

Supporting Information

Discriminatory antibacterial effects of calix[n]arene capped silver nanoparticles with regard to Gram positive and Gram negative bacteria

Samira Boudebouze^a, Anthony W. Coleman^{b,*}, Yannick Tauran^b, Hela Mkaouar^a, Florent Perret^c,
Alexandrine Garnier^a, Arnaud Brioude^b, Beomjoon Kim^d, Emmanuelle Maguin^a and Moez Rhimi^{a,*}

^a INRA, UMR 1319 Micalis, F-78350 Jouy-en-Josas, France.

Tel: +33 1 3465 2294; E-mail: moez.rhimi@jouy.inra.fr

^b LMI CNRS UMR 5615, Univ. Lyon 1, Villeurbanne, F69622, France.

Tel: +33 4 4243 1027; E-mail: antony.coleman@adm.univ-lyon 1.fr

^c ICBMS, UMR 5246, Univ. Lyon 1, Villeurbanne, F69622, France.

^d Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Contents:

.

Experimental details:

Synthesis of sulphonato-calix[n]arenes

Materials and reagents

All chemicals were purchased from ACROS Organics or Sigma Aldrich and used without further purification. Solvents were of chemical grade and were used without any purification. The structure and purity of the products were verified by ^1H NMR spectroscopy at 300K using a Bruker 500 MHz NMR spectrometer, with D_2O as solvent. All products were characterised by electrospray mass spectroscopy, using a Perkin-Elmer Sciex spectrometer.

The starting materials, calix[n]arenes, were prepared by debutylation of *para*-tert-butylcalix[n]arenes, using the procedure described by Gutsche. [1] All calix[n]arenes used in this work have been previously described [2].

Synthesis of sulphonato-calix[n]arene modified silver nanoparticles

The procedure of Xiong [3] was slightly modified as follows. 10 mL of 10^{-2} M AgNO_3 solution was added to 80 mL of deionized water. To this solution, 10 mL of 10^{-2} M of a sulphonato-calix[n]arene aqueous solution was added as stabilizer with stirring for 30 min. And then, 44 mg of NaBH_4 was added to the solution. Silver nanoparticle suspensions were obtained after 5 minutes. The silver nanoparticles were then diluted 10 fold for storage at a final concentration of 1×10^{-4} M.

All calix[n]arene capped silver nanoparticles were stable excepted for SC8c capped silver nanoparticles which precipitated after a few hours.

Characterisation of the Capped Nanoparticles

UV-Visible absorption assays

The mixture experiments were conducted by monitoring the absorbance intensity between 340 nm and 650 nm, using a 96 well titre visible spectrometer, (BioTek Power Wave 340).

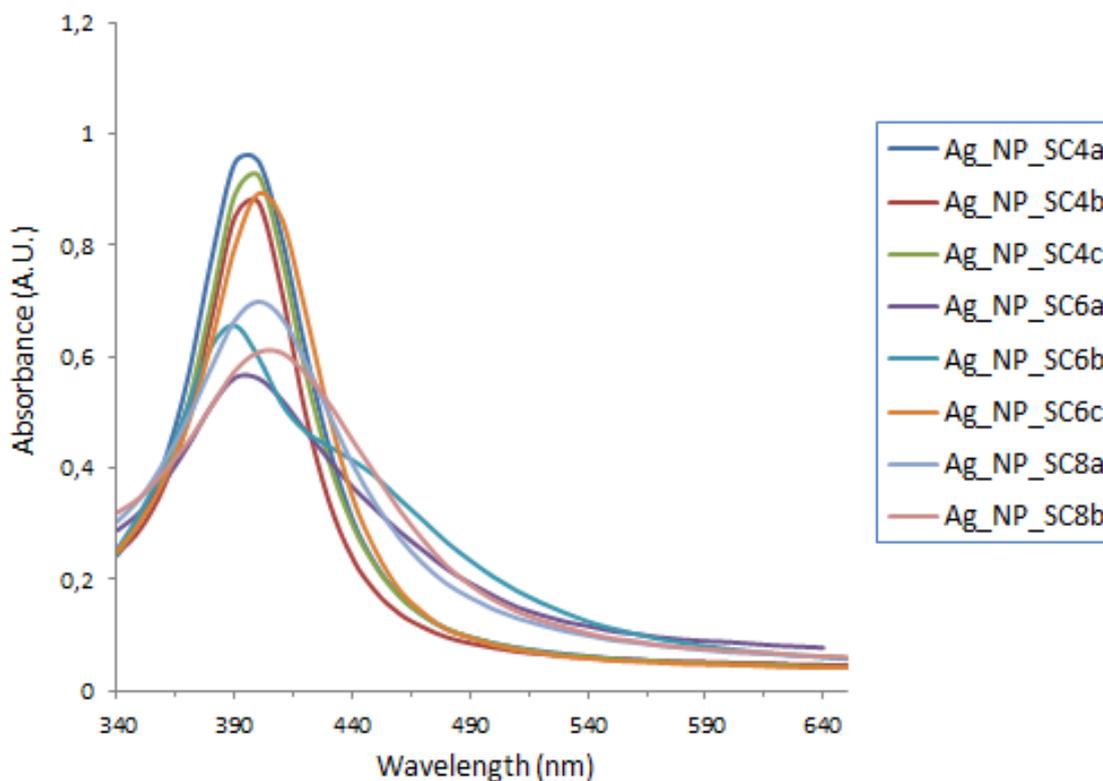


Fig. S1 UV-Visible spectra of the calix[n]arene capped silver nanoparticles.

Dynamic Light Scattering

Particle size measurements were performed on a Zetasizer Nano ZS (Malvern Instruments, UK) with a detection angle of 90°. The measurements were carried out in triplicate. The average hydrodynamic diameter (or Z average) was determined using the cumulant analysis provided by the instrument software with the assumption of spherical particles.

Table S1 Z average of calix[n]arene capped silver nanoparticles

Sample	Diameter (nm)	Polydispersity Index
Ag_NP_SC4a	32.99 ± 6.2	0.28
Ag_NP_SC4b	68.18 ± 2	0.185
Ag_NP_SC4c	45.41 ± 6.7	0.245
Ag_NP_SC6a	51.19 ± 9.8	0.137

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Ag_NP_SC6b	74.47	± 14.47	0.151
Ag_NP_SC6c	42.35	± 1.1	0.515
Ag_NP_SC8a	21.97	± 0.1	0.56
Ag_NP_SC8b	69.15	± 10.1	0.769

Zeta Potential

The zeta potential of the calix[n]arene capped silver nanoparticles was determined by Laser Doppler Micro electrophoresis on a Zetasizer Nano ZS (Malvern Instruments, UK). From the measurement of the electrophoretic mobility, the zeta potential and its distribution was calculated. The measurements were carried out in triplicate at 25°C.

Table S2 Zeta potential average of calix[n]arene capped silver nanoparticles.

Sample	Zeta Potential (mV)	Zeta deviation (mV)	Electrophoretic mobility ($\mu\text{m.cm/Vs}$)
Ag_NP_SC4a	-27.3	5.72	-2,139
Ag_NP_SC4b	-35.3	10.79	-2,765
Ag_NP_SC4c	-35.4	12.66	-2,775
Ag_NP_SC6a	-42.03	9.54	-3,296
Ag_NP_SC6b	-26.66	13.53	-2,11
Ag_NP_SC6c	-33.53	10.59	-2,414
Ag_NP_SC8a	-44.56	10.5	-3,494
Ag_NP_SC8b	-36.03	12.33	-2,822

Bacteria growth conditions and kinetics

B. subtilis and *E. coli* were cultured in Luria Bertani (LB) medium at 37 °C with agitation (220 rpm, Infors system). From overnight cultures we inoculated cultures at initial OD600

nm of 0.1. Growth kinetic was carried out by measurement of the OD₆₀₀ nm each hour using a visible spectrophotometer (BioPhotometer, Eppendorf) [4].

References and Note

[1] C. D. Gutsche and L.-G. Lin, *Tetrahedron*, 1986, **42**, 1633

[2] Y. Tauran, A. Brioude, P. Shahgaldian, A. Cumbo, B.J. Kim, F. Perret, A.W. Coleman, I. Montasser, *Chem. Commun.*, 2012, **48**, 9483-9485.

[3] D. Xiong, M. Chen and H. Li, *Chem. Commun.*, 2008, **7**, 880-882.

[4] G. Sezonov, D. Joseleau-Petit, R. D'Ari. *J. Bacteriology*, 2012, **189**, 8746-8749.