

# Polarity sensitive colloidal gold nanoparticles

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## ABSTRACT

Water soluble colloidal nanoparticles possess huge surface negative charge and this provides their colloidal stability [1]. The surface charge, therefore, ultimately demonstrate the overall behavior of the nanoparticles irrespective of core material. We demonstrate fluorescence based dual emission polarity sensor that is based upon hydroxyflavone derivative [2]. The NH<sub>2</sub> group at position 7 facilitates the conjugation to the carboxylic acid groups on the particle surface. Two important parameters can be addressed in parallel by using the sensor i) polarity and ii) Hydration [3]. The fluorescence read-out is either single peak (hydration, due to interaction of water molecules to the ketone group) or dual peak emission (polarity of environment). The influence of external factors such as alcohols, polyamines, detergents etc. has been investigated.

**Keywords** Nanoparticles, Polarity, Sensor, Fluorescence

## EXPERIMENTAL

Dodecanethiol stabilized Au nanoparticles were synthesized by conventional two phase method with slight modification (see figure 1) [4]. Amphiphilic polymer is constituted of backbone (Isobutylene-alt-maleic anhydride, average M<sub>w</sub> ~6,000 g/mol, Sigma, #531278) (see figure 2a); and sidechain (dodecylamine powder, ≥98%, Fluka, # 44170) (see figure 2b) [5]. The two constituents are mixed in molar concentrations 20mmol and 15mmol respectively for backbone and sidechain (see figure 2c). The 25% free rings can be utilized later for further functionalization. The polymer was modified with 2% FE-dye molecules (see figure 3) and then was wrapped around the particle surface to make them soluble in water [1]. The wrapping phenomenon is self triggered and is really efficient. The solvent (chloroform) was then evaporated completely and the particles were redissolved in buffer SBB 12. The anhydride rings open and we get negatively charged carboxylic groups on the surface. The highly negative

charged surface ensures the colloidal stability of particles in buffer due to steric hinderance.

## FIGURES AND CAPTIONS

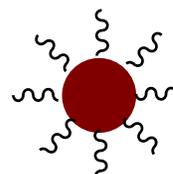


Figure 1: Dodecanethiol stabilized Au nanoparticles.

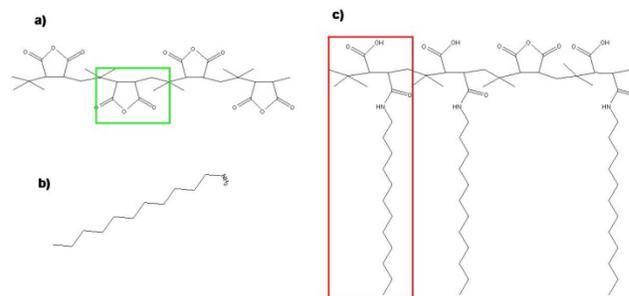


Figure 2: Amphiphilic polymer a) hydrophilic backbone consisting anhydride rings (open upon exposure to buffer) b) hydrophobic sidechains (ensure intercalation with dodecanethiol on the particle surface) and c) polymer with 75% anhydride rings modified with side chains.

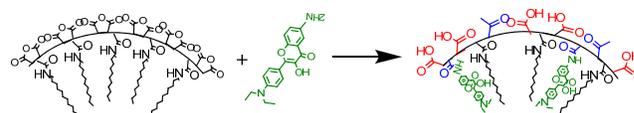


Figure 3: Amphiphilic polymer modified with 2% FE dye. The remaining rings open once dissolved in water.

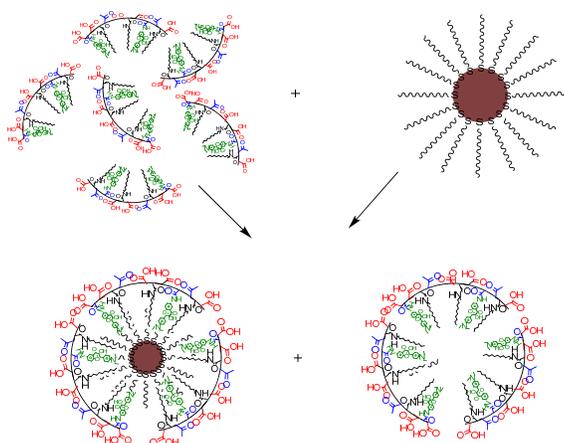


Figure 4: Polymer coating of Au nanoparticles with FE-modified amphiphilic polymer. The free polymer forms empty micelles and can be separated through either GEL electrophoresis or HPLC chromatography.

Au nanoparticles with FE dye exposed to the surrounding media via polyethylene glycol (PEG spacers) were prepared. The FE-PEG conjugates were prepared and purified through phase separation techniques. The Boc-group on the PEG was then deprotected through trifluoroacetic acid. The conjugation of modified PEG was mediated through coupling agent (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, Sigma-Aldrich # E7750). The ratio of EDC was kept to 32000/NP, based upon previous findings [6] whereas for PEG the ratio was kept to 500/NP.

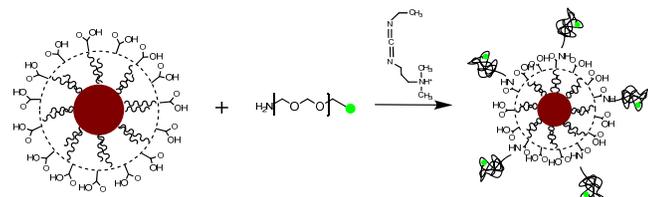


Figure 5: functionalization of plain polymer coated Au nanoparticles with FE-modified PEG spacers via EDC chemistry to keep the dye exposed to medium (Buffer).

## RESULTS

Fluorescence measurements of particles with dye embedded inside polymer shell and dye located outside polymer shell has been done. It was found that the dye embedded inside polymer shell can sense the interactions on the particle surface whereas the dye located in the media is unable to sense the changes occurring on the particle surface due to influence of certain stimuli (alcohol, plynamine, detergent). It was found that the dye is sensitive to environmental changes only if it located inside polymer shell. For dye

located outside shell the readout is single emission peak due to hydration effect.

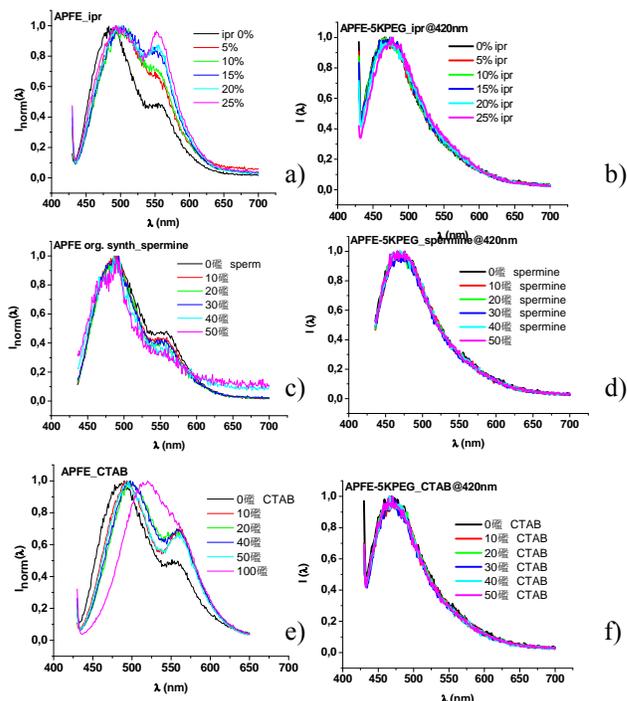


Figure 6: Comparison of Au nanoparticles with FE dye embedded in polymer shell [a), c) and e)] and FE dye exposed to buffer [b), d) and f)] under the influence of isopropanol (a, b), spermine (c, d) and CTAB (e, f).

## DISCUSSION

FE incorporated Au nanoparticles can be used to sense the polarity changes in the environment. The effect of different factors has been studied successfully. The effort to locate dye outside polymer shell keeping the sensitivity of fluorophore intact failed. The dehydration effect is quite dominant on the dye molecule once in water. PEG spacers hinder the approach of small molecules to the surface of particles. This was further verified by saturating FE-incorporated particles with PEG spacers of different lengths. It was found that longer the PEG spacer is better is the hindrance.

## FUTURE PERSPECTIVES

FE dye with ketone group protected with a benzyl group can resolve the hydration issue. Although hydration is an important parameter in the biological membrane still it is more worthy to know the polarity of the environment. Since the trafficking of micro- as well as macro-molecules is polarity dependent. Several studies has already been devoted but no published report is available with particles.

## REFERENCES

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