# Cyclodextrin-modified gold nanoparticle aggregate formed by simple host–guest interactions with 1,10-phenanthroline

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An aggregate of gold nanoparticles modified with thiolated β-cyclodextrin was fabricated through the linkage of PHEN and characterised by FT-IR, UV-vis, fluorescence and STM techniques, showing that the aggregate formation was a concentration-dependant behaviour.

**Keywords**: aggregate, gold nanoparticle, cyclodextrin, inclusion complexation, STM

In recent years, research works on metal clusters and colloidal particles,[1-5] especially the investigations on nanoparticle assemblies, have been widely focused owing to their potential applications in electronic circuit components of extraordinarily high integration.[6] Several research groups[7,8] are actively working on the modification of metal nanoparticle surfaces with synthetic receptors or substrates in order to use the molecular recognition mechanism to control particle assembly. For example, Rotello and co-workers reported that interparticle spacing can be controlled through self-assembly of gold nanoparticles and poly (amidoamine) dendrimers.[9] Mirkin *et. al.* demonstrated that gold colloidal particles modified with oligonucleotides can be used to direct the placement of two different particle types within extended particle assemblies.[1] Significantly, Kaifer and co-workers reported that water-soluble gold nanoparticles capped with thiolated γ-cyclodextrin hosts formed large network aggregates in the presence of $C_{60}$ molecules.[10] Therefore, studies on the adsorption of modified cyclodextrin (CD) onto the surface of gold or gold nanoparticle have become a greatly attractive topic in recent years,[11-15] since modified CDs can act as excellent molecular receptors to selectively bind a wide variety of organic, inorganic and biologic guest molecules to form host–guest inclusion complexes or nano-scale supramolecular assemblies. We now report our investigation results on the preparation of gold nanoparticles modified by mono-6-thio-β-CD (**1**)[16] and their assembly behavior in the presence of 1,10-phenanthroline (PHEN) in aqueous solution. The results obtained indicate that PHEN acts as a linker between different gold particles in the assembly formation, and the concentration of PHEN will affect the aggregating modes.

Similar to the report by Kaifer,[17] addition of mono-6-thio-β-CD **1** to a colloidal dispersion of gold nanoparticles[5f] (~1mM Au) results in the formation of the β-CD-capped gold nanoparticle (**2**). FT-IR experiments show that gold nanoparticle **2** displays the fairly analogous IR spectrum to that of parent **1**. In addition, the UV–vis spectrum of gold colloidal particles shows a characteristic absorption for the surface plasmon resonance absorption at 520 nm in aqueous solution, and this maximum obviously shifts to 532 nm after modification by **1**. These phenomena jointly provide the evidences for the attachment of thiolated CD to the gold nanospheres.

It is well known that CD cavity can bind guest molecule to give host–guest inclusion complex. In the present case, the interactions between PHEN and CD units in **2** are also observed. As can be seen from Fig. 1, the fluorescent intensity of PHEN ($6.0 \times 10^{-6}$ M, trace a) increases upon addition of 40.0 mg native β-CD (trace b), which could be ascribed to the inclusion of PHEN into the hydrophobic cavity of CDs. Moreover, the introduction of gold colloidal dispersion into the PHEN solution leads to the complete quenching of PHEN fluorescence under same condition (trace c). However, after the addition of **1**-modified gold nanospheres (0.4 mg) to the PHEN solution, only small decrease of PHEN fluorescence can be found (trace d). This indicates that the inclusion complexation of CD units with PHEN molecule cancels most of the fluorescence quenching effect of gold nanoparticle.

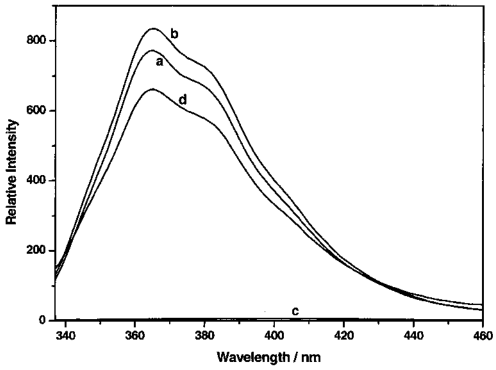

**Fig. 1** Fluorescence spectra of PHEN ($6.0 \times 10^{-6}$ M): (a) without and (b) with free β-CD (40.0 mg), (c) with colloidal dispersion of gold nanoparticles ([Au] ~1mM), and (d) with 1-modified gold nanoparticles (0.4 mg).

After verifying the host-guest inclusion complexation between CD-modified gold nanoparticle **2** and PHEN, we start to exploit this complexation to construct the aggregate of CD-modified gold nanoparticles by using PHEN as noncovalent linker between different nanoparticles. Scanning tunnel microscope (STM) image provides the direct evidence for the formation of aggregate. The specimens of STM was prepared by dripping the **2**-PHEN solution onto a freshly cleaned pyrolytic graphite (HOPG) surface, followed by evaporating the liquid at least 2 h *in vacuo*. From Fig. 2A, we can see clearly that, for **1**–modified nanosphere, every scattered gold nanoparticle does not display any aggregation. However, with the addition of PHEN (0.4 mM), simple aggregation between gold nanoparticles is found (Fig. 2B). Compared with the original size of nanoparticle **2** represented by one white dot in Fig. 2A (average diameter 10.0 ± 1.8 nm), the extended length of aggregate (32.5 ± 1.5 nm) is closely related to the summation of three nanoparticles' diameter, which indicates that the aggregate of gold nanosphere **2** is obtained from the present strategy.

Further investigations indicate that the aggregation of **2** is a concentration-dependant behaviour. For example, addition of a relatively concentrated PHEN (0.5 mM) to the colloidal dispersion of **2** will result in the purple precipitation within one week, while addition of the highly diluted PHEN (0.008 mM) does not cause any precipitation or flocculation even allowed to stay for several weeks. Moreover, **1**-modified nanoparticle presents a weak UV absorption at 532 nm (Fig. 3 line a), and this maximum shifts to 552 nm along with the obvious increase of the absorption intensity (line 3b) in the presence of concentrated PHEN (0.5 mM). However, addition

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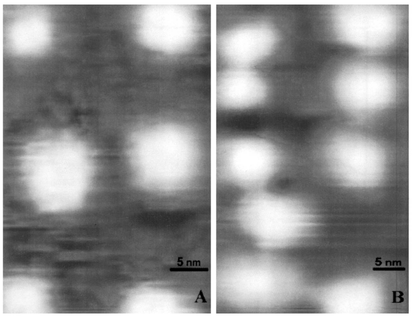


**Fig. 2** STM images of (A) **1**-modified gold nanoparticles ([Au] ~1mM) and (B) PHEN-induced aggregate ([PHEN] 0.4 mM).

of a diluted PHEN (0.008 mM) to an aqueous colloidal dispersion of **2** only induces a slight bathochromic shift (6 nm) of the corresponding peak with the absorption intensity remaining nearly unchanged (line 3c). These phenomena reveal that only under a relatively high concentration of PHEN, CD units immobilised on the surface of different gold nanoparticles can bind with PHEN guests through an intermolecular 2:1 mode (Scheme 1).

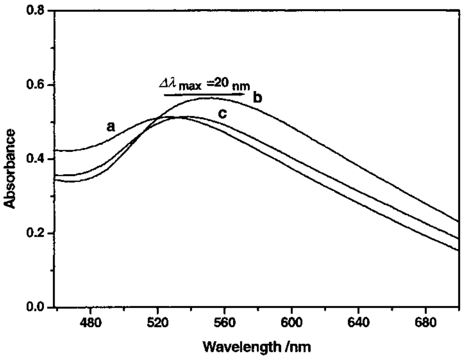
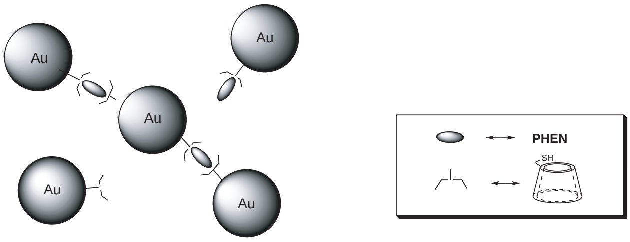


**Fig. 3** UV-visible spectra of aqueous solutions of **1**-modified gold nanoparticles: (a) before and after addition of PHEN; (b) PHEN 0.5 mM, trace; (c) PHEN 0.008 mM.



**Scheme 1**

In summary, we have demonstrated that particle aggregation formed by simple host–guest interactions between **1**-modified gold nanoparticles and 1,10-phenanthroline in aqueous solution. This aggregation phenomenon is driven by the formation of inclusion complexes between two CDs attached to different nanoparticles and one PHEN molecule, in which guest molecule acts as a sort of "molecular retractor". As a consequence, further investigation is in progress.

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## References

1 For gold colloidal particles derivatised with oligonucleotides, see: R.C. Mucic, J.J. Storhoff, C.A. Mirkin and R.L. Letsinger, *J. Am. Chem. Soc.*, 1998, **120**, 12674.
2 For polyfunctional monolayer-protected gold clusters, see: A.C. Templeton, M.J. Hostetler, E.K. Warmoth, S. Chen, C.M. Hartshorn, V.M. Krishnamurthy, M.D.E. Forbes and R.W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 4845.
3 For catalytic applications of metal nanoparticles, see: (a) M. Bartz, J. Kuther, R. Seshadri and W. Tremel, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2466; (b) G. Schmid, H. West, J.-O. Malm, J.-O. Bovin and C. Grenthe, *Chem. Eur. J.*, 1996, **2**, 1099; (c) M. Valden, X. Lai and D.W. Goodman, *Science,* 1998, **281**, 1647.
4 For analytical applications based on nanoparticles, see: C.R. Martin, *Anal. Chem.*, 1998, **70**, A322.
5 For film preparation using derivatized metal colloidal particles, see: (a) R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney and R.G. Osifchin, *Science*, 1996, **273**, 1690; (b) R.M. Bright, D.G. Walter, M.D. Musick, M.A. Jackson, K.J. Allison and M.J. Natan, *Langmuir,* 1996, **12**, 810; (c) M. Brust, D. Bethell, C.J. Kiely and D.J. Schiffrin, *Langmuir,* 1998, **14**, 5425; (d) H. Fan and G.P. Lopez, *Langmui,r* 1997, **13**, 119; (e) D.L. Feldheim, K.C. Crabar, M.J. Natan and T.E. Mallouk, *J. Am. Chem. Soc.*, 1996, **118**, 7640; (f) K.C. Grabar, R.G. Freeman, M.B. Hommer and M.J. Natan, *Anal. Chem.*, 1995, **67**, 735; (g) K.C. Grabar, P.C. Smith, M.D. Musick, J.A. Davis, D.G. Walter, M.A. Jackson, A.P. Guthrie and M.J. Natan, *J. Am. Chem. Soc.*, 1996, **118**, 1148; (h) K.C. Grabar, K.J. Allison, B.E. Baker, R.M. Bright, K.R. Brown, R.G. Freeman, A.P. Fox, C.D. Keating, M.D. Musick and M.J. Natan, *Langmuir,* 1996, **12**, 2353; (i) T. Vossmeyer, E. Delonno and J.R. Heath, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1080.
6 D.L. Feldheim and C.D. Keating, *Chem. Soc. Rev.*, 1998, **27**, 1.
7 (a) L. Cusack, S.N. Rao, J. Wenger and D. Fitzmaurice, *Chem. Mater.*, 1997, **9**, 624; (b) L. Cusack, X. Marguerettaz, S.N. Rao, J. Wenger and D. Fitzmaurice, *Chem. Mater.*, 1997, **9**, 1765; (c) D. Aherne, S.N. Rao and D. Fitzmaurice, *J. Phys. Chem. B,* 1999, **103**, 1821; (d) S. Fullam, S.N. Rao and D. Fitzmaurice, *J. Phys. Chem. B*, 2000, **104**, 6164; (e) D. Ryan, S.N. Rao, H. Rensmo, D. Fitzmaurice, J.A. Preece, S. Wenger, J.F. Stoddart, N. Zaccheroni, *J. Am. Chem. Soc.*, 2000, **122**, 6252.
8 (a) A.K. Boal and V.M. Rotello, *J. Am. Chme. Soc.*, 1999, **121**, 4914; (b) A.K. Boal, F. Ilhan, J.E. DeRouchey, T. Thurn-Albrecht, T.P. Russell and V.M. Rotello, *Nature,* 2000, **404**, 746.
9 B.L. Frankamp, A.K. Boal and V.M. Rotello, *J. Am. Chem. Soc.*, 2002, **124**, 15146.
10 J. Liu, J. Alvarez, W. Ong and A.E. Kaifer, *Nano Lett.*, 2001, **1**, 57.
11 H. Kitano, and Y. Taira, *Langmuir,* 2002, **18**, 5835.
12 S. Zapotoczny, T. Auletta, M.R. de Jong, H. Schönherr, J. Huskens, F.C.J.M. van Veggel, D.N. Reinhoudt and G.J. Vancso, *Langmuir,* 2002, **18**, 6988.
13 M.R. de Jong, J. Huskens and D.N. Reinhoudt, *Chem. Eur. J.*, 2001, **7**, 19.
14 M. Lahav, K.T. Ranjit, E. Katz and I. Willner, *Chem. Commun.*, 1997, 259.
15 G. Nelles, M. Weisser, R. Back, P. Wohlfart, G. Wenz and S. Mittler-Neher, *J. Am. Chem. Soc.*, 1996, **118**, 5039.
16 K. Fujita, T. Ueda, T. Imoto, I. Tabushi, N. Toh and T. Koga, *Bioorg. Chem.*, 1982, **11**, 72.
17 J. Liu, W. Ong, E. Román, M.J. Lynn and A.E. Kaifer, *Langmuir,* 2000, **16**, 3000.