# Light-induced flocculation of gold nanoparticles

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## Background to C6PAS photochemistry

Under UV irradiation akyl-phenylazosulfonates switch from a hydrophilic (surfactant-based) to a hydrophobic system (photoproducts). As shown in Figure S1, photoirradiation of sodium 4-hexylphenylazosulfonate (C6PAS) yields to the formation of two different photolysis products 4-hexylphenol and hexylbenzene.[1,2]

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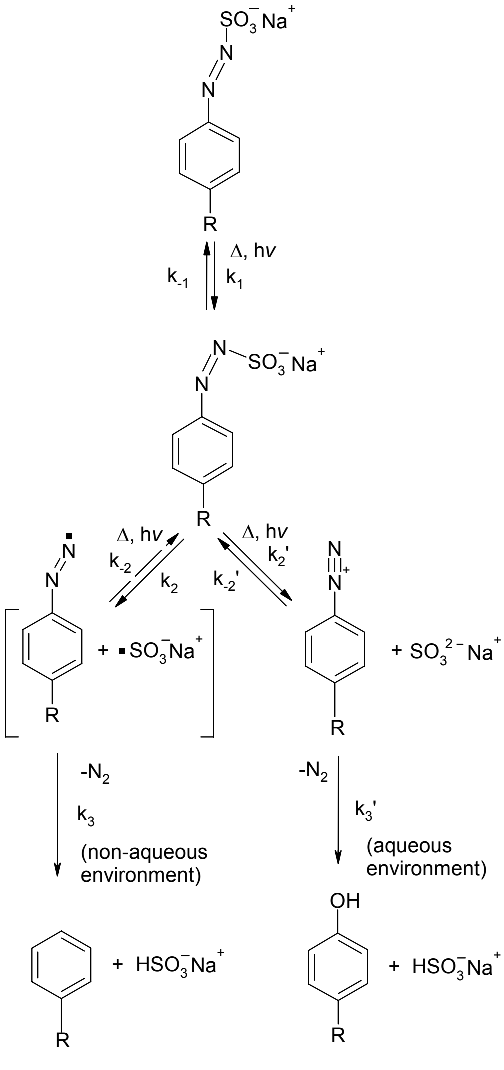


**Figure S1.** Mechanism of photolysis of $C_6$PAS (R=hexyl)

In sufficiently concentrated solution both mechanisms compete and the ratio of photoproducts depends of the solvent environment and concentration[1,2]. At high concentrations the cationic diazonium salt, precipitates after complexation with the remaining anionic azosulfonate.

## Sample appearance and UV-Vis spectra

Gold nanoparticles were obtained by chemical reduction of Au (III) salt with sodium borohydride, both dissolved in the aqueous core of reversed micelles.[3] The molar concentration ratio of $[NaBH_4]/[KAuCl_4]=3.4$ was kept constant for all preparations.

An initial solution of Au nanoparticles in reversed micelles of $H_2O/C_{12}E_6$ in isooctane was studied. The reduction of gold was followed by UV-Vis spectroscopy: the initial $Au^{III}$ microemulsion displayed a maximum peak at $\lambda_{max}$ 330nm, after the reduction reaction this peak disappeared and a new band characteristic of nanoparticle $Au^0$ appeared at $\lambda_{max}$ 525 nm. For this control system, which contained no C6PAS, no change in appearance or UV-Vis spectra was noticeable after UV irradiation for 150 minutes.

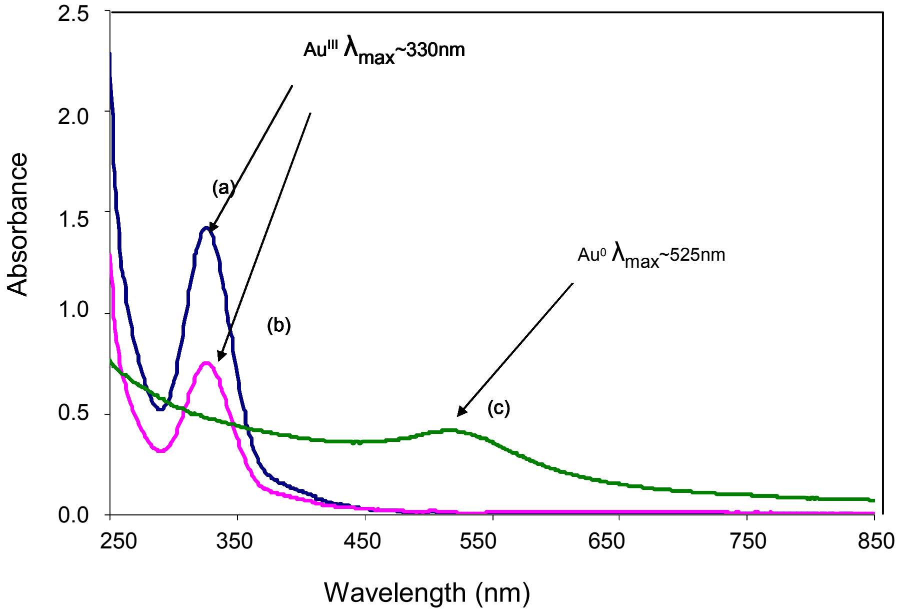


**Figure S2.** Absorption spectra of [Au]=0.02 M in the inverse micelle system $H_2O/C_{12}E_6$/isooctane, w =2 (a) Au before reduction (b) Au after addition of insufficient 0.32M $NaBH_4$ (c) Au after addition of 0.64 M $NaBH_4$, sufficient to generate $Au^0$.

Different Au nanoparticles in $H_2O/C_{12}E_6$/C6PAS/isooctane microemulsions were studied. The samples were prepared using the method outlined in the main paper. The compositions are summarized in Table S1

**Table S1.** Sample compositions.

| Sample | *w* | [surfactants]/M | $X_{C6PAS}$ (%) | [Au]/M |
|---|---|---|---|---|
| Au1 | 2 | 0.155 | 5 | 0.020 |
| Au2 | 2 | 0.070 | 10 | 0.020 |
| Au3 | 2 | 0.060 | 12 | 0.020 |
| Au4 | 9 | 0.350 | 10 | 0.085 |
| Au5 | 8 | 0.300 | 10 | 0.080 |

The photosurfactant C6PAS shows an intense UV absorption[2] at $\lambda_{max}$ 308nm, and a secondary peak at $\lambda_{max}$ 420 nm. Photolysis of C6PAS was studied by following the disappearance of the strong UV absorption peak, suggesting that the photoreaction is completed. Previous $^1$H NMR studies have established the nature of the photoproducts after irradiation.[4]

A solution of $C_{12}E_6$ (2 wt%) in isooctane was used as a background spectral reference. The presence of Au caused a blue-shift of the C6PAS absorbance, from $\lambda_{max}$ 308 nm to $\lambda_{max}$ 270 nm (Figure S3), hence a C6PAS-containing microemulsion could not be used as the blank.

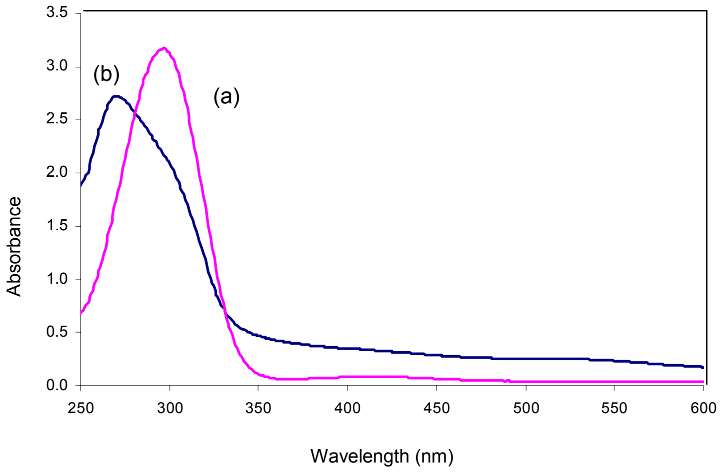


**Figure S3.** UV-visible spectra of (a) $H_2O$/C6PAS/$C_{12}E_6$/isooctane with *w* = 2, [surfactants] = 0.155M and $X_{C6PAS}$(%) = 2 and (b) Au/$H_2O$/C6PAS/$C_{12}E_6$/isooctane.

Irradiation of sample Au1, with the lowest C6PAS level (Table S1), showed no visible effect on the stability of the Au nanoparticles. This initial observation is supported by UV-Vis spectroscopy (Figure S4), which shows that the C6PAS has been destroyed but the Au nanoparticles are still present in the solution. It also showed that a small amount of unreduced gold is present corresponding to the absorbance at $\lambda_{max}$ 330nm. At $X_{C6PAS}$(%)=5 the concentration of C6PAS is not high enough to affect the nanoparticle stability, but this sample was used as a standard to check the effect of UV on a photostable gold colloid dispersion. Photolysis of C6PAS at this 5% level is insufficient to induce flocculation of the colloidal Au, and there is enough residual $C_{12}E_6$ to maintain particle stability after UV irradiation. To achieve effective UV-induced flocculation it was necessary to increase the C6PAS: $C_{12}E_6$ ratio and the overall surfactant concentration (see Table S1).

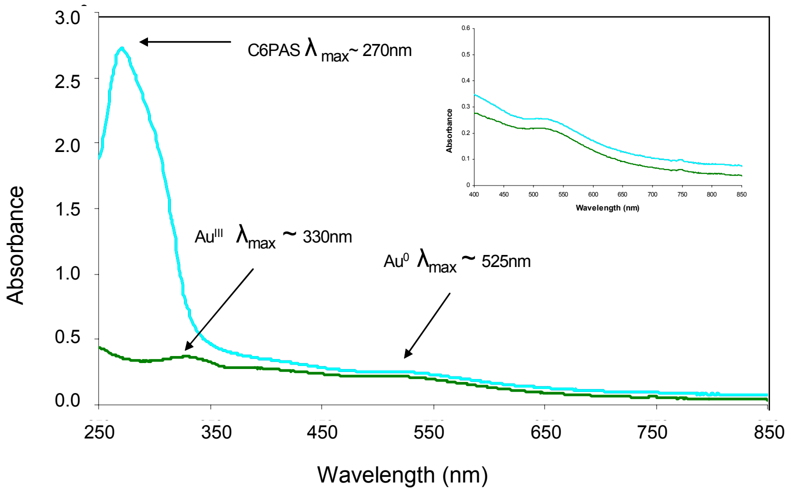


**Figure S4.** UV-Vis spectrum of Au1 before and after irradiation.

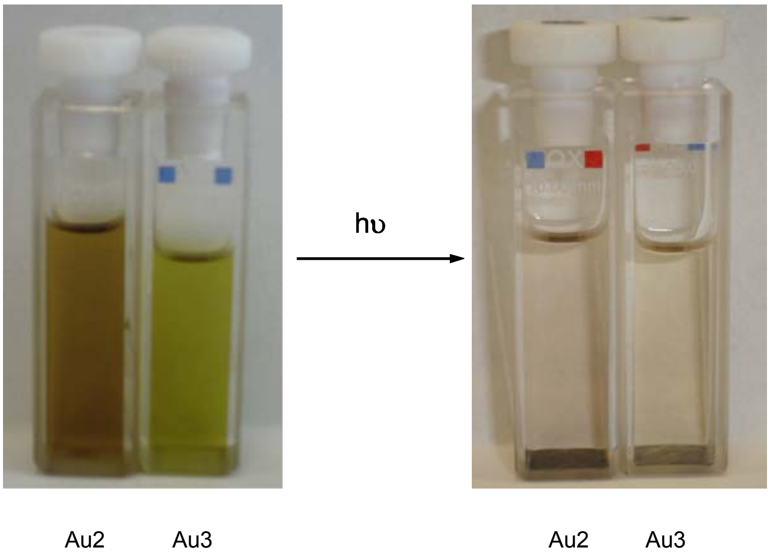


**Figure S5.** Samples Au2 (a) and Au3 (b) before (left) and after (right) UV irradiation.

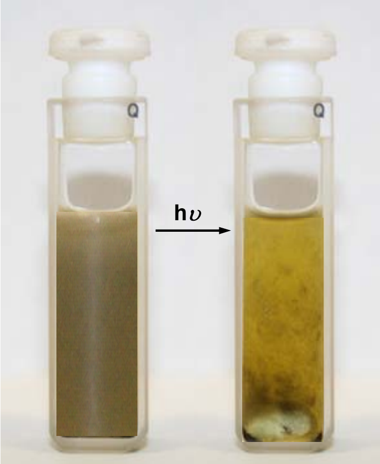


**Figure S6.** Sample Au4 before (left) and after (right) UV irradiation.

As seen in Figures S5, S6 and in main paper, samples Au2-Au5 resulted in destabilization of the Au nanoparticles after 130 min of UV exposure. UV-Vis spectra were consistent with full photolysis of C6PAS owing to disappearance of the $\lambda_{max}$ 420 nm peak. No absorption at $\lambda_{max}$ 525 nm from Au particles was observed in the postirradiated clear supernatant solution of these solutions. The wavelength range in Figure S7 is optimized for each system to minimize very strong absorbance in some cases.

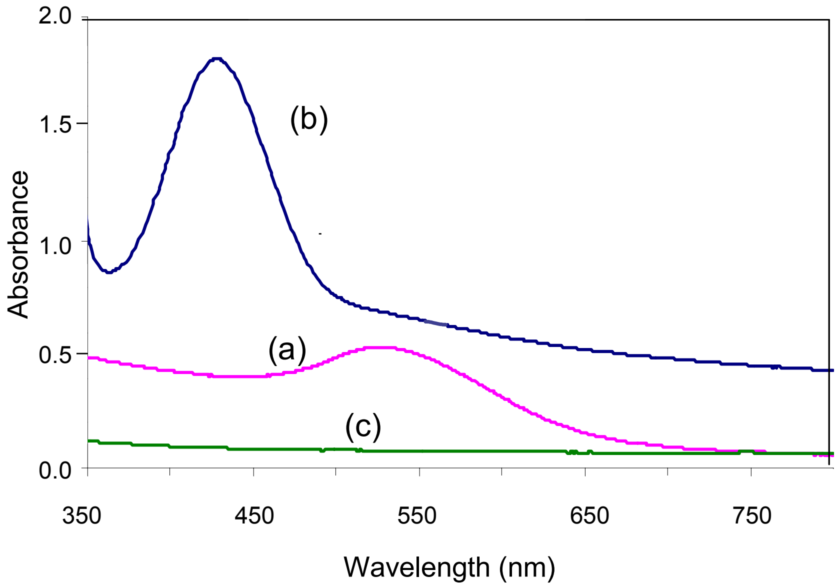


**Figure S7.** UV-Vis spectra of (a) background microemulsion equivalent to sample Au3 with no C6PAS added, (b) sample Au3 before and (c) the supernatant of sample Au3 after UV irradiation.

Samples Au4 and Au5 are darker in appearance before exposure to UV (Figure S6 and Figure 1 main paper) but UV-Vis spectra have similar behavior (Figure S7 and Figure 2 main paper). After irradiation no absorption for the Au nanoparticles or C6PAS was observed from the transparent supernatant liquid phases.

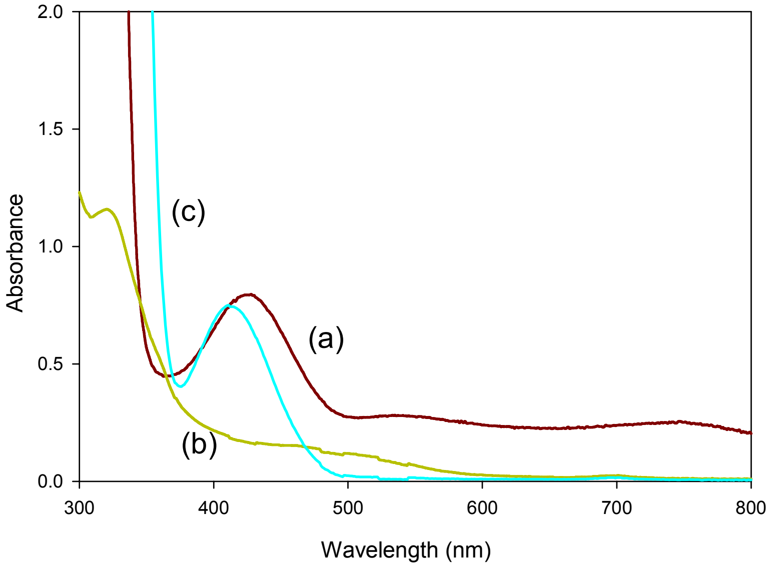
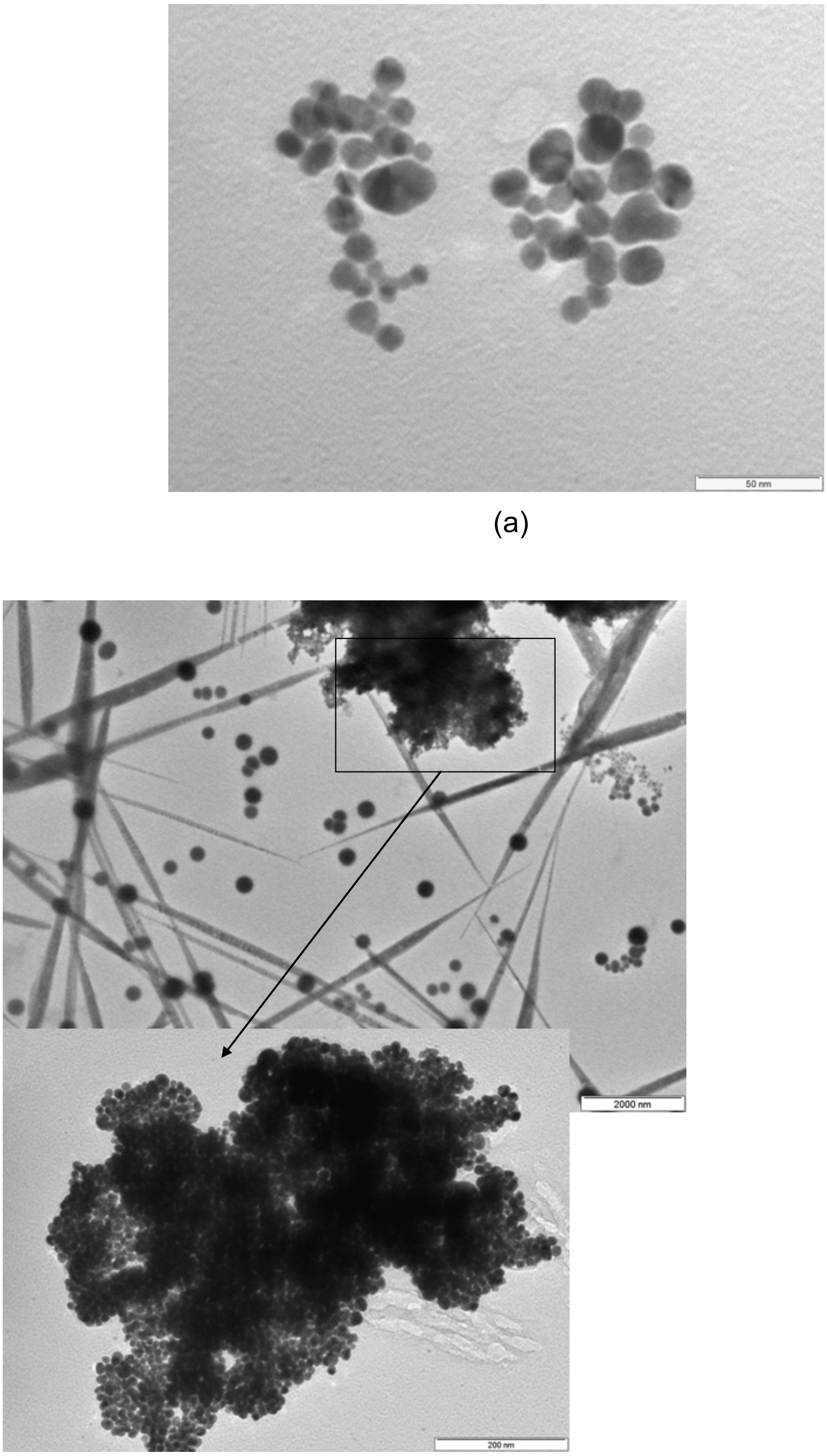


**Figure S7.** UV-Vis spectra of sample Au4 (a) before and (b) after UV irradiation, (c) background microemulsion of C6PAS equivalent to Au4 before irradiation, but without gold.

## Microscopy

TEM images of sample Au4 showed different shape and size of gold nanoparticles before irradiation (Figure S8), compared to sample Au5 described in the main paper. Gold particles before irradiation seem more rounded and smaller (8-29 nm). The post irradiated samples were separated, and the lower gold flocculated phases were imaged with TEM. Post-irradiated dense Au precipitates showed evidence for strong particle clustering, however the individual nanoparticles appeared to change size/shape compared to the pre-irradiated state.

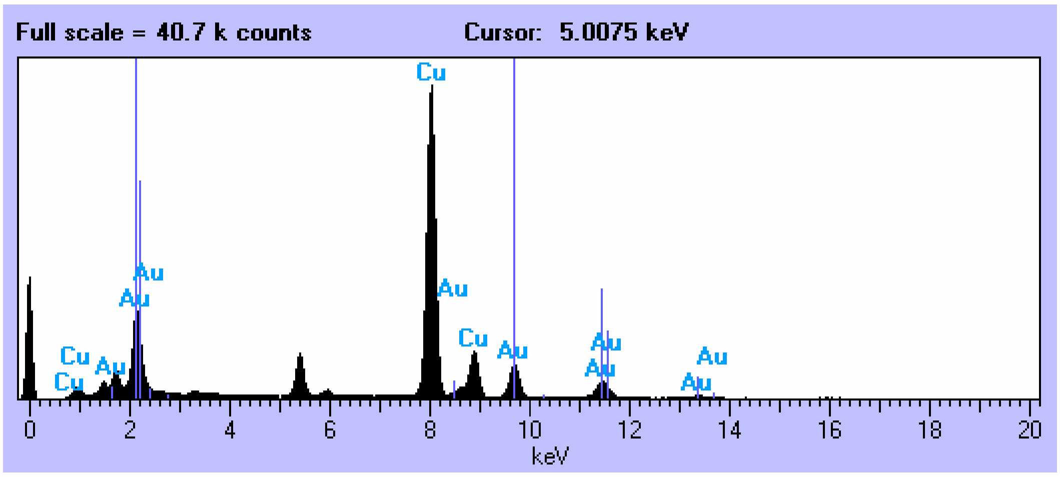


(a)

(b)

**Figure S8.** TEM images for sample Au4 before (a) and after UV irradiation (b).

As shown in Figure S9 composition of the particles before and after irradiation was confirmed by energy dispersive X-ray analysis (EDXA, Oxford Instruments ISIS 300 X-ray microanalysis system and silicon detector). The composition spectra are almost identical, showing no significant changes in chemical composition as a function of irradiation.



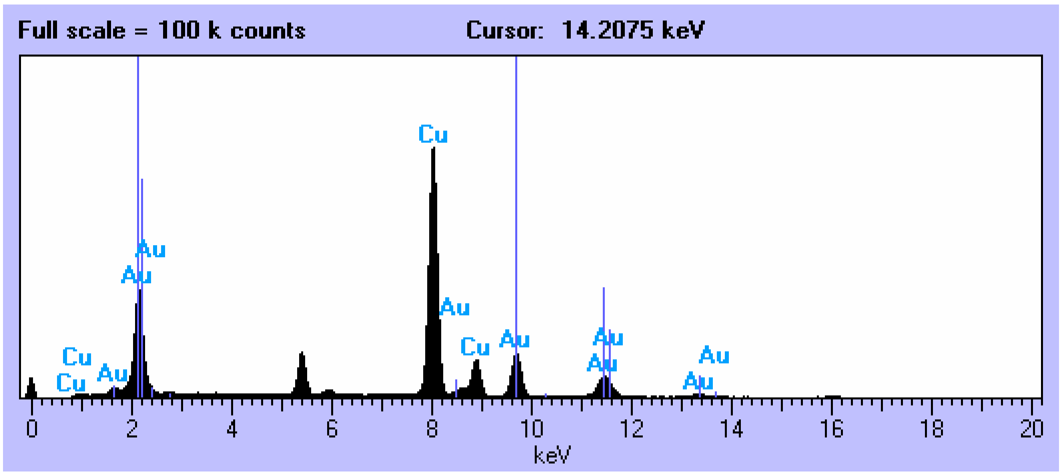


**Figure S9.** EDXA spectra of sample Au5 before and after irradiation.

A proposed mechanism for recovery of Au nanoparticles is shown schematically in Figure S10. Initially the system comprises stabilized gold nanoparticles, sterically stabilized in reverse micelles. Upon irradiation with UV light the C6PAS undergoes photolysis causing destruction of a portion of the steric stabilizing layer. The unstable particles can flocculate, then precipitate, or also regain stability by adsorption of residual inert $C_{12}E_6$ surfactant.

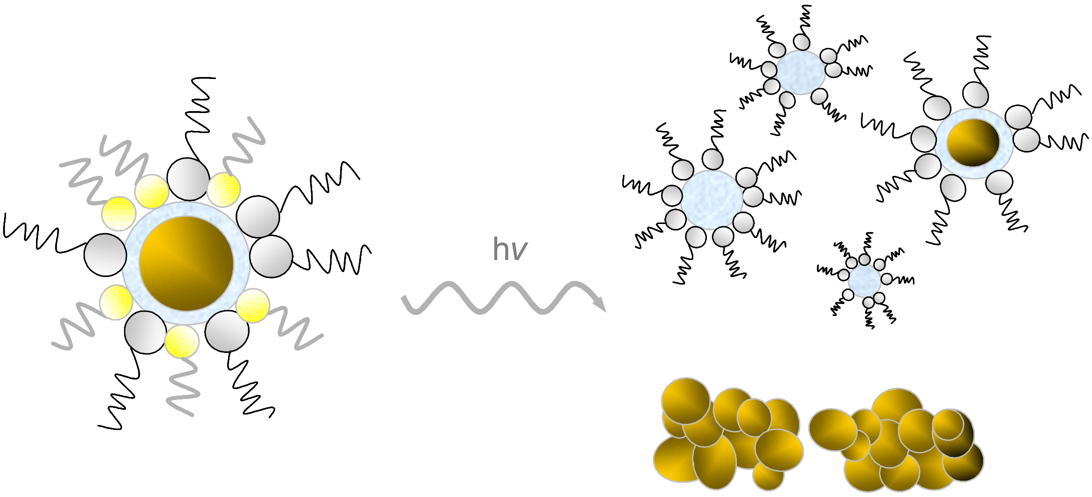


**Figure S10.** Schematic representation of the destabilization of Au nanoparticles in reverse micelles of $C_{12}E_6$ and C6PAS.

## References

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(2) Mezger, T.; Nuyken, O.; Meindl, K.; Wokaun, A. *Progr. in Org. Coatings* **1996**, *29*, 147.
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(4) Eastoe, J.; Sanchez Dominguez, M.; Cumber, H.; Wyatt, P.; Heenan, R. K. *Langmuir* **2004**, *20*, 1120