



U N I V E R S I T Y O F

L I V E R P O O L

Monodisperse Polymer-Stabilised Water Soluble Gold Nanoparticles

Nicolas SCHAEFFER

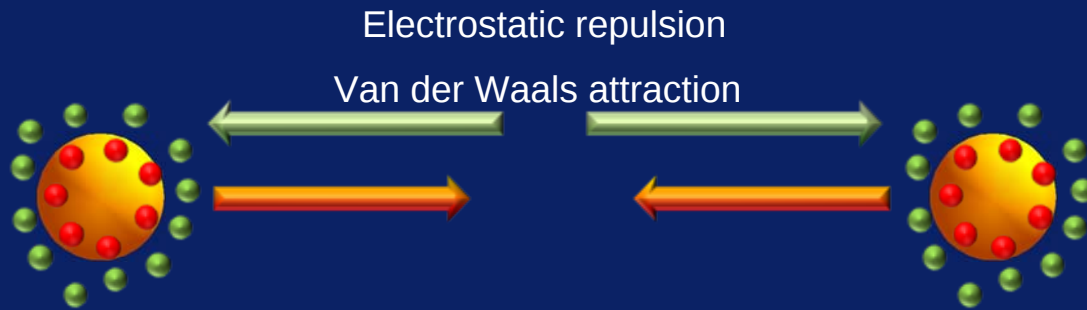
The University of Liverpool
Department of Chemistry
Crown street
Liverpool
L69 7ZD
U.K.



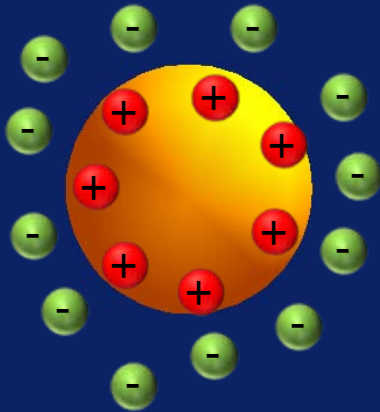
Stabilization



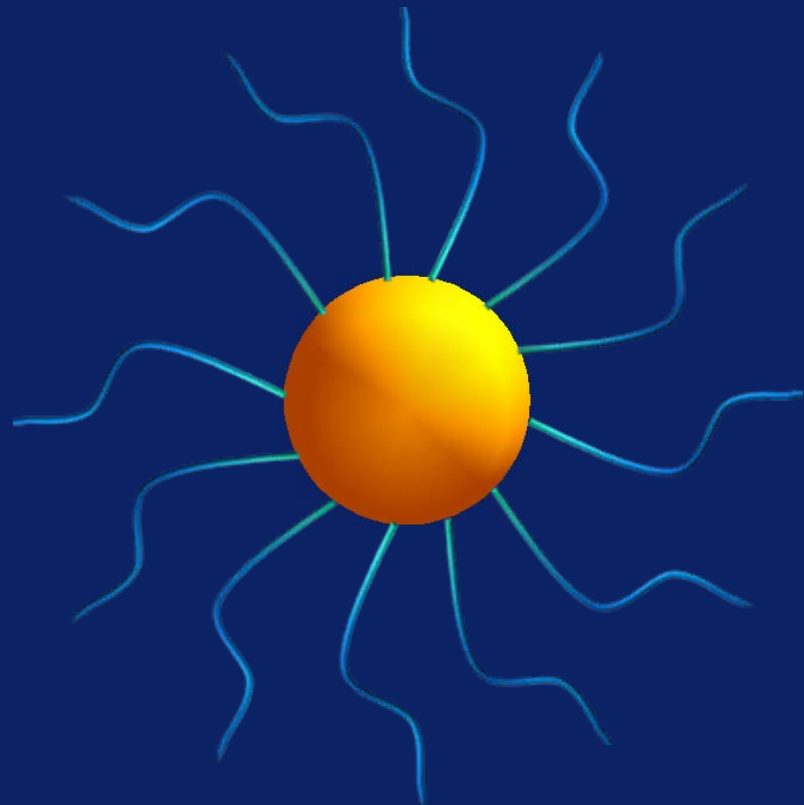
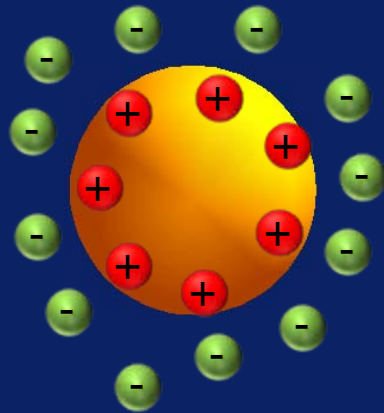
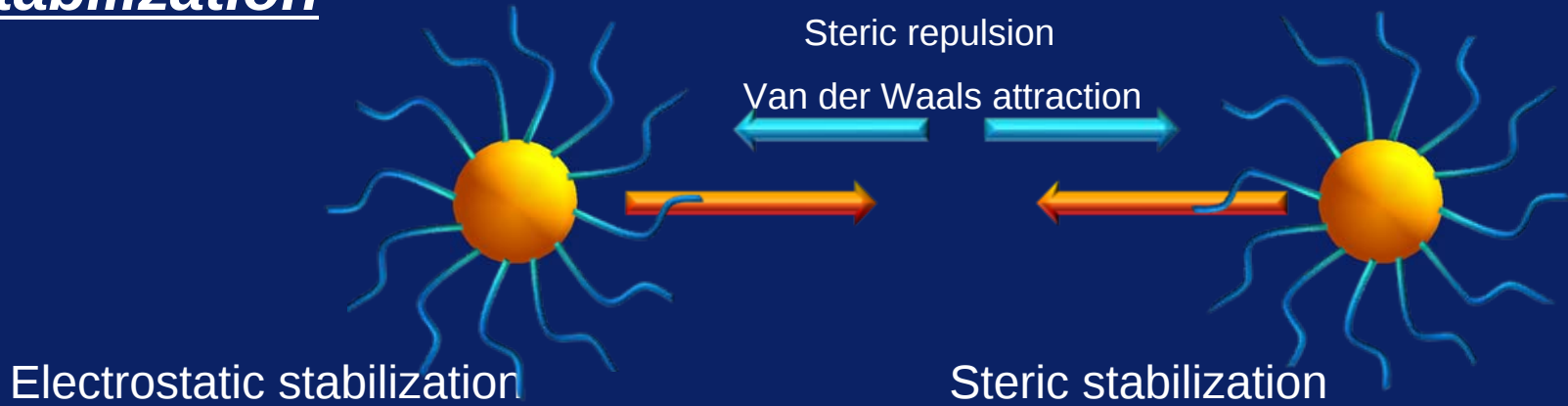
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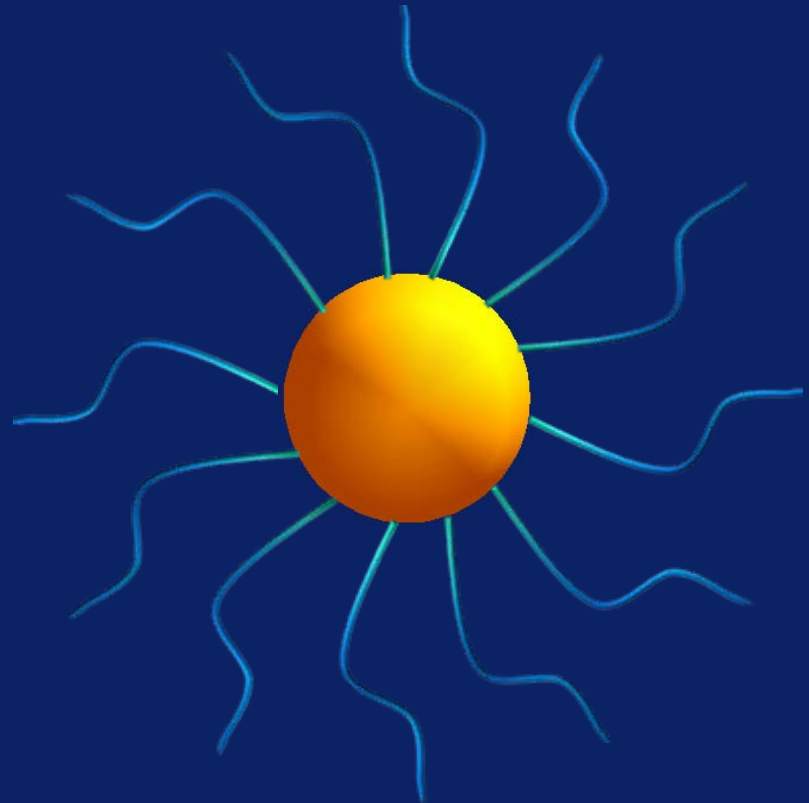
Electrostatic stabilization



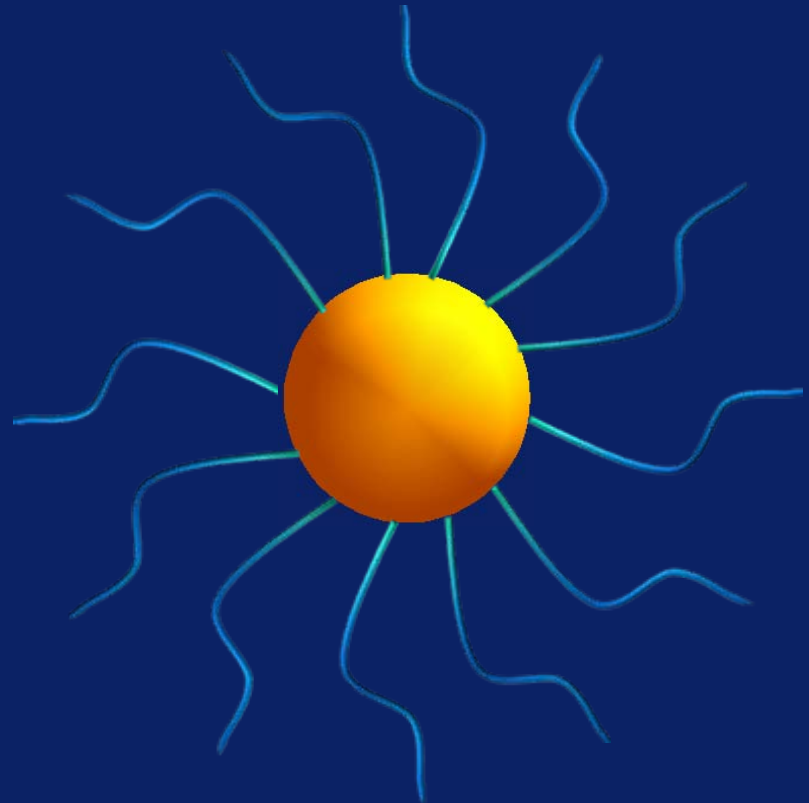
Stabilization



Polymeric stabilization



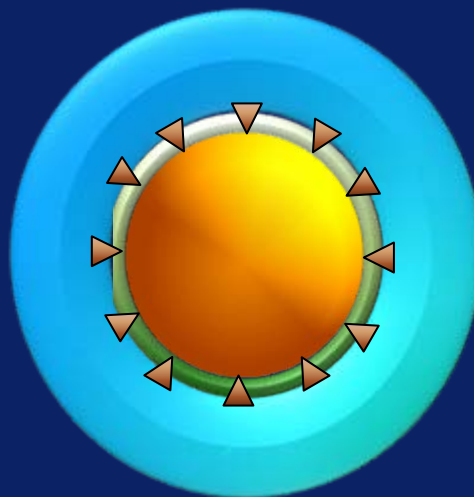
What makes a suitable stabilizer ?



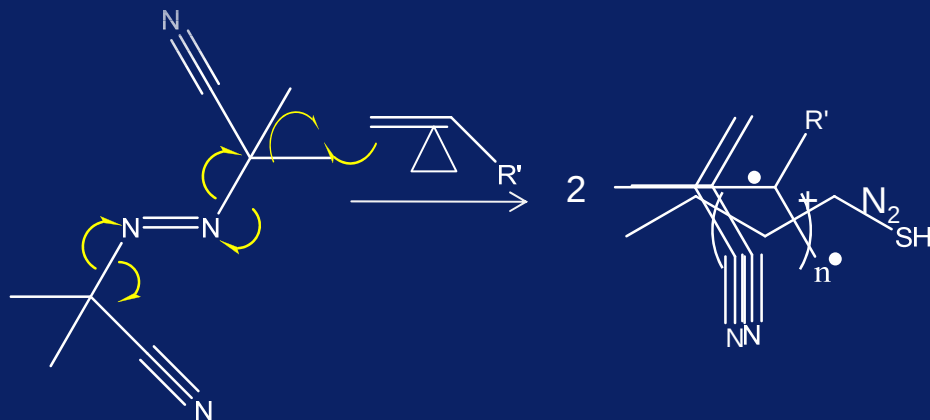
What makes a suitable stabilizer ?



- Binding site
- Hydrophobic end
- Hydrophilic tail

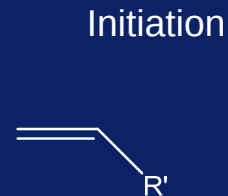


Chain transfer polymerization



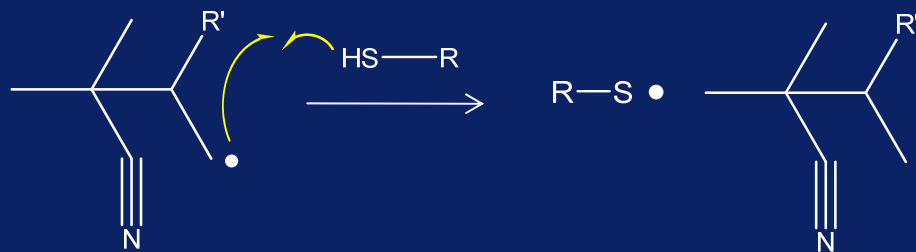
Initiator

Chain transfert agent



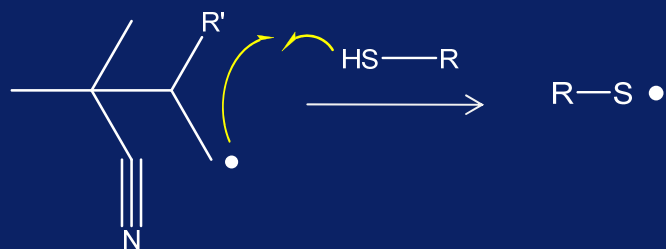
Monomers

Chain transfer polymerization

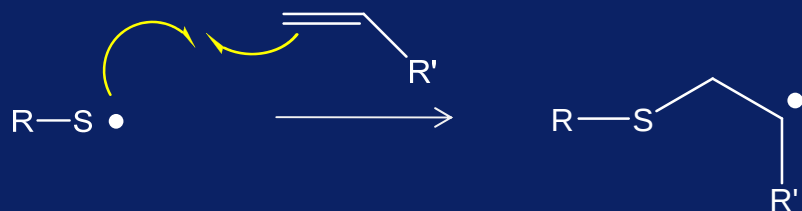


Chain transfer

Chain transfer polymerization

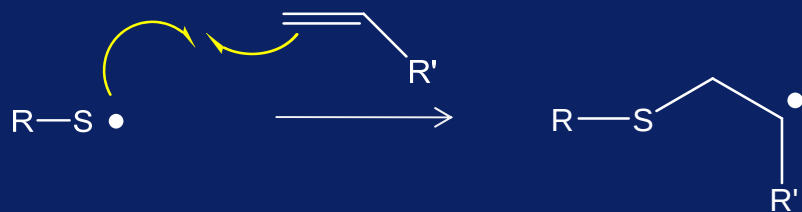


Chain transfer

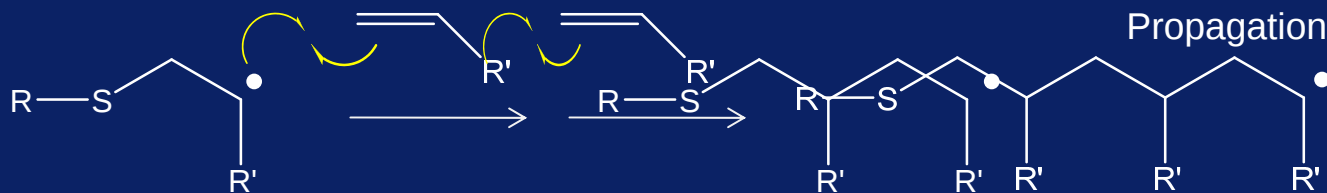


Initiation

Chain transfer polymerization

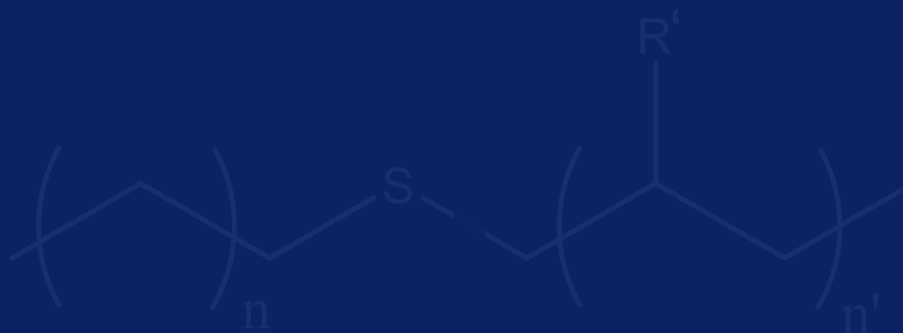
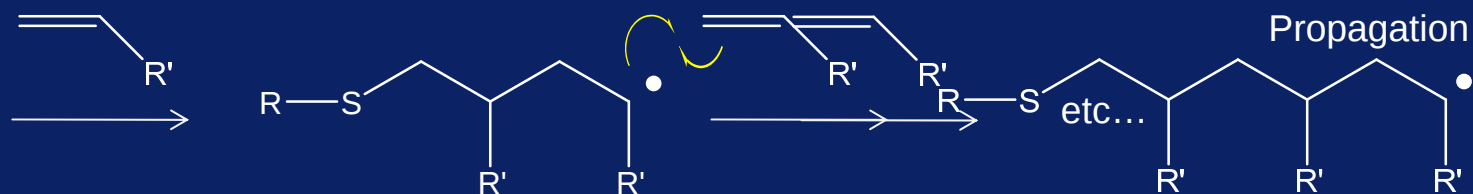
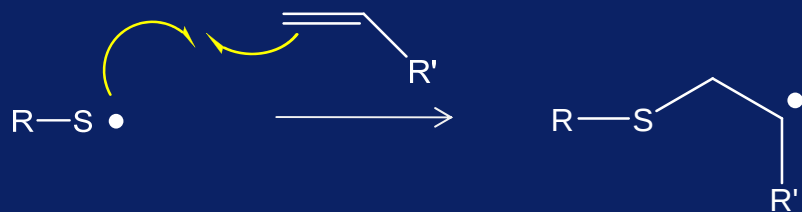


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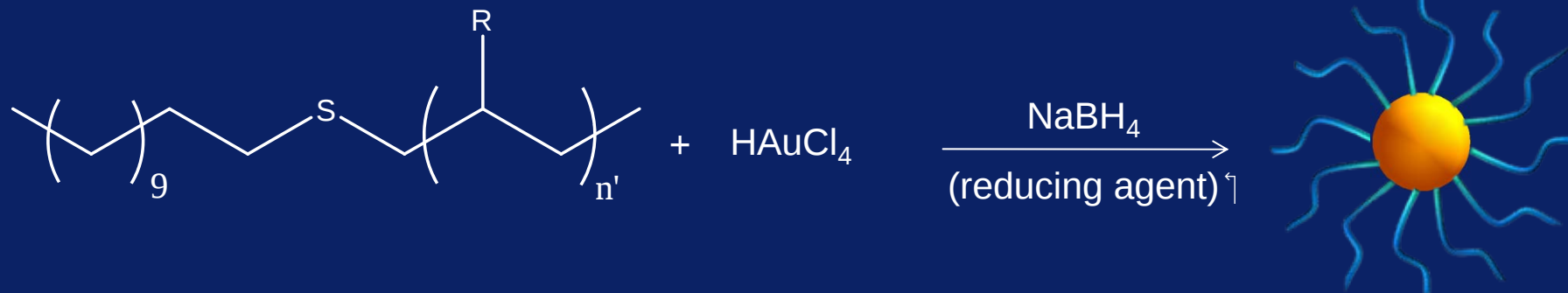


Propagation

Chain transfer polymerization

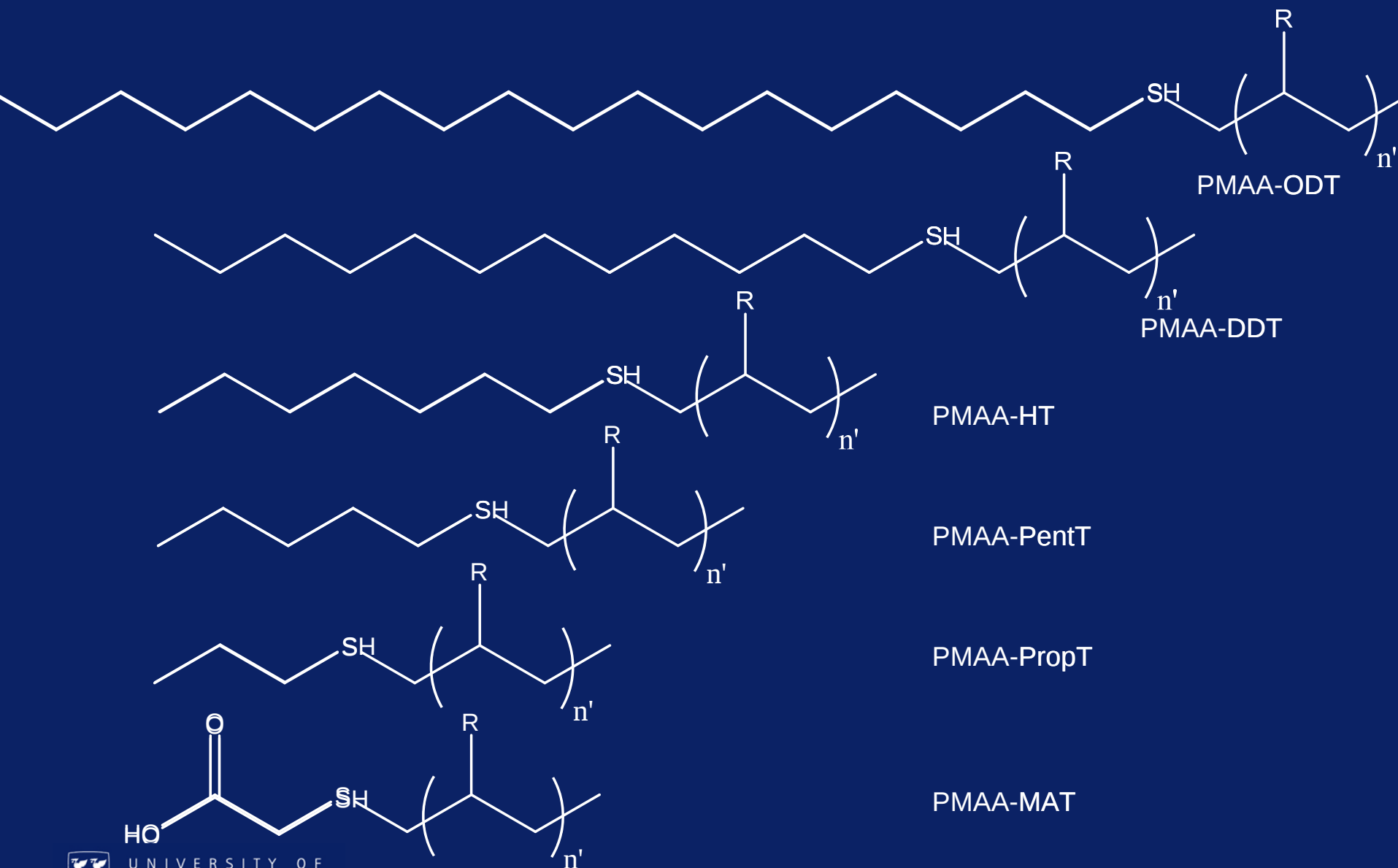


Gold nanoparticles synthesis



a) b) c) d)

End-group contribution



End-group contribution

End-group hydrophobicity

$\frac{C_{\text{polymer}}}{C_{\text{Au}}}$ increasing



PMAA-ODT

$M_n=2980$, $M_w=3480$

PMAA-DDT

$M_n=2550$, $M_w=3491$

PMAA-HT

$M_n=2180$, $M_w=2550$

PMAA-Pent

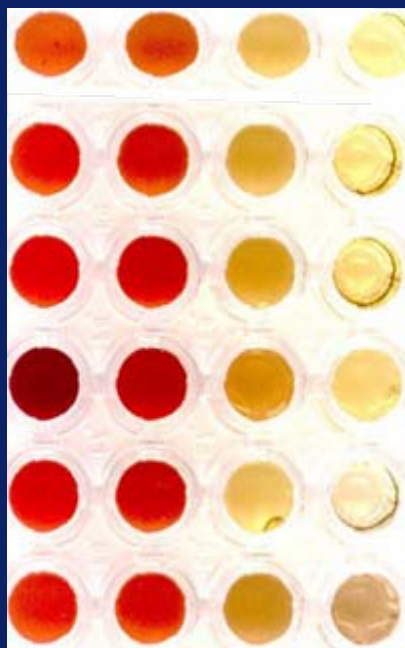
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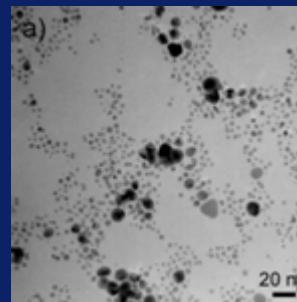
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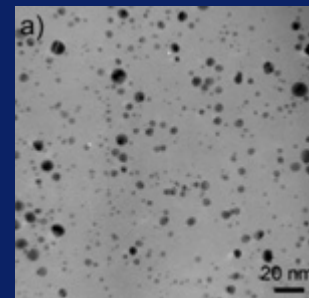
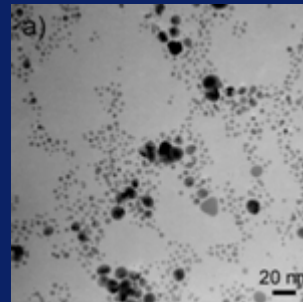
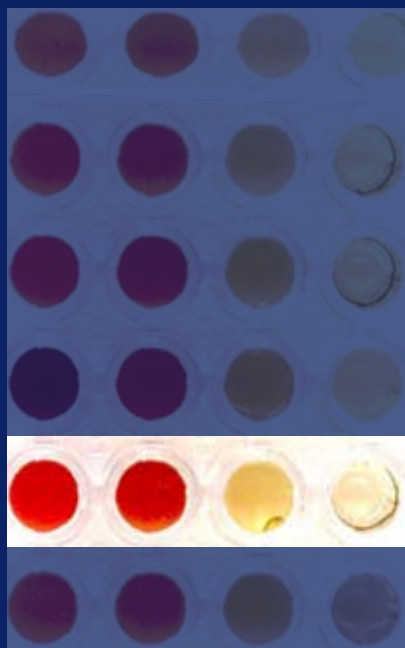
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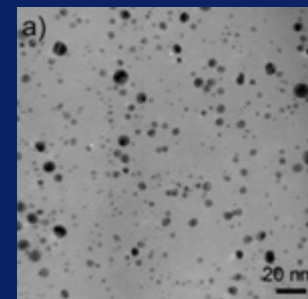
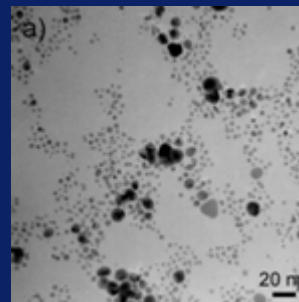
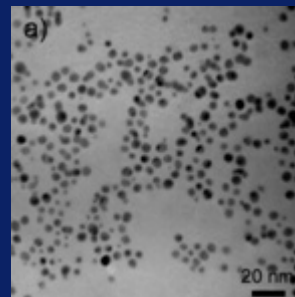
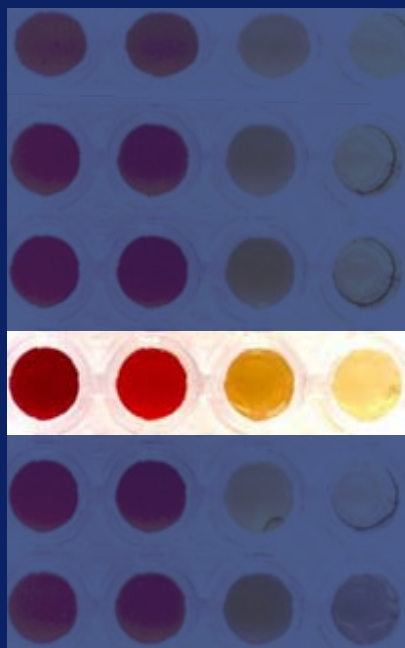
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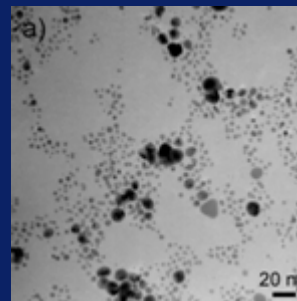
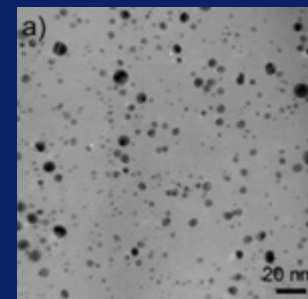
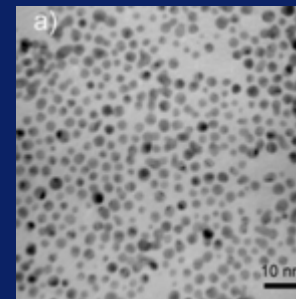
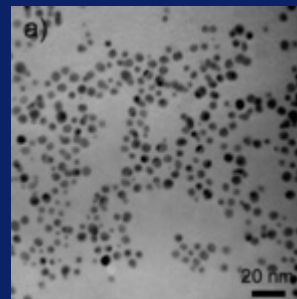
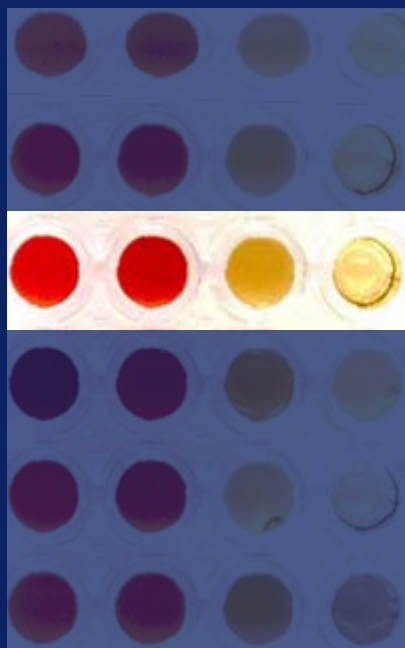
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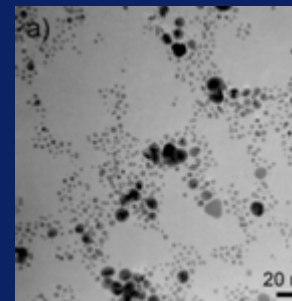
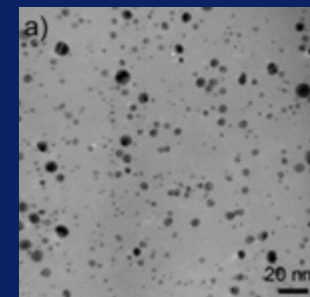
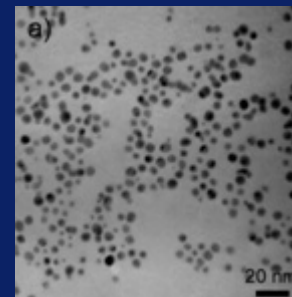
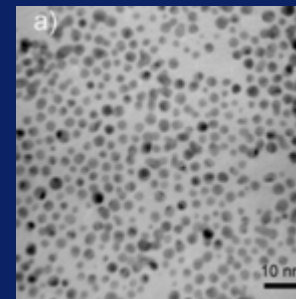
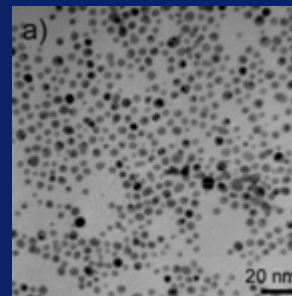
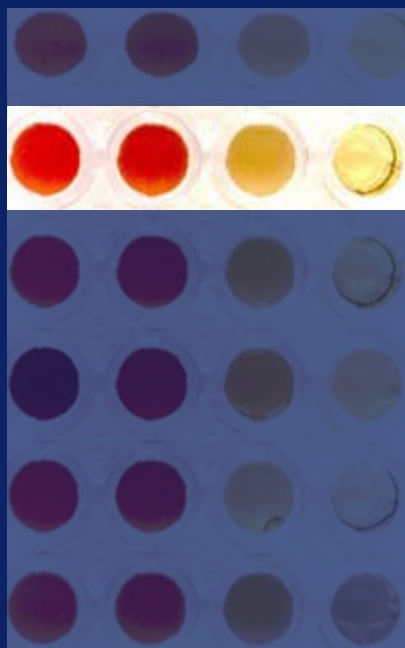
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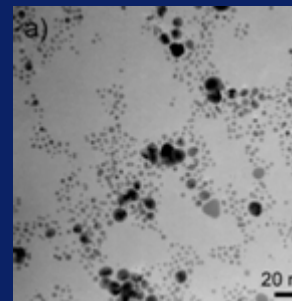
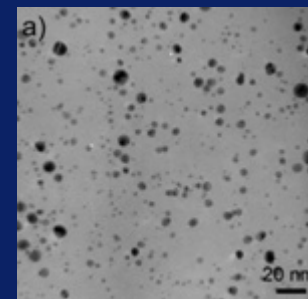
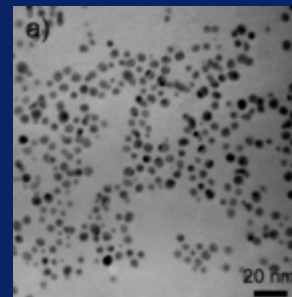
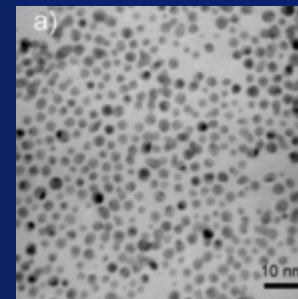
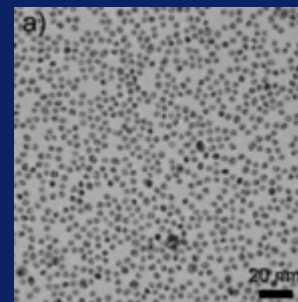
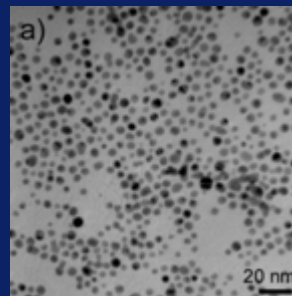
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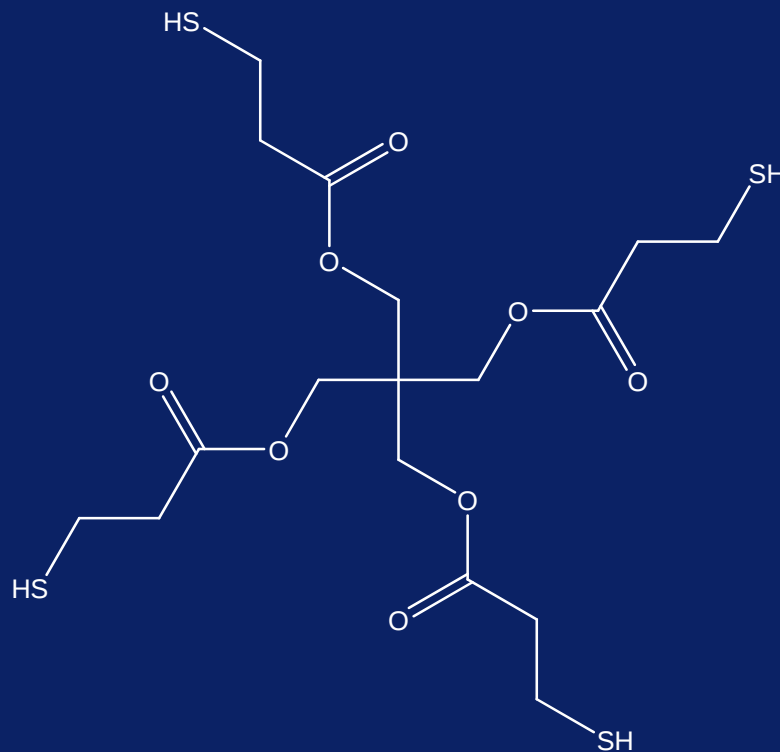
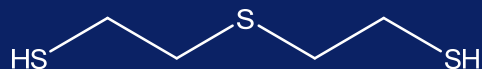
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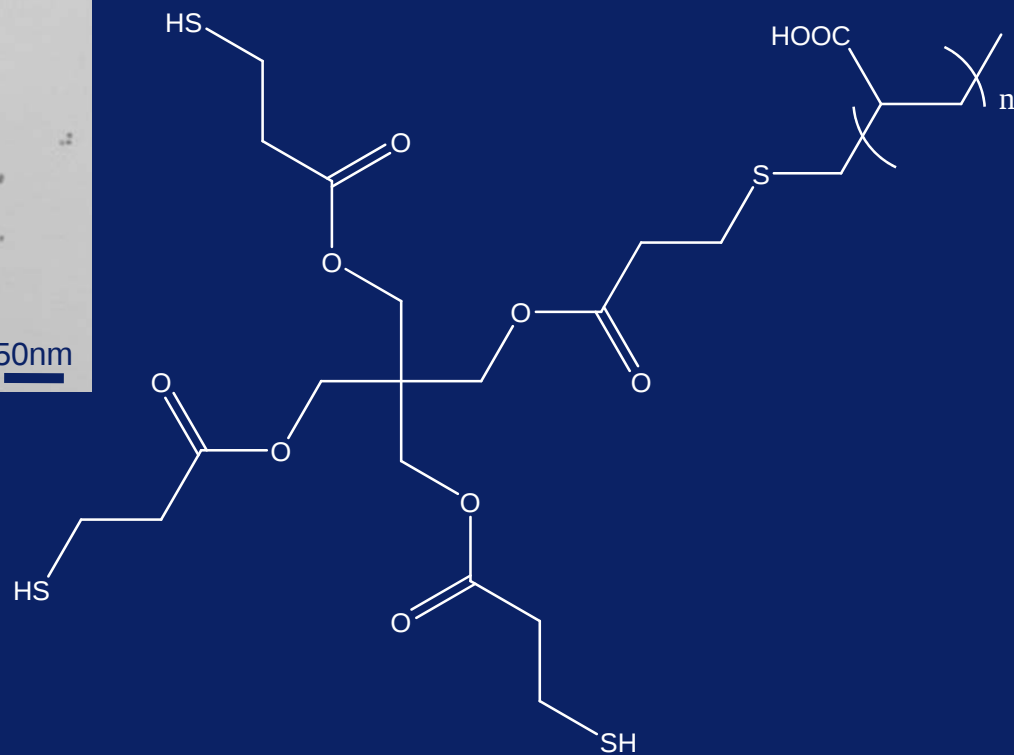
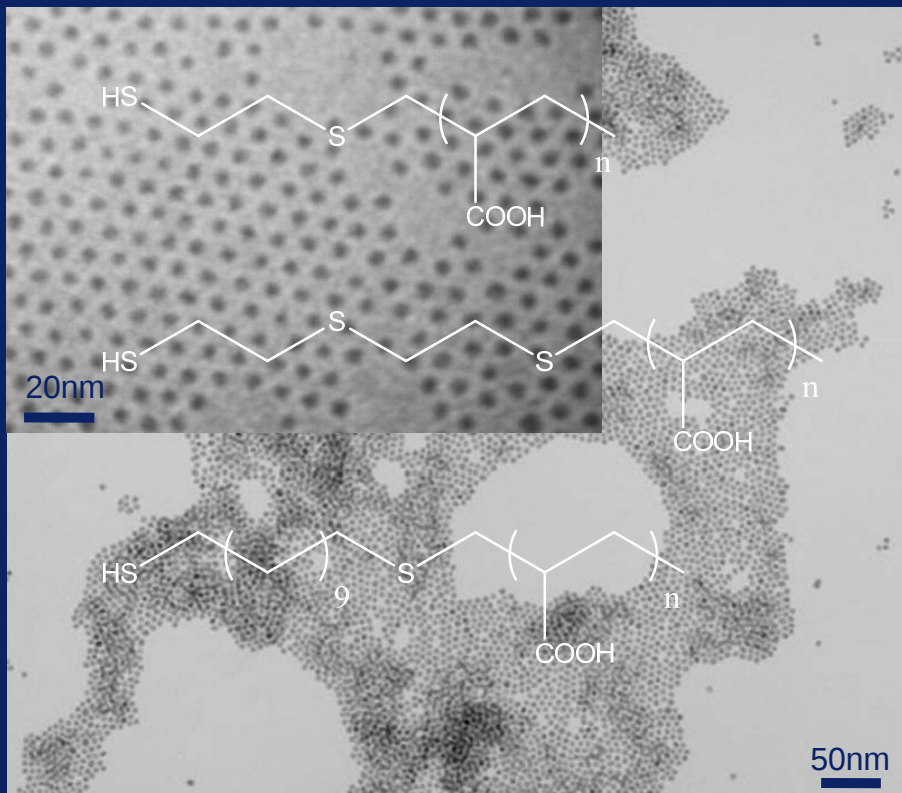
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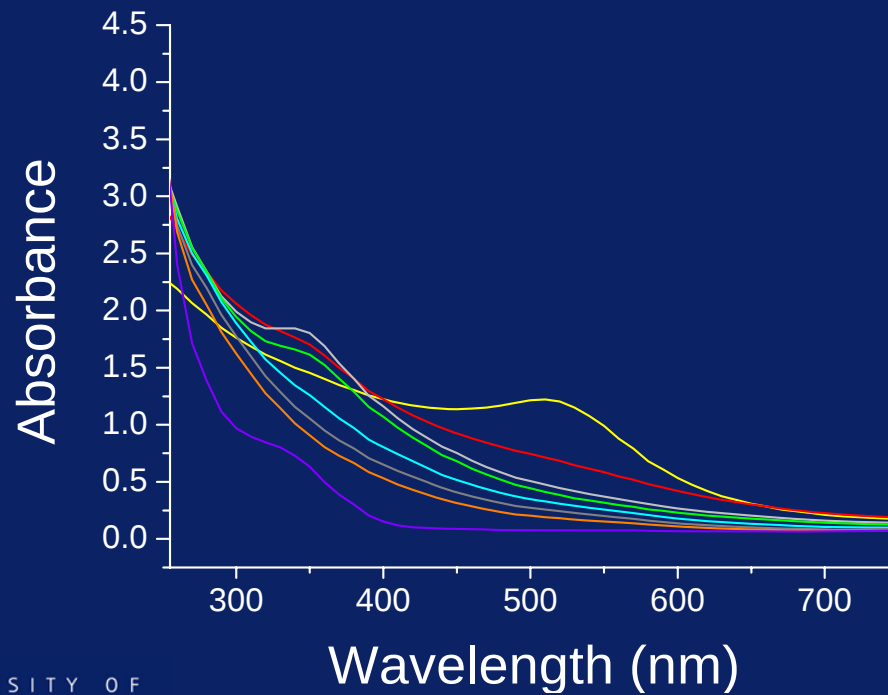
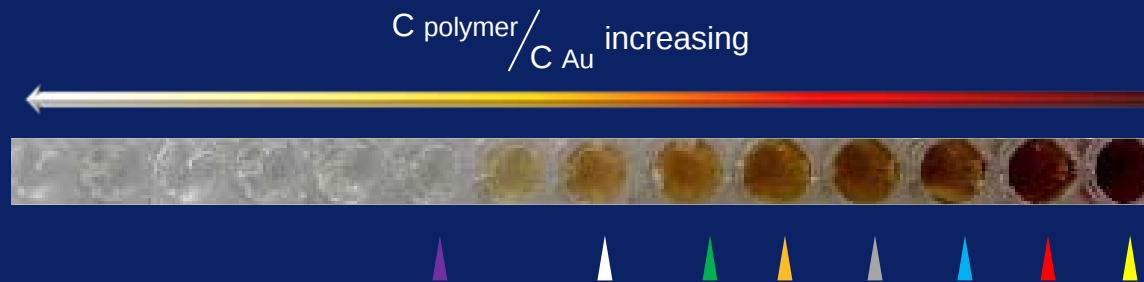
What about thiol(s) containing end-groups ?



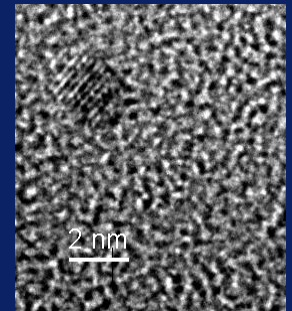
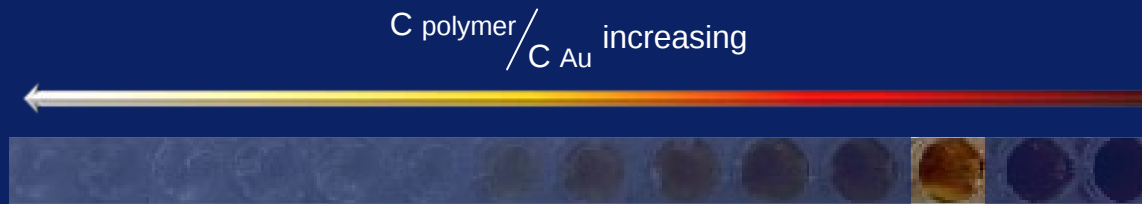
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« Small is beautiful »

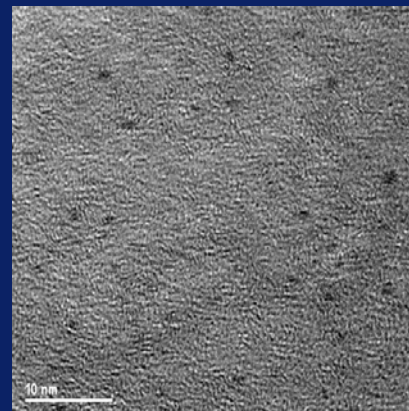
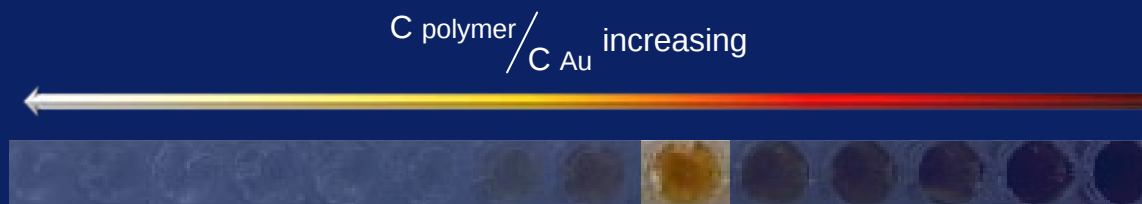


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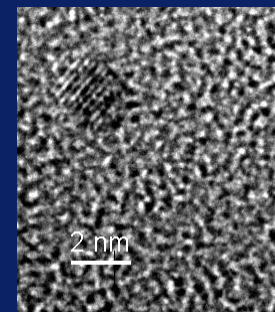


1.7 nm

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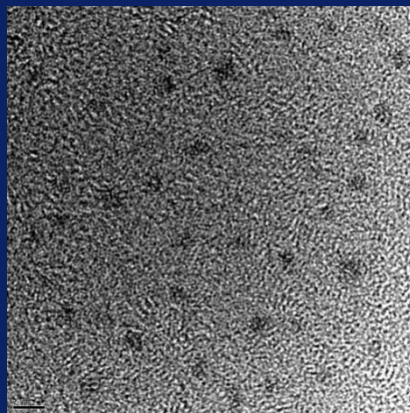
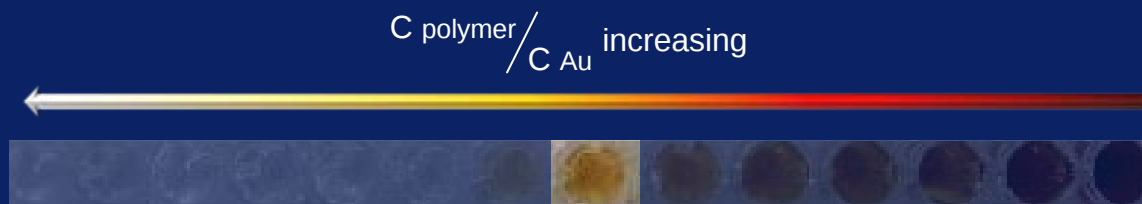


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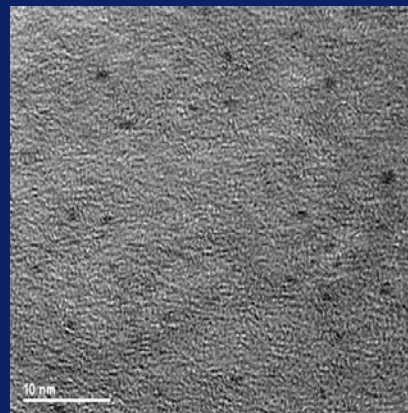


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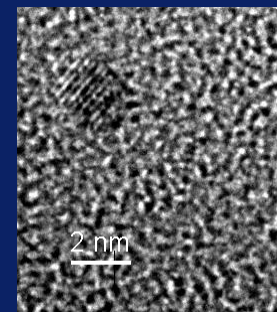
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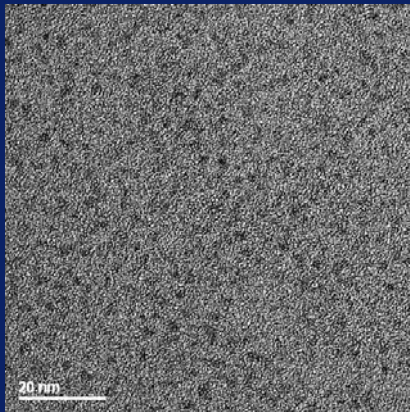
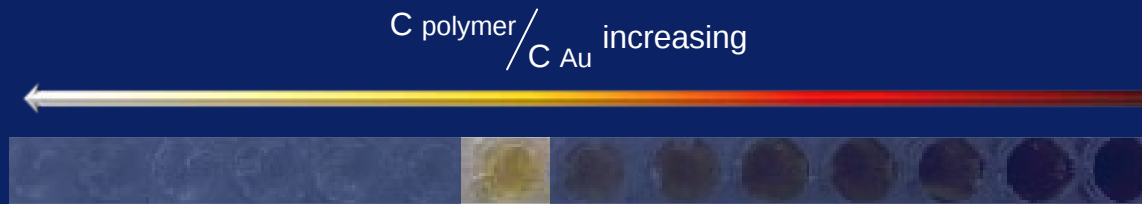


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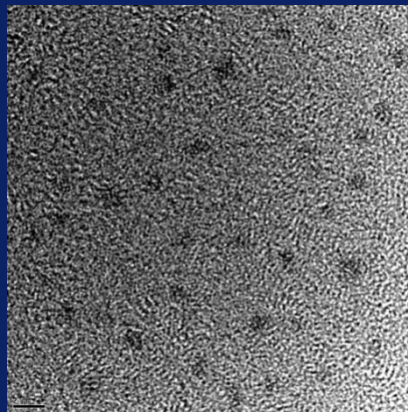


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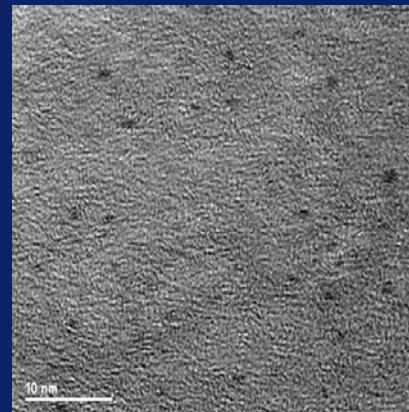
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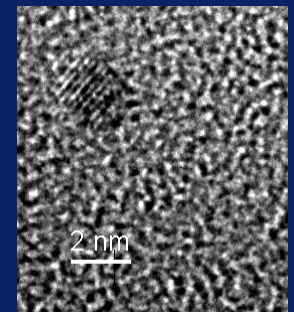
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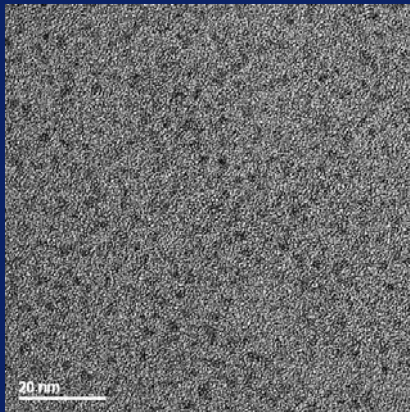
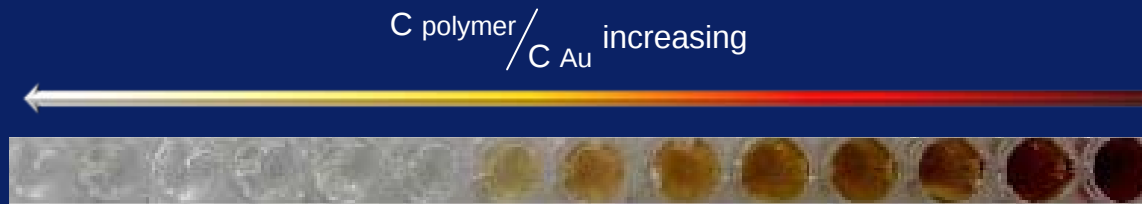


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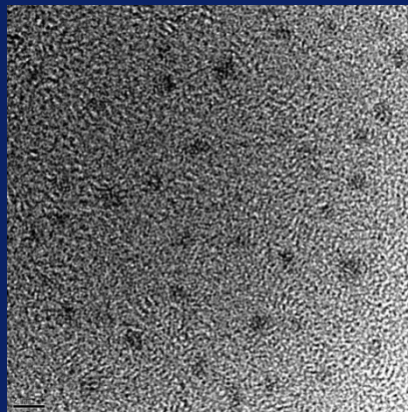


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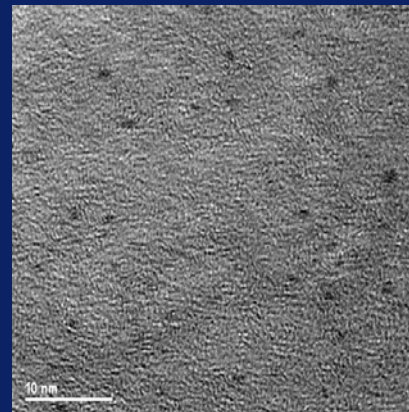
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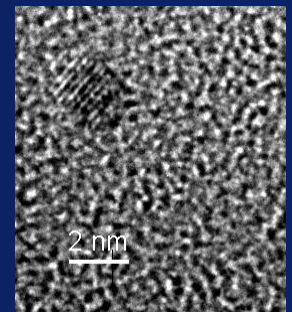
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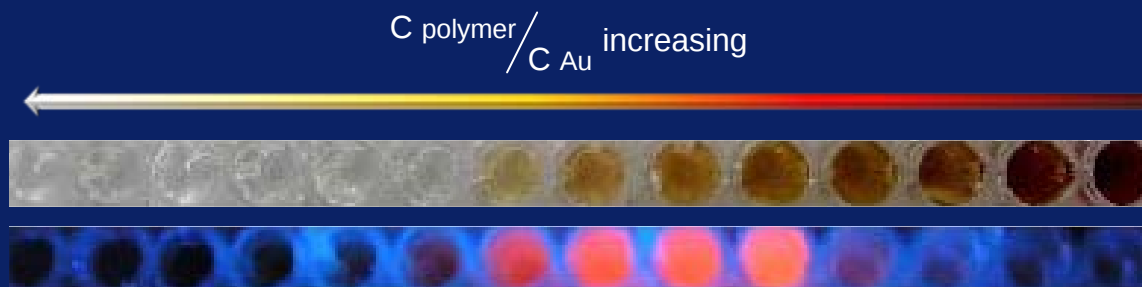


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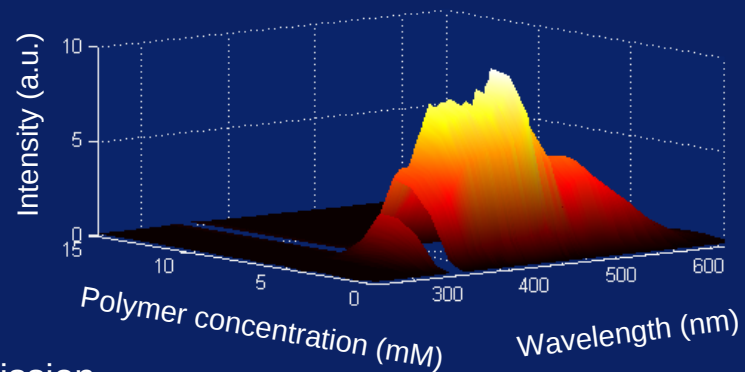


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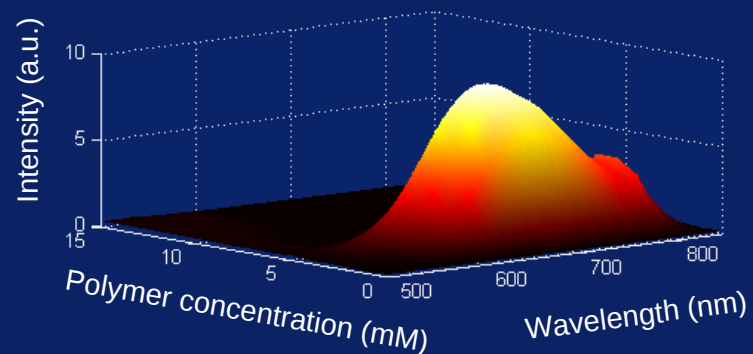
Photophysical properties



Excitation



Emission



Are they really fluorescent?

High Quantum Yield Blue Emission from Water-Soluble Au₈ Nanodots

JACS
COMMUNICATIONS

Published on Web 06/04/2003

High Quantum Yield Blue Emission from Water-Soluble Au₈ Nanodots

Jie Zheng, Jeffrey T. Petty,[†] and Robert M. Dickson^{*}

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Usually occurring at the nanoscale, material properties drastically change as their sizes approach characteristic length scales. Such confinement effects often yield nanomaterials with greatly improved and potentially controllable properties. Metals exhibit a particularly wide range of material behavior along the atom to bulk transition.^{1–11} At sizes comparable to the Fermi wavelength of an electron, optical properties are significantly modified, and discrete nanocluster energy levels become accessible.^{1–3} Such metal nanoclusters, composed of only several tens of atoms, exhibit molecule-like transitions as the density of states is insufficient to merge the valence and conduction bands.^{1,2–9} Such studies have yielded fluorescent, surface passivated Au nanoclusters ranging in size from 28 atoms to smaller particles (<1.2 nm) with emission in the near-IR,⁴ red,¹⁰ and blue.¹¹ With increasingly higher energy emission with decreasing nanocluster size. Although Au nanoclusters with million-fold enhanced fluorescence quantum yields Φ_f , relative to that of bulk gold films,¹² have been created, the 10^{-4} – 10^{-5} quantum yields and polydisperse nanoparticle size distributions have precluded them from being good fluorophores.^{4,10} Herein, we report water-soluble, monodisperse, blue-emitting Au₈ nanodots that, when encapsulated in and stabilized by biocompatible poly(amidoamine) (PAMAM) dendrimers,¹³ exhibit a fluorescence quantum yield of $41 \pm 5\%$, a more than 100-fold improvement over other reported gold nanoclusters.^{4,10}

Widely used to prepare larger metallic and semiconductor nanoparticles,^{14–17} second and fourth generation OH-terminated PAMAM (G2-OH and G4-OH, respectively, Aldrich) were utilized to stabilize and solubilize gold nanoclusters in both aqueous and methanol solutions. By dissolving 0.5 μmol of G4-OH or G2-OH and 1.5 μmol of HAuCl₄·xH₂O (Aldrich) into 2 mL of distilled water (18 M Ω), gold ions were sequestered into dendrimers and reduced by slowly adding an equivalent of NaBH₄ into the solution. Reduced gold atoms aggregate within the dendrimers to form small nanodots (dendrimer-encapsulated nanodots) and large nanoparticles. The solution was stirred for 2 days until reaction and aggregation processes are completed. Solutions were subsequently purified through centrifugation (13 000g) to remove the large gold nanoparticles,¹⁸ leaving a clear, colorless, Au nanodot solution. Although weak as compared to the 285 nm pure dendrimer peak, a clear absorption spectrum of dendrimer encapsulated gold nanodots is obtained by subtracting the pure dendrimer absorption. It can be seen from Figure 1B that a new absorption band at 384 nm with a bandwidth of ~60 nm (fwhm) appears in the final fluorescent Au nanodot solutions. Contrary to the absorption spectrum of large gold nanoparticles, no surface plasmon absorption at 520 nm is observed from this solution, indicating that the nanodots are smaller than ~2 nm.¹⁶

Strong blue luminescence with excitation at 384 and 450 nm, respectively, is dendrimer-encapsulated gold nanodot

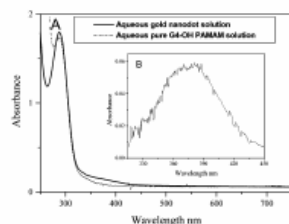


Figure 1. (A) UV-vis absorption spectra of aqueous gold nanodot and pure dendrimer solutions. (B) Subtraction of absorption spectra in A reveals the 384-nm absorption of PAMAM encapsulated Au nanodots.

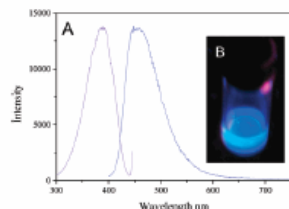


Figure 2. (A) Excitation and emission spectra of G4-OH PAMAM encapsulated gold nanodots at room temperature. (B) Emission from Au nanodots under long-wavelength UV lamp irradiation (366 nm).

fluorescence excitation maximum and bandwidth are identical to the nanodot absorption band in Figure 1. While G2-OH and G4-OH dendrimers yield indistinguishable fluorescent solutions, G0 dendrimers yield only nonfluorescent solutions with black gold solids under the same synthetic conditions. These heterogeneous solutions suggest that, unlike larger second and fourth generation PAMAM, small zeroth generation dendrimers do not adequately protect and stabilize gold nanoclusters. Amazingly, for 384-nm excitation, integrated fluorescence quantum yields for G4-OH and

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

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Dendrimers have recently been of interest as new templates for the preparation of quantum dots of nanometer- to a few nanometer dimensions,^{1–3} a size range where new optical, electrical, or magnetic properties are expected for metals or semiconductors. In addition the nanoclusters formed inside dendrimers are highly monodisperse, chemically stable, and free from agglomeration and are thus excellent systems for studies of quantum size effects. Au nanoclusters encapsulated in dendrimers reportedly produce strong blue photoluminescence at 450 nm,⁴ and we began an investigation of the electrochemistry and the production of ECL with such species. However, we found that photoluminescence with the same spectral profile was obtained without the addition of any Au species. Simple oxidation of OH-terminated PAMAM dendrimers, such as (fourth generation) G4-OH, G2-OH, or even G0-OH, e.g. with (NH₄)₂S₂O₈ (PS), produced species that showed blue photoluminescence with a high quantum yield.

The preparation method described below was quite simple and highly reproducible. A 0.2-mL aliquot of G2-OH (Aldrich, 20 wt % in MeOH) was added to 2.6 mL of distilled water, followed by addition of 0.2 mL of 0.1 M aqueous PS (Aldrich). After several hours, the colorless solution began to display blue luminescence under UV irradiation at 366 nm with the luminescence intensity gradually increasing with time up to several weeks. Moreover, the initially colorless solution changed to pale yellow after about a week. The UV-vis spectra shown in Supporting Information (Figure S1A) indicate that the characteristic absorption peak of pure PAMAM G2-OH dendrimer occurred below 300 nm. After the addition of PS, a new absorption band grew at around 380 nm, which slowly increased with time. This PS-treated G2-OH produced the strong blue luminescence shown in Figure 1. A PS-treated G2-OH aqueous solution, diluted to 10 μM showed an emission band at 450 nm with the excitation band at 380 nm, coincident with the UV-vis absorption band (Figure S1A), both bands gradually increased with time, while their peak positions remained unchanged. With 380-nm excitation, the fluorescence quantum yield for this PS-treated G2-OH was $38 \pm 5\%$ with quinine sulfate (dissolved in 0.1 M sulfuric acid), showing a similar luminescence spectrum, used as reference.⁵

When the same treatment was applied to PAMAM G4-OH or G0-OH (technical grade, Dendritech Inc.), virtually the same blue photoluminescence was observed, with emission and excitation spectra very close to those of G2-OH (Figure 1A). The same treatment for amine-terminated PAMAM dendrimers, such as G4-NH₂, G2-NH₂, and G1-NH₂, produced only very pale-blue

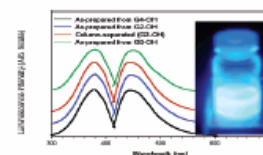


Figure 1. (A) Emission (EM) and excitation (EX) spectra for several PS-treated (OH-terminated) PAMAM dendrimers, concentrations of G4-OH, G2-OH, and G0-OH are 2.5, 10, and 40 μM , respectively. Each sample has been aged for 7 days. (B) Blue emission from the column-separated PS-treated G2-OH under 366-nm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

The chemical structure for this luminescence center is currently under investigation (see Supporting Information for preliminary characterization), but we speculate that the initial step of the reaction is the oxidation of a terminal -OH group by the PS, finally forming the blue-luminescent chemical species.

We also attempted to prepare Au₈ nanoclusters in the cavity of PAMAM G2-OH and G4-OH dendrimers by modifying the original procedure.⁴ Two micromoles of HAuCl₄ (Aldrich, 99.99%) was dissolved in 40 mL of MeOH (Aldrich, HPLC grade), and 5 μmol of G4-OH or 10 μmol of G2-OH was then added. The solution was magnetically stirred for 2 days in the dark. During this procedure some Au³⁺ ions were sequestered into the dendrimer, while other Au³⁺ ions precipitated as Au(OH) from the solution. Thirty micromoles of fresh NaBH₄ dissolved in MeOH was then added dropwise to this solution to complete the reduction of Au³⁺ ions to metallic Au. The resultant solution was stirred for 4 days until the formation of any Au clusters was complete. Any Au³⁺ ions not sequestered into the dendrimer precipitated by the reduction of dendrimer or NaBH₄. The precipitated Au was collected by centrifugation, and a gravimetric analysis showed the weight percentage of Au in the G2-OH dendrimer to be $49 \pm 5\%$. The luminescence properties of the prepared Au-G2-OH or Au-G4-OH samples after removal of the Au(OH) were the same as those in the earlier report⁴ and also the same as those of PS-treated dendrimers (Figure 2). However, the PS-treated dendrimers produced a 25–50 times higher luminescence intensity at the same dendrimer concentration.

We also prepared the Au-G2-OH in EtOH instead of MeOH under the same experimental conditions. In EtOH solution most

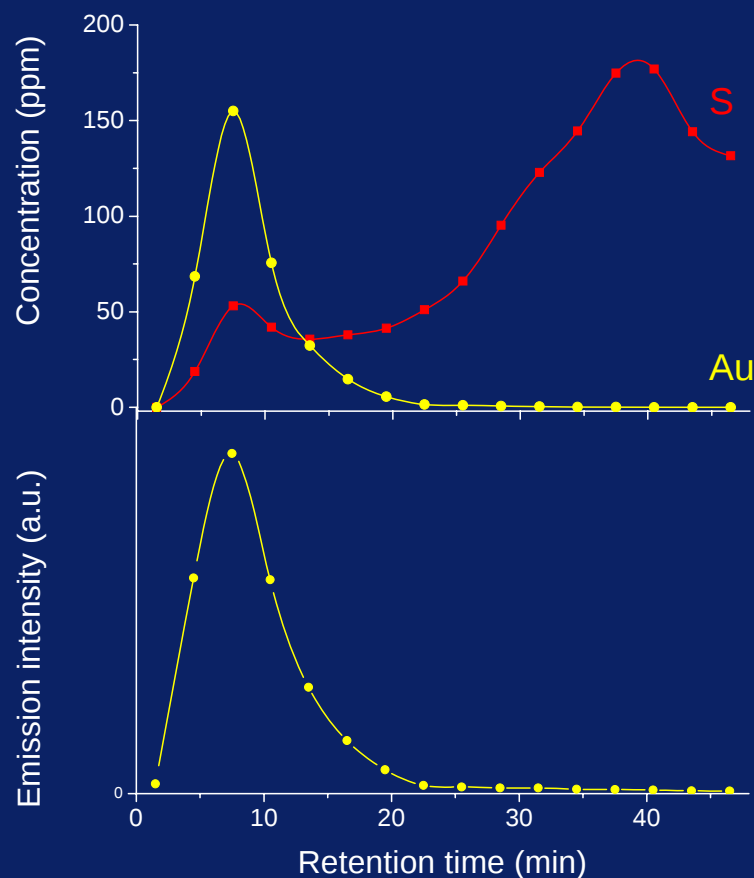
Strong Blue Photoluminescence and ECL from OH-Terminated PAMAM Dendrimers in the Absence of Gold Nanoparticles

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Are they really fluorescent ?

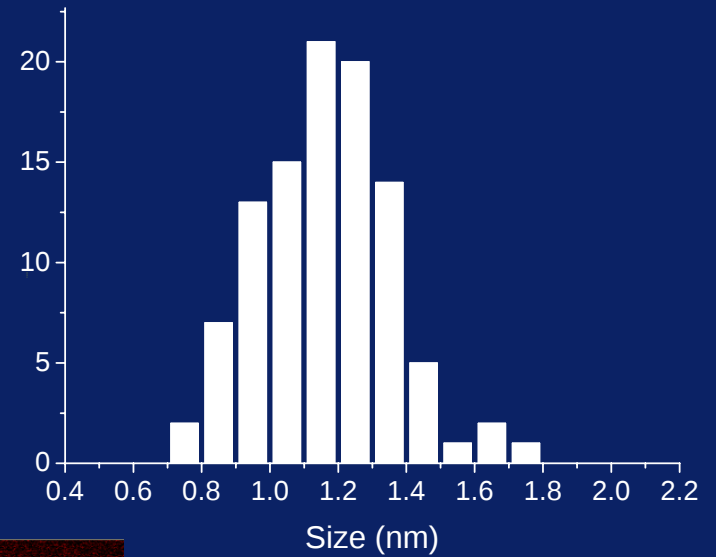
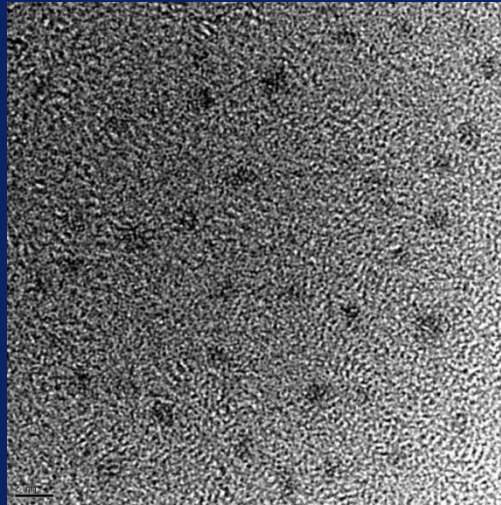
- The polymer is not fluorescent
- The polymer, after oxidation, is not fluorescent
- The polymer, after reduction, is not fluorescent
- The polymer, in the presence of HAuCl_4 , is not fluorescent

Purification/control by
size exclusion
chromatography

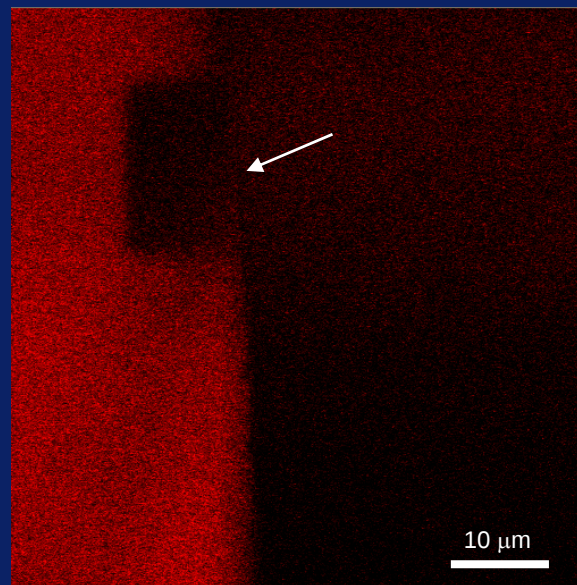


Core/shell structure

Core
(HR-TEM)

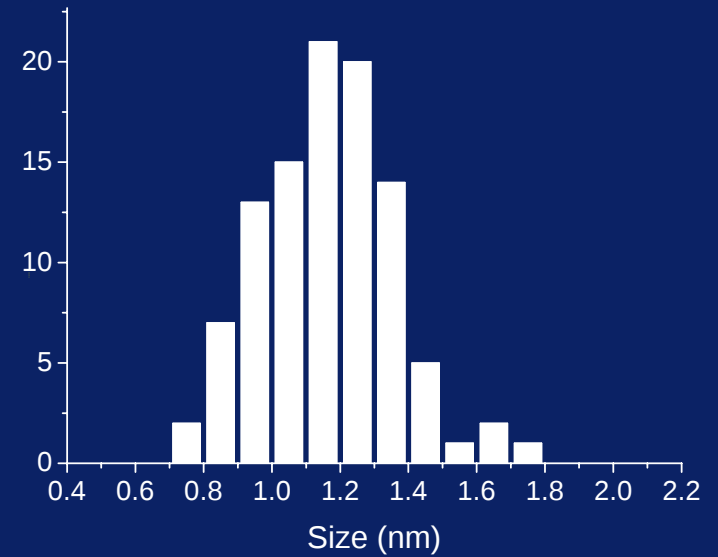
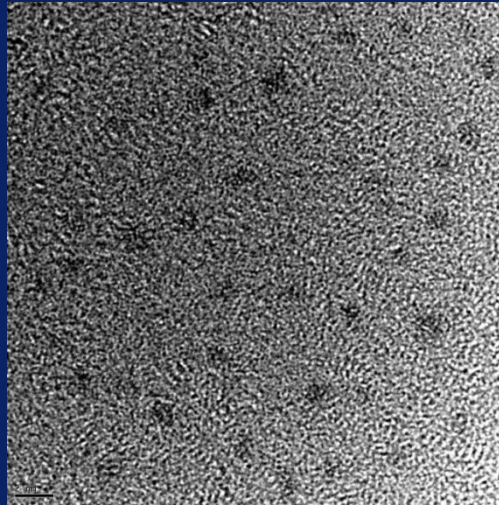


Shell
(???)

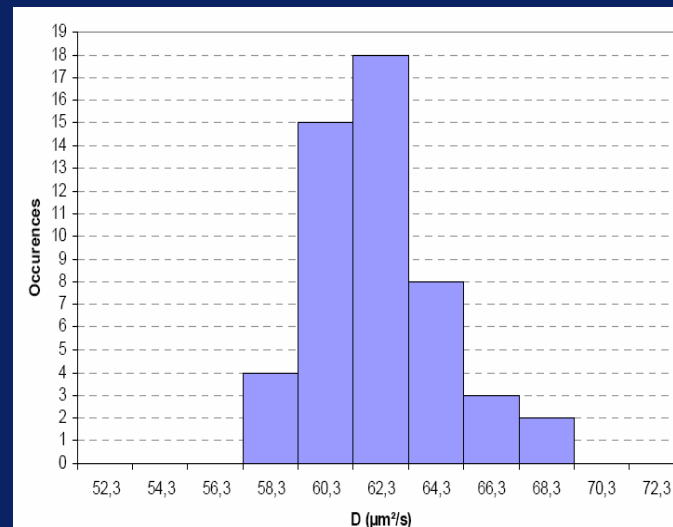


Core/shell structure

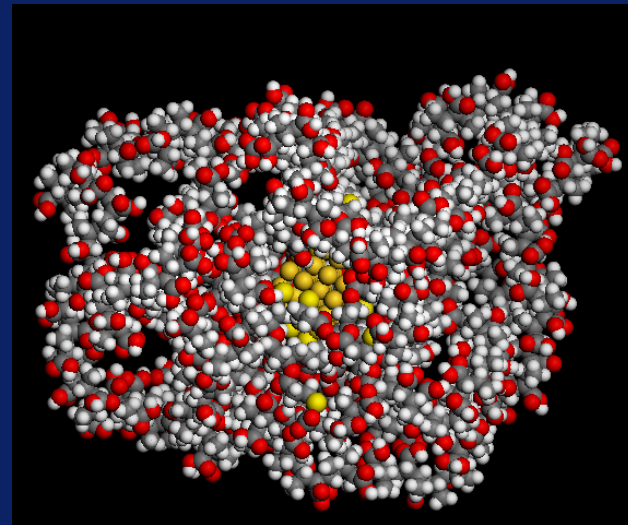
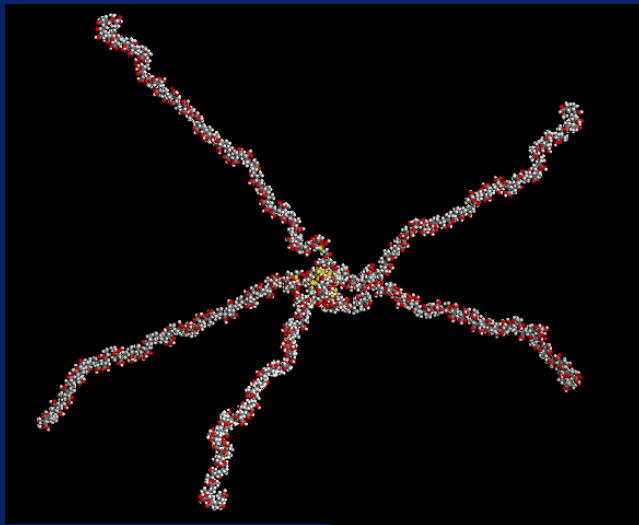
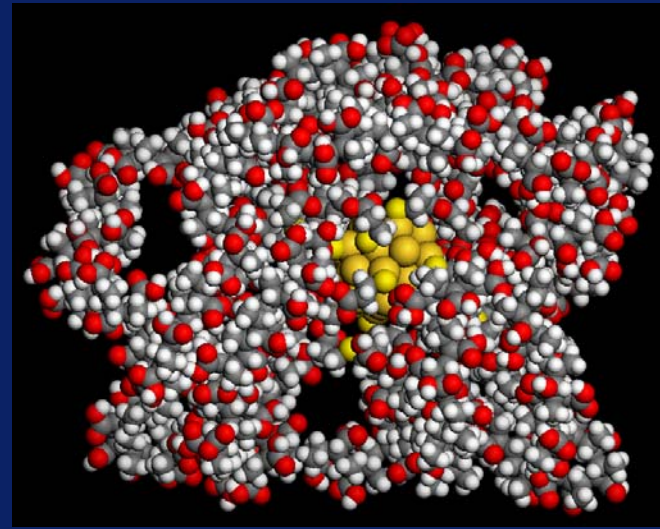
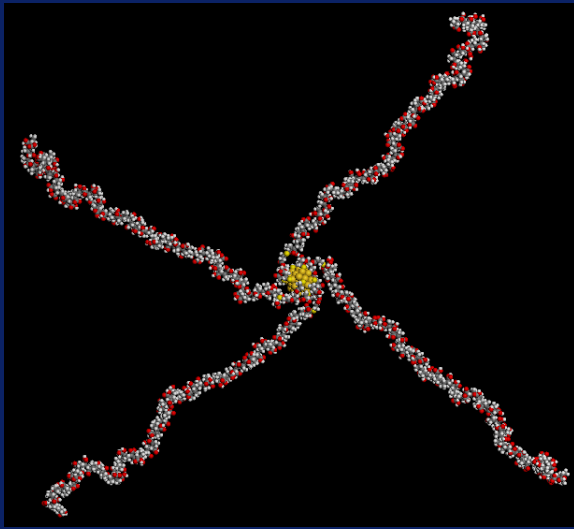
Core
(HR-TEM)



Shell
(Fluorescence recovery
after photobleaching)



Building a model



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 theoretical model of the most fluorescent nanoparticle solution

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