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Monodisperse Polymer-Stabilised Water Soluble Gold Nanoparticles

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n.schaeffer@liverpool.ac.uk

Stabilization

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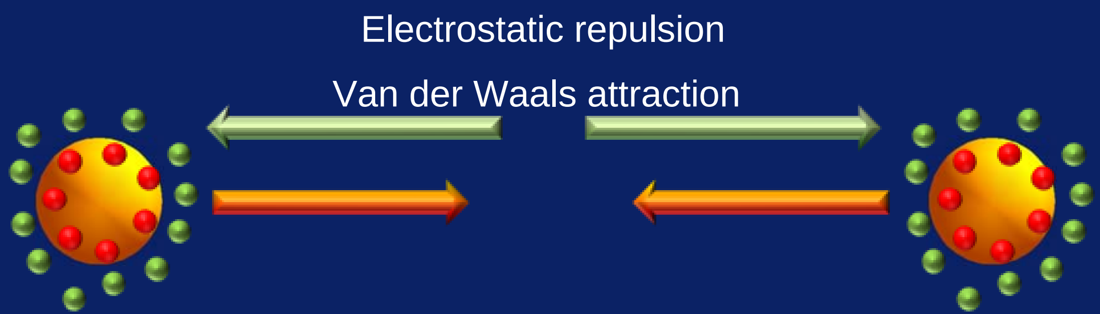
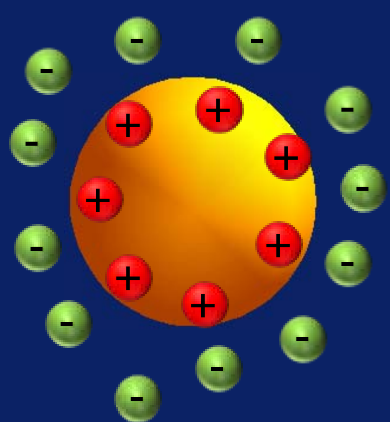


Electrostatic stabilization



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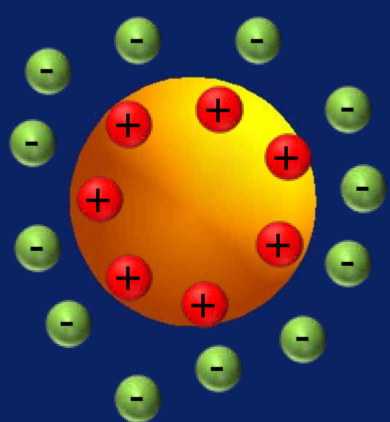
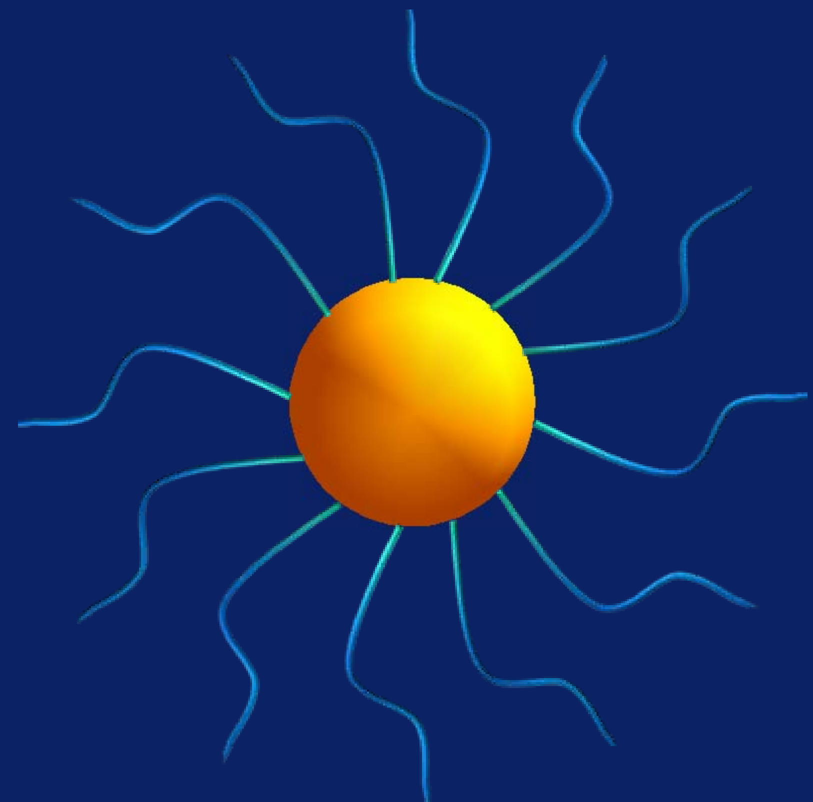
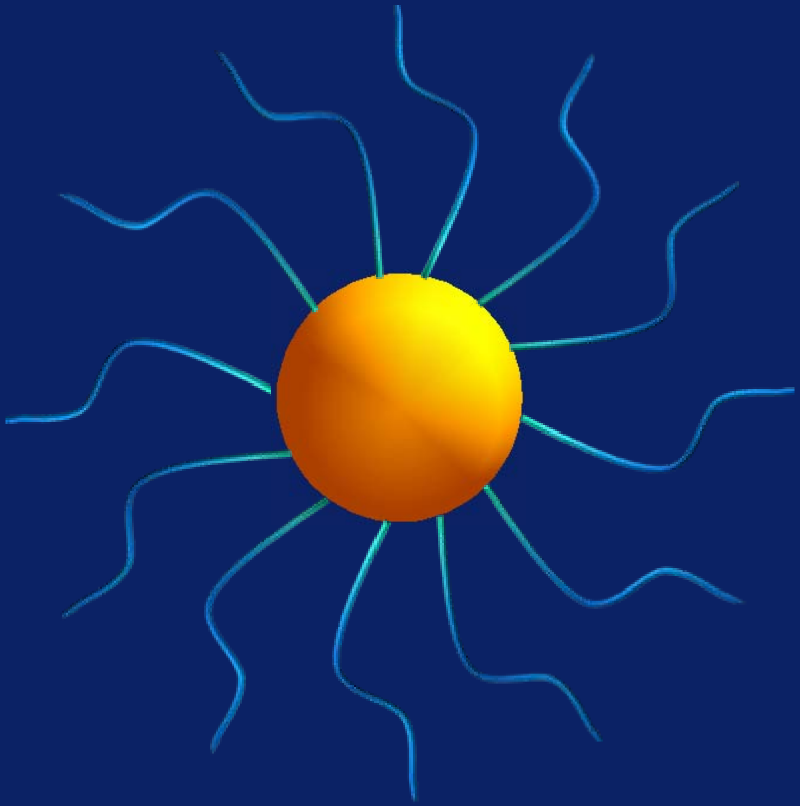


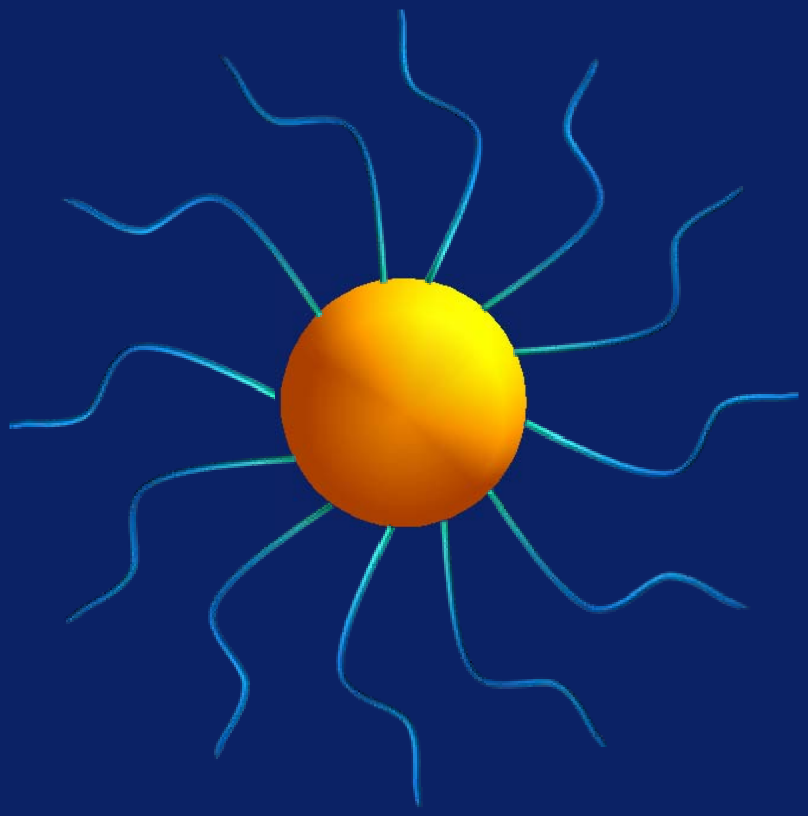
Steric stabilization



Polymeric stabilization



What makes a suitable stabilizer ?



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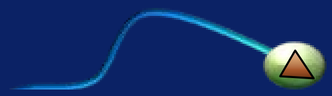
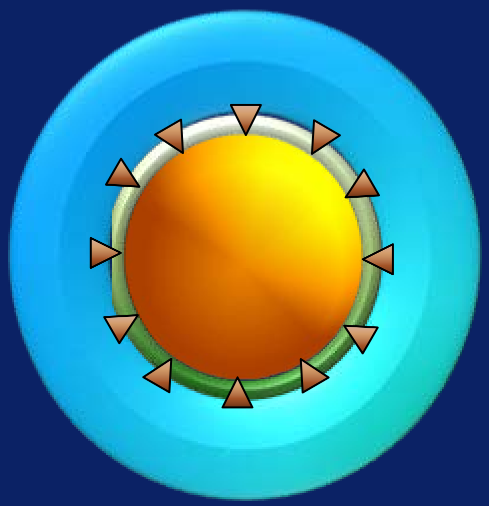


-Binding site

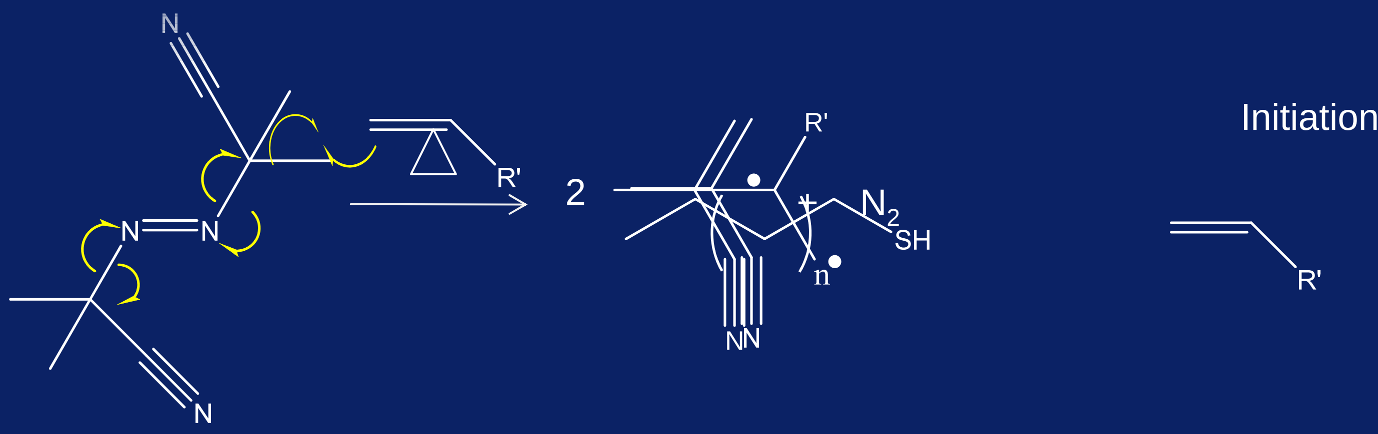
-Hydrophobic end

-Hydrophilic tail



J. Am. Chem. Soc.; 2004; 126; 10076

Chain transfer polymerization



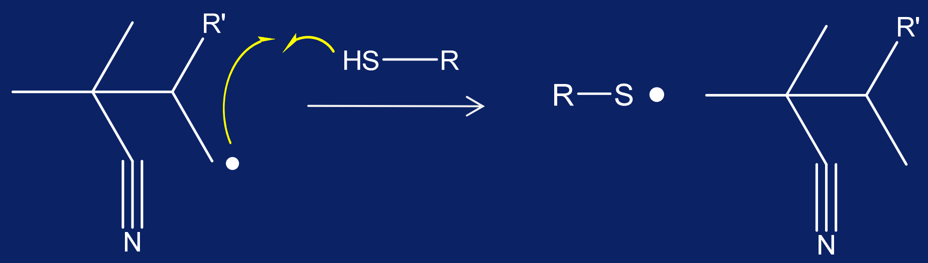
Initiator

Chain transfert agent

Monomers

J. Macrmol. Sc. Part A; 1999, 36, 51

Chain transfer polymerization



Chain transfer

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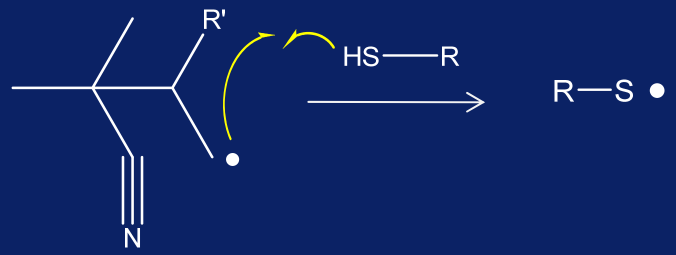

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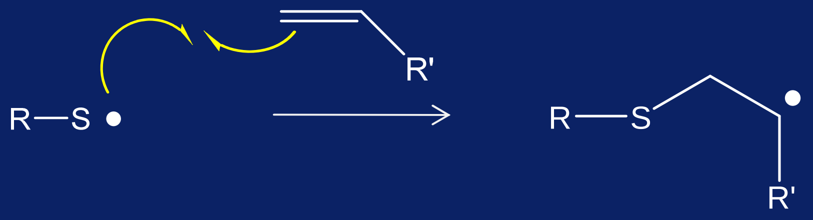

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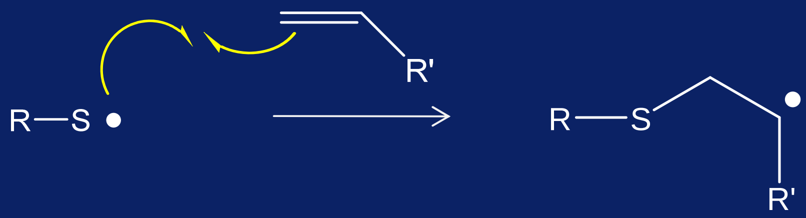
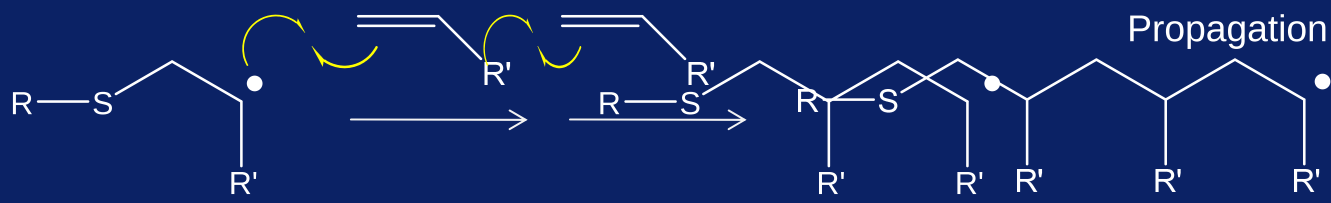


Propagation



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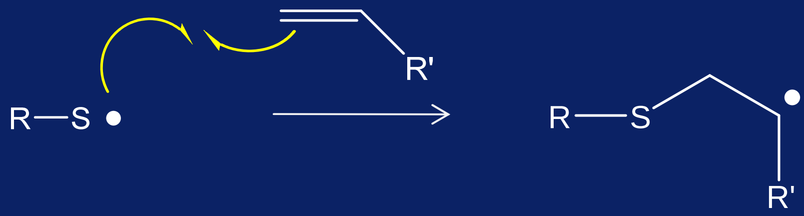

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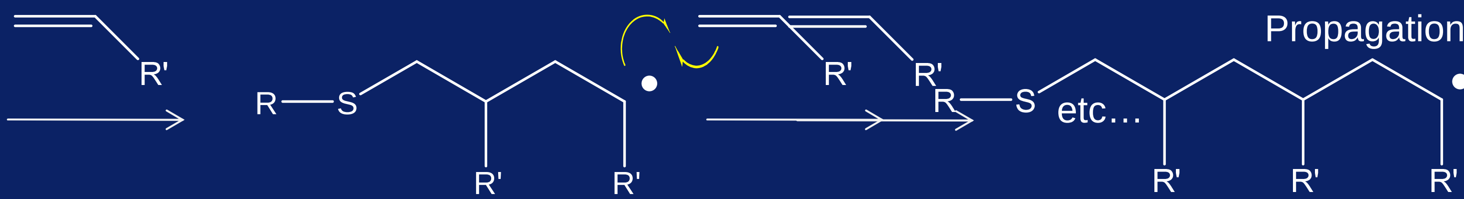

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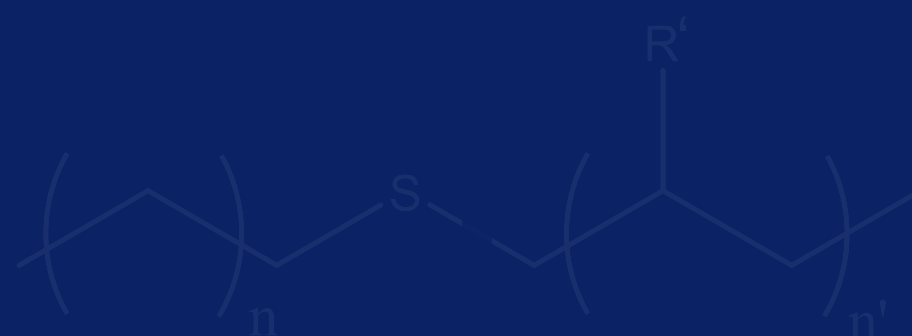

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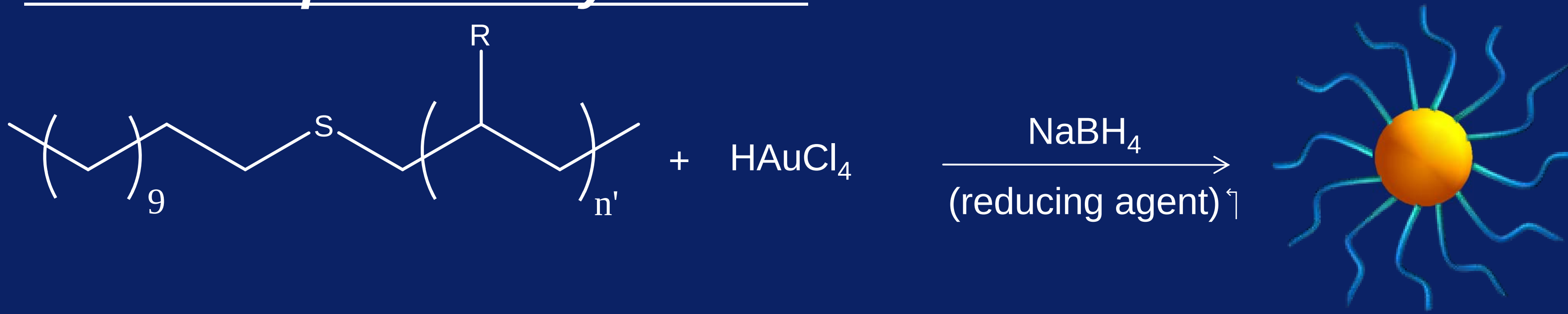
Gold nanoparticles synthesis



a) b) c) d)

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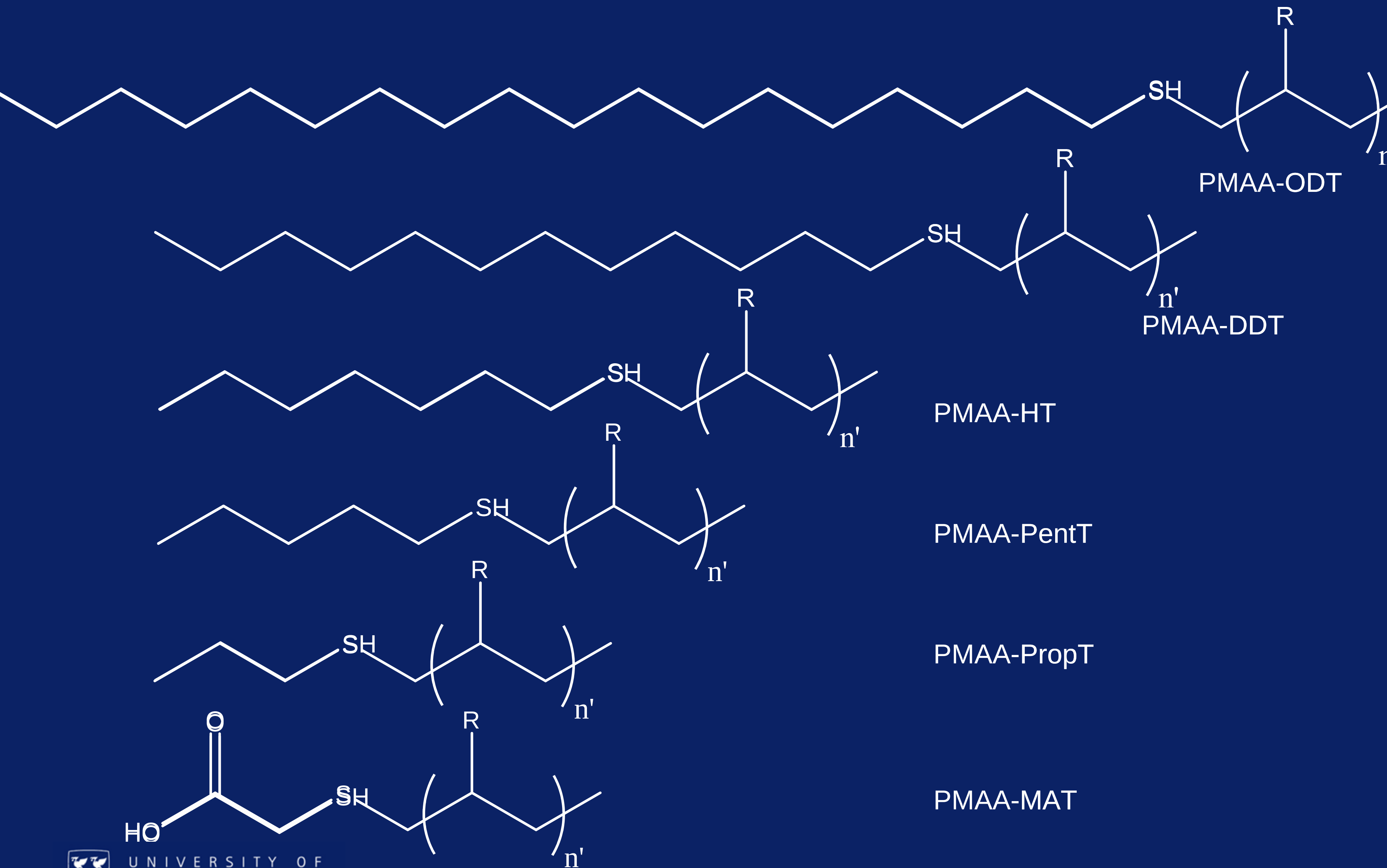
J. Am. Chem. Soc.; 2005; 127; 16398 & Langmuir; 2007;23; 885

End-group contribution



Langmuir; 2007;23; 885

End-group contribution

End-group hydrophobicity

$C_{polymer}/C_{Au}$ increasing

PMAA-ODT
M_n=2980, M_w=3480

PMAA-DDT
Mn=2550, Mw=3491

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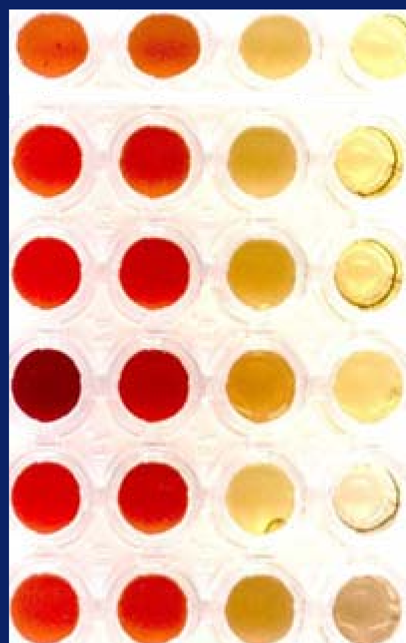

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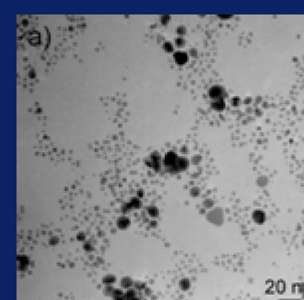

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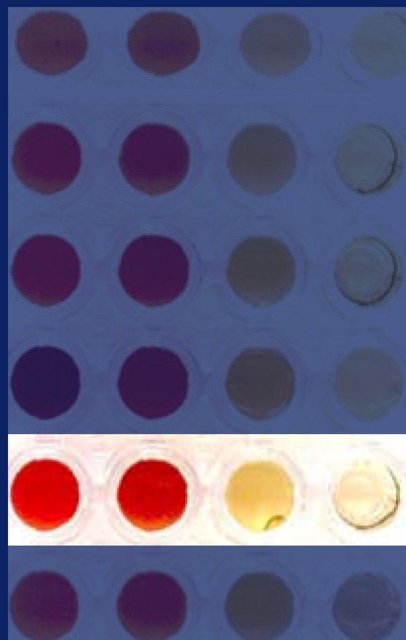

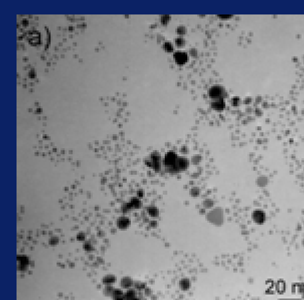

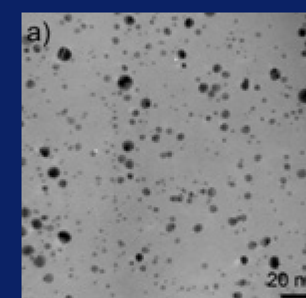

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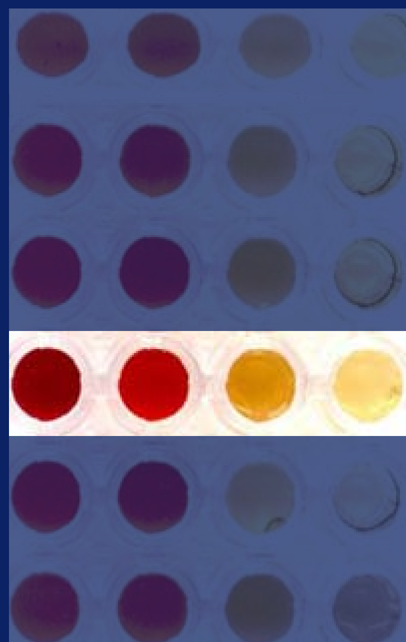

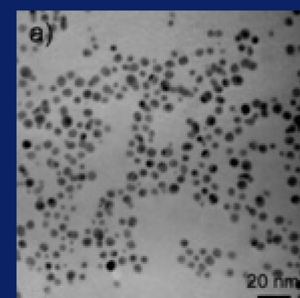

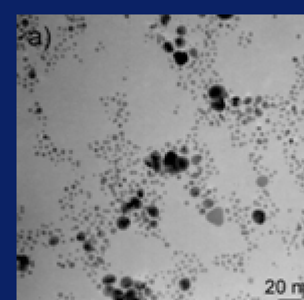

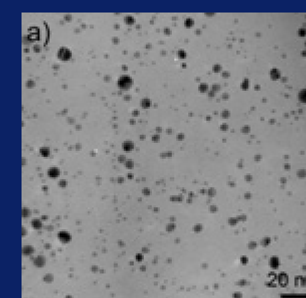

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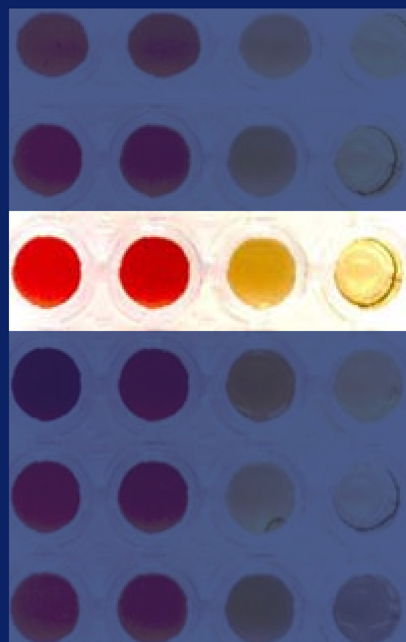

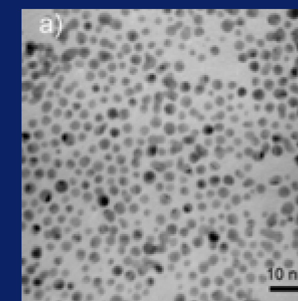

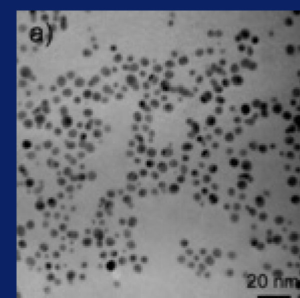

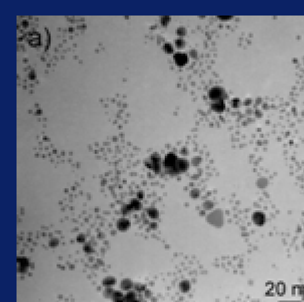

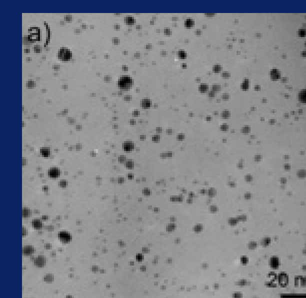

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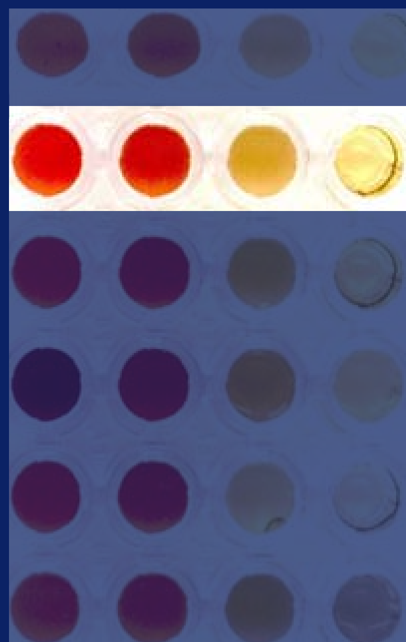

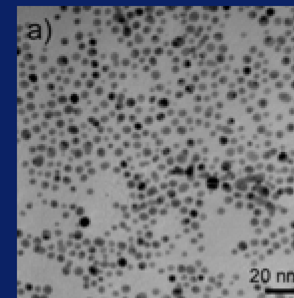

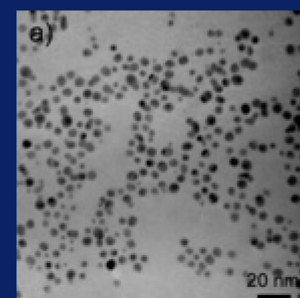

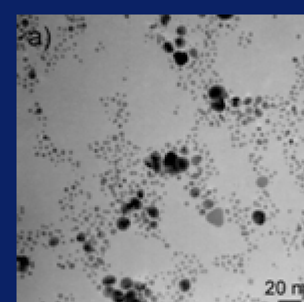

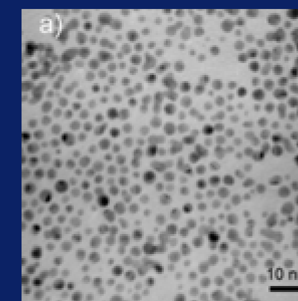

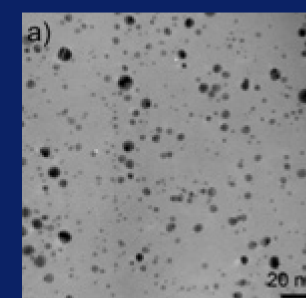

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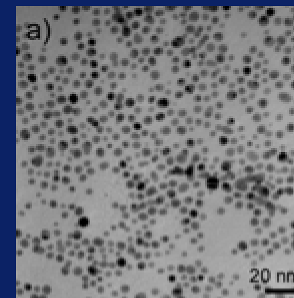

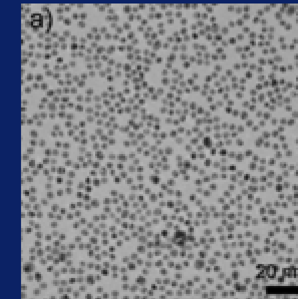

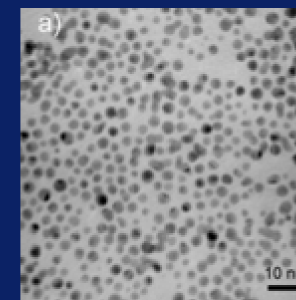

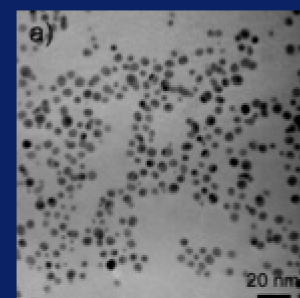

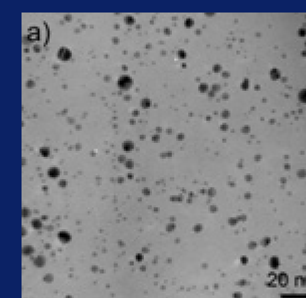

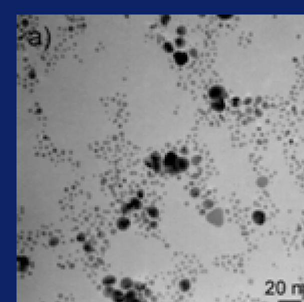

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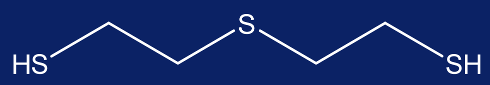
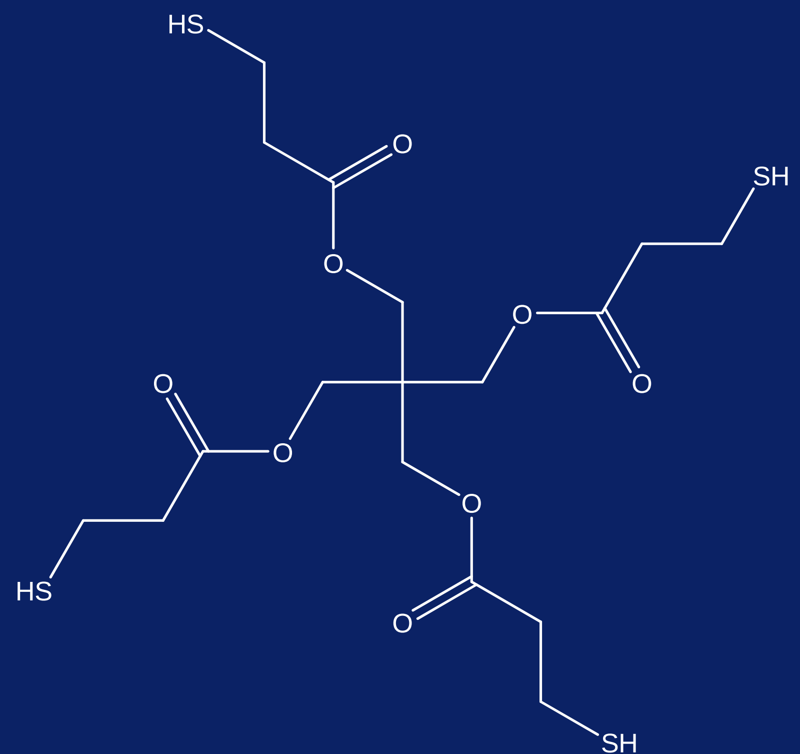
What about thiol(s) containing end-groups ?





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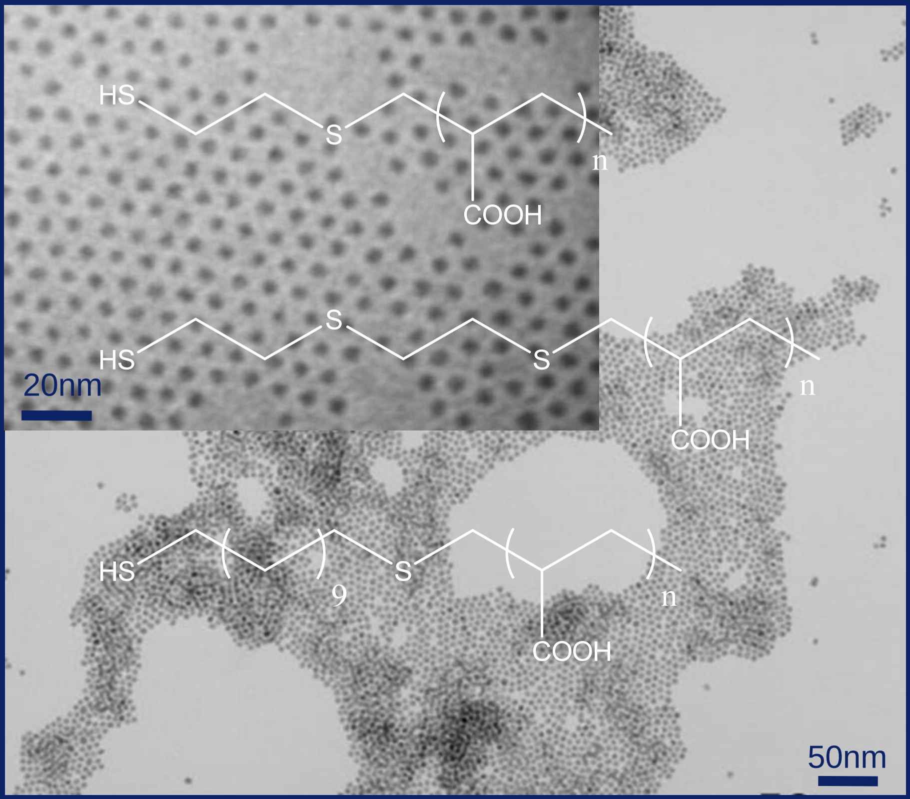

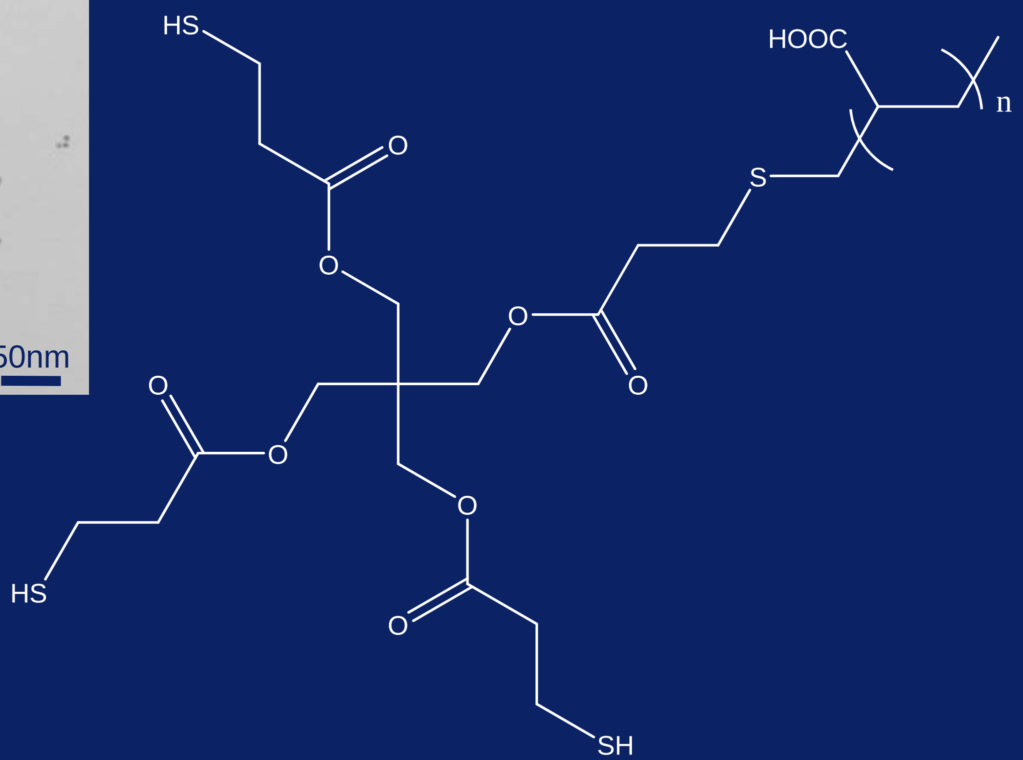

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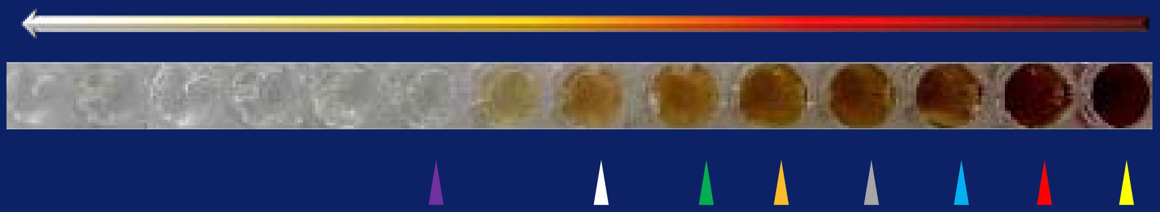
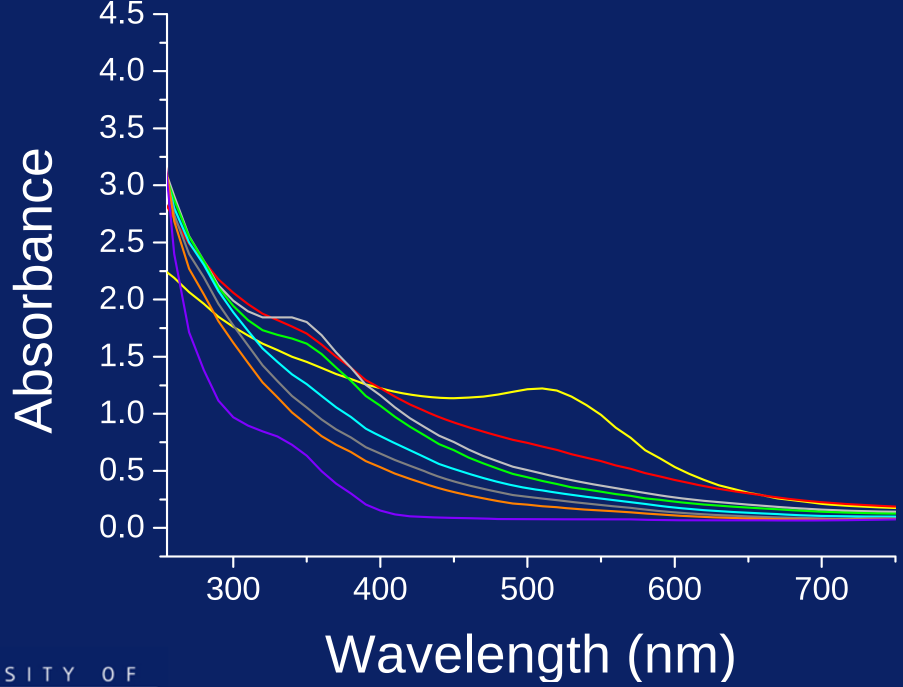
« Small is beautiful »

$C_{polymer}/C_{Au}$ increasing





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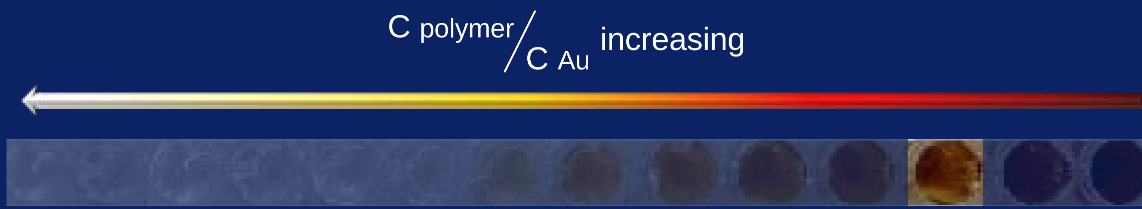

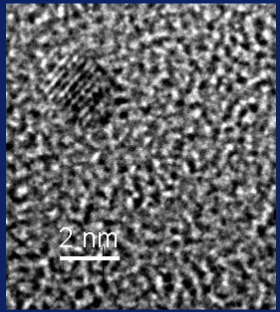

1.7 nm

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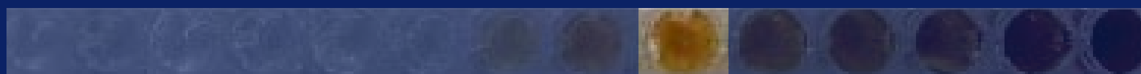
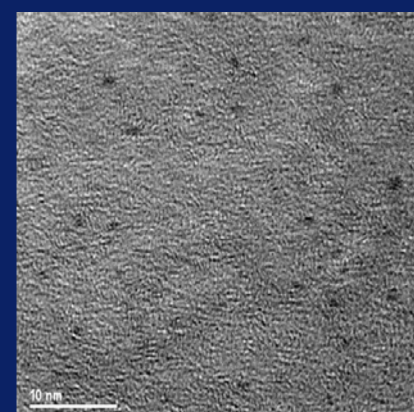
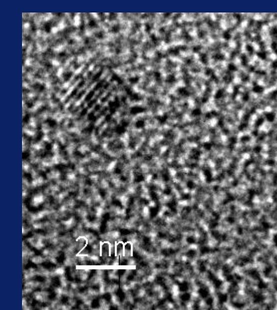




1.1 nm



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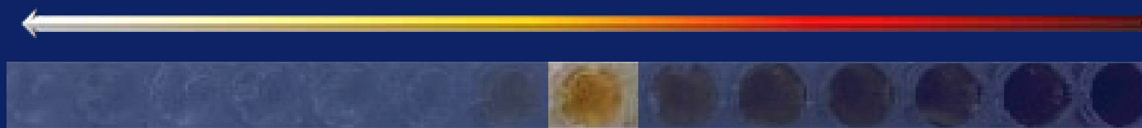

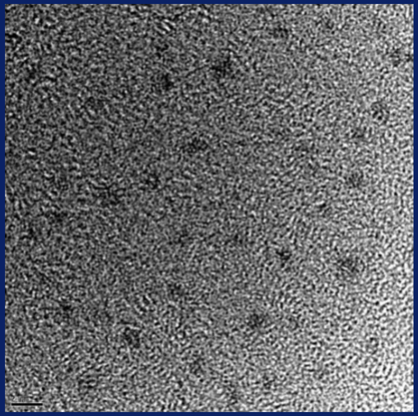

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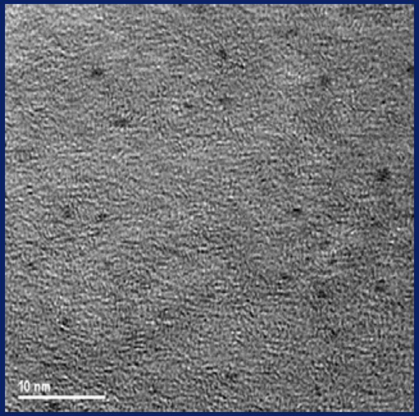

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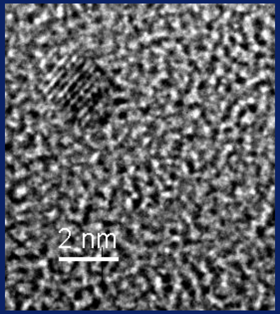

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« Small is beautiful »

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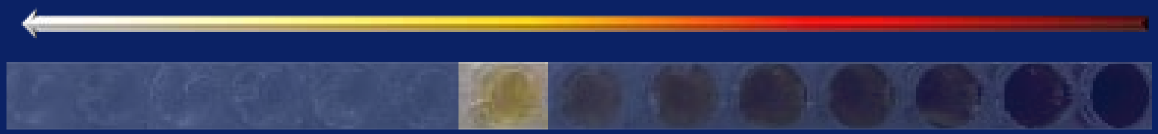
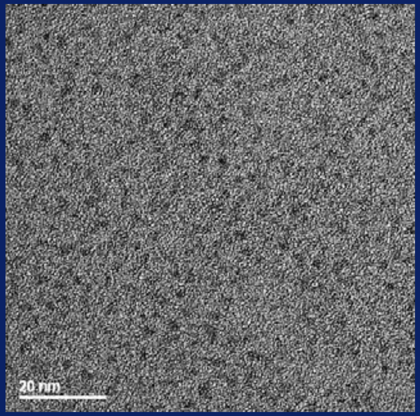
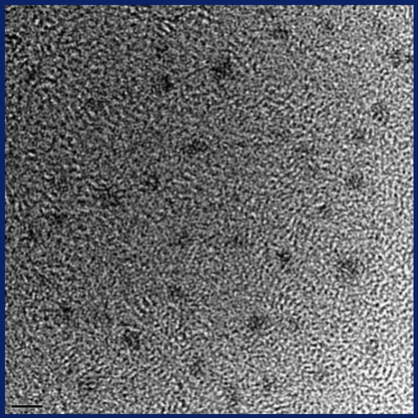
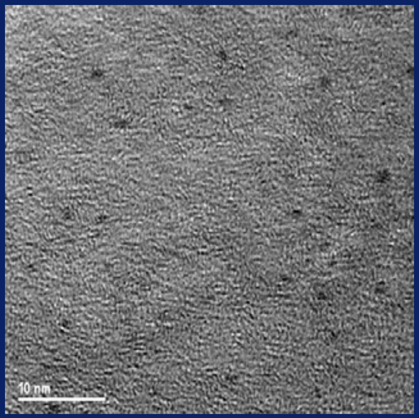




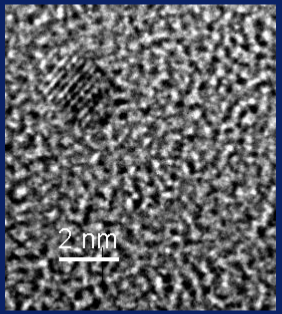
1.1 nm



1.1 nm



1.1 nm



1.7 nm

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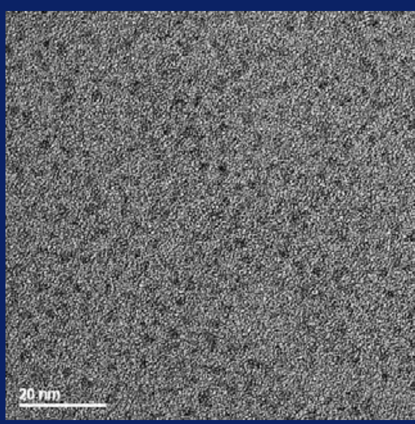
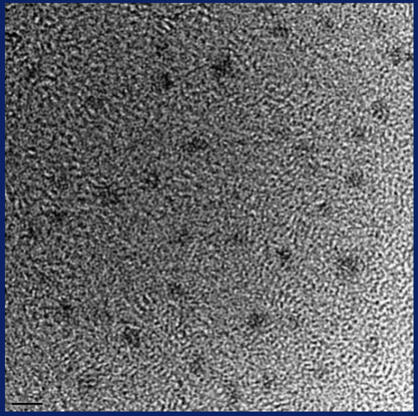
« Small is beautiful »

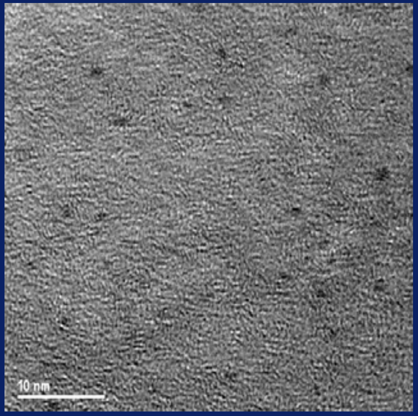
$C_{polymer} / C_{Au}$ increasing



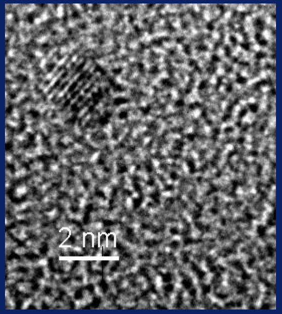
1.1 nm



1.1 nm



1.1 nm



1.7 nm

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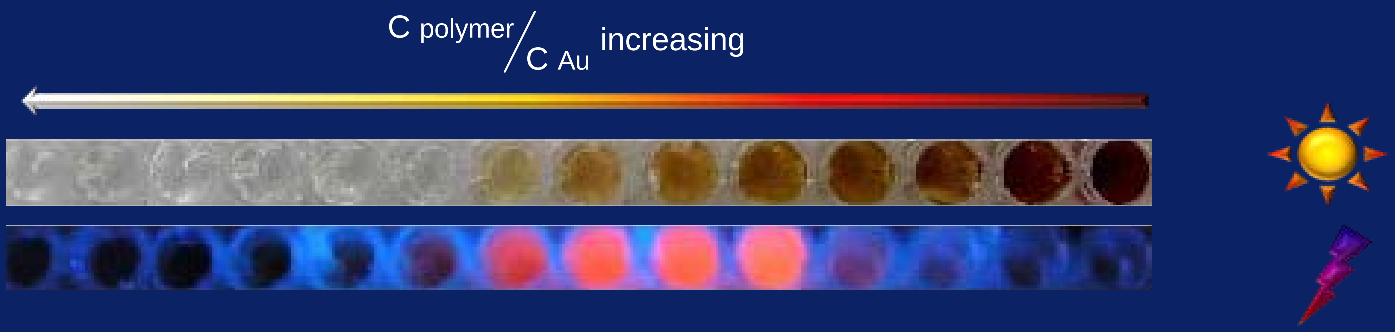
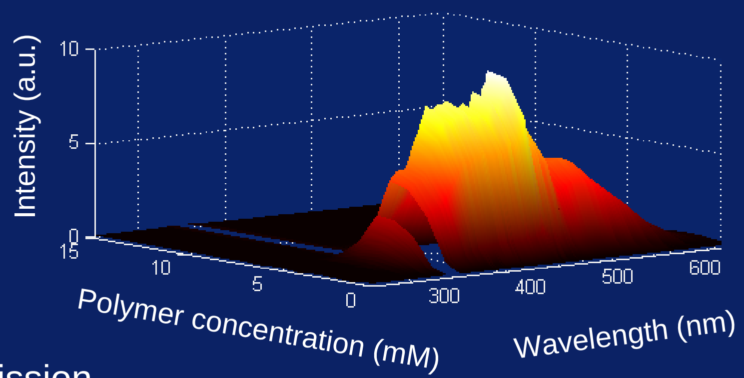
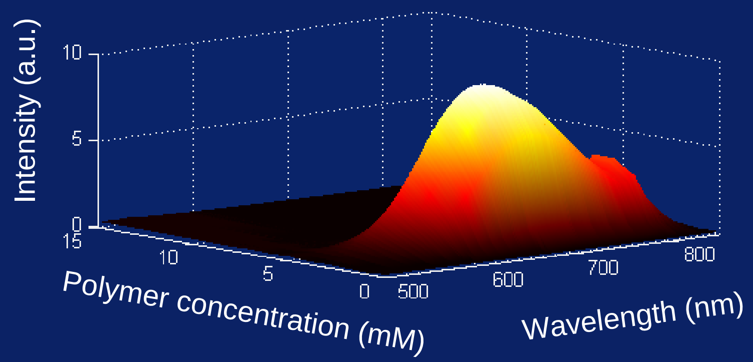
Photophysical properties



Excitation



Emission



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Are they really fluorescent ?

High Quantum Yield Blue Emission from Water-Soluble Au_8 Nanodots

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Published on Web 06/04/2003

High Quantum Yield Blue Emission from Water-Soluble Au_8 Nanodots

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School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

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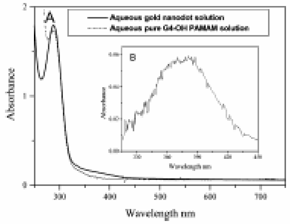

Figure 1. (A) UV−vis absorption spectra of aqueous gold nanodot and pure dendrimer solutions. (B) Subtraction of absorption spectra in A reveals the 384-nm absorption of PAMAM encapsulated Au nanodots.

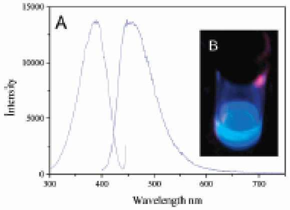

Figure 2. (A) Excitation and emission spectra of G4-OH PAMAM encapsulated gold nanodots at room temperature. (B) Emission from Au nanodots under long-wavelength UV lamp irradiation (366 nm).

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Strong Blue Photoluminescence and ECL from OH-Terminated PAMAM Dendrimers in the Absence of Gold Nanoparticles

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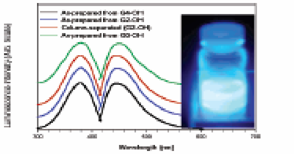

Figure 1. (A) Emission (EM) and excitation (EX) spectra for several PS-treated OH-terminated PAMAM dendrimers, concentrations of G4-OH, G2-OH, and G0-OH are 2.5, 10, and 40 μM, respectively. Each sample has been aged for 7 days. (B) Blue emission from the column-separated PS-treated G2-OH under 366-nm irradiation.

Strong Blue Photoluminescence and ECL from OH-Terminated PAMAM Dendrimers in the Absence of Gold Nanoparticles

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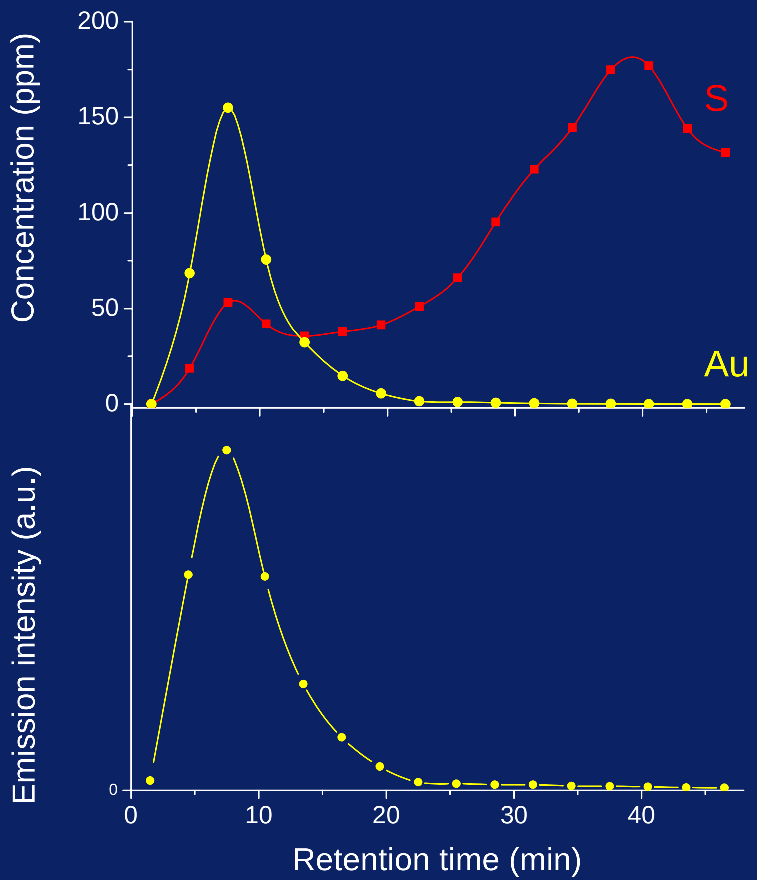
J. Am. Chem. Soc.; 2002; 125; 7780 & J. Am. Chem. Soc.; 2004; 126; 8358

Are they really fluorescent ?

- The polymer is not fluorescent
- The polymer, after oxidation, is not fluorescent
- The polymer, after reduction, is not fluorescent
- The polymer, in the presence of $HAuCl_4$, is not fluorescent

Purification/control by size exclusion chromatography



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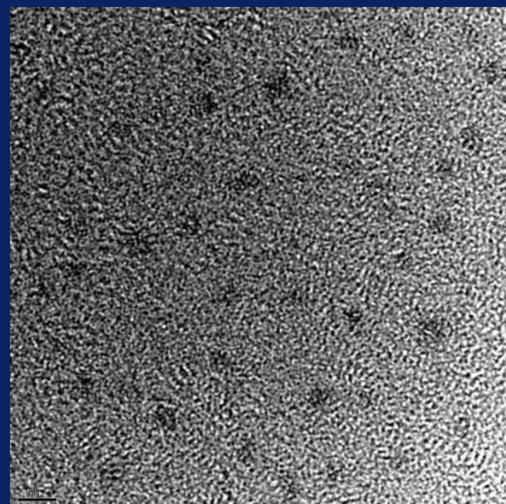
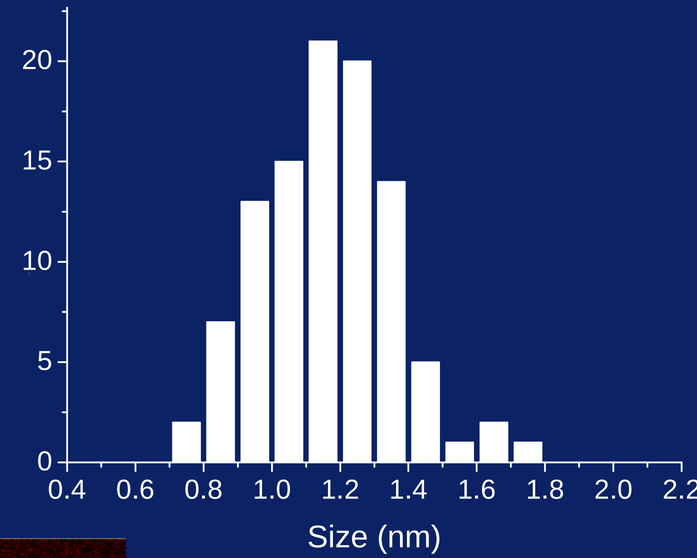
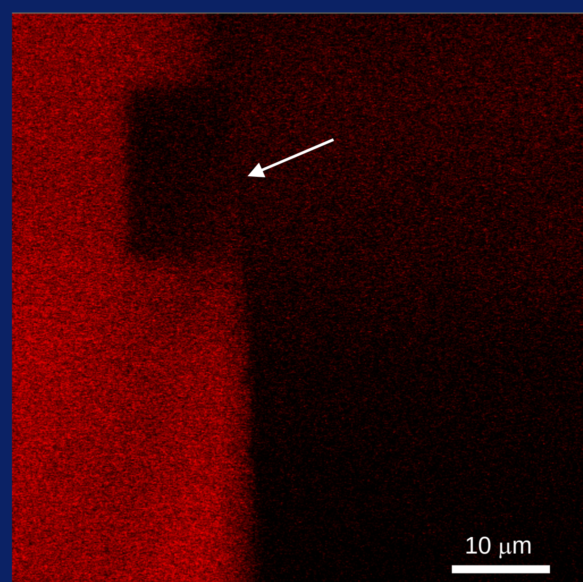
Core/shell structure

Core
(HR-TEM)





Shell
(???)



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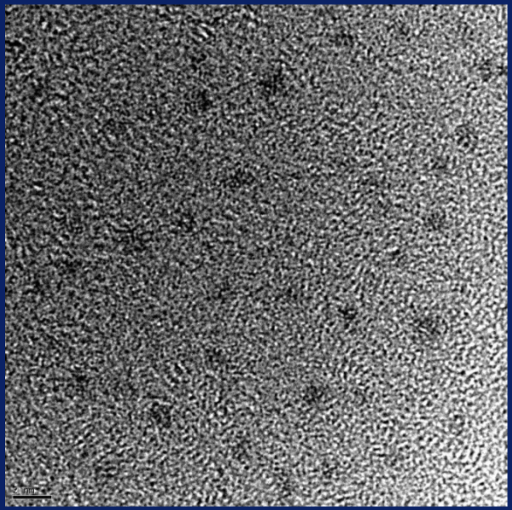
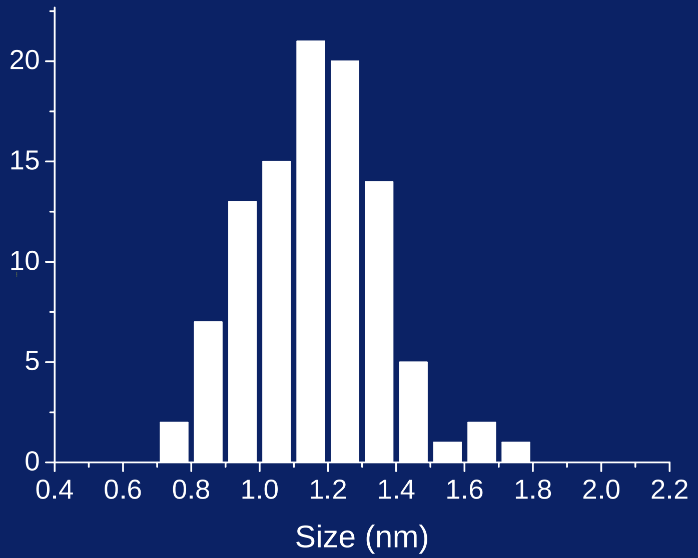
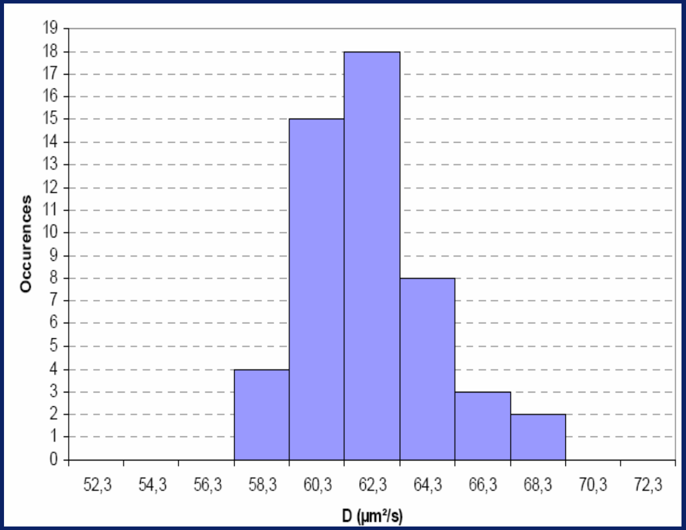
Core/shell structure

Core
(HR-TEM)





Shell
(Fluorescence recovery
after photobleaching)



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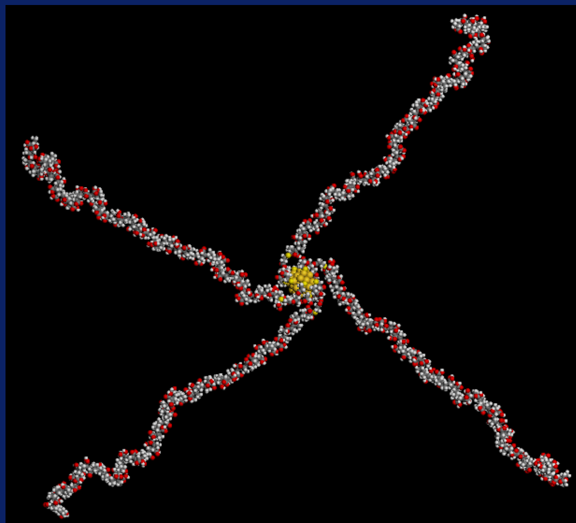
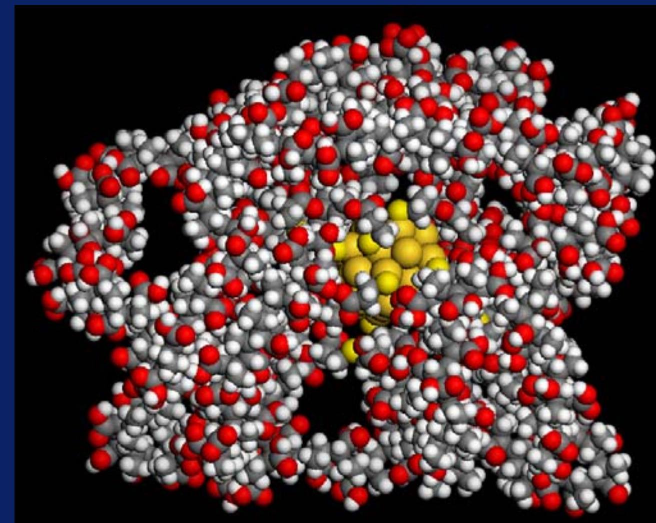
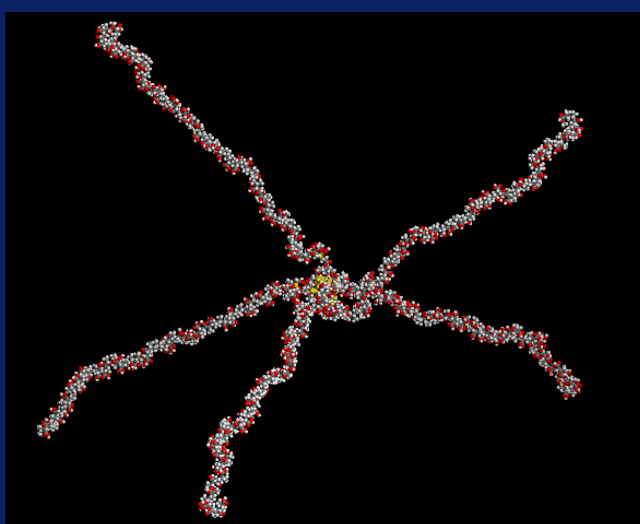
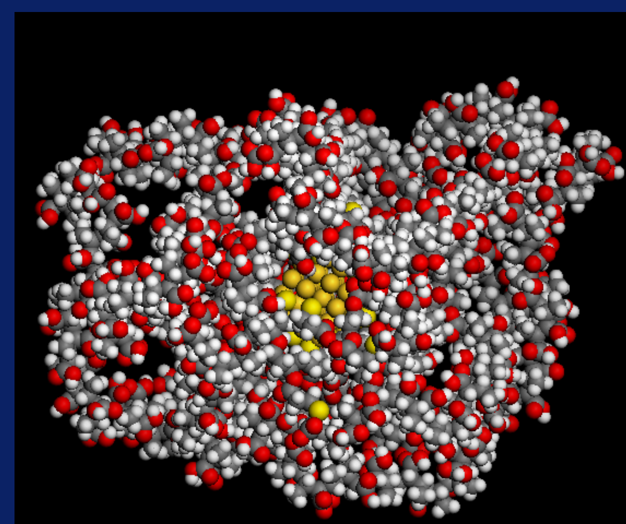
Building a model









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Conclusion

- A simple protocol for the preparation of near-monodisperse gold nanoparticles in the small size regime below 5 nm has been developed.
- Polymer structures have been optimized to control the growth of gold nanoparticles, leading to a narrow size distribution.
- By varying systematically the polymer to gold ratio, the size of the nanoparticles can be finely tuned and a transition from non-fluorescent to fluorescent nanoparticles is observed.
- A combination of characterization techniques allow us to propose a theoratical model of the most fluorescent nanoparticle solution

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