Synthesis of DPA dendron encapsulated gold clusters with metal-assembling function

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Abstract

Gold clusters modified with first, second and third generation dendritic polyphenylazomethines (DPA) were synthesized by an exchanged reaction of corresponding DPA dendron thiols. Measurements by high performance perfect sizer (HPPS) and TEM reveal that their diameters increase with a change in the chain length of the modifying molecules from the first to third generation. These gold clusters with DPA dendrons exhibit coordination quantitatively to metal ions such as Fe³⁺, Sn²⁺, etc., because of their imine groups; this then resulted in self-aggregation to form a large sphere.

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1. Introduction

Dendrimer, a monodispersed high-ordered branched macromolecule with an unusual tree-like topology, is widely interesting as a new nano-material [1]. Some with multiple coordination sites have been utilized to coordinate metal ions and synthesize metal clusters [2]. We reported the synthesis of π-conjugated dendritic polyphenylazomethines (DPA) with multiple imine groups with an increasing geometric series and found that this dendrimer structure can stepwise complex metal ions, such as Sn²⁺ and Fe³⁺, etc. at the imine groups from internal to outer generation because of a gradient in the electron density associated with the imine groups [3]. This is of interest for electron and energy transfers, especially in bio-systems [4]. Because of the gradient in the electron density, it is possible to control the number and the type of metal ions complexed in an additional generation dendrimer. The coordinate sites increase with the number of the generations, but a multi-generation dendrimer with more coordinate sites is rarely synthesized. Therefore, we choose gold clusters as a core to prepare a dendrimer with more coordinate sites than even a multi-generation dendrimer because a gold cluster core can load dozens of ligands. The combination of dendrimer and gold clusters will produce a new model of nano-particles, a true spherical dendrimer with more dendron units.

On the other hand, gold clusters are the most stable metal nano-particles and a topic in both basic research and applied field of nano-technology because of their unusual quantum size effect [5]. A number of functional groups have been utilized to modify gold clusters and above broaden the application of the gold clusters [6]. They not only preserve the intrinsic properties of gold clusters but also hold some new function from the modifying groups. In this report, we describe the synthesis of gold clusters that coordinate metal ions (Scheme 1). In addition, metal ion assembling is expected to result in tuning the function of the gold clusters through the change of the electronic state.

2. Experimental procedure

2.1. Materials

All solvents and chemicals were purchased from Kanto Kagaku Corporation, and used directly without further purification. Octanethiol-modified gold clusters (Au-OT) [7] and first, second and third generation DPA dendrons [3a] were prepared by a literature method. The other products and intermediate products were synthesized by slightly modified literature means.
2.2. Synthesis of 4-nitrophenylhexanethiol

4-Bromo-nitrobenzene (2.09 g, 10.3 mmol) and 1,6-hexanethiol (3.90 g, 26.0 mmol) were mixed with NaH (60% dispersed in paraffin liquid, 2.08 g, 52 mmol) in dehydrated THF (200 ml). The mixture was stirred for 6 h at room temperature, and poured into ice-water (200 ml) and acidified (pH 4, HCl). The solution was extracted with ether (4×100 ml), and the organic layer was washed with water and dried with over Na₂SO₄. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to give a yellow oil (0.930 g) in 33.3% yield. ¹H NMR (CDCl₃, 270 MHz) δ (ppm): 8.11 (m, 2H), 7.31 (m, 2H), 3.04 (m, 2H), 2.54 (m, 2H), 1.3–1.8 (m, 9H). TOF-Mass: 269.9 (M–1, 270.4).

2.3. Synthesis of 4-aminophenylthiohexanethiol

The powdered tin (1.00 g, 8.42 mmol) and concentrated HCl was successively added into the solution of 4-nitrophenylhexanethiol (0.30 g, 1.10 mmol) in ethanol (10 ml) in an ice-water bath. The mixture was stirred for 30 min. NaHCO₃ was employed to adjust the pH value of the solution to 4. The solution was extracted with chloroform (3×50 ml). The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to give a yellow oil (140 mg) with a yield of 52.7%. ¹H NMR (CDCl₃, 270 MHz) δ (ppm): 7.23 (m, 2H), 6.59 (m, 2H), 3.60 (s, 2H), 2.70 (m, 2H), 2.51 (m, 2H), 1.3–1.8 (m, 9H). MALDI-TOF-Mass: 241.20 (M, 241.40).

2.4. Synthesis of the G2-dendron-thiol [3a]

The G2-dendron (0.32 g, 0.59 mmol), 4-aminophenylthiohexanethiol (140 mg, 0.58 mmol), and 1,4-diazabicyclo[2.2.2]-octane (DABCO) (0.67 g, 6.0 mmol) were dissolved in chlorobenzene (15 ml). Titanium(IV) chloride (0.28 mg, 1.5 mmol) in chlorobenzene (2 ml) was added dropwise. The mixture was heated in an oil bath at 125 °C for 5 h. The precipitate was removed by filtration and the filtrate was concentrated. The G2-dendron-thiol (yellow solid, 81 mg, 18.3%) was isolated by silica gel column chromatography (chloroform:ethyl acetate=5:10:1). ¹H NMR (400 Hz, CDCl₃) δ (ppm): 7.74 (m, J = 7.2 Hz, 4H), 7.48 (m, J = 5.6 Hz, 4H), 7.43 (m, J = 6.4 Hz, 4H), 7.28 (m, J = 6.0 Hz, 8H), 7.15 (d, J = 6.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 6.8 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.54 (m, J = 4.0 Hz, 4H), 2.84 (t, J = 7.2 Hz, 2H), 2.51 (dd, J = 6.8 Hz, 2H), 1.6 (m, 4H), 1.40 (m, 4H), 1.31 (t, J = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.37, 168.00, 153.56, 151.66, 149.98, 139.08, 135.81, 135.65, 134.45, 130.88, 130.78, 130.58, 130.05, 129.92, 129.65, 129.36, 129.28, 128.76, 128.69, 128.16, 127.98, 127.78, 121.87, 120.47, 120.23, 34.82, 33.88, 29.15, 28.21, 27.94, 24.58, MALDI-TOF-Mass: 764.3 (calcd M⁺, 764.1).

2.5. Synthesis of the G1-dendron-thiol [3a]

The G1-dendron-thiol was synthesized by the same method as that above with a yield of 36.8%. ¹H NMR (270 MHz, CDCl₃) δ (ppm): 7.73 (d, J = 6.4 Hz, 2H), 7.43 (m, 3H), 7.27 (m, 3H), 7.11 (t, J = 8.2 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H). ¹³C NMR (67.8 MHz, CDCl₃) δ (ppm): 130.68, 130.44, 129.40, 129.21, 128.57, 128.10, 127.88, 121.61, 34.62, 33.86, 29.02, 28.16, 27.94, 24.62, MALDI-TOF-Mass: 404.3 (calcd, M–1, 404.6).

2.6. Synthesis of the G3-dendron-thiol [3a]

The G3-dendron-thiol was synthesized by the same method as that above with a yield of 8.5%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.74 (m, 8H), 7.35–7.50 (m, 18H), 7.38 (m, 6H), 7.21 (m, 4H), 7.14 (m, 8H), 7.01 (m, 4H), 6.85 (t, J = 7.6 Hz, 4H), 6.79 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.4 Hz, 4H), 6.64 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 8.0 Hz, 4H), 6.50 (d, J = 8.8 Hz, 2H), 2.77 (t, J = 7.0 Hz, 2H), 2.45 (d, J = 7.2 Hz, 2H), 1.4–1.6 (m, 4H), 1.2–1.4 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.80, 168.40, 168.18, 168.11, 167.79, 154.02, 152.00, 151.85, 149.98, 139.25, 139.06, 135.79, 135.59, 134.01, 130.88, 130.60, 130.37, 130.32, 130.18, 130.11, 130.04, 129.95, 129.36, 128.79, 128.72, 128.68, 128.16, 127.99, 127.82, 122.06, 120.80, 120.48, 120.24, 120.00, 34.61, 33.85, 29.00, 28.16, 27.92, 24.58. MALDI-TOF-Mass: 1479.3 (calcd M–1, 1479.8).

2.7. Synthesis of the dendron modified gold clusters

These clusters were synthesized by exchange reaction. Briefly, G2-dendron-thiol (G2-SH, 25.5 mg, 39.4 mmol) and Au-OT (39.2 mg, 0.525 mmol) were mixed in 15 ml toluene and stirred for 48 h. The solution was concentrated and kept under 0 °C after adding 10 times the amount of methanol. A precipitate was isolated as a black product, G2-dendron-thiol modified gold clusters (Au-G2). Yield: 42.5 mg, 89.87%. Similarly, the yields were 91.32% for Au-G1, and 90.21% for Au-G3. Their ¹H NMR spectra exhibited broad peaks at the same positions as those of corresponding dendron-thiols.
2.8. Measurements

NMR and UV–vis spectra were collected with a JEOL EX270 and a JEOL EX400 spectrometer, and a SIMAZU PC-2400, respectively. TEM image recorded on a FE-TEM TECNAIF20. The size dispersions of gold clusters were measured with a HPPS. The TOF-Mass of products were identified on.

3. Results and discussion

3.1. Synthesis of DPA dendron modified gold clusters

We have tried to synthesize DPA modified gold clusters directly by the Brust’s method through the reductive reaction of HAuCl₄ in the presence of a dendron-thiol and tetraoctylamine bromide, but have not obtained the proposed products because of a reduction of the imine of the DPA dendron by gold complexing catalysis. Therefore, the exchange reaction as a substitute was used to synthesize the DPA dendron-modified gold clusters. Gold clusters with first, or second or third generation DPA dendrons were prepared through exchange of the octanethiolate of Au-OT with first, or second or third generation DPA dendrons.

Field emission transmission electron microscope (FE-TEM) images of the Au-OT clusters prepared here determined that the average core diameter of the gold clusters was 2.2 nm corresponding to 309 Au atoms with a cuboctan-hedron core shape bearing approximately 95 octanethiolate chains on one clusters [11]. The core diameters of the dendron-modified gold
clusters were estimated to be the same as that of Au-OT based on their FE-TEM images, which suggests that the modification of the functional molecule does not change the structure of the core of the gold clusters (Figs. 1–4). The core diameter combines the length of the chain of the modified molecule outside the core (evaluated by ChemDraw simulation) to give the entire diameter of gold clusters summarized in Table 1. We also used high performance particle sizer (HPPS) to measure the entire diameters of all clusters as shown in Fig. 5. The values from the two measurements are in agreement (Table 1) and increase with a change of the chain lengths of substituent groups from octanethiolate, G1-, G2- to G3-thiolate. The data prove that functional molecules have modified gold clusters. Their $^1$H NMR spectra also support the results (vide infra).

### Table 1

| Clusters | Constitution | Diameter (nm)  |
|----------|--------------|----------------|
|          | TEM          | HPPS           |
| Au-OT    | Au$_{109}$(C$_8$H$_{17}$S)$_{95}$ | 4.2 | 4.0 |
| Au-G1    | Au$_{109}$(C$_8$H$_{17}$S)$_{68.5}$(G1)$_{26.5}$ | 6.4 | 6.2 |
| Au-G2    | Au$_{109}$(C$_8$H$_{17}$S)$_{70}$(G2)$_{25}$ | 6.8 | 6.7 |
| Au-G3    | Au$_{109}$(C$_8$H$_{17}$S)$_{74}$(G3)$_{21}$ | 7.2 | 7.1 |

In the $^1$H NMR spectrum of Au-G3, the signals of the dendron-phenyl appeared at $d$ 6.4–7.8 with broad peaks at the same position as that of the corresponding free G3-dendron-thiol molecule. The signal of the methyl of the octanethiolate appeared at $d$ 0.9, which suggests that the G3-dendron-thiol is attached to the gold clusters. According to the ratio of the peak integrals between the dendron-phenyl and the methyl of the octanethiolate, we evaluated the exchanged number of the DPA dendron-thiolate to be 21. The same calculations for Au-G2 and Au-G1 gave the number of exchanged DPA dendron-thiolsates as 25 and 26.5, respectively.

### 3.2. Metal-assembling on gold clusters

The optical properties of these gold clusters with dendrons were investigated by using UV–vis spectroscopy. In Fig. 6, the UV–vis absorption spectrum of the Au-G3 clusters shows intense bands at 284 and 359 nm and a weak broad band at 525 nm due to the surface plasmon. A brown chloroform–acetonitrile solution of the Au-G3 clusters changes to yellow upon the addition of FeCl$_3$, while the bands at 290 and 360 nm decrease in intensity and a new peak appears at 420 nm and increases. In addition, when monitoring the change of the absorbance of the solution at 500 nm (Fig. 6 inset), we found that the absorbance converged at 8 equiv. of FeCl$_3$ added.
which is equal to the sum of the nitrogen atoms and sulfur atom of the benzylthio group in one cluster. These changes are attributed to a quantitative complexation of Fe$^{3+}$ on the nitrogen atoms of the imine groups and the sulfur atom of the benzylthio group of the modified dendrons. The Au-G3 clusters also show quantitative complexation with other metal ions such as Sn$^{2+}$ and Au$^{3+}$.

We reported similar spectral changes by the corresponding dendrimers with titration of FeCl$_3$ or SnCl$_2$, which results from the stepwise coordination of metal ions from the core to outer shell [12]. Whereas, for the gold cluster Au-G3 we have not observed the same stepwise coordination of metal ions as the corresponding DPA dendrimer, though the complexation of metal ion in gold clusters with dendrons proceeds quantitatively similar to the previously reported manner. Perhaps, this is due to the electrostatic field outside of the gold clusters resulting from the charges absorbed around the gold clusters [13], which affect the distribution of electron density of the imine groups along the entire molecule. Anyway, we could prepare the gold cluster modified DPA dendron with a metal-assembling function as an advanced nano-material (Scheme 2).

3.3. Assembling structure of Au cluster

In fact, the stable existence of gold clusters is partially due to repulsion among the gold clusters with the same charge. An FE-TEM image of Au-G2 complexed with SnCl$_2$ (Fig. 9) shows large spheres different from that of the free Au-G2. According to the enlarged image of a ball, all of the spheres are assembled aggregates of a number of gold clusters. On the basis of the previous reported results [14], we assumed that the change on the surface charges of the gold clusters results in the aggregation of the gold clusters.
4. Conclusion

We succeeded in synthesizing gold clusters modified with first, second and third DPA dendrons, and demonstrated their quantitative assembly with metal ions. The assembly resulted in the aggregation of the gold clusters. The model provides a new method to adjust the properties of metal clusters through complexation of metal ions.

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