Reversible Self-Assembly

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Light-Induced Reversible Self-Assembly of Gold Nanoparticles Surface-Immobilized with Coumarin Ligands

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Abstract: *A novel light-induced reversible self-assembly (LIRSA) system is based on the reversible photodimerization and photocleavage of coumarin groups on the surface of gold nanoparticles (AuNPs) in THF solution. Facilitated by coumarin groups, light irradiation at 365 nm triggers the stable assembly of monodisperse AuNPs; the resulting self-assembly system can be disassembled back to the disassembled state by a relatively short exposure to benign UV light. The reversible self-assembly cycle can be repeated 4 times. A specific concentration range of coumarin ligand and the THF solvent were identified to be the two predominant factors that contribute to the LIRSA of AuNPs. This is the first successful application of reversible photodimerization based on a coumarin derivative in the field of AuNP LIRSA. This LIRSA system may provide unique opportunities for the photoregulated synthesis of many adjustable nanostructures and devices.*

Light-induced reversible self-assembly (LIRSA) has recently attracted considerable attention because of the advantages of easy, economical, and efficient control of higher-order domain structures for a wide range of practical applications.[1] Theoretically, most self-assembled nanostructures that respond to light in a reversible manner do so by either photoisomerization or photodimerization through the introduction of chromophores on the nanoparticle (NP) surface. Unlike photoisomerization,[2] the photodimerization process and its reverse do not significantly alter the atomic positions of the aromatic system. Each monomer unit remains essentially intact, and the photodimers formed by polycyclic aromatic hydrocarbons can be photodissociated to generate the original monomers.[3] The weakly toxic dye coumarin and its derivatives are found in many plants and constitute an important example of reversible photodimerization. Despite the use of coumarin derivatives in a wide variety of fields,[4] their potential application in the LIRSA of NPs to achieve good reversibility and high switching rates has been rarely investigated, possibly because of complex and sensitive issues.[3c,5] Solvent properties, such as solvent type and polarity, are found to play a critical role in both the percent conversion and the selectivity of photodimerization. The kinetic equilibrium depends on the solvent and can be interpreted using the proposal of Long et al.[6] Additionally, the optical absorption of the solvent must also be considered because of the detrimental optical filter effect. The reversible photoreaction of coumarin has been used to control the increase and decrease of colloidal clusters in tetrahydrofuran (THF); unfortunately, reversible photocrosslinking of the clusters failed, possibly because of the irreversible damage of coumarin molecules caused by strong UV irradiation.[3b,c] The recent report by Zhang et al.[5a] also concerns the use of coumarin groups as a phototrigger for light-induced assembling thiol-capped NPs into nanovesicles. Eighteen types of solvents with various polarities were tested, but the spontaneous aggregation process caused by the irradiation of acetone with UV light makes the system incompatible with its potential use as an optically controlled interlinker in the LIRSA of inorganic NPs. It is therefore highly desirable to explore a tolerant physical and chemical micro-environment for the delicate LIRSA system to realize the significantly reversible self-assembly of modified NPs by photodimerization and photocleavage of coumarin groups.

Herein, we report the design of colloidal coumarin-functionalized AuNPs capable of reversible self-assembly based on the photolysis of coumarin in response to light irradiation. Facilitated by coumarin groups, light irradiation at 365 nm triggers the stable assembly of monodisperse AuNPs; the resulting self-assembly system can be disassembled back to the disassembled state by a relatively short exposure to benign UV light, as shown in Figure 1a. We find that maintaining an appropriate concentration of coumarin ligand on the surface of NPs and the suppression of the *anti*-configuration dimers (*anti*-CDs) by THF during irradiation are key for successful LIRSA. This goal is achieved first by synthesizing a thiolated coumarin derivative 7-(11-mercaptoundecanoxy)coumarin (**1**), which was used as a photoresponsive interlinker for LIRSA of AuNPs under suitable irradiation. We use a nucleophilic THF as a moderately polar solvent to disperse coumarin-functionalized AuNPs (**1**-AuNPs). More importantly, THF was used as an electron donor to yield the charge-separated coumarin singlet excimer, ensuring effective photocleavage for the rapid disassembly of **1**-AuNPs. The LIRSA of the **1**-AuNP/THF system can be repeated with full recovery for four cycles, making them promising materials for light-driven actuating applications. Our work is the first successful application of a reversible photodimerization-based coumarin derivative in the LIRSA of AuNPs, and the obtained results are very promising.

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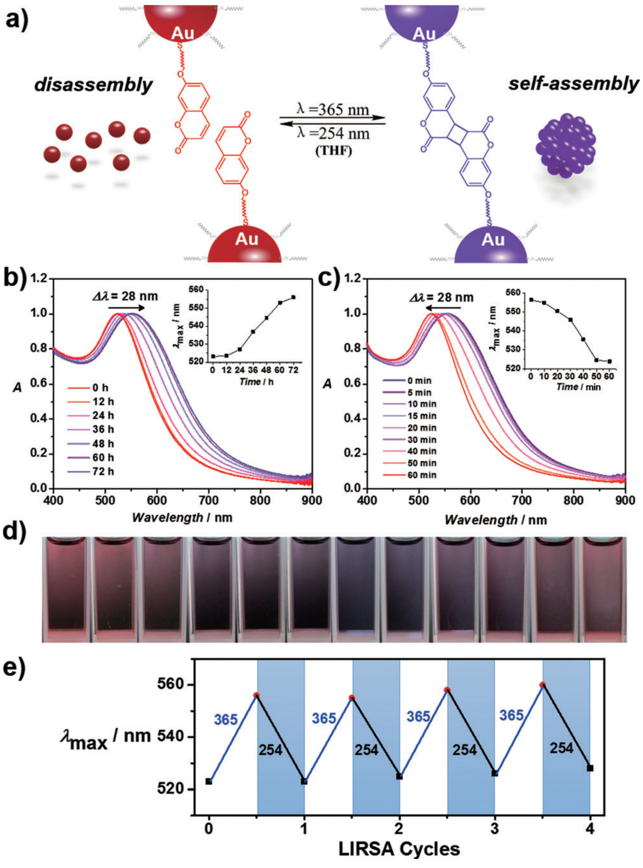

Figure 1. a) The LIRSA behavior of **1**-AuNPs. Normalized absorption spectra of **1**-AuNPs (0.01 mm) in THF after light exposure at b) 365 nm and c) subsequently, 254 nm. Inset: Changes in the wavelength maximum for **1**-AuNPs for increasing times. d) **1**-AuNP solutions corresponding to the points in the plot. e) Reversible change in the wavelength maximum during assembly of **1**-AuNPs with illumination at $\lambda = 365$ nm (72 h) and disassembly at $\lambda = 254$ nm (60 min).

Compound **1** was synthesized by a four-step synthesis, and its purity was confirmed by ^{1}H NMR spectroscopy and EI-MS analysis (Supporting Information, Figures S1–S4). The optical absorption spectral changes under irradiation are characteristic of the photodimerization and photocleavage of coumarin groups, as shown in the Supporting Information, Figure S5. AuNPs with a mean size of 7.6 nm were prepared using a modification of a procedure described previously.[7] Transmission electron microscopy (TEM) images and size-distribution histograms of as-prepared AuNPs are presented in the Supporting Information, Figure S6. The coumarin-functionalized **1**-AuNPs were prepared by mixing AuNPs with **1** under vigorous stirring. As shown by the first red line of Figure 1 b, the solution exhibits a strong surface-plasmon resonance (SPR) band of AuNPs at 523 nm. Light irradiation at 365 nm for 72 h leads to a red-shift of the SPR absorption from 523 nm to 556 nm ($\Delta\lambda_{max} = 29$ nm), while the irradiation of unmodified AuNPs with 365-nm light produces almost no changes in the SPR absorption (Supporting Information, Figure S7 b), clearly indicating that the self-assembly of **1**-AuNPs as caused by the photodimerization of coumarin groups on the NP surface.

After subsequent irradiation with 254-nm light, the SPR band was blue-shifted from 556 nm to 550, 536, and 523 nm by irradiation for 20, 40, and 60 min, respectively (Figure 1 c). Consistent with the spectral absorption change, the color of the solution first changed from deep red to purple during irradiation with 365-nm light and then gradually regained its initial deep red color under irradiation with 254-nm light, thus indicating light-induced self-assembly and disassembly in THF solution (Figure 1 d). As shown in Figure 1 e, λ_{max} of **1**-AuNPs shifted between 523 and 560 nm by alternating light exposure at 365 and 254 nm, suggesting that the four consecutive disperse-assemble-redisperse cycles of **1**-AuNPs in THF solution occur through the photodimerization and photocleavage of **1**.

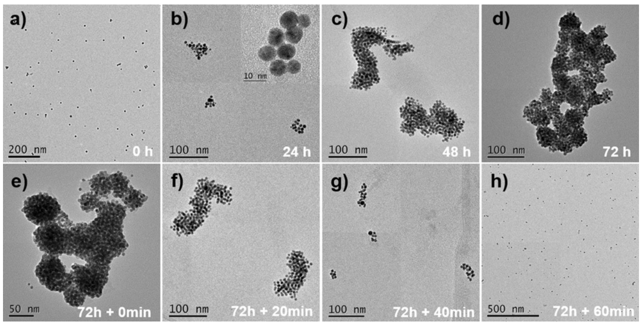

Figure 2. TEM images of **1**-AuNPs (0.01 mm) in THF solution a)–d) under irradiation with 365 nm and e)–h) subsequent irradiation with 254-nm light.

Figure 2 shows the changes in the cluster size with irradiation time. In the early stage, in the absence of light, **1**-AuNPs with a uniform size distribution were not aggregated (Figure 2 a). Following irradiation with 365-nm light, cluster aggregates were gradually formed because of the photodimerization of the coumarin groups on the surface of **1**-AuNPs. The clusters then gradually expanded ($t = 48$ h) and ultimately ($t = 72$ h) formed amorphous aggregates but did not precipitate out of the solution (Figures 1 c and 2 d). In contrast, a TEM image of the unmodified AuNPs collected after irradiation showed no obvious assembly of AuNPs upon irradiation with 365-nm light for 72 h (Supporting Information, Figure S6 d). Such **1**-AuNP aggregates were metastable and could be converted back into free NPs by irradiating with 254-nm light for another 60 min. As shown in Figures 2 e–h, TEM observations revealed that the size of the aggregates does indeed decrease with increasing UV irradiation time.

Furthermore, we found that a critical amount of **1** played an important role in achieving reversible **1**-AuNP self-assembly (Figure 3; Supporting Information, Figure S8). The number of **1** ligands per NP-*N* was calculated by thermodynamic analysis (Supporting Information, Table S1).[1f] When *N* was low (ca. 11), the SPR absorption shifted by $\Delta\lambda_{max} = 29$ nm during assembly, indicating that the 365-nm light-irradiated **1**-AuNPs organized into three-dimensional, reversible clusters (phase **RC1** in Figure 3). Taking the spatial configuration of each **1**-AuNP into account, the host NP allowed the reactive double bonds of the coumarin to be

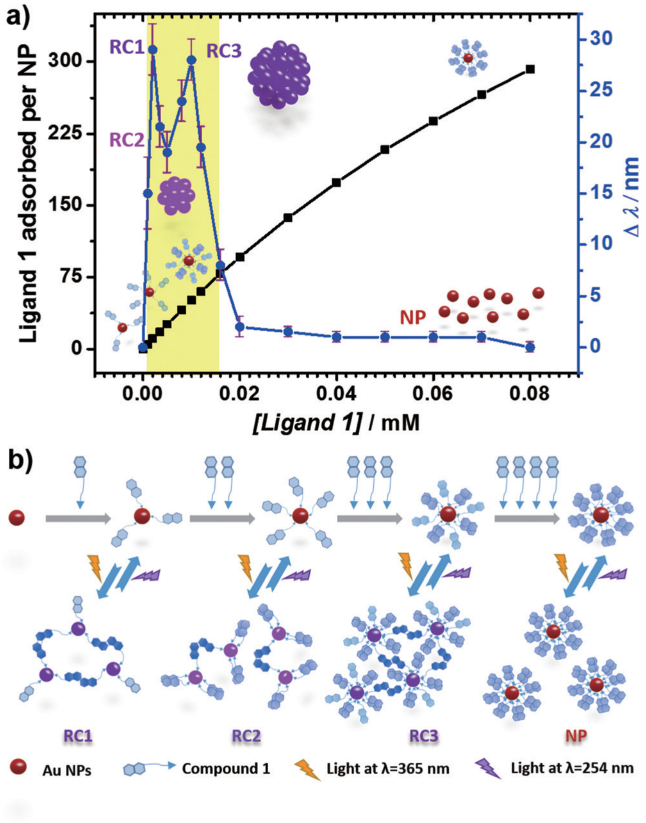

Figure 3. a) NPs covered with various numbers of coumarin ligands (black symbols) and the wavelength shifts of SPR absorption ($\Delta\lambda_{max}$, blue symbols) for **1**-AuNP self-assembly resulting from irradiation with 365 and 254 nm in THF according to the concentration of coumarin ligand **1**. b) Representation of the photodimerization and photocleavage of **1** ligands mediating the covalent self-assembly of AuNPs.

located less than 4.2 Å apart and aligned parallel to the adjacent coumarin groups. This facilitated the dimerization of the surface coumarin molecules, forming *syn*-configuration dimers (*syn*-CDs) upon irradiation.[8] As N increased, the system showed a lower LIRSA efficiency because a number of coumarin monomers were first consumed to form *syn*-CDs on their host NP (phase **RC2**). This explains the reduction of $\Delta\lambda_{max}$ when the concentration of ligand **1** was increased from 0.002 to 0.005 mM. The addition of 0.01-mM **1** again increased the $\Delta\lambda_{max}$ of **1**-AuNPs with a high self-assembly efficiency. In this case, the adequate coumarin end groups were stacked in parallel in the combination of *H*- and *J*-aggregates.[9] The *H*-aggregates on the same AuNP prefer to form *syn*-CDs because of their close proximity, and then, as the concentration of coumarin monomer decreases under 365-nm light irradiation, the neighboring coumarin groups in the *J*-aggregates between the two NPs yield *anti*-CDs (phase **RC3**), as shown by FTIR measurements (Supporting Information, Figure S10b and Table S2). However, when the concentration of ligand **1** was ≥ 0.02 mM, all of the sterically crowded coumarin units formed *syn*-CDs on their host NP surface and were not able to dimerize with the neighboring molecules from other NPs. As a result, the solution retains its uniform dispersion, even under prolonged 365-nm irradiation.

Thus, the photodimerization and photocleavage effects of **1**-AuNPs were "disabled" by further increasing the concentration of **1** (for example, 0.08 mM), demonstrating that LIRSA of **1**-AuNPs occurs only when **1** is added in a specific concentration range (thta is, 0.001–0.016 mM; yellow region in Figure 3a).

The solvent effect is also essential for the control of coumarin photolysis and therefore the LIRSA of **1**-AuNPs. When chloroform, which is another widely used solvent with $P' = 4.1$, comparable to that of THF, was used instead of THF and all other experimental conditions were kept the same, only irreversible red-shifted absorption accompanied with extensive broadening of the SPR adsorption signal was observed, and eventually heavily aggregated NPs were obtained (Supporting Information, Figure S11). Moreover, the photoreactions in the solutions decreased, and increased polarity led to aggregated clusters that could not be recovered back to the disassembled state (Supporting Information, Figure S12). Thus, LIRSA is mediated by ligand–solvent interactions, and possibly by the accompanying electronic coupling effects. As can be seen from Figure 4a, compound **1** shows intense solvent-dependent fluorescence at room temperature. The emission bands of **1** were centered on 380 nm, and increasing the solvent polarity slightly red-shifted and broadened the emission because of increased hydrogen bonding.[10] The weak fluorescence in THF is indicative of the shorter lifetime of its singlet excited state. It is reasonable to suggest that the excited coumarin groups were quenched by a photoinitiated electron-transfer reaction by THF because the first solvent coordination sphere of coumarin molecules consists solely of THF molecules.[11] Figure 4b shows the fluorescence emission spectra of **1** in THF before and after

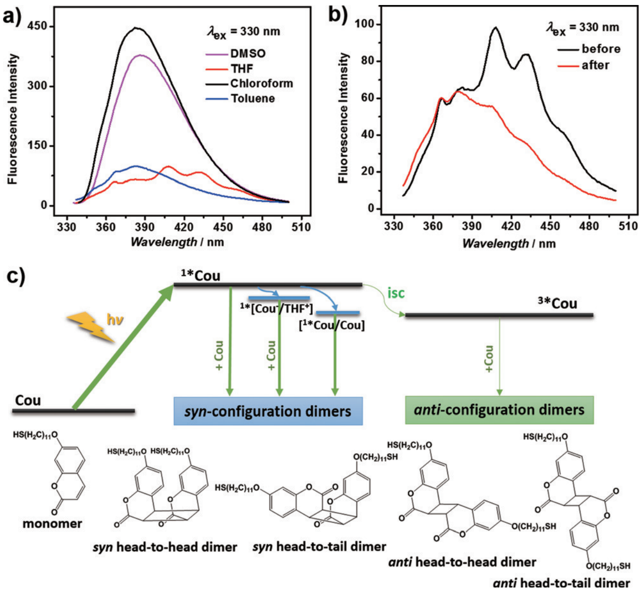

Figure 4. Fluorescence emission spectra of **1** a) in different solvents and b) in THF solution before and after irradiation with 350-nm light for 4 h; $\lambda_{ex} = 330$ nm. c) Simplified energy-level diagram for coumarin dimerization in THF solution under 350-nm light irradiation.

irradiation with 365-nm light for 4 h. Two peaks and a shoulder were detected at 408, 431, and 462 nm before irradiation, suggesting the formation of charge-separated singlet excimers.[12] In this photoinduced electron-transfer process, the charge is transferred during the irradiation from the lone pair of electrons located on the oxygen atom of THF to the excited coumarin. The simplified energy level diagram for coumarin dimerization in THF solution under 350-nm irradiation is shown in Figure 4c. The singlet excimers contribute to the longer singlet lifetime and the low efficiency of intersystem crossing from the singlet state to the triplet state.[13] The reduced triplet excited state population decreased the likelihood of the formation of *anti*-CDs and accelerated the formation of *syn*-CDs. The fluorescence decay of the singlet excimer moieties after 365-nm light irradiation for 4 h indicates that singlet excimers contribute substantially to the formation of *syn*-CDs.

In principle, very few *syn*-CDs can form between two different NPs because of conformational anchoring. In other words, upon irradiation, dimerization of the coumarin groups in THF preferentially leads to the formation of *syn*-CDs on the host NP surface, with only a small amount of *anti*-CDs remaining for the AuNP self-assembly. Clearly, THF selectively enhances the formation of coumarin *syn*-CDs and inhibits the formation of *anti*-CD components, and thus, the **1**-AuNP/THF system proceeds through a less efficient photocrosslink reaction but leads to more efficient photocleavage under irradiation. Another important factor is that THF is an excellent solvent for **1**-AuNPs and shows low absorption at 254 nm (Supporting Information, Figure S13), providing maximum support for the photocleavage of **1**-AuNPs assembles and the reversibility of LIRSA.

The necessity to use a 254-nm light as the trigger is the reason for the relatively poor reversibility of the system compared to previous reports. Control experiments were performed by exposing non-functionalized AuNPs to 254-nm light for a prolonged period of time. The results shown in the Supporting Information, Figures S14 and S15 clearly indicate that 254-nm light is energetic enough to desorb thiolates from AuNPs, but it can also readily affected by the solvent. The photochemical stability of AuNPs in THF solution is much better than the stability of AuNPs in toluene or chloroform solution. Note that the LIRSA of AuNPs by coumarin ligands is proposed for the first time by this work. Although further exploration is required to enhance their reversibility of LIRSA, it is reasonable to believe that coumarin derivative is a potential new ligand to control the aggregation process of NPs.

In summary, we have developed a LIRSA system by integrating coumarin photolysis with the assembly-driven color-change properties of AuNPs. Coumarin-functionalized AuNPs can be self-assembled from the red disperse state to the purple aggregate state by irradiation with $\lambda = 365$-nm light and can then be transformed back to the original disassembled state by UV irradiation; this reversible self-assembly cycle can be repeated four times. Compared with the previous photoreactive NP systems based on coumarin functionalization, the current system exhibits crucial advantages of simpler structure, highly efficient control, and higher cycling performance. We believe that this LIRSA system can potentially be used in the photoregulated synthesis of more complex and/or adjustable nanostructures and devices.

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