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Self-Assembly of Porphyrin Nanostructures

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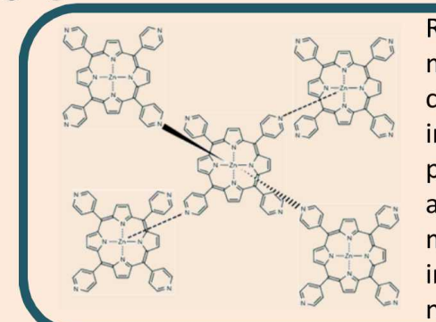
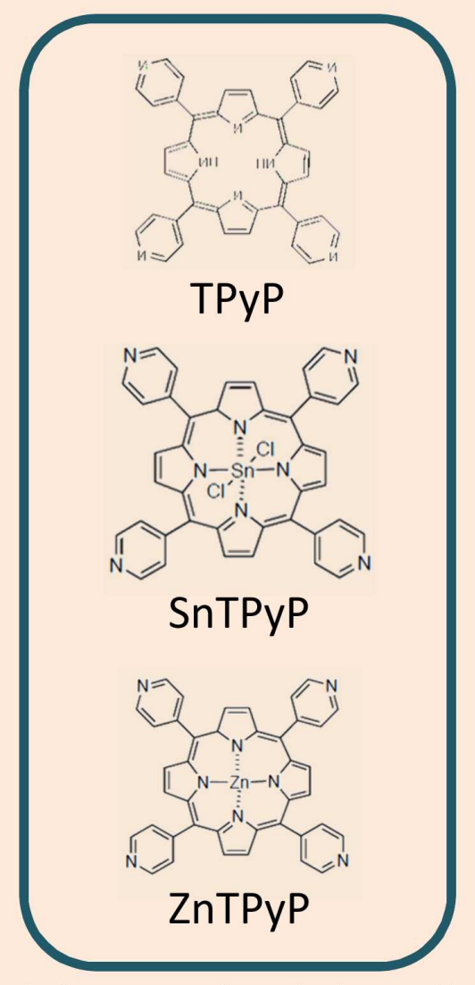
Background – Why Porphyrins?:



Representation of metal-ligand coordination interactions promoting self assembly of metalloporphyrins into organized nanostructures



Chemical structure of porphyrins used in our investigation of self-assembly methods. We focused on using meso-tetra pyridine type porphyrins for our study.

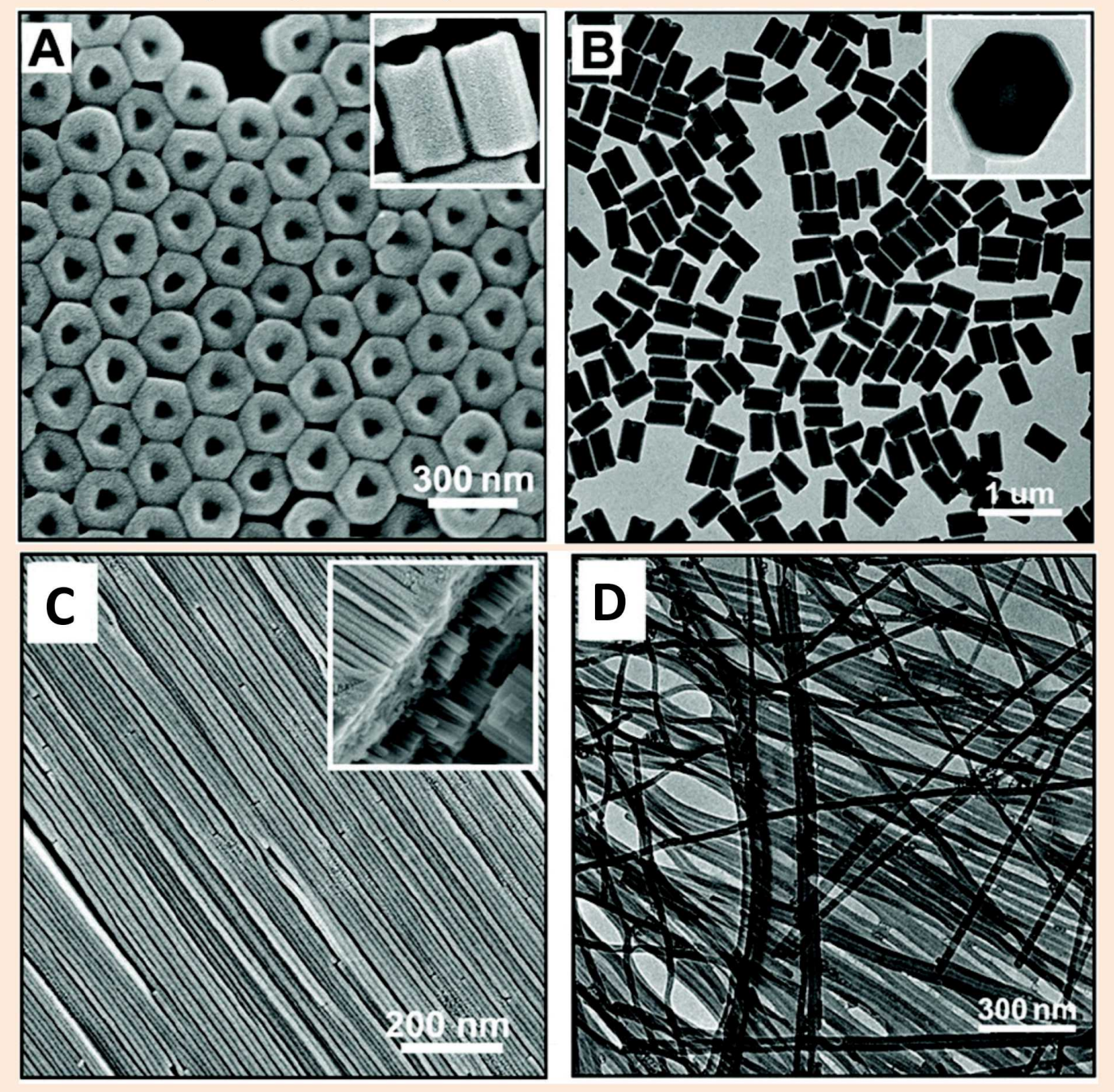
Porphyrins are a class of optically active biomacromolecular compounds which play critical roles in many biological energetic processes including photosynthesis, and also serve as colorful pigments covering a wide range of the visible spectrum. In an effort to utilize these versatile porphyrins for advanced materials development, organized porphyrin nanostructures with photoactive properties have been obtained through a surfactant-assisted non-covalent self-assembly method (π-π interactions and ligand coordination) through the cooperative interactions of the porphyrin building blocks including zinc meso-tetra(4-pyridyl)porphine, tin meso-tetra(4-pyridyl)porphine, and meso-tetra(4-pyridyl)porphine. This method takes advantage of porphyrin insolubility when deprotonated in solution due to acid-base neutralization, thereby forcing them into surfactant micelles which stimulates self-assembly and eventually yields well-defined controllable and reproducible external morphology. The unique collective optical properties displayed by self-assembled porphyrin nanostructures over their individual chromophores, appear highly favorable for exciton formation and transport. With active and responsive optical properties, these porphyrin structures look to serve as promising components for a wide range of practical applications including sensing, diagnostics, solar cells, photocatalysis, and photodegradation of pollutants.

Previously Achieved Structures:

Our following investigation is based on a previous paper published from our group: "Porous One-Dimensional Nanostructures through Confined Cooperative Self-Assembly" (Bai et al. *Nano. Lett. 2011, 11, 5196*)

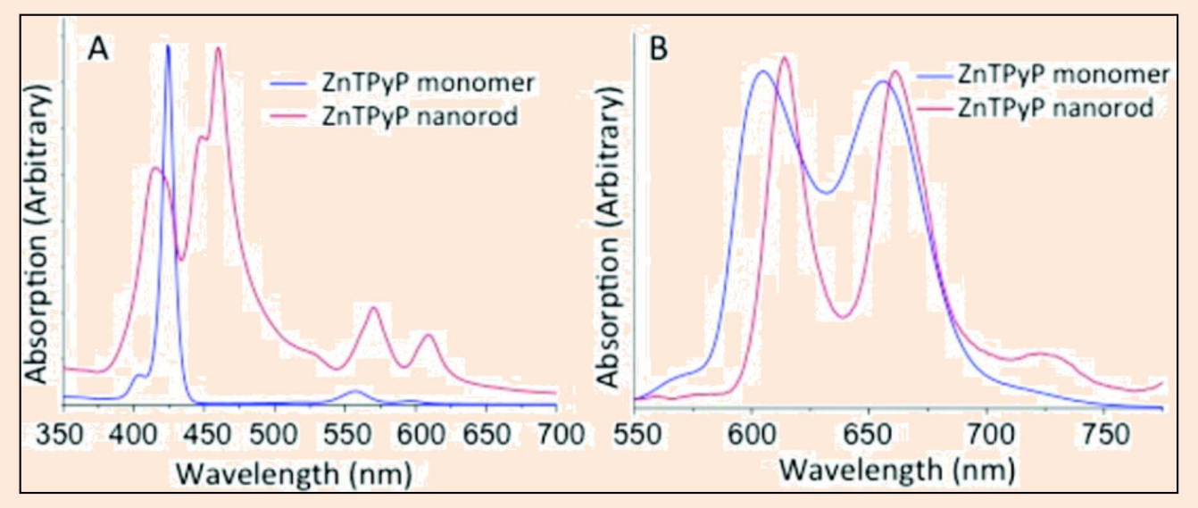
Some useful findings achieved include:

- ZnTPyP self-assembly
- Hollow hexagonal nanorods
- Thin nanowires & bundles
- Red shift in absorption and fluorescence
- Exciton coupling & transport



Some organized ZnTPyP nanostructures have previously been achieved by our group. A) SEM image and B) TEM image of hexagonal nanorods prepared through confined cooperative self-assembly of ZnTPyP using sodium dodecyl sulfate (SDS) as a stabilizing surfactant. C) SEM image and D) TEM image of nanowires prepared via confined cooperative self-assembly of ZnTPyP using cetyltrimethylammonium bromide (CTAB) as a stabilizing surfactant.

These structures represent only a portion of nanostructures possible for porphyrin self-assembly and their functional applications.

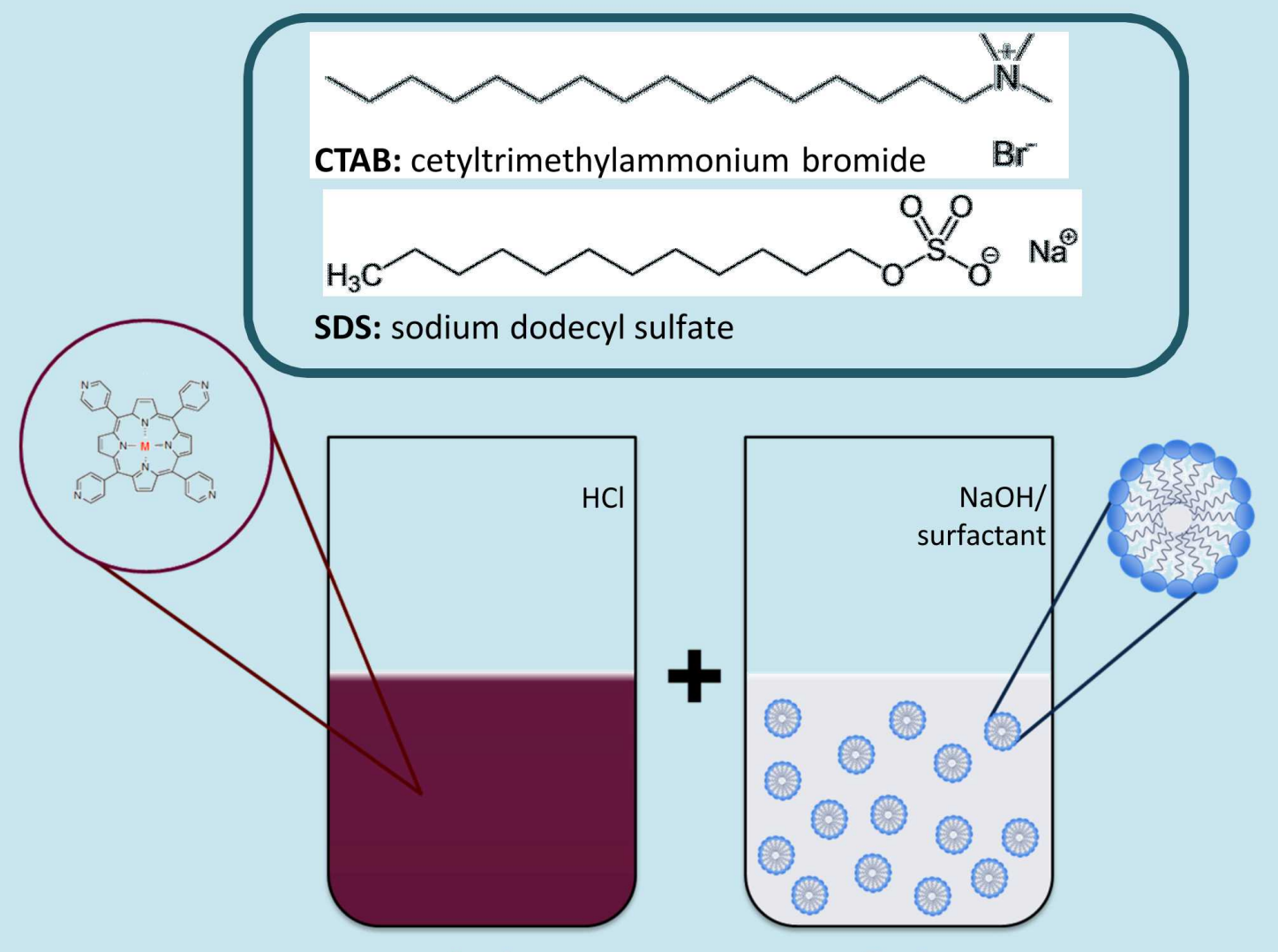


A) UV-Vis absorption and B) fluorescence spectra of ZnTPyP monomers compared to self-assembled nanorod structures. Assembled nanorods show a red shift indicative of exciton coupling.

Figures reproduced with permission from Bai et al. *Nano Lett. 2011, 11, 5196-5200*

Confined Cooperative Self-Assembly:

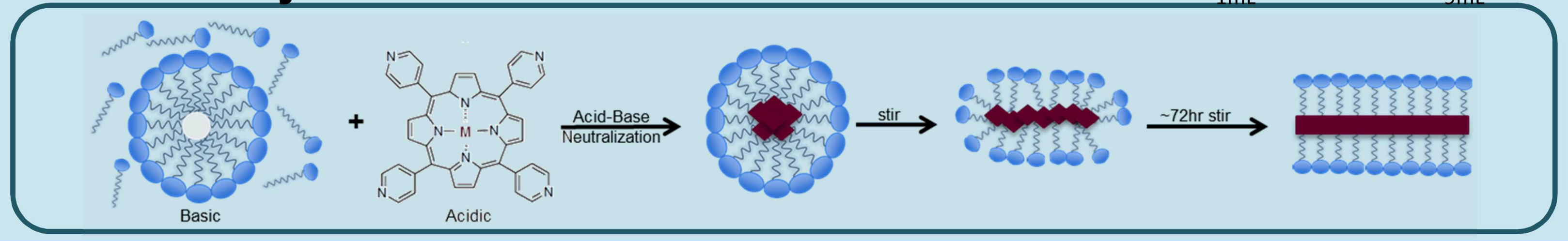
- Molecular porphyrin– 0.1M HCl (pH 1)
- Surfactant solution – 0.02M NaOH (pH 12.3)
- CTAB and SDS surfactants used to form micelles
- Acid-base neutralization causes deprotonation of porphyrin making it insoluble in the solution.
- Porphyrin becomes encapsulated in surfactant micelles promoting nanostructure self assembly.



CTAB: cetyltrimethylammonium bromide

SDS: sodium dodecyl sulfate

Self-Assembly Process:

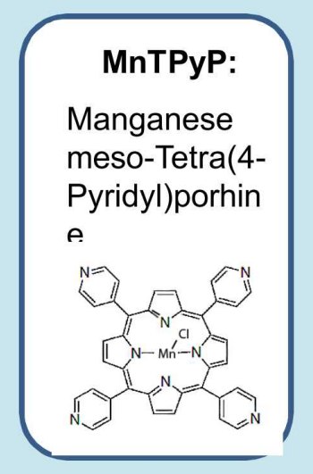


Controlling Parameters - Slow Injection:

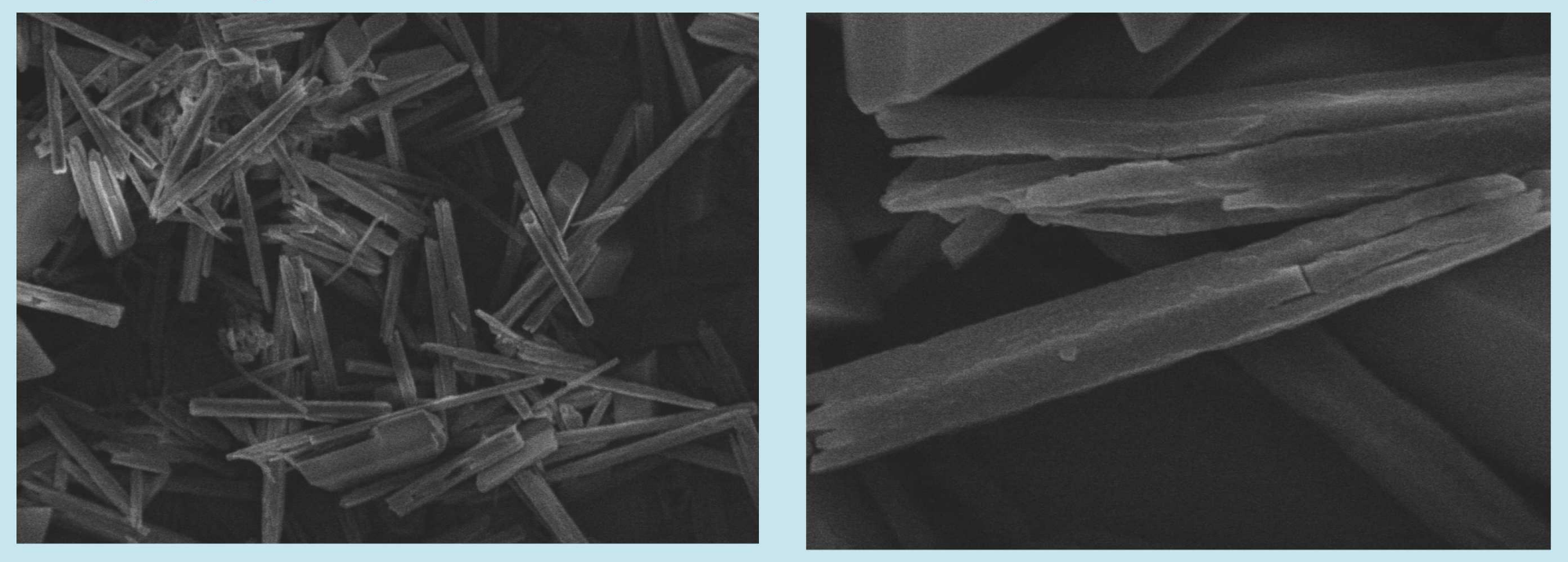
Alternate approach to inducing confined cooperative self-assembly of organized porphyrin nanostructures:

- Slow neutralization process
- Slow injection of base/surfactant solution - pH 12.34
- 1 mL/hr – 4.5 hr neutralization reaction
- Gradual porphyrin nanostructure nucleation
- Organized morphology, variable size
- Improvement on time constraints
- Optical activity

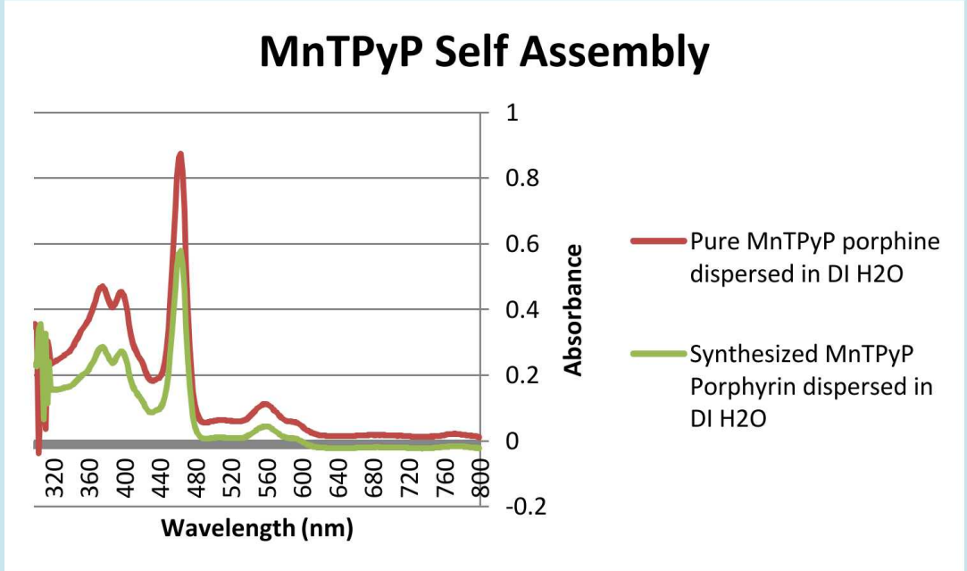
Metal Porphyrins:

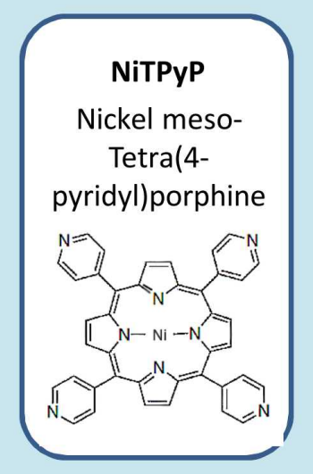


MnTPyP:
Manganese meso-Tetra(4-Pyridyl)porhine

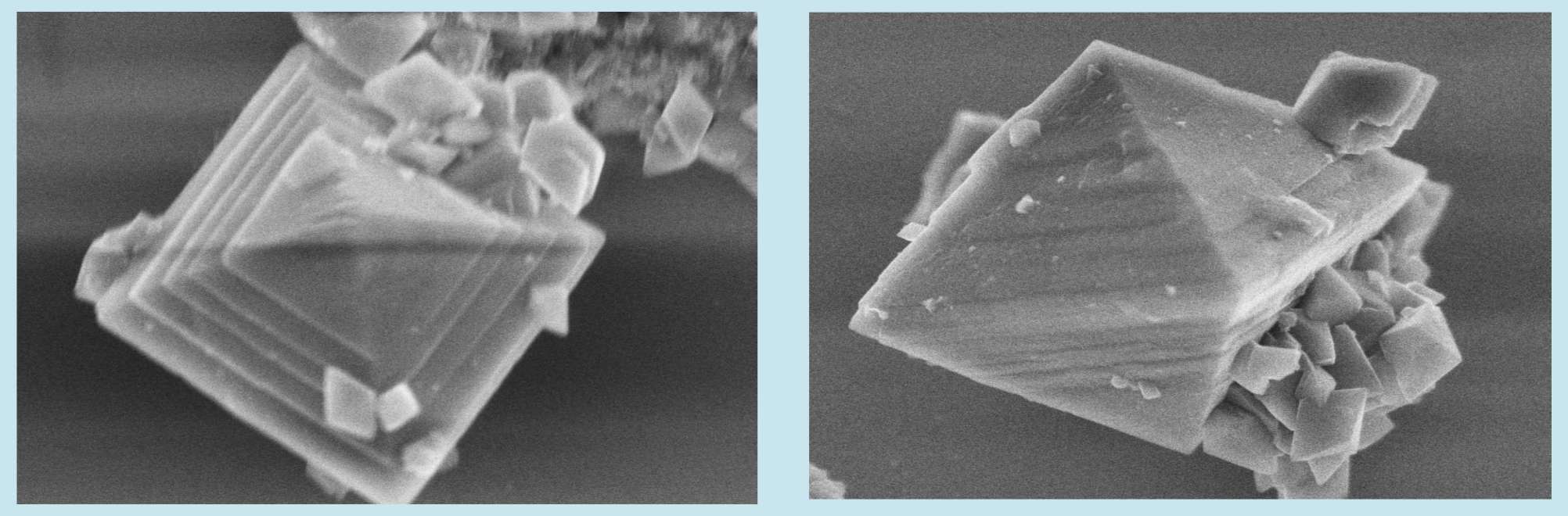


MnTPyP: Nanostructures obtained via slow injection with stirring using CTAB, over 4.5 hour period.

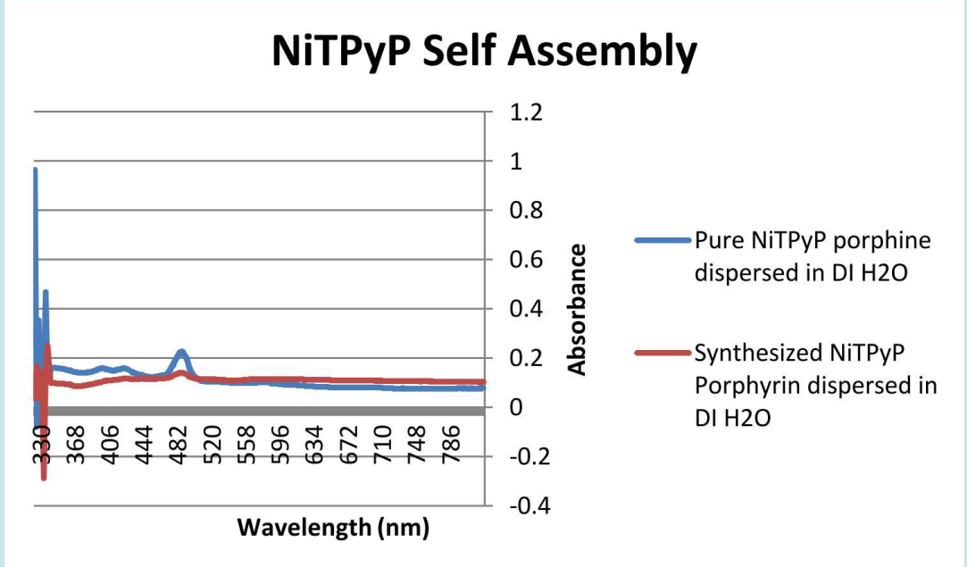


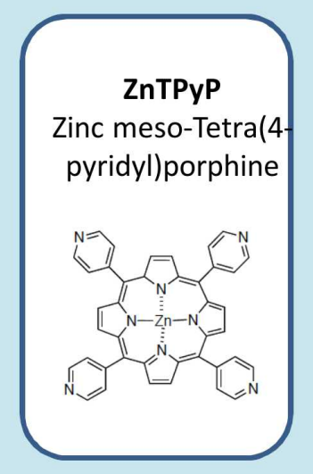


NiTPyP
Nickel meso-Tetra(4-pyridyl)porphine

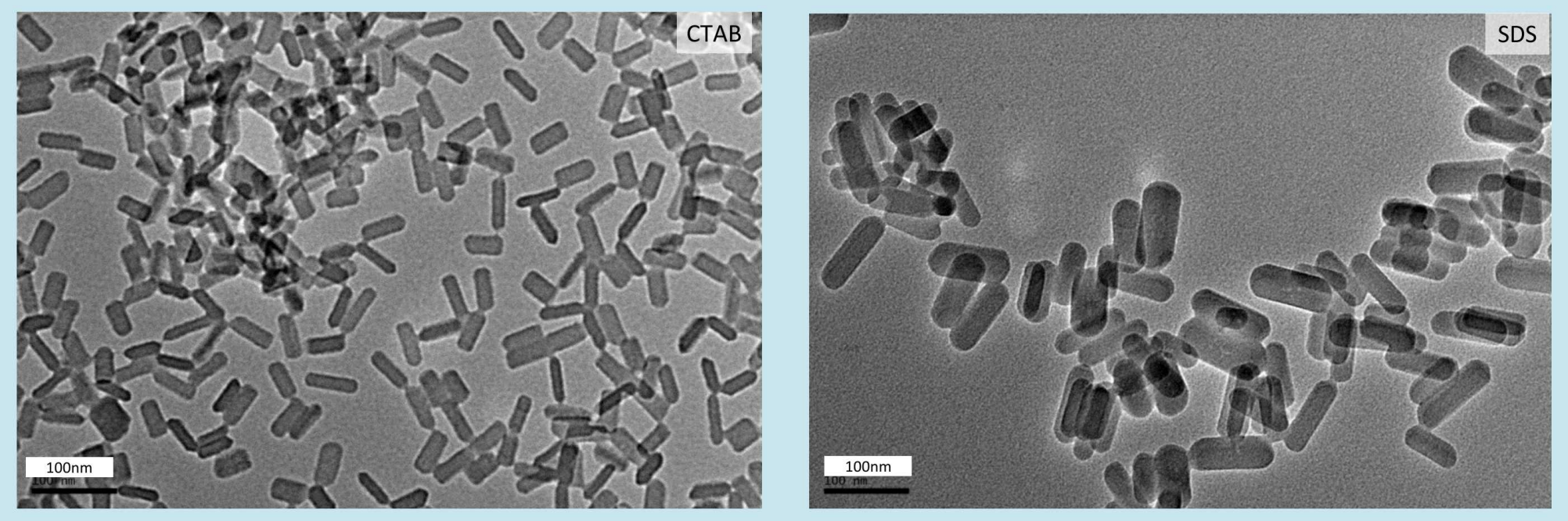


NiTPyp: Nanostructures obtained via slow injection method using CTAB with stirring, over 4.5 hour period.

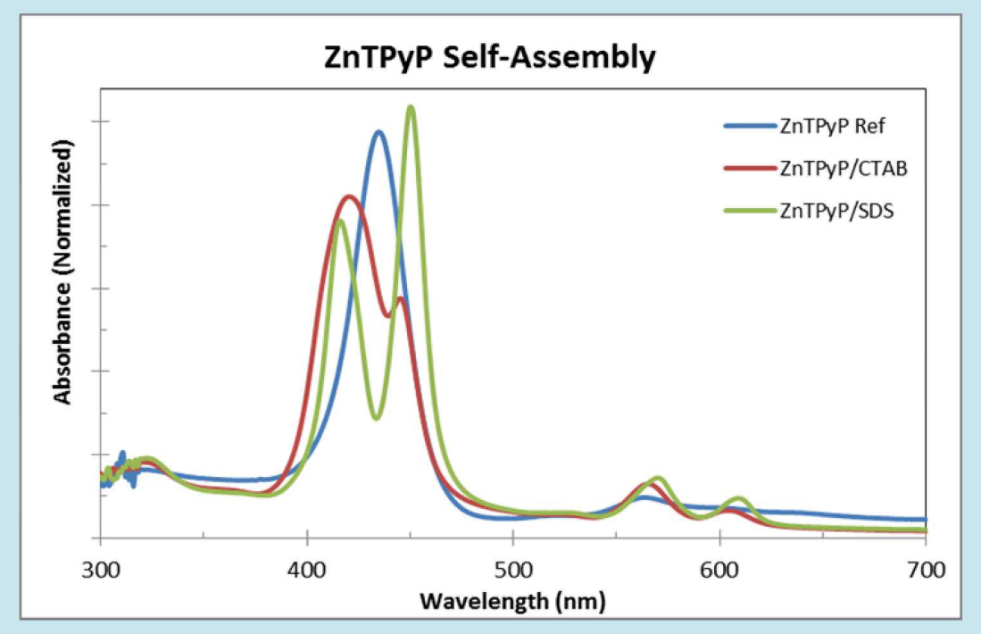


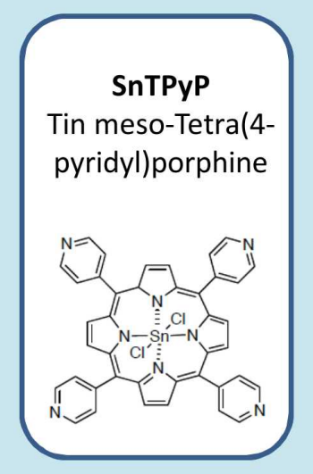


ZnTPyP
Zinc meso-Tetra(4-pyridyl)porphine

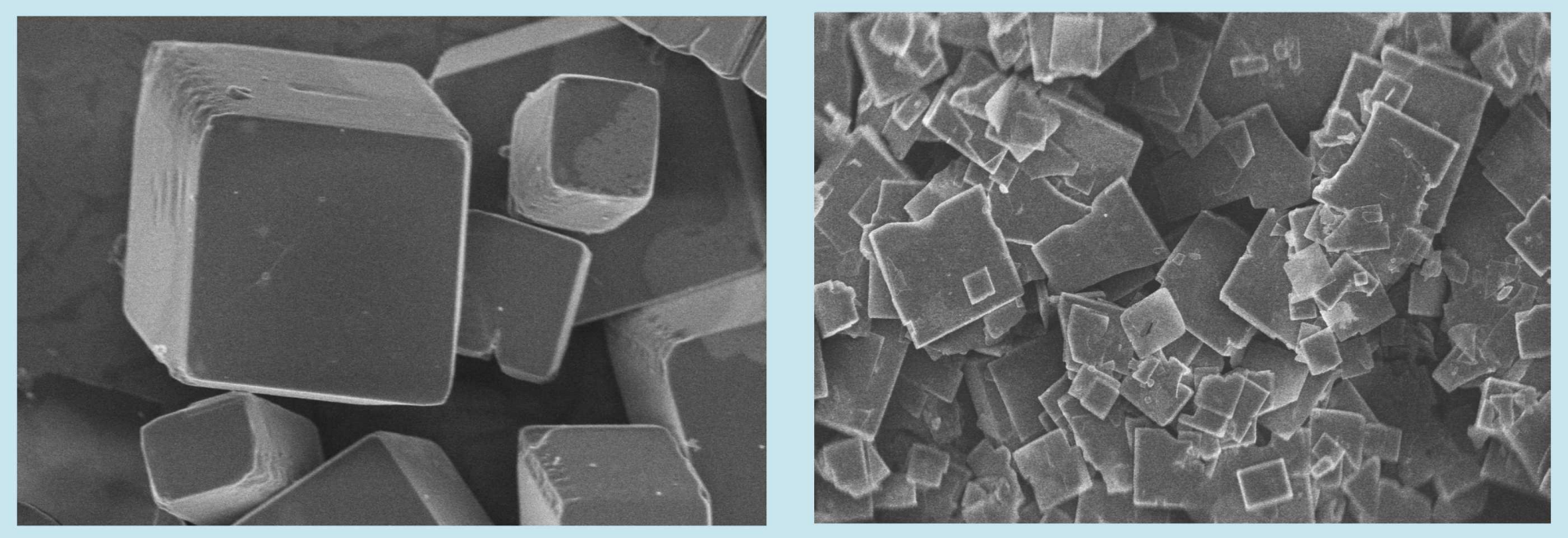


ZnTPyP: Nanostructures obtained via confined cooperative self-assembly using **CTAB** (left) and **SDS** (right), in an acid-base reaction stirred for 72hours.

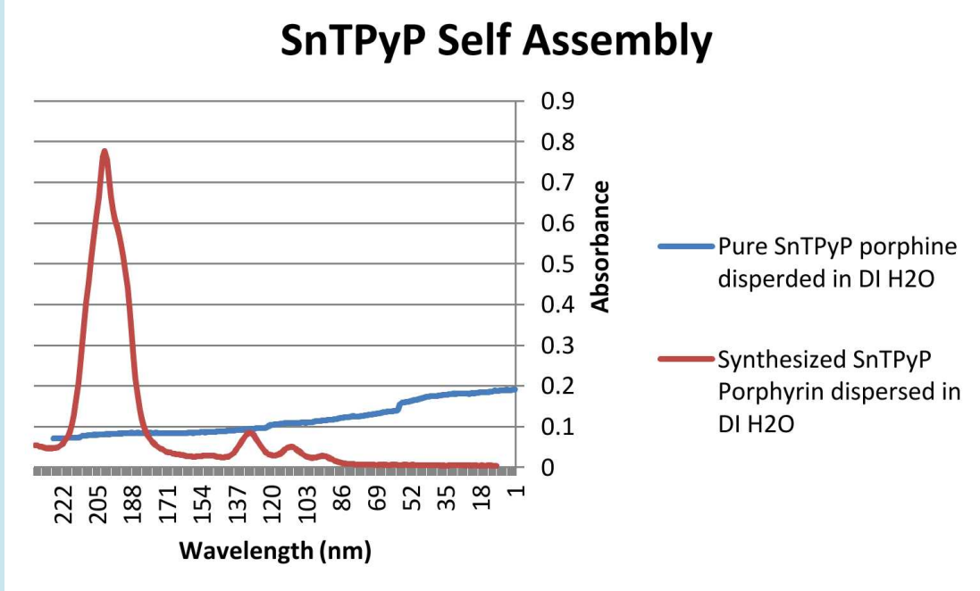




SnTPyP
Tin meso-Tetra(4-pyridyl)porphine



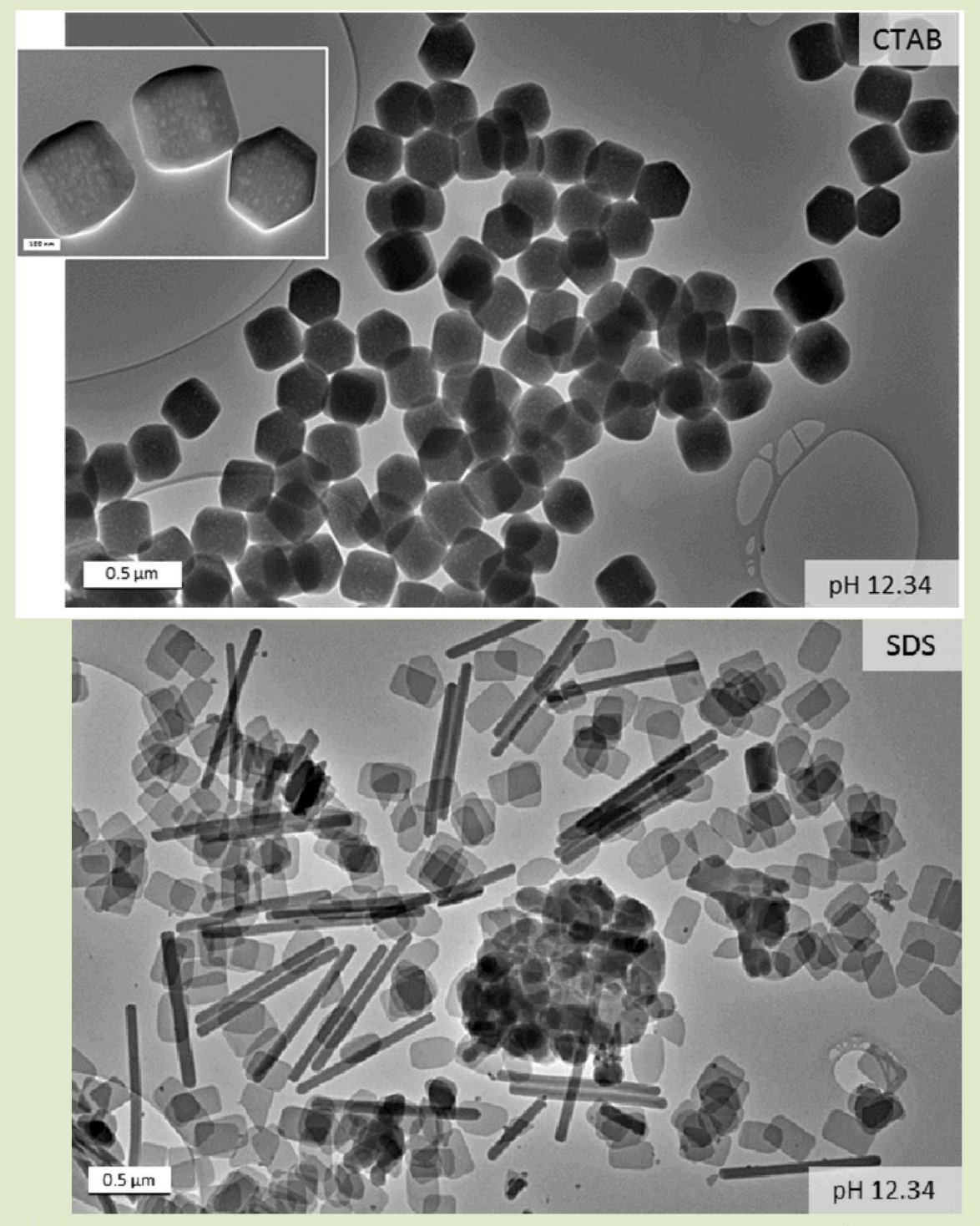
SnTPyP: Nanostructures obtained via emulsion sonication using SDS solution.



Method adapted from: Bai et al. *Nano Lett. 2011, 11, 5196-5200*

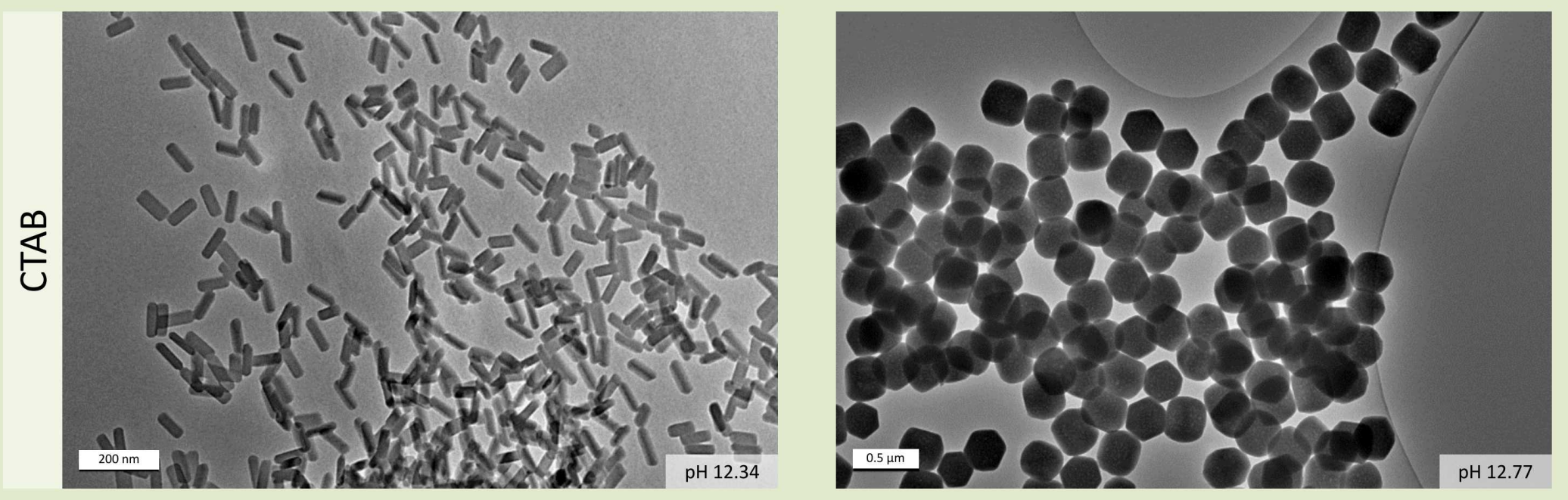
Controlling Parameters– pH tuning:

Shape and size of self-assembled nanostructures is extremely sensitive to pH of the reaction solution as influenced by tuning the initial pH of base used to initiate the neutralization reaction. When trying to replicate previously achieved short rod-like ZnTPyP nanostructures, instead a new morphology of hexagonal nanocylinders and a mixed morphology of short nanowires and rectangular nanoprisms was achieved by assembly in CTAB and SDS respectively. The difference in structure was determined to be an effect of varying pH from the previous trial. As a result a pH study was conducted to determine the effects of initial/final pH on the formation of self-assembled ZnTPyP nanostructures.

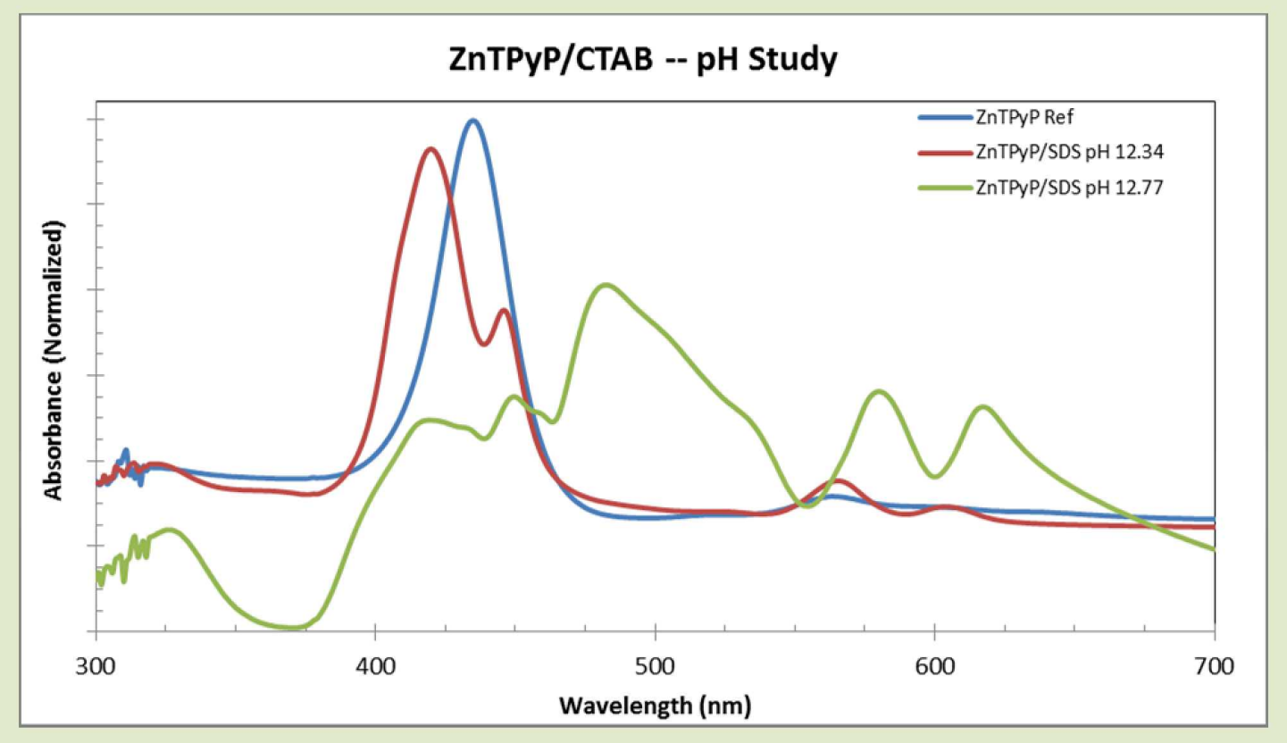


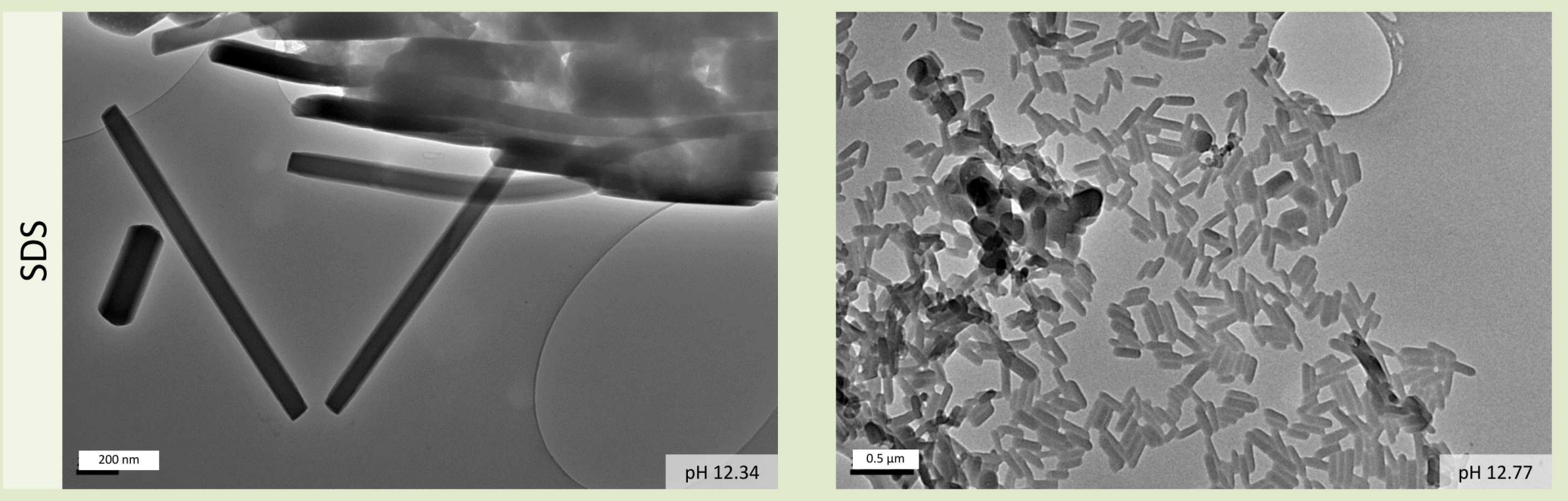
ZnTPyP nanostructures obtained through controlled cooperative self-assembly by CTAB (top) and SDS (bottom) surfactant solutions starting at a controlled pH of 12.34. CTAB assisted structure shows small nanocylinder like shapes with a hexagonal cross section (inset). SDS assisted structures show mixed morphology of short nanowires and small rectangular prisms.

ZnTPyP– pH Study:

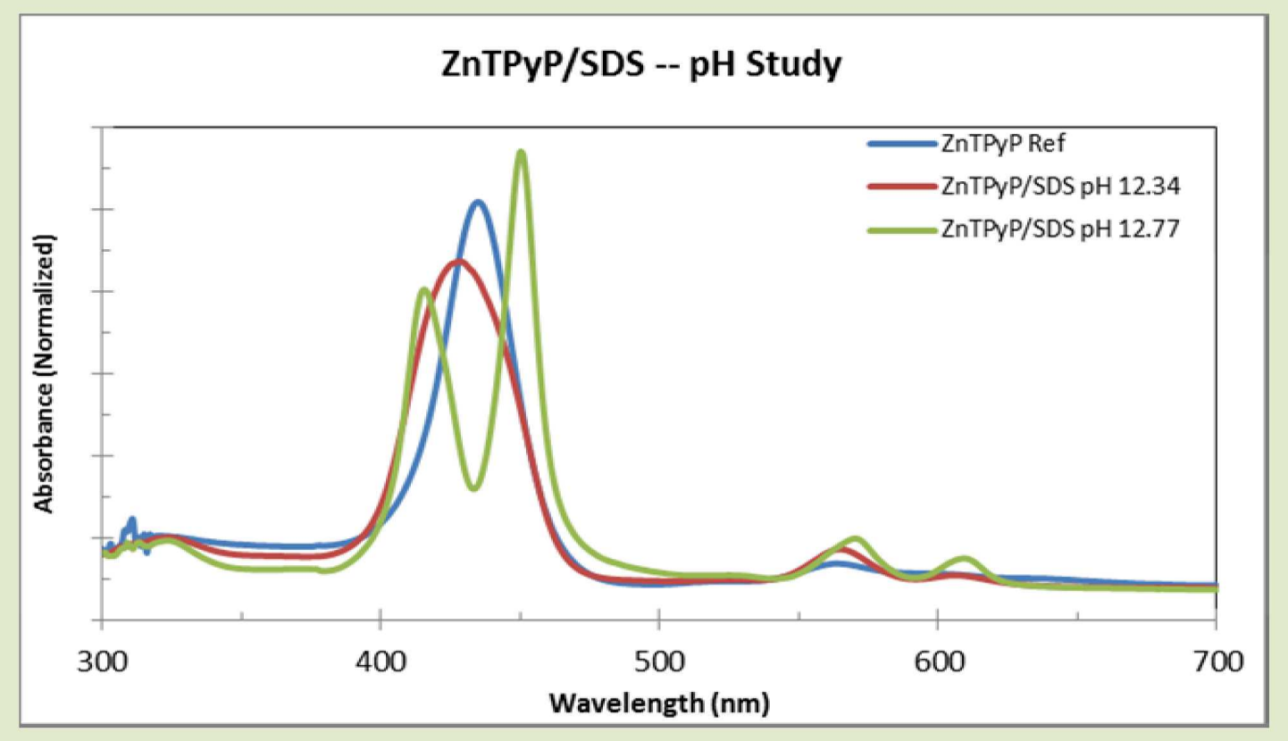


Shift in nanostructure morphology obtained through solution pH adjustment using confined cooperative self-assembly method with CTAB as the stabilizing surfactant. Increase of pH produces red shift in optical absorbance as well as a shape change towards larger surface area nanospheres.



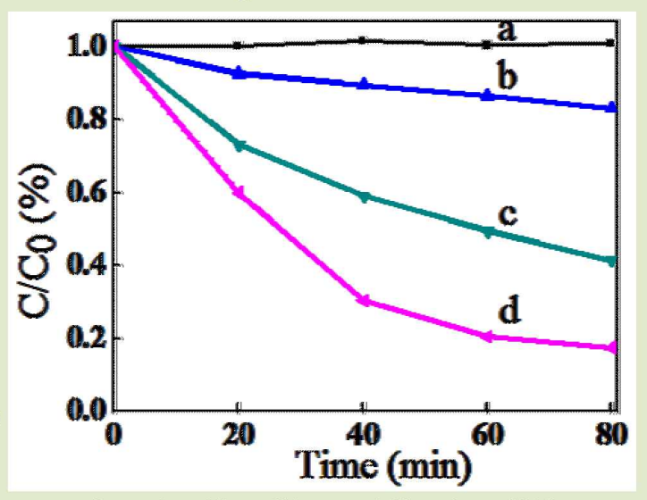


Shift of nanostructure morphology by pH adjustment using confined cooperative self=assembly and SDS as the stabilizing surfactant. An increase in the pH yields a red shift and splitting of optical absorbance along with a more uniform morphology of nanorod structures.



Applications:

- Dye sensitized solar cells
- Photocatalysis
- Photodegradation of pollutants
- Sensors
- Diagnostics



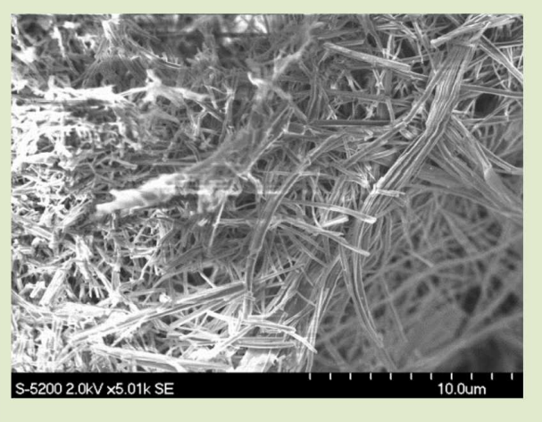
Photocatalytic activity of a) methyl orange (MO) and degradation of MO by porphyrin nanostructures: b) TPyP nanooctahedra, c) Zn metallized TPyP nanoparticles , and d) Zn metallized TPyP nanowires.

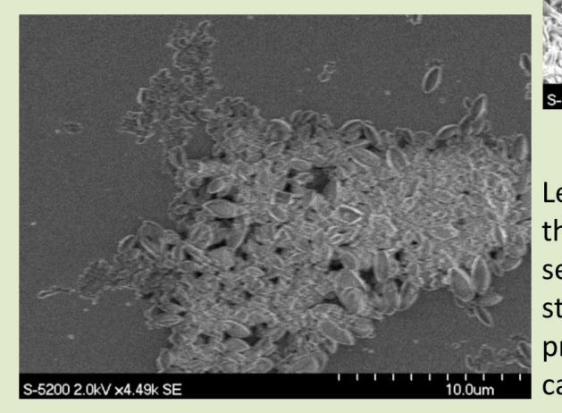
Reproduced from: Wang et al. *Nano Lett., 2016*

Future Work:

- Testing different metal and non-metal porphyrins
- Porphyrin solvent/anti-solvent interactions
- Slow diffusion
- Hot injection
- Micro-emulsion sonication

Right: Nanofiber structures produced through hot-injection assembly method using solvent/antisolvent interactions to rapidly insolubilize the porphyrin product.





Left: Nanostructures obtained through micro-emulsion process for self-assembly of TPyP porphyrin structures. Ultra sonication promotes nucleation within the cavities produced in the solution.

Conclusion:

Self-assembly of uniform porphyrin nanostructures has been most successful through use of the confined cooperative method, however its main drawback remains the long reaction time necessary to achieve nanostructure uniformity. The slow-injection method of confined cooperative self-assembly looks to solve the time constraints in producing organized porphyrin nanostructures, but will require tuning to achieve more monodisperse morphology. Optical characterizations of our porphyrin nanostructures show enhanced collective optical properties including a shifted and broadened absorbance as compared to that of the individual porphyrin chromophores, and appear favorable for electronic exciton coupling, formation, and transport.

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