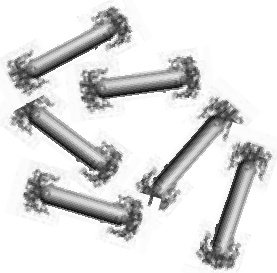
ADVANCED MATERIALS
Early view



Evolution of Self-Assembled Structures of Polymer-Terminated Gold Nanorods in Selective Solvents

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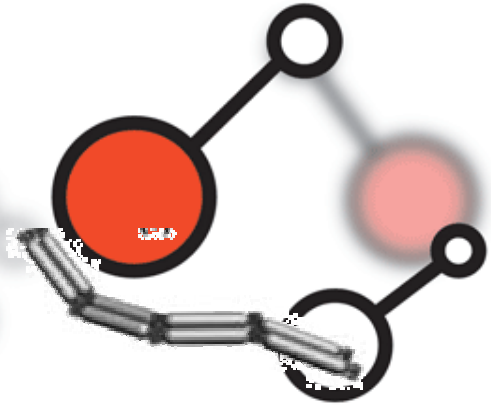

Sreeprasad T. S.

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- *Self-assembly of nanoparticles is fascinating*
- *Allows for the coupling of their size- and shape-dependent properties which makes them potentially useful in optoelectronics, sensing and imaging, and biomedical applications*
- *Compositional heterogeneity makes nanoparticles similar to amphiphilic molecules like surfactants or block copolymers*
- *Self-assembled structures with compositional heterogeneity can be made either by synthesizing nanoparticles from several different materials or by selectively attaching organic molecules to the different sites of the nanoparticles.*
- *a) The template-driven assembly b) the interactions between the ligands stabilizing NRs c) assembly induced by using external fields d) the organization of NRs by using controlled solvent evaporation.*
- *Thermodynamic approaches*

❖ *Polymer-tethered inorganic nanorods : compositional heterogeneity + asymmetric structure + shape-dependent properties.*

❖ *The organization of NRs enable tuning their properties by coupling of the optical and electronic properties of the adjacent individual NRs.*

❖ *Polymer-tethered inorganic NRs can be organized in a range of structures which include bundles, tubes and sheets, lamella and spherical micelles,and rings, chains, and spheres.*

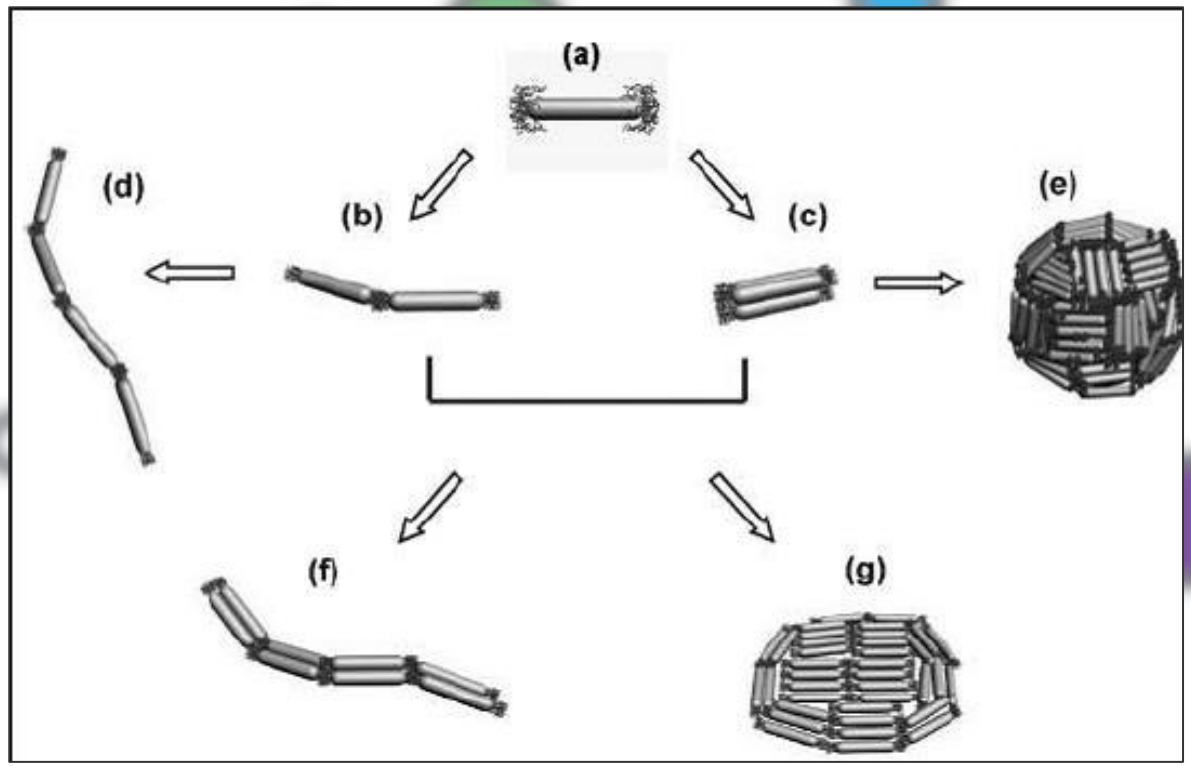
❖ *Recently, a ''block copolymer'' paradigm was proposed for the self-assembly of gold nanorods : "pom-pom" triblocks*

❖ *Multiple polymer chains are attached to the ends of the linear block(NR), and amphiphilic triblocks comprising a hydrophilic central metal block and two hydrophobic polymer end blocks were prepared. The triblocks were dispersed in DMF or THF.*

❖ *The self-assembly by adding water to change the quality of solvent for the hydrophilic and hydrophobic blocks.*

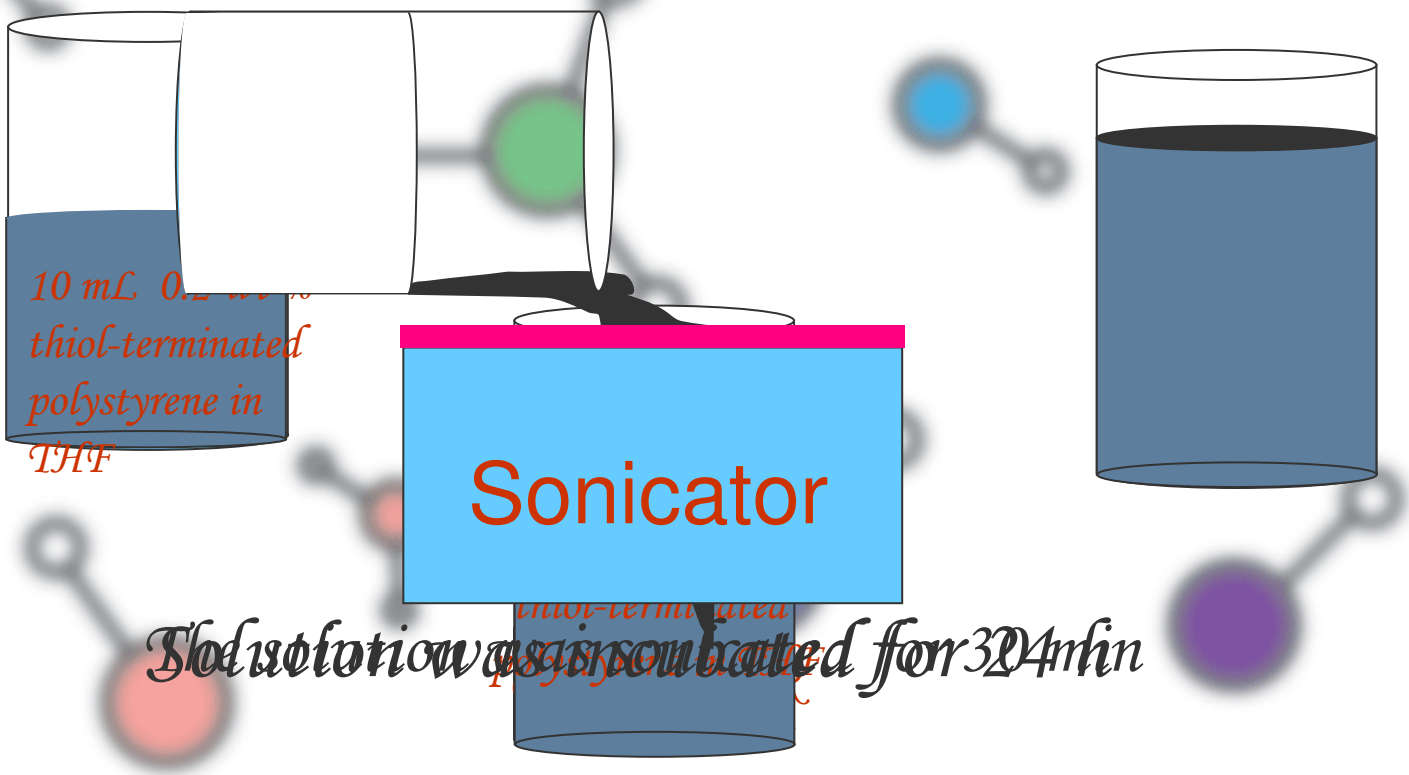
In this paper…

The evolution of the self-assembled structures of polymer-terminated gold NRs, following the gradual change in the selectivity of solvent for the central CTAB-coated metal block and polystyrene molecules is studied. The self-assembly experiments were conducted from ternary THF/DMF/water solutions of the polymer-terminated nanorods. It was observed that seven types of structures, namely, individual triblocks, chains, networks of chains, side-to-side chains, doublets and triplets, raft-like structures, and spheres were formed.



Experimental

Gold nanorods were synthesized following Nikoobakht and El-Sayed method. diameter of 8 nmand a length of 42nm. The NRs were purified using three 30 min long centrifugation cycles at 8000–10000 rpm



Solution was sonicated for 24 h

This modified NRs are referred to as **triblocks**

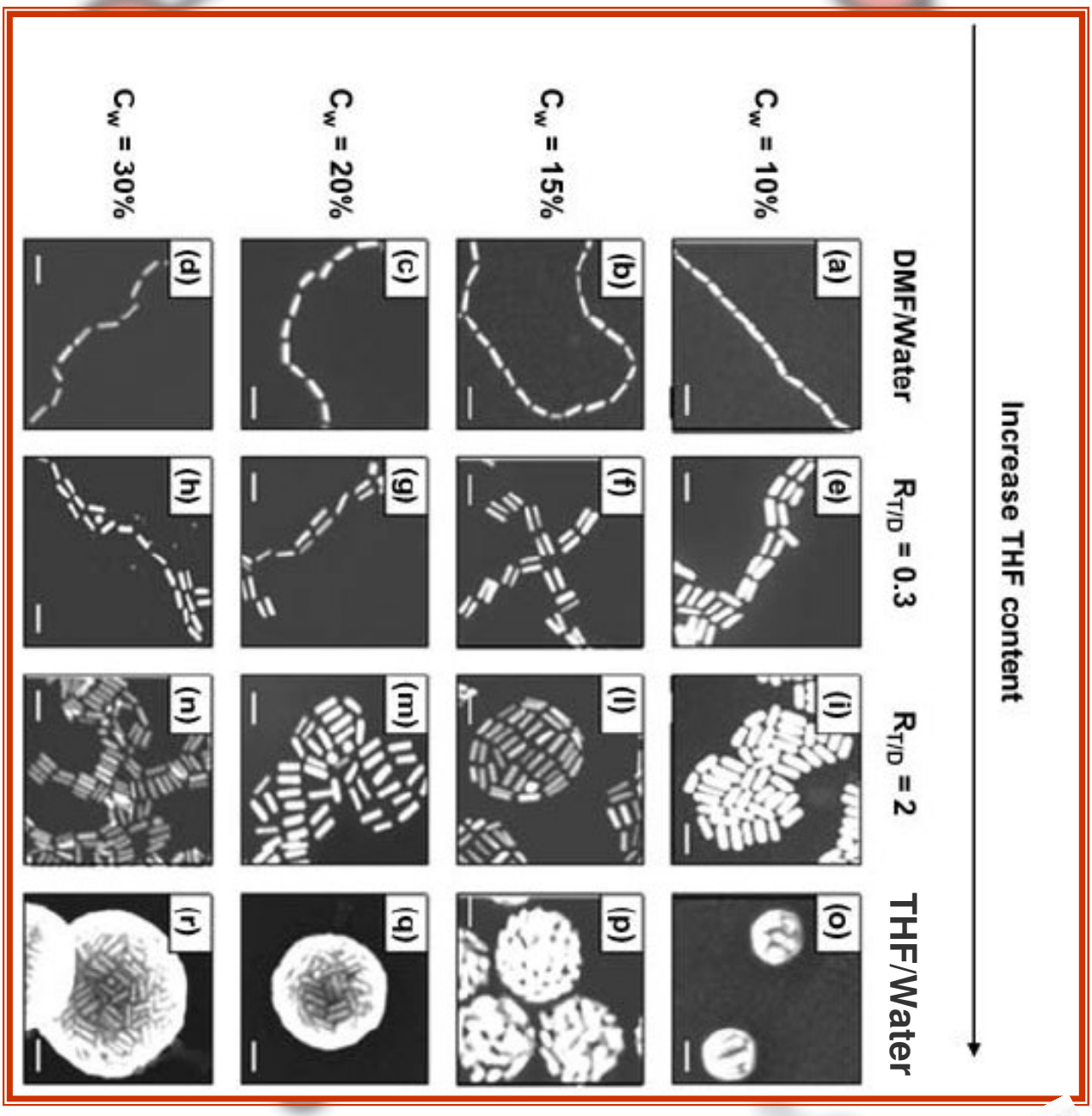
The triblocks were purified by 30 min long centrifugation cycles at 9000–10000 rpm and finally redispersed in 8mL of THF.

For the self-assembly , 0.5mL of the solution of Modified NRs in THF was dried and redispersed in 1mL of THF/DMF mixture at the desired solvent ratio.

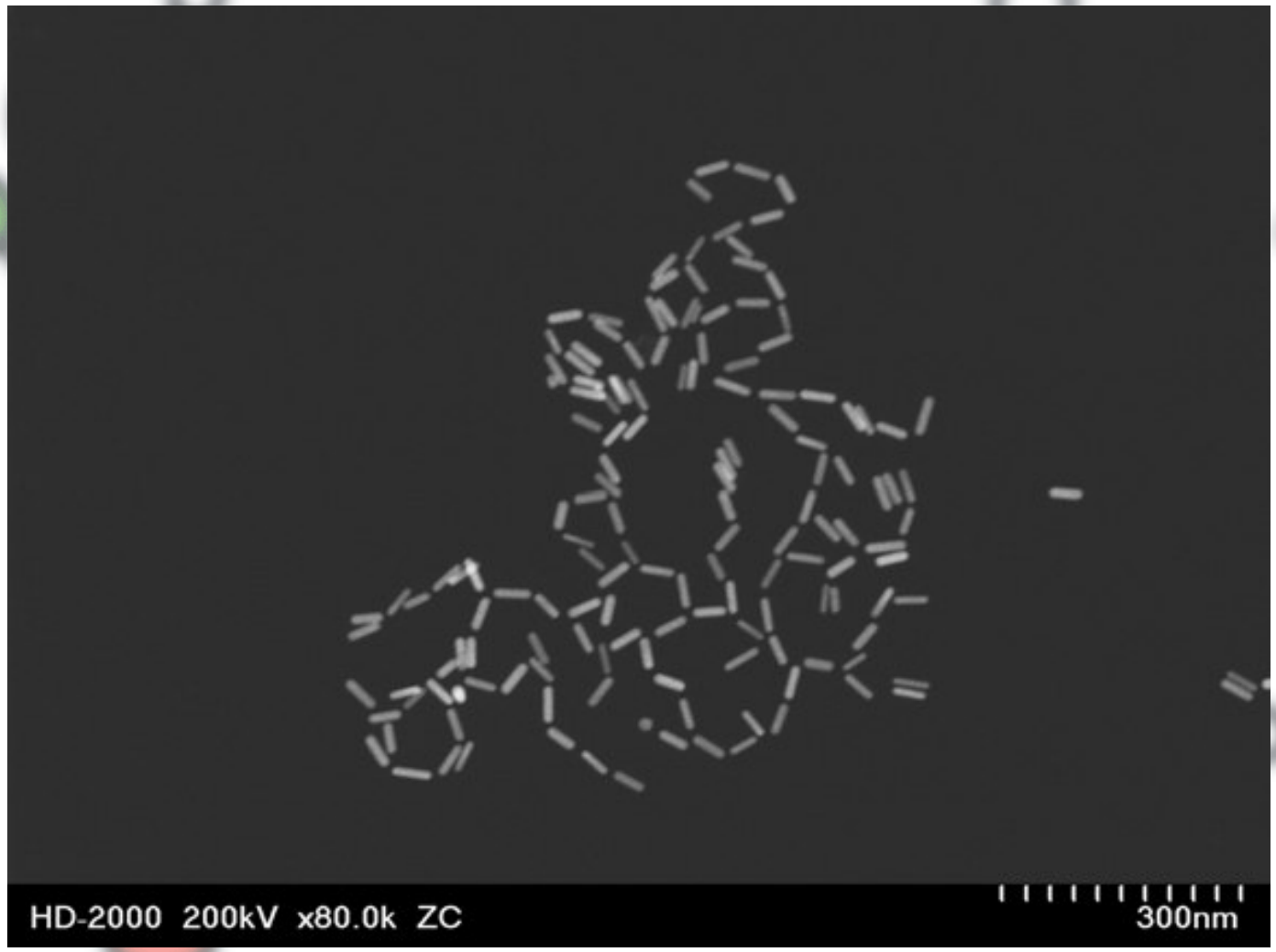
To this to trigger assembly, 1mL of THF/DMF/water at the desired composition was added dropwise under stirring.

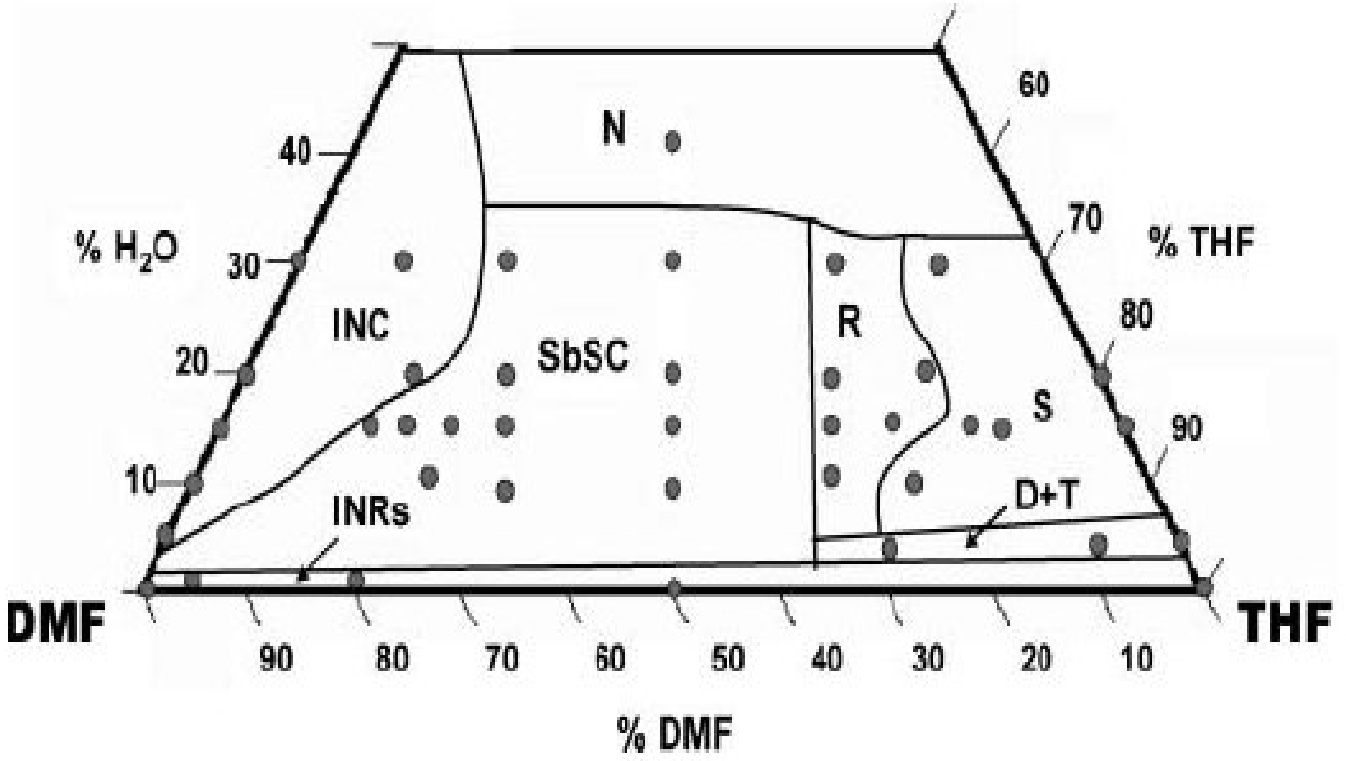
The final solution was equilibrated for 24 h and imaged

Self-assembled structures obtained at various THF/DMF ratios ($R_{T/D}$) and various water contents (C_W) in ternary solutions of triblocks. The scale bar is 50nm in panels (i), (m), (o), (p), and 60nm in all other panels

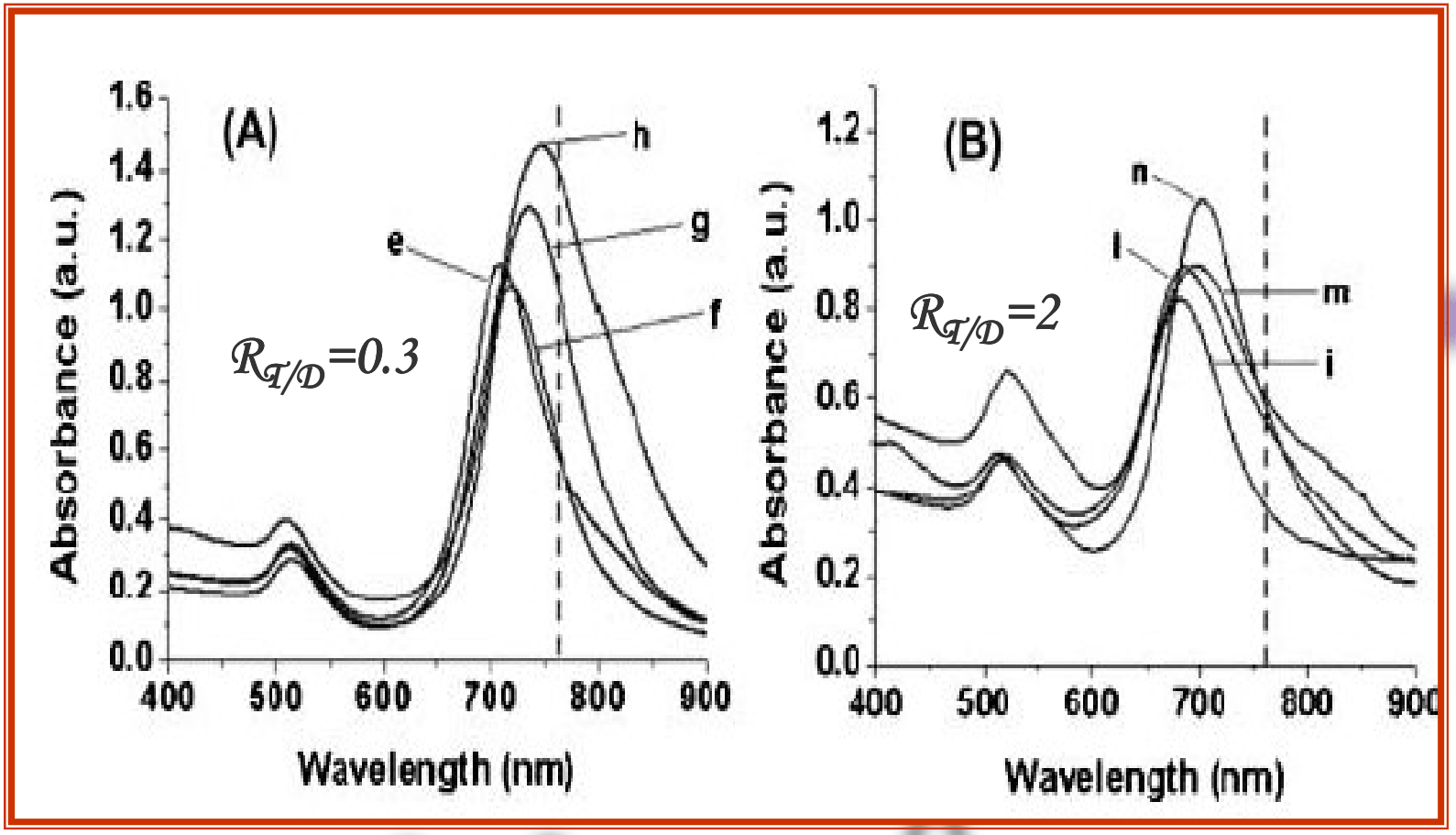


Network structures





Ternary phase diagram showing transitions in the self-assembled triblock structures. INC: individual nanorod chains; INR: individual nanorods; SbSC: NRs assembled side-by-side in chains; S: spheres; R: raft-like structures; D+T: doublets and triplets; N: network-like structures. At $R_{T/D} \geq 2$ and $C_W \geq 30\%$, the triblocks precipitated.



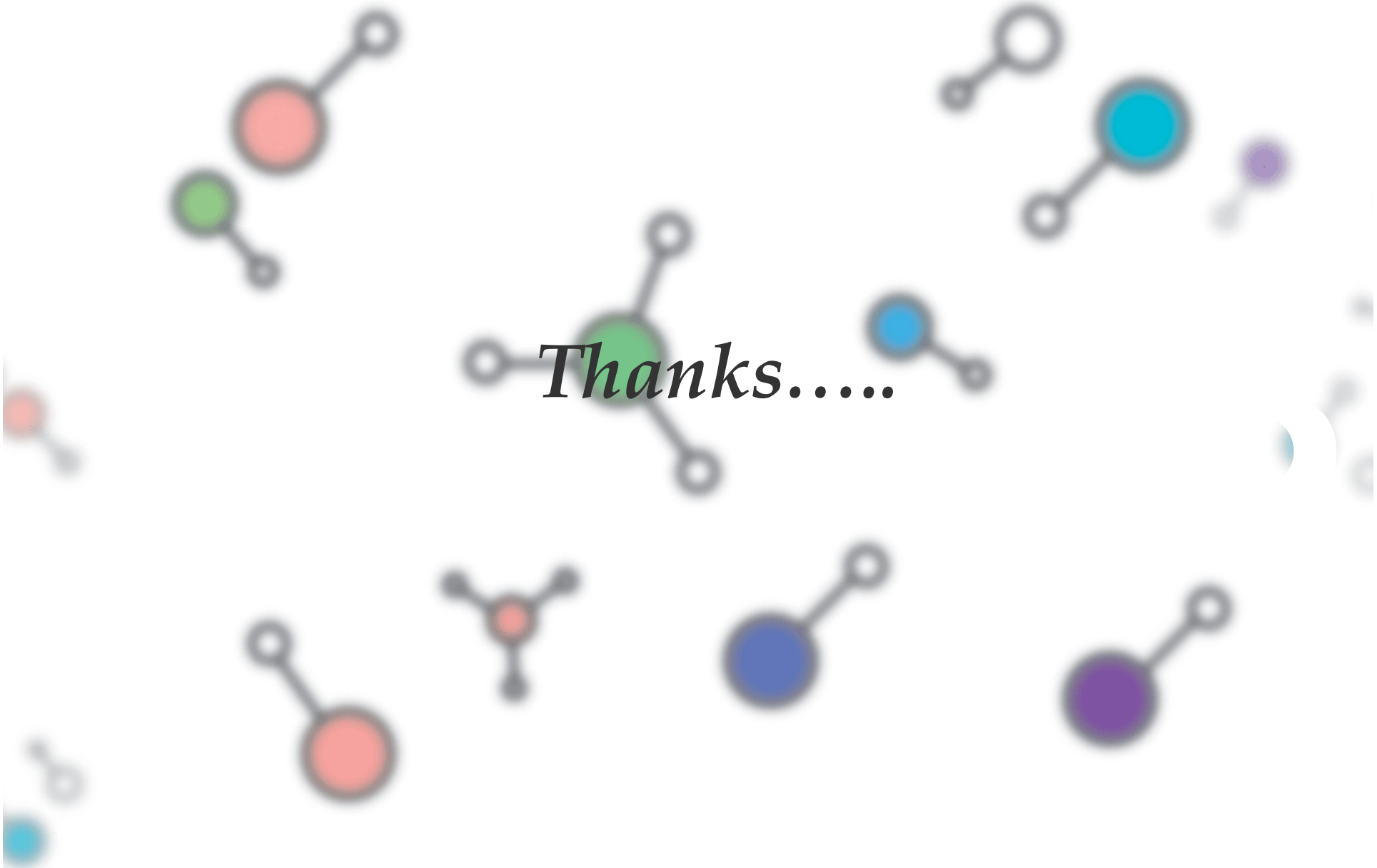
Absorption spectra of self-assembled structures of triblocks obtained at $\mathcal{R}_{T/D}$=0.3 (A) and at $\mathcal{R}_{T/D}$=2 (B). The spectra refer to the organic solvent/water mixtures with C_w, wt%: 10 (e, i), 15 (f, l), 20 (g, m), and 30 (h, n). The vertical dashed line indicates the position of the longitudinal plasmon of the individual triblocks in water (λ=760 nm).

Summary

❖A systematic study of the self-assembly of gold nanorods end terminated with polystyrene molecules shows that the evolution of structures occurs through competition between the side-to-side and end-to-end aggregation.

❖This competition arises from the different solubilities of the polystyrene and the CTAB-coated metal blocks in the solvent mixture.

❖ Its explained how the tendency towards side-to-side aggregation is dominant over most of the compositional range. This tendency is significantly reduced at high DMF or water content, and, at very low RT/D values, this tendency is suppressed


Thanks…..

Relevance

Assembly with diacid molecules of different length.

Use of bio-molecules as templates.