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Network Aggregates Formed by C_{60} and Gold Nanoparticles Capped with γ-Cyclodextrin Hosts

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ABSTRACT

Water-soluble gold nanoparticles (3.2 nm diameter) capped with thiolated γ-cyclodextrin hosts form large network aggregates (∼300 nm) in the presence of C_{60} fullerene molecules. This aggregation phenomenon is driven by the formation of inclusion complexes between two cyclodextrins—attached to different nanoparticles—and one molecule of C_{60}.

Research work on metal and semiconductor nanoparticles has flourished in the past few years, partially as a consequence of the development of methods to control particle size and to stabilize the particles in solution.[1] Considerable interest focuses on the possibility of nanoparticle assembly because of potential applications for electronic circuit components of extraordinarily high integration.[2] Several groups[3,4] are actively working on the modification of metal nanoparticle surfaces with synthetic receptors or substrates in order to use well-known molecular recognition interactions to drive and control particle assembly. We have recently reported on the modification of gold,[5,6] platinum,[7] and palladium[7] nanoparticles with cyclodextrin (CD) receptors. This research program[8] is geared toward the preparation of nanoparticles whose properties can be controlled via molecular recognition, using the well-known host properties of the CDs.[9] These receptors form inclusion complexes with many organic substrates in aqueous solution. A very relevant case for the work presented here is the stable 2:1 complex formed by γ-CD with C_{60}.[10] In this communication, we describe the formation of large network aggregates composed of gold nanoparticles bearing surface-immobilized γ-CD hosts whose assembly is driven by C_{60} molecules, acting as noncovalent molecular linkers between the nanoparticles.

The preparation of gold nanoparticles (2−7 nm in diameter) capped with CDs has been described in detail.[6] In this work, we have used a slightly modified version of our published procedure which we have found more effective to remove residual ionic species from the surface of the gold nanoparticles (see Supporting Information). The resulting γ-CD-modified gold nanoparticles can be isolated as a deep brown solid and are very soluble in water, where they remain dissolved without any apparent aggregation or precipitation for periods of time as long as several weeks. Figure 1 shows the ^{1}H NMR spectra (in D_2O, 400 MHz) of free γ-CD and γ-CD-capped gold nanoparticles. These data afford unequivocal evidence for the surface attachment of the CD hosts to the gold nanoparticles. The signal broadening for the proton resonances in the spectrum of the capped particles (Figure 1B) is consistent with previous observations in similar systems.[6] Photon correlation spectroscopy (PCS) was used to verify the absence of aggregates in aqueous solutions of the γ-CD-modified nanoparticles. Our PCS instrument did not detect any scattered light, revealing the absence of particles or aggregates with diameter significantly larger than its lower detection limit (3 nm). Particle size determinations using transmission electron microscopy (TEM) yielded an average diameter of 3.2 ± 0.7 nm (Figure 2A) with a reasonable degree of monodispersity.

Because C_{60} is extremely insoluble in aqueous media, we could not add it directly to solutions containing γ-CD-capped gold nanoparticles. However, the known formation of 2:1 complexes[10] between γ-CD and C_{60} led us to attempt fullerene extraction/solubilization experiments into aqueous solutions containing γ-CD hosts attached to the gold nanoparticles. For instance, we dissolved 50 mg of γ-CD-capped gold nanoparticles in 5.0 mL of water and stirred in a 10 mg portion of solid C_{60} into the resulting solution in the dark. After 2 days, the undissolved solid fullerene was removed by filtration. Water evaporation from the filtrate solution yielded a deep brown solid, which was dried overnight at 60 °C under high vacuum. The presence of fullerene in this solid was proven by the electronic absorption spectrum of its toluene extract, which presented all of the typical bands

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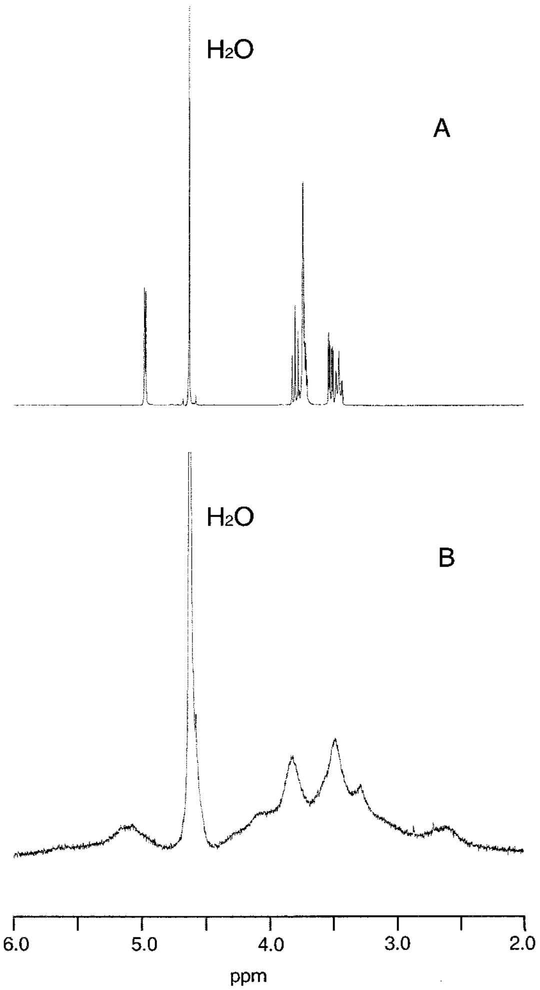


Figure 1. ^{1}H NMR spectra (400 MHz, D_2O) of (A) free γ-CD and (B) γ-CD-capped gold nanoparticles.

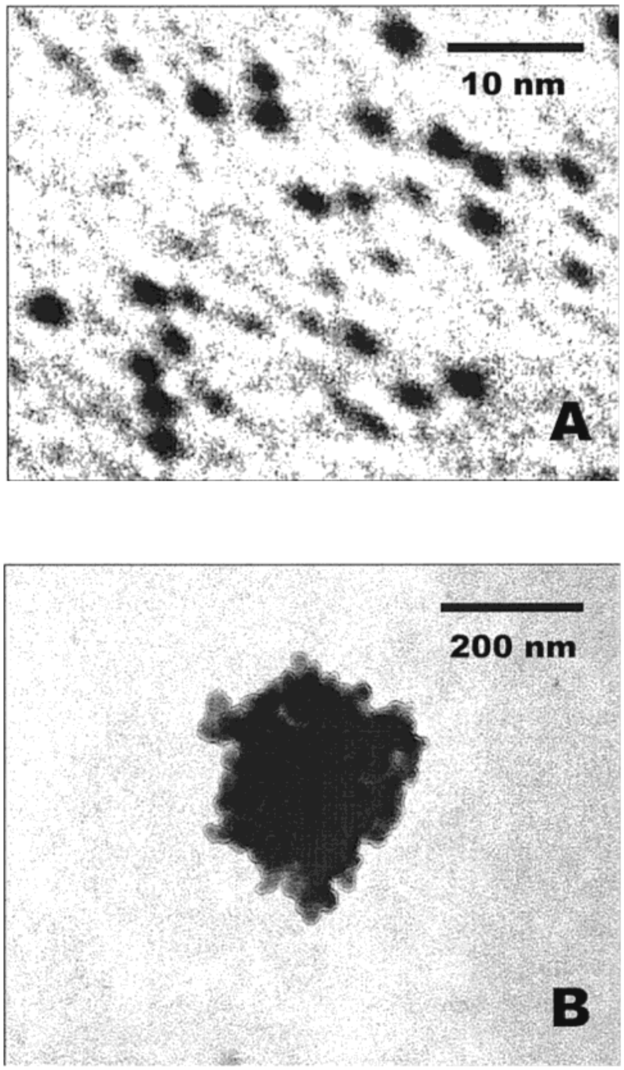


Figure 2. TEM images of (A) γ-CD- capped gold nanoparticles and (B) C_{60}-induced aggregate.

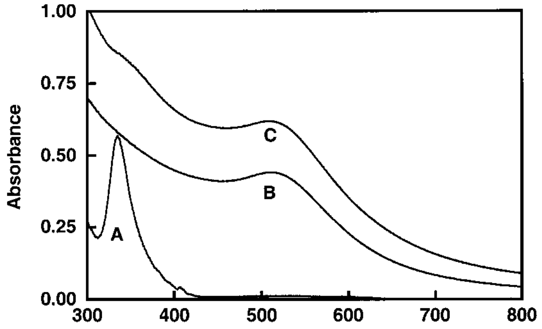
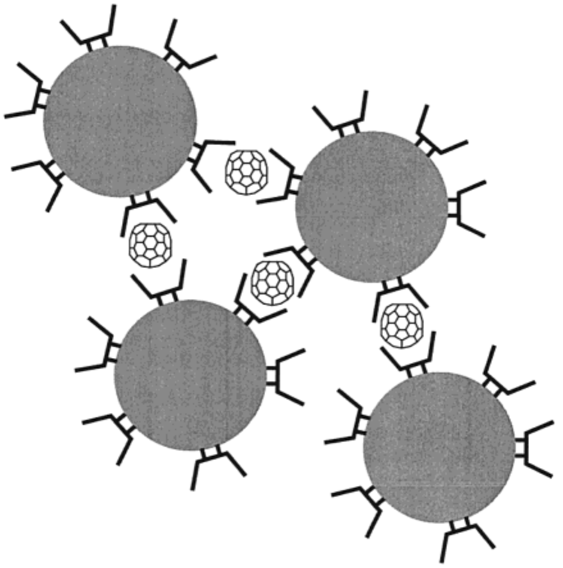


Figure 3. Electronic absorption spectra of (A) toluene extract from C_{60}/gold nanocomposite, (B) aqueous solution of γ-CD-capped gold nanoparticles (0.1 mg/mL) and (C) as in B after interaction with C_{60}.

of C_{60} (Figure 3A). This finding verifies the partial solubilization of the C_{60} sample in the aqueous solution of the γ-CD-capped nanoparticles. In a second type of experiment, a toluene solution of C_{60} (11.2 mg dissolved in 4 mL) was mixed with an aqueous solution of γ-CD-capped gold nanoparticles (50 mg dissolved in 5 mL). This mixture was gradually cooled to 0 °C and kept under fast stirring in the dark.[11] After 2 d, the aqueous phase was separated, and the water was removed. The resulting deep brown solid was dried under vacuum, and the presence of C_{60} was demonstrated by absorption spectroscopy of its toluene extract. Under the conditions described here, the first type of experiment (solubilization of solid C_{60}) was more efficient than the second one (extraction of C_{60} from toluene solutions). In the first case, 0.07 mg of C_{60} were found to dissolve in the aqueous nanoparticle solution (equivalent to $\sim$20 μM in C_{60}), whereas only 0.03 mg dissolved in the second case. These C_{60} amounts are larger than or similar to those solubilized by free γ-CD in aqueous solution. For instance, in control experiments, we determined that 0.03 mg of solid C_{60} could be extracted into a solution of 70 mg of γ-CD in 5.0 mL of water.

The solubilization of C_{60} is attributed to its complexation by the nanoparticle-attached γ-CD hosts. Interestingly, the 2:1 stoichiometry of this complex suggests that the fullerene molecules may behave as *noncovalent linkers* between the nanoparticles, leading to their aggregation (see Scheme 1). To investigate this point, we extracted solid C_{60} into a 1.0 mg/mL aqueous solution of γ-CD-capped gold nanoparticles. After filtering the undissolved fullerene, PCS analysis of the

Scheme 1. Fullerene-induced network of γ-CD-capped gold nanoparticles in aqueous solution



resulting solution at 20 °C clearly revealed a single particle population with an average size of 290 nm, thus confirming the C_{60}-induced aggregation of the γ-CD-capped gold nanoparticles. We performed some experiments at higher temperatures, 40 and 60 °C, obtaining average size values of 284 and 145 nm, respectively. These results are consistent with an inclusion complexation mechanism driving the aggregation of the nanoparticles, as an increase in temperature is expected to lower the corresponding association equilibrium constant, leading to a decrease in aggregate size, in agreement with the experimental observations. Further evidence for the aggregation of the nanoparticles was obtained from TEM experiments. A drop of the C_{60}-nanoparticle solution was deposited on a carbon coated copper grid, and the solvent was allowed to evaporate. The corresponding TEM image (Figure 2B) shows a typical aggregate found in this sample, with a size entirely consistent with the PCS data.

We performed control experiments to address the reversibility of the nanoparticle aggregation processes reported here.[12] For instance, after extracting C_{60} in a solution of γ-CD-capped gold nanoparticles and verifying the formation of large network aggregates (average diameter: 270 nm, in this case, as measured by PCS), we added free γ-CD (10 mM) to the solution. After stirring for 1 d, PCS measurements completely failed to detect any aggregates, revealing that, as anticipated, the free CD had broken up the linkages between the nanoparticles and fully reversed the aggregation process. The C_{60}/gold nanocomposites were also investigated with UV−vis absorption spectroscopy. In the absence of C_{60}, the γ-CD-capped nanoparticles presented a weak surface plasmon resonance absorption at 510 nm (Figure 3B). In the presence of C_{60}, this band remains essentially unchanged, only the scattering envelope of the spectrum increases, revealing the presence of larger particles that scatter light in this wavelength range more effectively. It is relevant to contrast this behavior with the results described by Mirkin and co-workers in a series of reports on the aggregation of gold nanoparticles driven by the binding interactions of surface-attached oligonucleotides.[13] Mirkin's particles are much larger (often as large as 30 nm) than the nanoparticles used in this work. As a result of their larger size, the surface plasmon resonance absorption of these particles is much more intense and, thus, sensitive to aggregation. Furthermore, we have also reported the aggregation of 13-nm gold nanoparticles with surface-attached β-CD hosts driven by the molecular linking effect of a soluble ferrocene dimer.[5] In that case, the dimer led to flocculation of the nanoparticle aggregates. In the case presented here, no flocculation was observed; the aggregates remain in solution. This difference is probably due to the lower solubility of C_{60} in the solution, which limits the number of possible linkages between nanoparticles, leading to aggregate size control and, thus, no flocculation. In addition, the smaller size of the gold particles used here is another factor that hinders flocculation. We should also note that Brust and co-workers have reported the C_{60}-mediated aggregation of gold nanoparticles in toluene solution through a mechanism entirely different to that reported here.[14]

In summary, we have demonstrated that C_{60} is partially solubilized in aqueous solution containing γ-CD-capped gold nanoparticles (3.2 nm diameter). This solubilization takes place due to the formation of complexes between one molecule of C_{60} and two γ-CD hosts attached to different nanoparticles (Scheme 1). Therefore, the fullerenes act as a sort of "molecular glue", leading to the formation of soluble nanoparticle aggregates with sizes around 290 nm. These results may find application in the assembly of three-dimensional nanoparticle arrays exhibiting long-range order, a current topic of active research work.[4b]

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Supporting Information Available: One page with additional experimental details. This material is available free of charge through the Internet at http://pubs.acs.org.

References

(1) Templeton, A. C.; Wuelfing, W. P.; Murray, R. C. *Acc. Chem. Res.* **2000**, *33*, 27.

(2) Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1.

(3) (a) Cusack, L.; Rao, S. N.; Wenger, J.; Fitzmaurice, D. *Chem. Mater.* **1997**, *9*, 624. (b) Cusack, L.; Marguerettaz, X.; Rao, S. N.; Wenger, J.; Fitzmaurice, D. *Chem. Mater.* **1997**, *9*, 1765. (c) Aherne, D.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **1999**, *103*, 1821. (d) Fullam, S.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **2000**, *104*, 6164. (e) Ryan, D.; Rao, S. N.; Rensmo, H.; Fitzmaurice, D.; Preece, J. A.; Wenger, S.; Stoddart, J. F.; Zaccheroni, N. *J. Am. Chem. Soc.* **2000**, *122*, 6252.

(4) (a) Boal, A. K.; Rotello, V. M. *J. Am. Chem. Soc.* **1999**, *121*, 4914. (b) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. *Nature* **2000**, *404*, 746.

(5) Liu, J.; Mendoza, S.; Román, E.; Lynn, M. J.; Xu, R.; Kaifer, A. E. *J. Am. Chem. Soc.* **1999**, *121*, 4304.

(6) Liu, J.; Ong, W.; Román, E.; Lynn, M. J.; Kaifer, A. E. *Langmuir* **2000**, *16*, 3000.

(7) Alvarez, J.; Liu, J.; Román, E.; Kaifer, A. E. *Chem. Commun.* **2000**, 1151.

(8) Liu, J.; Alvarez, J.; Kaifer, A. E. *Adv. Mater.* **2000**, *12*, 1381.

(9) For recent reviews, see: (a) Connors, K. A. *Chem. Rev.* **1997**, *97*, 1325. (b) Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875.

(10) (a) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerstrom, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604. (b) Yoshida, Z.; Takekuma, H.; Takekuma, S.; Matsubara, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1597.

(11) Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tsee, D. S.; Lorents, D. C. *Nature* **1993**, *362*, 140.

(12) We thank one of the reviewers for suggesting this experiment.

(13) Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 12 674.

(14) Brust, M.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 12 367.

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