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Reverse Micellar Synthesis of Dye/Gold Hybrid Nanocomposites

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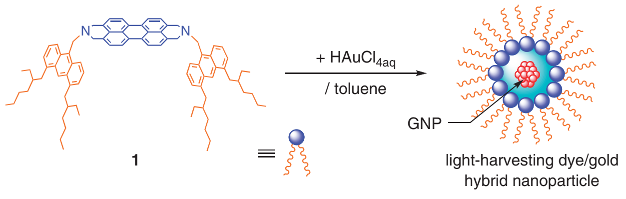
Complexation of a light-harvesting dye with hydrogen tetrachloroaurate led to spontaneous formation of gold nanoparticles within self-assembled reverse micellar aggregates, which generated stabilized dye/gold hybrid nanocomposites.

Gold nanoparticles (GNPs) have attracted broad attention in the fields of physics, chemistry, and biology because of their unique dielectric and electrodynamic properties[1–4] which have been employed for several emerging applications, such as bioanalytical labels,[5] phototherapeutic agents,[6] and plasmonic devices.[7] Of particular interest in the context of the present studies is surface functionalization of GNPs with organic molecules to introduce unique chemical and physical properties onto the resulting nanocomposites.[8–11] Nevertheless, there are only a few reports concerning convenient and general protocols for in situ preparation of organic/gold hybrid nanocomposites.[12–14] In a previous publication, we have reported that anthracene–perylene triad **1** exhibited light-harvesting functionality and self-assembled into nanoscopic reverse micelles through treatment with sulfuric acid.[15,16] Replacement of sulfuric acid with tetrachloroauric acid ($HAuCl_4$) will develop a new synthetic approach to organic/gold hybrid nanoparticles, since reduction of the tetrachloroaurate anions confined within the reverse micellar enclosure would yield stable GNPs (Scheme 1).[17,18] With this idea in mind, we set out to synthesize a new type of hybrid nanocomposite by the use of the light-harvesting reverse micellar system. In this publication, we disclose a new synthetic strategy for the preparation of organic/gold hybrid nanocomposites, where stabilized GNPs could be generated without any reducing agent at the core of the self-assembled light-harvesting dyes.

In a typical experimental procedure, a toluene solution of **1** ($c = 1.0\,\text{mM}$) was treated with 4.0 equiv of aqueous $HAuCl_4$, where the molar ratio of water to **1** (W_0) equals 50. Sonicating this mixture for 3 min resulted in an essentially clear solution of the complexes of the protonated dyes with aurate counter anions. The UV–vis spectrum of the resulting solution exhibited discernible broadening and bathochromic shift of the absorption peaks immediately after the reaction. Dark incubation of the solution at room temperature led to appearance of a pronounced absorption band at 518 nm whose intensity increased gradually over the course of about 9 h and reached a saturation value thereafter (Figure 1). Clearly, this absorption is assigned to the surface plasmon resonance (SPR) band characteristic of extremely small-sized GNPs presumably encapsulated within self-assembled molecular shells of the reverse micelles.[1] Another compelling evidence for the formation of the GNPs was obtained by steady-state fluorescence measurements upon excitation at 368 nm, where direct excitation of the anthracene chromophores essentially occurs. Under these conditions, weak emission bands attributed to monomeric anthracene chromophores were observed in the range from 400 to 550 nm through the measurements with incubated samples, whereas the reverse micelles prepared with sulfuric acid showed unstructured weak bands originating from monomeric and dimeric perylene emissions in the longer-wavelength region (450–650 nm) along with the monomeric anthracene emission (Figure S1).[19] We believe this different spectroscopic behavior can be explained on the basis of strong fluorescence quenching of the electronically excited perylene chromophores due to direct electron transfer from the adjacent GNPs.[20,21] This rationalization may account for emission behavior with the use of more polar solvents. Indeed, the sample diluted with 35% v/v ethanol/toluene gave enhanced intensities of fluorescence emissions from the perylene chromophores (Figure S2).[19] The effect of the solvent polarity can be interpreted in terms of solvent swelling of the dye/GNP aggregates, which may aid in dissociation of the bound dyes as a result of the change in degree of the solvation.



Scheme 1.

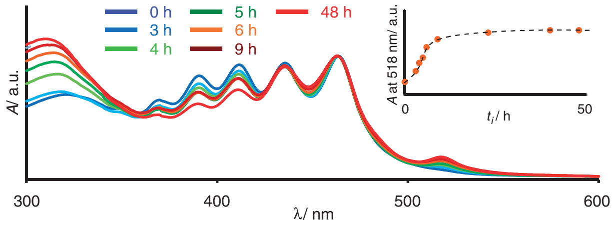


Figure 1. Absorption spectra of the **1**/$HAuCl_4$ complexes in toluene. Inset: Plot of incubation time vs. absorbance at 518 nm.

In an effort to gain insight into nanoscopic features, morphology of the dye/GNP aggregates was investigated by atomic force microscopy (AFM).[22] As shown in Figure 2, the AFM analysis revealed a number of small-sized spherical objects which possibly corresponded to the dye/gold hybrid nanocomposites. A cross-sectional view of the AFM image indicated that every object had a highly monodisperse size with

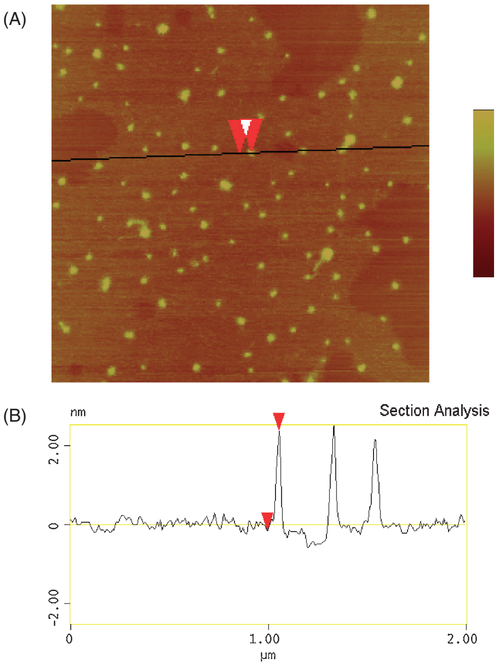


Figure 2. (A) AFM image of drop-cast of toluene solution of dye/GNP aggregates on HOPG. (B) Height profile on a cross section of the solid line in the AFM image.

peak height of about 2 nm. Considering that about 2.6 nm thickness of overall molecular layers should be included in the volume of the fully extended aggregate structures[23] and that their nonspherical collapsed forms could be detected by this analysis, an estimated size of the GNPs was obviously less than 2 nm, in agreement with the expectation from the observed absorption wavelength of the SPR band.

In conclusion, the complexation of **1** with $HAuCl_4$ has been demonstrated to produce a new type of organic/gold hybrid nanocomposite, where the surface of the GNPs is stabilized by the shell of the light-harvesting dye surfactants.[24] The synthetic method described herein has several advantages such as: (i) simplicity and ease of preparation without the need for any reducing agent, (ii) generation of the stabilized GNPs with narrow distribution, (iii) in situ surface functionalization of the GNPs to create a new class of organic/gold hybrid nanocomposites. Further discussion on mechanistic aspects of the spontaneous reaction will be given in the near future.

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References and Notes

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19 Figures S1 and S2 are shown in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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22 A solution of the dye/GNP aggregates diluted with dry toluene ($c = 0.1$ mM) was drop-cast on to the HOPG. Air-dried sample of this solution was examined by measurements in tapping mode.

23 Molecular modeling study of fully extended structure of **1** indicates that vertical distance from the perylene nucleus to the center of the molecular edges are estimated to be approximately 1.3 nm.

24 The observation that the sample incubated for 10 days revealed the SPR absorption band at the same wavelength suggested that nanostructures of the GNPs should be highly stabilized by the dye surfactants.