Studies of Nanoparticles Assemblies at Fluid Interfaces

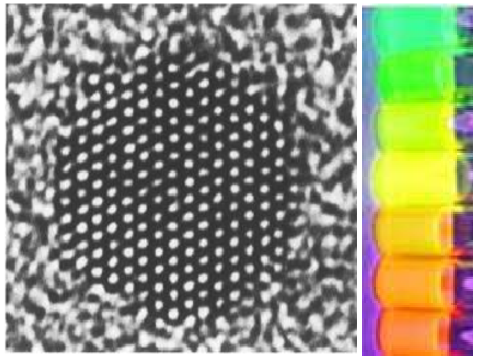
Motivation

- **Objective**: Simple routes to the fabrication of functional materials by hierarchical approaches to organize both organic and inorganic building blocks, with nanometer-level control.

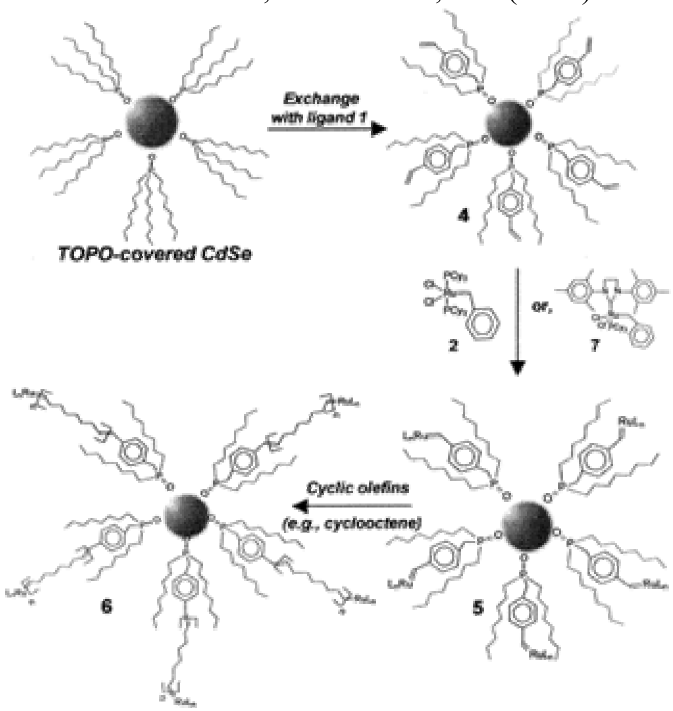
- **Approach**: Directed self-assembly of nanoparticles into 3-D structures at fluid-fluid interfaces, for sensing, bio-separation, encapsulation and delivery application…

Introduction: *Inorganic Nanoparticles*

Cadmium Selenide (CdSe) nanoparticles



Alivisatos, Science 271, 933 (1996).



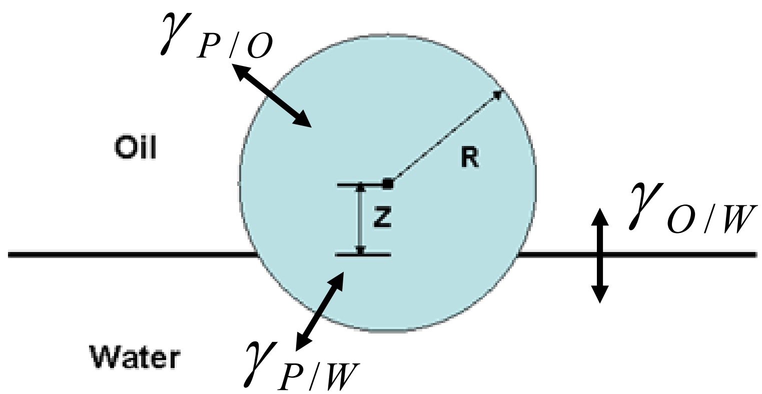
Skaff, *et. al*. JACS 124, 5729 (2002)

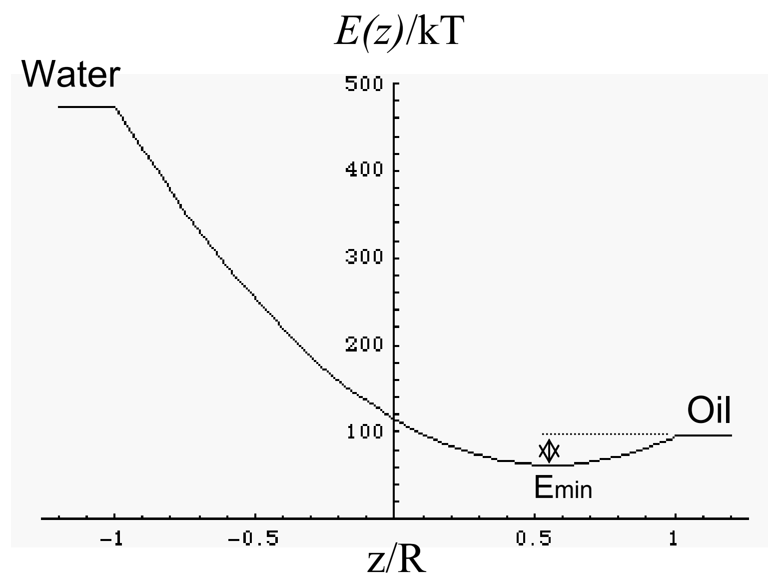
Ideal building blocks

- Inorganic Core ---
  Unique electronic, magnetic, and optical properties.
- Organic Ligands ---
  Chemical interaction with the surroundings, and can be functionalized.

Theory: *Driving Force for the Assembly*

Pieranski, P. PRL 45, 569 (1980).



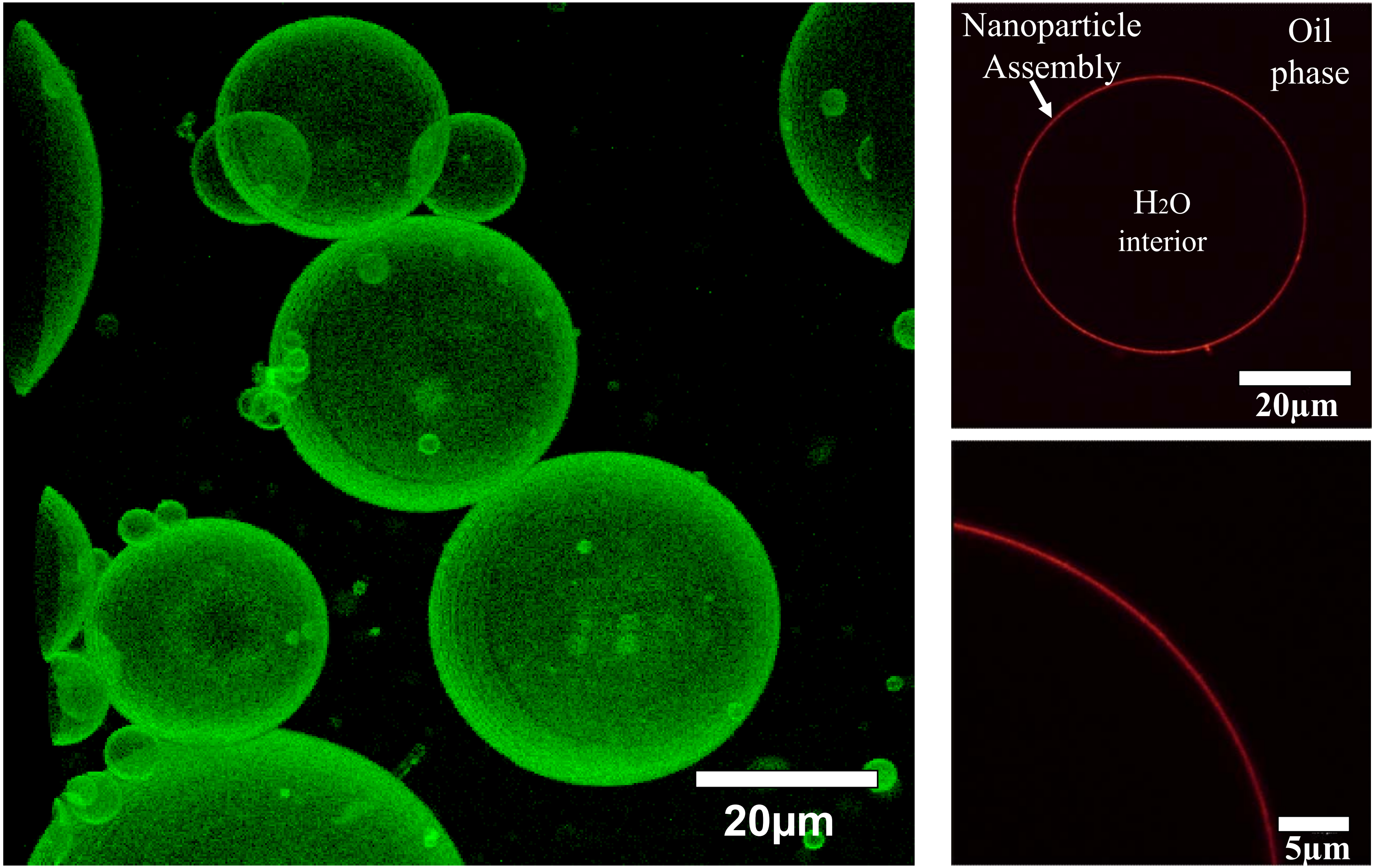


$$E(z) = \pi R^2 \gamma_{O/W} \cdot \left[\left(\frac{z}{R}\right)^2 + 2 \cdot \left(\frac{\gamma_{P/O}}{\gamma_{O/W}} - \frac{\gamma_{P/W}}{\gamma_{O/W}}\right) \cdot \left(\frac{z}{R}\right) + 2 \cdot \left(\frac{\gamma_{P/O}}{\gamma_{O/W}} + \frac{\gamma_{P/W}}{\gamma_{O/W}}\right) - 1 \right]$$

$$E_{\min} \text{ at } z = \frac{\gamma_{P/W} - \gamma_{P/O}}{\gamma_{O/W}} \cdot R$$

Interfacial Engery Well $\Delta E = E_{P/O} - E_{\min} = \frac{\pi R^2}{\gamma_{O/W}} \cdot \left[\gamma_{O/W} - \left(\gamma_{P/W} - \gamma_{P/O}\right)\right]^2$

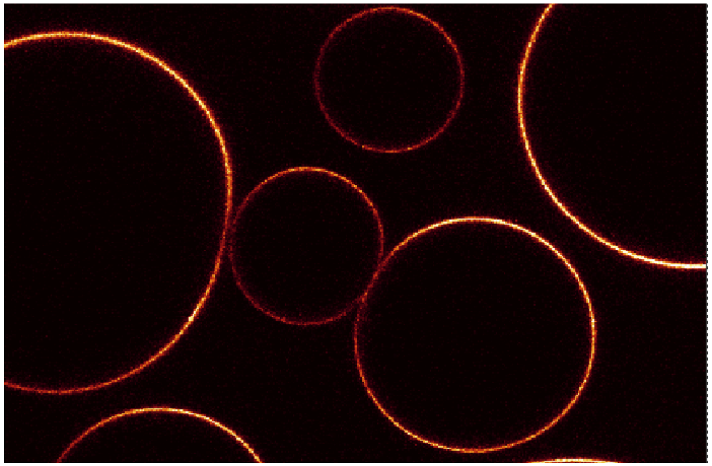
CdSe Nanoparticle Assembly: *Probed by Confocal Microscope*

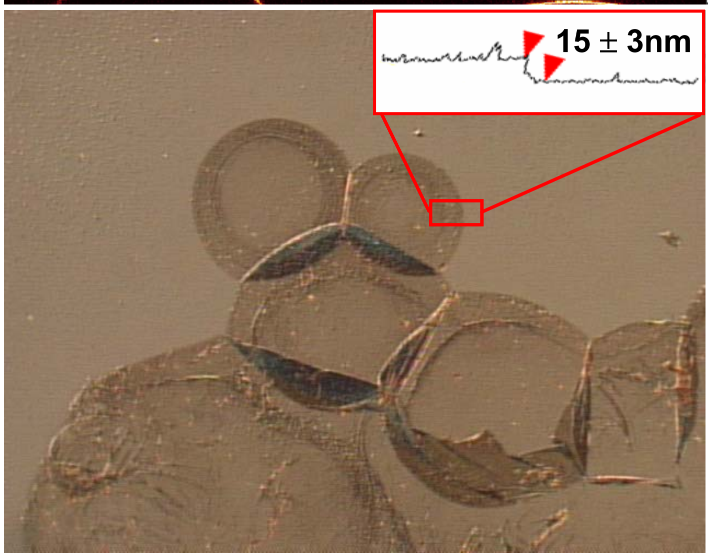


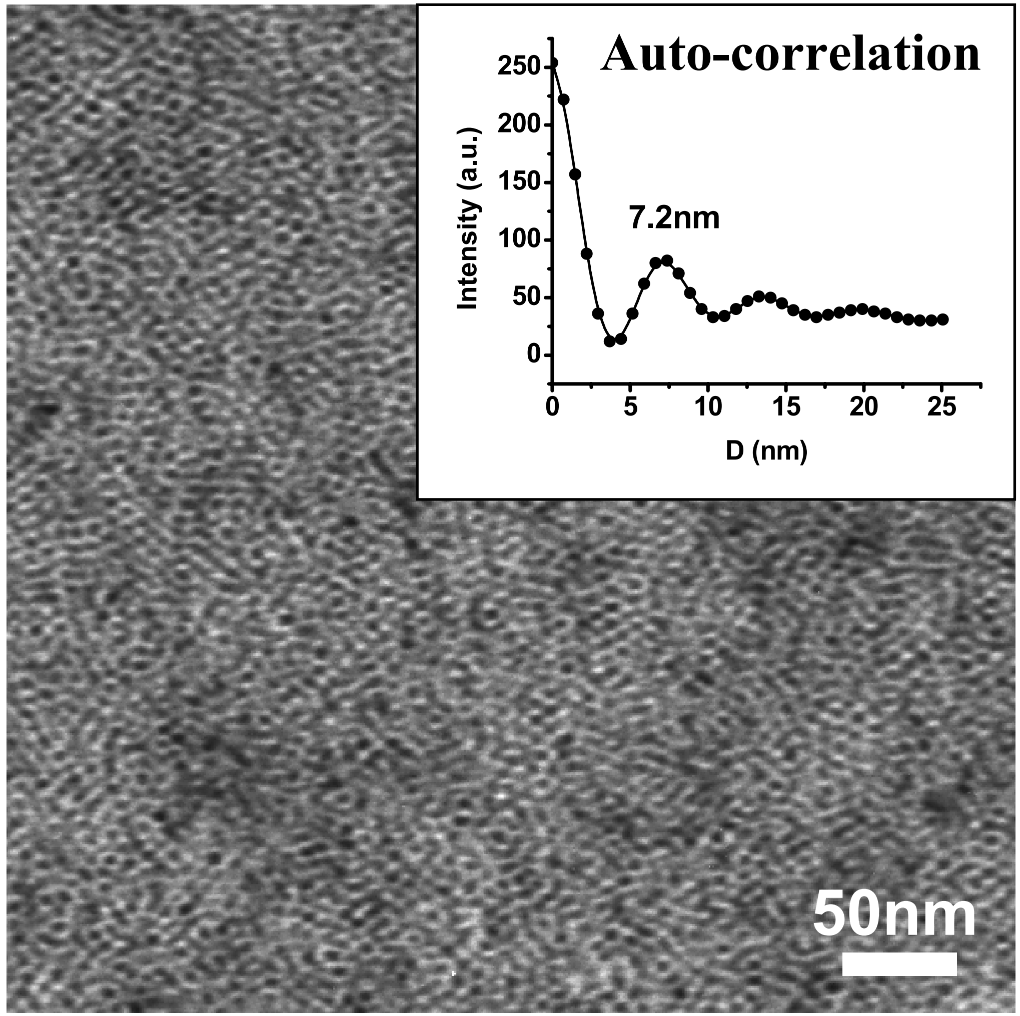
Fluorescence confocal images of nanoparticles at Oil-Water Interface

Assembly: *Morphology*

Nanoparticles: 4.6nm Core Diameter, Ligand Length ~0.8nm

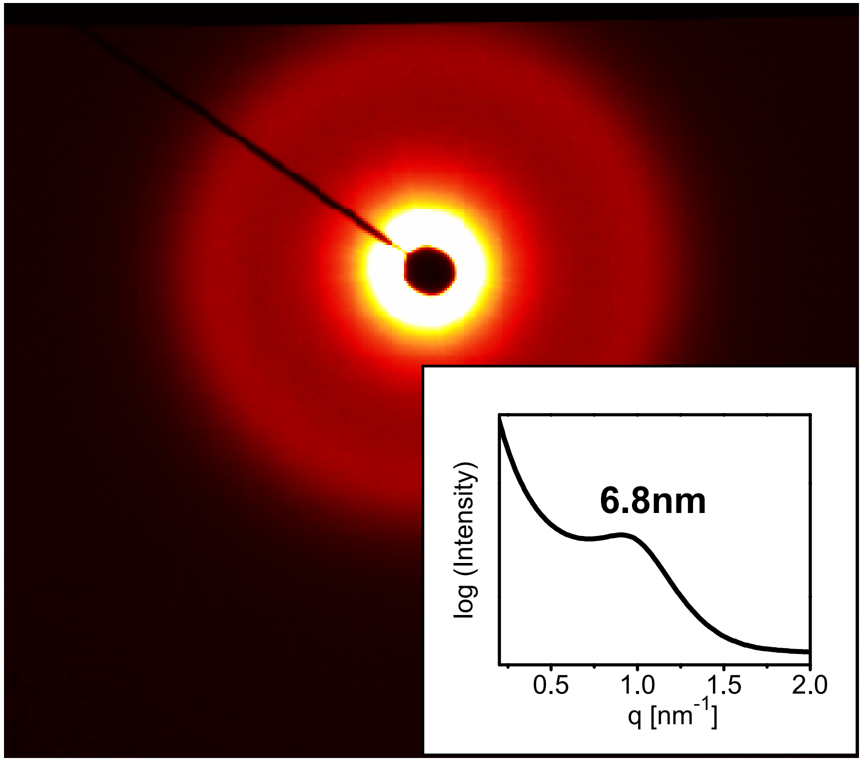




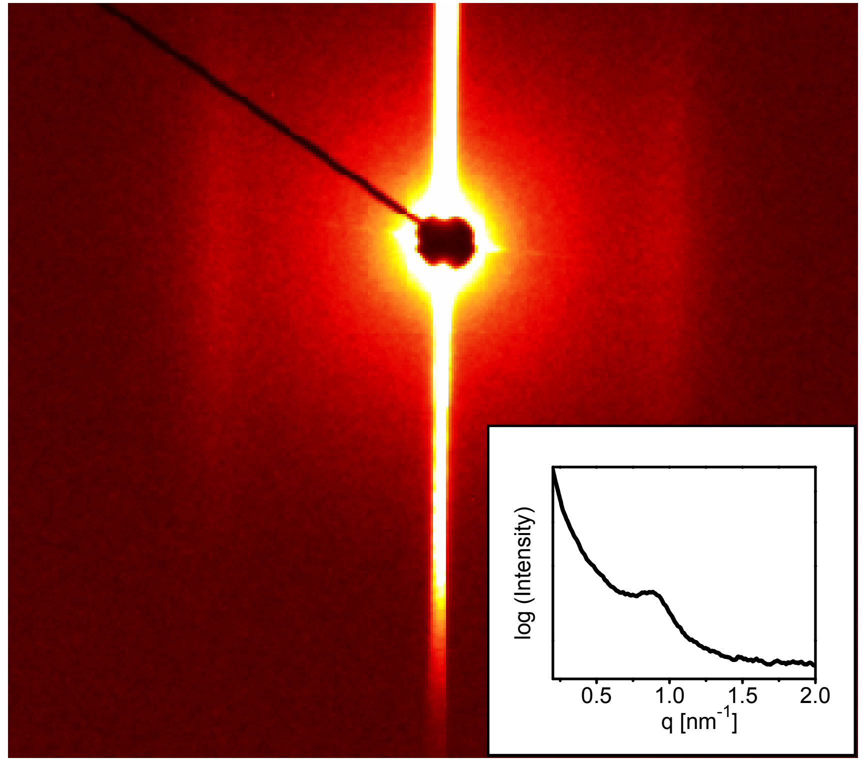


X-ray Scattering

Nanoparticles: 4.6nm Core Diameter, Ligand Length ~0.8nm



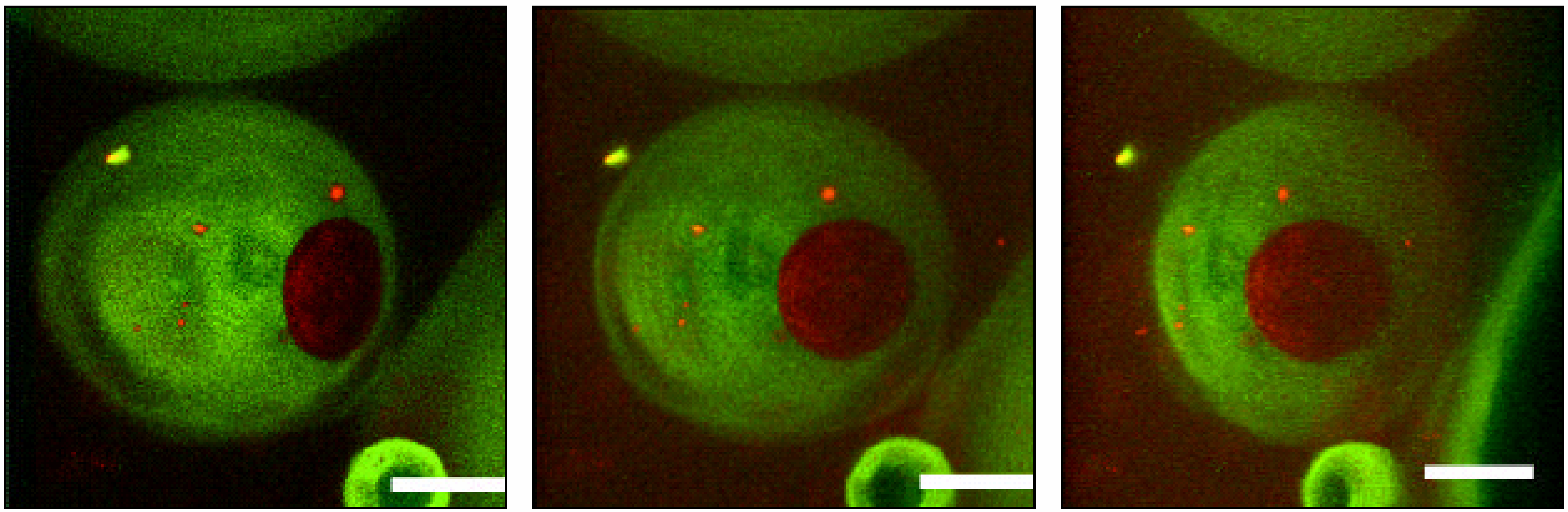
SAXS on nanoparticle-stabilized water droplets



GISAXS on nanoparticle-stabilized Planar oil-water interface

2-D Phase Separation at the Interfaces

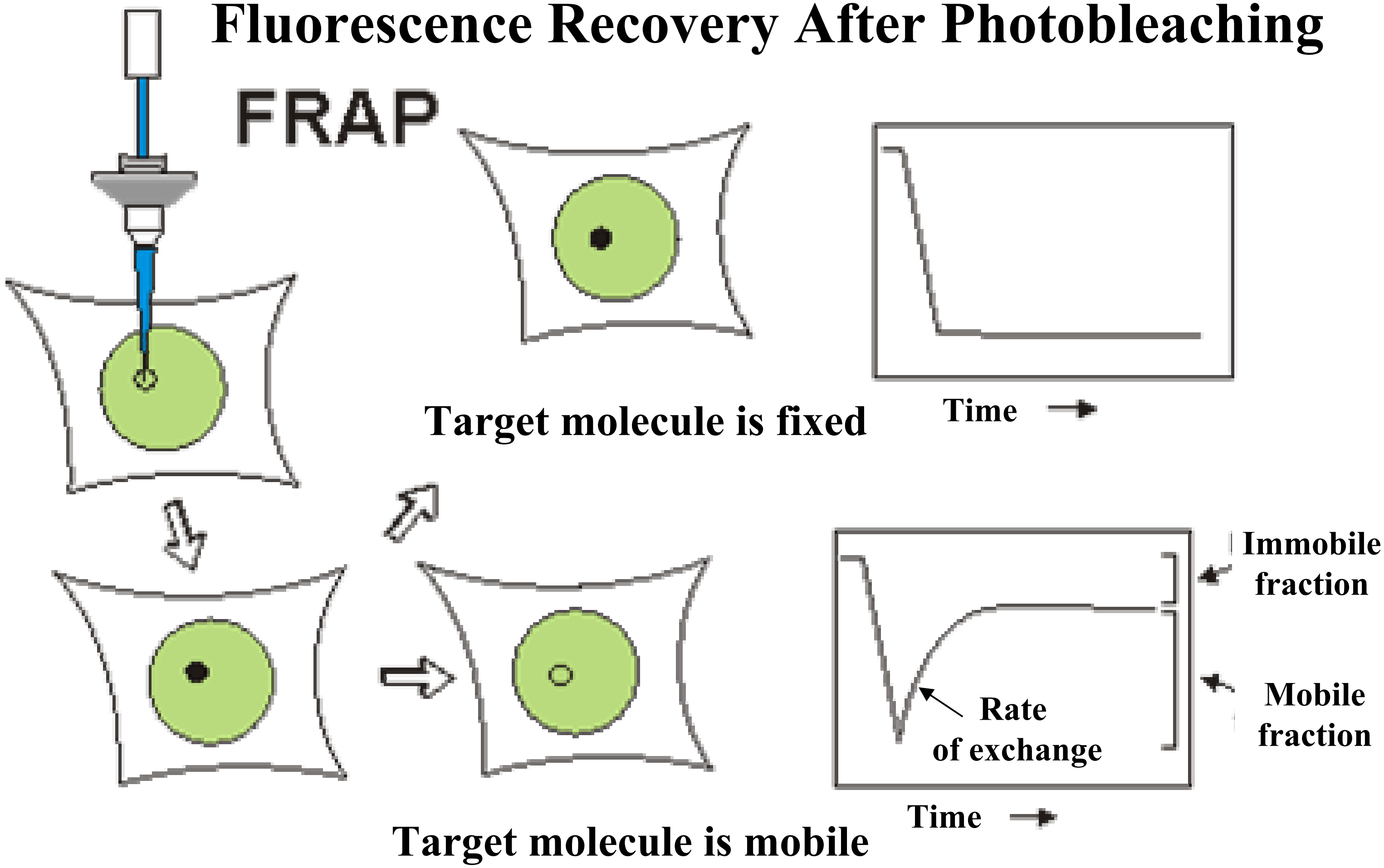
3nm particles:	**Green Fluorescence**
5nm particles:	**Red Fluorescence**



LCSM image of phase-separated nanoparticles on a water droplet
(3-D views from different angle, scale bar: 16μm).

Dynamics: *Studies by Photobleaching*

Fluorescence Recovery After Photobleaching



Elson & Webb Biophys. J. 16, 1055 (1976); Blonk J. Microscopy 169, 363 (1992)..

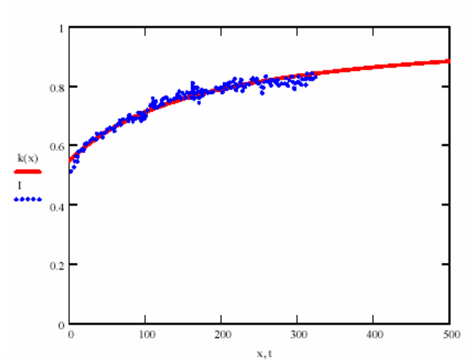
Dynamics: *Fitting by Different Models*

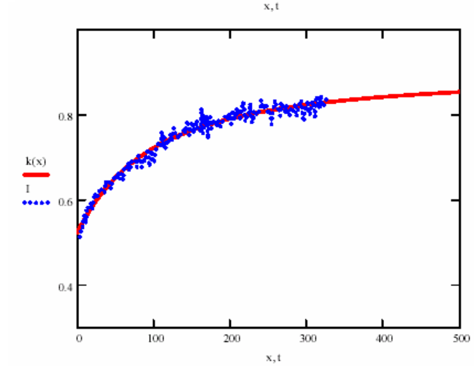
2-D Diffusion Model

$$f(t)=\sum_{0}^{\infty}\frac{(-\kappa)^n}{n!}\frac{1}{1+n\left(1+\left(\frac{2t}{\tau_D}\right)\right)}$$

3-D Diffusion Model

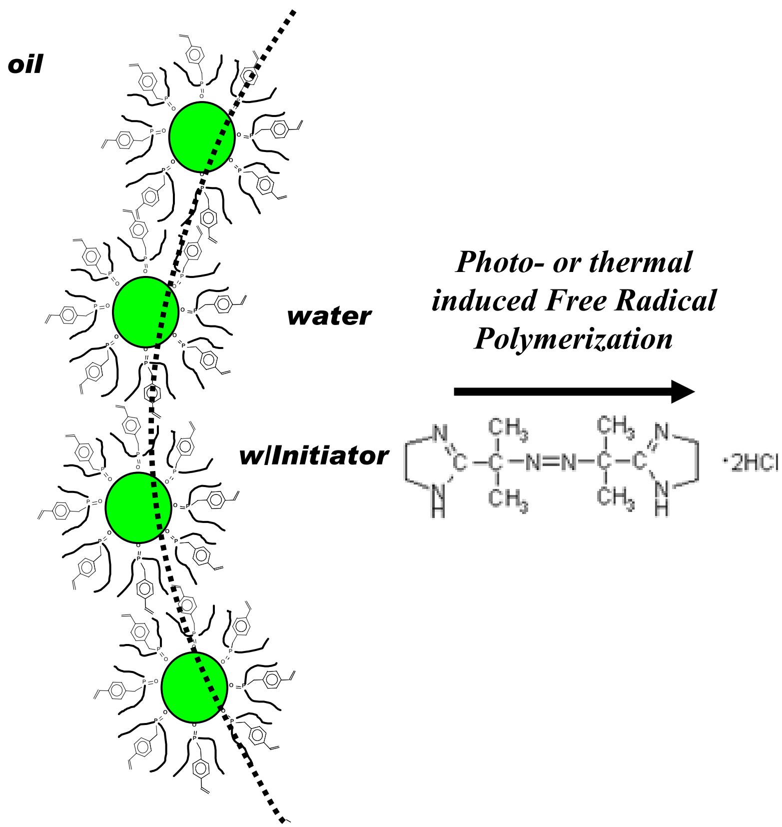
$$f(t)=\sum_{0}^{\infty}\frac{(-\kappa)^n}{n!}\frac{1}{\sqrt{1+n\left(1+\left(\frac{2t}{\tau_{Dz}}\right)\right)}}\bullet\frac{1}{1+n\left(1+\left(\frac{2t}{\tau_{Dr}}\right)\right)}$$



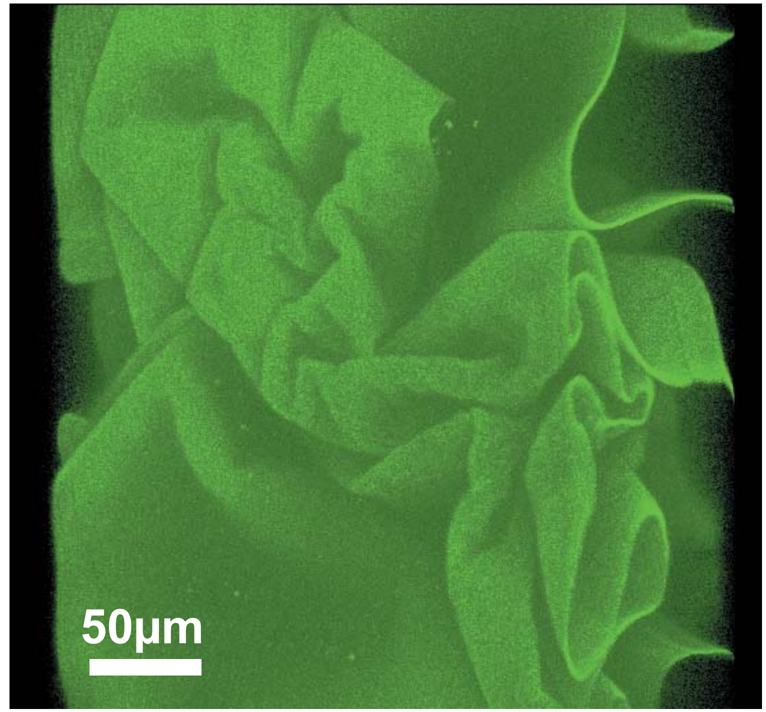


	2D model		3D model τ_{Dr}(s)
	τ_D(s)	D= $\omega^2/4\tau_D$ (cm^2/s)	τ_D(s)
FRAP	190 ± 54	1.3 (± 0.3) * 10^{-10}	121 ± 42
FLIP	70 ± 15	3.3 (± 0.7) * 10^{-10}	126 ± 12

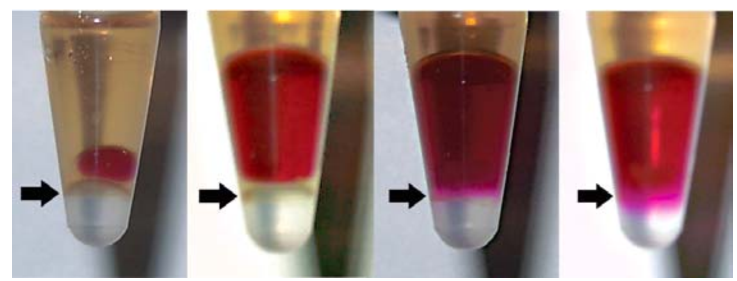
Crosslinking: *Ultrathin Membranes*



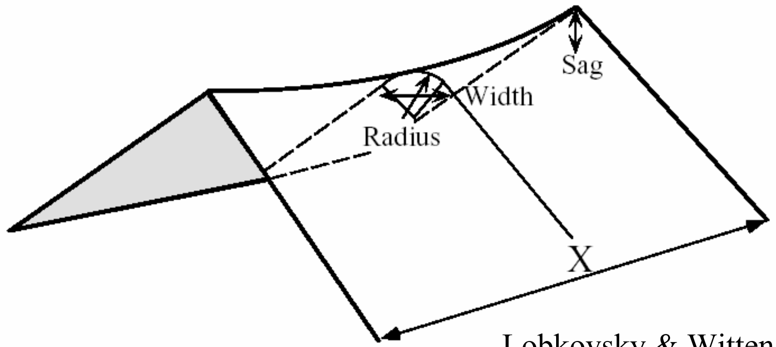
Membrane taken out from flat interface

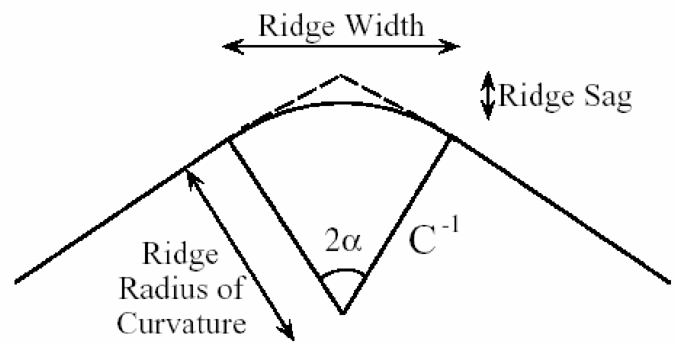


Membrane as a diffusion barrier

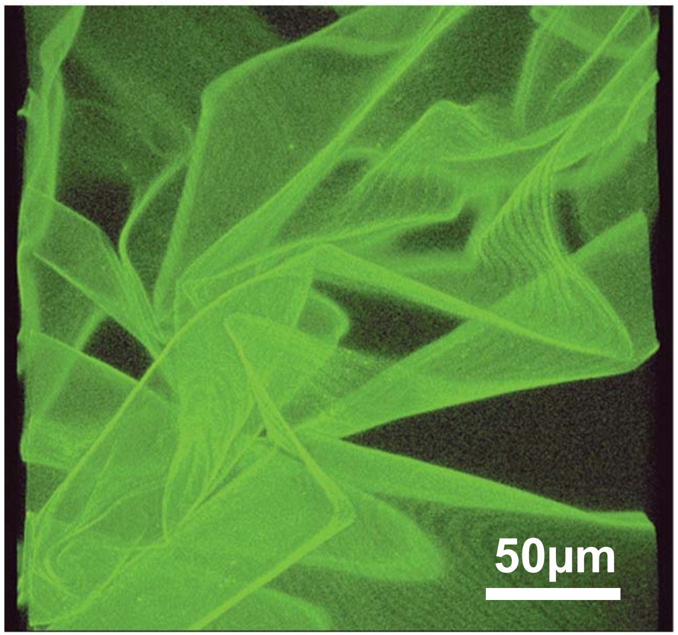


Ultrathin Membrane: *Bending Modulus*





Lobkovsky & Witten. Science 270, 1482 (1995).



Thickness of Membrane

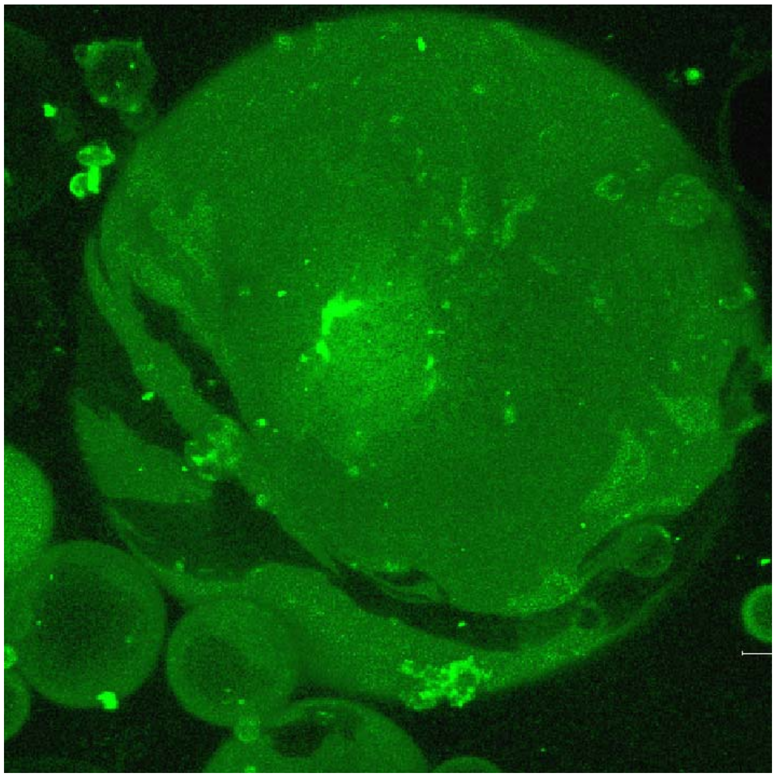
$$h \sim (\kappa / G)^{1/2} \approx 1/(X^2 C^3) \Rightarrow \underline{2 \sim 7nm}$$

Bending Modulus

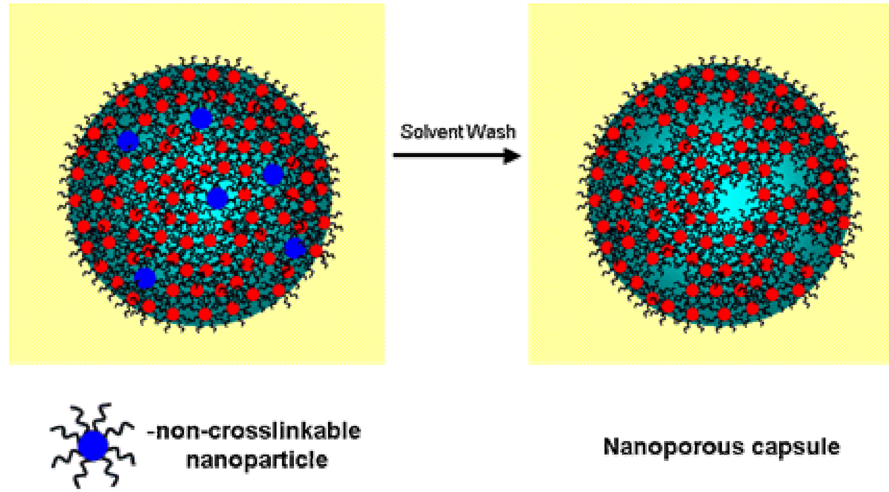
$$\kappa = Eh^3/12(1-\nu^2) \Rightarrow \underline{10^3 \sim 10^5 k_B T}$$

Crosslinked Capsules/Membranes with Nanopores

Crosslinked Capsule
(Droplet surface)



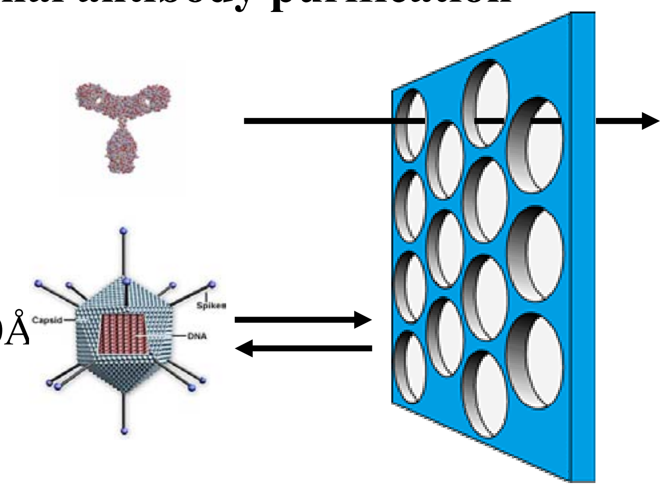
Pore size controllable from 3nm to 30nm



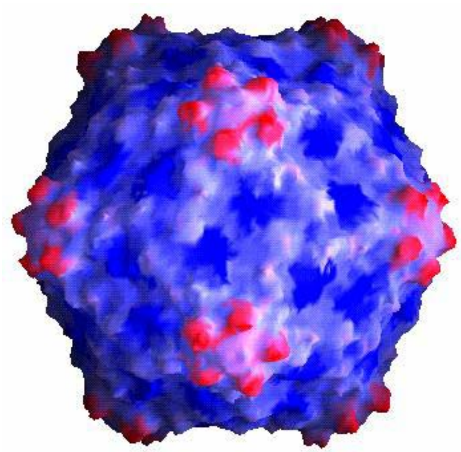
monoclonal antibody purification

Antibodies:
150Å

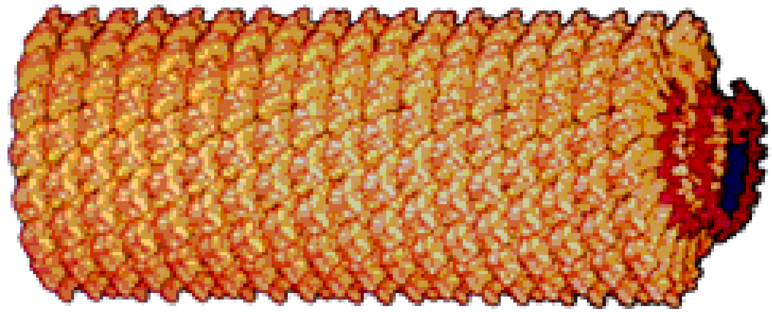
Viruses: 180-3000Å



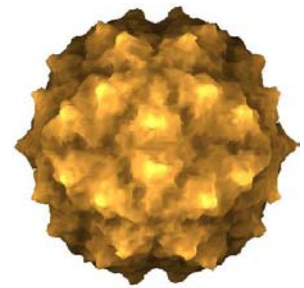
Building Blocks from the Nature: *Bio-nanoparticles*



CPMV



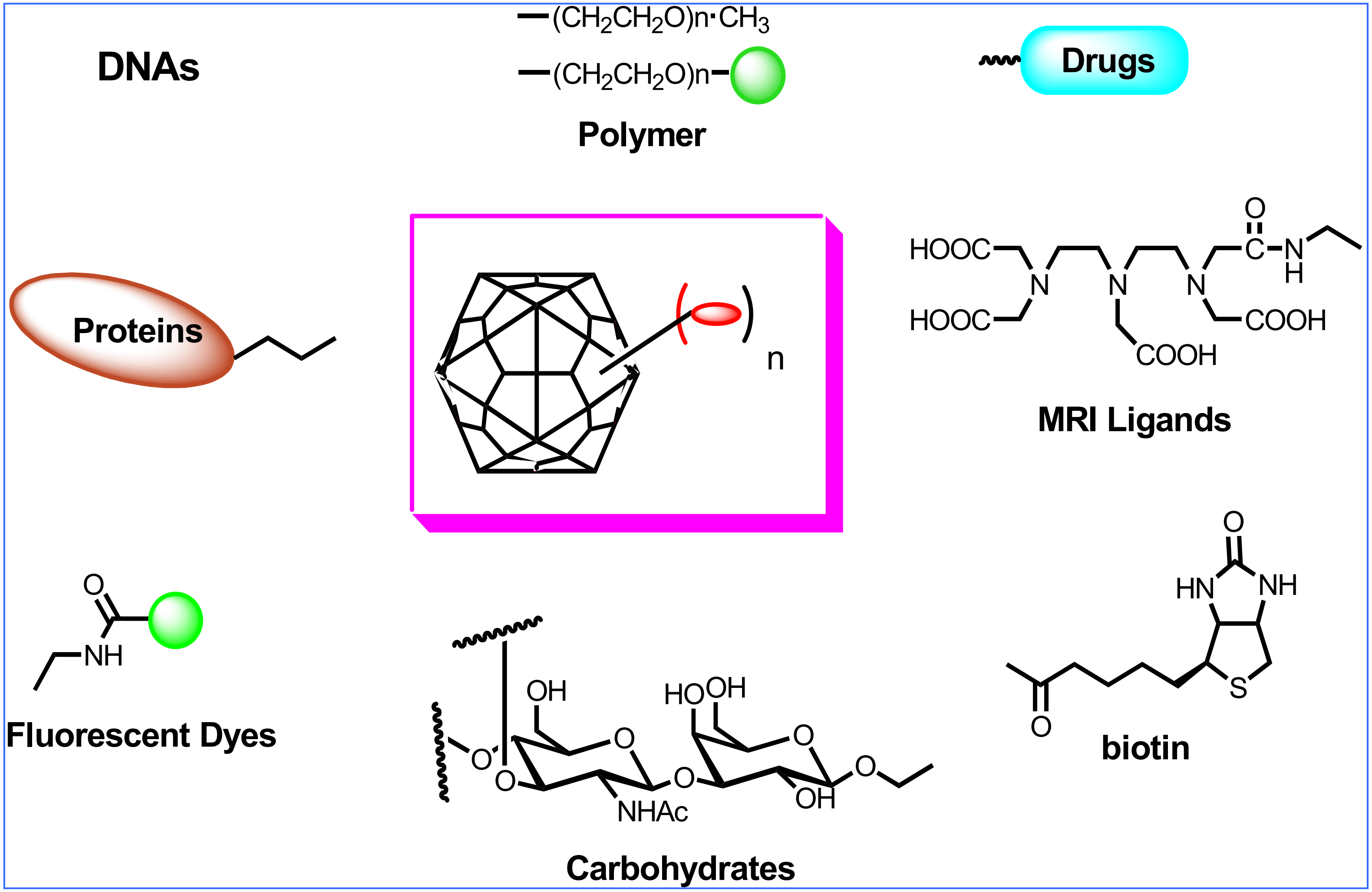
TMV



HSF

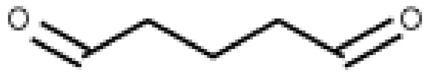
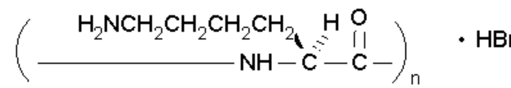
- Many bioparticles can be readily isolated in pure form in <u>gram quantities</u>.
- They are stable and have no infectivity to mammals.
- The structures of many bioparticles are known to near atomic resolution.
- Plasmids containing the coat protein sequence are available and readily modified.

A Programmable Supramolecular Platform



Q. Wang, M. G. Finn et. al. Angew. Chem. Int. Ed. ***2002****, 41*, 459; *Chem. & Biol.* **2002**, *9*, 805 & 813; *Biomacromolecules*, **2003**, *4*, 472; *Bioconjugate Chem.* **2003**, *14*, 38; *Nano Lett.* **2003**, 3, 883.

Physical or Chemical Crosslinking of Bioparticle Assemblies

Crosslinker	***Glutaraldehyde*** 	***Avidin***	***Poly-L-lysine*** 
Targeted Bioparticles	wt-CPMV and ferritin	Biotin-CPMV	CPMV and ferritin
Mechanism	Links covalently to the amine groups of lysine/hydroxy-lysine in proteins.	Binds four vitamin biotins per molecule with high affinity and selectivity.	Positively-charged, binds negatively-charged surface proteins electrostatically.

Conclusion

- Nanoparticles can self assembly at the Oil/Water interface to form liquid-like, densely packed monolayer.
- Due to the weak confinement of the interfacial well, the assembly of nanoparticles at the interface show interesting size-dependence.
- Nanoparticles are mobile at the interface. When mixture of different sized nanoparticles are used, they show unique size dependent 2-D phase separation at the interface.
- Crosslink the nanoparticle assembly at the interface can lead to robust membrane or capsules.
- The strategy can be applied to the bioparticles like cowpea mosaic virus particles and ferritin particles.

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