

## ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

### Light-responsive reversible solvation and precipitation of gold nanoparticles

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#### Experimental

All the reagents, solvents included, except water, were purchased from Aldrich. The MilliQ water was provided in our laboratory using a MQ water filter (Millipore-Direct Q 3). The UV-Vis studies were made thanks to a Spectrophotometer UV-Vis-NIR (Shimadzu UV-3600). The irradiation lamp was a UV lamp with  $\lambda_{\max}$  of emission centered around 366 nm (Benda NU-8 KL). All the images were acquired with a FIB (model FEI Dual Beam Strata 235) equipped with a STEM detector (TEM module, FEI). Samples for electron microscopy were prepared by drop casting, on carbon-copper grids, a solution of **AZOAuNP3** with the same concentration either in the *cis* or *trans* form in toluene.

#### Synthesis AuNP1

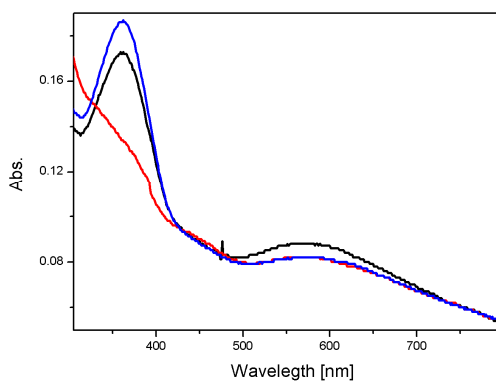
Once  $\text{HAuCl}_4$  was dissolved in water (MilliQ, 11.36 mM, 3ml) tetraoctylammonium bromide (TOAB) in toluene was added (26.68 mM, 3ml) and stirred until the solution became colorless. Later octadecylamine in toluene (124 mM, 3ml) and after a few minutes  $\text{NaBH}_4$  in water (MilliQ, 174.4 mM, 3ml) was added. The reaction equilibrium was reached after 12 h of stirring. After separation from the aqueous solution an organic (toluene) colloidal dispersion of nanoparticles was obtained.

#### Synthesis AuNP2

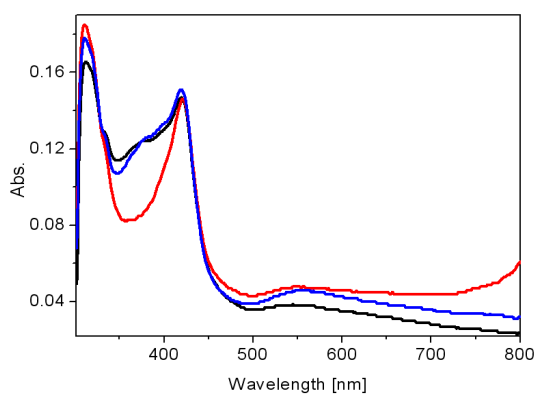
A water solution of  $\text{HAuCl}_4$  was prepared and stirred until boiling. Once at the boiling point an amount of citrate salt (30 times more than the gold) was added and stirred another hour. Then the heating was stopped and the solution was stirred over night.

#### UV-Vis study of AuNP1 and AuNP2

In Figs. S1 and S2 are shown the UV-Vis spectra of the smaller nanoparticles (AZOAuNP1 and AZOAuNP2) after being subjected to UV or visible light. These samples displayed the same kind of behavior than the biggest one (AZOAuNP3). This happens even if the spectral evidence of aggregation-disaggregation behavior is less pronounced, maybe due to the lower SPR coupling between near nanoparticles due to dimensional-issues. There is, in fact, a dependence of the coupling interaction not only on the distance between the nanoparticles but even on the sizes.



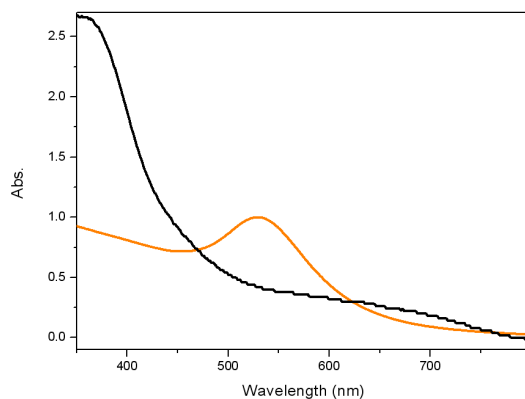
**Figure S1:** UV-Vis spectra of the AZO AuNP1 sample upon irradiation: a) black line, before irradiation; b) red line, after irradiation with UV light at 366 nm; c) blue line, after irradiation with visible light at 450 nm.



**Figure S2:** UV-Vis spectra of the AZO AuNP2 sample upon irradiation: a) black line, before irradiation; b) red line, after irradiation with UV light at 366 nm; c) blue line, after irradiation with visible light at 450 nm. The spectral features in the near IR region, i.e. around 800 nm, may be due to measurement artefact.

### Behavior of the SPR on substituted particles

Figure S3 displays the UV-Vis spectrum of the gold nanoparticles AuNP3 before and after substitution.

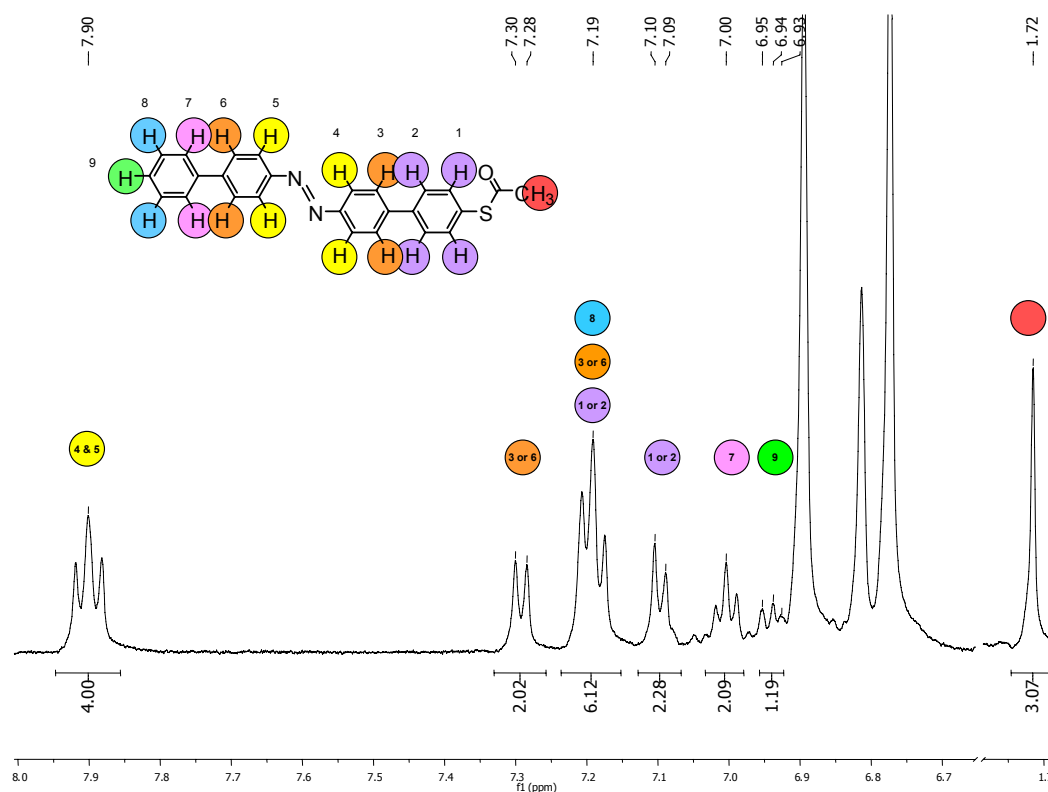


**Figure S3:** UV-Vis spectra of AuNP3 before (orange line) and after (black line) substitution.

## <sup>1</sup>H-NMR spectra

<sup>1</sup>H-NMR spectroscopy was employed to gain a detailed insight into the composition AZO AuNPs.

The <sup>1</sup>H-NMR spectrum of the *trans*-form of AZO in d8-toluene was recorded as basis for the comparison with the spectrum of AZO AuNPs. The <sup>1</sup>H-NMR spectrum of the *trans*-form of AZO in d8-toluene is displayed in Figure S4. The assignment of the chemical shifts is based on a COSY experiment.

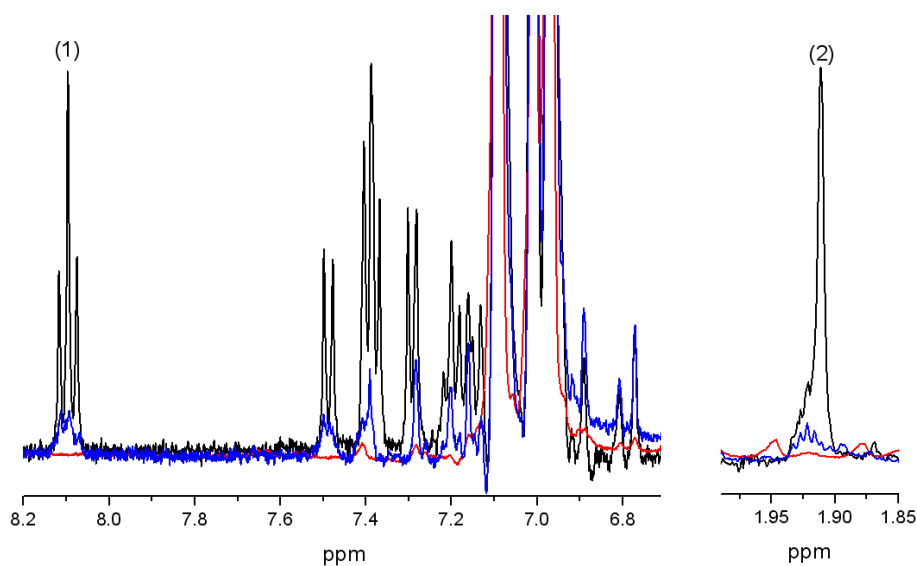


**Figure S4:** <sup>1</sup>H-NMR spectrum of the AZO molecule recorded in d8-toluene. The assignment of the signals to particular hydrogens was made based on a COSY experiment.

It is noteworthy that additional signals appear between 6.5 and 7.2 ppm upon irradiation with UV light. These signals disappear after storing in the dark and are thus attributed to the *cis*-form of the AZO molecule.

The spectra of the AZO AuNPs were recorded in d8-toluene as the solvent of choice to provide the required solvation of the nanoparticles. In Figure S5 the spectra of AZO AuNPs are displayed together with those of the AZO molecule and of the parent Au nanoparticle. The spectrum of the AZO AuNP displays a series of weak signals due to the limited available surface resulting in a rather low concentration of organic structures immobilized on the Au nanoparticle. However, the comparison with the spectrum of the AZO molecule clearly demonstrates the exchange of the stabilizing ligands by the AZO molecules. Moreover the effects of the covalent tethering of the AZO-ligand to the AuNP induces a shift only in the signals of the protons near the sulphur atom that covalently interacts with the AuNP.<sup>1-3</sup> We have therefore focused our attention to two different proton-signals, one at  $\delta = 8.1$  ppm (1) and the other at  $\delta = 1.9$  ppm (2). The first one is due to the protons near the N=N double bond (hydrogens No. 4 & 5 in Figure S4) and it is present if the AZO molecule is in the solution. The second can be ascribed to the methyl unit of the acetyl group once it is

fully solvated, whereas it does not appear for AZO molecules that are chemically tethered to the AuNP. The region between 1.93 and 1.90 ppm presents one sharp peak, which can be ascribed to the acetyl group once the molecule is in its *trans* isomer, and another broad signal at higher ppm. This last signal is the typical signal of the acetyl group when the AZO is in its *cis* isomer. The combined analysis of the two signals therefore provides direct information on the stoichiometry of the AZO/AuNP and AZO ratio in the solution. By purpose the analysis was not extended to the spectral range typical of the alkyl chains because we could not unambiguously assign the detected weak signals of surfactant's aliphatic hydrogens to either molecules solvated or left-over of chemisorbed molecules on the AuNP.

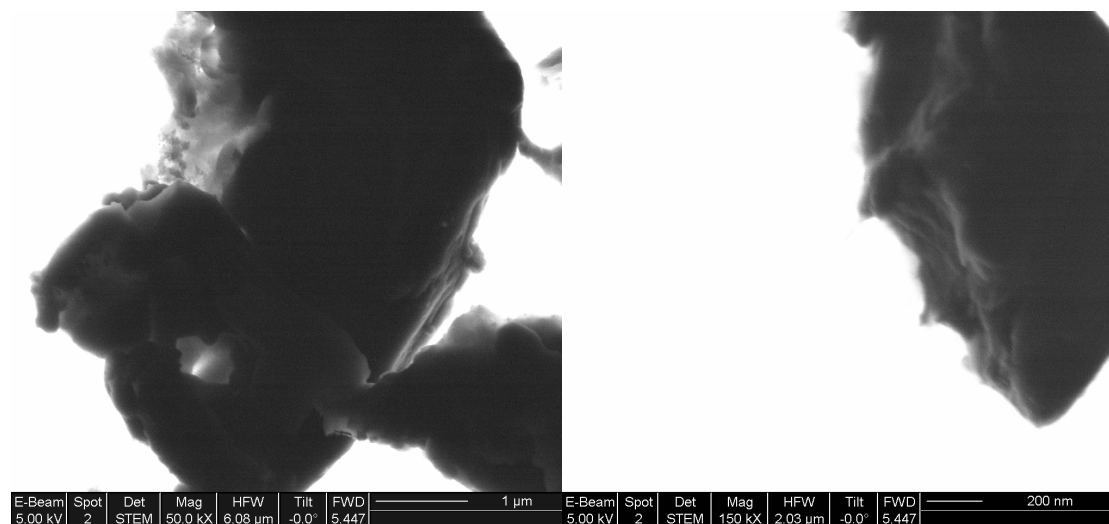


**Figure S5:**  $^1\text{H-NMR}$  spectrum of AZO molecule (black line), AuNP18 (red line), AZO/AuNP18 (blue line). (1) is the peak corresponding to  $\delta = 8.1$  ppm indicative of the substitution, (2) is the peak corresponding to  $\delta = 1.9$  ppm indicative of AZO molecule free in solution.

### Electron Microscopy

STEM microscope was employed to gain images of the nanoparticles before and after ligand-exchange reaction and UV. These measurements provided direct and unambiguous evidence for monodisperse character of the AuNP (Fig. 3a), and on the photo-triggered aggregation-solvation (Fig. 3a and 3c, respectively). On the several tens of micron scale the films obtained by spinning AZO/AuNP3 in the *trans* form are very inhomogeneous exhibiting uncoated areas and large aggregates (see Fig. 3b and S6). Conversely, on the same scale the naked AuNP3 (Fig. 3a) and the films of *cis*-AZO/AuNP3 are homogeneous. This different observation for the *trans* and *cis* AZO/AuNP3 should not be ascribed to the concentration of the solution applied to the substrate, which indeed was identical,

Figure S6 shows two images of AZO/AuNP3 after substitution that were recorded before irradiation with UV light; in their *trans*-form the AZO/AuNP3s strongly aggregate forming 3D disordered structures.



**Figure S6:** STEM images of **AZO AuNP3** after substitution, before irradiation with UV light.

#### Literature

1. V. Naponen, S. Bhat, E. Sievanen, E. Kolehmainen, *Mater. Sci. Eng., C*, 2008, **28**, 1144.
2. S. Aryal, R. B.K.C., N. Dharmaraj, N. Bhattarai, C.H. Kim, H.Y. Kim, *Spectrochim. Acta, Part A*, 2006, **63**, 160.
3. T. Peterle, A. Leifert, J. Timper, A. Sologubenko, U. Simon, M. Mayor, *Chem. Commun.*, 2008, **29**, 3438.