Understanding the Self-Assembly Behavior of Nanoparticles and Polymers

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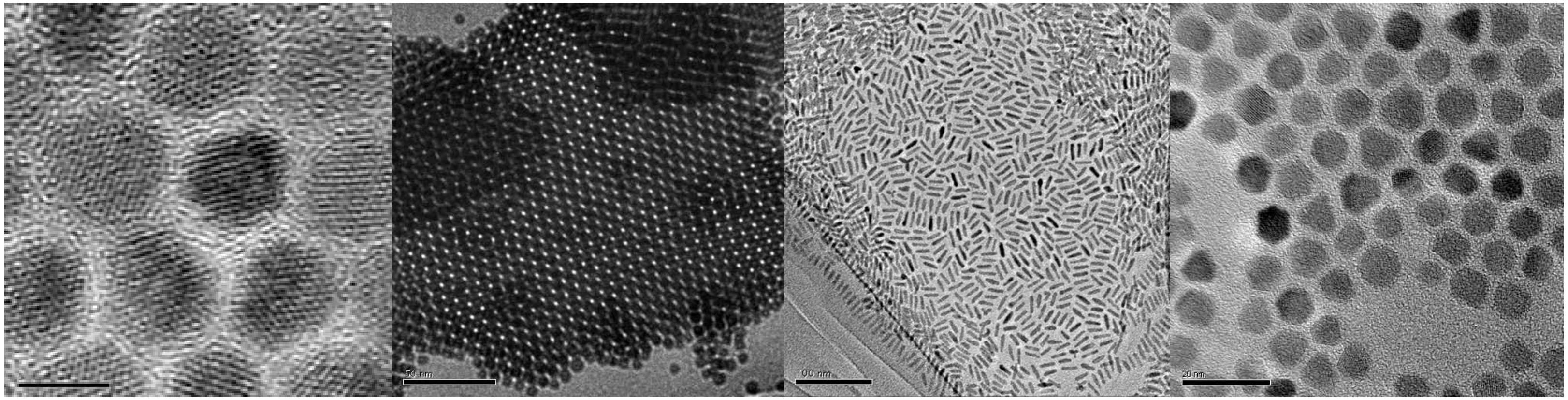
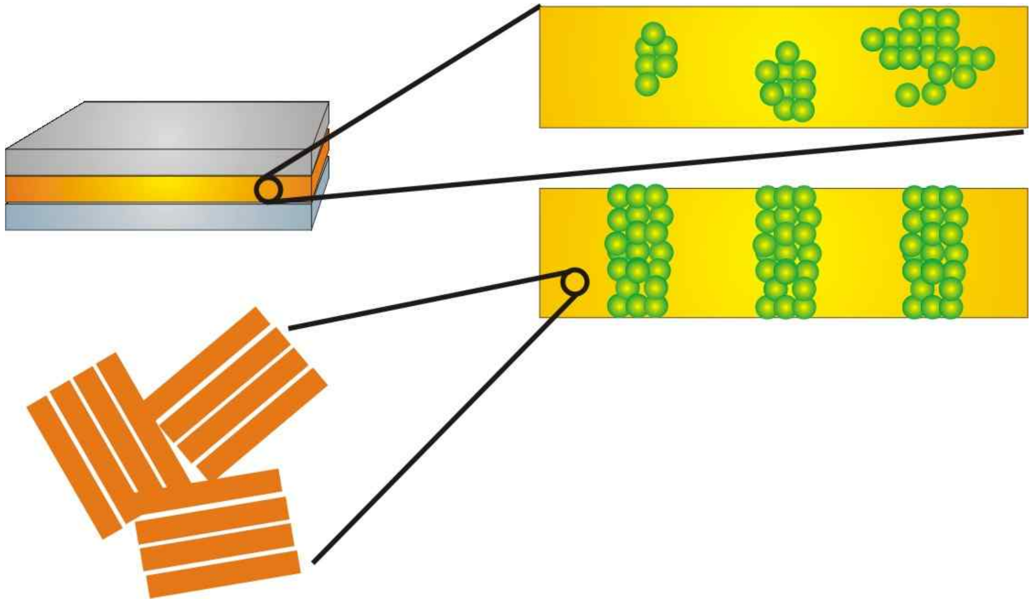
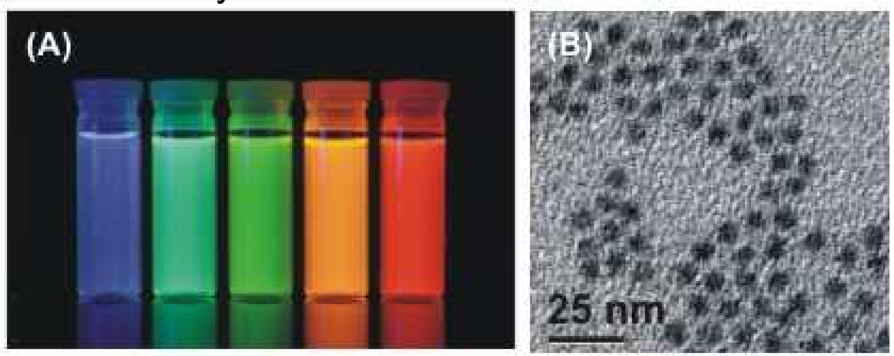
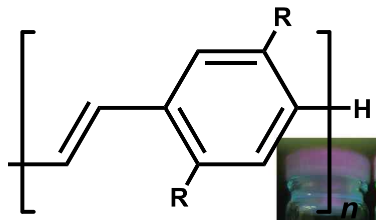


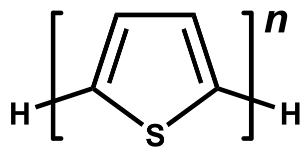
Inorganic Nanoparticle/Polymer Hybrid Materials for Alternative Energy

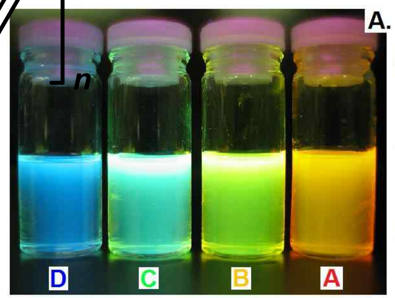


CdSe nanocrystals



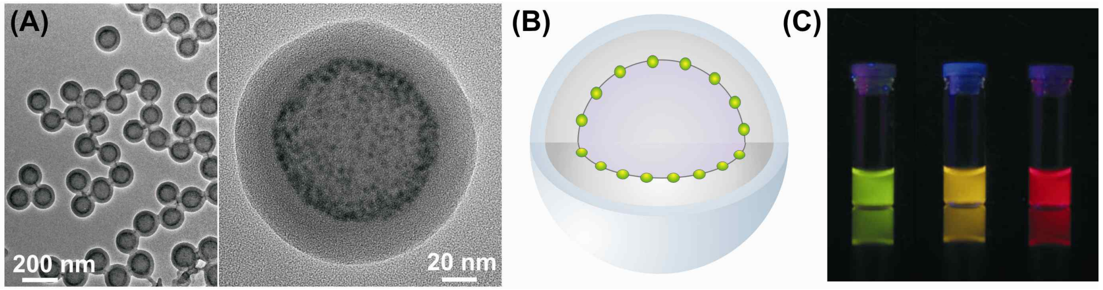






Overview

1. Cooperative Assembly of Nanoparticles and Block-Copolymers



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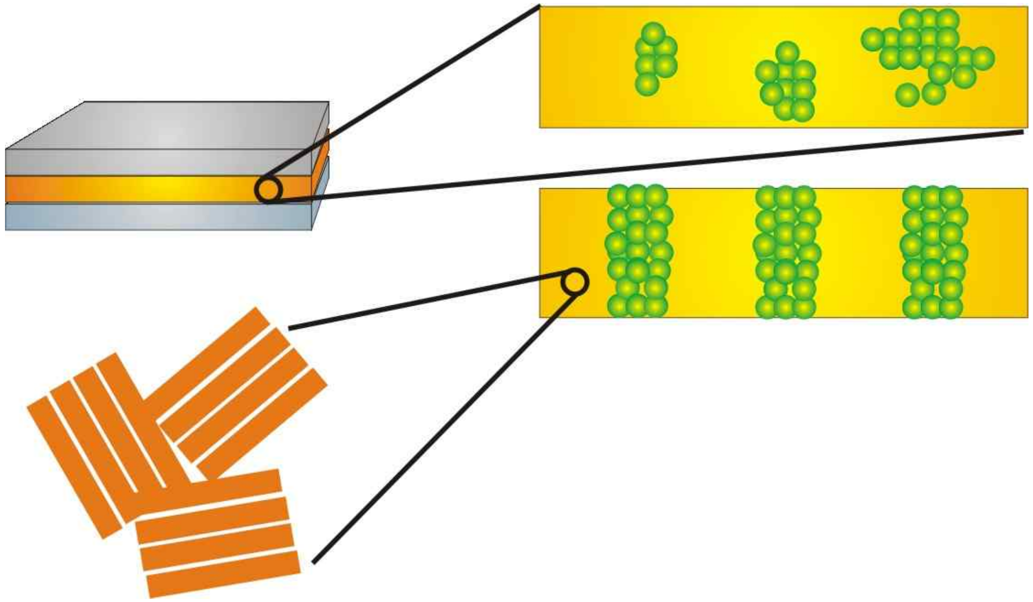

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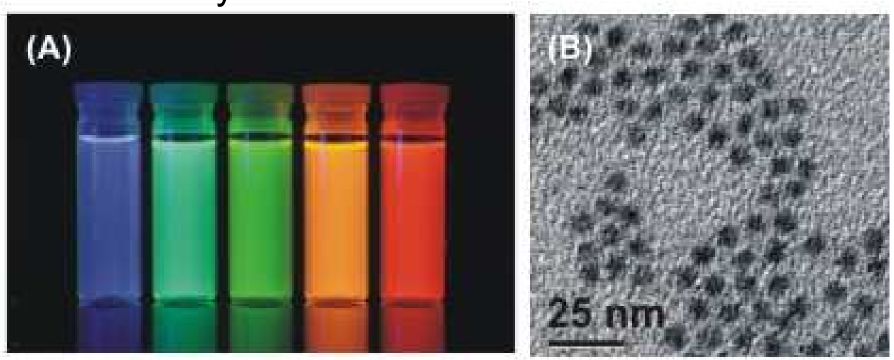

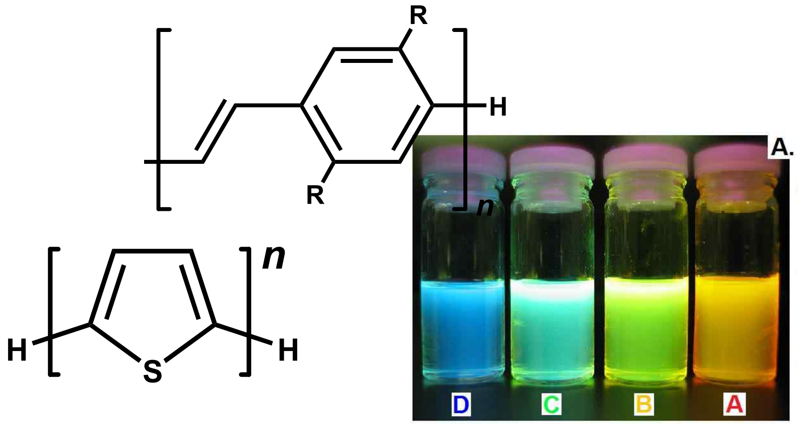

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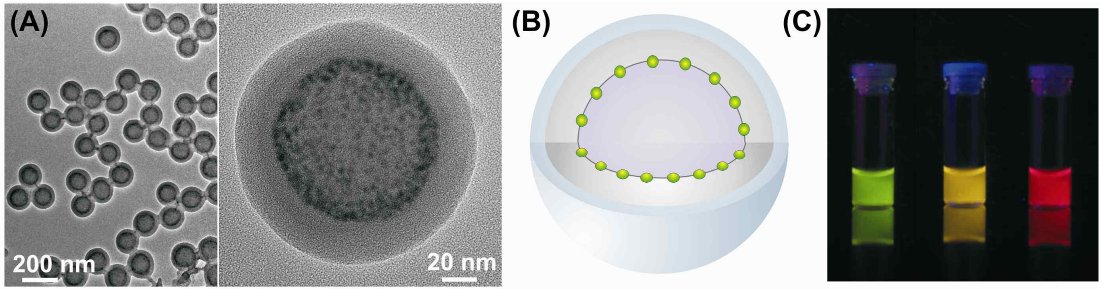
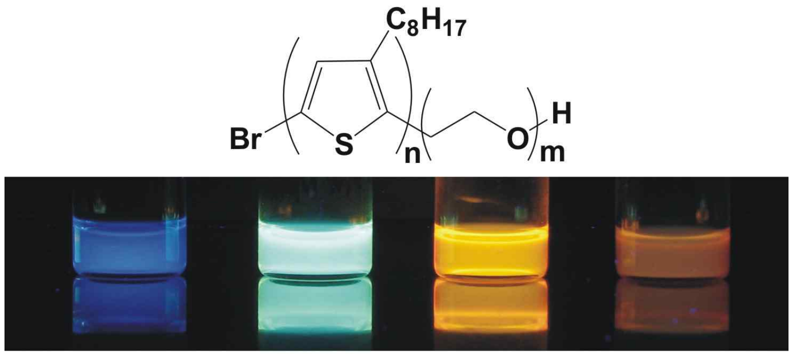
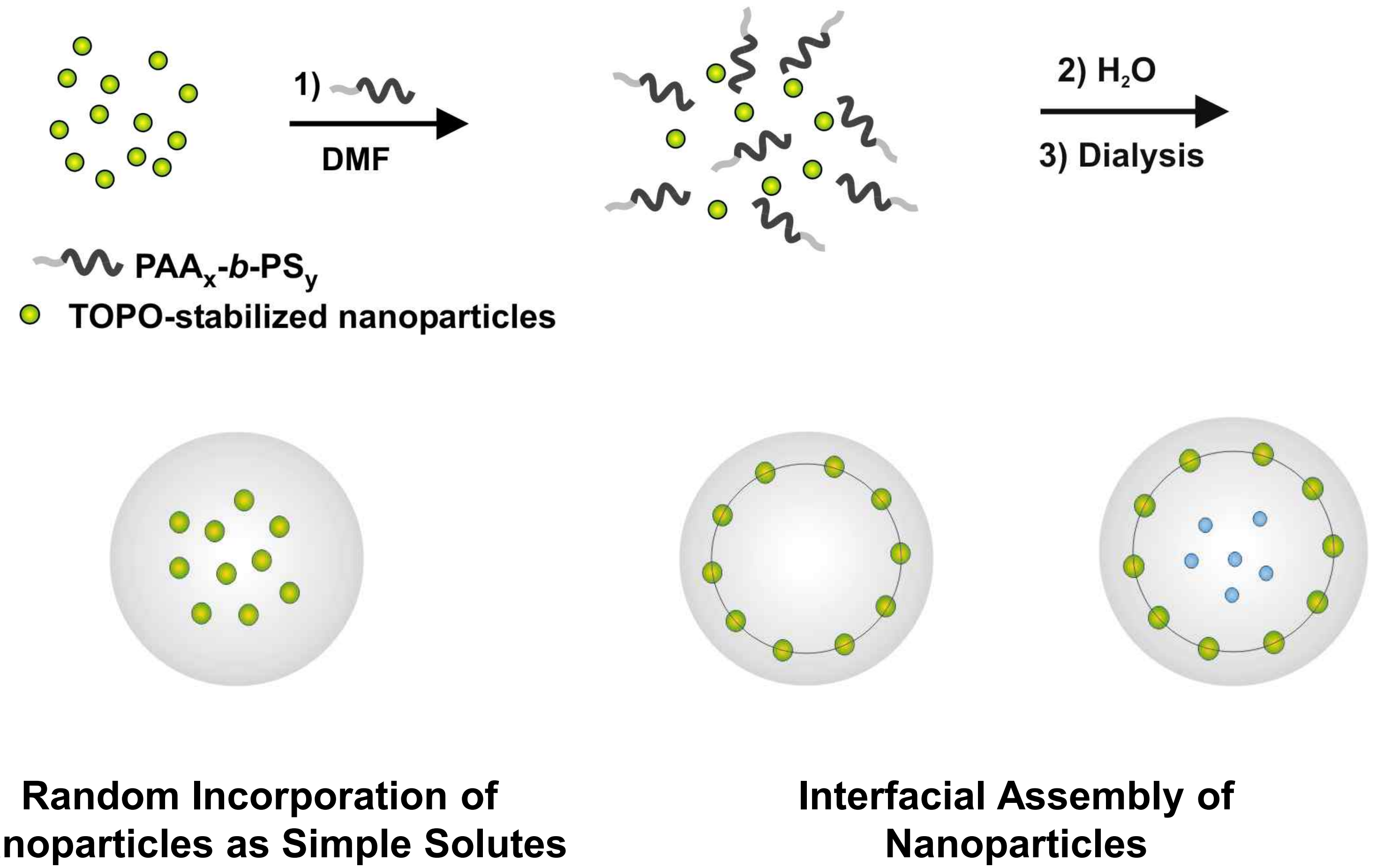


2. Self-Organizing Organic Electronic Materials

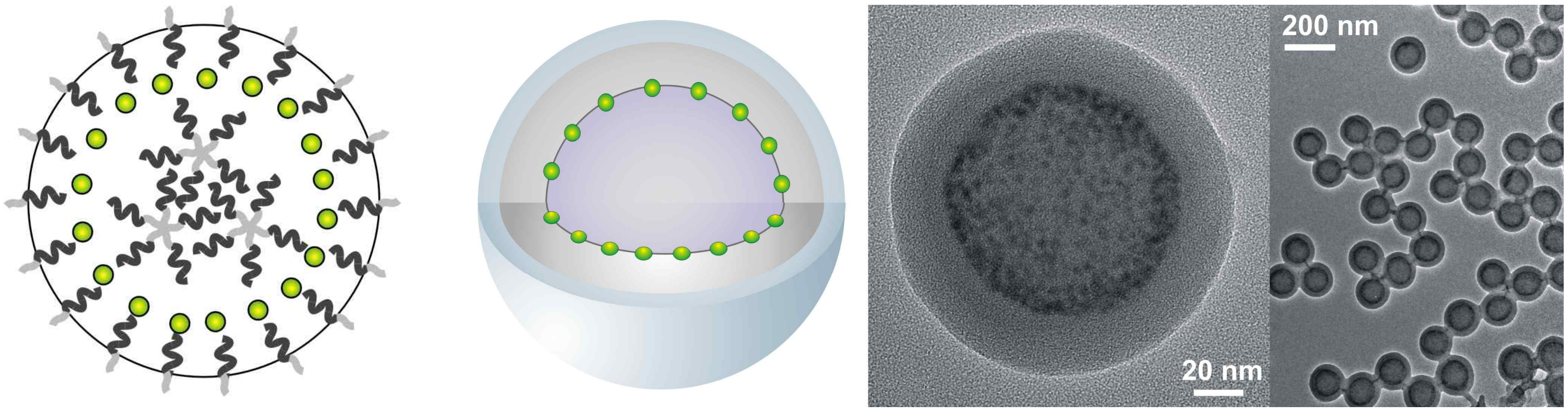


CH_3OH $CH_3OH: K^+$ THF H_2O

Cooperative Assembly of Nanoparticles and Block-Copolymers



Interfacial Assembly of Quantum Dots in Discrete Block-Copolymer Aggregates



Co-assemblies of PAA_{41}-*b*-PS_{193} and CdSe nanocrystals in water

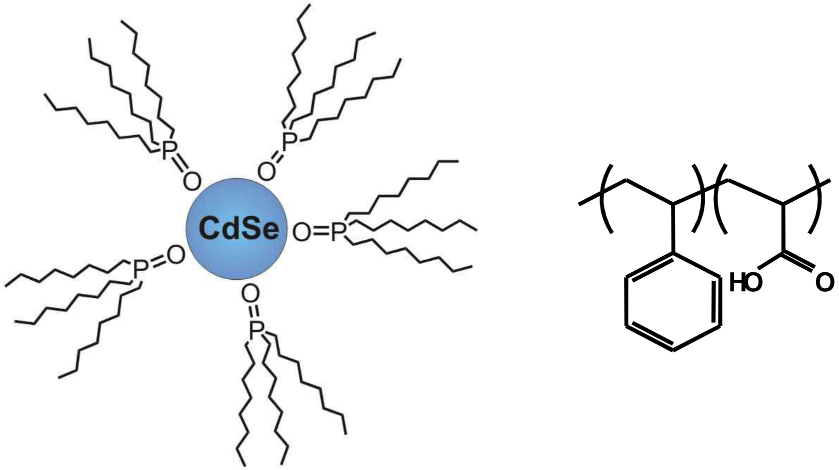
Cavity-like Structure of Nanoparticles

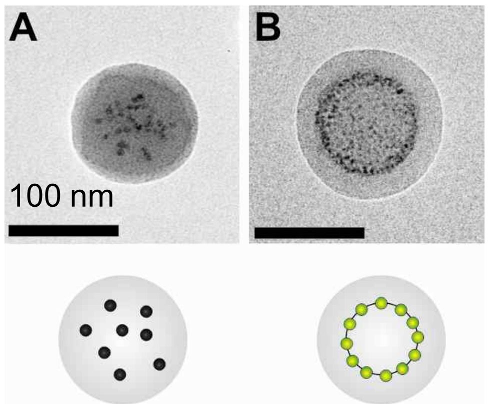
- Polymer shell: A monolayer of block-copolymers with PAA at the exterior
- Polymer core: Reverse micelles of block-copolymers
- QDs arranged at the interface between the polymer core and the polymer shell.

Park and coworkers, *Angew. Chem. Int. Ed.*, **2007**, *119,* 9395.

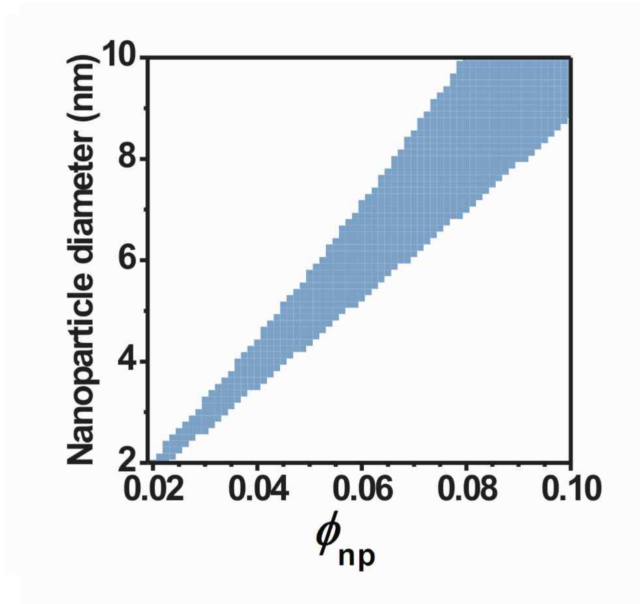
Origin of the Interfacial Assembly

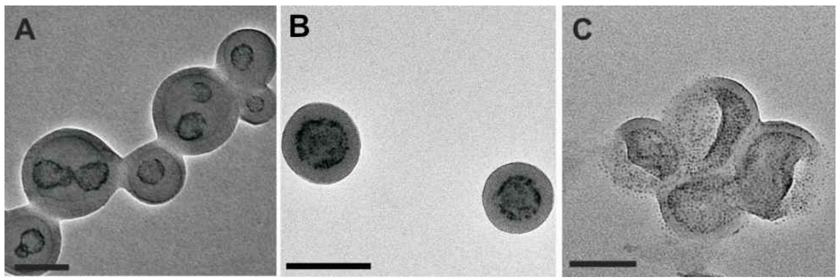
- *Enthalpic Effect*



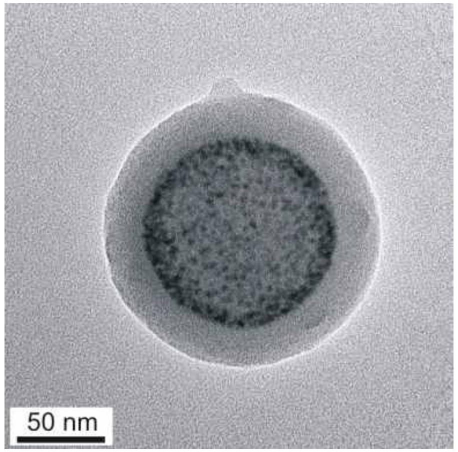


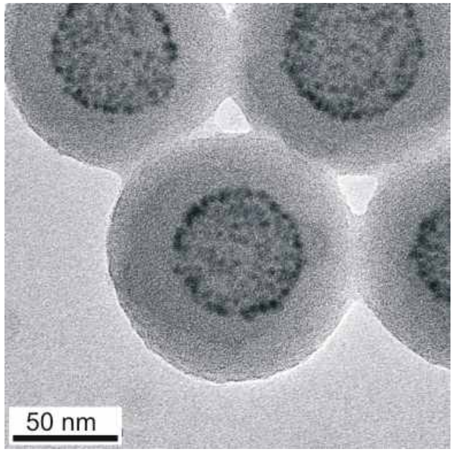
- *Entropic Effect*



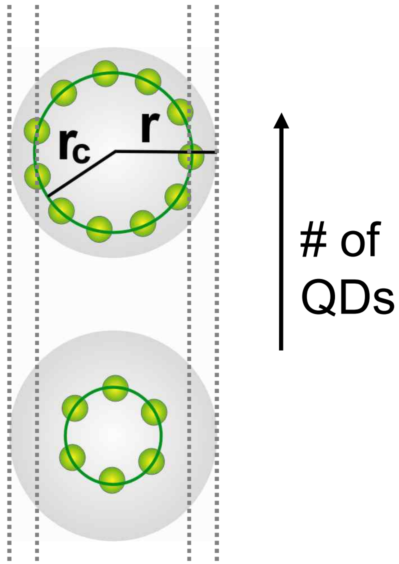


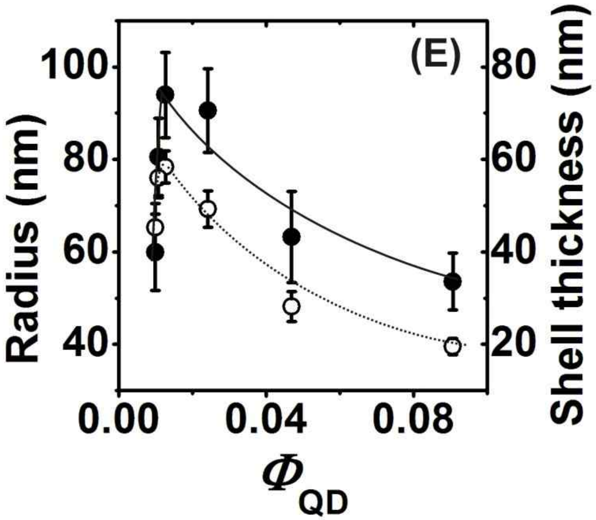
Control of the Location of Nanoparticles

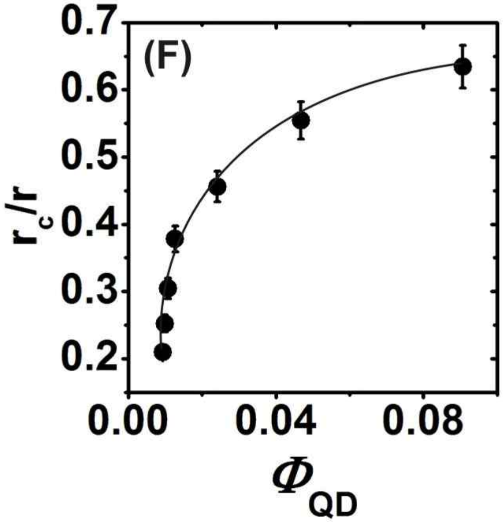




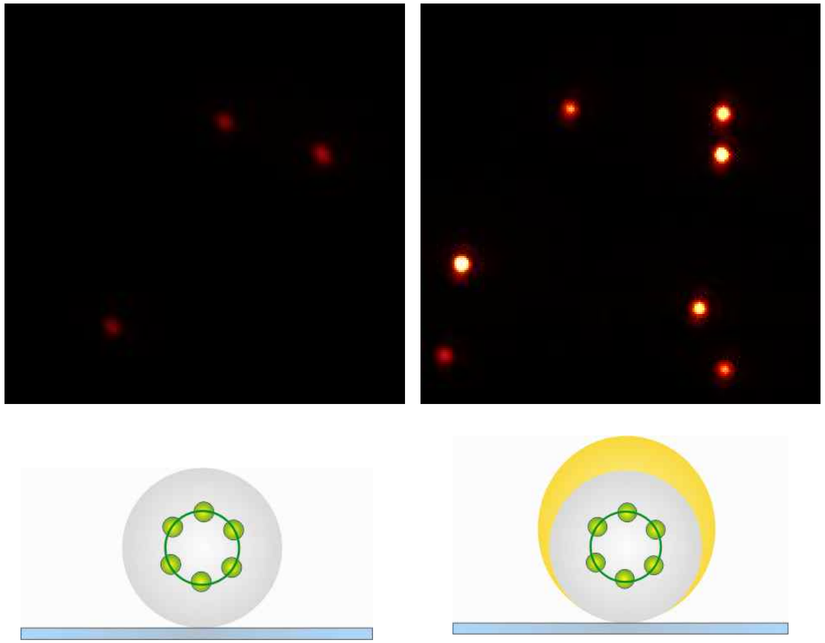
Polymer/QD = 100 Polymer/QD = 400

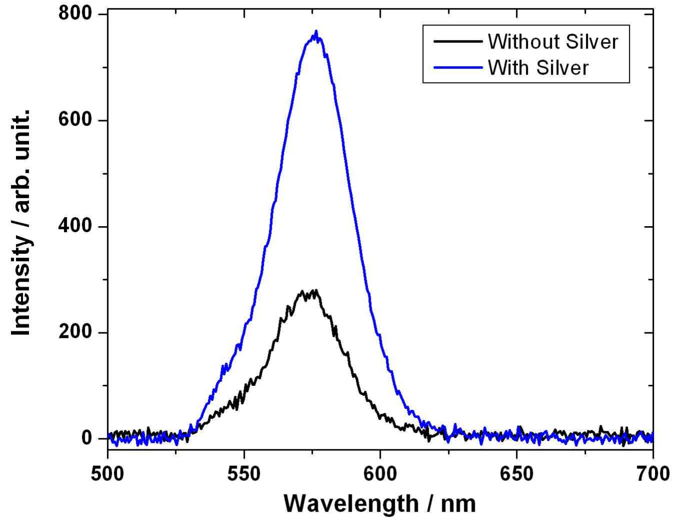






Distance Dependence Studies Using the Controllable Shell Thickness





No silver: 84.38 $\pm$ 50.66 cts/ms
with silver: 281.59 $\pm$ 126.01 cts/ms

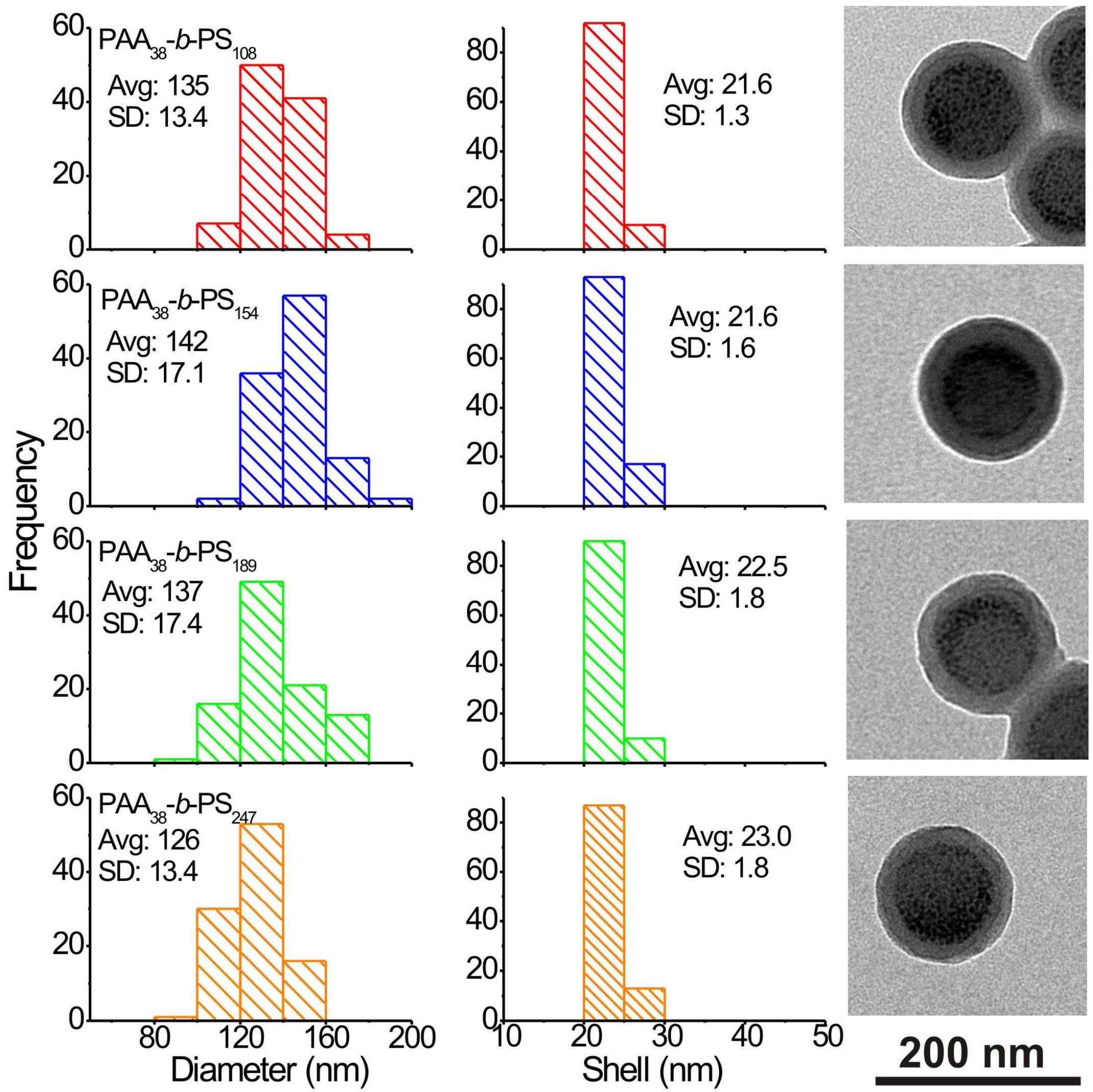
What Controls the Structural Parameters?

PAA$_{38}$-*b*-PS$_{108}$

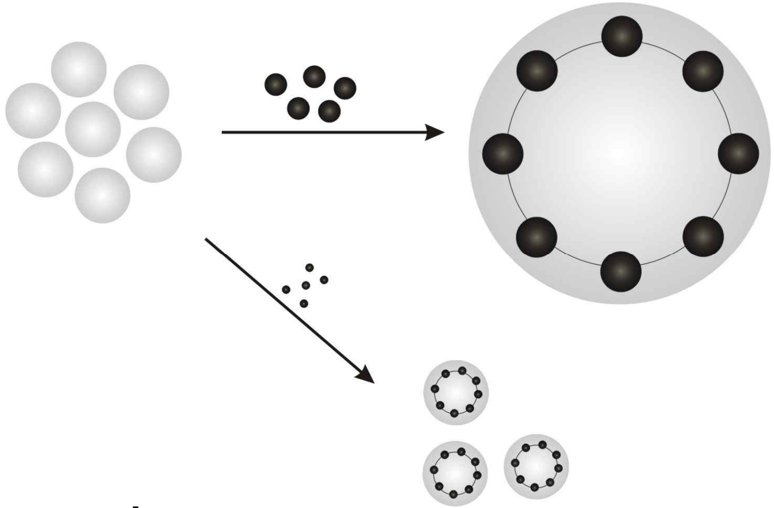
PAA$_{38}$-*b*-PS$_{154}$

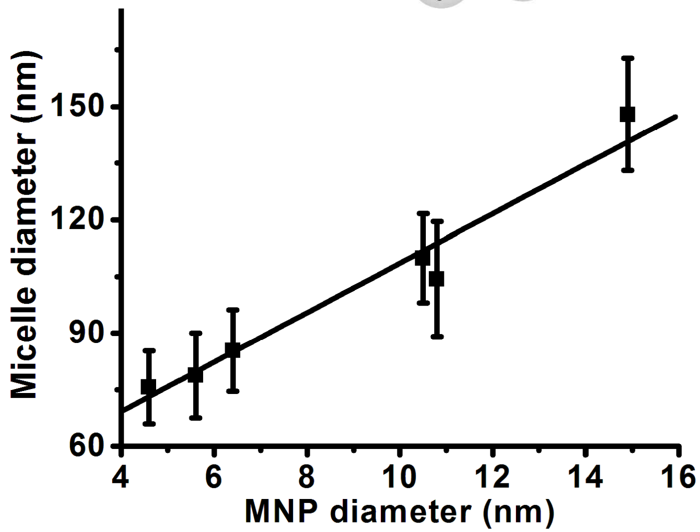
PAA$_{38}$-*b*-PS$_{189}$

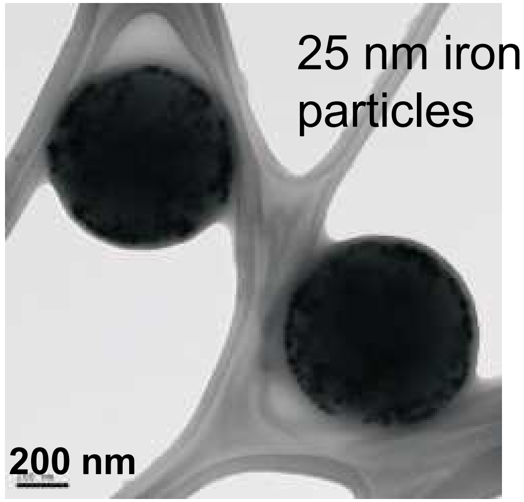
PAA$_{38}$-*b*-PS$_{247}$



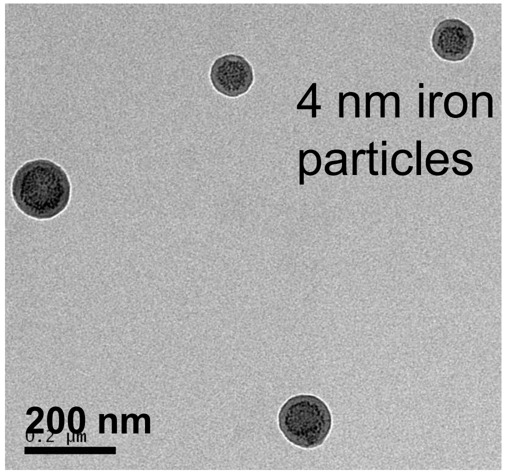
Nanoparticle Size Determines the Size of Co-assemblies





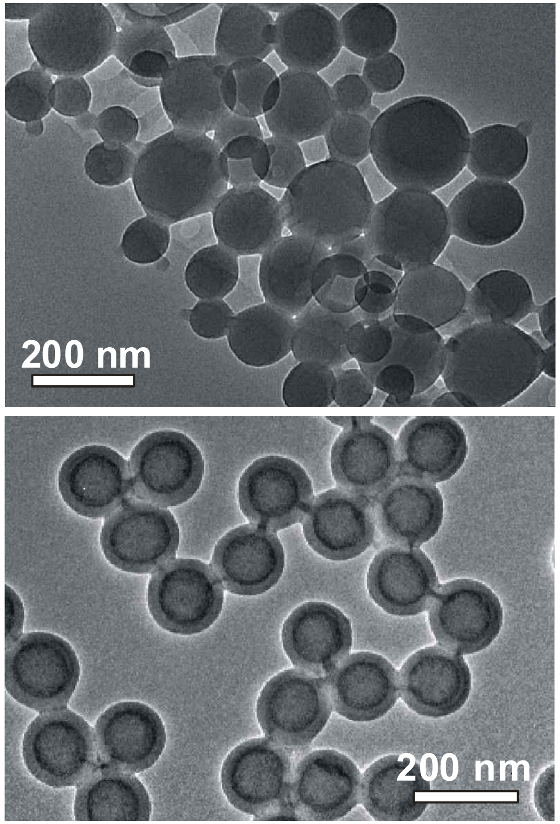


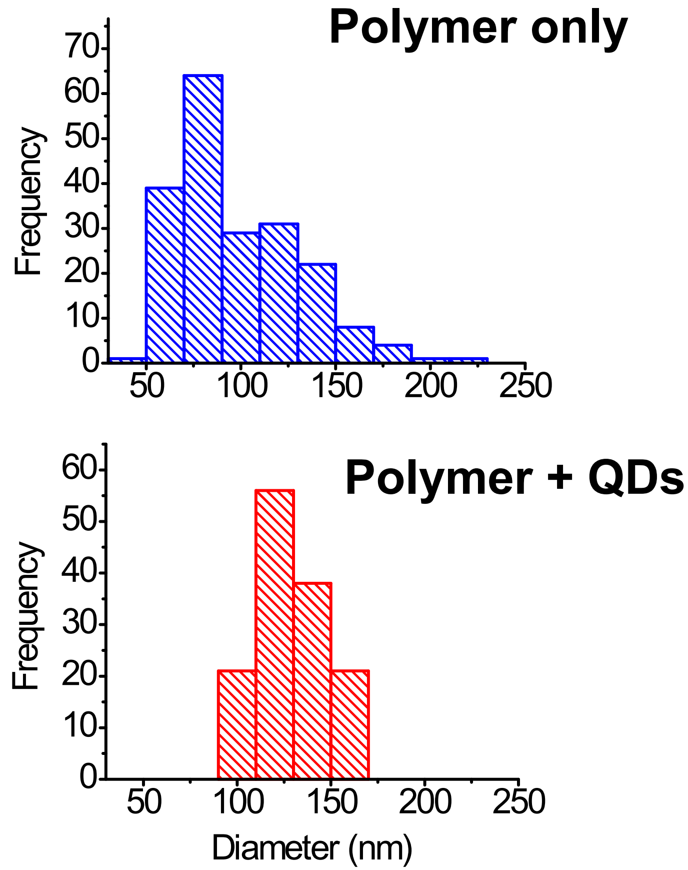
25 nm iron oxide particles



4 nm iron oxide particles

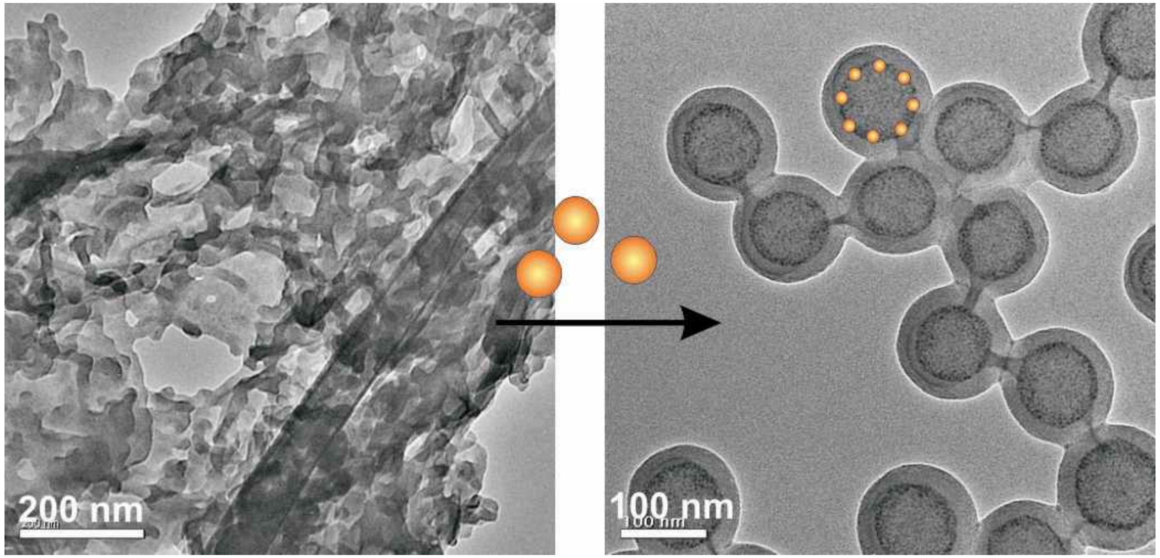
The Incorporation of Nanoparticles Reduces the Size Distribution.





- Nanoparticles narrow the size distribution of the assemblies formed.
- As the concentration of nanoparticles is decreased, the size distribution gradually gets larger.

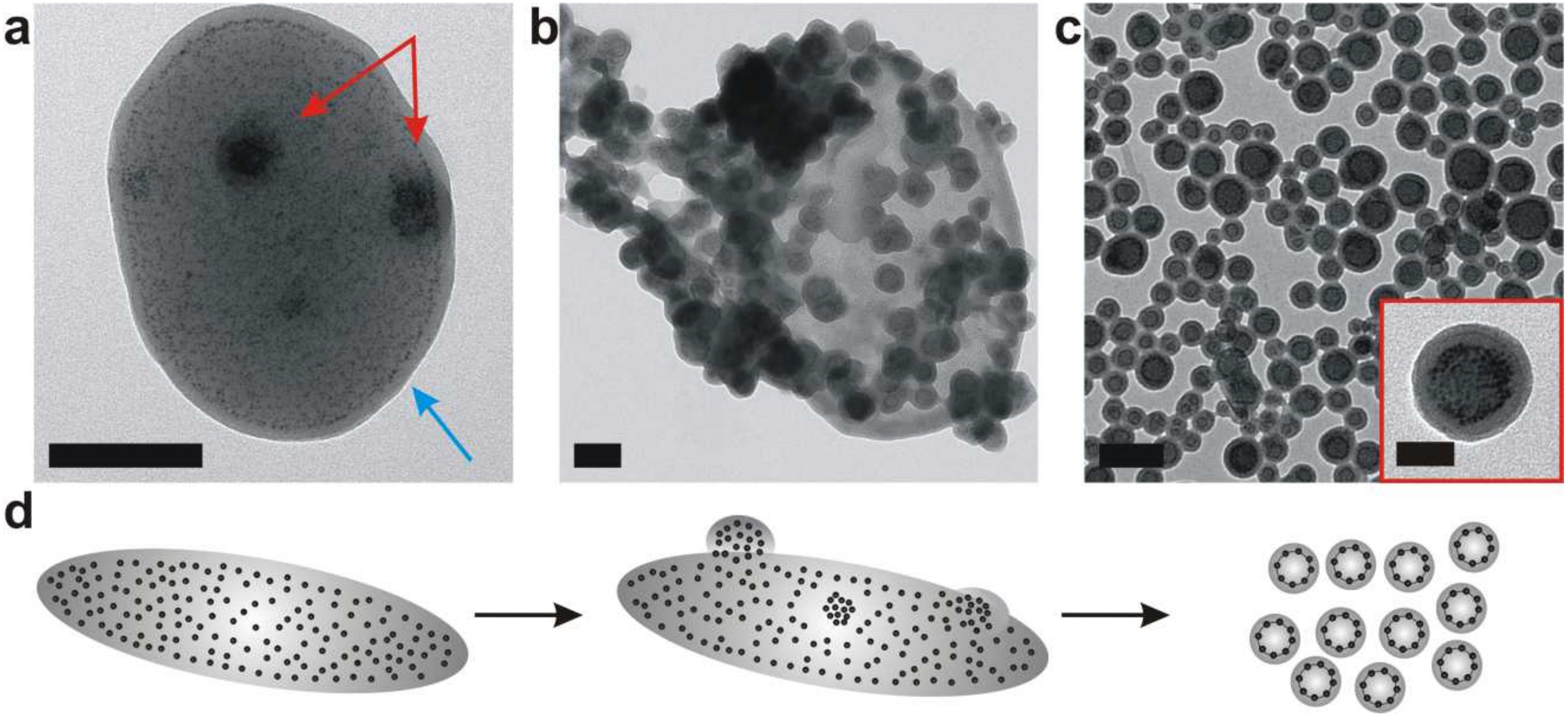
Nanoparticle-Induced Morphological Changes



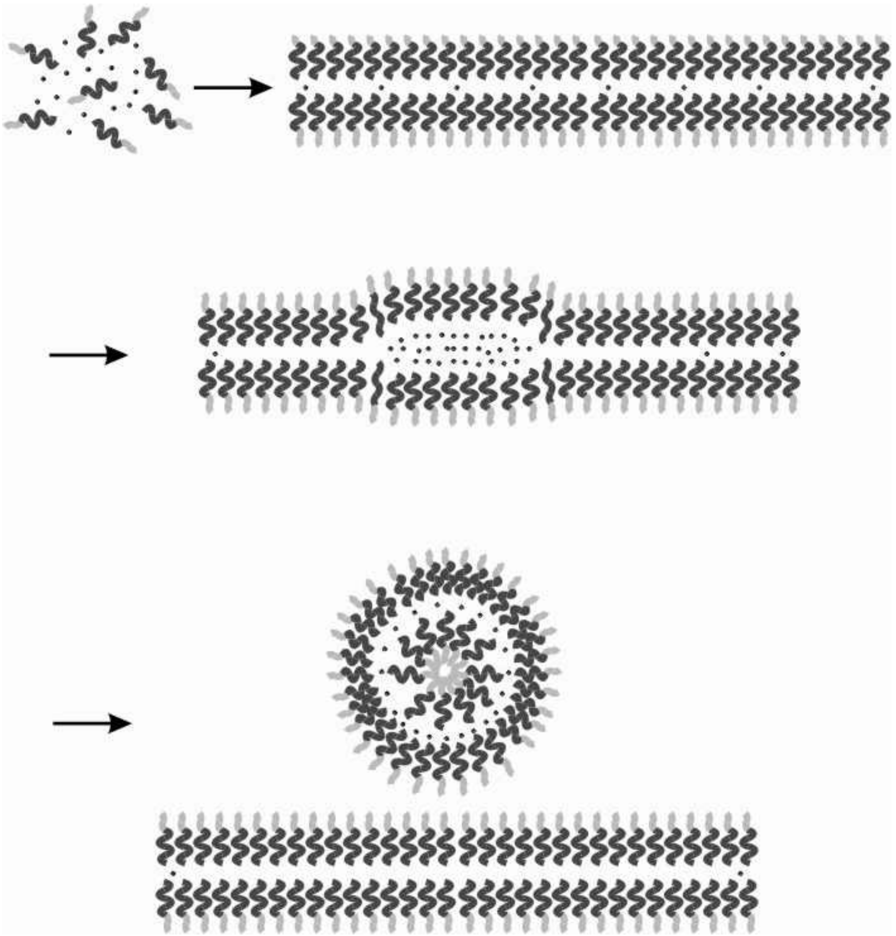
Polymer only **Polymer + QDs**

- Nanoparticles play an active role in the block-copolymer assembly processes rather than simply being incorporated passively in the hydrophobic domain as solutes.
- Nanoparticles cause a drastic morphology change of block copolymer assemblies.

Morphological Transition Induced by Nanoparticle Clustering



Membrane Curvature Change Induced by Nanoparticle clustering



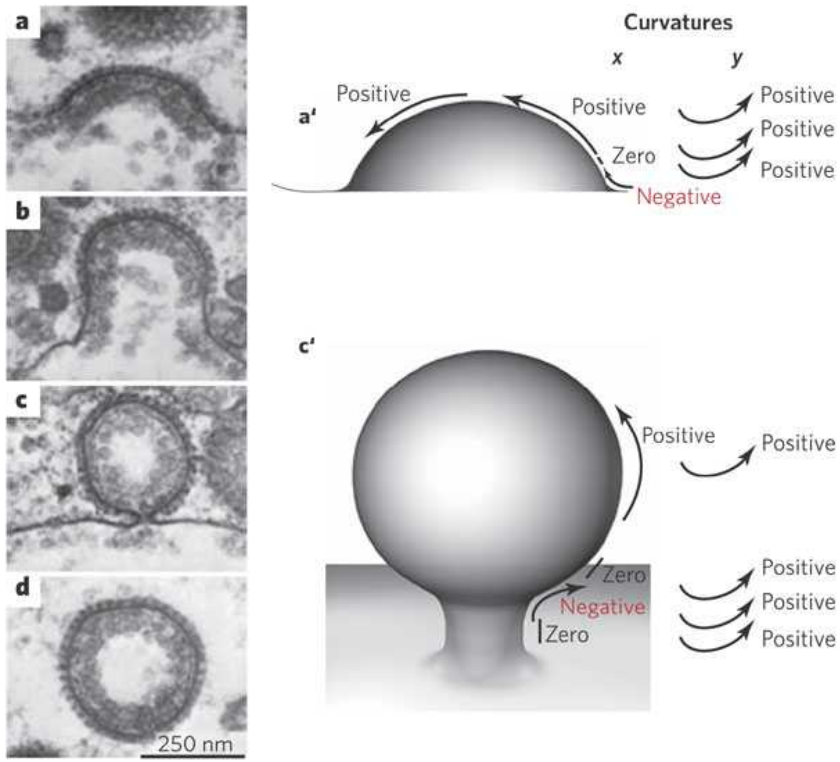


Figure 2: Clathrin-coated vesicle budding where yolk protein is being incorporated into vesicles in oocytes. *Taken from McMahon et al. Nature, 438, 590 (2005).*

Overview

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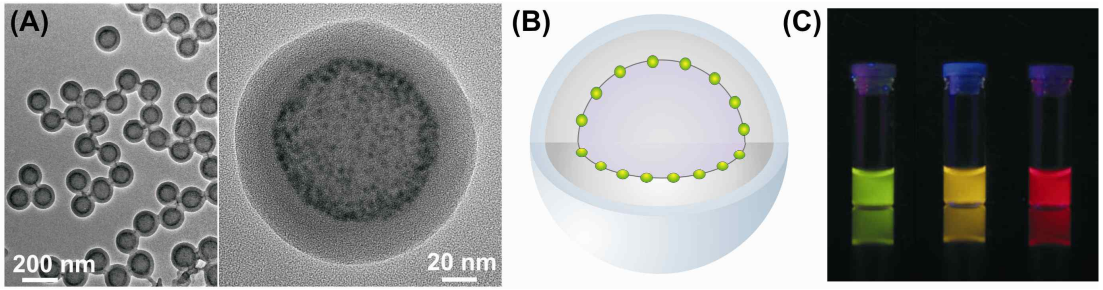

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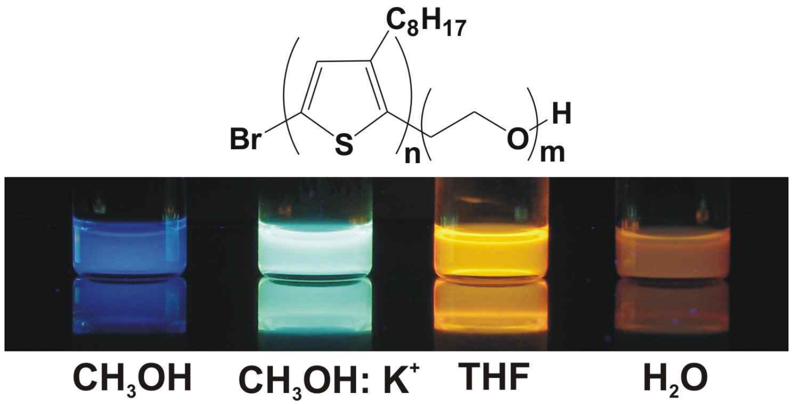
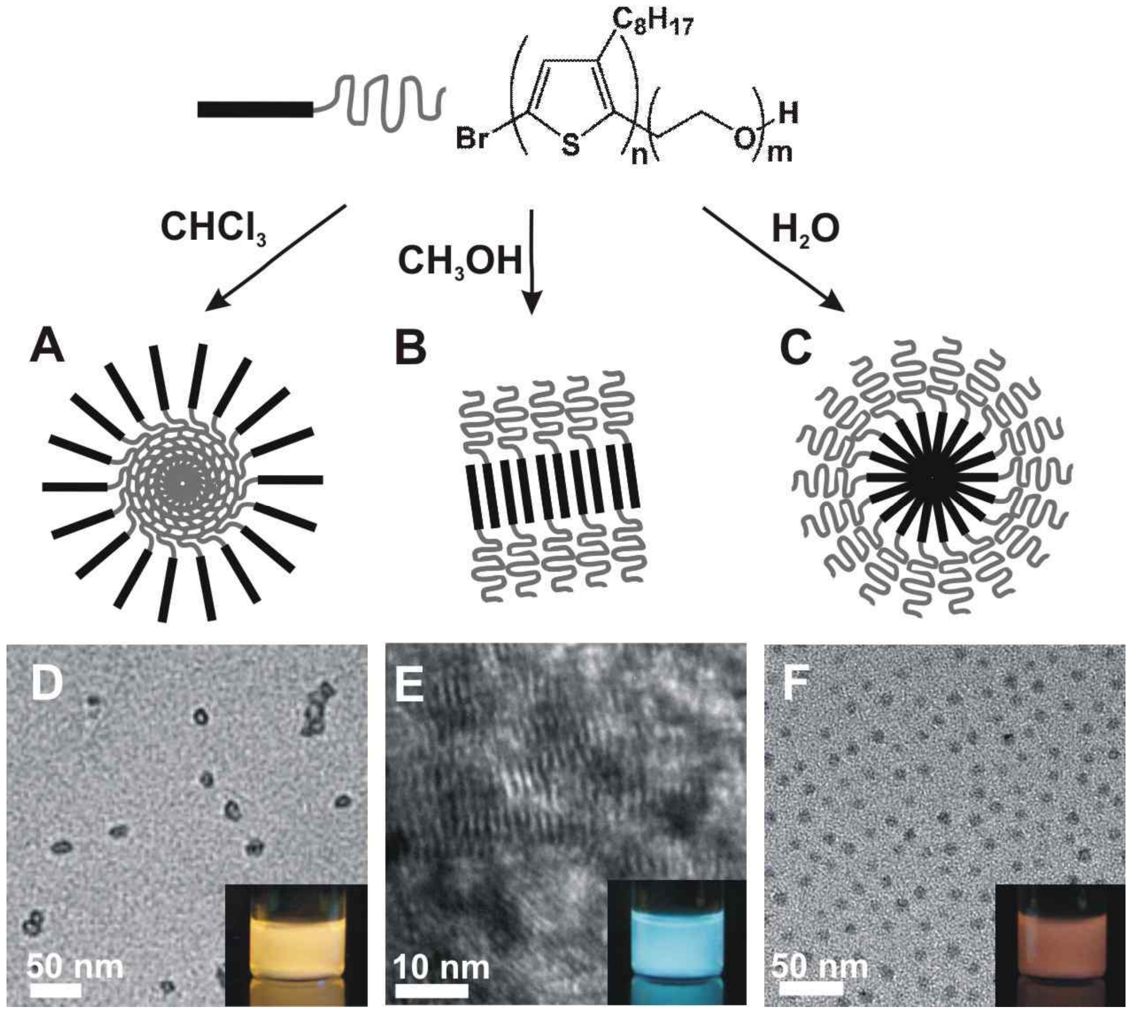
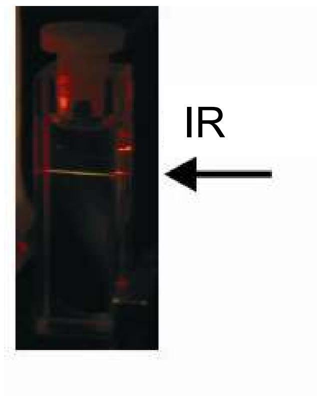
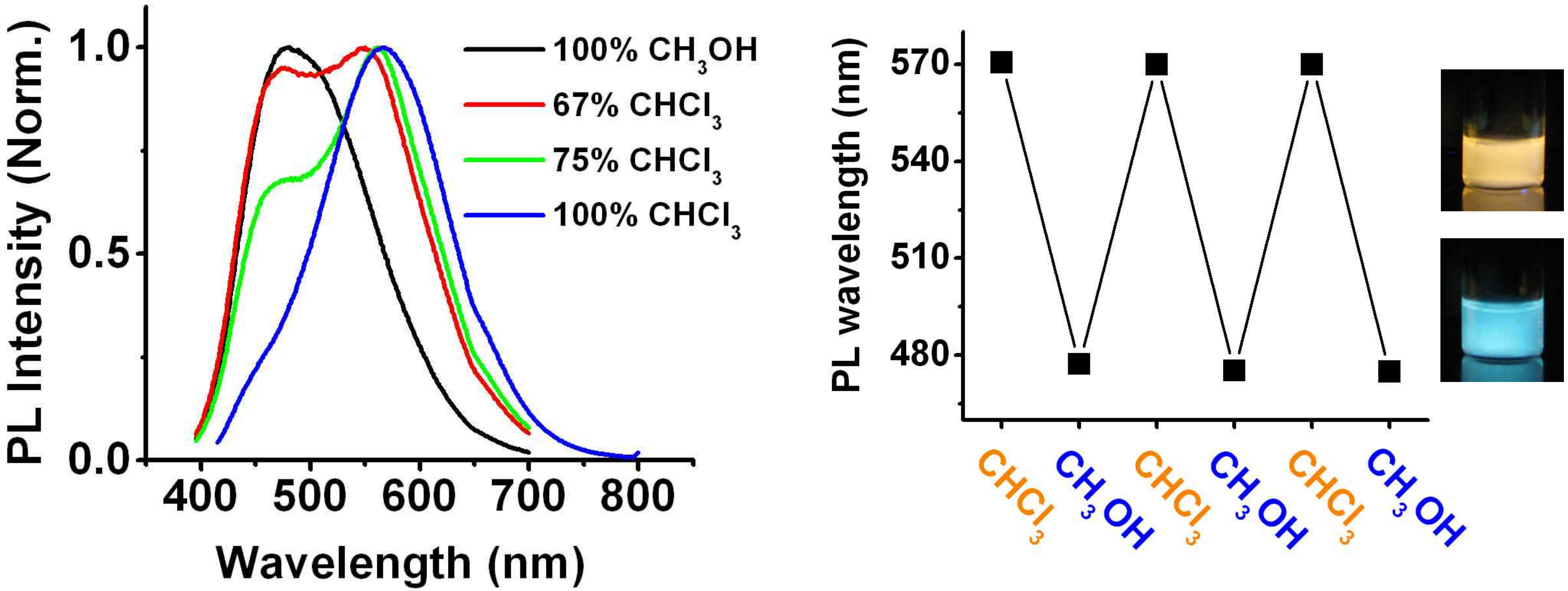


Self-Organizing, Optically Active Organic Materials

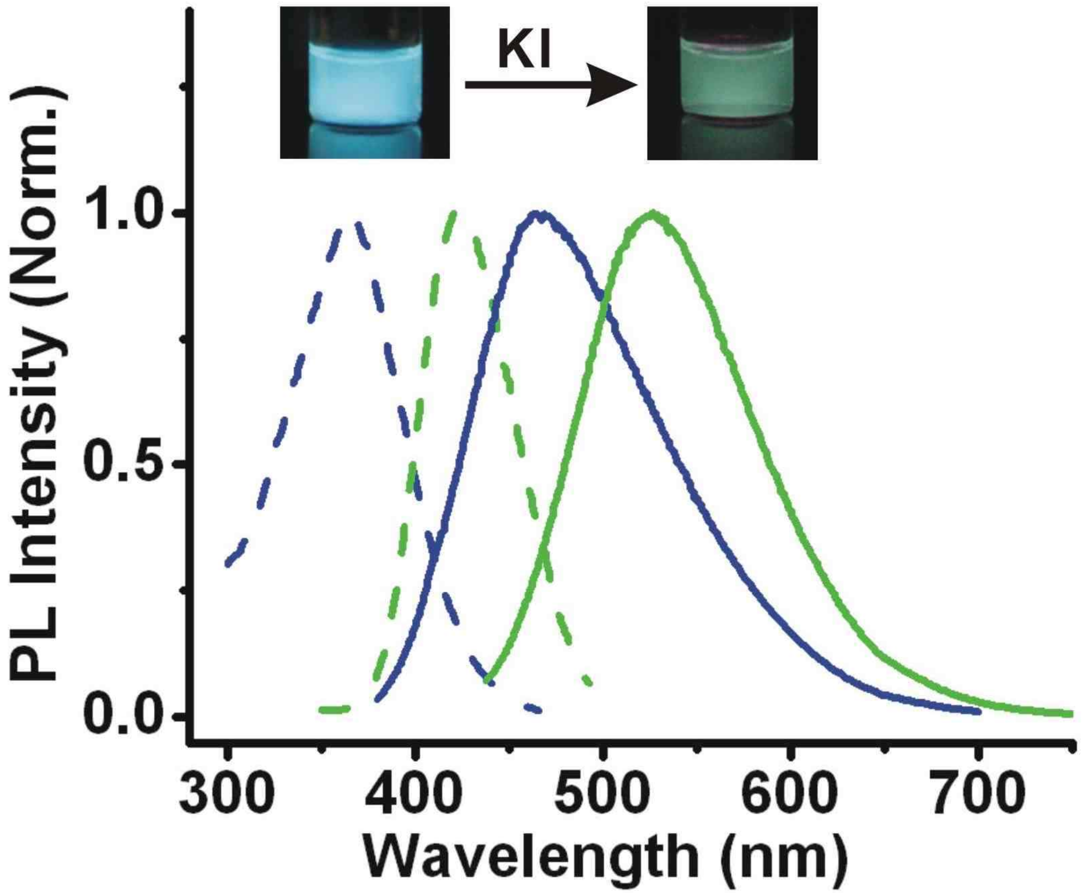




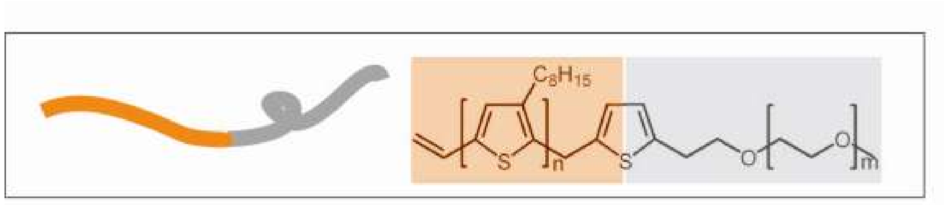
Reversible Morphology and Emission Color Changes



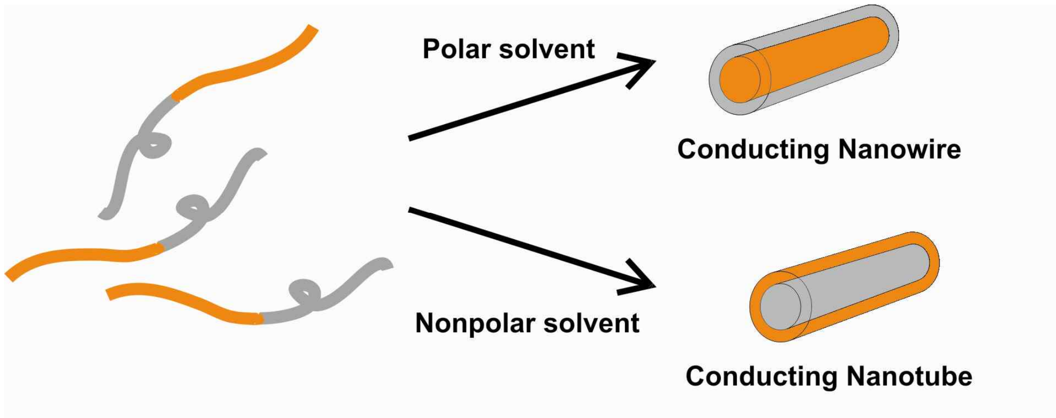
Fine Tuning of Emission Colors: Salt Effect

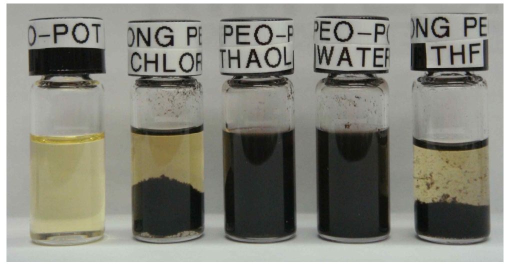


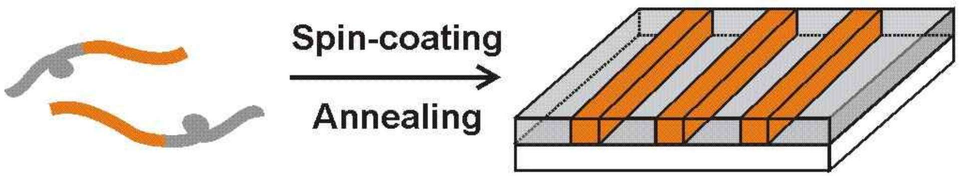
Self-Assembled Building Blocks for Inorganic/Organic Hybrid Materials



Nanotubes wrapped in conjugated block-copolymers







Summary

- Nanoparticles play an active role in the self-assembly process of block-copolymers, and they can drastically alter the behavior of polymers and the co-assembly structure.

- Cooperative self-assembly of nanoparticles and block-copolymers offer a facile way to control the arrangement of nanoparticles in discrete block-copolymer assemblies.

- We developed conjugated block-copolymers that can self-assemble into various morphologies including core-shell particles, rods, nanowires and layered structures.

- Their band gap and the photoluminescent properties are highly tunable by simply controlling their assembly structures.

Acknowledgements

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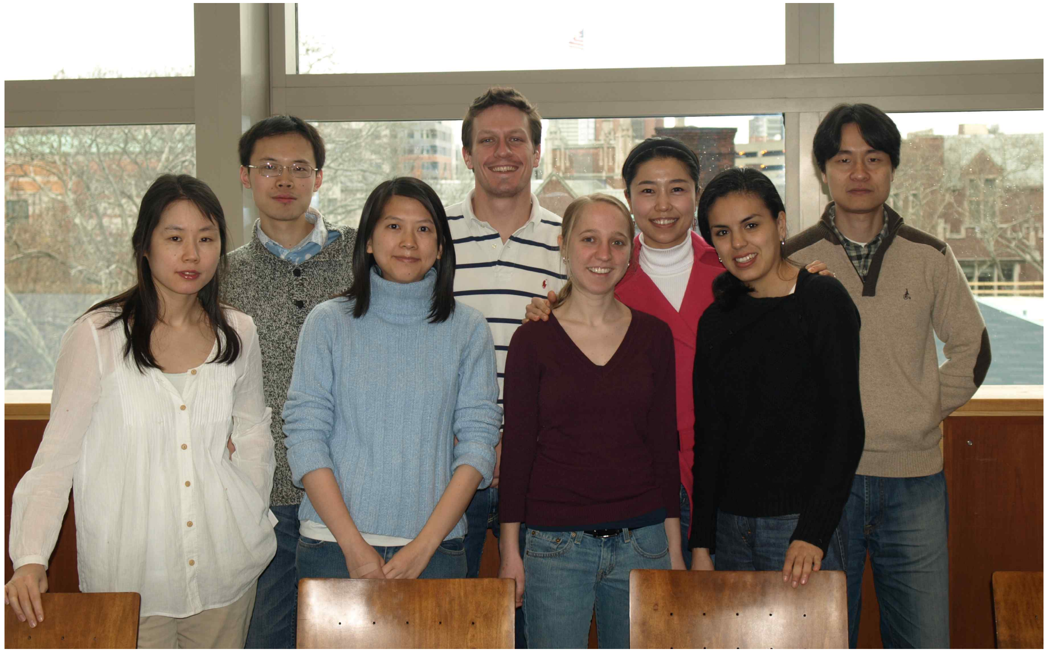

Collaborators

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