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Interfacial Self-Assembly of Hierarchically Structured Nanoparticles with Photocatalytic Activity

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Acknowledgements

Ashley Bowman Hattie Schunk Leanne Alarid Kaifu Bian

Casey Karler Feng Bai Raid Haddad

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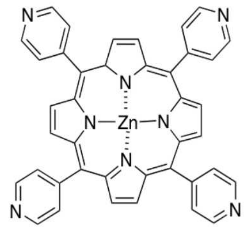
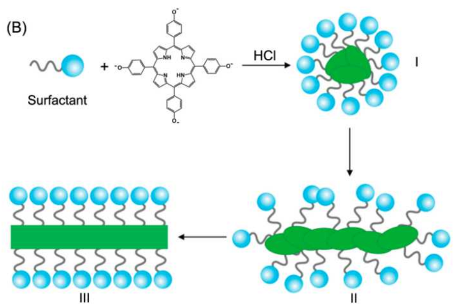
Outline

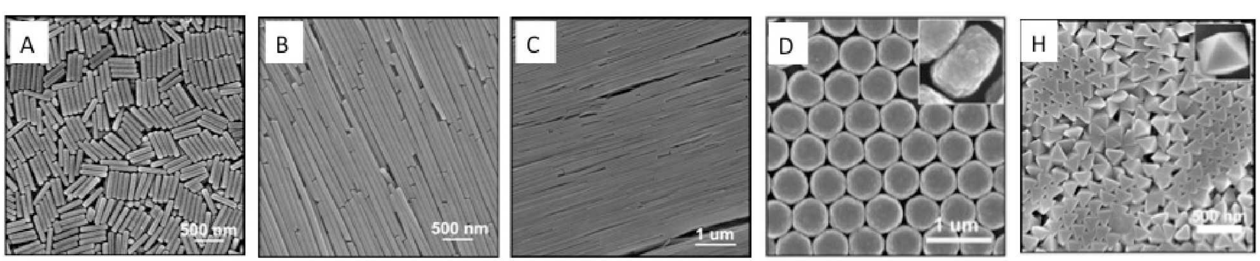
- Why Porphyrin?



- Method – confined noncovalent self-assembly



- Self-assembly and optical property



- Applications - Photocatalysis

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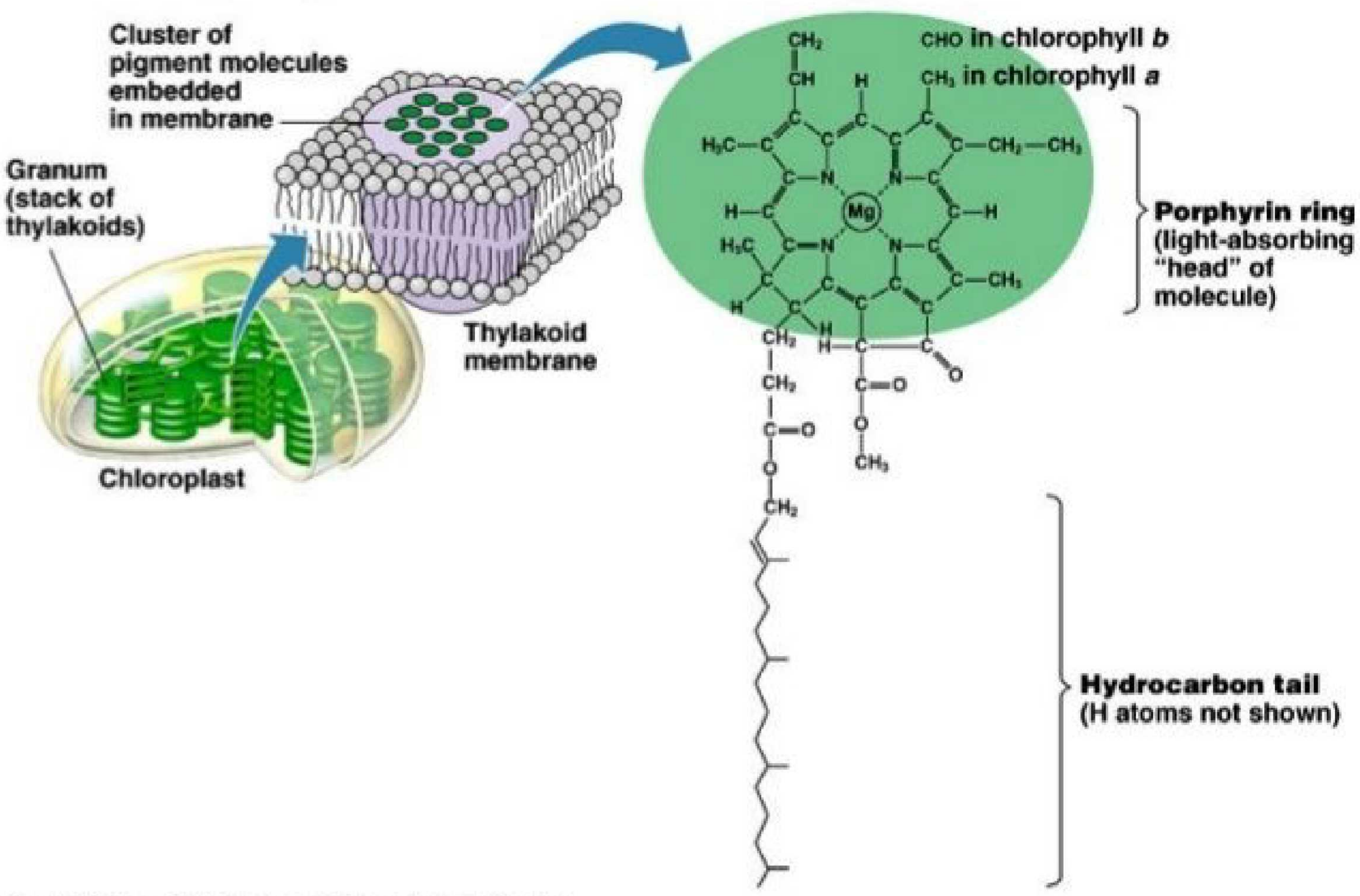
Chlorophyll Structure and Function

Biomacromolecules (e.g., chlorophyll, heme, etc.) with well-defined size and chemistry are essential pigments in many biological energy transduction processes in plants, algae, and bacteria including photosynthesis (absorb light, transfer energy, etc), water splitting, etc.



https://www.pinterest.com/katidavis86/structure-and-function/

Why porphyrins?

Inspired by biological nature, many synthetic molecule building blocks such as porphyrins, organic dyes, etc have been demonstrated for new optical and electrical applications in areas of molecule electronics, photovoltaics, and sensors.

Well-defined size and chemistry:

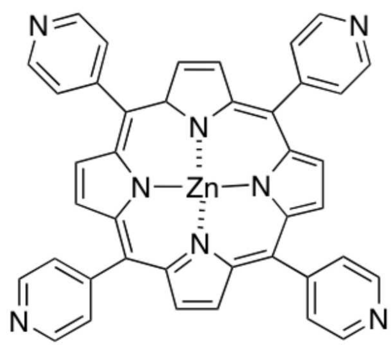
- Well-defined size and surface chemistry,
- Optical and electrical activity due to the conjugated aromatic π system,
- Covering wide range of visible spectrum.

Applications in energy conversion/storage and sensors:

- Photocatalysts,
- Sensors,
- Phototherapy,
- Dye sensitized solar cells.

Driving forces for self-assembly:

- Hydrophobic-hydrophobic,
- π-π stacking,
- Metal-ligand coordination,
- Ionic interactions.

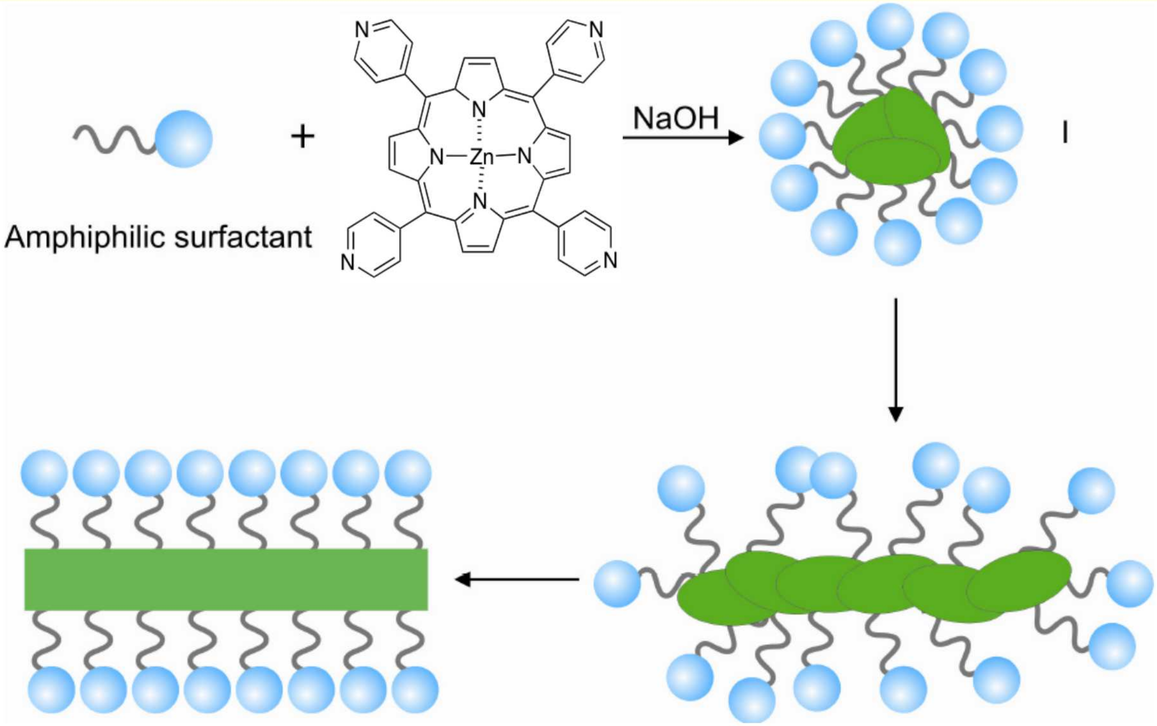


ZnTPyP

Interfacial Self-Assembly and Confined Crystallization

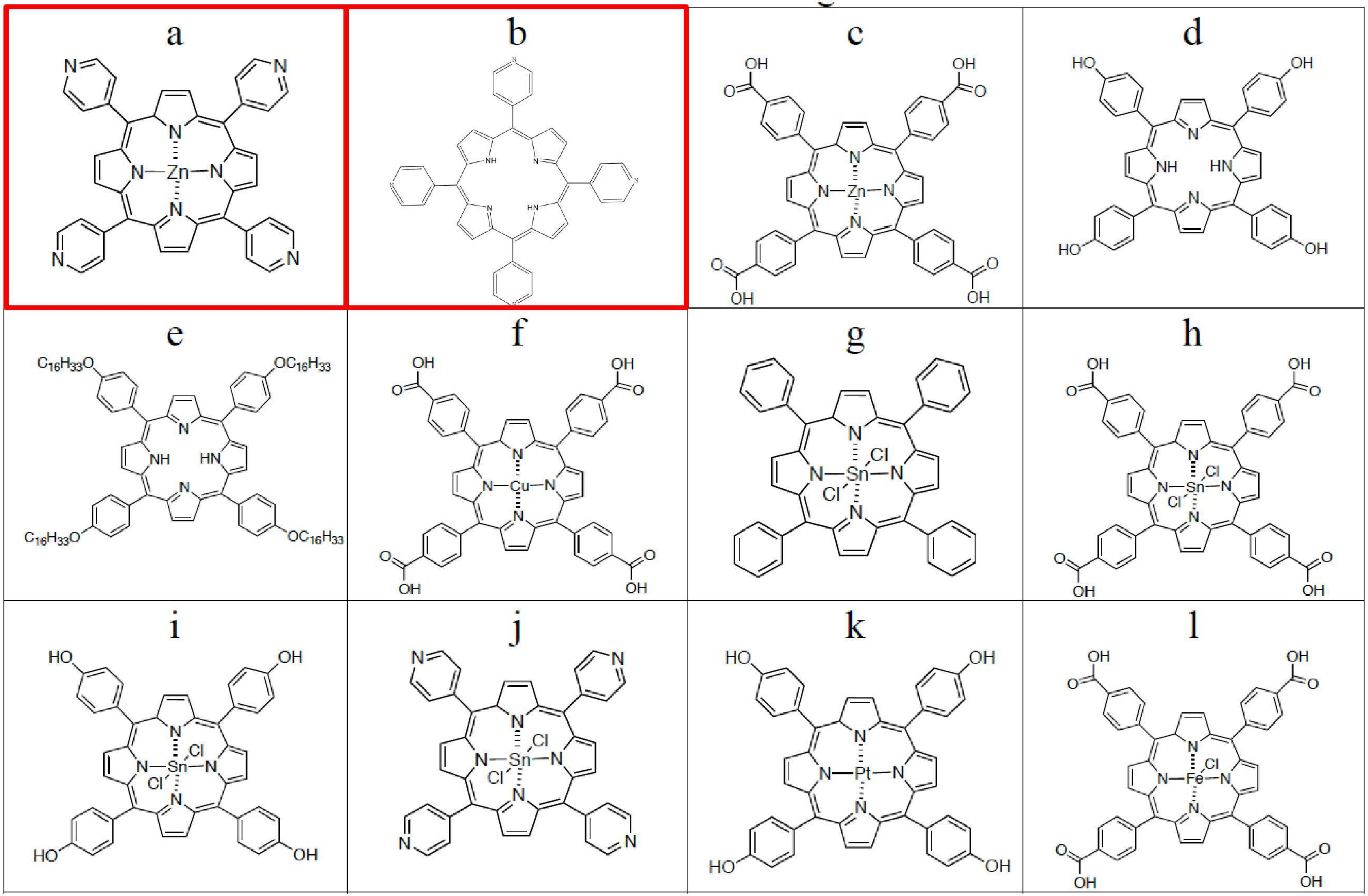
Surfactant assisted confinement of non-covalent interactions:

- Hydrophobic-hydrophobic interactions,
- π-π stacking,
- Metal-ligand coordination.

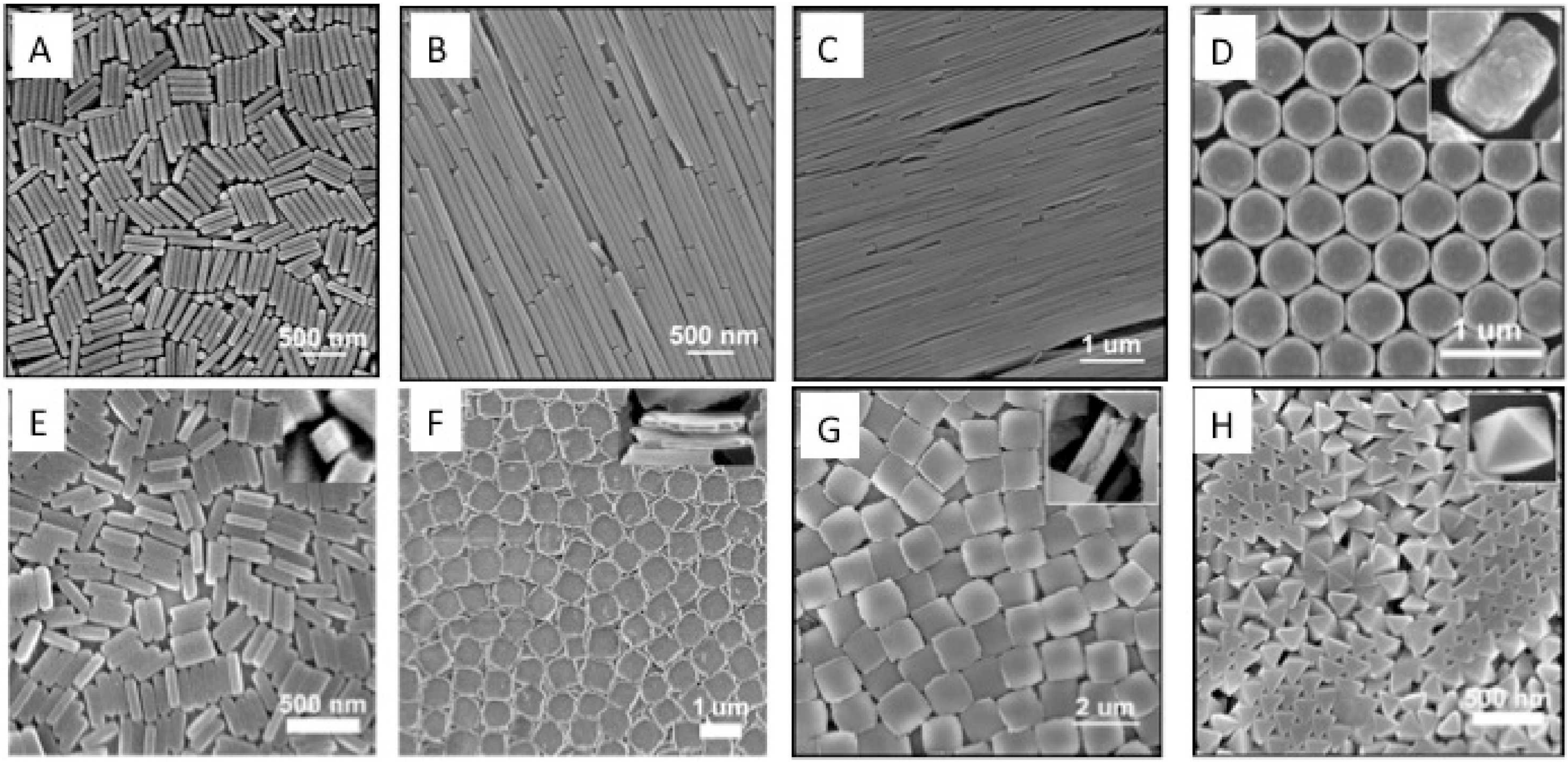


Y. Liu, et al. *Nano Lett*. 2019.
K. Bian, et al. *Nature Communicitons*, **2018**.
K. Bian et al. *MRS Adv.*, **2018**, 3 (45), 2757-2762.
N. Zhang, et al. *Nano Lett.*, **2018**, 18 (1), 560–566.
D. Wang, et al. *ACS Nano*, **2018**, 12 (4), 3796-3803.
J. Wang, et al. *Nano Lett.*, **2017**, 17 (11), 6916–6921.
J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528.
F. Bai, et al. *Adv. Mater*. **2016,** 28, 1989-1993.
Y. Zhong, et al. *Nano Lett.* **2014,** 14, 7175-7179.
Y. Zhong, et al. *ACS Nano*, **2014**, 8 (1), 827–833.
F. Bai, et al. *Nano Lett.* **2011**, 11, 3759–3762.
F. Bai, et al. *Nano Lett.* **2011**, 11, 5196–5200.
F. Bai, et al. *Chem. Commun.*, **2010**, 46, 4941–4943.

Porphyrins Used in Our Research



Hierarchically Structured Porphyrin Nanocrystals



K. Bian et al. *Nature Communicitons*, **2018**.
K. Bian et al. *MRS Adv.*, **2018**, 3 (45), 2757-2762.
D. Wang, et al. *ACS Nano*, **2018**, 12 (4), 3796-3803.
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Y. Zhong, et al. *ACS Nano*, **2014**, *8* (1), 827–833.
F. Bai, et al. *Nano Lett.* **2011**, 11, 3759–3762.
F. Bai, et al. *Nano Lett.* **2011**, 11, 5196–5200.
F. Bai, et al. *Chem. Commun*., **2010**, 46, 4941–4943.

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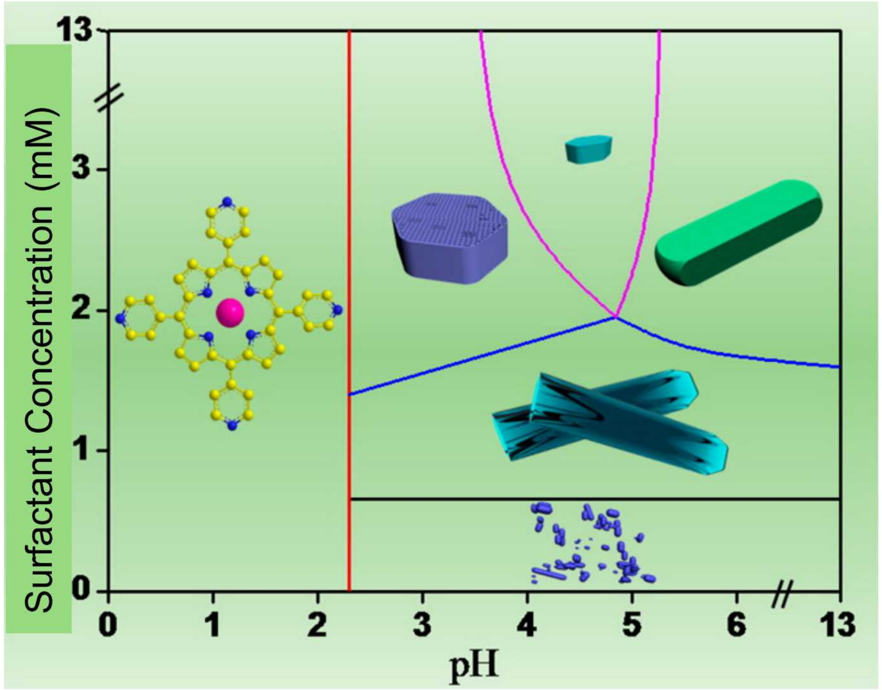
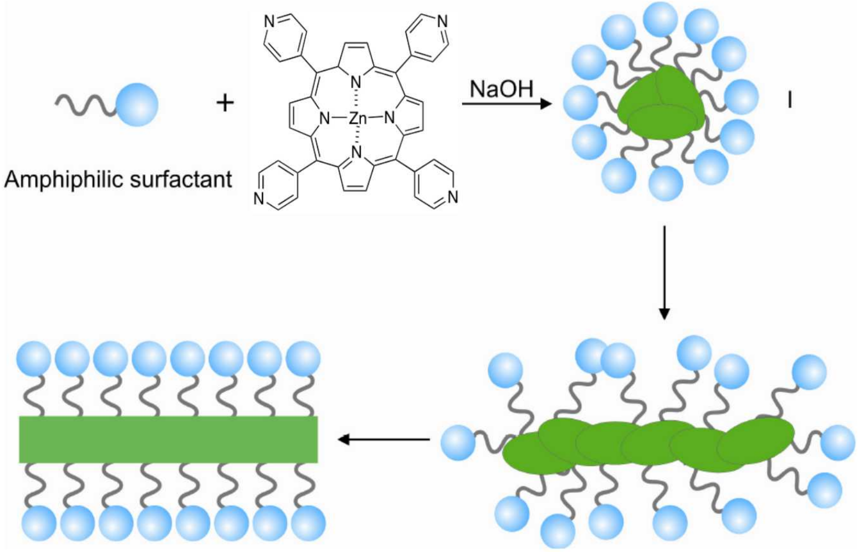
Summary of Crystal Structures

Space Group	Unit Cell Dimension	Packing Mode	Energy (eV)	Morphology
Hexagonal R-3 (148)	$a = b = 33.110$ Å $c = 9.273$ Å $\alpha = \beta = \gamma = 120^\circ$	Metal-ligand coordination (N-Zn-N)	-0.68	Hexagonal nanorod and nanowire, bundle, hexagonal tube
YOVTAE Monoclinic P 21/c (14)	$a = 11.187$ Å $b = 13.825$ Å $c = 22.172$ Å $\alpha = 90^\circ$, $\beta = 100.52^\circ$, $\gamma = 90^\circ$	Metal-ligand coordination (N Zn-N) & π-π stacking	-1.08	Rectangular rod
Tetragonal	$a = b = 19.754$ Å $c = 16.311$ Å $\alpha = \beta = \gamma = 90^\circ$	π-π stacking	-0.48	Nanosheet and nanosheet stacking
Monoclinic Cc (09)	$a = 13.760$ Å $b = 20.925$ Å $c = 11.675$ Å $\alpha = 90^\circ$, $\beta = 117.73^\circ$, $\gamma = 90^\circ$	π-π stacking	-0.52	Octahedron

Phase Diagram of Self-Assembled Porphyrins





Nano Lett. **2014,** 14, 7175-7179.

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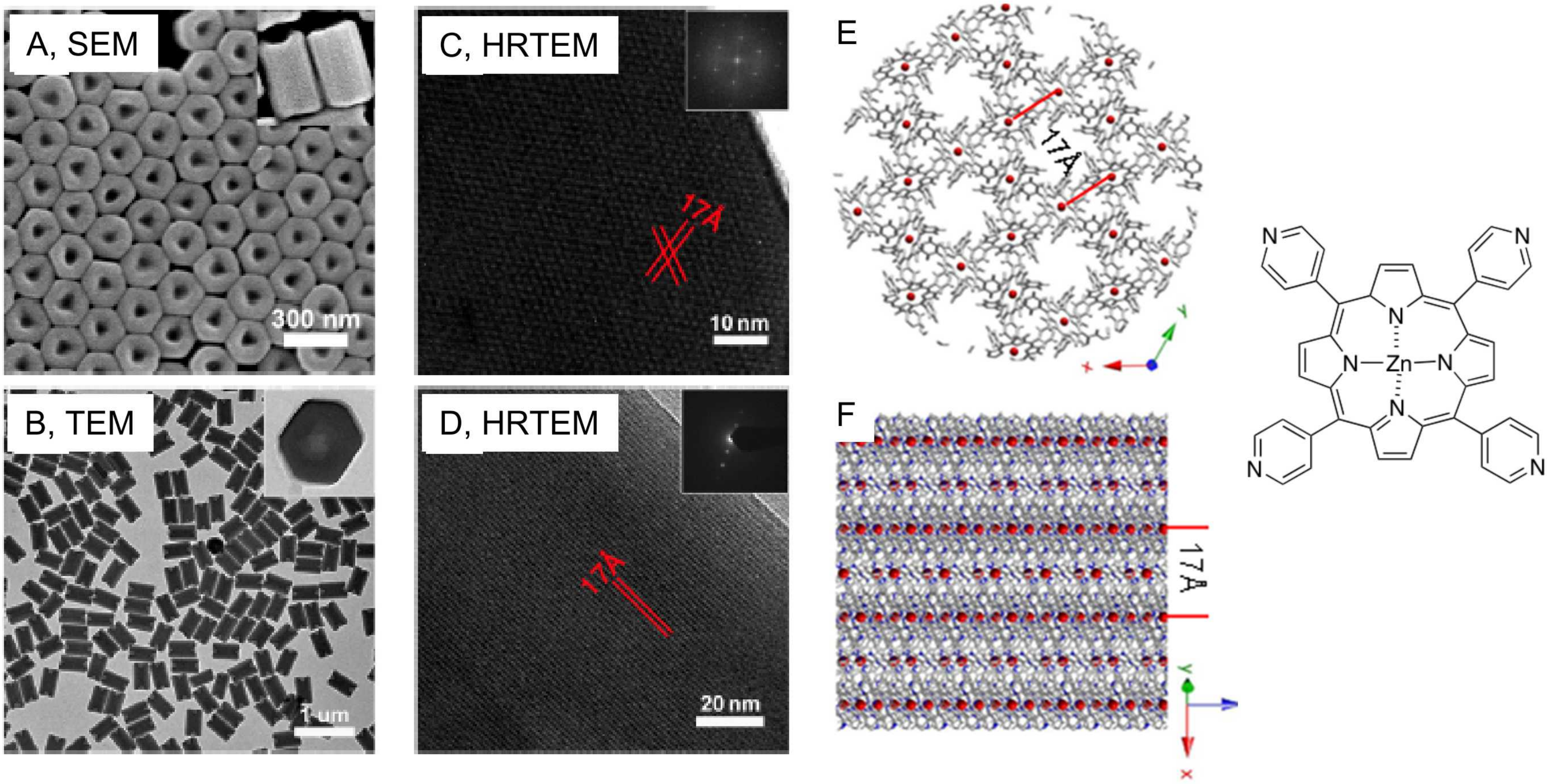
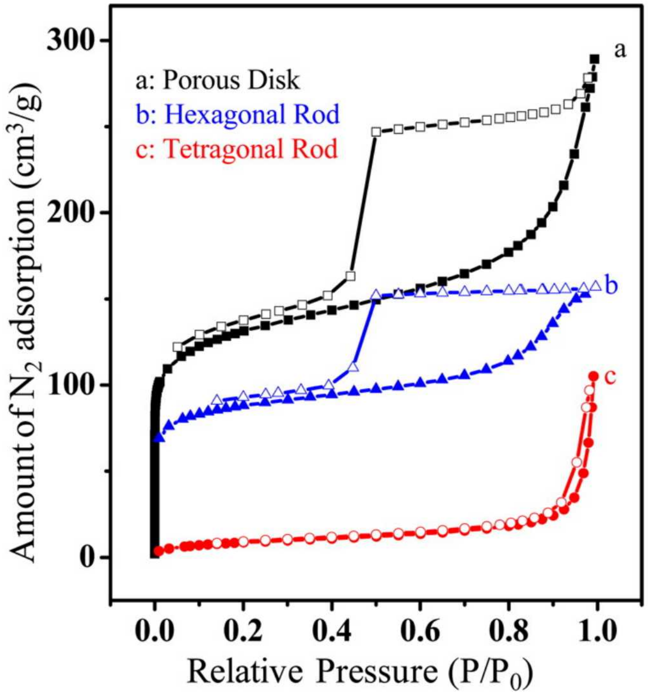
Hierarchically Structured Porphyrin Nanorods

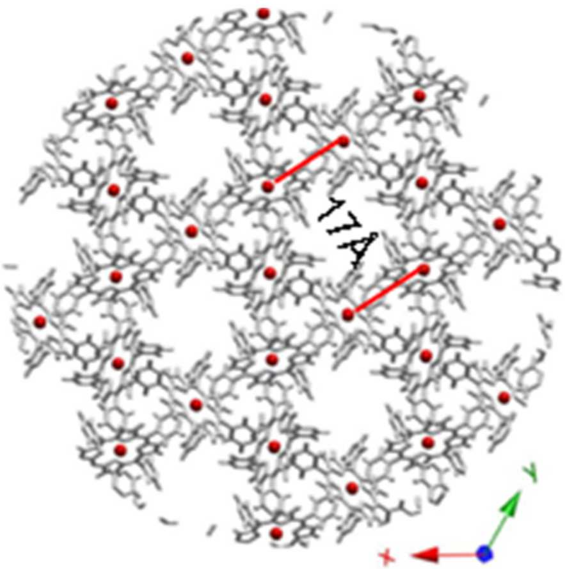


E, simulated crystal structure, viewed along the crystallographic z axis, Zn (red).
F. simulated crystal structure, viewed along the nanowire.
Crystal structure: Hexagonal R-3 (148) a=b= 33.110, c= 9.273; α=β=γ=120

J. Wang, et al. *Nano Lett.*, **2017**, *17* (11), 6916–6921. J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528. F. Bai; et al. *Nano Lett.* 2011, 11, 3759–3762; *Nano Lett.* 2011, 11, 5196–5200.

Nitrogen Sorption Isotherms of Different ZnTPP Nanocrystals





	Porosity (%)	Surface area (m^2/g)	Pore size (nm)
Tetragonal rod	34.3	371	0.81
Hexagonal rod	20.1	327	0.79
Long wire	16.1	294	0.78

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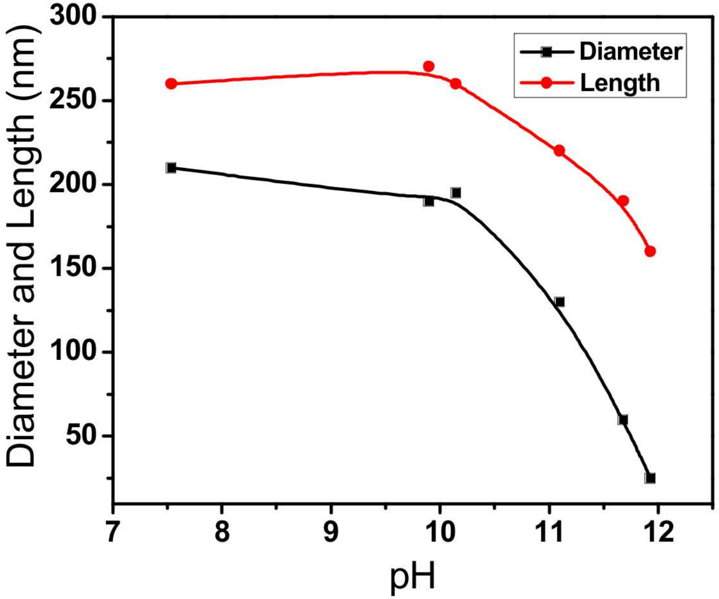
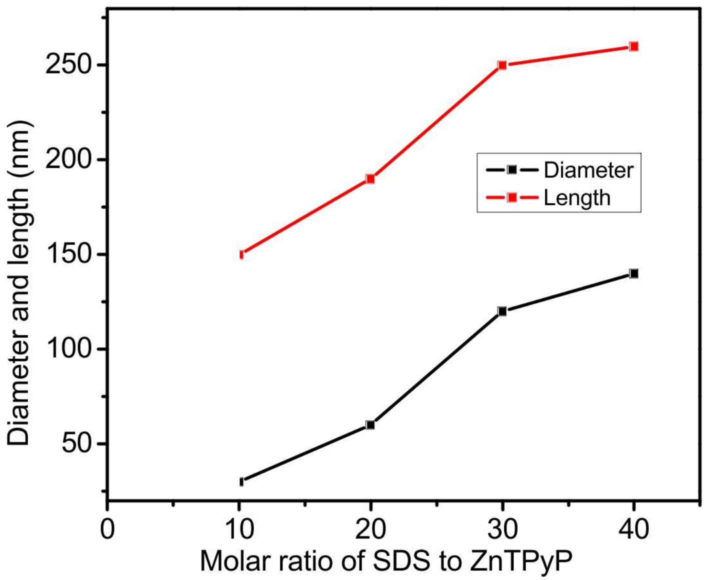
Nano Lett. **2014,** 14, 7175-7179.

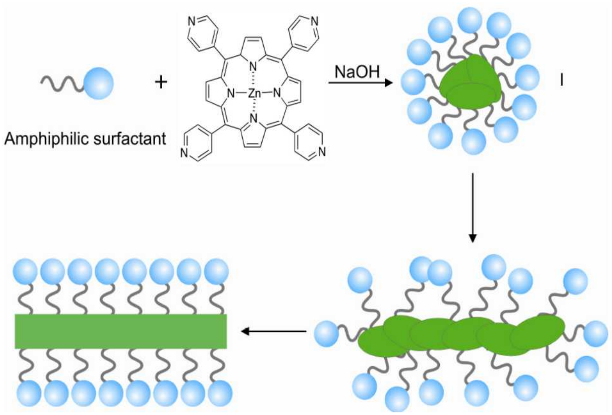
Size Control of Hexagonal Rods

A, pH



B, Ratio of surfactant to porphyrin





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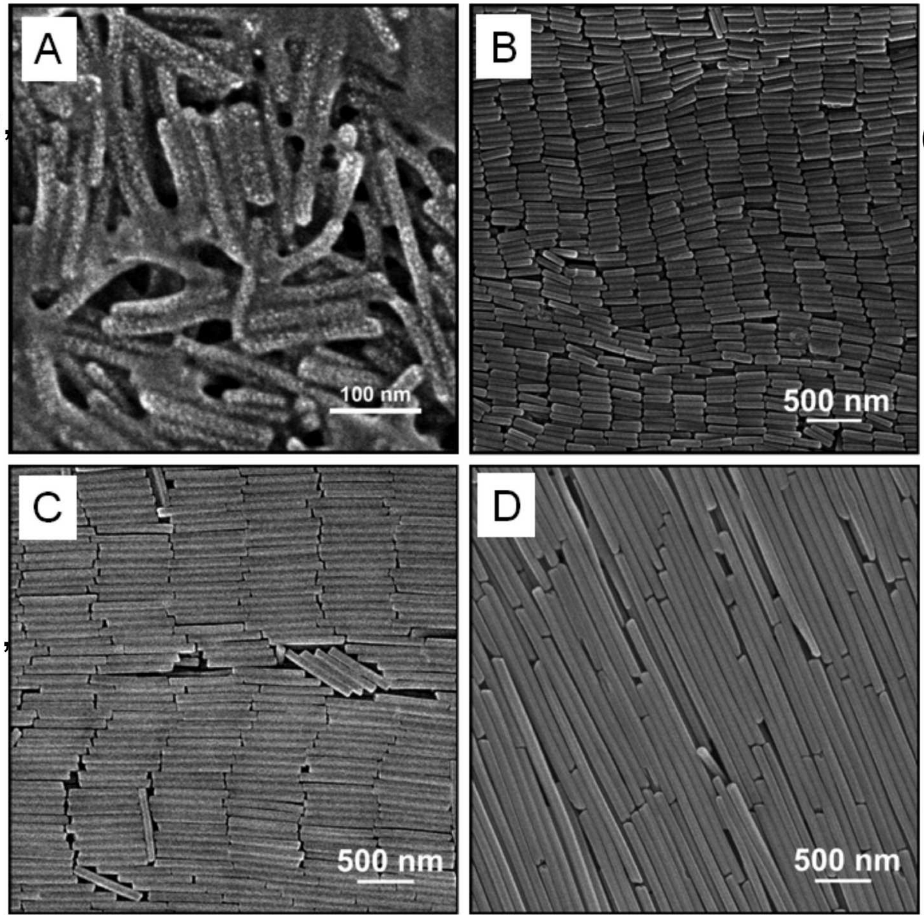
Control of One Dimensional Nanorods and Nanowires

(A) diameter (d) = 15 nm, length (l) = 120 nm.

(B) diameter (d) = 35 nm, length (l) = 280 nm.



(C) diameter (d) = 75 nm, length (l) = 800 nm.

(D) diameter (d) = 100 nm, length (l) = 2.5 μm.

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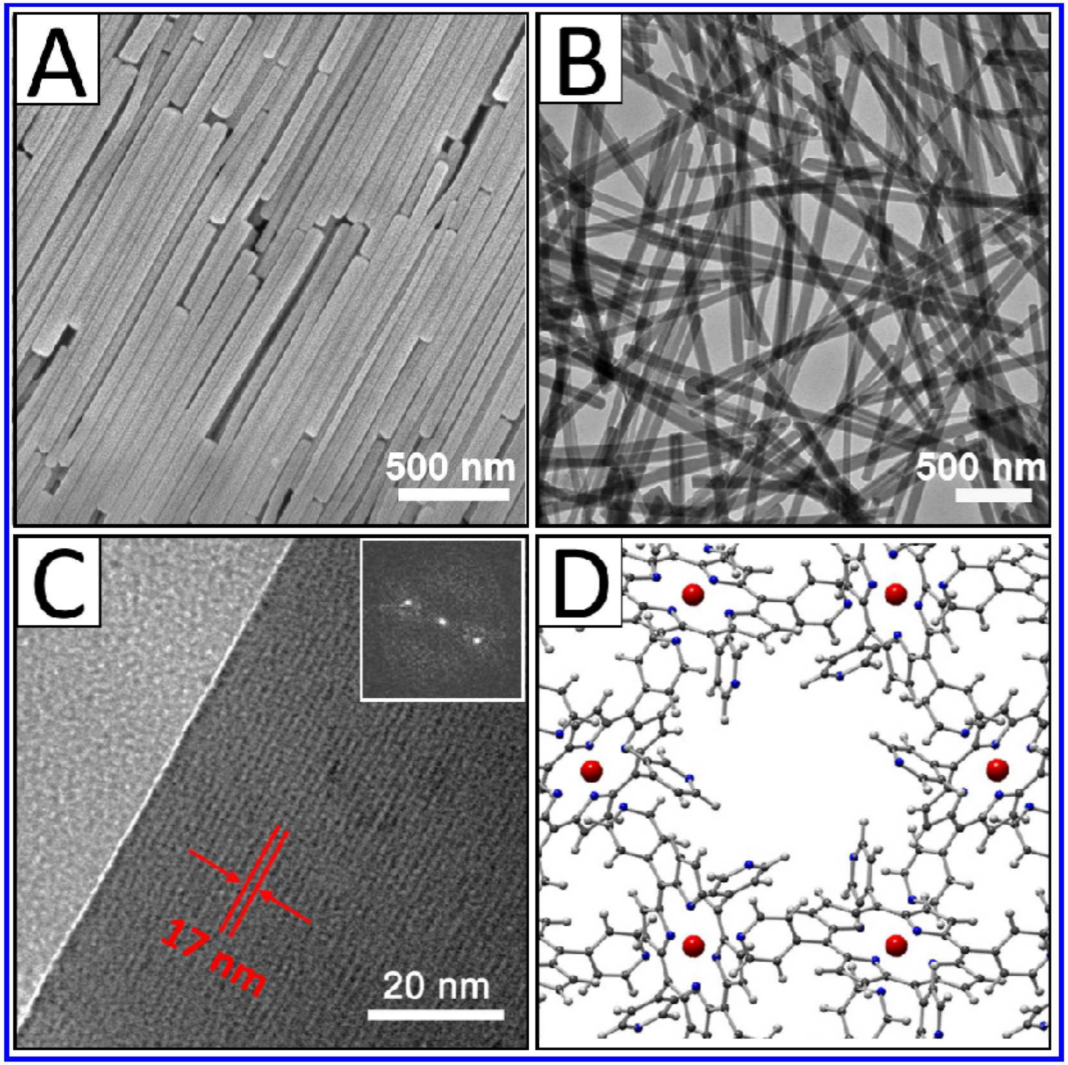
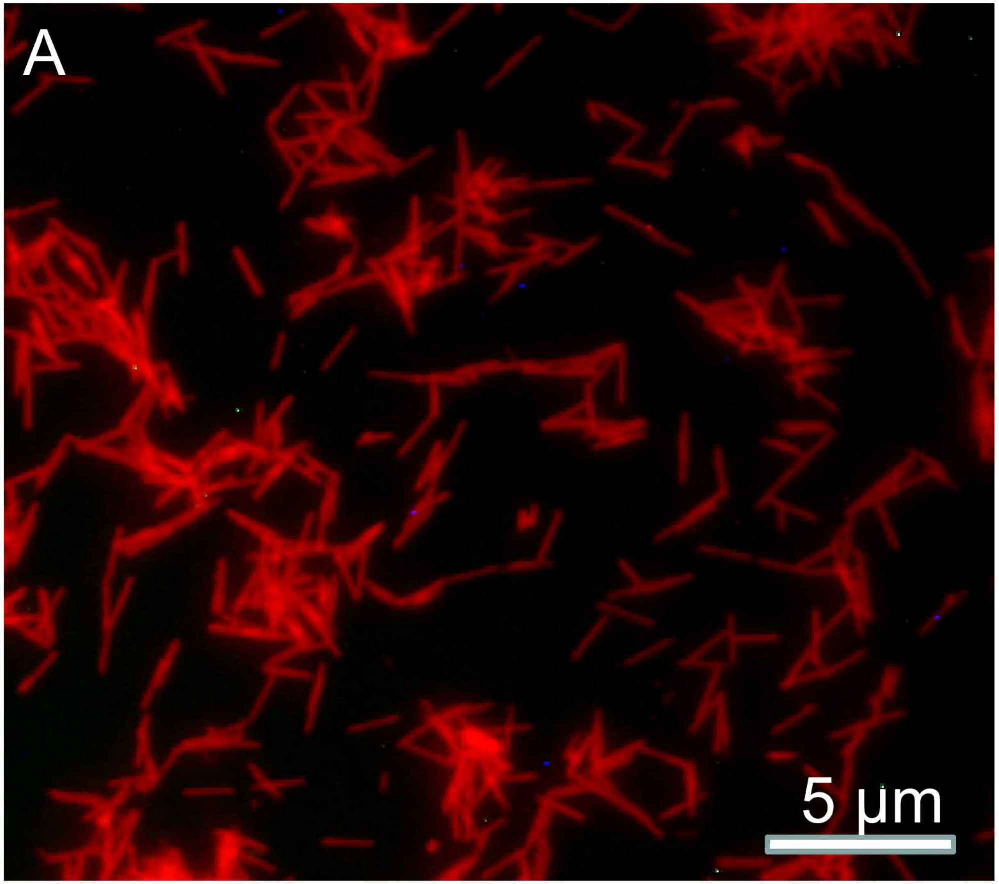
J. Wang, et al. *Nano Lett.*, **2017**, *17* (11), 6916–6921. J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528. F. Bai; et al. *Nano Lett.* 2011, 11, 3759–3762; *Nano Lett.* 2011, 11, 5196–5200.

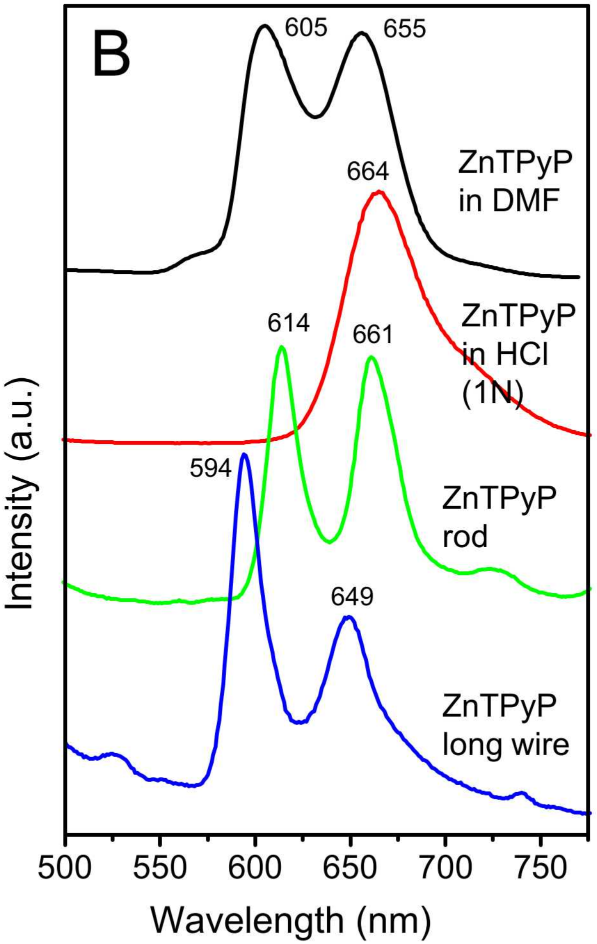
Hexagonal Nanowires



J. Wang; et al. *Nano Lett.* **2016,** 16, 6523-6528.

Optical Property of Nanowires





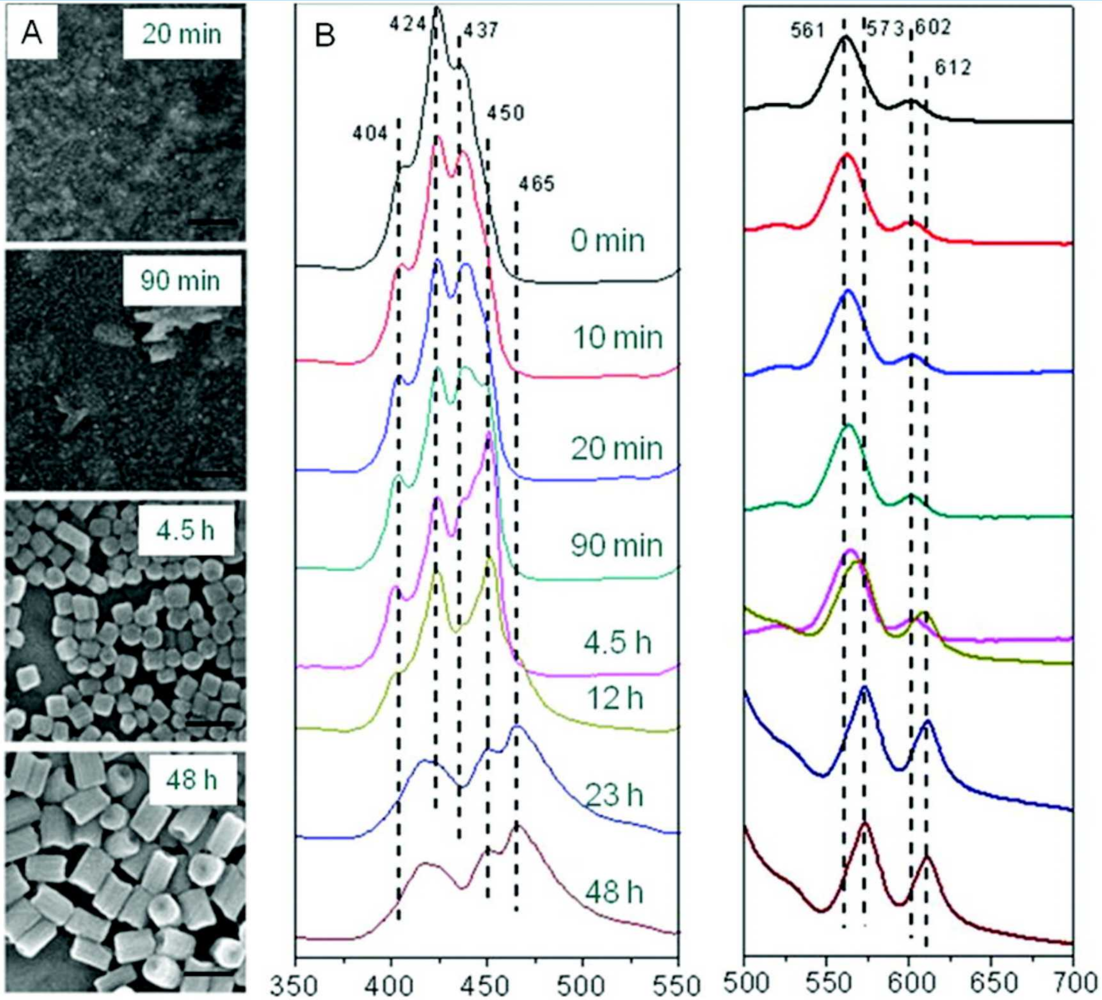
A, Fluorescence image of ZnTPyP long-wire.

B, Fluorescence spectra of different ZnTPyP nanostructures,

J. Wang; et al. *Nano Lett.* **2016,** 16, 6523-6528.

Structural Evolution during Self-Assembly

SEM images of hexagonal nanorods and UV-spectra of the reaction solution at different reaction times.



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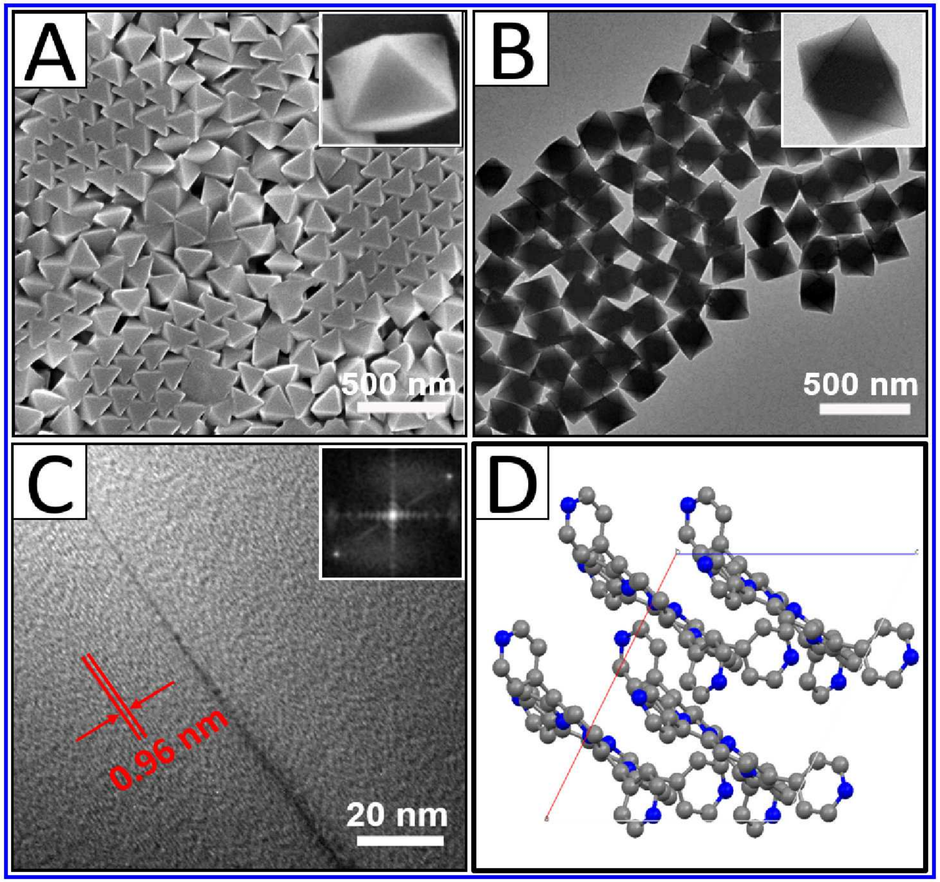
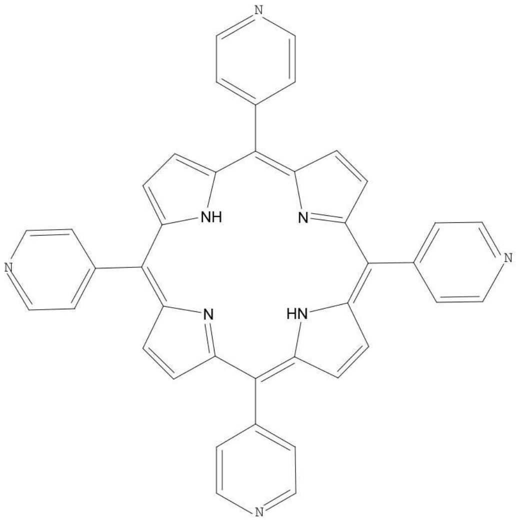
Self-assembled Octahedra





H2TPyP

(A) SEM image of the octahedra prepared using H2TPyP and 0.01 M CTAB. pH was adjusted at 11.44.
(B) TEM image of the octahedra; inset shows a large image of a nanooctahedron.
(C) High-resolution transmission TEM and fast Fourier transformation (FFT).
(D) Simulated crystal structure of nanooctahedra (plan view), N (blue), and C (gray).

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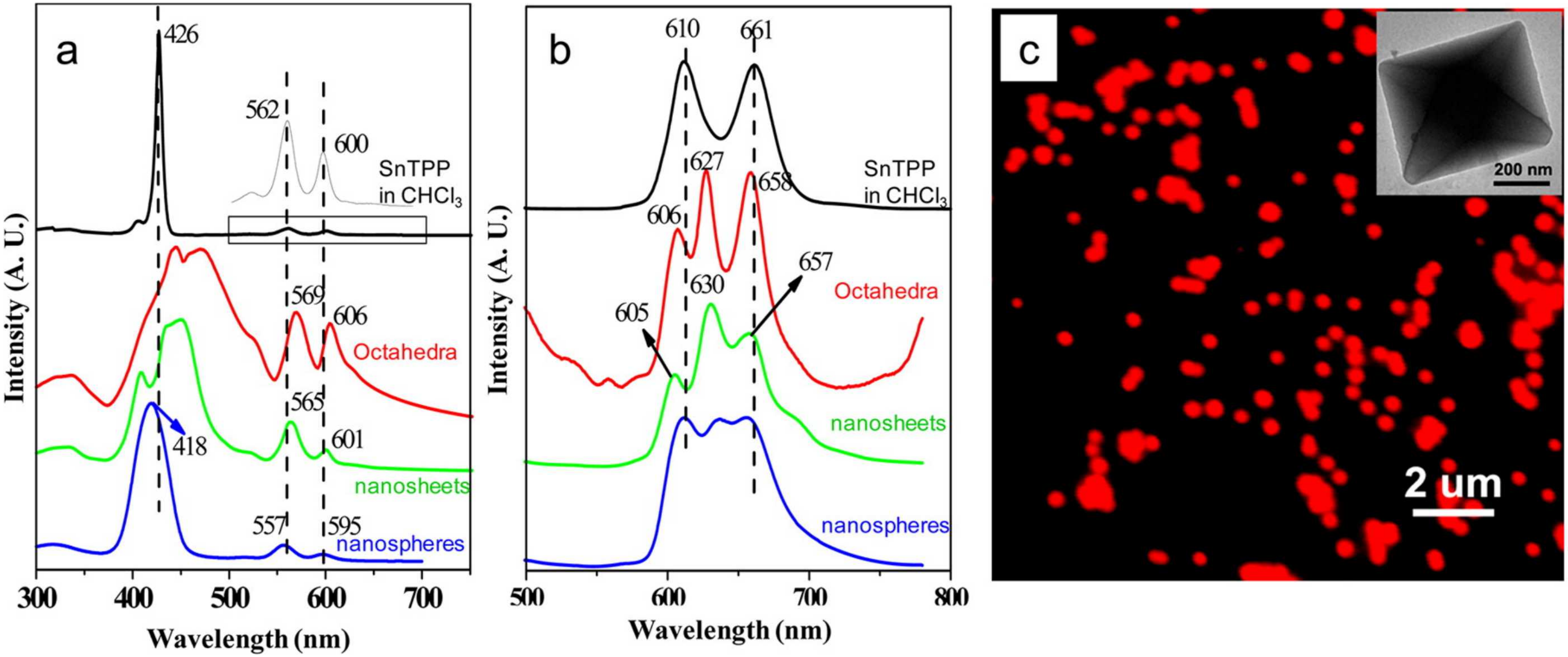
Nano Lett. **2016,** 16, 6523-6528.

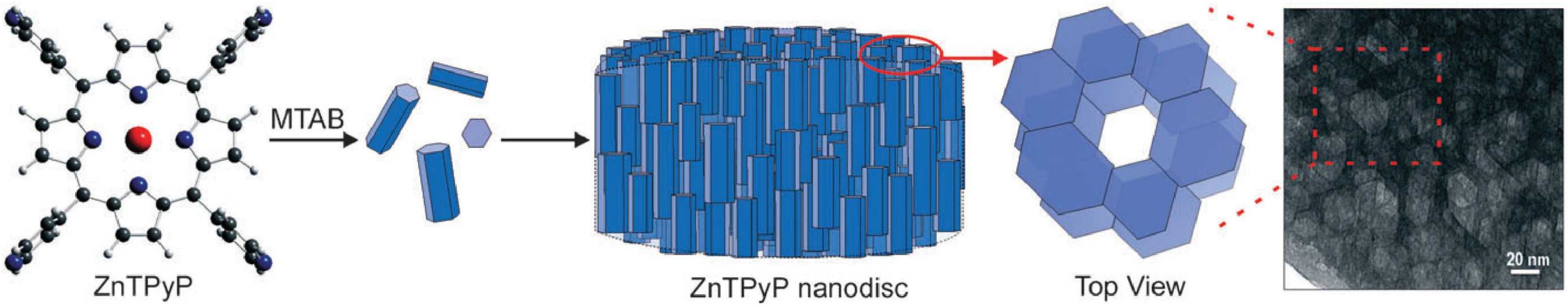
Optical Property of Porphyrin Nanocrystals - Octahedra

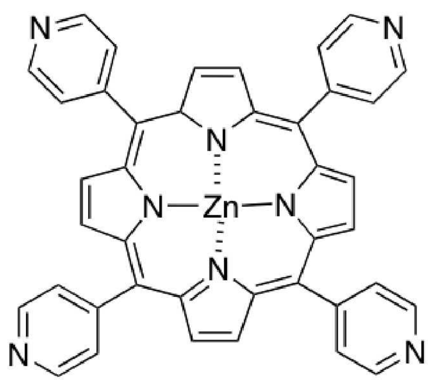


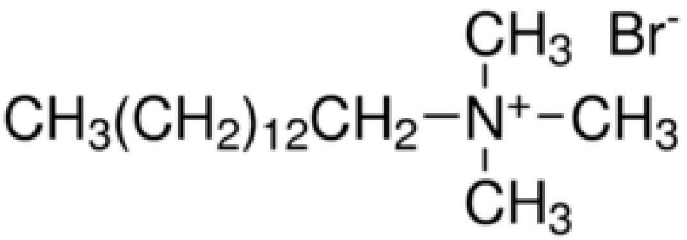
Optical characterization of hierarchically structured tin porphyrin nanocrystals: (a) UV–vis and (b) fluorescence spectra of different tin porphyrin nanocrystals as well as tin porphyrin molecules in CHCl3. (c) Fluorescence image of tin porphyrin octahedra.

Zhong et al. *ACS Nano* **2014,** 8, 827-833.

Formation of Monodisperse Porous Nanodiscs

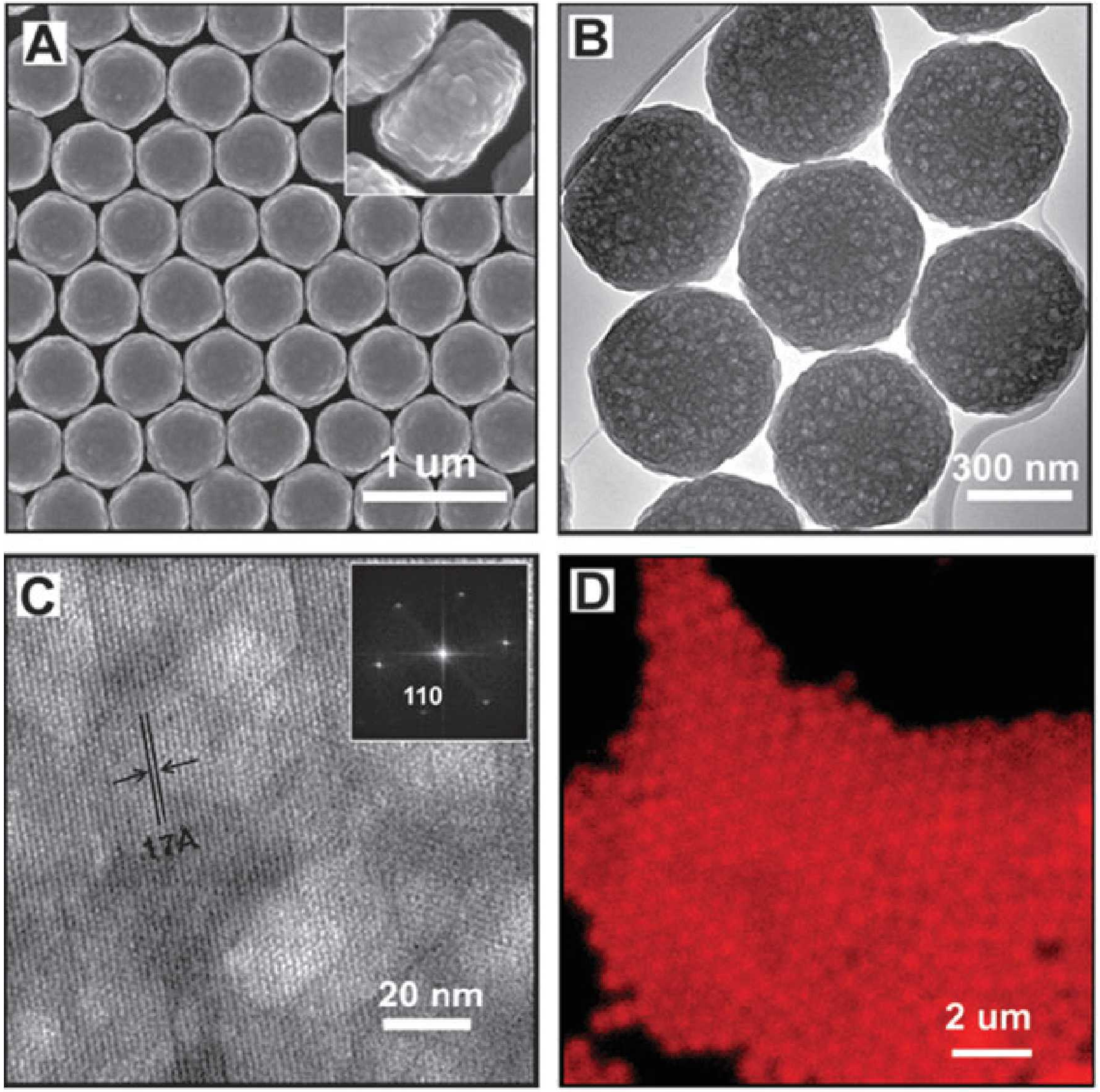






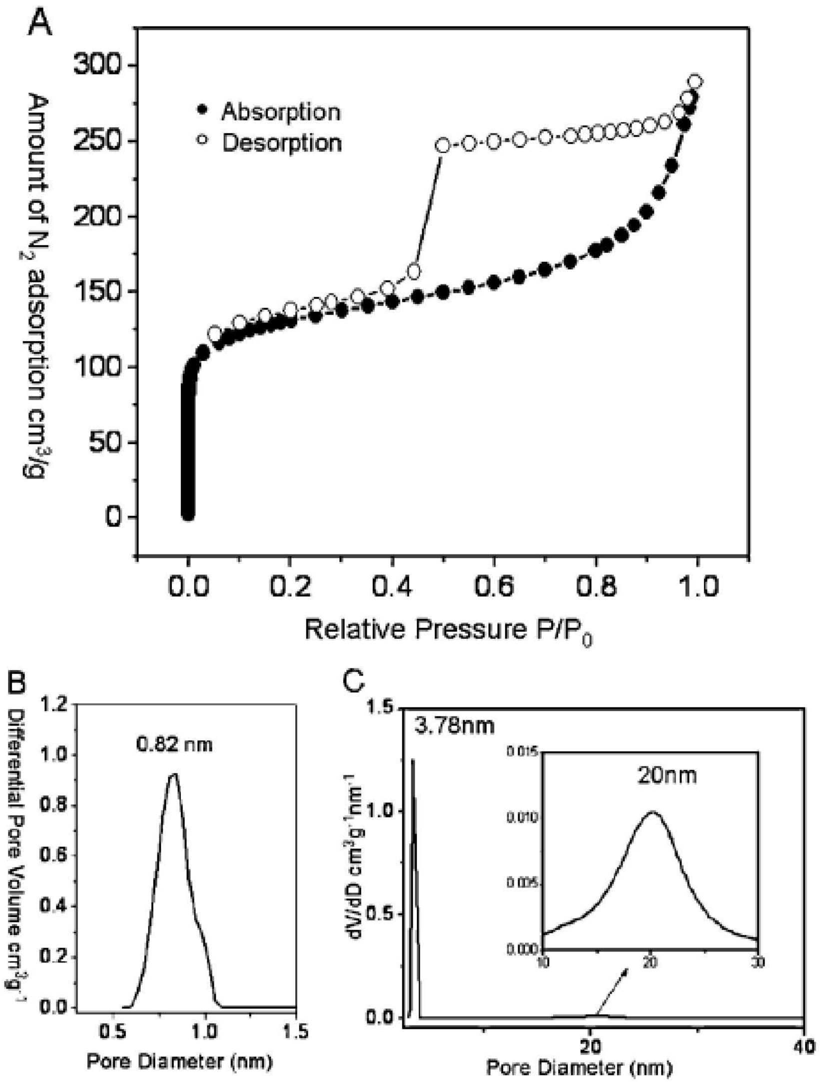
F. Bai, et al. *Chem. Commun.*, 2010, 46, 4941–4943.

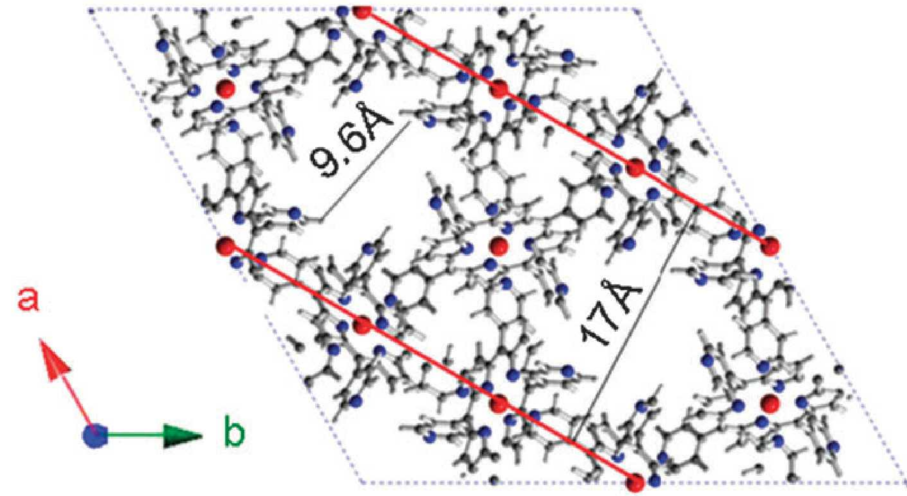
Monodisperse Porous Nanodiscs

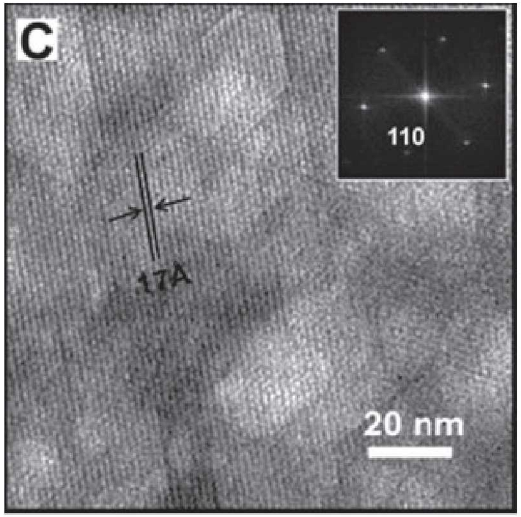


F. Bai, et al. *Chem. Commun*., 2010, 46, 4941–4943

Monodisperse Porous Nanodiscs

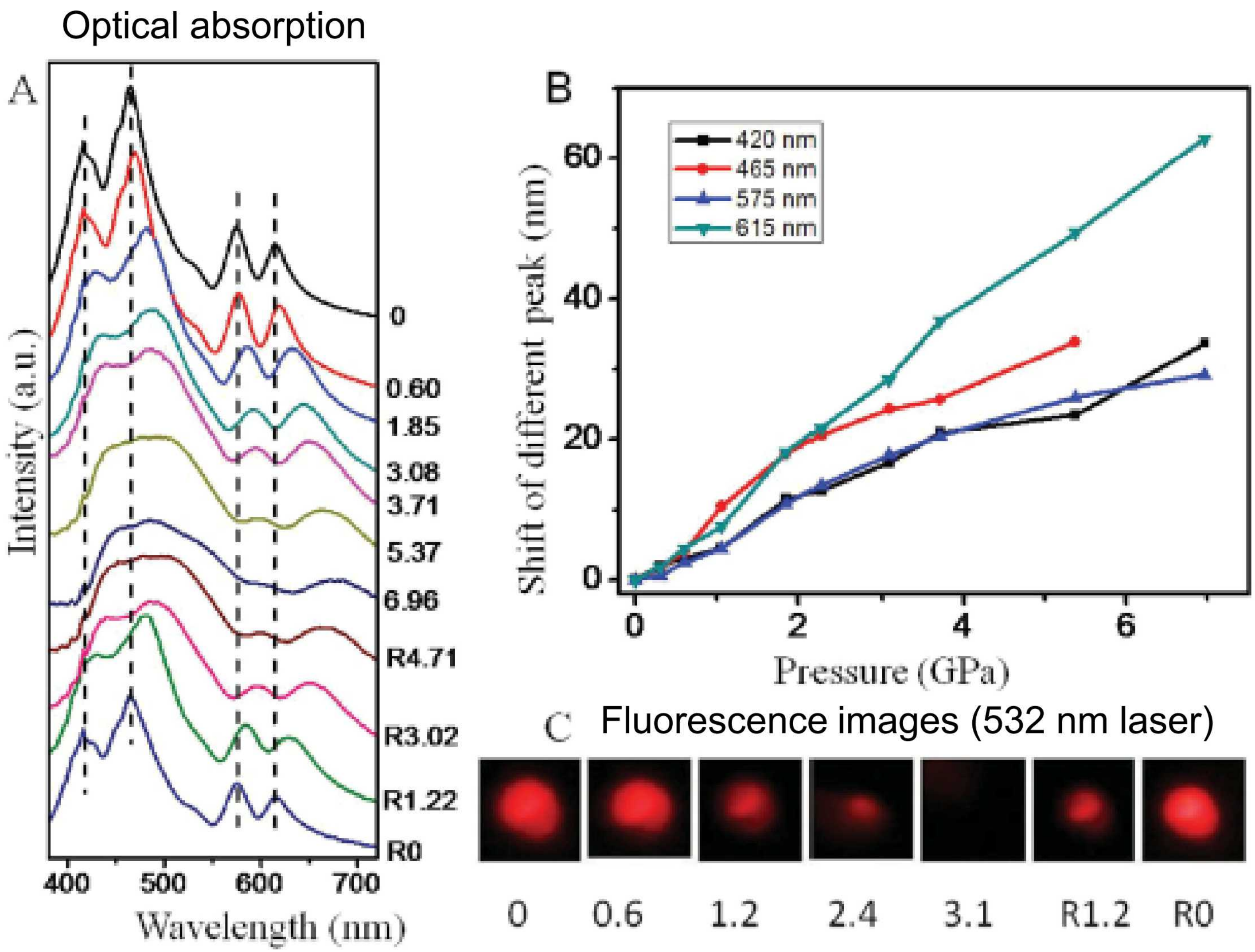






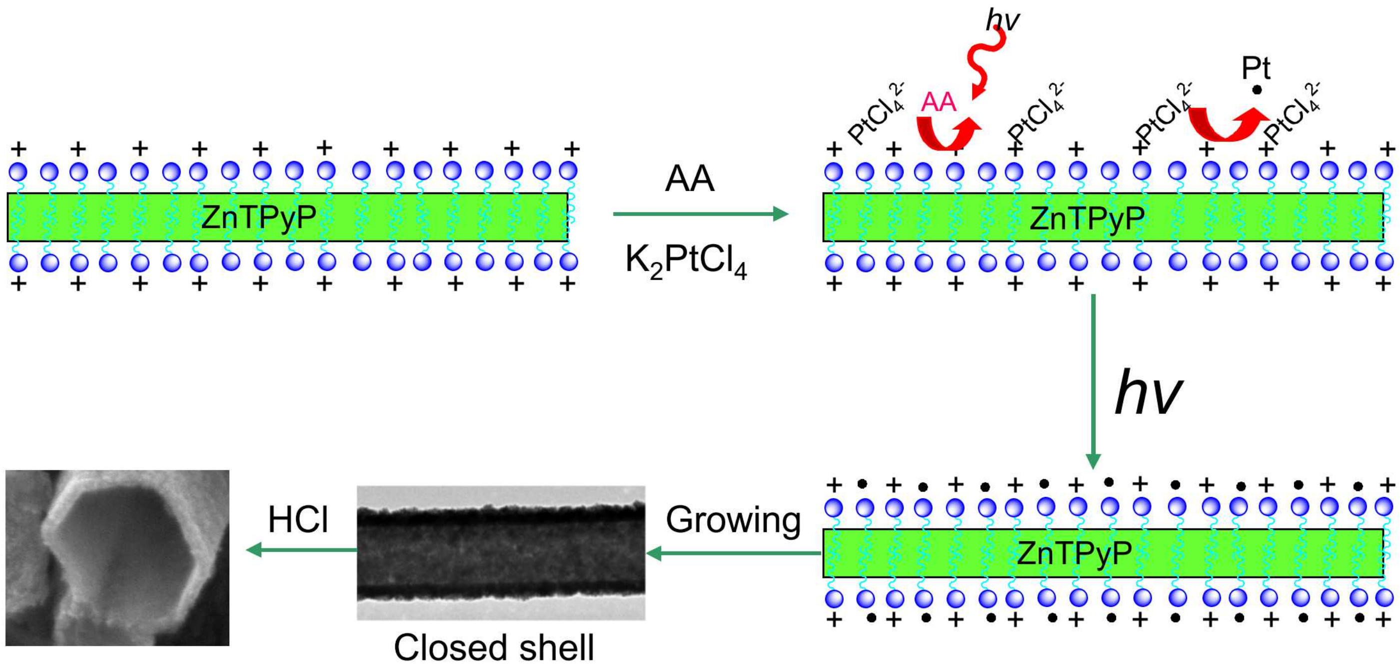
F. Bai, et al. *Chem. Commun.*, 2010, 46, 4941–4943

Reversible Tuning Optical property - Stress Sensor

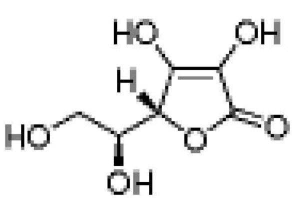


F. Bai, et al. *Adv. Mater*. **2016,** 28, 1989-1993.

Photocatalytic Synthesis of Hollow Pt Nanostructures



CTAB



Ascorbic Acid: AA **E**lectron **D**onor

$$\mathrm{ZnTPyP} \xrightarrow{h\nu} \mathrm{ZnTPyP^*} \quad \text{(excited triplet } \pi\text{-}\pi^* \text{ state)}$$

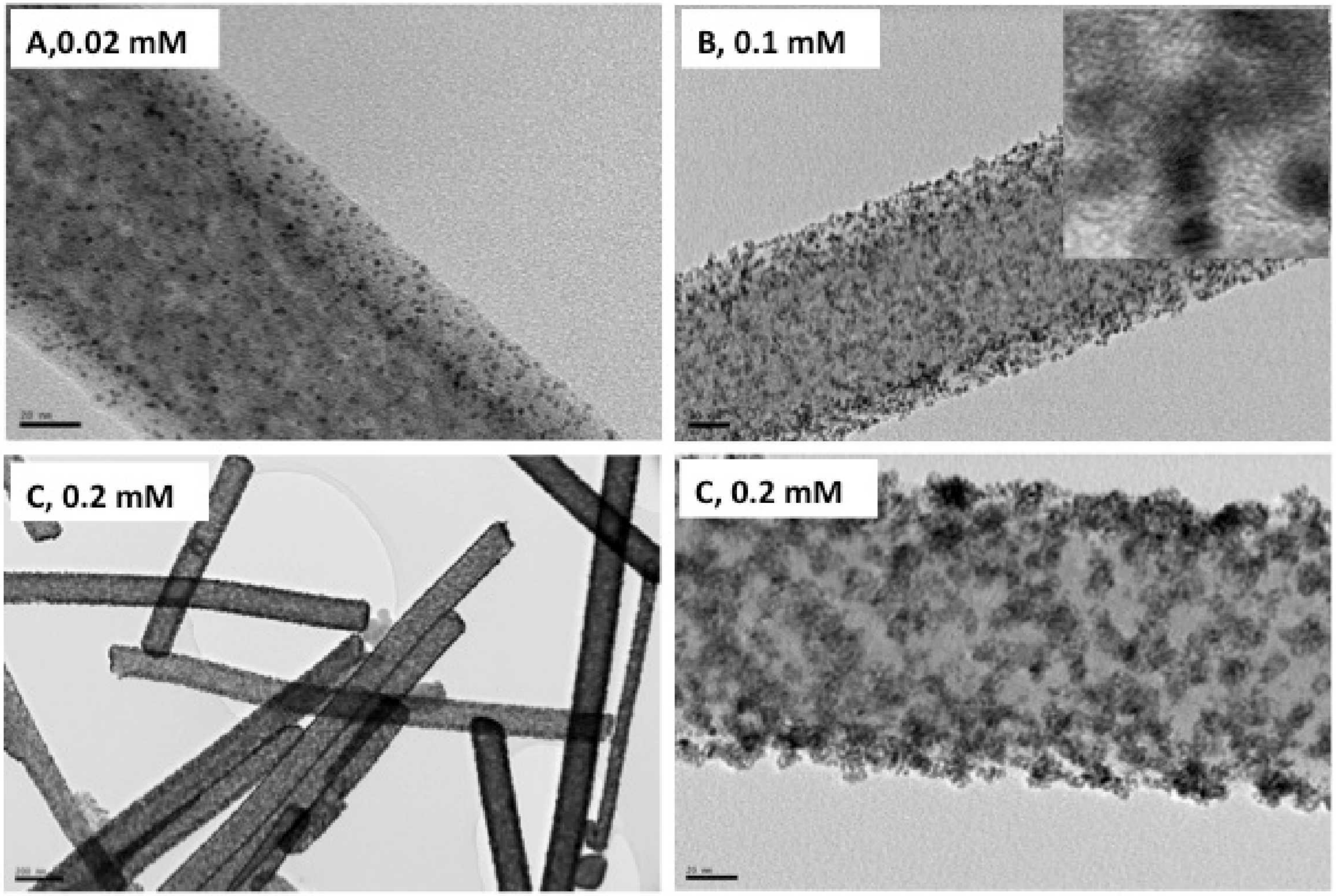
$$\mathrm{ZnTPyP^*} + \mathrm{AA} \longrightarrow \mathrm{ZnTPyP^{-\cdot}} + \mathrm{ED_{0x}}$$

$$4\mathrm{ZnTPyP^{-\cdot}} + \mathrm{PtCl_4^{2-}} \longrightarrow 4\mathrm{ZnTPyP} + \mathrm{Pt^0}$$

(radical anion)

J. Wang, et al. *Nano Lett.*, **2017**, *17* (11), 6916–6921. J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528. F. Bai; et al. *Nano Lett.* 2011, 11, 3759–3762; *Nano Lett.* 2011, 11, 5196–5200.

Controlled Growth of Pt Nanoparticles and interconnected Networks



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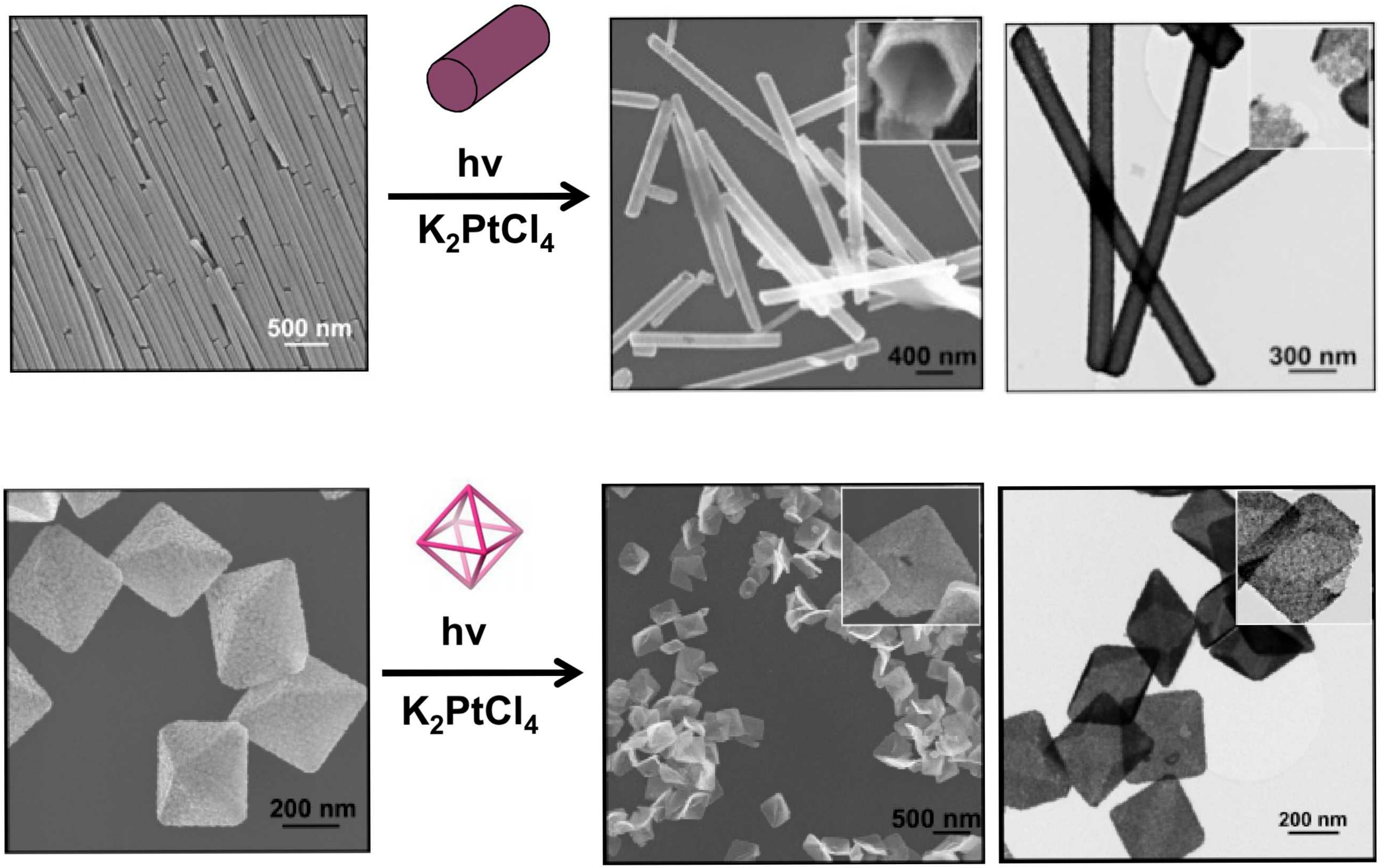
Photocatalytic Synthesis of Hollow Pt Nanostructures through Porphyrin Nanocrystals



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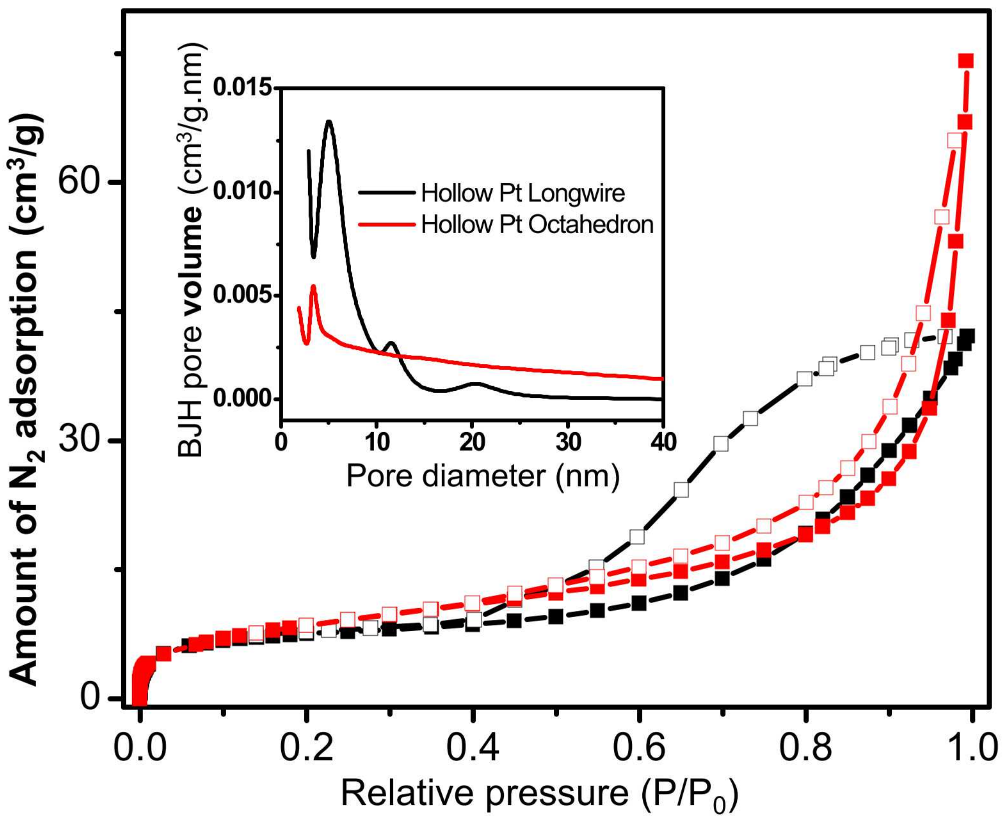
Nitrogen Sorption Isotherms of Pt Hollow Nanotructures



	Surface area (m^2/g)	BJH desorption pore size (nm)
Hollow Pt Nanotube	27.1	5.55
Hollow Pt Octahedron	31.9	13.0

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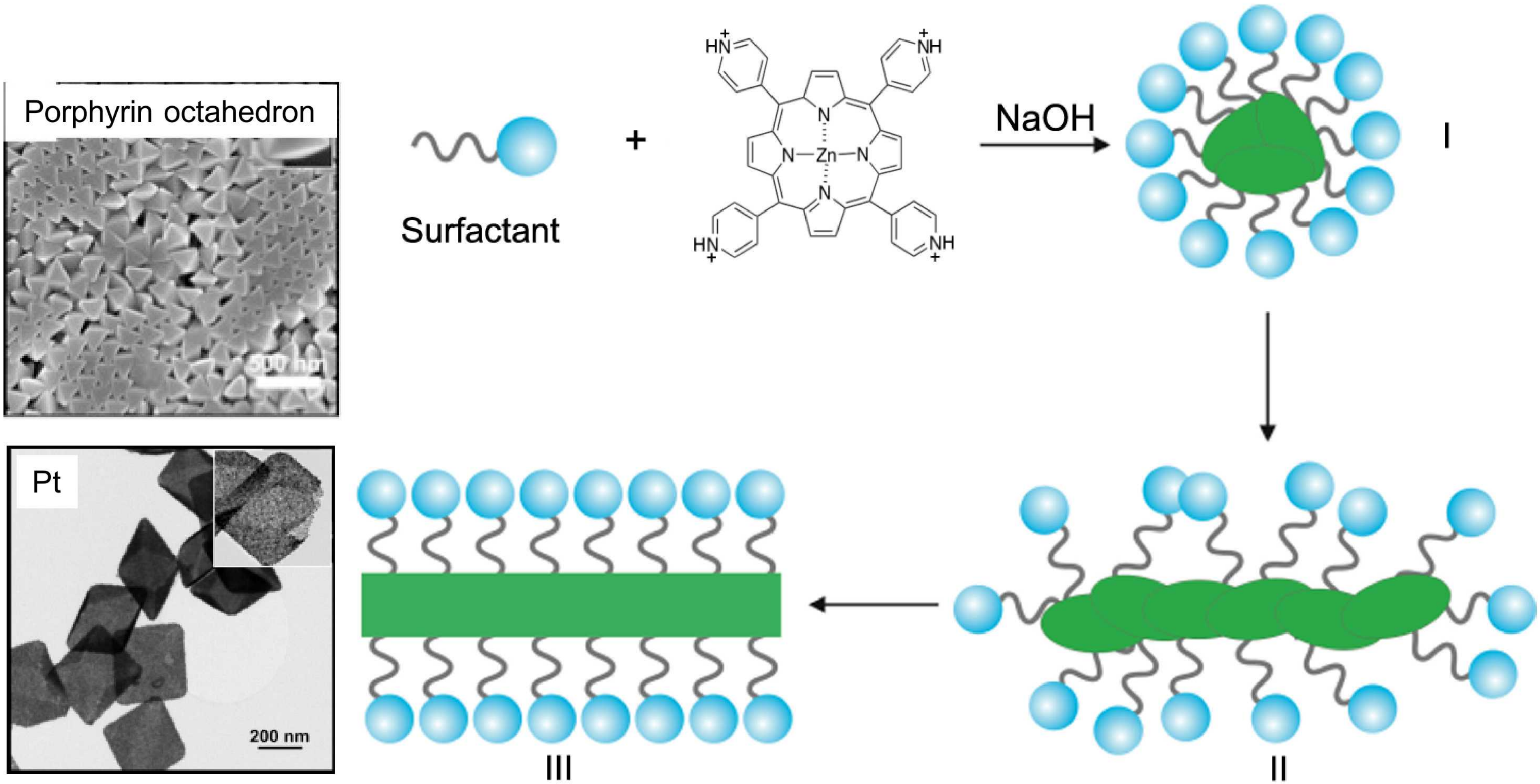
J. Wang, et al. *Nano Lett.*, **2017**, *17* (11), 6916–6921. J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528. F. Bai; et al. *Nano Lett.* 2011, 11, 3759–3762; *Nano Lett.* 2011, 11, 5196–5200.

Summary

Surfactant assisted self-assembly produces porphyrin nanostructures with controlled shape, size, and optical properties for photocatalytic applications.



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Self-assembled porphyrin and macrocycle derivatives