.8 nm, which is in good agreement with those previously reported^[13,17].

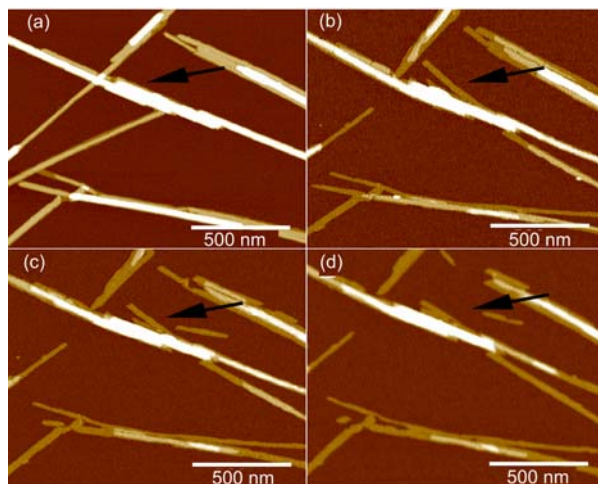


Fig.2 AFM images indicating evolution of the supramolecular nanorods of $H_4TPPS_4^{2-}$ on mica substrate, incubated at 30°C and 100% RH.

AFM images of the $H_2TPPS_4^{4-}$ nanorods on mica substrate incubated at 30°C and 100% RH showed a clear transformation of the self-assembled nanostructures (Fig.2). The time interval between two successive AFM images in Fig.2 is 10 hours. The AFM observation was carried out in a dry condition (~30% RH). After 10-h incubation, some nanorods decreased greatly in height and transformed into a film-like structure, with an anomalous fringe being lower than the nanorods (Fig.2b). By further incubations, the lower film structure grew in numbers (Figs.2c and 2d), until almost all the nanorods were transformed into films. Transformation of the nanorod bundles was also evident, with a slower rate though. Furthermore, the films formed in 100% RH condition could not re-transform into nanorods by incubating in a dry environment for several months, indicating the transformation process was irreversible.

A statistical analysis was done on the height distributions of the self-assembled nanostructures of $H_4TPPS_4^{2-}$ before and after high RH incubation. In Fig.3, the height distributions of the self-assembled

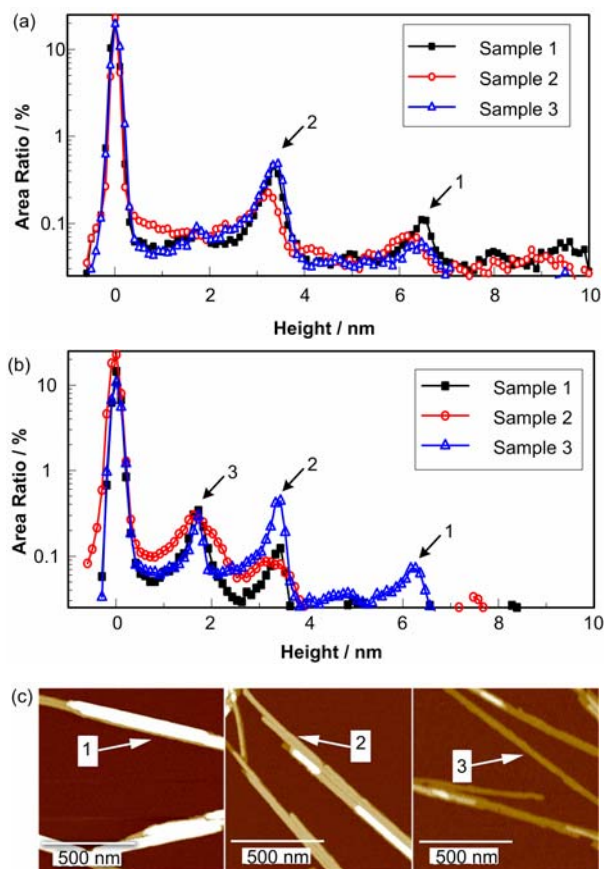


Fig.3 Height distribution of the self-assembled $H_4TPPS_4^{2-}$ structures on the mica surface. (a) Before incubation in high RH. There are two main histogram peaks correspond to the nanorod structure in different assembling states. (b) After incubation in 100% RH, a new peak appeared at 1.9 nm corresponding to the film structure. (c) Typical topographic images of the supramolecular structure corresponding to Peaks 1, 2 and 3 in Fig.3a and 3b.

$H_4TPPS_4^{2-}$ nanostructures in the three AFM images (500 nm×500 nm scan size) were counted. Before incubation (Fig.3a), the nanorods in height of 3.8 ± 0.4 nm (**2** in Figs.3a and 3c) were the dominating nanostructures self-assembled on the substrate. There was also a lower peak (**1** in Figs.3a and 3c) originated from the bundles of single nanorods, with a doubled height of individual nanorods. After incubation at 30°C and 100% RH for 30 h, a new peak, Peak **3**, appeared in the height distribution profile (Fig.3b). It corresponds to the lower film nanostructure with a height of 1.9 ± 0.4 nm (**3** in Fig.3c), which is half of the height of the nanorods. The film structure shows a very flat surface, suggesting that the $H_4TPPS_4^{2-}$ nanorods may not be randomly organized.

A series of experiments indicated that the $H_4TPPS_4^{2-}$ nanostructure transformation was highly related with the RH. The results showed that the

samples incubated in a dry environment (e.g. ~40% RH at room temperature) were very stable. As shown in Fig.4a, no changes were found on topography of the nanorods and the bundles were there after incubation of even one month. In contrast, when the samples were incubated at 70% RH and 30°C, the nanorod structure transformed a little after 30 h. Most of the film structures were found at the terminal parts of the nanorod, as pointed out by the white arrows in Fig.4b. Comparing with the samples incubated at 100% RH, the transformation rate was much slower.

It was found that the environment temperature affected strongly the transformation of $H_4TPPS_4^{2-}$ nanorods. At room temperature, the nanorod tended to transform into lower film structure, whereas at 37°C the transformation accelerated notably. However, the nanorods and film-like structures prepared under the two conditions were not stable. For example, after incubation at 37°C and 100% RH for 4 h, all the nanorod structures disappeared in Fig.4c, where only some small dots could be found on the mica substrate.

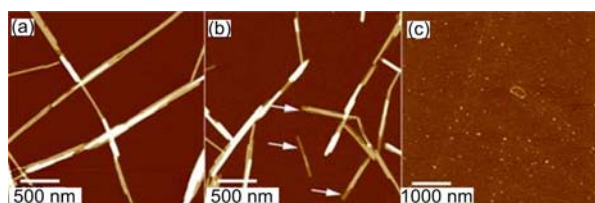


Fig.4 AFM images of the $H_4TPPS_4^{2-}$ supramolecular structures after incubations of (a) one month at room temperature and <40 % RH, (b) 30 h at 30°C and 70% RH, and (c) 4 h at 37°C and 100% RH.

It was reported that nanorod structures were stable, or kept growing at even 60°C in bulk solution^[13]. So the $H_4TPPS_4^{2-}$ supramolecular structures with decreased stability in a water vapor environment on the mica substrate is abnormal. This suggests that the transformation of the nanorod structures into flat film-like features may partly due to the alteration of the ionic strength around the $H_4TPPS_4^{2-}$ rods at a high RH. For the $H_4TPPS_4^{2-}$ nanorods formed in a bulk- solution environment (pH<4.8), the ionic strength around the nanorods was uniform and the electrostatic interaction was a major factor to stabilize the nanorod structures. However, when the $H_4TPPS_4^{2-}$ nanorods were deposited on mica surface and incubated at a high RH, a water nano-film was introduced onto the sample surface. Such kind of water nano-film on a mica substrate has been reported,

with a thickness of around several nanometers^[26,27]. In such a water nano-film, diffusion rate of the ions and the ionization of water molecules may differ greatly from the bulk conditions^[28]. The changes in ion strength around the $H_4TPPS_4^{2-}$ molecules can result in instability of the nanorod structures.

On the other hand, the lateral capillary forces at the surface of water nano-film may enhance the instability of $H_4TPPS_4^{2-}$ nanorods^[29]. It was found that some nanorods and film structures would move on the mica substrate during incubation at 100% RH, as pointed out by the black arrows in Fig.2. The film structure near the arrow (Fig.2b) was broken and separated into several parts (Fig.2c). Small pieces of individual nanorods and film structures were pushed by the water molecules around them and moved randomly on the substrate. As a result, the $H_4TPPS_4^{2-}$ supramolecular structures were forced to transform from nanorod into the lower film-like feature. At high temperatures, the water molecules and ions on the substrate experience enhanced thermo movements, hence the accelerated transformation of nanorod structure.

4 Conclusion

The stability of $H_4TPPS_4^{2-}$ nanorod structures on the mica substrate is very sensitive to the environmental RH. In a high RH, the nanorods transform into a lower film structure. And high temperatures accelerate this process. Our results indicate that a well-controlled low humidity condition is necessary for long term stability of the $H_4TPPS_4^{2-}$ nanorod structures, and it is also important to develop methods for maintaining self-assembled porphyrin structures in practical applications. The transformation of nanorod structure into film structure in a saturated water vapor condition may serve as a new way to generate $H_4TPPS_4^{2-}$ monolayer film on a substrate, without any surfactant.

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