

Dendritic effects on the ordered assembly and the interfacial one-electron oxidation of redox-active dendron-functionalized gold nanoparticles†

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A higher generation dendron with a long-alkyl chain thiol (DA2-SH) induced the formation of nanoparticles with a small core with quite a narrow size distribution (1.5 ± 0.1 nm), the self-assembly of one-dimensional arrays of these gold nanoparticles (DA2-Au), and the stabilization for the formation of the radical cation of the phenothiazine of DA2-Au nanoparticles from the interfacial one-electron oxidation of the nanoparticles with NOBF_4 .

Metal nanoparticles are of interest due to the unique catalytic, optical, and electronic properties arising from their size.^{1,2} Control of the surface properties and reactivity is an important aspect of developing nanomaterial applications. It is necessary for reliable nanoscale devices to control the size and shape of metal nanoparticles. The size, shape, and interparticle separation and assembly of metal nanoparticles are crucially controlled by the nature of capping ligands. Recently, there has been a remarkable increase in interest in the preparation of metal nanoparticles modified with dendrimers as capping agents.^{3,4} In contrast, very few papers have described the preparation of gold nanoparticles modified with dendrons bearing pyridone⁵ and thiols, e.g. Fréchet-type poly(alkyl or phenyl ether)dendrons with *benzyl*- or *aryl*-thiol groups at the focal point, in which the dendrons do not have a *long-alkyl chain thiol*.⁶ No clear-cut example has been hitherto known for the control of the surface properties and reactivity of gold nanoparticles modified with a redox-active dendron having a *long-alkyl chain thiol* at the focal point. Understanding the reactivity of gold nanoparticles provides very valuable information for applications such as nanoscale chemical sensing, electronics, and catalysis, but reports concerning the reactivities of the monolayer-protected gold nanoparticles are rather limited.^{7a}

In our recent research efforts, special emphasis has been placed on the elucidation of structural driving forces in the control of particle size and shape, self-assembly, and the reactivity of redox-active dendron-thiol modified metal nanoparticles. The key structural elements of the new redox-active dendrons in this study consist of phenothiazine branches for redox-active electron-donor and π - π stacking functions, thiol functionality at the focal point, and alkylthiol chain length for the stabilization of assembled structures *via* van der Waals interactions (Fig. 1). We have synthesized new redox-active dendron-thiols (Fig. 1) which are

potential candidates as capping agents to control not only the particle size but also the interfacial reactivity of metal nanoparticles.† We have found that the cores of redox-active dendron-thiol modified gold nanoparticles decrease in size and dispersity with increasing dendron generation and alkyl chain length of the thiol at the focal point. Particularly, the gold nanoparticles (DA2-Au) modified with a higher generation dendron bearing a *long-alkyl chain thiol* (DA2-SH) at the focal point have a much smaller core size with quite narrow size distribution and remarkably high stability. DA2-Au nanoparticles also exhibit the spontaneous formation of one-dimensional arrays. One-dimensional arrays of metal nanoparticles are becoming the subject of increasing interest. However, there are only limited reports on studies of self-assembled one-dimensional arrays of gold nanoparticles.^{1c,1d} Moreover, we have found that DA2-SH prevents decomposition of the nanoparticles from the interfacial one-electron oxidation of DA2-Au with NOBF_4 , in which the radical cation of the phenothiazine of DA2-Au is formed at the nanointerface. The decomposition of other dendron-modified gold nanoparticles (M-Au, D1-Au, D2-Au, and DA1-Au) has been found, due to the one-electron oxidation of their nanoparticles with NOBF_4 . This communication presents the dendritic effects on the particle size and assembly, and the interfacial one-electron oxidation of redox-active dendron-modified gold nanoparticles.

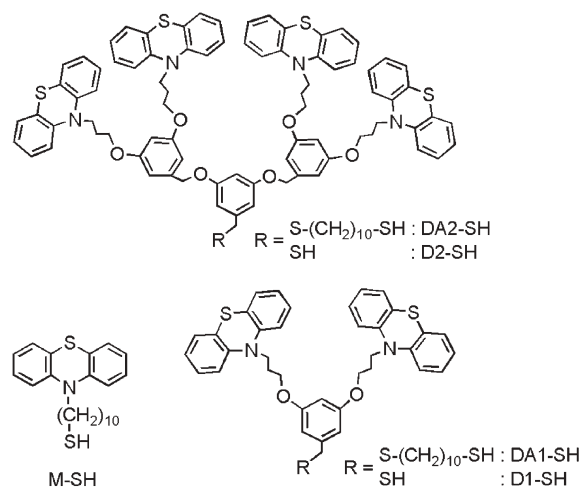


Fig. 1 Structures of the dendron-thiols. Thiols (M-SH, D1-SH, D2-SH, DA1-SH, and DA2-SH) derived the dendron-thiol modified gold nanoparticles (M-Au, D1-Au, D2-Au, DA1-Au, and DA2-Au).

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The redox-active dendron–thiol modified gold nanoparticles (M–Au, D1–Au, D2–Au, DA1–Au, and DA2–Au) were prepared by the two-phase method.^{7b} Typical procedure for the preparation of gold nanoparticles (DA2–Au) is as follows. To a vigorously stirred solution of tetraoctylammonium bromide (656 mg, 1.20 mmol) in 15 mL of toluene was added HAuCl₄·4H₂O (112 mg, 0.27 mmol) in 9 mL of deionized water. A solution of the thiol DA2–SH (386 mg, 0.25 mmol) in 9 mL of toluene was added, and the resulting solution was stirred for 20 min at room temperature. NaBH₄ (113 mg, 3.0 mmol) in 8 mL of deionized water was then added. The mixture was stirred for 3 h at room temperature. The resulting precipitate was collected by filtration and washed serially with acetone. The nanoparticles were redissolved in CH₂Cl₂ to purify and precipitated with acetone, and then the particles were isolated by filtration. These processes were repeated until no free thiol or phase transfer catalyst remained, as detected by TLC and ¹H and ¹³C NMR spectroscopy.

These nanoparticles were soluble in benzene, toluene, CH₂Cl₂, CHCl₃, and THF. They were highly stable both in solution, as well as in the solid state. In Fig. 2, the UV-vis spectra of M–Au and D2–Au in CH₂Cl₂ show a surface plasmon absorption at ~520 nm, whereas DA2–Au exhibits no significant plasmon resonance, which is consistent with its smaller particle size and narrower distribution as evidenced from TEM observation (*vide infra*).⁸ The X-ray photoelectron spectrum of DA2–Au showed the Au 4f binding energies at 84.1 and 87.8 eV, corresponding to the Au⁰ state.

The core size of the redox-active dendron–thiol modified gold nanoparticles was examined by transmission electron microscopy (TEM). The nanoparticles were redissolved in CH₂Cl₂ (1 mg mL⁻¹) and a drop of the resulting dispersion was placed on a carbon coated copper grid. The particle sizes of M–Au, D1–Au, D2–Au, DA1–Au, and DA2–Au are as follows: 2.1 ± 0.4 nm for M–Au, 1.9 ± 0.3 nm for D1–Au, 1.6 ± 0.4 nm for D2–Au (Fig. 3a), 1.7 ± 0.3 nm for DA1–Au, and 1.5 ± 0.1 nm for DA2–Au (Fig. 3b and Figure S1 in Electronic Supplementary Information†).⁹ These results indicate a small decrease in the mean size with increasing dendron generation and alkylthiol chain length. In contrast to our system, it has been reported that for higher generation dendrons both core size and size distribution

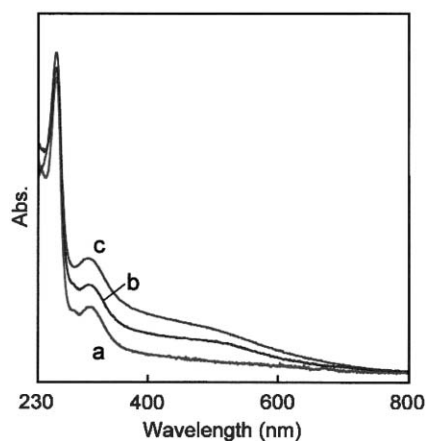


Fig. 2 UV-vis spectra of (a) DA2–Au, (b) D2–Au, and (c) M–Au in CH₂Cl₂.

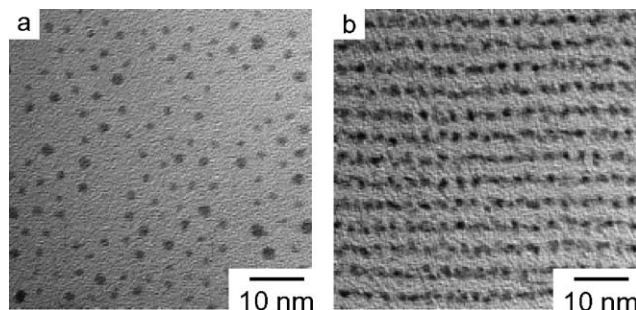
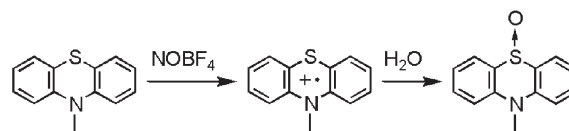


Fig. 3 TEM micrographs of (a) D2–Au and (b) DA2–Au.

remarkably increased with increasing generations of Fréchet-type poly(alkyl or phenyl ether)dendrons with a *benzyl*- or *aryl*-thiol group at the focal point, in which the dendrons do not have a *long-alkyl chain thiol*.⁶ Significantly, DA2–Au showed smaller core size and quite narrower size distribution, and the spontaneous formation of the stripe structure shown in Fig. 3b was reproducibly observed for DA2–Au, while such stripe structure was not found in M–Au, D1–Au, D2–Au, and DA1–Au. The stripe structure covers an area of *ca.* 100 × 100 nm and can be attributed to a one-dimensional self-assembly of the nanoparticles.¹⁰ The line spacing (interparticle edge-to-edge distance) of parallel stripes is about 2.8 nm. This distance is remarkably shorter than twice the focal-point-to-terminal distance (3.1 nm) of DA2–SH calculated from a MOPAC simulation. It is presumed that the intermolecular π – π stacking interaction of the thiol-terminated phenothiazine contributes to the self-organization of DA2–Au. While the phenothiazine sulfoxide (*vide infra*) of DA2–Au did not show the stripe structure, suggesting that the π – π interaction may play an important role in the formation of the one-dimensional arrays of DA2–Au, it is very difficult to explain the formation mechanism of one-dimensional arrays.^{1c,1d,6b} One-dimensional assembly provides a good model to study the size-dependent electronic and optical properties of metal nanoparticles.

The phenothiazine of the redox-active gold nanoparticles having been readily oxidized electrochemically,¹¹ was then treated with NO⁺BF₄⁻ as a one-electron oxidant. It is well known that the oxidation of phenothiazine derivatives with NOBF₄ leads to the formation of the radical cation which is further reacted with H₂O to give the phenothiazine sulfoxide (Scheme 1).¹² The oxidation of the gold nanoparticles (M–Au, D1–Au, D2–Au) with NOBF₄ in CH₂Cl₂–CH₃CN resulted in the decomposition of the nanoparticles.^{13,14} Interestingly, however, the oxidation of DA2–Au with NOBF₄ led to the formation of the radical cation of phenothiazine as evidenced by the UV-vis spectral data (λ = 516 nm).¹² In addition, the chemical evidence for the formation of the radical cation was obtained from the hydrolysis of the reaction mixture of DA2–Au with NOBF₄, *i.e.*, its hydrolysis gave the phenothiazine



Scheme 1 Formation of the phenothiazine sulfoxide from hydrolysis of the radical cation generated from one-electron oxidation of phenothiazine with NOBF₄.

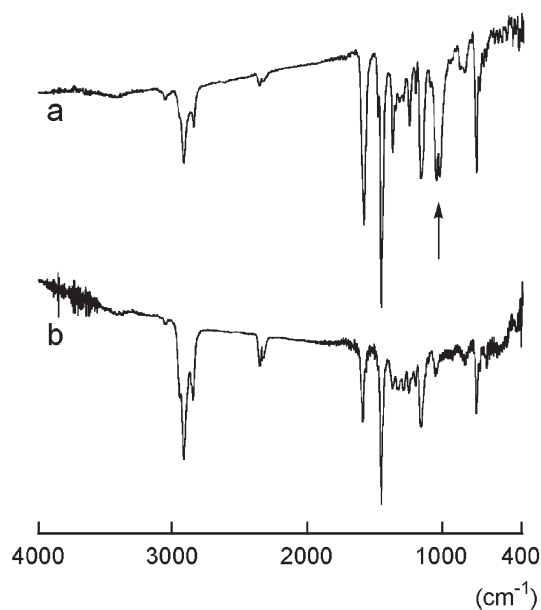


Fig. 4 The FT-IR spectra of (a) the phenothiazine sulfoxide of DA2-Au and (b) DA2-Au.

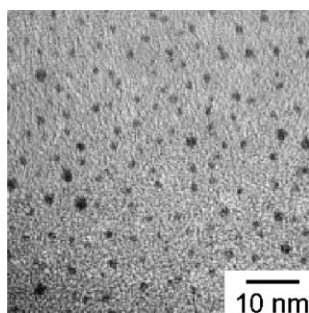


Fig. 5 TEM micrograph of the phenothiazine sulfoxide of DA2-Au.

sulfoxide of DA2-Au which was characterized by FT-IR spectroscopy and TEM measurement. The FT-IR spectrum of the phenothiazine sulfoxide of DA2-Au exhibited the S=O stretching vibration at 1025 cm^{-1} (Fig. 4). The TEM micrograph revealed the formation of dispersed particles with a diameter of $1.5 \pm 0.3\text{ nm}$ (Fig. 5), but the stripe structure was not observed in the phenothiazine sulfoxide of DA2-Au. These findings indicate that DA2-Au did not undergo decomposition of the gold nanoparticles upon treatment with NOBF_4 . The interfacial one-electron oxidation accompanying the electron-transfer pathway of the redox-active site at the periphery of the gold nanoparticles has been accomplished without decomposition of the nanoparticles by using our new type of redox-active dendron. These results may open a new route for the control of surface reactions on metal nanoparticles.

In summary, the particle size and shape, and the reactivity of the redox-active dendron-modified gold nanoparticles are greatly affected by the dendron generation and the difference in the alkyl chain length of the thiol at the focal point. Particularly, DA2-Au

exhibits the spontaneous formation of one-dimensional arrays, which are expected to play a dominant role in future nanoelectronics. A new type of interfacial redox reaction accompany electron-transfer can be performed without decomposition of the nanoparticles by the redox-active dendron functionality, such as DA2-SH. Our findings provide a general approach to tuning the surface properties of metal nanoparticles by using redox-active dendrons possessing various abilities. Further work is currently in progress in this and related areas.

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Notes and references

- (a) G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994; (b) D. L. Feldheim and C. A. Foss, Jr., *Metal Nanoparticles*, Marcel Dekker, Inc., New York, 2002; (c) G. Schmid, *Nanoparticles*, Wiley-VCH, Weinheim, 2004; (d) C. N. R. Rao, A. Muller and A. K. Cheetham, *The Chemistry of Nanomaterials*, Wiley-VCH, Weinheim, 2004, vol. 1.
- M. Tamura and H. Fujihara, *J. Am. Chem. Soc.*, 2003, **125**, 15742.
- (a) R. M. Crooks, B. I. Lemon, III and Y. M. Zhao, in *Dendrimers III*, ed. F. Vogtle, Springer, Berlin, 2001, pp. 81–135; (b) K. Esumi, in *Colloid Chemistry II*, ed. M. Antonietti, Springer, Berlin, 2003, pp. 31–52.
- V. Chechik and R. M. Crooks, *Langmuir*, 1999, **15**, 6364.
- R. Wang, J. Yang, Z. Zheng, M. D. Carducci, J. Jiao and S. Seraphin, *Angew. Chem., Int. Ed.*, 2001, **40**, 549.
- (a) M.-K. Kim, Y.-M. Jeon, W. S. Jeon, H.-J. Kim, S. G. Hong, C. G. Park and K. Kim, *Chem. Commun.*, 2001, 667; (b) S. Nakao, K. Torigoe, K. Kon-No and T. Yonezawa, *J. Phys. Chem. B*, 2002, **106**, 12097.
- (a) A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27; (b) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.
- M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafiqullin, I. Vezmar and R. L. Whetten, *J. Phys. Chem. B*, 1997, **101**, 3706.
- (a) The particle size and distribution of DA2-Au were determined from another domain in the same TEM grid (Electronic Supplementary Information, Figure S1†); (b) The TEM image at lower magnification of DA2-Au is shown in Figure S2 of Electronic Supplementary Information†.
- A similar result was recently reported for gold nanoparticles modified with Fréchet-type poly(phenyl ether)dendrons having an arylthiol group at the focal point (ref. 6b).
- The cyclic voltammogram (CV) of the gold nanoparticles in $\text{CH}_2\text{Cl}_2 + 0.1\text{ M Bu}_4\text{NPF}_6$ at a glassy carbon electrode showed the reversible redox wave at the following potential ($E_{1/2}$ vs. $\text{Ag}/0.1\text{ M AgNO}_3$): +0.52 V for D1-Au and DA1-Au, +0.46 V for D2-Au and DA2-Au.
- (a) H. J. Shine, in *Organic Free Radicals*, ed. W. A. Pryor, Am. Chem. Soc., Washington, 1978, ch. 22; (b) E. Bosch and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1057.
- Similar decomposition (desorption) was observed in the self-assembled monolayers (SAMs) with a phenothiazine-thiol (M-SH as shown in Fig. 1) on a gold electrode by treatment with NOBF_4 , i.e., the CV of the M-SH-SAMs on a gold electrode showed the reversible redox peak at +0.48 V, however the redox peak disappeared after treatment with NOBF_4 .
- (a) The reaction of octanethiol-stabilized gold nanoparticles with NOBF_4 in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ resulted in the decomposition of the nanoparticles; (b) The one-electron oxidant mediated decomposition of the gold core has not been reported. We propose that the NO^+ oxidant may attack the gold surface of the particles. Mechanistic studies on its decomposition are in progress.