



Light-induced self-assembly of gold nanoparticles with a photoresponsive polymer shell



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ABSTRACT

The light-induced self-assembly of gold nanoparticles was studied systematically. A methacrylate type monomer with an azobenzene sidechain was polymerized in a reversible addition–fragmentation chain transfer (RAFT) polymerization. The resulting light responsive polymer was grafted to gold nanoparticles via the RAFT group. UV-light induced *trans* to *cis* isomerization of the azobenzene moieties triggers the aggregation of the polymer–gold hybrid particles in toluene dispersion. The thermally induced *cis* to *trans* relaxation was found to be significantly slower than for small molecules at gold surfaces. The self-assembly was followed by dynamic light scattering (DLS), UV/vis spectroscopy and transmission electron microscopy (TEM). The density of primary gold particles within the self-assembled aggregates can be tuned by varying the molar mass of the grafted polymer.

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1. Introduction

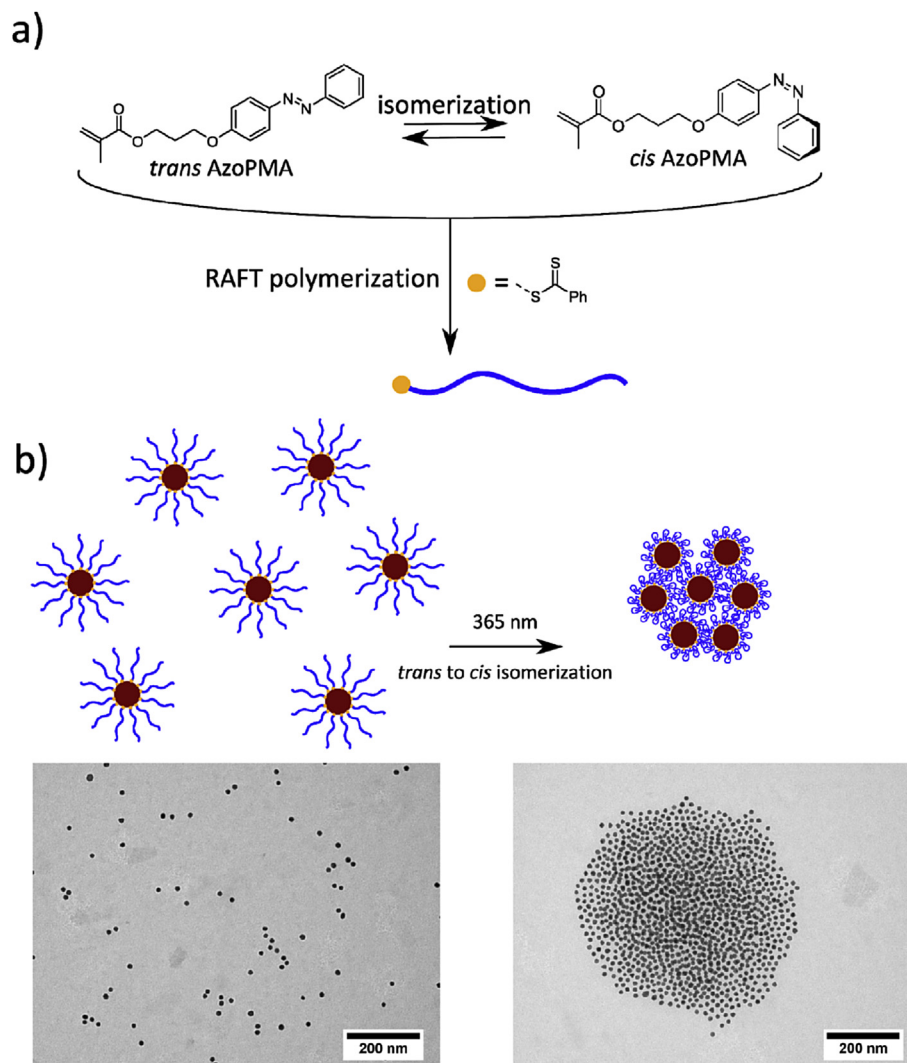
Gold nanoparticles stabilized with a photoresponsive shell have gained importance in recent years due to various possible applications like self-erasing ink [1] and micrometer sized supracrystals [2]. Especially systems using light as a trigger are in the focus of research because it is easy to handle and applicable very fast and precise. Among the possible photoswitches, azobenzene is probably the most used functional group in literature [3–5]. Upon irradiation with UV-light, the azobenzene moiety undergoes a $\pi \rightarrow \pi^*$ transition which induces *trans* \rightarrow *cis* isomerization. The configurational isomers are also often referred to as *E* and *Z*. It is important to note that this isomerization is fully reversible [6]. The *cis* \rightarrow *trans* isomerization can be induced thermally or by light. The *cis* isomers are not planar and the phenyl groups come closer to each other than in the *trans* isomer [6,7]. This molecular motion can be used to induce macroscopic motion [8] to be applied in e.g. artificial cilia [9] or micromachines [10]. Another important change during *trans* \rightarrow *cis* isomerization is the significant increase of the dipole moment [5,11]. This effect was e.g. used for switchable wettability surfaces [12–14] and light-induced self-assembly (LISA) of colloidal systems [2,15,16]. In the latter case, several examples

use gold nanoparticles as a core stabilized with small molecules comprising an azobenzene moiety and a thiol as an anchor group for the gold surface [1,2,15,16]. Is e.g. toluene used as a solvent these particles are well dispersed if all azobenzene groups are in the *trans* state. Irradiation with light will induce *trans* \rightarrow *cis* isomerization which increases the shell polarity and thereby switches the hybrid particles to be insoluble. The switched solubility induces aggregation of the primary particles as long as the shell is in the *cis*-state.

The here presented study is focused on the photoresponsive shell. We decided to make use of the well investigated azobenzene moiety as a molecular switch and possibilities of using a polymeric shell rather than a small molecule based one. Therefore, we designed a methacrylate type monomer carrying a propyl ether as a linker to the azobenzene group (AzoPMA, Scheme 1a). The substitution pattern determines the wavelengths of the absorption maxima. In this case, the $\pi \rightarrow \pi^*$ absorption maximum is at 346 nm. AzoPMA can easily be polymerized in a reversible addition–fragmentation chain transfer (RAFT) polymerization using 2-cyano-2-propyl benzodithioate as a control agent. The RAFT polymerization allows a good control over molar mass with a low dispersity [17]. The core material in our work is chosen to be gold, taking advantage of the possibility of its very straightforward functionalization with RAFT polymers [18–20], which can be much easier achieved than in case of e.g. silica nanoparticles [21]. The RAFT dithiobenzoate end group is working as an effective anchor group for the grafting to the gold surface [22–24]. The polymer

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Scheme 1. a) Structure of the monomer AzoPMA in its *trans* and *cis* state. b) PAzoPMA-coated gold nanoparticles in the well dispersed *trans* state (left) and its aggregated *cis* form (right).

chains can be immobilized at the gold nanoparticles very efficiently just by mixing both under sonication. The obtained hybrid particles can then be used in a light triggered self-assembly (Scheme 1b). One potential benefit of polymers as a shell material is the accessible variety of different architectures. Complementing our earlier work focusing on cross-linked gold-nanoparticle networks [25,26] rather than triggered self-assembly, we demonstrate how tailored molar masses can tune the inter-particle distances within the aggregated structures. Another expected benefit from using polymers is their high switching efficiency without the use of any additional surfactant as a spacer as required in some small molecule based systems [1,5]. Due to the long polymer chain and the surface curvature, enough free volume is present to ensure efficient isomerization. Furthermore, gold surfaces are known to catalyze the thermal *cis* → *trans* isomerization by introducing electrons to or withdrawing electrons from the azo group [27]. As a consequence of that, the thermal relaxation from the *cis* isomer to the *trans* isomer is up to several orders of magnitude faster in the presence of gold surfaces than in their absence [28,29]. By using polymer we expect to overcome this effect because of the shielding of the surface. Only the surface-near azobenzene units are influenced by the surface. The outer azobenzene groups should hardly

be able to efficiently diffuse to the surface because of the steric hindrance. The acceleration of the thermal (back-)isomerization should therefore be less pronounced than in small molecule coated particles.

2. Experimental section

2.1. Synthesis of AzoPMA

The synthesis was similar to a literature procedure [30]. A solution of 4-(phenyldiazenyl)phenol (24.0 g, 121 mmol, 1 equiv.), potassium carbonate (24.9 g, 180 mmol, 1.5 equiv.) and potassium iodide (10 mg) in DMF was stirred for 1 h at ambient temperature. After 3-bromopropan-1-ol (25 g, 180 mmol, 1.5 equiv.) was added dropwise, the mixture was refluxed for 16 h. DMF was removed under reduced pressure. The residue was dissolved in diethyl ether (300 ml) and extracted with hydrochloric acid (1 M, 150 ml). The organic phase was dried over sodium sulfate and purified via column chromatography (silica gel, pentane:ethyl acetate, 2:1). 3-(4-(phenyldiazenyl)phenoxy)propan-1-ol was obtained as an orange solid (25.7 g, 100 mmol, 83%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm) = 1.88 (s, 1 H, C–OH), 2.07 (quin, $J = 6.0$ Hz, 2 H,

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