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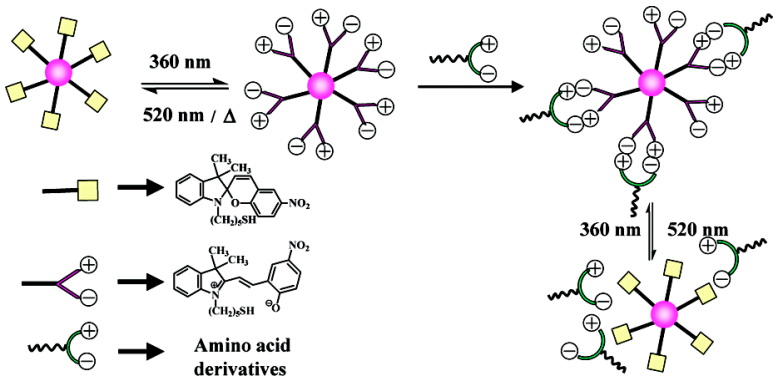

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Light-Induced Modulation of Self-Assembly on Spiropyran-Capped Gold Nanoparticles: A Potential System for the Controlled Release of Amino Acid Derivatives

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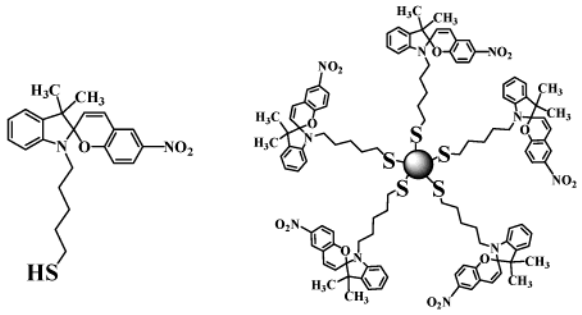
The design of nanostructured molecular architecture through the "bottom-up approach" offers a wide range of possibilities, particularly due to the size-dependent optoelectronic properties of nanomaterials, for the construction of newer types of hybrid organic−inorganic systems.[1−3] Chemical linkage of biologically relevant molecules such as proteins, peptides, carbohydrates, lipids, and DNA to gold nanoparticles has led to the development of novel probes for biochemical investigation, with better sensitivity and greater penetration through tissues.[4] The quantized capacitance is yet another interesting property of Au nanoparticles capped with organic molecules,[5a,b] and this has been recently exploited for the electrochemical modulation of fluorescence on nanostructured films.[5c] Furthermore, nanoparticle arrays and superstructures on surfaces are promising in sensory applications and possess several advantages over single-monolayer arrays.[6] Herein we report the design of the first photoswitchable double-shell structure on a Au nanoparticle core, consisting of photochromic spiropyran as the first shell (**Au-SP**), which regulates the assembly and release of an outer shell of an amino acid derivative on irradiation.



The rationale behind the design of light-mediated self-assembly is based on the fact that the discrete photoisomeric states of spiropyrans exhibit distinctly different physical properties.[7] Under dark conditions, the majority of spiropyran molecules exist in their "closed" spiro form (colorless and nonpolar),[7a] which when excited with UV light undergo photoisomerization to the "open" merocyanine form (highly polar and zwitterionic), absorbing in the visible region. The ring closure to the spiropyran form can occur either thermally or by exposure to visible radiation. The ability of zwitterionic merocyanines to bind with charged molecules[8] was further exploited for organizing a second layer of amino acid derivatives around the core−shell structures.

The photochemical ring opening of **SP** as well as the thermal/photochemical ring closure of the merocyanine form is similar to that of other reported spiropyran systems. Absorption spectra of spiropyran-capped gold nanoparticles, **Au-SP** (trace b) and **SP** (trace a) in methanol are presented in Figure 1.

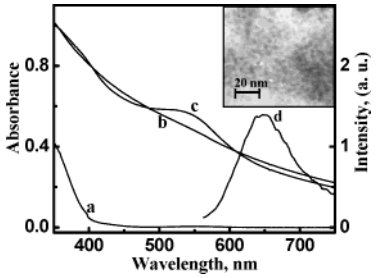
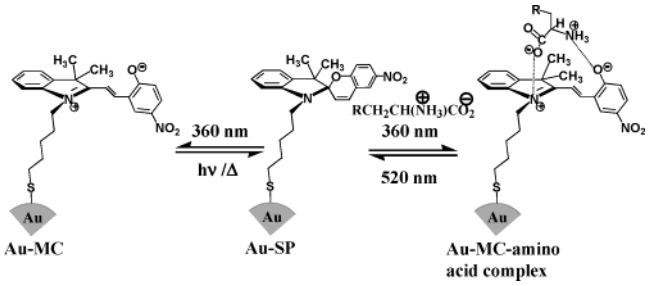


Figure 1. Absorption spectra of (a) **SP**, (b) **Au−SP**, and (c) **Au-MC** and (d) emission spectrum of **Au-MC** (excitation at 520 nm). Inset: TEM image of **Au-SP**.

Scheme 1. Schematic Representations of the Photochemical Ring Opening and Closing of **Au-SP** in the Absence and in the Presence of Amino Acids



The broad absorption observed in the visible region for **Au-SP** is attributed to the surface plasmon absorption of gold nanoparticles, which is significantly dampened as well as broadened (characteristic of smaller Au nanoparticles[9]). Based on the particle size (diameter of 1.5−2.0 nm), approximately 130 molecules of **SP** are capped on each nanoparticle. Irradiation of **Au-SP** in methanol with a 360-nm band-pass filter resulted in the formation of an absorption band around 500 nm (trace c in Figure 1), which corresponds to the formation of the zwitterionic merocyanine form (**Au-MC**) as represented in Scheme 1 (the isomer equilibrium constant of the chromophore at the photostationary state was estimated as 0.25; see Supporting Information).

Photoswitching of **Au-SP** was investigated in the presence of various amino acid derivatives such as L-tryptophan, L-tyrosine, L-DOPA (note that L-DOPA is effective for the treatment of Parkinson's disease and hypertension), and α-methyl-L-DOPA. The absorption of **Au-SP** remains unaffected on addition of a saturated solution of various amino acid derivatives under dark conditions (e.g., trace a in Figure 2A), ruling out the possibility of any ground-state interactions. Formation of a visible absorption band (trace b in Figure 2A) was observed on irradiation with a 360-nm band-pass filter. In contrast to the quick thermal ring closure of **Au-MC** in the absence of amino acids, an initial decrease in the intensity of the visible absorption band was observed and the absorbance

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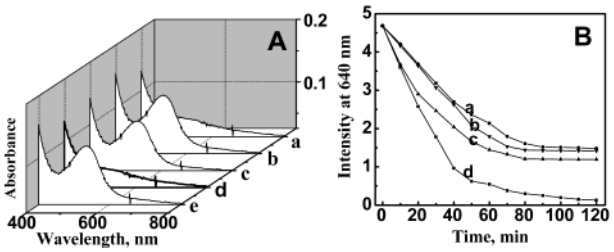

Figure 2. (A) Absorption spectra of (a) a methanolic solution of **Au-SP** containing L-DOPA (42 mM), (b) immediately after irradiation with UV light (360-nm band-pass filter), (c) after 2 h, (d) after further irradiation with visible light (520-nm band-pass filter), and (e) after subsequent irradiation with UV light (360-nm band-pass filter). (B) Changes in fluorescence intensity of **Au-MC** at 640 nm in the presence of (a) L-tyrosine (14.2 mM), (b) L-DOPA (42 mM), and (c) L-tryptophan (16.7 mM) and (d) in the absence of amino acid derivatives.

persisted, indicating the stabilization of the zwitterionic merocyanine form (trace c in Figure 2A). The two-point electrostatic interaction between the zwitterionic merocyanine form on Au nanoparticles and amino acid derivatives may result in the formation of a stable complex (e.g., **Au-MC**: : : : L-DOPA complex), which in turn prevents the thermal ring closure of **Au-MC** (Scheme 1). The zwitterionic nature of the open form of spiropyran derivatives was utilized earlier for the transport of tryptophan across bilayers[8a] and membranes.[8b] Comparison of traces b and c in Figure 2A indicates that only a part of the merocyanine capped on Au nanoparticles gets complexed with amino acid derivatives.[10] The **Au-MC**: : : : amino acid complex dissociates on photoirradiation at 520 nm and undergoes thermal ring closure to **Au-SP**, releasing the amino acid derivatives (trace d in Figure 2A), and the complexation/dissociation cycles could be repeated many times. Further the **Au-MC**: : : : amino acid complexes were quantitatively characterized using steady-state and time-resolved fluorescence techniques. The details regarding (a) the concentration of the amino acids complexed as a second layer on the Au core−shell structures in the photostationary state and (b) the rate constants for the thermal dissociation/ring closure of different **Au-MC**::::amino acid complexes in methanol [e.g., the half-life ($t_{1/2}$) of **Au-MC**::::tyrosine complex is ∼14 h, whereas the $t_{1/2}$ of **Au-MC** → **Au-SP** is 23 min] are given in the Supporting Information.

Recent investigations on the fluorescence properties of spiropyran-based systems indicate that (i) the closed spiro form has no strong emission, while the zwitterionic merocyanine form emits around 650 nm,[7a] and (ii) the multiexponential decay of merocyanine, observed in time-resolved fluorescence, is attributed to various isomeric species.[11a] The emission spectrum of **Au-MC** is shown in trace d of Figure 1. A solution of **Au-SP** was irradiated using a 360-nm band-pass filter for 3 min in the absence and in the presence of various amino acid derivatives. The irradiation source was turned off, and the emission intensity at 640 nm was recorded at intervals of 10 min for all the samples (Figure 2B). In the case of **Au-MC**, the emission intensity decreased gradually with time, and the solution became practically nonfluorescent after 120 min.[11b,c] Interestingly, in the presence of various amino acids, an initial decrease in emission intensity was observed (traces a−c in Figure 2B), and then the fluorescence persisted for a long time.[11c] The complex is further characterized by investigating the singlet lifetimes. The unbound merocyanine, **MC**, followed a biexponential decay in methanol, with two short-lived species (100 and 266 ps). The lifetime and relative abundance of both these species remain more or less unaffected by linking onto Au nanoparticles (**Au-MC**) (Supporting Information). Interestingly, an additional component, with a long lifetime (∼3 ns), was observed in the presence of tryptophan. The long-lived species is assigned to the **Au-MC**: : : : tryptophan complex, and its relative abundance increased with increasing tryptophan concentration. The two-point electrostatic interaction between **Au-MC** and tryptophan may restrict the torsional dynamics of merocyanine, leading to longer lifetimes.

In conclusion, we have demonstrated the photoswitchable self-assembly of various amino acid derivatives by anchoring spiropyrans onto the three-dimensional surface of Au nanoparticles. It is possible to control the local concentration of amino acid on the Au nanoparticle scaffold by suitably regulating the number of spiropyrans capped on the surface. The ability of these systems for light-mediated binding and release of molecules offers intriguing possibilities for designing drug delivery systems with controlled release abilities. The site-specific binding properties of Au nanoparticles observed in biological systems make them more attractive for such applications.

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Supporting Information Available: Experimental section including the synthesis and characterization of **Au-SP**, **SP**, and its intermediates, details of the photophysical investigations, and singlet lifetime data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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