pH Dependence of the Physical and Electronic Structure of a Supramolecular Porphyrin Assembly

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Abstract
Porphyrins are essential molecules to many biological processes, and have potential applications ranging from light energy harvesting to photodynamic therapy. Under certain conditions, porphyrins self-assemble into novel supramolecular structures. We are investigating the effects of changes in pH on assemblies of meso-tetra(carboxyphenyl)porphyrin (TCPP) using electronic spectroscopy and atomic force microscopy (AFM). Nanorods with high aspect ratios are formed at low pH, notably without the use of a stabilizing compound. Future work will involve determining the conductivity of the nanorods.

Introduction
- Porphyrins can self-assemble into supramolecular structures via noncovalent forces
- Porphyrin assemblies in nature can act as electron transport chains and chemical sensors
- Protonation of inner nitrogens can result in physical and electronic distortions.
- In acidic solutions (pH< 5) successive protonation of the pyrrole nitrogens results in monoacid and diacid forms of the porphyrin molecule.

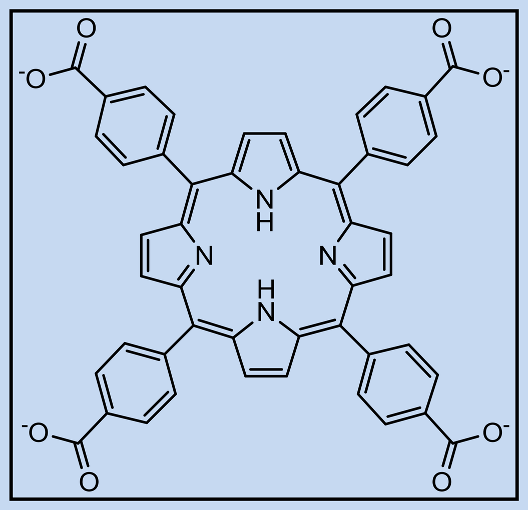


Figure 1. Ionized form of the free base form of TCPP

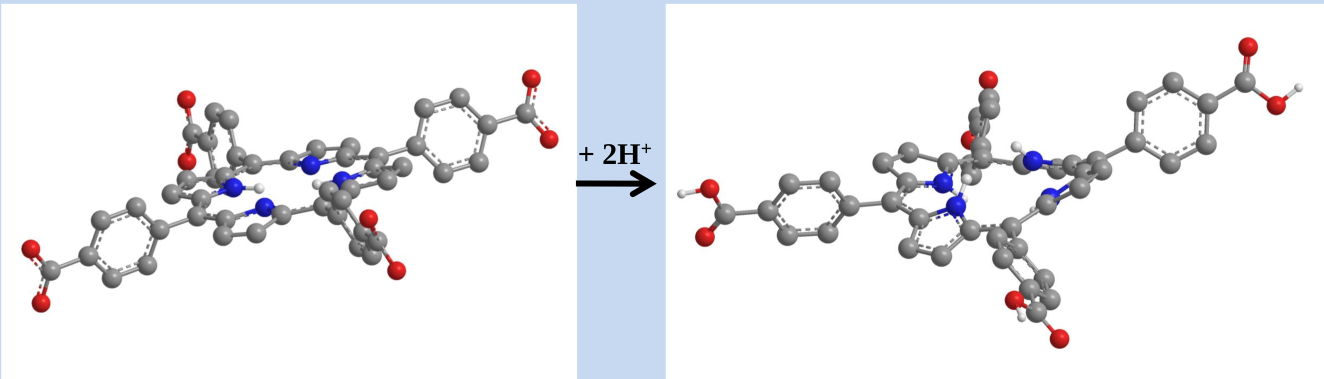


Figure 2. Molecular models of a TCPP distorted by pyrrole nitrogen protonation

- The TCPP monoacid is difficult to isolate
- We want to determine the protonation states and associated chemical and morphological properties of TCPP nanostructures

Experimental
TCPP solutions were made by dissolving solid TCPP in dilute ammonium hydroxide, then titrating with HCl to a desired pH[1].
UV-Vis. A Perkin-Elmer 330 Spectrophotometer with 0.1578 cm quartz cuvettes was used to collect TCPP solution UV-Vis spectra.
AFM. TCPP solution was deposited on a HOPG substrate, followed by spin drying and washing with HCl. Nanorods were imaged on a Digital Instruments AFM operated in tapping mode using silicon cantilevers under ambient conditions. A setpoint of ~2 V and resonant frequency of ~393 kHz were used.
XPS. TCPP nanorods were filtered and air dried. Powder and nanorod TCPP samples were pressed into indium foil, then analyzed with a Kratos X-Ray Photoelectron Spectrometer.

Results and Discussion

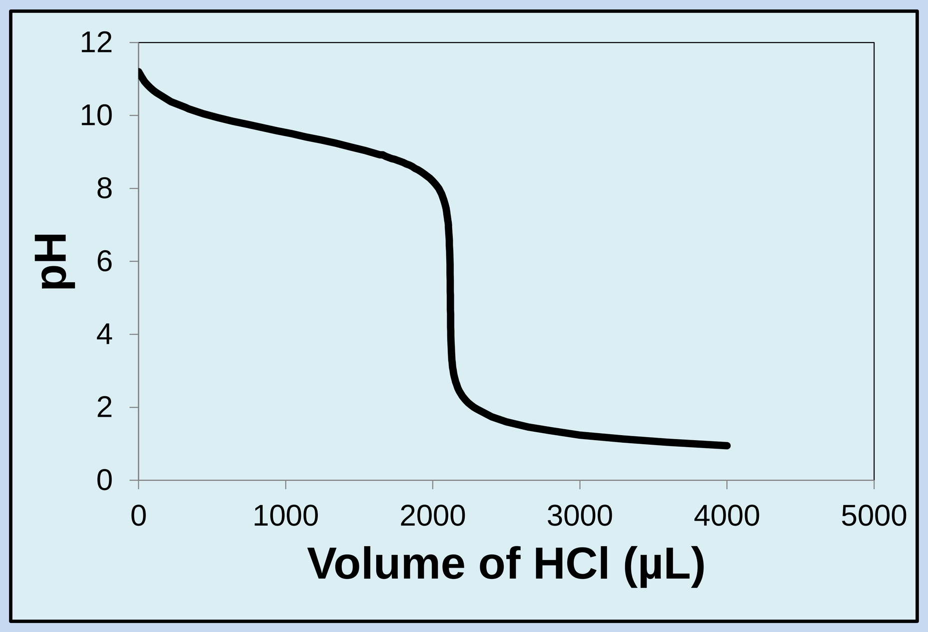
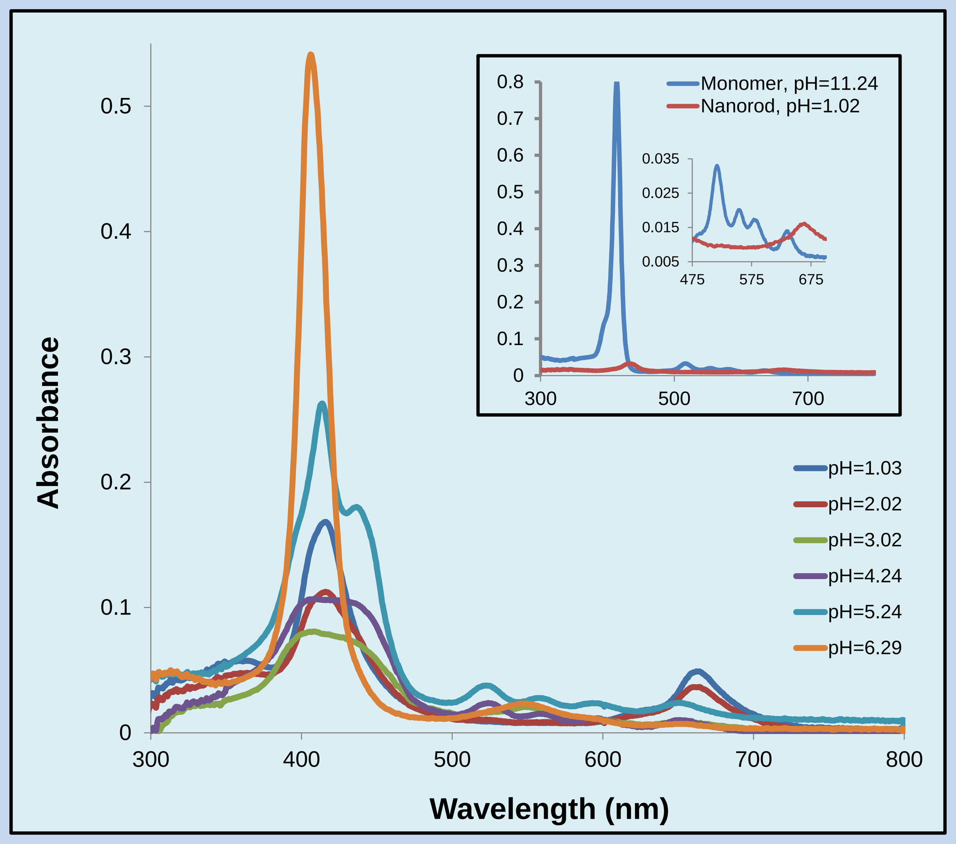


Figure 3. Titration curve of TCPP in NH_4OH with HCl

Only one equivalence point (~ pH 5) is observed even though TCPP has several unique basic moieties: the carboxylates and the pyrrole nitrogens.

Figure 4. UV-Vis spectra of aqueous TCPP solutions. Inset shows the spectral differences between TCPP monomer and self-assembled species, with the 475-700 nm region offset to highlight the redshift and collapse of the Q bands



- TCPP in free base form is present at basic pH.
- Near pH 5 the carboxyl groups become protonated. Subsequently, diacid species form. This is signaled by a slightly red-shifted Soret band near 415 nm and the appearance of a new band near 430 nm. There is also a change in the position of the Q bands.
- Self-assembly ensues as the pH decreases further.
- Nanorods form around pH 1 and precipitate out of solution. This causes light scattering, which decreases the measured absorbance.

pH	Soret Bands (nm)	Q bands (nm)
0.01	419	666
1.03	415.5	663.4
2.02	416.5	666
3.02	407.5, 426.5 (shoulder)	551.5, 658.9
3.86	408, 419 (shoulder)	525.5, 558.5, 595, 654
4.75	411.5, 434.5 (shoulder)	520.5, 566, 599, 664
5.74	412.5	525.5, 558, 601.5, 652

Figure 5. Absorption bands of TCPP as a function of solution pH

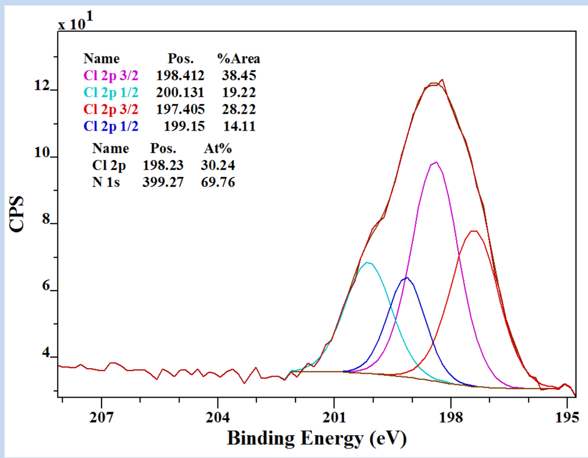


Figure 6. Cl 2p XPS of TCPP nanorods formed at ~ pH 1

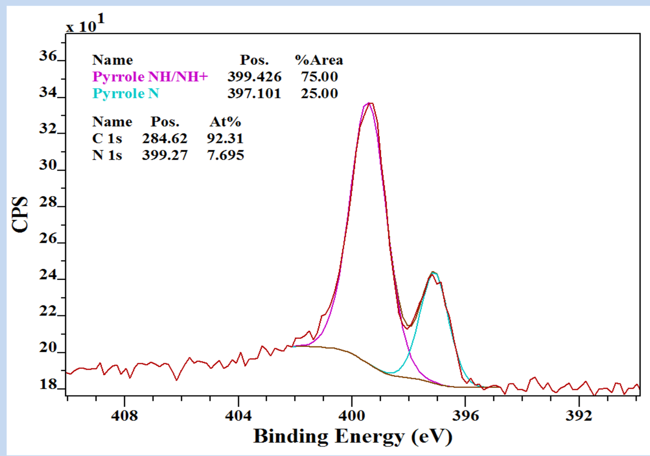


Figure 7. N 1s XPS of TCPP nanorods formed at ~ pH 1

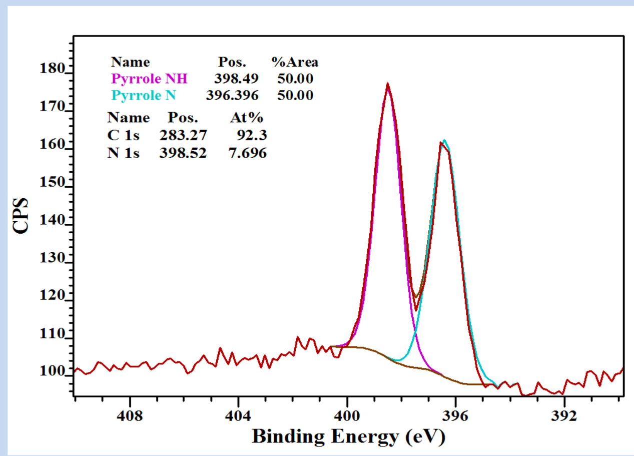


Figure 8. N 1s XPS of TCPP powder

- Two unique chlorines observed in TCPP rods: one associated with TCPP and one with NH_4Cl.
- Presence of unprotonated nitrogen in nanorods can be due to the presence of either monoacid or free base TCPP, or both.

	NH:N ratio
TCPP free base	1:1
TCPP nanorods	3:1

Figure 9. Relative ratios of protonated to unprotonated nitrogens

Figures 10 – 15. Tapping mode AFM images of TCPP nanorods prepared at various pHs and washed with dilute HCl unless indicated otherwise

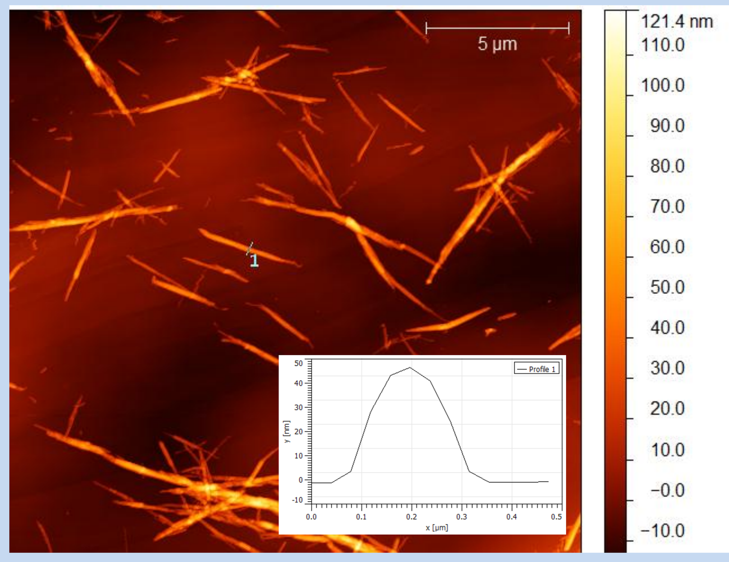


Figure 10. pH 1.02, not washed with HCl. Inset shows cross section of a single nanorod

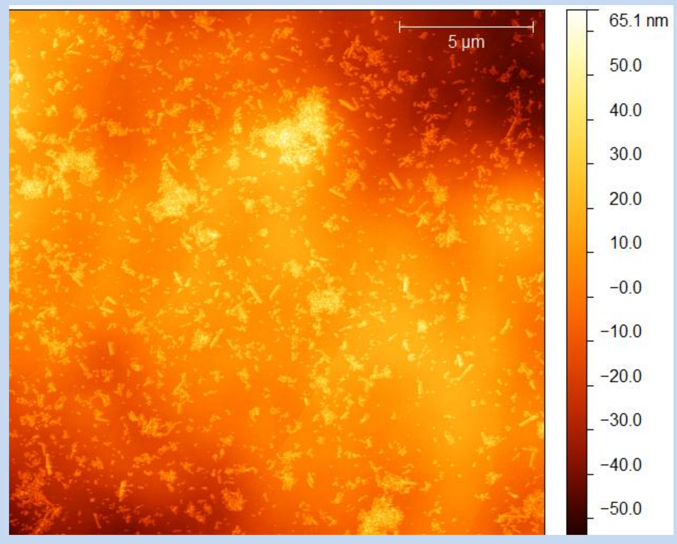
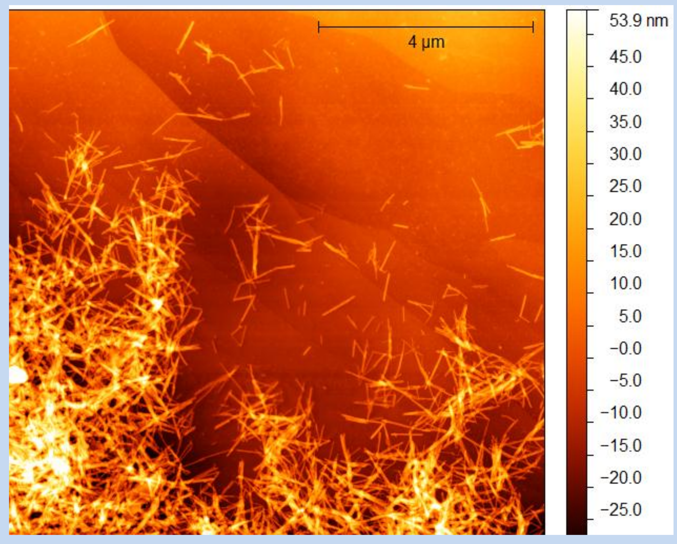


Figure 11. pH -0.42



Fgure12. pH 0.52

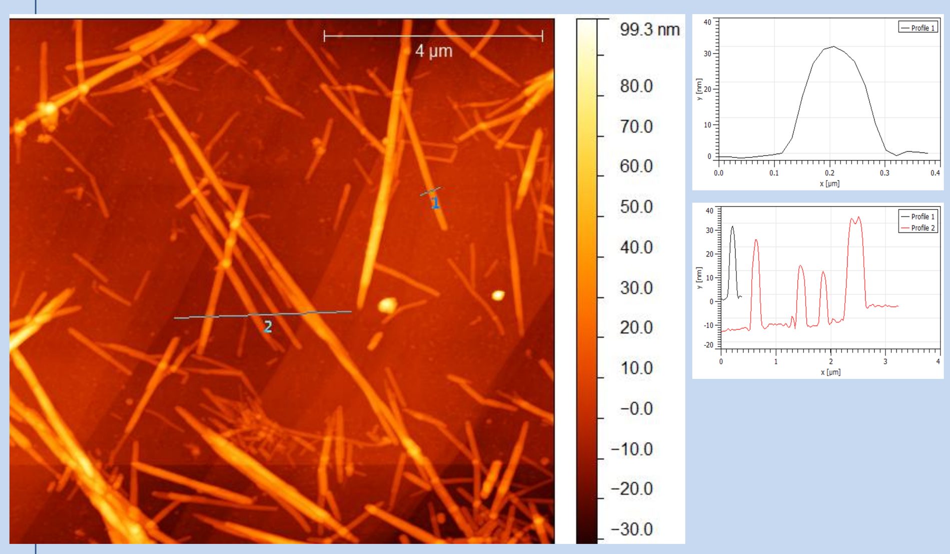


Figure 13. pH 1.03 and cross sections of several nanorods

- Longest nanorods occur around pH 1.
- Similar width and height for all rods
- Rods not washed with HCl solution appear similar to those that were (compare Figures 10 and 13).

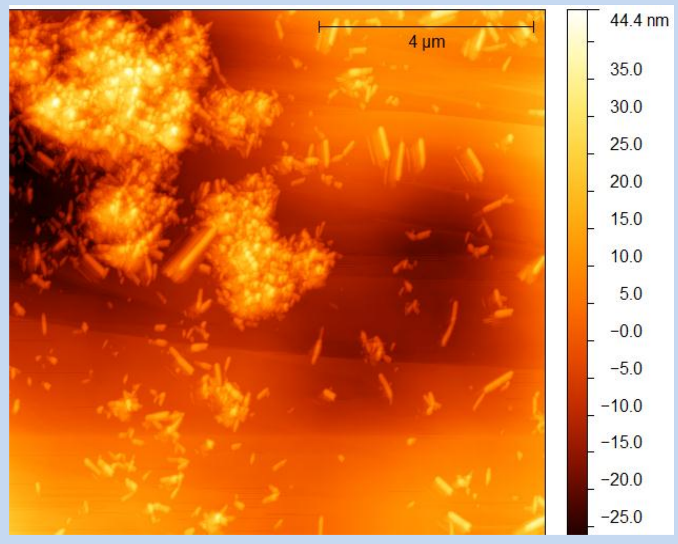


Figure 14. pH 1.57

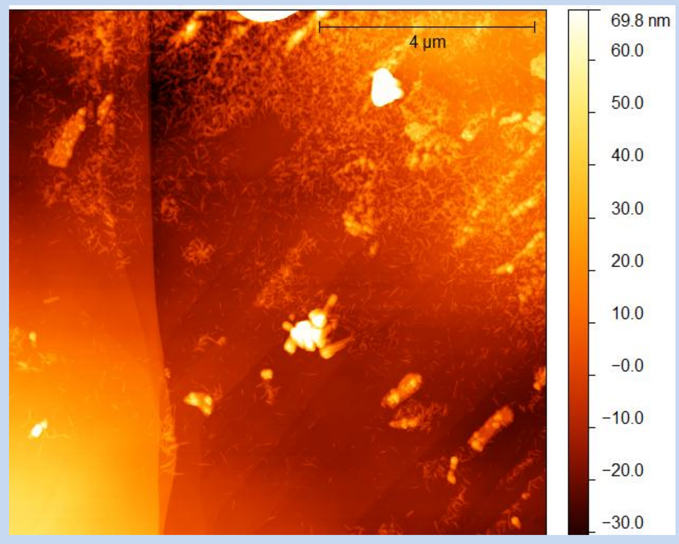


Figure 15. pH 4.04

Conclusions
- UV-Vis spectra indicate several different species are present in pH 0 to pH 6 TCPP solutions.
- XPS shows that the ratio of NH:N in TCPP powder is 1:1 and in the nanorods that ratio is 3:1. Cl is present in the nanorods.
- High aspect ratios of TCPP nanorods are most favored at pH 1.
- Washing the nanorods with HCl solution removes the NH_4Cl salt but does not appear to effect the nanorod's morphology.
- Future work: Conducting AFM will be used to determine the conductivity of individual nanorods.

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References: 1. Wan, A.; Bueso-Mendozal, D.; Luo, Z.; Batteas, J. D. Directed assembly of Porphyrin Nanostructure. *Polymer Preprints* **2011**,*52*,807.