

## Ionic self-assembly of porphyrin nanostructures on the surface of charge-altered track-etched membranes

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**ABSTRACT:** Track-etched polymer membranes are typically used as templates in the synthesis of various nanowires or nanotubes arrays. The unique advantages of track-etched membranes, such as uniform pore structure, excellent porosity, easily tailored pore sizes, and a well characterized surface chemistry, may find use in self-assembly strategies where colloidal nanostructures can be tethered to a suitable substrate to produce devices of interest. *Meso*-tetrakis(4-phenylsulfonic acid)porphyrin dihydrochloride and Sn(IV) tetrakis(4-pyridyl)porphyrin were used to synthesize ionic self-assembled porphyrin nanorods. The track-etched membranes surface charge was changed from negative to positive using polyethyleneimine. The porphyrin nanorods were either filtered through or self-assembled onto the surface of track-etched membranes. Comparisons were made with track-etched membranes modified with, and without, polyethyleneimine. Assembly of the porphyrin nanotubes only occurred on the surface of positively charged track-etched membranes, and filtration of the porphyrin nanorods produced a mesh-like structure on the surface of the membrane irrespective of the track-etched membrane pore diameter. In each case the characteristic absorbance profiles of the porphyrin nanorods was maintained. Transmission electron microscopy, scanning electron microscopy, atomic force microscopy, and UV-vis spectroscopy were used to characterize the various systems.

**KEYWORDS:** porphyrin nanotubes, poly-(ethylene-terephthalate) track-etched membranes, self-assembly, consolidated nanomaterial, UV-vis spectroscopy, atomic force microscopy.

### INTRODUCTION

Currently, there is a significant amount of interest in the design rationale of organized molecular assemblies with well-defined geometric shapes. One of the underlying principles behind such efforts is the possibility to use such structures in areas such as photonics, molecular electronics, solar energy conversion, catalysis, electrochemical energy devices, and host-guest chemistries.

Porphyrins are a class of macrocyclic compounds with a tetrapyrrolic ring system and have been the subject of intense research for several years. Utilizing various synthetic strategies, the ring system can be modified with a wide range of hydrophobic or hydrophilic moieties, which can then be exploited in different self-assembly based chemistries. Tailoring the core porphyrin structure allows for further self-assembly whilst maintaining the ability to exploit the unique  $\pi$ - $\pi^*$  transitions in nonlinear optics, molecular electronics, chemical sensing, or other previously mentioned applications.

On the nano-scale, the ability to produce various geometric shapes allows for the expression and exploitation of specific properties not seen in the corresponding bulk-scale. In this respect, the self-assembly of porphyrin

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systems into different nano-scale geometric structures has been an intense area of research. Using the free-base and diacid forms of tetrakis(4-sulfonatophenyl)porphine, and by varying the ionic strength of aqueous solutions used, Schwab *et al.* were able to form single and bundled nanorods [1], whereas Wang *et al.* used a mixture of tetrakis(4-sulfonatophenyl)porphine and Sn(IV) tetrakis(4-pyridyl)porphyrin to form a mixture of nanotubes and nanorods [2]. Both groups used non-covalent methods to produce the porphyrin-based nanostructures. Similar methods have been used by various researchers to form porphyrin nanotubes or nanorods for gas-sensing applications [3] and determination of optical properties [4], and so-called pea pod-based porphyrin systems using similar non-covalent assembly [5]. It is interesting to note that rectangular porphyrin-based nanotubes have been successfully synthesized using a thermal method, vaporization condensation re-crystallization, which may allow for new approaches in the utilization of porphyrin nanostructures in device fabrication [6].

Once they have been synthesized, the incorporation of porphyrin nanostructures into a functional device presents its own set of unique problems. One promising approach is to incorporate the nanotubes onto a support to obtain an array that can be directly used as a device. When two or more nanostructured materials are used to make a new structure, which can be simply described as a consolidated nanomaterial, it is possible to observe some kind of synergistic effect. For example, porphyrin- and fullerene-based nanoclusters have been shown to have relatively enhanced photovoltaic efficiencies [7], and the growth of carbon nanotubes on micro-wire arrays showed greater electrochemical activity than the separate nanotubes or micro-wires [8]. Track-etched polymeric membranes have a well-defined structure, and a wide range of controllable pore diameters, porosity and thickness. In addition, the physical-chemical properties have been well investigated [9–12]. For example, the electrokinetic behavior of track-etched membranes made from poly(ethylene terephthalate) (PET), with pore diameters between 20–580 nm, was investigated by Déjardin *et al.* [13], and the adsorption of proteins and water-soluble dyes on track-etched PET membranes were reported by Khataibe *et al.* [14]. It is interesting to note that the proposed mechanism of adsorption on the surface of the membranes took into account ionic, hydrophobic and hydrophilic interactions [10]; these may be exploited in porphyrin self-assembly onto similar PET substrates.

We report on the synthesis of a consolidated nanostructured material that consists of a porous PET membrane and a dispersed second phase of self-assembled porphyrin nanostructures. This second phase may alter the consolidated nanomaterial's optical, electronic, mechanical or physical-chemical properties. Consequently the surface of the consolidated nanomaterials can be tailored to specific requirements by selecting a suitable template support and secondary phase. The porphyrin membrane

composites were investigated using UV-vis spectroscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM).

## EXPERIMENTAL

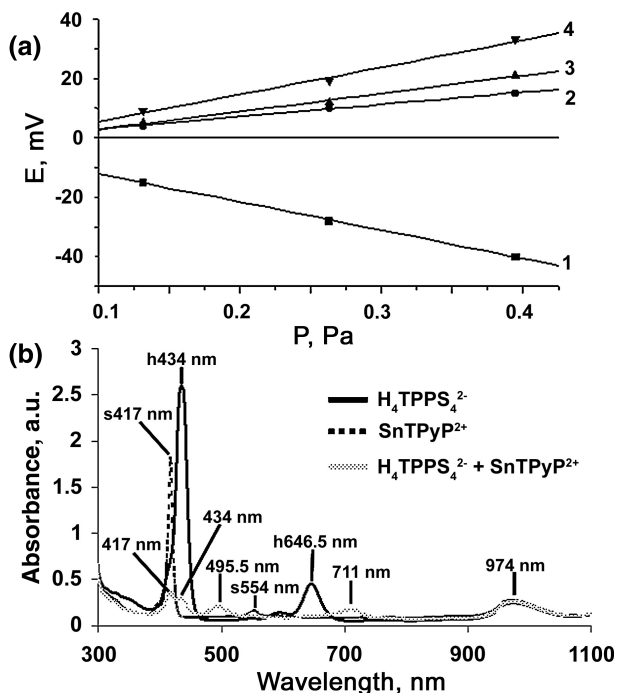
### Poly(ethylene terephthalate) (PET) track-etched membranes

PET track-etched membranes with pore diameters of 30 nm to 1  $\mu\text{m}$ , and thickness between 10 nm and 20  $\mu\text{m}$  were received from Flerov Laboratory of Joint Institute for Nuclear Research (Dubna, Russia). The original membranes are negatively charged in water-based solutions in the pH range 2.8–9 [10, 11].

In order to use the track-etched membranes as supports for the ionic self-assembly of porphyrin nanostructures, the surface charge needs to be elucidated since ionic interactions play a crucial role in the assembly of positively and negatively charged monomers of porphyrins. To alter the surface charge, membranes were modified with water-soluble polyethyleneimine (M.W. 1800, 99%, Lancaster). Where mentioned, membranes were modified with 0.01%, 0.10%, and 1.00% (w/w) aqueous solutions of polyethyleneimine by simply immersing the membranes for 24 hours at ambient conditions. In a typical experiment, the membrane is placed in a petri dish and 30 mL of the desired solution is poured over the membrane. The sample is then left for 24 hours, after which it is removed from the solution and air-dried under ambient conditions. Electrokinetic measurements were done to determine the changes of surface charge on the membranes. Method and installation for electrokinetic measurements were done according to procedures reported by Berezkin *et al.* [15]. Figure 1(a) illustrates typical results for electrokinetic measurements on the PEI-modified membrane. The electrokinetic data is similar to previous results reported in the literature, and clearly shows the change of the membrane surface charge from negative to positive for all PEI-modified membranes [9, 11]. It must be noted that the PEI layers on the surface of track-etched membrane are stable, and that varying the pH values does not change the electrokinetic properties of the membranes [9, 11].

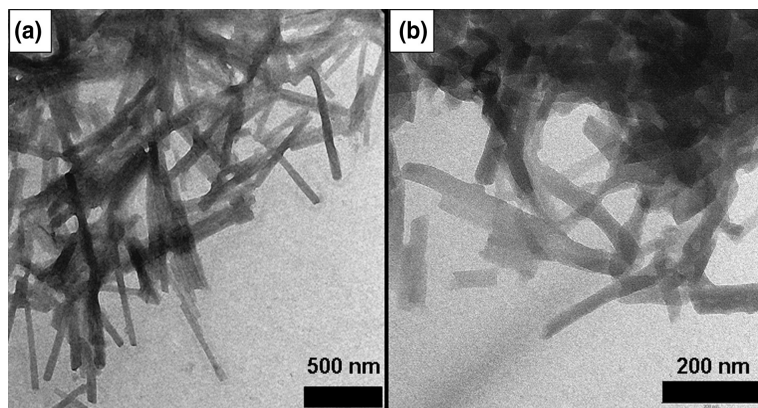
### Self-assembly porphyrin nanorod

The porphyrin nanorods were synthesized via ionic self-assembly technique by mixing aqueous solutions of two porphyrins using procedures developed by Wang *et al.* [2]. *Meso*-tetrakis(4-phenylsulfonic acid)porphyrin ( $\text{H}_2\text{TPPS}_4$ ) dihydrochloride and Sn(IV) tetrakis(4-pyridyl)porphyrin ( $\text{SnTPyP}^{2+}$ ) dichloride were purchased from Frontier Scientific and used without further purification. To obtain porphyrins self-assembly nanorods, equal volumes of an acidified  $\text{H}_4\text{TPPS}_4^{2-}$  solution (10.5  $\mu\text{M}$ ) and a Sn(IV)-tetrakis(4-pyridyl)porphyrin



**Fig. 1.** (a) Dependence of streaming potential (E) on pressure difference (P) TM (1: initial TM; 2: TM, modified by 1% water solution of PEI; 3: TM, modified by 0.1% water solution of PEI; 4: TM, modified by 0.01% water solution of PEI). Concentration of KCl = 0.01 M at pH = 6.0. (b) UV-vis of the precursors and porphyrin nanorods formed after mixing of the precursors. Peak labels with the letter 's' are for the  $SnTPyP^{2+}$  monomer, the values with an 'h' are for the  $H_4TPPS_4^{2-}$  monomer, and the remaining values are for the porphyrin nanorods formed

( $Sn(IV)TPyP^{2+}$ ) dichloride solution (3.5  $\mu$ M) were mixed and left undisturbed in the dark for  $\sim$ 72 hours at 25  $^{\circ}$ C. Rod formation is very sensitive to solution conditions, especially pH, because it alters the charge balance and hence the synthesis was conducted under acidic conditions of pH  $\sim$  2. Nanorod solutions were analyzed with UV-vis spectroscopy (CECIL 2021 UV-vis spectrophotometer, scanned from 250–900 nm, using scan rate of 200 nm/min, slit width of 0.2 nm) and TEM. For TEM



**Fig. 2.** Typical TEM micrographs on the porphyrin nanostructures obtained via ionic self-assembly (a) in solution, (b) from membrane surface after filtration of solution

observations, a few drops of solutions were drop-dried onto a 200 mesh copper grid and then examined.

Typically, UV-vis spectroscopy is used to characterize porphyrin self-assembled nanostructures [1]. Figure 1(b) shows the UV-vis spectra of the precursors and the resulting nanorods in solution. The decrease in the main absorbance peaks of the precursors and the several peaks identified in the spectrum for the nanorods — 417, 434.5, 495.5, 711 and 974 nm — are similar to what has been reported before [1, 2, 16].

In general, high porphyrin concentrations results in self-assembly of rod-like arrangement and with further increase in porphyrin concentration, the aggregates maintain rod-like shape but tend to be shorter [1, 17]. Experimental methods used in this study were similar to those used by Wang *et al.* [2], and thus favors the formation of nanotubes. However, the TEM images in Fig. 2 show solid cylindrical shapes with diameters between 20 nm and 60 nm, and lengths as small as 400 nm. The difference is attributed to the light sensitivity of these structures, and the ease of the nanostructures' transition from nanotubes to nanorods when exposed to light [2].

### Assembly of porphyrin nanorods and tubes on track-etched membranes

Methods used to assemble porphyrin nanorods on the membranes included filtration of pre-assembled nanorods and exposure of track-etched membranes, with different surface charges, to porphyrin solutions. Specifically, for the filtration of porphyrin nanorods, the mixture of  $H_4TPPS_4^{2-}$  and  $SnTPyP^{2+}$  porphyrins was filtered through unmodified 0.03  $\mu$ m, 0.2  $\mu$ m and 1  $\mu$ m track-etch membranes using a simple Millipore vacuum filtration setup.

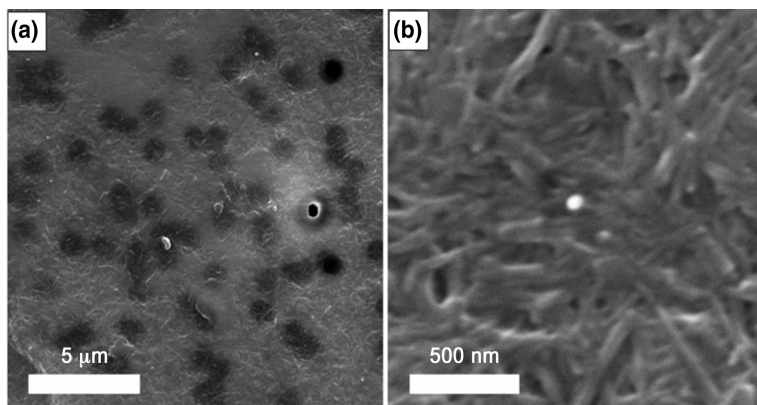
For self-assembly of porphyrin nanorods, a “layer-by-layer” growth regime on the surface of the charge modified membrane was utilized. The modified track-etched membrane was first immersed in a solution of porphyrin  $H_4TPPS_4^{2-}$  for 24 hours, followed by exposure to a solution of positively charged monomer of  $SnTPyP^{2+}$  for 24 hours. In parallel, un-modified and PEI-modified membranes were immersed for 72 hours in the mixture of  $H_4TPPS_4^{2-}$  and  $SnTPyP^{2+}$  porphyrins solution described above.

## RESULTS AND DISCUSSION

### Assembly of porphyrin nanorods on the surface of track-etched membrane via filtration

**SEM of porphyrin nanorods on track-etched membranes.** The mixture of  $H_4TPPS_4^{2-}$  and  $SnTPyP^{2+}$  porphyrins was filtered through 0.03  $\mu$ m, 0.2  $\mu$ m and 1  $\mu$ m track-etched membranes. Some nanorods were randomly distributed on the surface

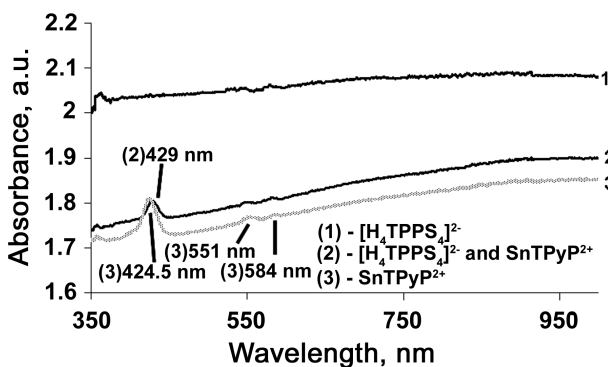




**Fig. 3.** (a) and (b) are SEM micrographs of porphyrin nanorods filtered through track-etched membranes

and others trapped on the membrane pores irrespective of the pore diameter used. There were a few pores that were not blocked by the nanorods, indicating that the porphyrin nanorods do not completely block the membranes, and although this is a simple method to stabilize the porphyrin nanorods, it has the disadvantage of blocking the supports pores, which is an undesirable outcome considering that the composite should have similar or enhanced properties to the individual components. However, as shown in Fig. 4, the optical properties were only slightly altered with this method of immobilization.

**UV-visible absorption porphyrin nanorods on unmodified membranes.** The UV-visible absorption bands of the porphyrin result from electronic transitions from ground state (S<sub>0</sub>) to the two lowest singlet-excited states S<sub>1</sub> (Q state) and S<sub>2</sub> (S state) [19, 18]. Exciton theory states that when molecules lie in a head-to-tail arrangement (J-aggregation) the allowed state is lower in energy, hence producing a red-shift to the monomer [19], and since the S band of [H<sub>4</sub>TPPS<sub>4</sub>]<sup>2-</sup> is red-shifted upon aggregation (J-aggregate), it implies the planar porphyrin molecules are stacked in an arrangement where individual porphyrin units are not positioned directly one on top of the other [1]. The nanorods composed of [H<sub>4</sub>TPPS<sub>4</sub>]<sup>2-</sup> J-aggregates are photoconductive and hence the higher absorbance peak of [H<sub>4</sub>TPPS<sub>4</sub>]<sup>2-</sup> in near UV region (400–460 nm).



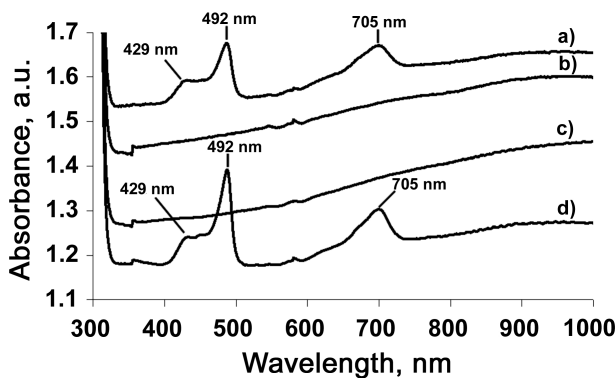
**Fig. 4.** UV-vis of various porphyrins filtered through the unmodified membrane

In Fig. 4 the featureless UV-vis trace of the [H<sub>4</sub>TPPS<sub>4</sub>]<sup>2-</sup> solution filtered through the unmodified membrane indicates that no aggregates formed on the surface of the membrane, an expected result due to the negative charge on the surface of the unmodified membrane. In contrast, the SnTPyP<sup>2+</sup> solution that was filtered through the unmodified membrane had a peak at 424.5 nm, compared to 417 nm for the free solution. This shift in the Soret and B bands (554 nm, vs. 551 nm and 584 nm) is an indication of self-aggregation of porphyrin structures. At pH 2, SnTPyP<sup>2+</sup> solution shows little to no aggregation

[2]; however, simple filtration of a solution of SnTPyP<sup>2+</sup> results in self-aggregation of porphyrin structures. This is a unique result and clearly demonstrates how ionic interactions can induce porphyrin self-aggregation on a solid surface. The nanorod solution filtered through the membrane did produce some expected bands (Fig. 4).

#### Assembly of porphyrin nanorods using a layer-by-layer technique

**UV-visible absorption porphyrin nanorods on PEI-modified membranes.** Modified track-etched membrane were inserted in solutions of H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>, SnTPyP<sup>2+</sup>, and the nanorod solution made from a mixture of H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> and SnTPyP<sup>2+</sup>. Figure 5 shows the UV-vis spectra of the PEI-modified membrane samples exposed to the various solutions. The characteristic absorption peaks for SnTPyP<sup>2+</sup> are not observed, whereas there is a distinctive change in absorbance peaks with the membranes exposed to H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>. Absence of absorbance peaks from the SnTPyP<sup>2+</sup> exposed membranes is expected, and confirms the positive charge of the membrane as determined by electrokinetic measurement. The change in the spectrum of H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> can be attributed to nanorod formation on the



**Fig. 5.** UV-visible absorption spectra of (a) modified membrane in the mixture of H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> and SnTPyP<sup>2+</sup>, (b) modified membrane before exposure to any solution, (c) modified membrane exposed to SnTPyP<sup>2+</sup> only, and (d) modified membrane in H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> solution

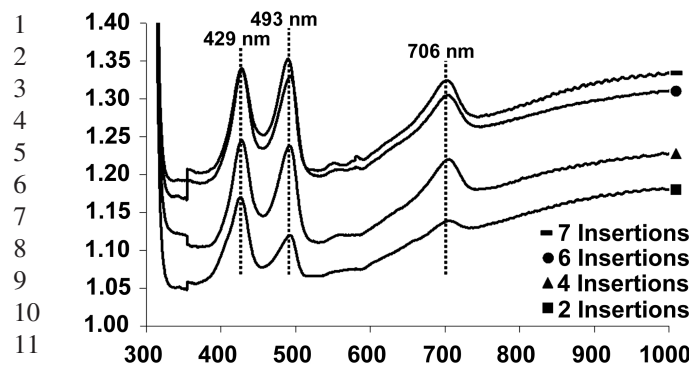


Fig. 6. Layer-by-layer deposition of porphyrin nanorods on the surface of PEI-modified track-etched membrane

charged membrane surface; a similar result was obtained by Schawb *et al.* on glass and mica substrates [1]. The formation of nanostructured aggregates, nanorods, by  $H_4TPPS_4^{2-}$  on the charged membrane surface can be attributed to the ionic interaction between the negatively charged  $H_4TPPS_4^{2-}$  and the positively charged surface. This is in line with literature reports of ionic interactions favoring nanorod and nanotube formation [1, 2, 4].

The peaks at 492 nm and 705 nm are characteristic of J-aggregate structures, particularly porphyrin nanorods [1, 4]. The peak at 429 nm is attributed to H-aggregates and the absorbance feature between 492 and 429 nm is most likely due to a mixture of aggregates and monomer [1]; however, the relatively strong absorbance peak on the modified membrane exposed to  $H_4TPPS_4^{2-}$  and then a mixture of  $H_4TPPS_4^{2-}$  and  $SnTPyP^{2+}$  does suggest the absorbance event is due to various aggregates of  $H_4TPPS_4^{2-}$ .

The PEI-modified membrane was inserted in a negatively charged porphyrin nanorod solution for about a day and the UV-visible absorption measured. This was repeated a number of times and the UV-vis absorption measured after each insertion. A distinct difference in the absorbance spectrum after set number of insertions was observed. Figure 6 shows that after two insertions there are three main absorption bands with peaks at 429, 493, and 706 nm, respectively, and the absorption event between 429 nm and 493 nm is no longer observed (see Fig. 5). A maximum absorbance was quickly observed after six insertions (Fig. 6), which indicates a complete coverage of the surface of the membrane by the nanorods and at the same time provides a relatively easy method to track the extent of surface coverage on the membrane. The change in absorbance profile between 429 nm and 493 nm (see Figs. 5 and 6) can be attributed to the lack of smaller aggregates or monomer on the PEI-modified membrane due to the

longer exposure times. The peaks at 493 nm and 706 nm after insertion are attributed to J-aggregation, and the change in the intensity after each insertions is most likely due to an increase in surface coverage of the J-aggregates, specifically, the porphyrin nanorods. However, the peak at 429 nm undergoes very little change with each insertion, indicating the H-aggregates of  $H_4TPPS_4^{2-}$  (from free monomer left in the solution porphyrin nanotube solution, see Fig. 1) on the membrane surface have reached maximum coverage and thus do not change with the subsequent insertions. This could account for an alternative explanation for the change in the intensity of the J-aggregates. The lack of any significant changes with the peak at 429 nm may indicate that the H-aggregates are tethering the nanorods to the membrane surface, and the change in peak intensity, at 493 nm and 706 nm, may not be a simple nanorod attachment to the system but more of a re-aggregation of porphyrin structures onto the membrane surface. However, the AFM results do not support this scenario, but rather a simple case where the increase in the intensity is due to an increase in the number of porphyrin nanorods.

A good UV-vis absorbance from the porphyrin nanorods assembled on the PEI-modified membranes could find potential use as chemical or biological sensors, or in photonic applications.

**AFM of porphyrin nanorods on track-etched membranes.** AFM observations on the membranes after 0, 4, and 6 insertions are presented in Fig. 7. Some of

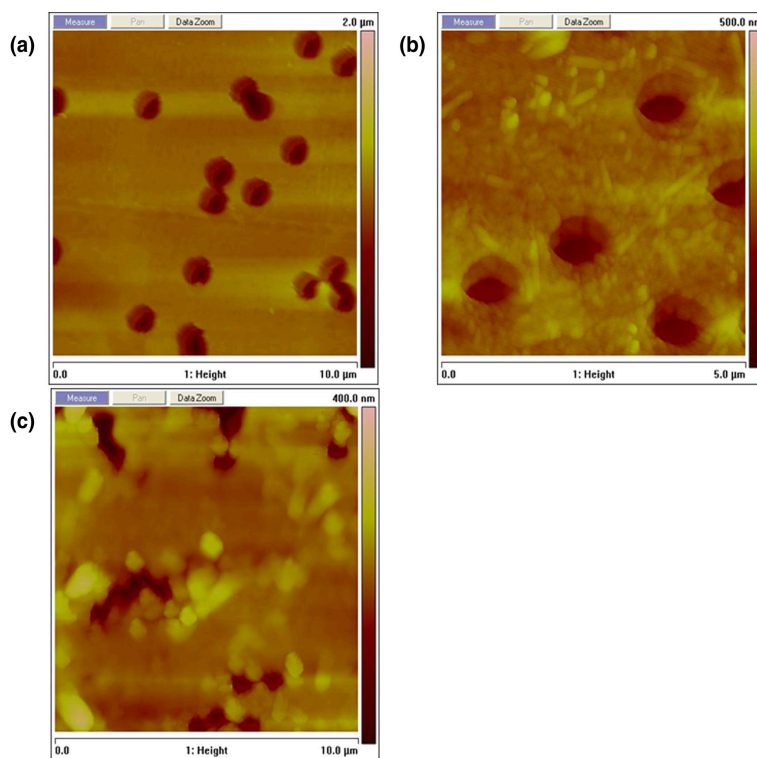


Fig. 7. (a) AFM image of the unexposed PEI-modified membrane, (b) the PEI-modified membrane after four exposures to the mixture of  $H_4TPPS_4^{2-}$  +  $SnTPyP^{2+}$ , and (c) the PEI-modified membrane after six exposures to the  $H_4TPPS_4^{2-}$  +  $SnTPyP^{2+}$  solution

the porphyrin nanostructures were aligned vertically and the membrane pores were not blocked by the porphyrin nanostructures.

However, by the sixth insertion (Fig. 7c) the pores on the PEI modified membrane had lost the characteristic circular shape and adopted a more irregular and slit-like appearance. The use of the layer-by-layer technique allows for the vertical alignment and immobilization of the porphyrin nanorods, and when compared to the filtered system, it is expected there will be a greater surface area. The orientation may explain the slightly better absorbance values obtained with the composite system made using the layer-by-layer technique.

An excellent review by Ariga *et al.* describes various assembly strategies to produce two-dimensional assemblies of porphyrin molecules on various surfaces [20]. In contrast our work has produced three-dimensional arrays of porphyrin molecules on porous substrates via self-assembly strategies, and by altering the surface charge we can induce the assembly of porphyrin molecules of interest.

## CONCLUSION

PEI was successfully used to modify the overall surface charge of PET track-etched membranes from net negative to positive at a pH = 6.0. The PEI-modified membrane was then used as a template for the ionic self-assembly of porphyrin nanotubes via a layer-by-layer technique. Characteristic absorption peaks at 423, 493, and 706 nm, indicative of porphyrin nanotubes, were observed using UV-vis spectroscopy.

Unmodified and modified membranes were able to induce self-aggregation of porphyrin molecules with the corresponding charges. Use of the unmodified membrane resulted in nanostructure formation with SnTPyP<sup>2+</sup>, whilst the modified membrane induced similar aggregation with the H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>.

Colloidal solution of porphyrin nanorods, obtained using similar methods developed by Wang *et al.*, were filtered through track-etched membranes with diameters 20–1000 nm. The nanorods formed an interwoven network on the surface of the membranes even at pore diameters greater than the average length of the nanorods (400–600 nm). UV-vis comparison of filtration and layer-by-layer technique resulted in slightly better absorbance values, and may be attributed to the difference in orientation of the nanorods on the surface of the membrane.

The assembly of porphyrin nanotubes on track-etched membranes can be easily achieved through altering the surface charge of the respective membranes. Surface coverage of the modified membranes using a layer-by-layer technique is maximized after only a few insertions, and the resulting modified membrane has an excellent absorbance signature which may be exploited in porphyrin sensor or photonic applications.

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