

Synthesis of small gold nanoparticles: Au(I) disproportionation catalyzed by a persulfurated coronene dendrimer†

Giacomo Bergamini,^a Paola Ceroni,^{*a} Vincenzo Balzani,^a Marc Gingras,^{*b} Jean-Manuel Raimundo,^b Vittorio Morandi^c and Pier Giorgio Merli^c

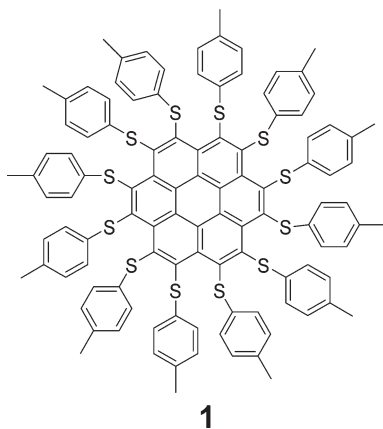
Received (in Cambridge, UK) 30th May 2007, Accepted 13th July 2007

First published as an Advance Article on the web 7th August 2007

DOI: 10.1039/b708115d

Gold nanoparticles with average diameter of 1.0 nm and narrow size distribution can be easily obtained by disproportionation of Au⁺ ions, in the presence of a persulfurated coronene dendrimer that favors encounters between Au⁺ ions and protects the resulting small nanoparticles from further aggregation.

Two of the most exciting topics in the field of nanoscience are those of dendrimers^{1,2} and nanoparticles.^{3,4} It has already been shown⁵ that these two research areas can profitably overlap to yield a variety of intradendrimer encapsulated⁶ and interdendrimer stabilized⁷ nanoparticles.



Gold nanoparticles are usually obtained by reducing HAuCl₄ with NaBH₄,⁸ but reduction of HAuCl₄ by a stabilizing polymer⁹ or by light excitation in ethylene glycol,¹⁰ and reduction of Au⁺ phosphine complexes by a borane complex¹¹ have also been reported. In this paper we describe the synthesis of small gold nanoparticles with narrow size distribution by a novel method, *i.e.* the disproportionation of Au⁺ catalyzed by compound **1**, consisting of a coronene-core appended with 12 thiophenyl units.¹²

^aDipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy. E-mail: paola.ceroni@unibo.it; Fax: +39 051 2099456; Tel: +39 051 2099535

^bNice Institute of Chemistry, Université de Nice-Sophia Antipolis, 28 Av. Valrose, 06108 Nice Cedex 2, France. E-mail: Marc.GINGRAS@unice.fr; Fax: +33 0492076578; Tel: +33 0492076578

^cCNR-IMM Sezione di Bologna, 40129 Bologna, Italy. E-mail: piergiorgio.merli@imm.cnr.it; Fax: +39 051 6399216; Tel: +39051 6399101

† Electronic supplementary information (ESI) available: experimental details. See DOI: 10.1039/b708115d

Compound **1** is the smallest member of a family of dendrimers obtained by persubstitution of aromatic cores with thiophenyl units.¹³ The coronene chromophoric unit that constitutes the core of **1** is strongly perturbed by the appended thiophenyl substituents, as evidenced by comparing the absorption spectrum of **1** with that of coronene (Fig. 1).

Compound **1**, as well as larger members of the same family, can coordinate a variety of soft metal ions, *e.g.* Ag⁺,¹⁴ thanks to the presence of sulfur atoms. Titration of **1** dissolved in dichloromethane (7.5 × 10⁻⁶ M) with an acetonitrile solution of HAuCl₄ (2.5 × 10⁻³ M) causes the spectral changes displayed in Fig. 2a. A substantial perturbation of the bands at 320 and 435 nm is accompanied by the formation of a broad band in the near infrared spectral region (λ_{max} = 840 nm, ε_{max} ≈ 1500 M⁻¹ cm⁻¹, Fig. 2a). The two isosbestic points at 390 and 460 nm are no longer maintained after addition of about 1.5 equiv. of HAuCl₄. A plot of the absorption changes at 435 nm as a function of Au³⁺ concentration reaches a plateau upon addition of one equiv., suggesting that **1** coordinates Au³⁺ to give a 1 : 1 species.

Since Au³⁺ can be easily reduced¹⁵ and **1** undergoes oxidation at 0.72 V vs NHE, we assign the new weak and broad band with λ_{max} = 840 nm to ligand-to-metal charge-transfer transitions. Such an assignment is supported by the fact that upon titration with HAuCl₄ of the analogous benzene-cored compound, which is much more difficult to oxidize (E_{1/2} = 1.08 V vs NHE), a similar band is formed with maximum at 565 nm. Experiments on solutions of **1** containing an excess of HAuCl₄ by high resolution transmission electron microscopy (HR-TEM) did not show any evidence of nanoparticle formation.

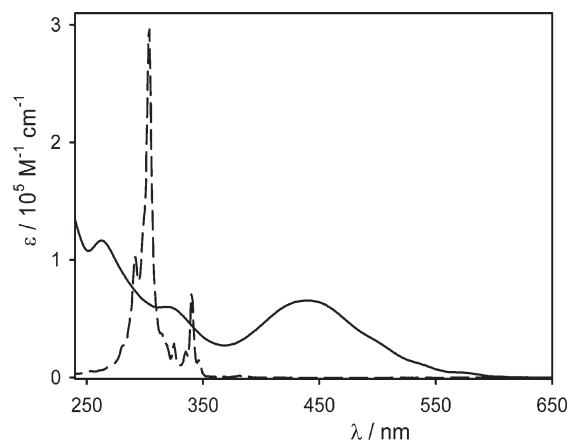


Fig. 1 Absorption spectra of coronene (dashed line) and compound **1** (full line) in dichloromethane solution at 298 K.

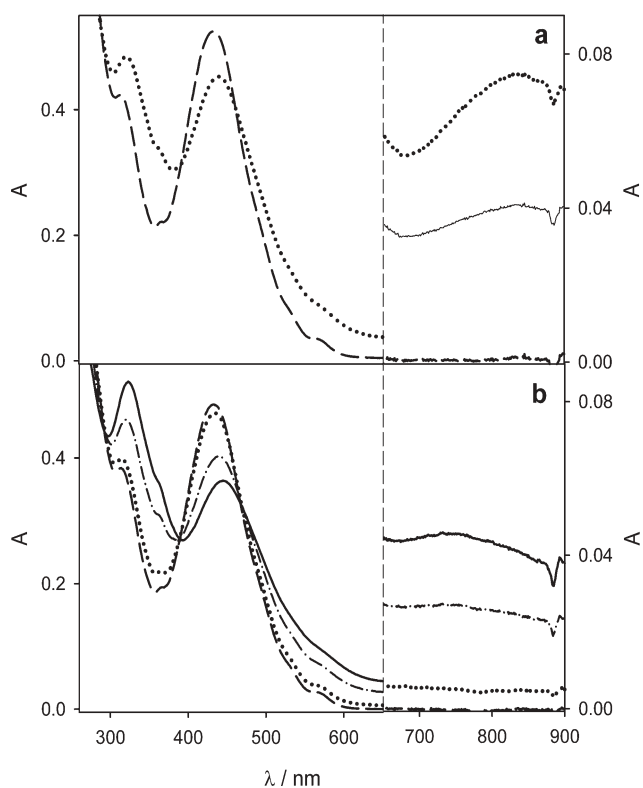


Fig. 2 Spectral changes observed upon titration of compound **1** in dichloromethane (7.5×10^{-6} M) with (a) H[AuCl₄]⁻ and (b) AuCl: 0 (dashed line) and 1.5 equiv. of gold ions (dotted line). In panel b, absorption spectra upon addition of 15 (dashed dotted line) and 30 (thick solid line) equiv. of AuCl are reported.

Titration of **1** in dichloromethane solution (7.5×10^{-6} M) with up to 1.5 equiv. of an acetonitrile solution of AuCl caused only very minor spectral changes (dotted line in Fig. 2b) in the 300–600 nm region, qualitatively similar to those observed upon titration with H[AuCl₄]⁻ (Fig. 2a), and the formation of a tail at lower energy. Because of the well known tendency of AuCl solutions to undergo disproportionation,¹⁶ we assign such spectral changes to the presence of small amounts of Au³⁺ in the AuCl solution (2.2×10^{-3} M) used for titration. Indeed, in that solution the ratio [Au³⁺]/[Au⁺] is 1/10, as estimated from the molar absorption coefficient of H[AuCl₄]⁻ in acetonitrile. Apparently, **1** either does not coordinate Au⁺ or, more likely, the concentration of complexes between Au⁺ and **1** is always very small because of Au⁺ disproportionation (*vide infra*).

Isosbestic points are maintained upon addition of 30 equiv. of AuCl per dendrimer (thick solid line in Fig. 2b) and a proportional increase of the tail at low energy is observed. This tail is consistent with formation of dispersed nanoparticles. Examination of the titrated solution with HR-TEM indeed showed the presence of very small nanoparticles ($d = 1.0 \pm 0.3$ nm) with narrow size distribution (Fig. 3).[‡] EDX (Energy Dispersive X-ray) spectra clearly indicated that the observed particles were made of gold. Magnification of the TEM images (Fig. 3c) has evidenced linear arrays of atoms with an interlayer distance of 0.234 nm, consistent with Au (101) crystals. The small size of the nanoparticles is in agreement with the absence in the absorption spectrum of the plasmon resonance band typical of larger nanoparticles.¹⁷

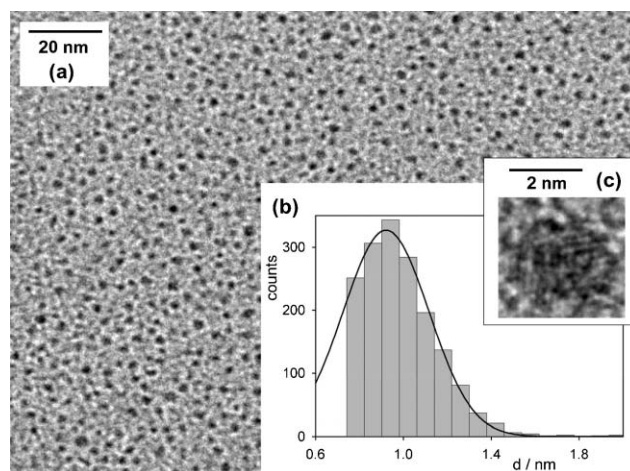


Fig. 3 (a) HR-TEM images of gold nanoparticles formed upon titration of a dichloromethane solution of compound **1** with 30 equiv. of AuCl. (b) Histograms, obtained by evaluation of 2225 nanoparticles, showing their size distribution. (c) Detailed view of a nanoparticle with interlayer distance (0.234 nm) consistent with that of Au (101) crystals.

Since the observed gold nanoparticles have been directly obtained by titration of **1** with AuCl without addition of any reductant, two reaction mechanisms can be taken into consideration, namely: (i) reduction of Au⁺ by compound **1**, and (ii) disproportionation of Au⁺ to Au⁰ and Au³⁺. Mechanism (i) is plausible since formation of nanoparticles upon “spontaneous” reduction of H[AuCl₄]⁻ by a stabilizing polymer has been previously reported.⁹ For our system, however, involvement of **1** as a reductant seems unlikely for the following reasons: a) judging from the absorption spectra, formation of nanoparticles upon titration with AuCl is not accompanied by a decrease of the concentration of **1** since isosbestic points are maintained upon addition of up to 30 equiv. of Au⁺; b) addition of an excess of 11-mercapto-1-undecanol liberates molecules of **1**, as evidenced by the fact that the absorption spectrum of **1** is completely recovered. Therefore, we believe that the observed gold nanoparticles are formed from the disproportionation of Au⁺ to Au⁰ and Au³⁺, with a mechanism similar to that proposed by Eustis and El-Sayed to interpret generation of gold nanoparticles by photochemical reduction of H[AuCl₄]⁻.¹⁰

In blank experiments we have verified that nanoparticles are not formed from Au⁺ alone, **1** and Au³⁺, coronene and Au³⁺ or Au⁺. We must conclude that formation of nanoparticles requires participation of species in which Au⁺ ions are coordinated by compound **1**. The disproportionation of Au⁺ is known to be very slow for Au⁺ halides,¹⁸ because it requires formation of a bimolecular species involving a gold-gold bond. Compound **1**, presenting multiple coordination sites, likely favors encounters of two Au⁺ ions in polymetallic species (*e.g.*, **1** \supset (Au⁺)₂), thereby catalyzing disproportionation. Encounters of Au atoms should then rapidly lead to formation of gold nanoparticles, most likely stabilized by dendrimer molecules. Stability of the gold nanoparticles in the presence of **1** is demonstrated by the fact that TEM experiments do not show any substantial variation in the nanoparticle size distribution with aging of the solutions or by removal of the solvent and redissolution.

In conclusion, we have discovered a new route to obtain gold nanoparticles with average diameter of 1.0 nm and narrow size distribution. The process is based on the disproportionation of Au⁺ in the presence of the relatively simple compound **1**, which not only favors encounters between Au⁺ ions, but also protects the resulting small nanoparticles from further aggregation. The effects of reactant concentrations, dendrimer generation, and nature of the dendrimer core on the efficiency of the process and on the size of the resulting particles are under investigations.

This work has been supported in Italy by University of Bologna and in France by the French Ministry of the National Education and Research.

Notes and references

‡ Particles with $d < 0.7$ nm are not reported because they are below instrument resolution.

- (a) G. R. Newkome and F. Vögtle, *Dendrimers and Dendrons*, Wiley-VCH, Weinheim, 2001; (b) *Dendrimers and Other Dendritic Polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, John Wiley & Sons, Chichester, UK, 2001; (c) D. A. Tomalia and J. M. J. Fréchet, *Prog. Polym. Sci.*, 2005, **30**(3–4), 217–505; Special issue, Dendrimers and Dendritic Polymers.
- For some recent reviews, see: (a) P. A. Chase, R. J. M. Klein Gebbink and G. van Koten, *J. Organomet. Chem.*, 2004, **689**, 4016; (b) W. Ong, M. Gomez-Kaifer and A. E. Kaifer, *Chem. Commun.*, 2004, 1677; (c) M. Ballauff and C. N. Likos, *Angew. Chem., Int. Ed.*, 2004, **43**, 2998; (d) A.-M. Caminade and J.-P. Majoral, *Acc. Chem. Res.*, 2004, **37**, 341; (e) D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852; (f) P. Ceroni, G. Bergamini, F. Marchioni and V. Balzani, *Prog. Polym. Sci.*, 2005, **30**, 453.
- (a) *Metal Nanoparticles: Synthesis, Characterization, and Applications*, ed. D. L. Feldheim and C. A. J. Foss, Dekker, New York 2002; (b) *Nanoparticles*, ed. G. Schmid, Wiley-VCH, Weinheim, 2004.
- (a) G. Schmid and L. F. F. Chi, *Adv. Mater.*, 1998, **10**, 515; (b) A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27; (c) E. Katz and I. Willner, *Angew. Chem., Int. Ed.*, 2004, **43**, 6042; (d) Y. Yadong and A. P. Alivisatos, *Nature*, 2005, **437**, 664; (e) M. Brust, *Nat. Mater.*, 2005, **4**, 364; (f) C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025; (g) A. B. Descalzo, R. Martínez-Mañez, F. Sancenón, K. Hoffmann and K. Rurack, *Angew. Chem., Int. Ed.*, 2006, **45**, 5924.
- (a) R. M. Crooks, B. I. Lemon, III, L. Sun, L. K. Yeung and M. Zhao, *Top. Curr. Chem.*, 2001, **212**, 81; (b) M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; (c) I. Willner, R. Baron and B. Willner, *Adv. Mater.*, 2006, **18**, 1109.
- (a) R. M. Crooks, M. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181; (b) J. J. Michels, J. Huskens and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 2002, **1**, 102; (c) R. W. J. Scott, O. M. Wilson and R. M. Crooks, *J. Phys. Chem. B*, 2005, **109**, 609; (d) S. Dend, J. Locklin, D. Patton, A. Baba and R. C. Advincula, *J. Am. Chem. Soc.*, 2005, **127**, 1744; (e) G. Schmid, W. Meyer-Zaika, R. Pugin, T. Sawitowski, J.-P. Majoral, A.-M. Caminade and C.-O. Turrin, *Chem.-Eur. J.*, 2000, **6**, 1693.
- (a) T. Ishii, A. Suzuki, N. Aihara, K. Usui and K. Torigoe, *Langmuir*, 1998, **14**, 3157; (b) M. E. Garcia, L. A. Baker and R. M. Crooks, *Anal. Chem.*, 1999, **71**, 256; (c) A. D'Aleo, R. M. Williams, F. Osswald, P. Edamana, U. Hahn, J. van Heyst, F. D. Tichelaar, F. Vögtle and L. De Cola, *Adv. Funct. Mater.*, 2004, **14**, 1167.
- (a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801; (b) M. R. Knecht, J. C. Garcia-Martinez and R. M. Crooks, *Langmuir*, 2005, **21**, 11981; (c) S. Wu, H. Zeng and Z. A. Schelly, *J. Phys. Chem. B*, 2005, **109**, 18715.
- (a) T. Ishii, H. Otsuka, K. Kataoka and Y. Nagasaky, *Langmuir*, 2004, **20**, 561; (b) T. Sakai and P. Alexandridis, *J. Phys. Chem. B*, 2005, **109**, 7766.
- S. Eustis and M. A. El-Sayed, *J. Phys. Chem. B*, 2006, **110**, 14014.
- M. F. Bertino, Z.-M. Sun, R. Zhang and L.-S. Wang, *J. Phys. Chem. B*, 2006, **110**, 21416.
- J. H. R. Tucker, M. Gingras, H. Brand and J.-M. Lehn, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1303.
- M. Gingras, J.-M. Raimundo and Y. M. Chabre, *Angew. Chem., Int. Ed.*, 2006, **45**, 1686.
- R. D. Johnson, A. Pinchart, I. H. A. Badr, M. Gingras and L. G. Bachas, *Electroanalysis*, 2002, **14**, 1419.
- E. Gachard, H. Remita, J. Khatouri, B. Keita, L. Nadjo and J. Belloni, *New J. Chem.*, 1998, **22**, 1257.
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 4th edn., 1980, 966.
- A. Moores and F. Goettmann, *New J. Chem.*, 2006, **30**, 1121.
- (a) S. Eustis, H.-Y. Hsu and M. A. El-Sayed, *J. Phys. Chem. B*, 2005, **109**, 4811; (b) C. H. Gammons and Y. Yu, *Geochim. Cosmochim. Acta*, 1997, **61**, 1971.