Subnanometer-sized Gold Clusters with Dual Molecular Receptors: Synthesis and Assembly in One-dimensional Arrangements

Yuichi Negishi,† Hironori Tsunoyama, Yasushi Yanagimoto, and Tatsuya Tsukuda*†
Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science, Myodaiji, Okazaki 444-8585
†Department of Photoscience, School of Advanced Sciences, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193

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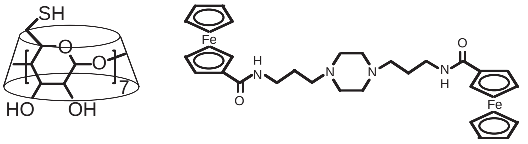
Subnanometer-sized gold clusters protected by thiolated β-cyclodextrin (HS-β-CD) were successfully isolated using polyacrylamide gel electrophoresis. Thermogravimetric measurements reveal that two β-CD ligands are bound to the Au clusters. One-dimensional assemblies of the β-CD-modified gold clusters are formed through binding interactions with ferrocene dimers.

Hybrid systems composed of metal clusters and organic monolayers have attracted considerable attention, because they exhibit novel and tunable physicochemical properties arising from the core-size effect and functionalities of the organic moieties. Among others, metal clusters capped by thiolated cyclodextrins (HS-CD) developed by Kaifer's group are appealing, especially because of the molecular recognition ability of the protecting layers.[1] By utilizing binding interactions between the CD receptors and the complementary guest molecules, large network aggregates of Au:S-CD clusters (>3 nm) have been successfully constructed.[2] However, the clusters were not assembled in well-ordered arrangements in the aggregates, and this was probably due to the large number (ca. 10) of CD receptors.[3] One may anticipate that smaller gold clusters, having a limited number of binding sites, may be assembled in predetermined and low-dimensional patterns. With an aim to develop a fabrication of ordered arrays of clusters and to study their collective properties, we report the preparation of subnanometer-sized gold clusters modified with two thiolated β-CD molecules (**1**; HS-β-CD), in addition to their assembly into one-dimensional arrangements via the interaction with ferrocene dimers (**2**).



1 **2**

Scheme 1. Structures of the compounds used in this work.

The thiolated β-cyclodextrin **1** and ferrocene dimer **2** (Scheme 1) were synthesized by the methods reported previously[2a,4] and characterized by ^{1}H NMR and FAB (Fast atom bombardment) mass spectrometry. The gold clusters protected by thiolated β-CD (Au:S-β-CD) were prepared by reduction of $AuCl_4^-$ with $NaBH_4$ in the presence of **1** in DMSO at ambient temperature:[5] the concentration ratio of $[\mathbf{1}]/[AuCl_4^-]$ was fixed at 1 (see ref 6 for details of the preparation). The ligation of cyclodextrin to the Au core via Au–S binding was confirmed by the absence of the peak at ν(S–H) = 2526 cm^{-1} in the FTIR spectrum of the Au:S-β-CD clusters. Figure 1a shows a representative TEM picture of the as-prepared Au:S-β-CD clusters. The size distribution of the gold cores is presented by a histogram in Figure 1b. Interestingly, the Au:S-β-CD clusters exhibit bimodal core-size distribution centered at ca. 1.0 and 2.4 nm. The smaller Au:S-β-CD clusters (ca. 1 nm), not reported hitherto, are formed preferentially because of the shorter reaction time (2 h)[6] compared with previous studies (24 h).[2] These two components were successfully separated using polyacrylamide gel electrophoresis (PAGE), which has been demonstrated as a powerful technique for the size separation of metal clusters protected by hydrophilic thiolates.[7] The Au:S-β-CD clusters are negatively charged in a buffer solution (pH = 8.3), because some of the secondary hydroxyl groups of the S-β-CD ligands are deprotonated. As a result, the Au:S-β-CD clusters are fractionated using PAGE, into two bands colored yellow and brown (Figure 2a); the clusters contained in these bands are hereafter referred to as **Au-1** and **Au-2**, respectively. The low-mobility clusters **Au-2**

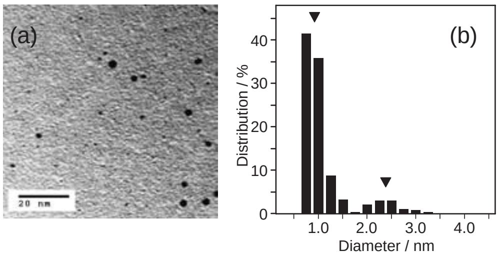


Figure 1. (a) TEM image and (b) size distribution of the as-prepared Au:S-β-CD clusters.

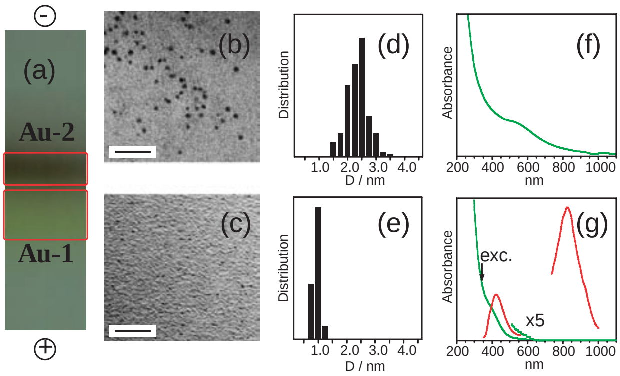


Figure 2. (a) PAGE separation of the as-prepared Au:S-β-CD clusters. TEM images of (b) **Au-2** and (c) **Au-1**. The scale bars represent a length of 20 nm. Size distributions of (d) **Au-2** and (e) **Au-1**. Optical absorption spectra of (f) **Au-2** and (g) **Au-1** (green). Red curves in (g) represent photoemission spectra of **Au-1** excited at 340 nm.

contain Au cores with an average diameter of 2.3 ± 0.4 nm (Figures 2b and 2d). The optical absorption spectrum of **Au-2** exhibits the surface plasmon band peaked at ca. 520 nm, as shown in Figure 2f. The **Au-2** clusters are essentially similar to the Au:S-β-CD clusters reported previously by Kaifer[2,3,5] and Chechik.[8]

In contrast, the Au clusters with a size of ca. 1 nm are barely discernible in the TEM image of the high-mobility clusters **Au-1** (Figure 2c). XPS measurements of **Au-1** show that the small particles in the TEM image are not Au(I)–thiolate complexes, but Au(0) clusters: the Au($4f_{7/2}$) and Au($4f_{5/2}$) peaks were observed at 84.4 and 88.1 eV, respectively. From the TEM image, the average core size is determined to be 1.0 ± 0.2 nm (Figure 2e). However, this value is only regarded as an estimate, owing to the difficulty in determining the core sizes from the poorly contrasted subnanometer-sized clusters in the TEM image. More reliable information for the core size (distribution) of **Au-1** can be derived from a comparison of the optical absorption spectrum (Figure 2g) with those of thiolated Au_n clusters ($n = 10$, 12, 15, 18, 22, 25, 29, 33, and 39).[7d,9] The peak structure at 400 nm suggests that thiolated Au_{12-15} clusters are the main components. The absorption onset at ca. 650 nm suggests the Au_n clusters with sizes up to $n = 22$ are present as minor species. The photoemission observed at 420 and 830 nm, upon photoexcitation at 340 nm (Figure 2g), supports the formation of subnanometer-sized Au clusters.[7d]

The number of S-β-CD ligands attached in **Au-1** is an important quantity to be determined. The chemical compositions of **Au-1** were examined using thermogravimetry (TG). The weight percentage of organics (S-β-CD) and Au were determined to be 51.2 and 48.8%, respectively. This result suggests that two S-β-CD ligands are contained in each cluster, based on the assumption that the gold core is composed of 12–15 atoms. The diameter of the ring formed by the seven sulfur atoms of S-β-CD is ca. 0.8 nm,[4] and this is comparable to the size of the Au core. This implies that two S-β-CD ligands are attached to the Au core so that the hydrophobic cavities are oriented toward opposite sides. To confirm this structural hypothesis, assemblages of **Au-1** and a ferrocene dimer **2** were prepared as follows. Addition of an aqueous solution of **Au-1** (0.1 mM, 10 mL) on top of a CH_2Cl_2 solution of **2** (0.1 mM, 10 mL) caused the complete bleach of the aqueous phase and formation of a transparent film at the biphasic interface within 15 min. In the TEM images of the film (See: Supporting Information), one-dimensional arrays of **Au-1** with the interparticle distances of ca. 2 nm are frequently observed (Figure 3). We believe that these structures are formed as a result of a host–guest interaction between the two S-β-CD receptors of **Au-1** and **2**, because the interparticle distances are comparable to the length of **2** (ca. 1.7 nm) and such structures are rarely observed in TEM images of **Au-1** in the absence of **2** (Figure 2c). On the basis of on these results, it was concluded that **Au-1** is composed of Au_{12-15} clusters capped by two S-β-CD ligands. The results given in Figure 3 clearly show that protection with small numbers of S-CD ligands is a promising method to assemble clusters in low-dimensional arrangements without using a template.[10]

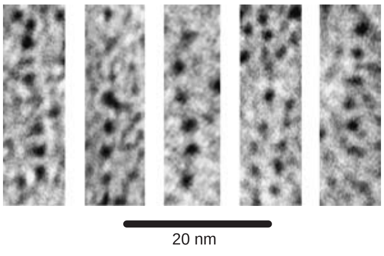


Figure 3. Portions of TEM images of the film formed at the biphasic interface in the reactions of **Au-1** and **2**.

Finally, we offer a discussion for the reason why a bimodal distribution of the gold cores was observed for the Au:S-β-CD clusters. It was found that the Au:S-β-CD clusters with core diameter dimensions between those of **Au-1** and **Au-2** could not be prepared, even when preparative conditions such as the [**1**]/[$AuCl_4^-$] ratio and the reaction temperature were changed. This implies that the Au clusters missing from this size region cannot be stabilized by HS-β-CD ligands. The seven thiol groups of **1** aligned in a ring with a diameter of ca. 0.8 nm cannot bind to small facets of the gold nanocrystals. Thus, our interpretation is that the gold clusters with a core size of 2.3 nm are the smallest clusters whose facets are strongly ligated. On the other hand, when the core size is reduced to ca. 0.8 nm, two HS-β-CDs can be bound to the equatorial areas of the clusters in order to stabilize them.

To summarize, subnanometer-sized gold clusters protected by two thiolated β-cyclodextrin ligands were synthesized. These Au:S-β-CD clusters can be arranged in one-dimensional arrays via binding interaction with a ferrocene dimer. By use of tailor-made molecules as linkers, the Au:S-β-CD clusters would be assembled in well-ordered arrangements with desired symmetry and interparticle distance.

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6 The HS-β-CD (0.75 mmol) was added to the DMSO solution (150 mL) of $HAuCl_4$ (0.75 mmol). Then, the DMSO solution of $NaBH_4$ (7.5 mmol, 30 mL) was injected rapidly into this mixture under vigorous stirring. After the reaction for 2 h, 150 mL of acetone was added to precipitate the CD modified gold clusters, which were collected by centrifugation (4000 g). The precipitate was redissolved in water (40 mL) and washed by centrifugal ultrafiltration (14000 g) twice to remove small impurities; a filter with cutoff molecular weight of 5 kDa was used. Finally, the precipitate was dried in vacuo to obtain the CD-modified gold clusters as a bright-brown powder.

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