Silver nanoparticles from hydrogen-bonded supramolecular scaffolds†

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Received (in Montpellier, France) 21st May 2008, Accepted 11th August 2008
First published as an Advance Article on the web 9th September 2008
DOI: 10.1039/b808561g

Silver nanoparticles were generated *in situ* under an electron beam from hydrogen-bonded double rosette-silver complexes.

Self-assembly is an attractive approach for creating functional molecular structures.[1] It is a fundamental principle in various natural phenomena, generating complex nanoarchitectures such as cells and viruses.[2] Moreover, current bottom-up nanotechnology approaches utilize the self-assembly of small building blocks as a nanofabrication tool,[3] and as an alternative to the lithography-based top-down methods of nanofabrication.[4] Previously, our group has reported the synthesis and organization of supramolecular structures based on hydrogen bonding.[5–7] These superstructures can be formed in solution and efficiently transferred onto surfaces.[8] The rosette assemblies are based on the self-assembly of calix[4]arene dimelamines and barbituric acid (or cyanuric acid) derivatives (Fig. 1), which are held together by complementary hydrogen bonding between the donor–acceptor–donor (DAD) array of calix[4]arene dimelamine derivatives and the acceptor–donor–acceptor (ADA) array of their BAR (barbituric acid) or CYA (cyanuric acid) counterparts. We have also reported the synthesis and organisation of gold- and silver-containing self-assembled rosettes as scaffolds for growing metallic nanostructures.[9] Furthermore, thiol-functionalized double rosettes have been used to control nanoparticle assembly.[10]

There are several methods for the synthesis of Ag nanoparticles, such as metal salt reduction, electroless deposition and the sonochemical irradiation or thermal decomposition of zero-valent metal precursors.[12] Most of these methods yield large and polydisperse nanoparticles. Ag nanoparticles show very interesting properties that are strongly dependent upon their size and shape, which might be useful for applications such as optical wave-guides, catalysis and medical treatments.[11] Previously, Mertig *et al.*[13] reported that electron beam reduction generated gold nanoparticle arrays from self-assembled proteins as templates. We report in this Letter that monodisperse Ag nanoparticles are generated by the reduction of Ag complexes of synthetic rosette scaffolds using electron beam reduction.

Double rosette assemblies **1a**$_3$·(DEB)$_6$ and **1b**$_3$·(CNPhCYA)$_6$ were synthesized as previously described,[7] by mixing calix[4]arene dimelamine derivatives **1a** (or **1b**) with DEB (5,5-diethyl barbituric acid) or CNPhCYA (*para-cyano*-phenyl cyanuric acid) in a 1 : 2 ratio in CHCl$_3$. In their ^{1}H NMR spectra, the characteristic signals around 13-15 ppm for the hydrogen-bonded imide protons (–NH) on the barbituric acid or cyanuric acid derivatives confirmed the formation of the double rosette assemblies (see ESI, Fig. SI 1†).

Ag complexes of double rosette assemblies are formed due to the strong affinity of π-donor or cyano functionalities for metal ions (Fig. 1).[14] Ag atoms could be incorporated in the double rosette assemblies **1a**$_3$·(DEB)$_6$ and **1b**$_3$·(CNPhCYA)$_6$ by reacting a 5–10 mM solution of these assemblies in CHCl$_3$ with 1.5 equivalents of Ag$^+$CF$_3$COO$^-$ for 24 h at room temperature. MALDI-TOF analysis of the Ag-functionalised assemblies showed intense signals in their spectra[15] at m/z = 4278.3 (calc. 4276.1 for C$_{228}$H$_{276}$N$_{48}$O$_{30}$ ·^{107}Ag$^+$)

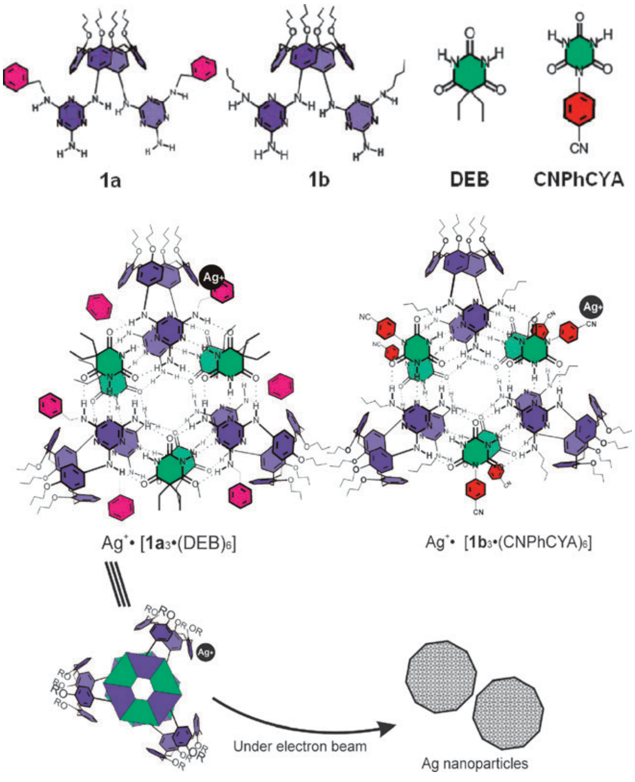

Fig. 1 Different building blocks of double rosette assemblies and Ag$^+$-functionalised double rosette assemblies.

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of double rosette assemblies **1a**$_3$·(DEB)$_6$ and **1b**$_3$·(CNPhCYA)$_6$ recorded in d_8-toluene at 300 MHz. See DOI: 10.1039/b808561g

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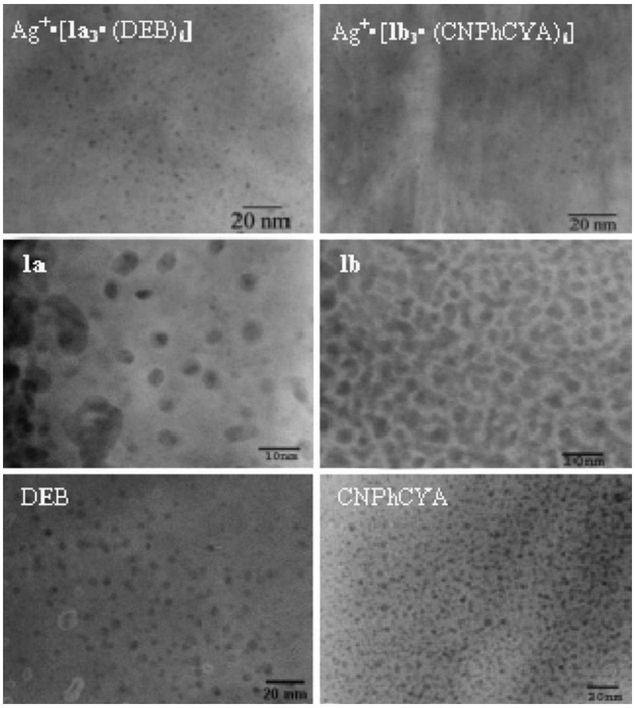

Fig. 2 TEM photos of Ag nanoparticles formed in the presence of the assemblies or the individual building blocks.

for the assembly $Ag^+\cdot[\mathbf{1a}_3\cdot(DEB)_6]$ and 4347.9 (calc. 4348.1 for $C_{222}H_{246}N_{66}O_{42}\cdot{}^{107}Ag^+$) for the assembly $Ag^+\cdot[\mathbf{1b}_3\cdot(CNPhCYA)_6]$, indicating the incorporation of Ag atoms into the rosette architecture. Presumably, in the assembly $Ag^+\cdot[\mathbf{1a}_3\cdot(DEB)_6]$, the Ag ions coordinate to the benzyl aromatic rings on the calix[4]arene dimelamine moieties, forming a sandwich-type complex with the benzyl substituent on the melamine. In the assembly $Ag^+\cdot[\mathbf{1b}_3\cdot(CNPhCYA)_6]$, the Ag ions coordinate to the CN– functionalities of the cyanurate derivatives.

The Ag-functionalised double rosette assemblies were subjected to an electron beam at 200 KeV *in situ* on a TEM grid. A 1mM solution of these rosette assemblies were deposited on the copper grid. When exposed to the electron beam in an electron microscope, metal nanoparticles were formed by reduction of the metal salts. This process lead to the generation of very small, monodisperse Ag nanoparticles (∼2 nm) (Fig. 2). Furthermore, energy-dispersive X-ray (EDX) analysis confirmed the formation of zero-valent Ag nanoparticles. The monodispersity of the particles was very good compared to most other Ag nanoparticle synthesis methods.§[12] Higher resolution TEM (HRTEM) images of the nanoparticles are shown in Fig. 3. Based on the HRTEM images, it is evident that these particles are crystalline in nature, as lattice fringes are clearly detectable. The HRTEM analysis revealed Ag lattice fringes with a spacing of 0.235 nm, corresponding to the cubic Ag(111) planes. It seems that the double rosettes play an important role in stabilizing the nucleation sites during nanoparticle formation (Fig. 1). The typical dimensions of a double rosette assembly are 1.3 by 3 nm;[9] the internal cavity is approximately 1 nm^3. However, subsequent growth probably leads to the formation of larger nanoparticles, which cannot be stabilized by these structures, but are instead held together *via* relatively weaker hydrogen bonds. To validate this argument, different precursor solutions were separately analysed under the electron beam in the presence of the salt $Ag^+CF_3COO^-$; the results are given in Fig. 2 and summarized in Table 1. Whereas the Ag rosette complexes yielded small Ag nanoparticles, the reduction of $Ag^+CF_3COO^-$ in presence of DEB, CYA, **1a** or **1b** yielded much larger Ag nanoparticles with a broad size distribution. This confirms the role of double rosettes in the formation of small-sized Ag nanoparticles.

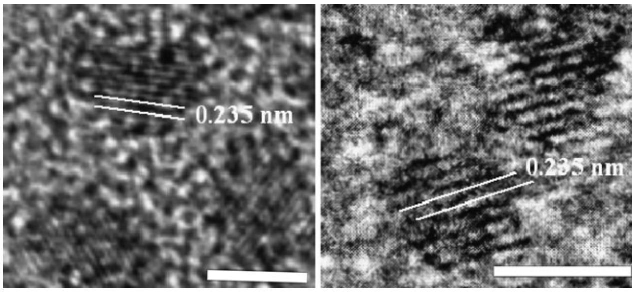

Fig. 3 HRTEM analysis of Ag nanoparticles formed in the presence of $Ag^+\cdot[\mathbf{1a}_3\cdot(DEB)_6]$ (right) and $Ag^+\cdot[\mathbf{1b}_3\cdot CNPhCYA)_6]$ (left) assemblies. Scale bars 5 nm.

In summary, *in situ* electron beam-induced reduction during TEM analysis leads to the formation of monodisperse zero-valent Ag nanoparticles from Ag complexes of synthetic double rosette scaffolds.

We thank Mark Smithers from MESA$^+$ Institute for Nanotechnology for numerous TEM analyses and many helpful discussions. This work was financially supported by the ESF-SONS-FunSMARTs project.

Experimental

All experiments were performed under an argon atmosphere. 5,5′-Diethyl barbiturate (DEB) (Aldrich), 2,5-dihydroxybenzoic acid (DHB) (Aldrich) and $Ag^+CF_3COO^-$ (ACROS) were purchased and used as received. Calix[4]arene dimelamine derivatives **1a**, **1b** and CNPhCYA were synthesized according to a previous synthesis protocol.[7] ^1H NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 instrument. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). Matrix-assisted laser desorption ionisation (MALDI) time-of-flight (TOF) mass spectra were recorded on a Voyager-DE-RP mass spectrometer (Applied Biosystems/PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction. A 337 nm UV nitrogen

Table 1 Particle sizes of Ag nanoparticles obtained in presence of the different assemblies and the individual building blocks

Assembly/component	Particle size/nm
$Ag^+\cdot[\mathbf{1a}_3\cdot(DEB)_6]$	2.3 ± 0.3
1a	7.3 ± 3.0
DEB	4.5 ± 1.2
$Ag^+\cdot[\mathbf{1b}_3\cdot(CNPhCYA)_6]$	2.1 ± 0.1
1b	6.8 ± 2.1
CNCPhCYA	3.6 ± 1.0
$Ag^+CF_3COO^-$	Polydisperse

laser producing 3 ns pulses was used, and mass spectra were obtained in the linear and reflectron mode. Samples for TEM were prepared by the deposition and evaporation of a drop of a $CHCl_3$ solution onto amorphous graphite. TEM images were recorded with a Philips CM-30 Twin operating at 300 kV.

Synthesis of Ag^+ complexes of the hydrogen-bonded assemblies

The assemblies $\mathbf{1a}_3\cdot(DEB)_6$ and $\mathbf{1b}_3\cdot(CNPhCYA)_6$ were prepared by mixing the components in $CHCl_3$ to yield a 5–10 mM solution concentration. Next, the hydrogen-bonded assemblies $\mathbf{1a}_3\cdot(DEB)_6$ and $\mathbf{1b}_3\cdot(CNPhCYA)_6$ in $CHCl_3$ were stirred for 24 h at room temperature with 1.5 equivalents of $Ag^+CF_3COO^-$. Subsequently, an aliquot of this solution (10 μL) was mixed with an aliquot (30 μL) of a solution of DHB (3 mg L^{-1}) in $CHCl_3$. A portion (1 μL) of the resulting solution was loaded onto a sample plate, the solvent removed in warm air and the sample transferred to a mass spectrometer for analysis. ^1H NMR was used to characterize the formation of the double rosette assemblies. The characteristic signals around 13–15 ppm of the hydrogen-bonded imide protons (–NH) on the barbituric acid or cyanuric acid derivatives confirmed their formation (see ESI, Fig. SI 1†). MALDI-TOF analysis of the Ag-functionalised assemblies showed intense signals in the spectra[15] at m/z = 4278.3 (calc. 4276.1 for $C_{228}H_{276}N_{48}O_{30}\cdot{}^{107}Ag^+$) for the assembly $Ag^+\cdot[\mathbf{1a}_3\cdot(DEB)_6]$ and 4347.9 (calc. 4348.1 for $C_{222}H_{246}N_{66}O_{42}\cdot{}^{107}Ag^+$) for the assembly $Ag^+\cdot[\mathbf{1b}_3\cdot(CNPhCYA)_6]$, indicating the incorporation of Ag atoms into the rosette architecture.

Synthesis of Ag nanoparticles

Ag-functionalised double rosette assemblies were reduced with an electron beam at 200 KeV *in situ* on the TEM grid. A 1 mM solution of these rosette assemblies was deposited on the copper grid and exposed to the electron beam of an electron microscope. This process lead to the generation of very small, monodisperse Ag nanoparticles (∼2 nm).

References

§ Previously, we have reported Au (covalently)-functionalized double rosettes. In this case, nanoparticles were not generated as the Au atoms were covalently bound to the assembly components.[9]

1 (*a*) J.-M Lehn, Supramolecular Chemistry and Self-Assembly, *Science*, 2002, **295**, 2400; (*b*) V. Balzani, A. Credi, B. Ferrer, S. Silvi and M. Venturi, *Top. Curr. Chem.*, 2005, **262**, 1; (*c*) J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte, *J. Mater. Chem.*, 2003, **13**, 2661; (*d*) H. M. Keizer and R. P. Sijbesma, *Chem. Soc. Rev.*, 2005, **34**, 226.

2 (*a*) S. G. Zhang, *Biotechnol. Adv.*, 2002, **20**, 321; (*b*) A. M. Bouchard and G. C. Osbourn, *Lect. Notes Comp. Sci.*, 2004, **3141**, 95.

3 (*a*) S. W. Lee, W. J. Chang, R. Bashir and Y. M. Koo, *Biotechnol. Bioprocess Eng.*, 2007, **12**, 185; (*b*) M. de Wild, S. Berner, H. Suzuki, L. Ramoino, A. Baratoff and T. A. Jung, *Ann. N. Y. Acad. Sci.*, 2003, **1006**, 291; (*c*) M. de Wild, S. Berner, H. Suzuki, L. Ramoino, A. Baratoff and T. A. Jung, *Chimia*, 2002, **56**, 500.

4 (*a*) P. S. Peercy, *Nature*, 2000, **406**, 1023; T. Ito and S. Okazaki, *Nature*, 2000, **406**, 1027; (*b*) G. M. Whitesides and J. C. Love, *Sci. Am.*, 2001, **285**, 38; (*c*) B. D. Gates, Q. B. Xu, J. C. Love, D. B. Wolfe and G. M. Whitesides, *Annu. Rev. Mater. Res.*, 2004, **34**, 339.

5 (*a*) L. J. Prins, F. de Jong, P. Timmerman and D. N. Reinhoudt, *Nature*, 2000, **408**, 181; (*b*) L. J. Prins, J. Huskens, F. de Jong, P. Timmerman and D. N. Reinhoudt, *Nature*, 1999, **398**, 498.

6 D. N. Reinhoudt and M. Crego-Calama, *Science*, 2002, **295**, 2403.

7 P. Timmerman, R. H. Vreekamp, R. Hulst, W. Verboom, D. N. Reinhoudt, K. Rissanen, K. A. Udachin and J. Ripmeester, *Chem.–Eur. J.*, 1997, **3**, 1823.

8 (*a*) H. Schonherr, V. Paraschiv, S. Zapotoczny, M. Crego-Calama, P. Timmerman, C. W. Frank, G. J. Vancso and D. N. Reinhoudt, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5024; (*b*) J. M. C. A. Kerckhoffs, M. A. Mateos-Timoneda, D. N. Reinhoudt and M. Crego-Calama, *Chem.–Eur. J.*, 2007, **13**, 2377.

9 (*a*) H. J. van Manen, V. Paraschiv, J. J. Garcia-Lopez, H. Schonherr, S. Zapotoczny, G. J. Vancso, M. Crego-Calama and D. N. Reinhoudt, *Nano Lett.*, 2004, **4**, 441; (*b*) S. Kinge, M. Peter, M. Crego-Calama and D. Reinhoudt, *Supramol. Chem.*, 2008, **20**, 593.

10 S. S. Kinge, M. Crego-Calama and D. N. Reinhoudt, *Langmuir*, 2007, **23**, 8772.

11 (*a*) F. Hache, D. Ricard and C. Flytzanis, *J. Opt. Soc. Am. B*, 1986, **3**, 1647; (*b*) Y. Y. Chen, C. A. Wang, H. Y. Liu, J. S. Qiu and X. H. Bao, *Chem.Commun.*, 2005, 5298; (*c*) R. W. Y. Sun, R. Chen, N. P. Y. Chung, C. M. Ho, C. L. S. Lin and C. M. Che, *Chem. Commun.*, 2005, 5059.

12 (*a*) Y. S. Shon and E. Cutler, *Langmuir*, 2004, **20**, 6626; (*b*) A. K. Kalkan and S. J. Fonash, *J. Phys. Chem. B*, 2005, **109**, 20779; (*c*) A. Henglein and M. Giersig, *J. Phys. Chem. B*, 1999, **103**, 9533; (*d*) N. Arai, H. Tsuji, K. Ueno, T. Matsumoto, N. Gotoh, K. Aadachi, H. Kotaki, Y. Gotoh and J. Ishikawa, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2006, **242**, 217; (*e*) J. P. Zhang, P. Chen, C. H. Sun and X. J. Hu, *Appl. Catal., A*, 2004, **266**, 49.

13 M. Mertig, R. Wahl, M. Lehmann, P. Simon and W. Pompe, *Eur. Phys. J. D*, 2001, **16**, 317.

14 (*a*) M. Karas, D. Bachmann, U. Bahr and F. Hillenkamp, *Int. J. Mass Spectrom.*, 1987, **78**, 53; (*b*) F. Hillenkamp, M. Karas, R. C. Beavis and B. T. Chait, *Anal. Chem.*, 1991, **63**, 1193A.

15 (*a*) K. A. Jolliffe, M. Crego-Calama, R. Fokkens, N. M. Nibbering, P. Timmerman and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 1998, **37**, 1247; (*b*) P. Timmerman, K. A. Jolliffe, M. C. Calama, J. L. Weidmann, L. J. Prins, F. Cardullo, B. H. M. Snellink-Ruel, R. H. Fokkens, N. M. M. Nibbering, S. Shinkai and D. N. Reinhoudt, *Chem.–Eur. J.*, 2000, **6**, 4104.