

# Formation of Dendrimer-like Gold Nanoparticle Assemblies

Shufeng Pang, Takeshi Kondo, and Takeshi Kawai\*

Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo, Japan

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Dentritic microstructures formed by gold nanoparticles have been fabricated by a wet-chemical protocol.  $\text{HAuCl}_4$  was reduced in an aqueous surfactant solution of 3-heptadecafluorooctylsulfonylamino-propyltrimethylammonium iodide ( $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{NH}-(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3\text{I}^-$ , HFOTAI) and the solution was allowed to stand for different time periods (incubation times), including very long periods of up to over 50 days at room temperature. The dendrimer structures were found to depend on the concentration of HFOTAI and the incubation time.

## Introduction

A significant challenge faced in material synthesis and device fabrication is the development of methods to organize interconnecting and patterned assemblies of individual components at all dimensions, from the nanoscale to the macroscale. Many attempts have been made to assemble nanostructures and to study their properties.<sup>1–3</sup> Significant success has been achieved based on different driving mechanisms<sup>4–10</sup> including using conventional lithographic processes,<sup>11</sup> nanoscale template approaches<sup>12</sup> and LB techniques.<sup>13</sup> For example, Hutchison et al. have reported the linear assembly of gold nanoparticles on a DNA scaffold.<sup>14</sup> Mitov et al.<sup>15</sup> have achieved success in assembling platinum nanoparticles into periodic ribbons by mimicking the well-known “fingerprint” cholesteric texture. Furthermore, special nano-architectures such as nanocombs, nanowindmills and nanotetrapods have recently been reported.<sup>16–18</sup>

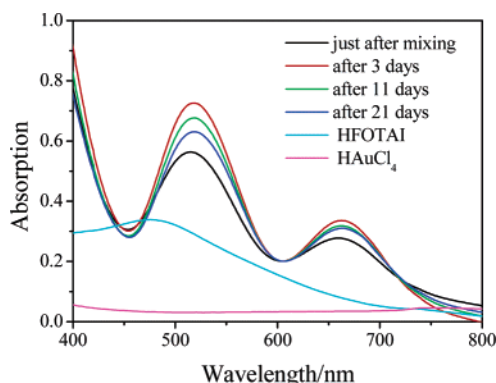
In addition, despite some degree of success in aligning nanowires and patterning them into novel meso-scale structures, such as, dandelions,<sup>19</sup> snowflakes,<sup>20</sup> nanoflowers<sup>21</sup> and tubular metal–polymer assemblies,<sup>22</sup> attempts at spontaneously assembling nanoparticles into novel mesostructures have been met only with limited success. Except for long-range linear Au assemblies directed by templates<sup>14,15,23,24</sup> and ordered 2D superlattices,<sup>25</sup> there are very few reports of special meso-architectures using gold nanoparticles as building blocks.<sup>26</sup> Esumi et al. and other groups have used dendrimer compounds as reducing agent and template to get dendrimer nanostructure, however the generation of aimed dendrimer is very low.<sup>27</sup> In this study, we demonstrate a facile wet-chemical method for the synthesis of dendrimer-like structures that are spontaneously assembled using Au nanoparticles by a one-pot route, wherein a novel surfactant solution of  $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{NH}-(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3\text{I}^-$  (HFOTAI), is used not only as a reducing agent, but also as an assembling agent. We have also examined the effects of varying the incubation time and the  $\text{HAuCl}_4$ :HFOTAI ratio on the organization of the dendrimer-like structures.

## Experimental Section

**Materials.** Hydrogen tetrachloroaurate(III) tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  99.99%, Adrich), 3-heptadecafluorooctylsulfonylamino-propyltrimethylammonium iodide (HFOTAI, Adrich) were used as received without further purification. Deionized water was doubly distilled throughout the experiments.

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**Figure 1.** UV-vis spectra of the reaction solution for different incubation times by the reaction of 50 mL of 0.48 mM  $\text{HAuCl}_4$  with 11.4 mg HFO-TAI.

**Synthesis.** In a typical procedure, 4.6–18.6 mg of HFO-TAI was added to a 0.48 mM aqueous solution of  $\text{HAuCl}_4$  (50 mL), and the mixture was stirred for ca. 30 min. The solution was allowed to stand for up to 60 days or more at room temperature (this standing time is termed the “incubation time”).

**Measurements.** Transmission electron microscope (TEM) samples were prepared by placing a drop of the solution on a 400-mesh, carbon-covered, copper TEM grid and then drawing off the excess solution using lint-free paper. The sample grids were examined using an H-9000 transmission electron microscope (HITACHI) operating at 200 kV. The composition of the products was determined by energy-dispersive X-ray analysis in a scanning electron microscope, SEM-EDX (HITACHI, S-5000). The powder samples for XRD and FT-IR measurements were obtained by centrifuging the solution of the products. The precipitates were washed with water thrice before being examined. A Rigaku RINT-2000 instrument and a Nicolet 510M instrument were used for the XRD and FT-IR measurements, respectively.

## Results

The addition of HFO-TAI to the aqueous solution of  $\text{HAuCl}_4$  caused an immediate color change from yellow to red. Figure 1 shows the UV-vis spectra of the mixture of HFO-TAI and  $\text{HAuCl}_4$  solution as a function of reaction time (incubation time). In the spectra of the mixed solution of HFO-TAI and  $\text{HAuCl}_4$ , new bands at 520 and 670 nm appeared. These band intensities increased for early incubation times, but they decreased after 3 days due to the sedimentation of the products. The band at 520 nm can be attributed to the surface plasmon band of Au particles.<sup>28</sup> The band at 670 nm is probably due to aggregated particles and/or larger particles of Au.<sup>28</sup> Thus, the UV-vis spectra indicate that Au particles were formed by the reaction of  $\text{HAuCl}_4$  with HFO-TAI, though the details of the chemical reaction of HFO-TAI are still unknown. The formation of Au particles

was also confirmed by the XRD patterns of the precipitates of the products, for which the [111] and [200] diffraction peaks of a Au crystal were observed at  $38.0^\circ$  and  $44.2^\circ$ , respectively.<sup>29</sup>

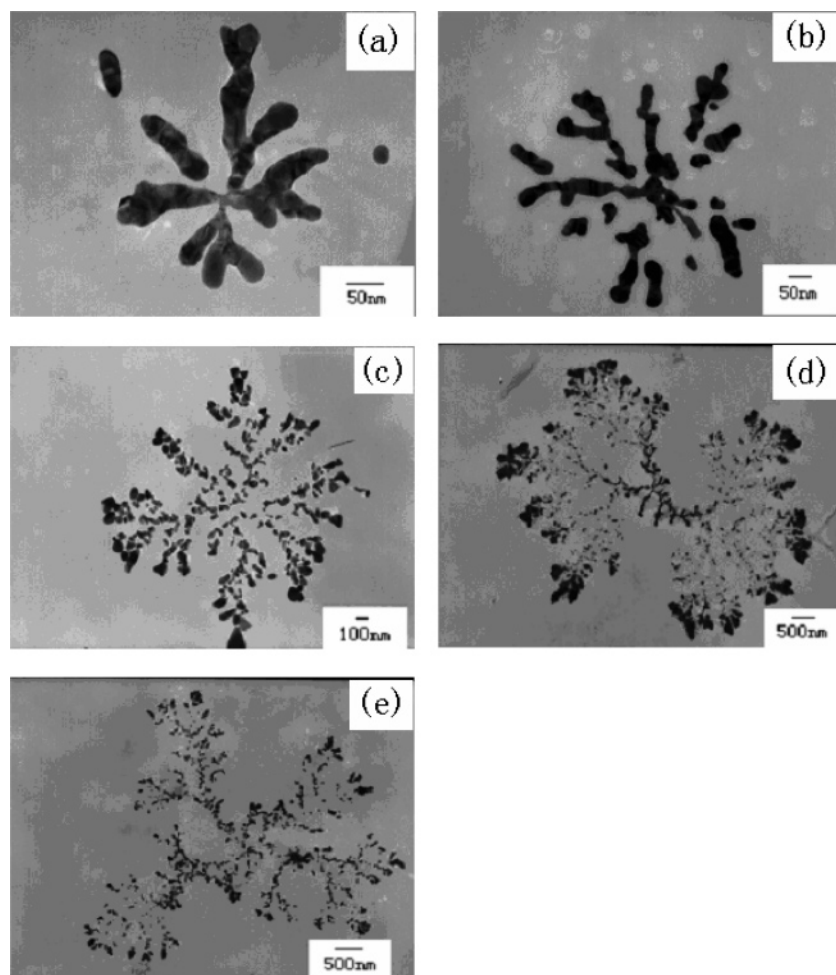
**Influence of Concentration of HFO-TAI on the Morphologies of Au Assemblies.** TEM and SEM observations of the products revealed the morphology of the Au particles. Interestingly, the products for an incubation time of a few weeks assembled into dendritic structures and the dendrimers on copper mesh did not change their shape after 1–2 months. Figure 2 shows the evolved dendritic assemblies obtained for various concentrations of HFO-TAI. Figure 3 shows enlarged TEM images of typical particles as building blocks. It can be seen that particles with various shapes and sizes were included in the present architecture. With increasing concentration of HFO-TAI, the number of branches and the size of each branch increased, and an interconnected dendrimer structure was formed (Figure 2 d,e). In addition, at higher concentrations, another significant feature is the larger particle size at the outer edges of the assemblies (Figure 2c–e). The particles at the outer edges were in contact with each other (Figure 3a,b) but were not in contact in the center of the assemblies (Figure 3c,d).

To confirm that the dendrimer assembly was organized by Au particles, we performed SEM-EDX analysis by using the  $\text{M}\alpha$  line of Au (2.121 keV). Figure 4 shows the normal SEM micrograph (Figure 4a) and the associated EDX image (Figure 4b) of the corresponding area. Although the spatial resolution of the latter is not very good, the EDX image is in agreement with the SEM image. Thus, it is reasonable to conclude that the dendritic assemblies are made of Au particles.

**Evolution of Dendrimer-like Assemblies.** Figures 5 and 6 demonstrate the representative evolution process of the Au nanoparticle assemblies at  $[\text{HFO-TAI}] = 4.6$  mg and 15.0 mg, respectively. For the lower concentration of  $[\text{HFO-TAI}] = 4.6$  mg, spherical nanoparticles with an average size of ca. 12 nm were present (Figure 5a) for a short incubation time. After one week, a satellite-like assembly was formed in which a larger gold nanoparticle (ca. 30 nm diameter) was surrounded by a few small particles as shown in Figure 5b. Furthermore, branched assemblies (Figure 5c) composed of large and various shapes of gold particles were formed after one month. Interestingly, after 50 days, there were no branched assemblies, but only isolated particles with diameters of ca. 40 nm (Figure 5d). For the system with a higher concentration of HFO-TAI, spherical nanoparticles were produced within a short incubation time, such as the system of  $[\text{HFO-TAI}] = 4.6$  mg in Figure 5a. After 20 days, branched assemblies (Figure 6a) appeared. The assemblies became more complex structures with increased incubation times and then formed interconnected dendrimers (Figs. 6b – 6d). In addition, the size of the dendrimers increased from several hundreds of nanometer to several micrometers, while the particle size at the outer edges of the assemblies became larger than the particle size at the center. After 90 days, the evolved dendritic assemblies in Figure 6d were broken into

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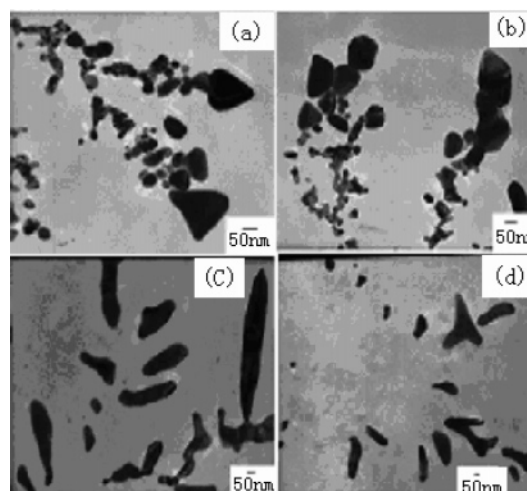
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**Figure 2.** Evolved dendrimers obtained by the reaction of 50 mL of 0.48 mM  $\text{HAuCl}_4$  with different amounts of HFOTAI. (a) 4.6 mg at 30 days (b) 7.4 mg at 35 days (c) 11.4 mg at 40 days (d) 15.0 mg at 45 days (e) 18.6 mg at 50 days. small particles (such as Figure 5d) in the end.

### Discussion

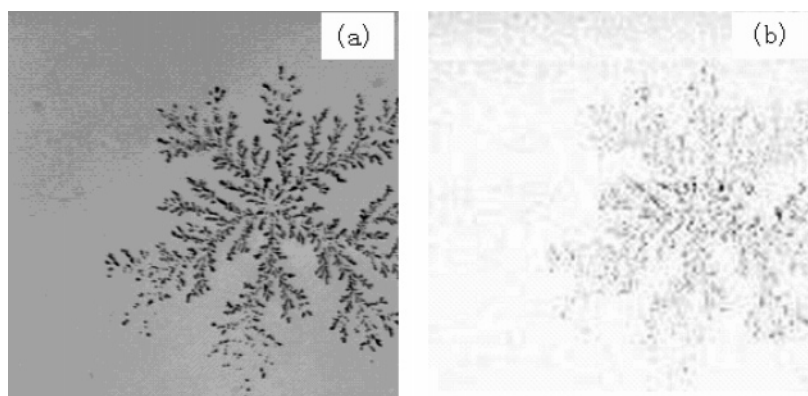
By comparing Figures 2 and 6, it is found that the structures of the assemblies in the course of the microstructural evolution are similar to those of the evolved assemblies of lower HFOTAI concentrations. For example, the assembly structure of  $[\text{HFOTAI}] = 15.0$  mg at 20 days (Figure 6a) and 50 days (Figure 6c) are similar to those of  $[\text{HFOTAI}] = 7.4$  mg (Figure 2b) and  $[\text{HFOTAI}] = 11.4$  mg (Figure 2c), respectively. To examine the effect of the concentration of HFOTAI on the evolution process of the gold assembly in detail, we observed the evolution process of the dendritic assemblies within the concentration range of HFOTAI from 4.6 mg to 18.6 mg. Figure 7 shows a schematic illustration of the evolution process estimated from the experimental results. For the whole concentration (from  $[\text{HFOTAI}] = 4.6$  mg to  $[\text{HFOTAI}] = 18.6$  mg) of HFOTAI, Au particles only exist in the early stages and in the final stages of the evolution process. The structures of the assemblies at high concentrations of HFOTAI for short incubation times are similar to those of the evolved assemblies for lower concentrations of HFOTAI for longer incubation times. In other words, the assemblies for higher concentrations in the evolution process follow the evolved assemblies produced at lower concentrations. In addition, the formation rate of a younger assembly increases with increasing concentration of HFOTAI.



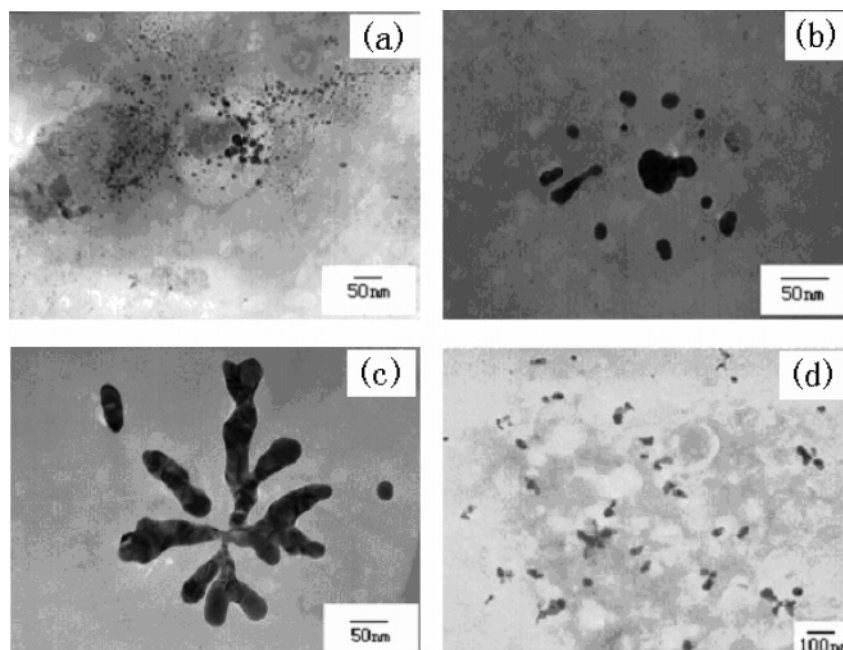
**Figure 3.** Representative areas of the Au assemblies for 11.4 mg HFOTAI at 40 days.

The very slow evolution process of the assemblies shows that the supply of gold is constant for a long time. Possible sources of the gold are (a) the reduction product of  $\text{HAuCl}_4$  and (b) gold nanoparticles produced during the early period evolution. The possibility of the former is not high, because the band intensity of  $\text{HAuCl}_4$  at 220 nm in the UV-Vis spectra almost disappeared within one week for  $[\text{HFOTAI}] = 4.6$  and 7.4 mg. Unfortunately, for  $[\text{HFOTAI}] > 11.4$  mg,





**Figure 4.** (a) SEM micrograph of the Au assembly, and (b) the corresponding EDX mapping.



**Figure 5.** The growth process of simple dendrimers ([HFOTAI] = 4.6 mg) for different incubation times. (a) Within 24 h, (b) after one week, (c) after one month, and (d) after 50 days.

it is difficult to determine the amounts of  $\text{HAuCl}_4$  because the HFOTAI band and the 220 nm band of  $\text{HAuCl}_4$  overlap. On the other hand, Cheng et al.<sup>30</sup> have reported that the development of gold particles, such as by fusion, fragmentation and aggregation, is enhanced by the presence of iodine ions. They suggested the existence of a water-soluble gold-iodide/iodine species. In the present system, iodine ions, which are the counterions of HFOTAI, probably affect the evolution of the Au nanoparticles. That is, the iodine ions enhance the rate of the Ostwald ripening process (i.e. change of atomic gold between particles). Thus, a selected gold particle or assembly grows due to the supply of atomic gold generated by the slow reduction of  $\text{HAuCl}_4$  and/or gold nanoparticles produced in a short incubation time.

Dendritic crystal growth has been observed under various conditions such as electrodeposition,<sup>31</sup> dielectric breakdown<sup>32</sup> and viscous fingering instability.<sup>33</sup> Leontidis et al.<sup>34</sup>

have showed that dendritic assemblies of gold were obtained by the photochemical reduction of  $\text{HAuCl}_4$  in an aqueous solution of a cationic surfactant and NaCl. Wang et al.<sup>35</sup> have prepared dendritic patterns of Ag by the  $\gamma$ -irradiation on  $\text{AgNO}_3$  dissolved in deionized water. The formation of these dendritic assemblies were explained by diffusion-limited aggregation (DLA).<sup>35</sup> In the DLA model,<sup>36</sup> aggregates are formed by the adhesion of a particle by a random walk process to a selected seed on contact. Thus, there should be continuity in one aggregate produced. The gold branches in the present assemblies, however, did not connect among themselves but were formed in isolation (as shown in Figure 3c, d). Thus, the formation process of the present dendritic assemblies cannot be explained by the DLA of gold.

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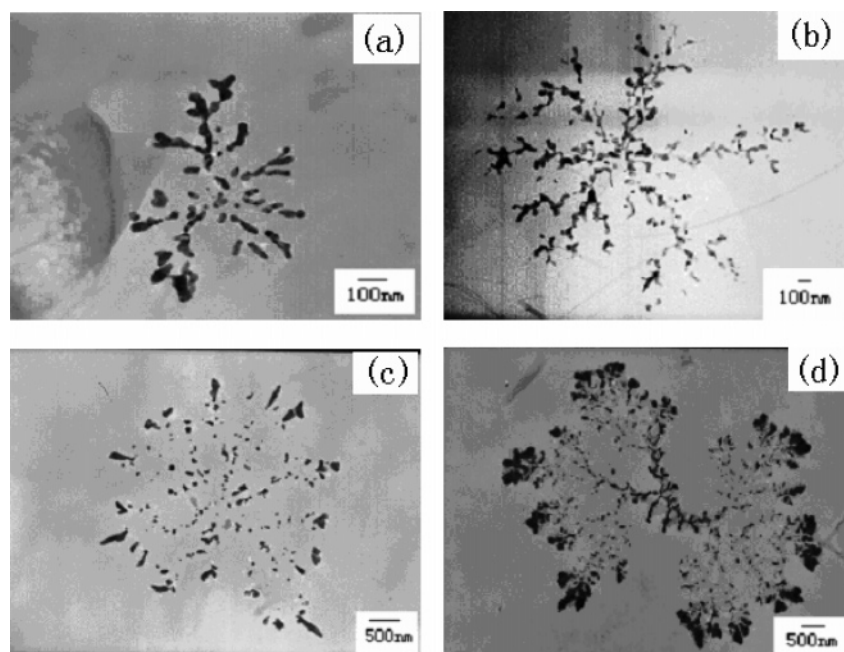
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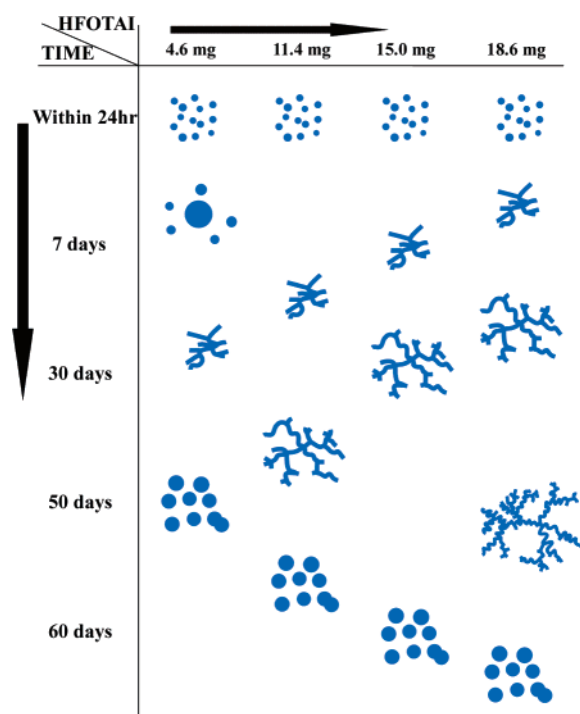
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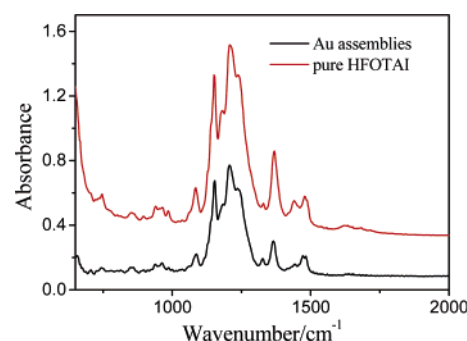


**Figure 6.** The growth process of simple dendrimers ([HFOTAI] = 15.0 mg) with different incubation times of (a) 20 days (b) 40 days, (c) 50 days and (d) 55 days.



**Figure 7.** The schematic illustration of the microstructural evolution process for various HFOTAI concentrations.

An important factor for the possible explanation of the dendritic assembly formation is the role of HFOTAI. TEM observations confirmed that HFOTAI formed vesicles in an aqueous solution. Since, in the mixture solution of  $\text{HAuCl}_4$  and HFOTAI, surfactant assemblies of HFOTAI were not observed in TEM micrographs, HFOTAI molecules probably interacted with the Au particles. We then measured the infrared spectra of centrifuged products (centrifugation and washing over 3 times). Figure 8 shows the IR spectra of the centrifuged products and pure HFOTAI. It can be seen that the characterized peaks of HFOTAI are well matched for



**Figure 8.** IR spectra of Au nanoparticle-assemblies and pure HFOTAI.

both spectra. This result indicates that the Au particles are covered with HFOTAI molecules and that the dendritic assemblies consist of Au particles and HFOTAI. Thus, HFOTAI molecules probably serve as a binder of the Au particles. However, further work is required to fully understand the assembly mechanism of the Au particles.

In addition, we have tried to add gold nanoparticles into an aqueous solution of HFOTAI under the same conditions used in the study, including HFOTAI concentrations and temperature. The gold nanoparticles were prepared by the traditional sodium citrate reduction method, wherein the gold nanoparticles were covered by citrate ions. The resulting product was not dendritic assemblies of Au particles but larger spherical and cubic particles. In conclusion, HFOTAI molecules covering the gold particles play an important role for the formation of the dendritic assembly structures observed in the present study.

## Conclusion

In summary, the complex dendrimer-like gold assembly was spontaneously formed. The present work opens the door

for the assembly of particles for architectures ranging from the nanoscale to the microscale via the wetting method. The assembly mechanism still needs to be understood to be able to tailor more elaborate structures. These assemblies have great potential for even larger structures and for utilization as engineered materials.

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