



Spontaneous formation of dye-functionalized gold nanoparticles using reverse micellar systems

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ABSTRACT

Detailed exploratory and mechanistic investigations on spontaneous formation of dye-functionalized gold nanoparticles (GNPs) using dye-based reverse micellar systems are described in this publication. The accumulated results from spectroscopic and microscopic investigations demonstrated that water molecules confined within nanoscopic enclosure of the self-assembled reverse micelles played critical role in the redox processes of aurate ions to produce GNPs, which are assumed to have approximately constant size distributions. The resulting dye-functionalized GNPs were found to offer their absorption and fluorescence emission tunability by changing the medium polarity as well as to exhibit excellent film-forming properties to give optically homogeneous polystyrene thin films. These key findings in addition to broad applicability of the self-assembling process with a variety of dye analogues have led to a conclusion that the protocol presented here serves as a versatile synthetic method to provide a potential convenience for future development of new organic–inorganic hybrid nanomaterials.

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1. Introduction

Hybrid nanomaterials, composed of both organic and inorganic components, have attracted a great deal of interest in the past few years as advanced materials with desirable optical, electrical and magnetic properties [1], which have been employed for several emerging applications such as imaging agents [2], semiconductors [3–5] and photoelectric devices [6–8]. Engineering surfaces of inorganic nanomaterials with functional dyes provides the ability to independently tune the energy levels of each component, and thus will pave the way for the development of new photonic devices with finely-tuned optoelectronic properties [9,10]. On the basis of the idea that the rapidly emerging field of the plasmonics can be applied to construction of not only superior photonic devices based on surface electromagnetic field enhancement [11,12], but also efficient solar energy conversion systems [13], considerable effort has been devoted to develop efficient synthetic routes for the generation of

Abbreviations: GNP, gold nanoparticle; NTCA, naphthalene-1,4,5,8-tetracarboxylic dianhydride; PTCA, perylene-3,4,9,10-tetracarboxylic dianhydride; NMP, N-methylpyrrolidone; THF, tetrahydrofuran; SPR, surface plasmon resonance; W_0 , molar ratio of water to dye molecules; t_s , sonication time for complexation of dye with HAuCl_4 ; t_i , incubation time for complexation of dye with HAuCl_4 ; r , stoichiometric ratio of $\text{HAuCl}_4/\text{dye}$.

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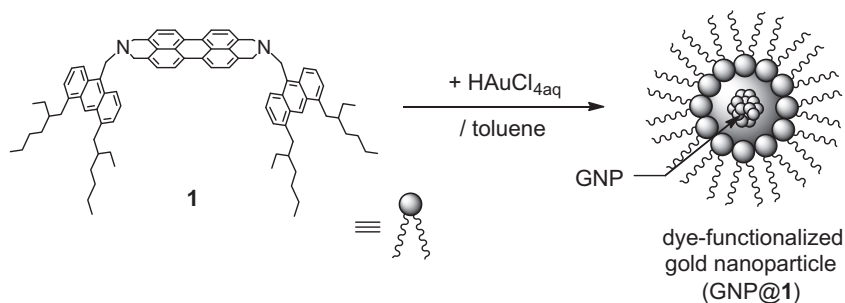
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organic–inorganic hybrid nanomaterials [14–16]. In a previous publication, we have discovered spontaneous formation of organic–inorganic hybrid gold nanoparticles (GNPs) through treatment of trichromophoric light-harvesting dye **1**, which has been designed to funnel absorbed photons from anthracene units to perylene core [17], with aqueous hydrogen tetrachloroaurate in toluene (Scheme 1) [18]. Of particular interest in this context is demonstration that the gold cations of the dye-aurate salts were spontaneously reduced in the absence of any reducing agents to give the GNPs, accompanied by self-assembly of the protonated dyes into spherically shaped reverse micelles, where the gold nanoparticles would be encapsulated within the reverse micellar shells. Driven by these intriguing findings, we decided to pursue our research on this poorly understood phenomenon to gain insight into the mechanism and the scope of these chemical processes in more details as well as to show broad applicability of this protocol as a potential method for the synthesis of many types of organic–inorganic hybrid nanomaterials. In the present publication, we describe the complete details of exploratory and mechanistic investigations on the production of the dye-functionalized GNPs by the use of the trichromophoric dye **1** and related analogues **2–5** (Fig. 1).

2. Material and methods

2.1. General

All solvents and reagents were of reagent grade quality from Wako Pure Chemicals and Tokyo Chemical Industry (TCI) used



Scheme 1. Schematic representation of the production of the dye-functionalized GNPs from **1**.

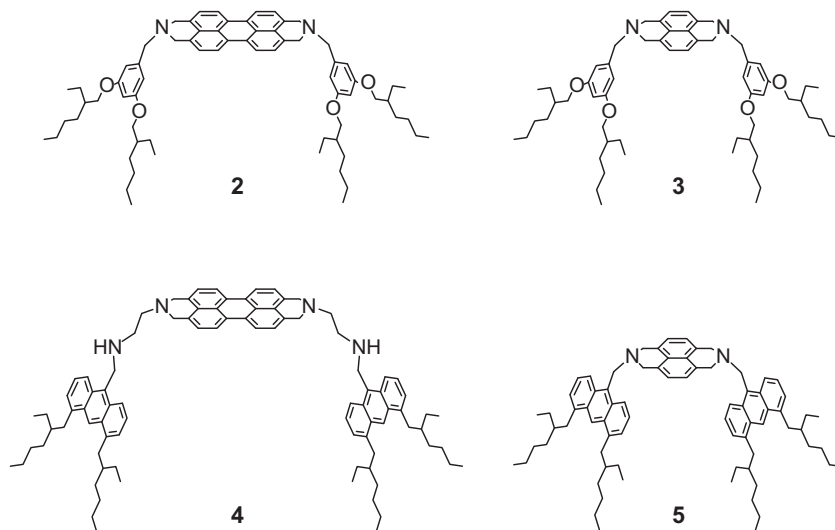


Fig. 1. Structures of dyes **2–5**.

without further purification, except for polystyrene beads with average molecular weight of 250,000 from Acros Organics. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra operating at the frequencies of 300 and 75 MHz, respectively, were recorded on a JEOL JNM-AL300 spectrometer in chloroform- d (CDCl_3). Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV-vis and fluorescence (excitation) spectra were recorded on a JASCO V-530 spectrophotometer and a JASCO FP-6200 spectrofluorometer, respectively. Elemental analyses were performed by JSL Model JM 10 instruments. The atomic force microscope (AFM) analyses were performed on a Veeco NanoScope IIIa microscope for GNP@**3** and a Keyence VN-8010 for all other samples. The trichromophoric dye **1** and the two related analogues **2** and **5** were prepared according to already published reaction protocol and used for experiments [17,19]. The other materials **3** and **4** were synthesized as described in the following procedures.

2.2. Materials

2.2.1. Synthetic procedure for **9**

A solution containing 9-(chloromethyl)-4,5-bis(2-ethylhexyl)anthracene **8** (0.100 g, 0.222 mmol) in THF (10 mL) was added to vigorously stirred ethylene diamine (5 mL) at room temperature under nitrogen atmosphere. After 2 h, the reaction mixture was quenched by addition of water (50 mL), and extracted with hexane (50 mL). The organic layer was washed with brine

(30 mL), dried over anhydrous Na_2SO_4 . The filtrate was concentrated *in vacuo* to give the corresponding diamine derivative **9** (0.198 g, 85%) as a yellow oil: IR (NaCl) 3266 cm^{-1} (N–H), 3299 cm^{-1} (N–H), 1617 cm^{-1} (C=C); ^1H NMR δ 8.84 (s, 1H, ArH), 8.21 (d, $J = 9.0$ Hz, 2H, ArH), 7.33 (dd, $J = 9.0, 5.4$ Hz, 2H, ArH), 7.27 (d, $J = 5.4$ Hz, 2H, ArH), 4.71 (s, 2H, CH_2), 3.27 (d, $J = 7.4$ Hz, 4H, CH_2), 3.13 (dd, $J = 7.2, 14.1$ Hz, 4H, CH_2), 2.95 (t, $J = 5.4$ Hz, 2H, CH_2), 2.85 (t, $J = 5.4$ Hz, 2H, CH_2), 2.0–1.9 (m, 2H, CH), 1.5–1.2 (m, 19H, CH_2 , NH, NH_2), 0.9–0.8 (m, 12H, Me); ^{13}C NMR δ 138.7 (C) 132.6 (C), 130.3 (C), 125.9 (C), 125.9 (C), 125.6 (CH), 122.4 (CH), 119.6 (CH), 53.1 (CH_2), 46.3 (CH_2), 41.8 (CH_2), 39.7 (CH), 38.5 (CH_2), 32.6 (CH_2), 28.9 (CH_2), 25.6 (CH_2), 23.1 (CH_2), 14.0 (CH_3), 10.5 (CH_3). Anal. Calcd. for $\text{C}_{33}\text{H}_{50}\text{N}_2$: C, 83.48; H, 10.62; N, 5.90. Found: C, 83.72; H, 10.31; N, 6.02.

2.2.2. Synthetic procedure for **7**

A solution containing 3,5-bis(2-ethylhexyloxy)benzylamine **6** (1.05 g, 2.89 mmol) and NTCA (0.260 g, 0.969 mmol) in NMP (30 mL) was heated at 110°C with stirring under argon atmosphere. After 3 h, the reaction mixture was cooled to room temperature, quenched by addition of water (50 mL), and then extracted with hexane (50 mL). The organic layer was washed with water (100 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give **7** (0.498 g, 0.519 mmol, 54%) as a yellow solid: IR (NaCl) 3018 cm^{-1} (C–H), 2961 cm^{-1} (C–H), 2928 cm^{-1} (C–H), 1706 cm^{-1} (C=O), 1670 cm^{-1} (C=C); ^1H NMR δ 8.77 (s, 4H, ArH), 6.64 (d, $J = 2.2$ Hz, 4H, ArH), 6.35 (t, $J = 2.2$ Hz, 2H, ArH), 5.31 (s, 4H, CH_2), 3.79 (dd,

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