AFM Imaging of Binary Porphyrin Nanostructures

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Introduction:
Porphyrrins are known to form self-assembled supramolecular structures with useful electrical and optical properties. Although there is a great deal of research on the photonic properties of such materials, not much is known about the internal structure of the nanometer scale aggregates that they form. In this project we examine such a structure formed from two ionic porphyrin molecules, tetra(sulfonatophenyl)porphyrin (TSPP) and tetra(pyridyl)porphyrin (TPyP).

Atomic force microscopy (AFM), ultraviolet-visible (UV-vis) spectroscopy and transmission electron microscopy (TEM) were used to examine the structure of the rods. AFM displays a topographical image of a surface by detecting the deflection of a cantilever as it moves across the surface. UV-vis measures the absorption of molecules at different wavelengths within the ultraviolet and visible spectrum. TEM sends an electron beam through a thin sample and an image is produced from the interaction between the sample and electron beam.

Methods:
To prepare a 15 μM: 15 μM TPyP:TSPP solution sample at pH 2, 100 μl of 1M HCl was added to a flask, followed by 309 ul of a 485 μM TPyP solution and 275 ul of a 546 μM TSPP solution. This mixture was then diluted up to 10 ml with MilliQ H2O (18 MΩ). 5 μM: 5 μM solutions were also prepared in a similar manner. The solution sat up to a day to allow the aggregates to form before depositing. In order to get an even distribution of nanorods on the surface of the substrate, 1-2 drops of the solution were deposited for 1 min, followed by a 30 sec spin and repeated 10 times.

AFM was used to determine the best deposition times as well as view the heights and lengths of the TSP-TPyP nanorods. UV-vis was used to look at both the monomer (unaggregated molecules) and aggregate solutions to compare their electronic absorption spectra. TEM was used to obtain higher resolution images of the rods.

Results:
The UV-vis data of the TPyP, TSPP, and mixture of TSPP:TPyP suggested that the transformation from monomer to aggregate occurs in solution. This is based on the shifts in the Soret and the Q bands. The aggregate solution also has a peak at 490 nm, showing a change in the electronic properties between the monomer and aggregate solutions. The TSP-TPyP aggregates form in clumps and can grow quite large, as seen in AFM images (Fig. 2). In order to prevent clumping on the substrate surface, a shorter deposition time was used (1 min deposition, 30 sec spin, 10 times). The average height of the rods was 60 nm and the average length was 5 μm. AFM also allowed us to follow the progress of the nanorod growth (Fig. 3). After 24 hours, the rods had already grown to be over 5 μm in length and over 30 nm in height. Because of tip convolution in AFM, TEM was utilized to confirm the widths of the aggregates and to investigate their internal structure. From the TEM images, the TSP-TPyP aggregates are nanorods and not nanotubes, as can be seen in the absence of a tubular wall.

Conclusions:
UV-vis data shows a change in electronic structure between the monomer and mixed solutions indicating aggregate formation. From AFM and TEM images we have been able to observe the aggregate structures formed by TSP and TPyP at pH 2. These images confirm a solid, layered nanorod structure. The actual inner structure of the nanorods is unknown. However, spectroscopic and microscopic studies are underway to further elucidate their internal structure. Understanding the structure would be simplified by finding a way to form smaller rods, such as determining an optimum time to deposit after mixing. Access to small rods would allow for the application of scanning tunneling microscopy (STM) and would potentially provide atomic scale images.

References:

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