Highly photoresponsive monolayer-protected gold clusters by self-assembly of a cyclodextrin–azobenzene-derived supramolecular complex†‡

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Reversibly-photoswitchable gold nanoparticles containing azobenzene and exhibiting a light response "virtually identical" to that of the free chromophore were achieved by self-assembling a host–guest inclusion complex between α-cyclodextrin and an azobenzene-terminated alkanethiol in an aqueous medium.

The investigation of thiol-stabilized gold nanoparticles, commonly referred to as monolayer-protected clusters (MPCs), constitutes an extremely active area of modern materials science.[1–4] In this context, MPCs performing specific functions, exclusively controlled by external inputs, are of great importance in the perspective of new generation nanocomposite devices for multi-faceted applications in fields spanning microelectronics and photonics to biology and medicine.[5] Light is a very appealing trigger. Its ease of availability and manipulation, coupled with the fast response of photochemical reactions, makes light-controlled systems particularly fascinating. Nevertheless, in the massively explored arena of MPCs, only a limited number of reports have been centered on metal nanoparticles modified with photoactivatable chromophores.[6]

Intriguing nanoarchitectures, whose properties can be reversibly switched by appropriate light stimuli, can be created by functionalizing the metal nanoparticles with photochromic units. Of these, azobenzene is one of the most widely employed by virtue of its superior characteristic of undergoing reversible $trans \rightleftarrows cis$ photoisomerization upon UV and visible light illumination, respectively.[7] This process is accompanied by significant changes in its optical absorption spectrum and molecular dipole moment. In the case of azobenzene-based MPCs, photoconversion efficiency comparable to that of the free chromophore is, of course, highly desirable. Fox and co-workers have shown that in the case of gold nanoparticles supporting azobenzene-terminated alkanethiolates,[8] the aggregation between the nearest neighbors of the photoactive units is weaker than that occurring on two-dimensional self-assembled monolayers. This makes the resulting MPCs moderately photoresponsive, opposite to the observed non-reactivity of the same capping agents self-assembled on planar gold surfaces.[9] Recently, Tamada et al. have optimized the photoisomerization of

azobenzene-based MPCs, soluble in low polarity solvents, by using an unsymmetrical azobenzene disulfide as the capping agent; obtaining a photoresponse nearly equivalent to that of the free azobenzene in solution.[10] Such high photoreactivity is the result of a complementary effect of the 50% dilution of the azobenzene moiety. This effect is due to the unsymmetrical disulfide structure and the curved colloidal gold surface that makes the interaction between the photoactive units negligible and enables effective photoconversion.[10]

Here we show that highly photoresponsive MPCs with polar characteristics can be achieved by self-assembling a host–guest complex between the azobenzene-terminated alkanethiol **1** (Fig. 1) and α-cyclodextrin (**α-CD**) on the surface of colloidal gold nanoparticles. In addition to our continuing interest in exploring novel aspects related to the photoreactivity of supramolecular **CD** complexes,[11] this work was inspired by the excellent paper of Kaifer and co-workers that reported the surface derivatization of gold colloidal particles through the aqueous solubilization of alkanethiols by **α-CD**.[12] We envisage that, in our case, besides delivering **1** to the metal surface, **α-CD** could also exert some control on the chemisorption process, acting as a suitable spacer between the alkyl chains of **1**, reducing their intermolecular interactions and, as a consequence, increasing the sweep volume to allow an effective photoresponse from the resulting MPCs.
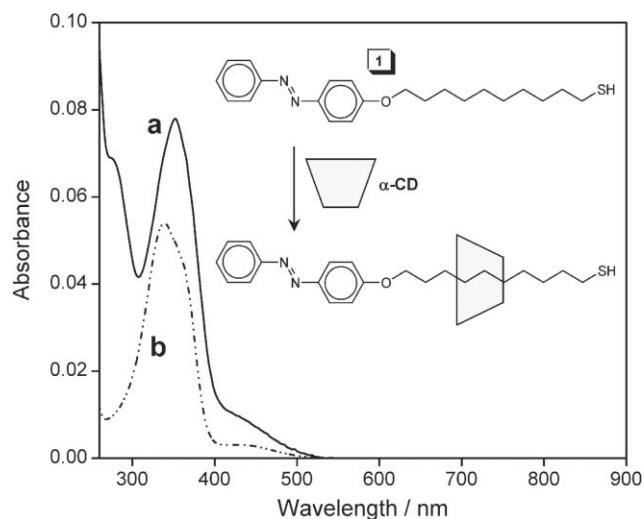
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Fig. 1 (a) Absorption spectrum of **1** in the presence of a 20 mM aqueous solution of **α-CD** and, (b) for comparison, in acetonitrile.

Gold nanoparticles were prepared through reduction of $AuCl_4^-$ by citrate in an aqueous medium, according to the method proposed by Natan et al.[13] After filtration with a 0.8 μM membrane filter, the gold colloid exhibited the characteristic visible plasmon absorption band at 516 nm. TEM micrographs confirmed the average diameter of these metal nanoparticles to be 13 nm, in good agreement with the literature.[13]

Alkanethiol 1 is insoluble in aqueous solution. On the other hand, it is fairly soluble in the presence of **α-CD** as result of the formation of a host–guest inclusion complex. This is demonstrated by the appearance of the characteristic absorption for the *trans* isomer with a maximum at 350 nm, corresponding to the $\pi \rightarrow \pi^*$ transition, similar to that obtained in acetonitrile (Fig. 1).§ Analogously to others alkanethiols,[12,14] an inclusion complex, in which the **CD** cavity preferentially includes part of the hydrophobic alkyl chain of 1, can be conceived (see Fig. 1). This hypothesis is corroborated by the absence of any significant induced circular dichroism signal, in correspondence with the absorption bands of the azo-chromophore that are typically observed whenever azobenzene interacts with **CD** cavities.[15]

In a typical preparation of the photoactive MPC–1, 1 mg of 1 was added to 50 mL of the gold colloidal solution containing 20 mM **α-CD** and the resulting mixture stirred for 3 days at room temperature. The dark precipitate obtained was collected by centrifugation and washed several times with first water and then acetonitrile in order to remove the large excess of **α-CD** and unreacted 1, respectively.¶ The resulting dried precipitate was insoluble in chloroform and dichloromethane but very soluble in dimethylformamide (DMF), different to the gold nanoparticles capped with azobenzene-terminated alkanethiols in the absence of **CD**.[6,8] Absorption spectrum (a) in Fig. 2 clearly exhibits the absorption features of the azo-compound, together with those of the metal nanoparticles. In particular, it can be noted that the plasmon absorption band is slightly shifted compared to that of the unfunctionalized gold nanoparticles (compare spectra (a) and (e) in Fig. 2), consistent with the modification of the gold surface
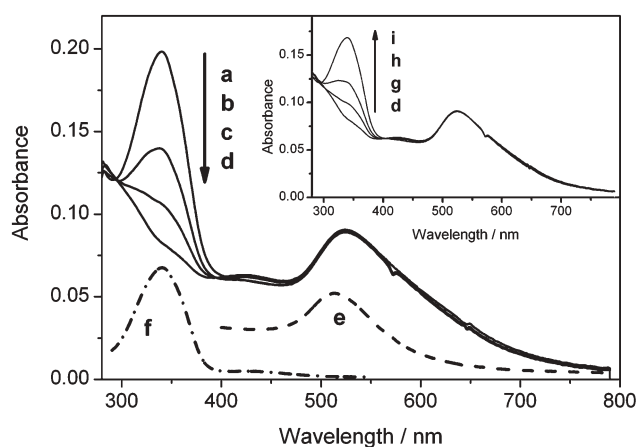
upon covalent binding of the alkanethiol group.[8] On the other hand, a comparison of the absorption spectrum of MPC–1 with that of free 1 in the same solvent (spectra (a) and (f) in Fig. 2) shows no evidence of a shift in the absorption maximum of the azo-chromophore at 340 nm. This result proves the absence of π-stacking interactions between the azobenzene units, in excellent agreement with the results observed for gold nanoparticles, in which the azobenzene units are interspaced with alkyl chains,[10] and differently to MPCs, based on densely-packed azobenzene-terminated alkanethiols.[8]

The solubility of MPC–1 in a polar solvent such as DMF is a clear indication that the **α-CD** does not unthread upon the chemisorption of 1 due to the presence of the bulky azobenzene and the gold nanoparticle on opposite ends of the alkyl chain, resulting in the achievement of a rotaxane-like structure[12] with polar characteristics (Scheme 1).

The irradiation‖ of a DMF solution of MPC–1 with 340 nm light induces the *trans → cis* isomerization of the azobenzene unit. Consistently, the absorbance at 340 nm for the $\pi \rightarrow \pi^*$ transition of the *trans* isomer decreases and two clear isosbestic points appear at 294 and 405 nm (Fig. 2, spectra (a–d)). As shown in the inset of Fig. 2 and pictorially illustrated in Scheme 1, the process is fully reversible. Upon irradiation at 450 nm, the *cis* isomer reverts back to the original *trans* form, restoring almost totally the initial absorption spectrum.

It is worth noting that no variation of the gold plasmon absorption is observed upon photoswitching. This finding indicates that the number of gold nanoparticles dispersed in DMF does not change when the azobenzene shell switches from the *trans* to the *cis* form, in contrast to the partial sedimentation observed upon irradiation of gold nanoparticles capped with unsymmetrical azobenzene disulfides in a toluene solution.[10]

The efficiency of the photoisomerization was examined by analyzing the absorbance changes at 340 nm for DMF solutions of MPC–1 and free 1 when absorbing the same quantity of incident photons by using a first-order plot based on the method of Mita et al.[16] The results, reported in Fig. 3, provide an unequivocal indication that the photoinduced reaction in the case of MPC–1 proceeds with an identical reaction rate to that of the free chromophore, in accordance with the absence of any significant steric hindrance.

Fig. 2 Absorption spectra of MPC–1 (6×10^{-6} M) in DMF solution, observed (a) before and after (b) 2, (c) 6 and (d) 12 min of 340 nm light irradiation. The spectra of the (e) unfunctionalized gold colloids and (f) free 1 in DMF solution are shown in arbitrary absorbance units for the sake of comparison. The inset shows the spectral changes of the MPC–1 solution observed after (g) 5, (h) 10 and (i) 20 min of 450 nm light irradiation.
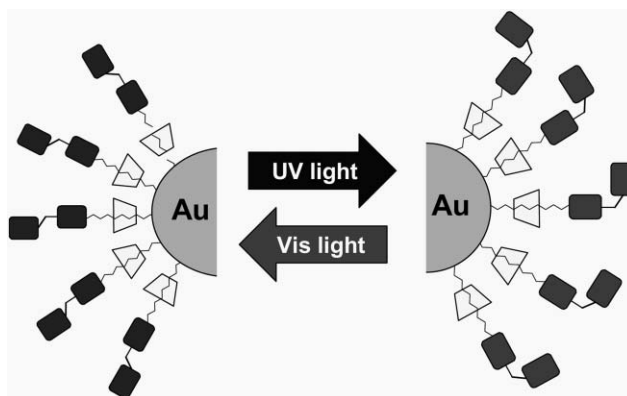

Scheme 1 Idealized representation for the photocontrolled switching of MPC–1.
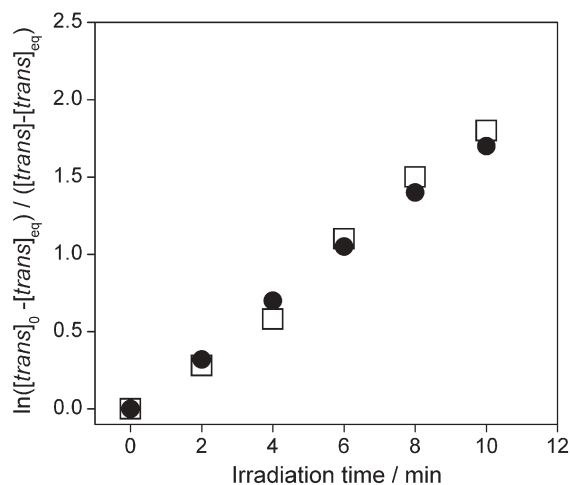
Fig. 3 First-order plots for the *trans* to *cis* photoisomerization of MPC–**1** (●) and free **1** (□) in DMF solution.

This result is in line with the proposed host–guest association model, not implying the inclusion of the azobenzene unit within the **α-CD** cavity. Actually, it is well known that in such a case, reduced photoisomerization efficiency would have been expected as result of the relevant steric constraints of the host's cavity.[15]

In summary, we have demonstrated that highly photoresponsive gold nanoparticles containing azobenzene can be prepared from aqueous solutions by using an **α-CD** supramolecular complex. The role of the host cavity is threefold: (i) Conveying the photoactive unit, insoluble in water, to the metal surface, (ii) allowing the solubilization of the resulting MPCs in a polar solvent, both in their *trans* and *cis* forms, and (iii) exerting control in the chemisorption process of the photoactive unit, increasing the inter-chain distance of the adsorbed species. This latter effect is crucial for a high photoresponse to be observed. Actually, complementary to the curvature of the metal nanoparticles, the sweep volume further increases to allow a light response "virtually identical" to that of the free alkanethiol in solution. To the best our knowledge, this represents the first example of an enhanced photoresponse of photochromic-based materials achieved through a host–guest complex with **CD**s. We believe that an extension of the present study to MPCs containing azobenzenes, tailored with specific functional elements, may be of general relevance to the construction of smart, highly photoresponsive nanocomposite devices.

Notes and references

§ The absorption spectrum in the presence of **α-CD** was recorded after stirring 1 mg of **1** in a 20 mM aqueous solution of **α-CD** for 3 h at 40 °C and then filtering the suspension to remove the unincluded alkanethiol.
¶ The absence of **α-CD** and free alkanethiol were verified by TLC and spectrophotometric analysis, respectively.
‖ Irradiation was carried out by using the monochromatic light sources of a Spex Fluorolog-2 (mod. F-111) spectrofluorimeter.

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