Supporting Information

Calix-arene silver nanoparticles interactions with surfactants are charge, size and critical micellar concentration dependent

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Experimental details:

Synthesis of *para*-sulphonato-calix[n]arene

Materials and reagents

All chemicals were purchased from Acros Organics or Sigma Aldrich and used without further purification. The starting materials, calix[n]arenes, were prepared by debutylation of *para*-t-butylcalix[n]arenes, using the procedure described by Gutsche. [1] Solvents were of chemical grade and were used without any purification. The structure and purity of the products were verified by ^{1}H NMR spectroscopy at 300K using a Brucker 300 MHz, D_2O as solvent. All products were also characterised by electrospray mass spectroscopy, using a Perkin-Elmer Sciex spectrometer.

General procedure for the preparation of *para*-sulphonato-calix[n]arenes SC4a, SC6a and SC8a

para-sulphonatocalix[n]arenes have been synthesized according to the procedure described by Shinkai *et* al. [2]

Calix[n]arenes (3 mmol) was mixed with concentrated sulfuric acid (10ml) and the solution was heated at 60°C for 24h. The completion of the reaction is followed by withdrawing an aliquot from the reaction mixture into water. When no water insoluble material was detected, the reaction was completed. After cooling, the reaction mixture is added on diethyl

ether solution for precipitating the sulfonato-calix[n]arene. After filtration, the reaction was washed with cold acetone and dried under vacuum.

All the NMR, Mass spectra and I.R. spectra were conform to literature data.

Calix[4]arene-*para*-tetrasulphonic acid SC4a
Yield 95% , m.p. > 300 °C, IR. ν (cm^{-1}): 3430 (OH), 1040 and 1178 (SO), 1H NMR (D_2O, 300MHz) δ (ppm) : 4.12 (8 H, s, $ArCH_2Ar$) and 7.74 (8 H, s, ArH), ES m/z $[M+H]^+$: 745,2 (100,0%), $[M+Na]^+$: 767,3 (57,0%)

Calix[6]arene-*para*-hexasulphonic acid SC6a
Yield 80% , m.p. > 300 °C, IR. ν (cm^{-1}): 3430 (OH), 1045 and 1190 (SO), 1H NMR (D_2O, 300MHz) δ (ppm) : 4.10 (12 H, bs, $ArCH_2Ar$) and 7.65 (12 H, s, ArH), ES m/z $[M+H]^+$: 745,2 (100,0%), $[M+Na]^+$: 767,3 (57,0%), ES m/z $[M+H]^+$: 1119,1 (100,0%), $[M+Na]^+$: 1131,3 (35,0%)

Calix[8]arene-*para*-octasulphonic acid SC8a
Yield 85%, m.p. > 300 °C, IR. ν (cm^{-1}): 3425 (OH), 1050 and 1190 (SO), 1H NMR (D_2O, 300MHz) δ (ppm) : 4.11 (16 H, bs, $ArCH_2Ar$) and 7.61 (16 H, s, ArH); ES m/z $[M+H]^+$: 1489,2 (100,0%), $[M+Na]^+$: 1511,4 (51,0%).

General procedure for the preparation of calix[n]arenes propane-3-sulphonic acid. SC4b, SC6b, SC8b
Compounds SCnb were synthesized by the reaction of these calix[n]arenes with propane-1,3-sultone described for t-Bu calix[6]arene by Shinkai et al. [3]

Calix[n]arene (2 mmol) was dissolved in tetrahydrofuran (THF) (100 ml) at 50°C under a stream of nitrogen. After cooling, sodium hydride (5eq. per hydroxyl group) was added and the mixture was stirred until evolution of hydrogen ceased (ca. 1 h). Propane- 1,3-sultone (3eq. per hydroxyl group) was then added dropwise and the mixture was stirred at room temperature for 24 h. Remaining NaH was decomposed by addition of methanol, after which the solvent was evaporated under reduced pressure, and the residue dissolved in hot water (500 ml). Any insoluble material was removed by centrifugation. Finally, SCnb was precipitated by the salting-out method with sodium acetate: yielding to a precipitate. After drying and purification by preparative HPLC, the desired compound in acidic form is obtained in good yield.

Calix[4]aryloxy-25,26,27,28-tetrakis(propane-3-sulphonic acid) SC4b
Yield 45%, m.p. > 300°C; 1H NMR (D_2O, 300MHz) δ (ppm) : 2.22 (8H, m, CH2CH2O), 2.96 (8H, t, CH_2S), 3.25 and 4,36 (8H, 2 x d, $ArCH_2Ar$), 4.04(8H, t, OCH_2), 6.59 (4H, s, ArH*para*), 6,75 (8H, s, ArH*meta*); 13C NMR (D_2O, 100MHz) δ (ppm) : 25.56 (O-CH_2-CH_2), 31.06 (Ar-CH_2-Ar), 48.28 (CH_2-S), 73.54 (CH_2-O-Ar), 128.66 (*para*C-Ar), 135.35 (*meta*C-Ar), 156.26 (*ortho*C-Ar), 181.91 (ArC-O-CH_2); ES m/z neg $[M-H]^-$: 911.3 (100,0%)

Calix[6]aryloxy-37,38,39,40,41,42-hexakis(propane-3-sulphonic acid) SC6b

Yield 35%, m.p. > 300°C; 1H NMR (D_2O, 300MHz) δ (ppm) : 1.80 (12H, m, CH2CH2O), 2.81 (12H, t, CH_2S), 3.39 (12H, d, O-CH2), 3.81(12H, bs, $ArCH_2Ar$), 6.69 (6H, s, ArH*para*), 6.75 (12H, s, ArH*meta*); 13C NMR (D_2O, 100MHz) δ(ppm) : 25.60 (O-CH_2-CH_2), 30.77 (Ar-CH_2-Ar), 48.31 (CH_2-S), 71.80 (CH_2-O-Ar), 114.78 (*para*C-Ar), 118.65 (*meta*C-Ar), 134.53 (*ortho*C-Ar), 163.17 (ArC-O-CH_2); ES m/z neg $[M-H]^-$: 1367.2 (100,0%)

Calix[8]aryloxy-49,50,51,52,53,54,55,56-octakis(propane-3-sulphonic acid) SC8b

Yield 23%, m.p. > 300°C; 1H NMR (D_2O, 300MHz) δ (ppm) : 2.04 (16H, m, CH_2CH_2O), 2.84 (16H, t, CH_2S), 3.60 (16H, d, O-CH_2), 3.74 (16H, bs, $ArCH_2Ar$), 6.79 (8H, s, ArH*para*), 6.92 (16H, s, ArH*meta*); 13C NMR (D_2O, 100MHz) δ(ppm) : 25.63 (O-CH_2-CH_2), 32.57 (Ar-CH_2-Ar), 48.51 (CH_2-S), 71.80 (CH_2-O-Ar), 116.70 (paraC-Ar), 118.80 (metaC-Ar), 134. 35 (orthoC-Ar), 164.07 (ArC-O-CH_2); ES m/z neg $[M-H]^-$: 1823.6(20,0%), $[M-2H]^{2-}$: 911.9 (100,0%).

General procedure for the preparation of *para*-sulphonatocalix[n]arene propane-3-sulphonic acids. SC4c, SC6c, SC8c.

para-sulphonato-calix[n]arene propane-3-sulphonic acids (SCnc) have been prepared following the procedure described by Hwang et al. [4] and adapting the procedure of Shinkai et al. [5]

para-sulphonato calix[n]arene (SCna) (2 mmol) was mixed with NaOH (10 eq. per OH group) in DMSO (15 mL) . Propane- 1,3-sultone (3eq. per hydroxyl group) was then added dropwise and the mixture was heated at

60°C for 2 days. DMSO is then distilled under reduced pressure. The obtained orange solid is dissolved in a minimum of water and then the product was precipitated from the solution by diluting with ethanol. This operation was repeated 3 times in order to remove inorganic salts. The obtained precipitate is filtered off, dried under vaccum and purified on HPLC.

para-sulphonato-calix[4]aryloxy-25,26,27,28-tetrakis-(propane-3-sulphonic acid) SC4c

Yield 35%, m.p. 20°C; 1H NMR (D2O, 300MHz) δ (ppm) 2.27 (8H, m, CH_2CH_2O), 3.32 (8H, t, SCH2), 3.75 (8H, bs, $ArCH_2Ar$), 3.94(8H, t, OCH_2), 7.43(8H, s, ArH), ES m/z neg $[M-H]^-$: 1231.3 (60,0%), $[M-2H]^{2-}$: 615.1 (100,0%).

para-sulphonato-calix[6]aryloxy-37,38,39,40,41,42-hexakis-propane-3-sulphonic acid) SC6c

Yield 20%, m.p. > 290°C; 1H NMR (D_2O, 300MHz) δ (ppm) 2.18 (12H, m, CH_2CH_2O), 3.36 (12 H, t, SCH_2), 3.74(12H, t, OCH_2), 4.05 (12H, bs, $ArCH_2Ar$), 7.53(12H, s, ArH)

ES m/z neg $[M-H]^-$: 1849.1 (50,0%), $[M-2H]^{2-}$: 924,1 (100,0%).

para-sulphonato-calix[8]aryloxy-49,50,51,52,53,54,55,56-octakis-(propane-3-sulphonic acid) SC8c

Yield 23%, m.p. > 300°C; 1H NMR (D_2O, 300MHz) δ (ppm) : 2.14 (16H, m, CH_2CH_2O), 3.18 (16H, t, SCH_2), 3.66 (16H, d, O-CH2), 4.04 (16H, bs, $ArCH_2Ar$),

7.59 (16H, s, ArH). ES m/z neg $[M-H]^-$: 2463.1 (45,0%), $[M-2H]^{2-}$: 1231.1 (100,0%).

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

The procedure of Xiong[6] 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 the various sulphonato-calix[n]arene aqueous solutions were added as stabilizers with stirring for 30 min. And then, 44 mg of $NaBH_4$ was added to the solution. The colloidal silver l suspensions were obtained after 5 minutes.

UV-Visible Absorption assays

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

DLS experiments

Particle size measurements were performed on a Zetasizer Nano ZS (Malvern Instruments, UK) with an angle of detection of 90°. The measurements were done 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.

SEM experiments

Samples for SEM acquisitions were prepared by spreading 3 µl of the nanoparticle suspensions on freshly cleaved mica surfaces. After drying at room temperature and Au-Pd sputter coating (15s at 15mA), micrographs were acquired using a Supra 40V system (Carl Zeiss, Switzerland) at an accelerating voltage of 20 kV using an in-lens detector. Statistical size measurements were performed measuring the diameter of at least 50 nanoparticles using the analysis® (Olympus, Germany) software package.

References and Note

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

[2] S. Shinkai, K. Araki, T. Tsubaki, T. Arimura, and O. Manabe, J. *Chem. Soc. Perkin Trans. 1*, 1987, 2297-2299

[3] S. Shinkai, T. Arimura, K. Arak, and H. Kawabata, *J. Chem. Soc. Perkin Trans. 1*, 1989, 2039-2045

[4] K.M. Hwang et al., Antithrombotic treatment with calixarene compounds, 1995, US54099959, p.46

[5] Shinkai, S. Mori, H. Koreishi, T. Tsubakiand O. Manabe, *J. Am. Chem. Soc.*, 1986, 2409-2416

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

[7] T. V. Kharitonova, N. I. Ivanova, B. D. Summ, *Colloid J.*, 2002, 64, 620-630.

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Supporting Figures:

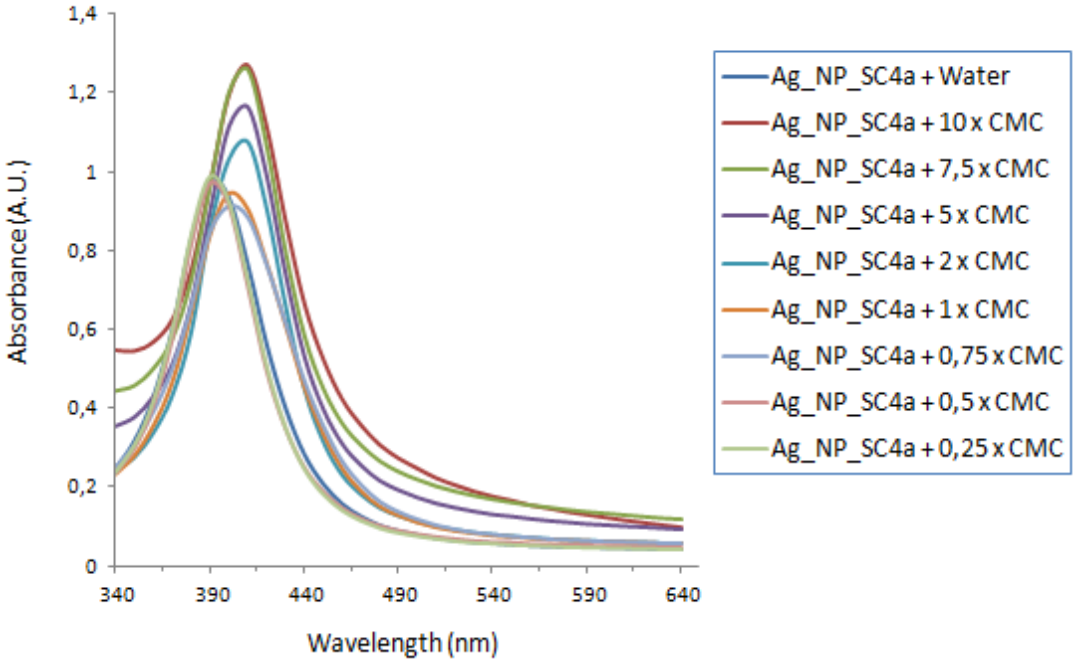

Fig. S1 UV-Visible spectra of *para*-sulphonato-calix[4]arene capped silver nanoparticles (Ag_NP_SC4a) as a function of cetyl pyridinium bromide concentration.

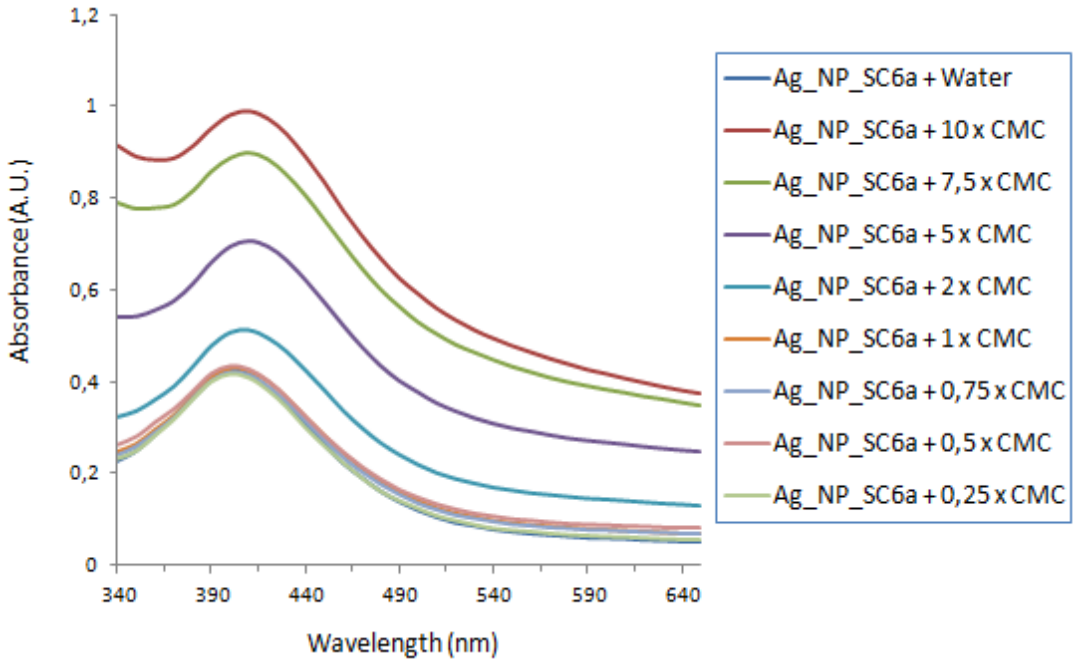

Fig. S2 UV-Visible spectra of *para*-sulphonato-calix[6]arene capped silver nanoparticles (Ag_NP_SC6a) as a function of cetyl pyridinium bromide concentration.

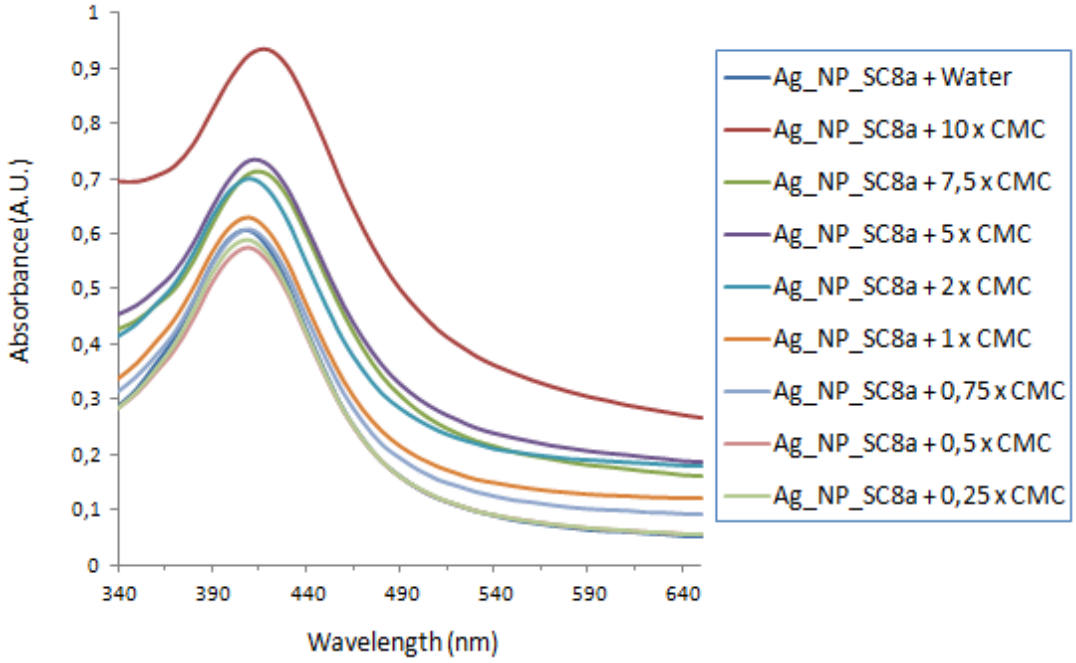

Fig. S3 UV-Visible spectra of *para*-sulphonato-calix[8]arene capped silver nanoparticles (Ag_NP_SC8a) as a function of cetyl pyridinium bromide concentration.

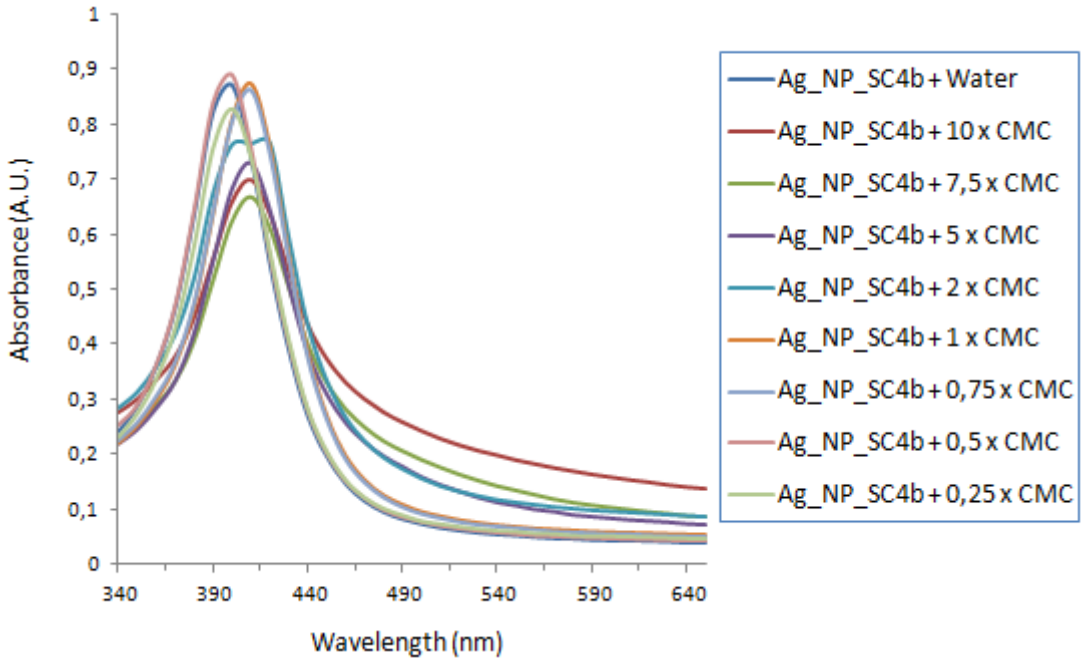

Fig. S4 UV-Visible spectra O-propoxysulphonate -calix[4]arene capped silver nanoparticles (Ag_NP_SC4b) as a function of cetyl pyridinium bromide concentration.

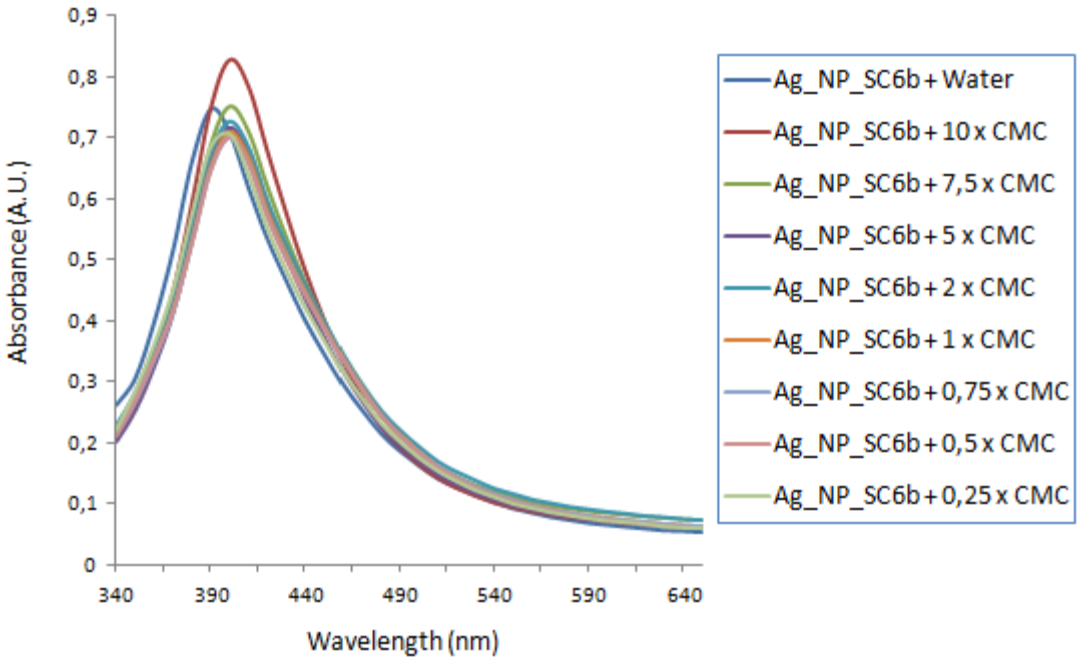

Fig. S5 UV-Visible spectra of O-propoxysulphonate -calix[6]arene capped silver nanoparticles (Ag_NP_SC6b) as a function of cetyl pyridinium bromide concentration.

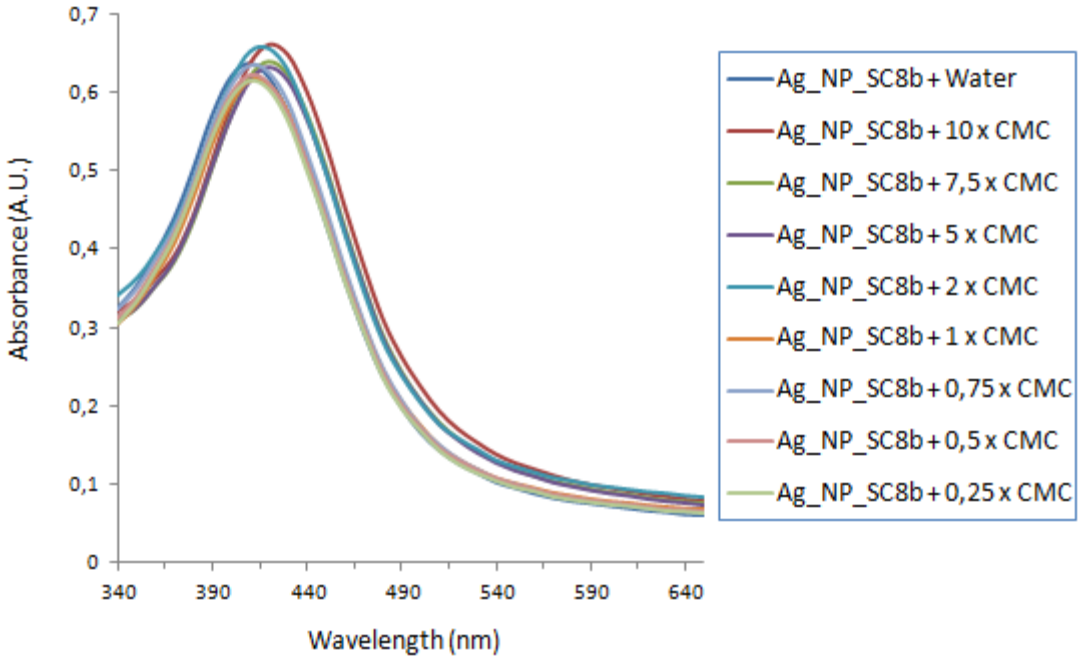

Fig. S6 UV-Visible spectra of O-propoxysulphonate -calix[8]arene capped silver nanoparticles (Ag_NP_SC8b) as a function of cetyl pyridinium bromide concentration.

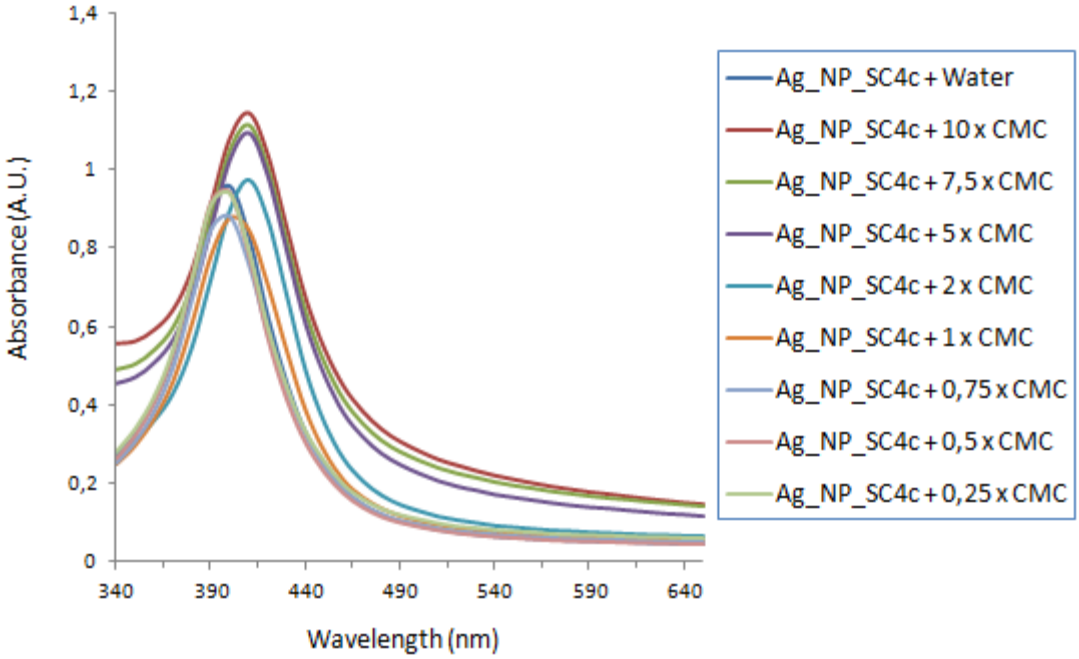

Fig. S7 UV-Visible spectra of *para*-sulphonato-calix[4]arene O-propoxysulphonate capped silver nanoparticles (Ag_NP_SC4c) as a function of cetyl pyridinium bromide concentration.

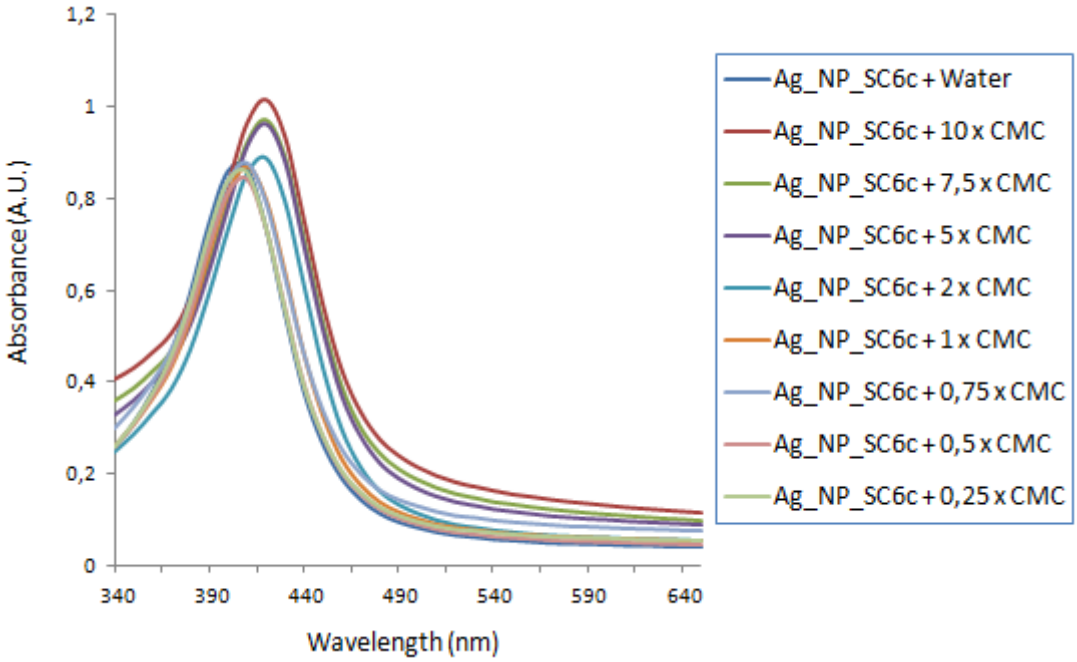

Fig. S8 UV-Visible spectra of *para*-sulphonato-calix[6]arene O-propoxysulphonate capped silver nanoparticles (Ag_NP_SC6c) as a function of cetyl pyridinium bromide concentration.

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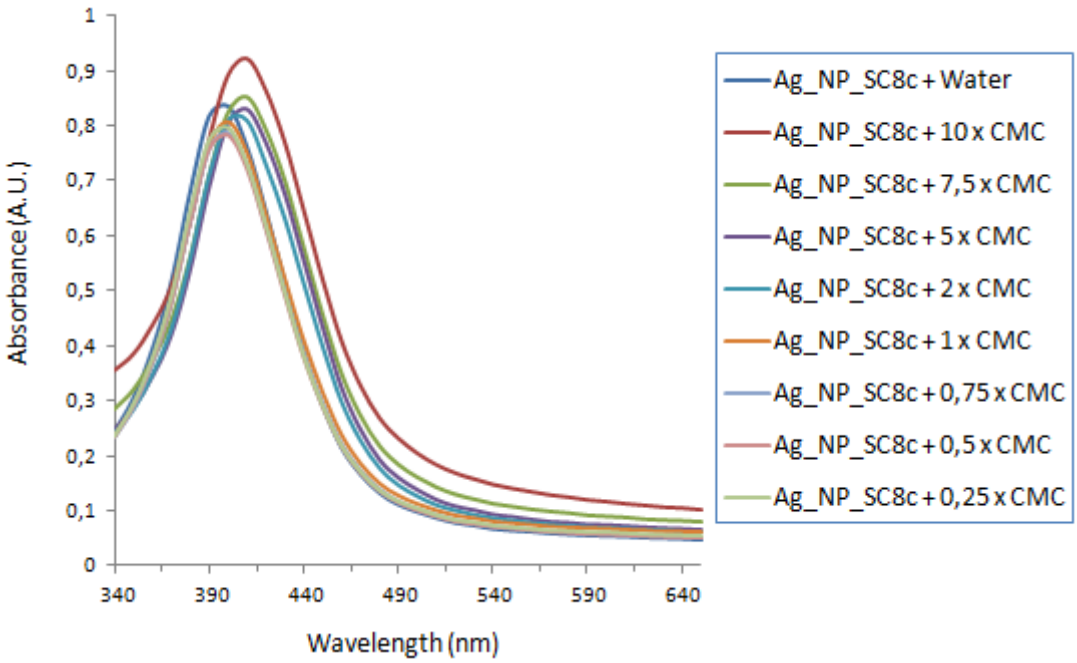

Fig. S9 UV-Visible spectra of *para*-sulphonato-calix[8]arene O-propoxysulphonate capped silver nanoparticles (Ag_NP_SC8c) as function of cetyl pyridinium bromide concentration.

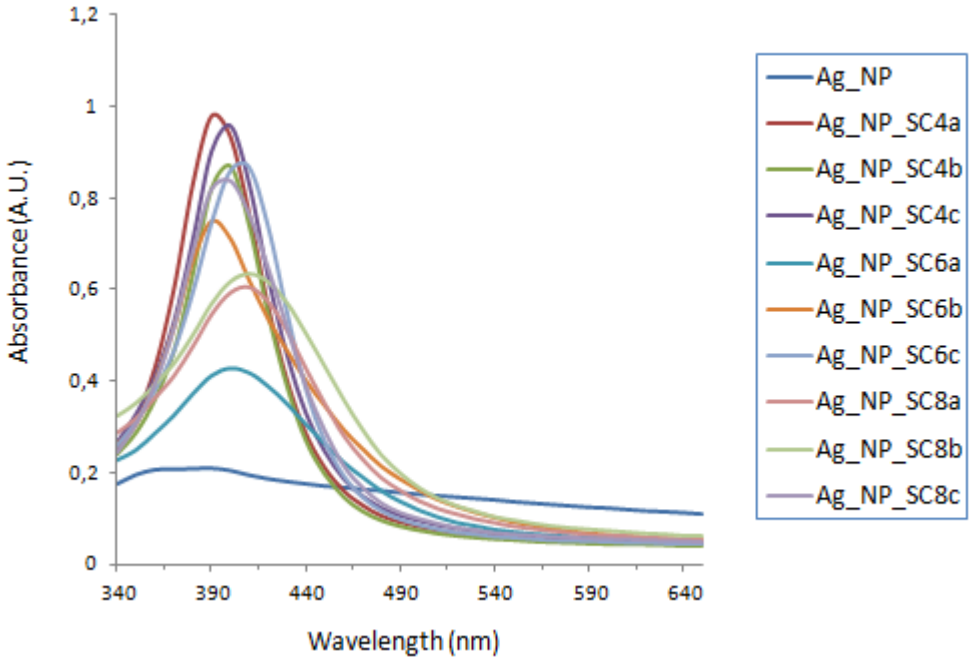

Fig. S10 UV-Visible spectra of calix[n]arene capped silver nanoparticles after one hour of their preparations. Ag_NP represents a solution of silver nitrate reduced by $NaBH_4$ in the ansence of calix[n]arene as stabilizer.

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Electron Microscopy

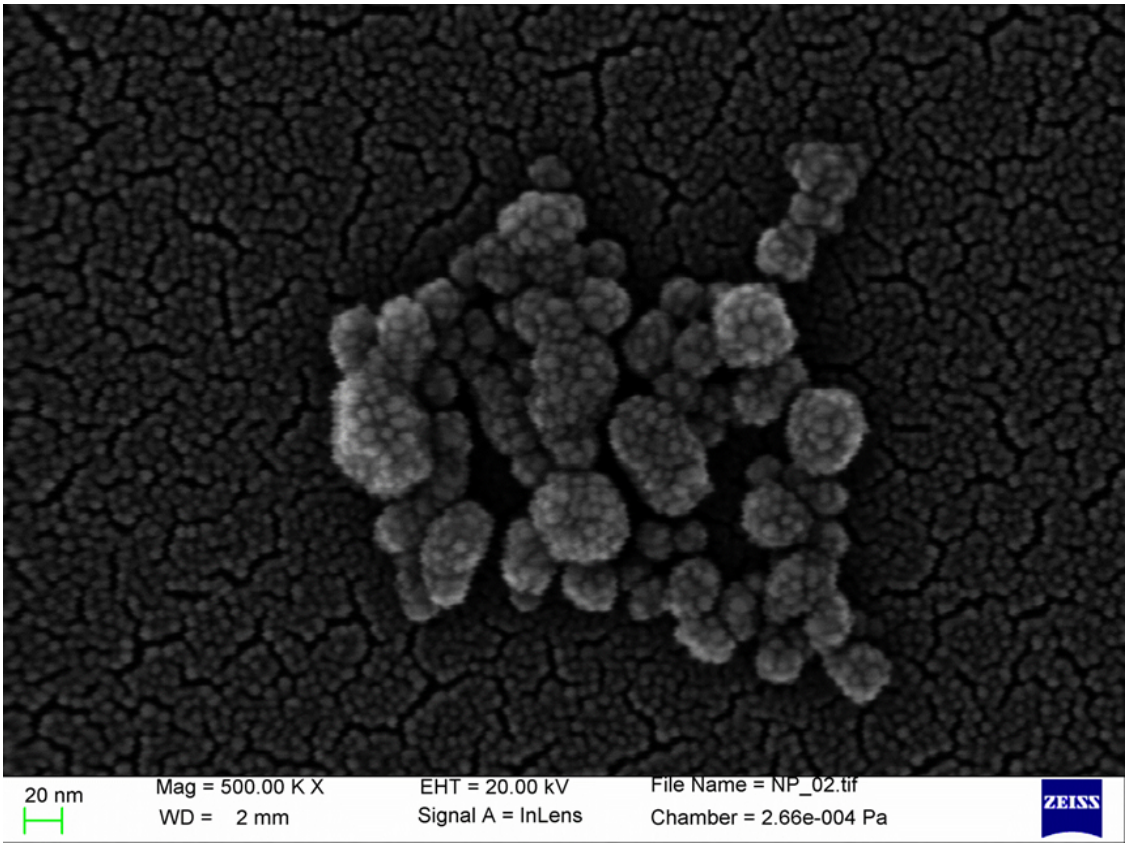

Fig. S11 SEM image of Ag_NP_SC4a

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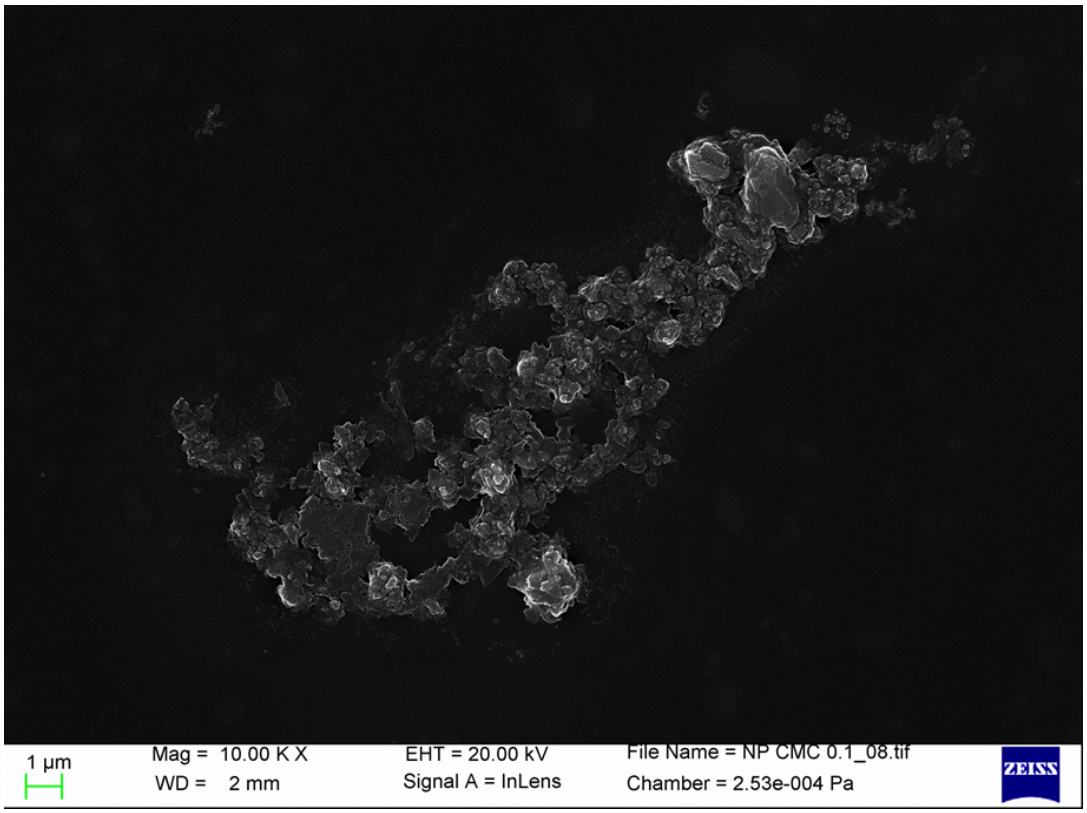

Fig. S12 SEM image of Ag_NP_SC4a mixed with of cetyl pyridinium bromide at 0.1 x CMC (ratio surfactant:nanoparticle = 1:1)

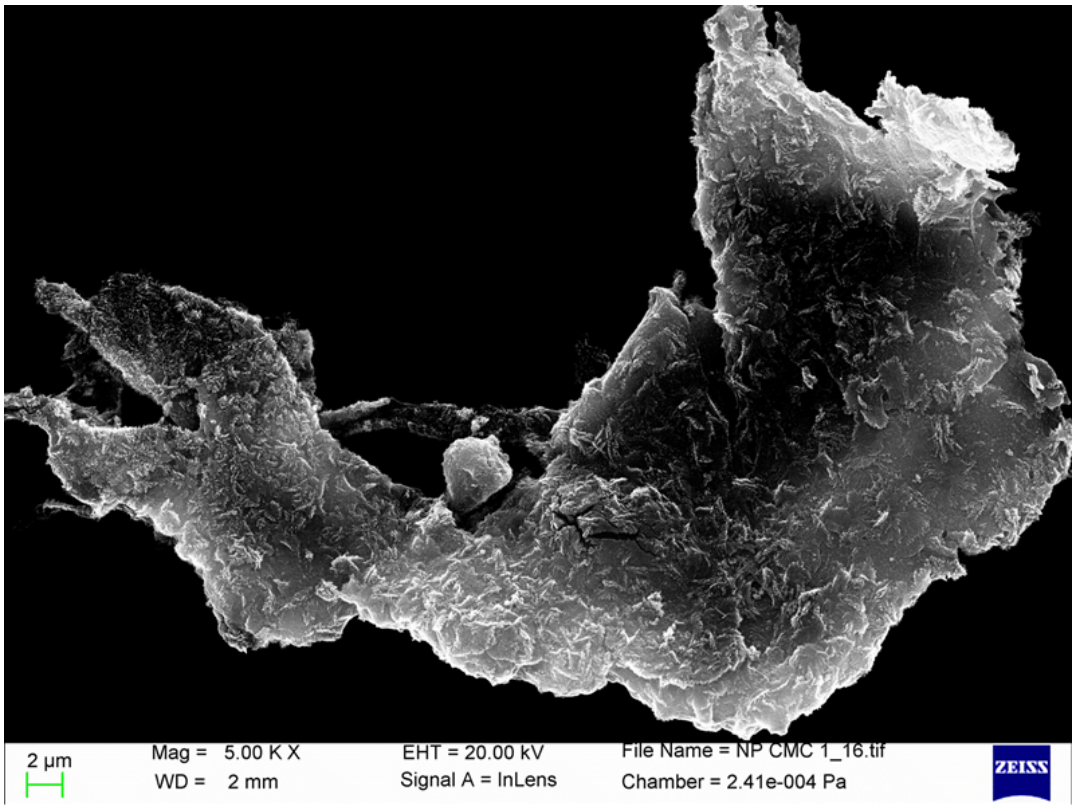

Fig. S13 SEM image of Ag_NP_SC4a mixed with of cetyl pyridinium bromide at 1 x CMC (ratio surfactant:nanoparticle = 10 : 1)

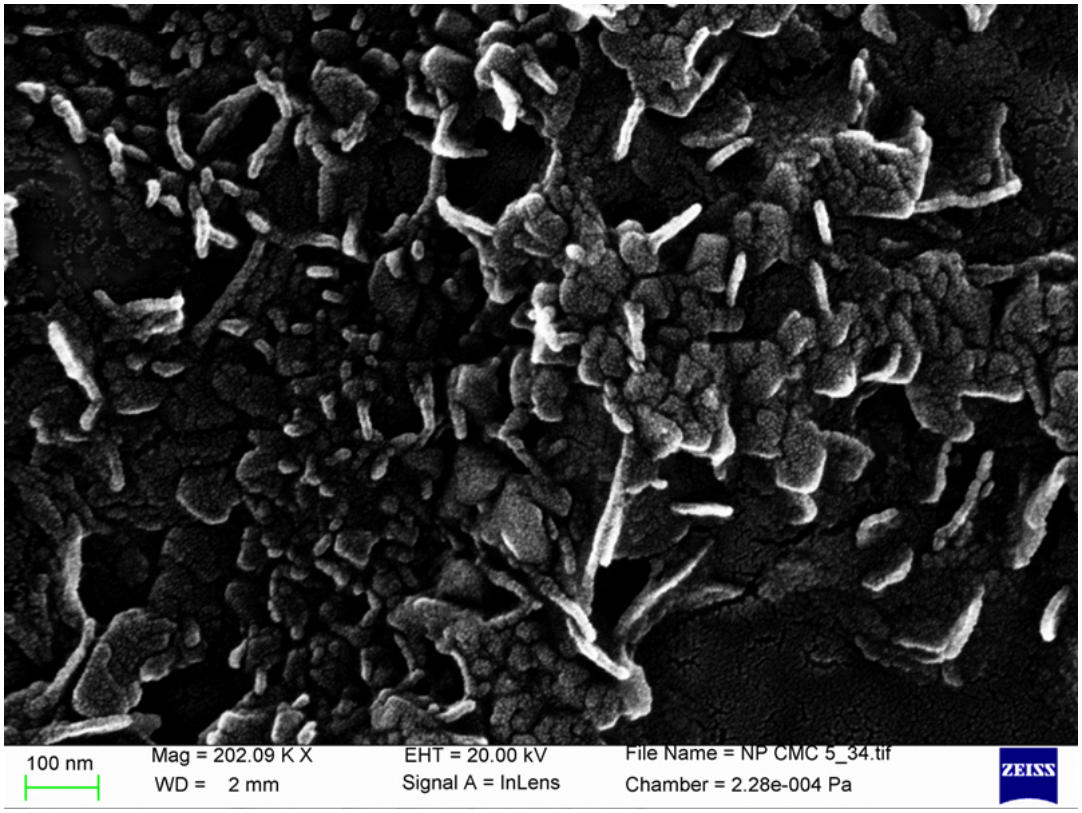

Fig. S14 SEM image of Ag_NP_SC4a mixed with cetyl pyridinium bromide at 5 x CMC (ratio surfactant:nanoparticle 50 : 1)

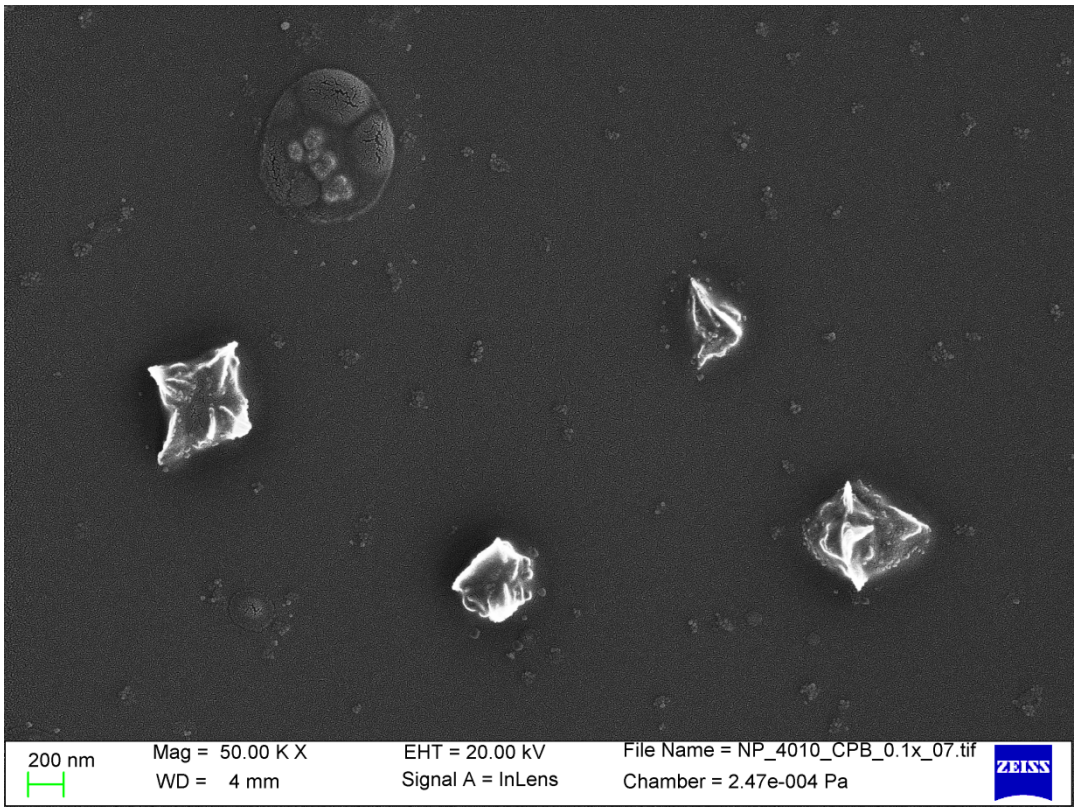

Fig. S15 SEM images of Ag_NP_SC4b mixed with cetyl pyridinium bromide at 0.1 x CMC (ratio surfactant:nanoparticle 1: 1)

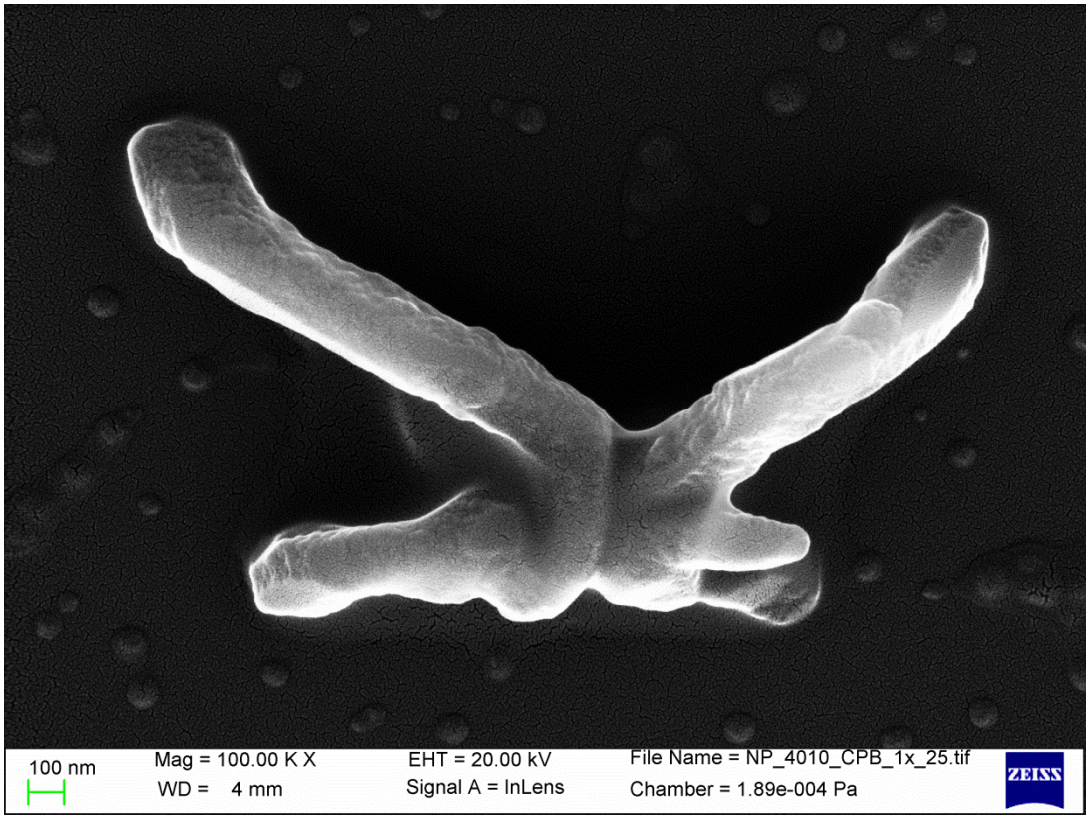

Fig. S16 SEM images of Ag_NP_SC4b mixed with cetyl pyridinium bromide at 1 x CMC (ratio surfactant:nanoparticle 10 : 1)

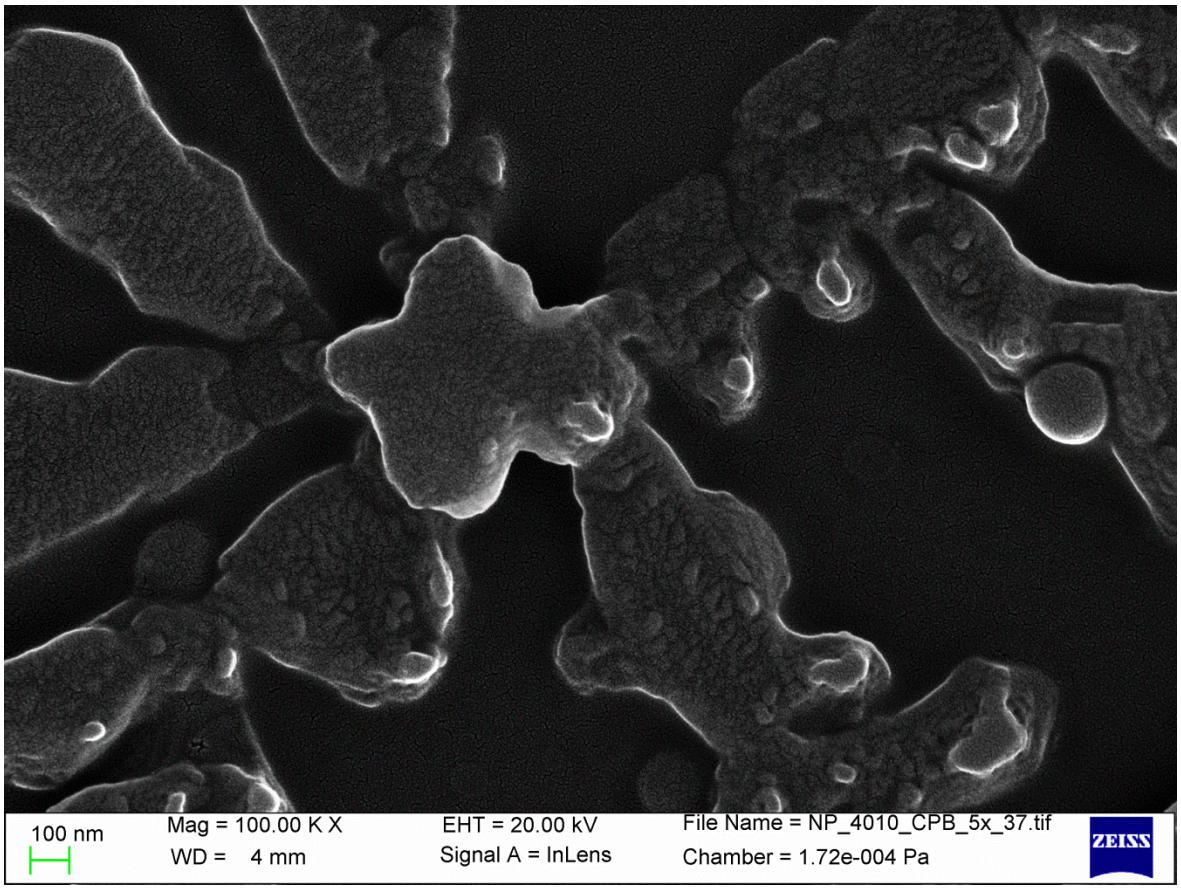

Fig. S17 SEM images of Ag_NP_SC4b mixed with cetyl pyridinium bromide at 5 x CMC (ratio surfactant:nanoparticle 50 : 1)

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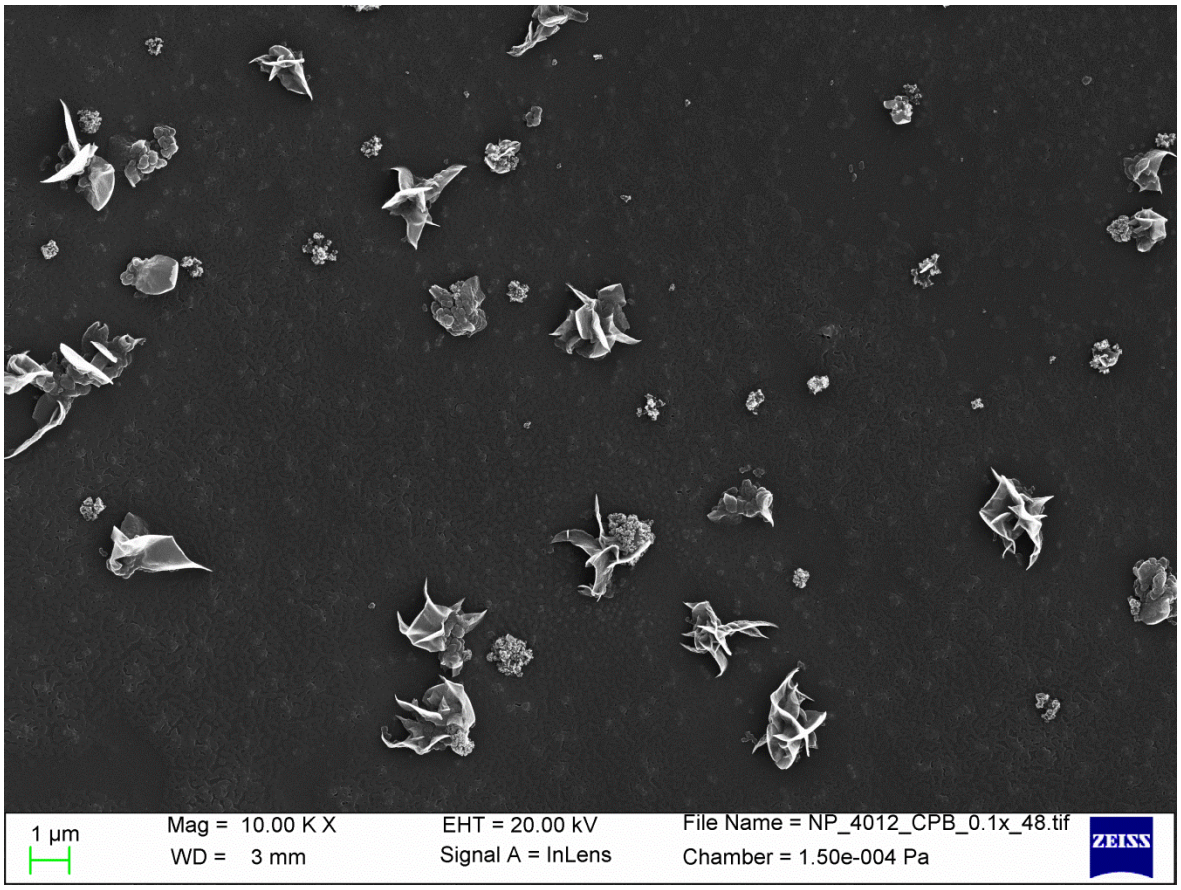

Fig. S18 SEM images of Ag_NP_SC4c mixed with cetyl pyridinium bromide at 0.1 x CMC (ratio surfactant:nanoparticle 1: 1)

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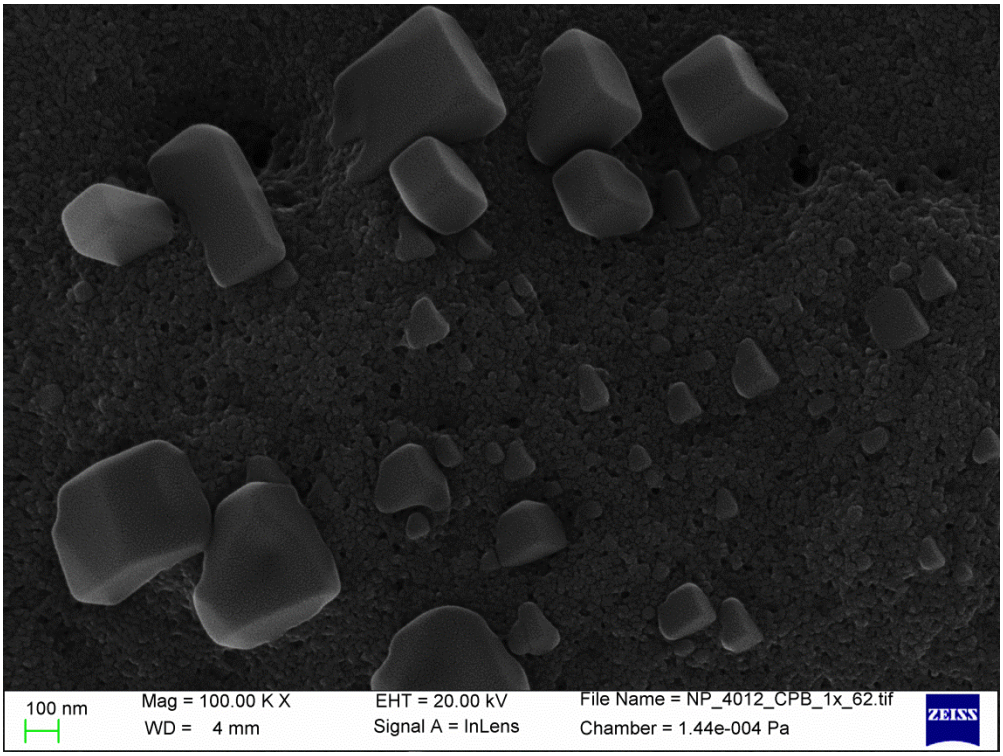

Fig. S19 SEM images of Ag_NP_SC4c mixed with cetyl pyridinium bromide at 1 x CMC (ratio surfactant:nanoparticle 10 : 1)

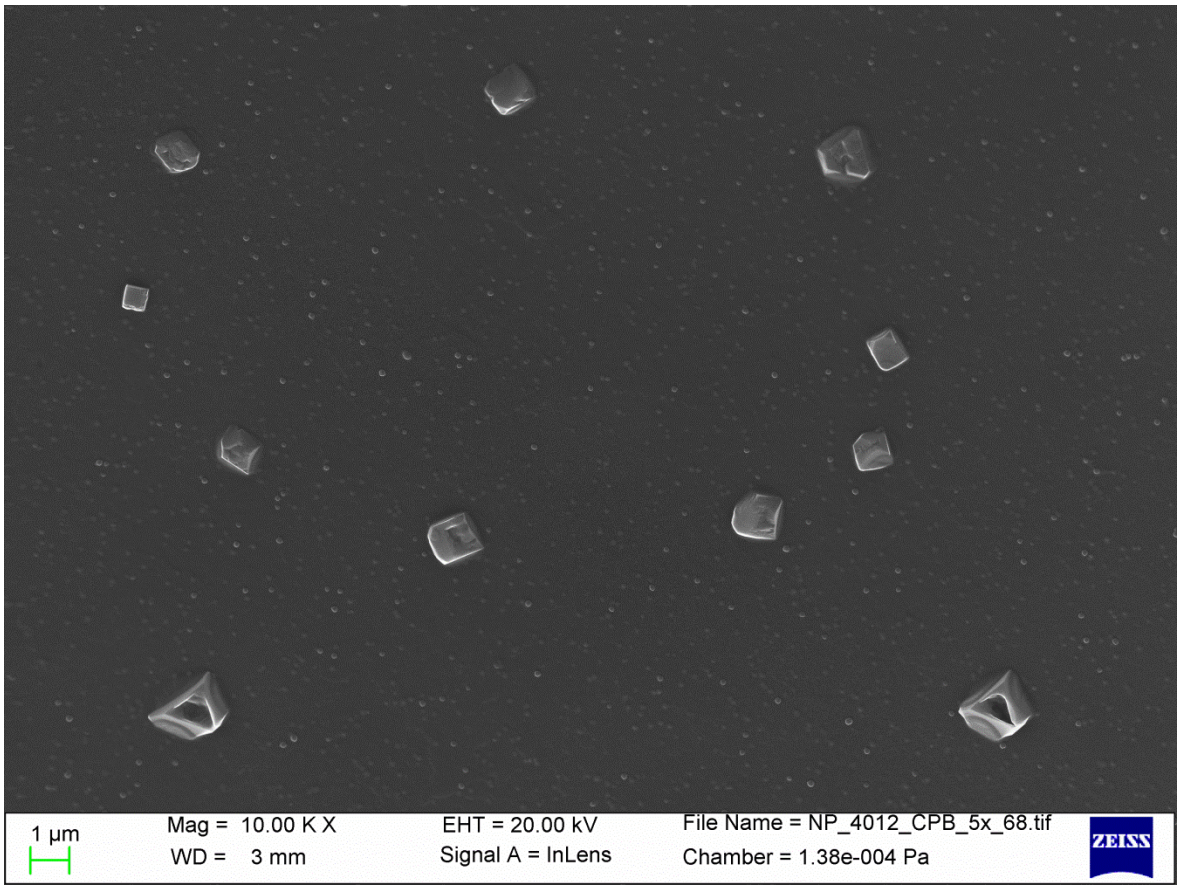

Fig. S20 SEM images of Ag_NP_SC4c mixed with cetyl pyridinium bromide at 5 x CMC (ratio surfactant:nanoparticle 50 : 1)

Dynamic Light Scattering

Sample	Diameter (nm)	PdI
Ag_NP_SC4a	32,99 ± 6,2	0,28
Ag_NP_SC4a + CPB 5x CMC	139,13 ± 0,33	0,16
Ag_NP_SC4a + CPB 1x CMC	60,82 ± 1,2	0,53
Ag_NP_SC4a + CPB 0,1x CMC	31,2 ± 0,96	0,47
Ag_NP_SC4a + CTAB 5x CMC	445,1 ± 9,4	0,26
Ag_NP_SC4a + CTAB 1x CMC	152,2 ± 0,4	0,3
Ag_NP_SC4a + CTAB 0,1x CMC	40,39 ± 5,46	0,28

Sample	Diameter (nm)	PdI
Ag_NP_SC4b	56,98 ± 0,92	0,099
Ag_NP_SC4b + CPB 5x CMC	69,38 ± 6,26	0,717
Ag_NP_SC4b + CPB 1x CMC	41,21 ± 1,59	0,467
Ag_NP_SC4b + CPB 0,1x CMC	596,26 ± 24,96	0,409
Ag_NP_SC4b + CTAB 5x CMC	53,8 ± 17,26	0,381
Ag_NP_SC4b + CTAB 1x CMC	44,07 ± 1,45	0,447
Ag_NP_SC4b + CTAB 0,1x CMC	99,98 ± 2,02	0,572

Sample	Diameter (nm)	PdI
Ag_NP_SC4c	62,25 ± 15,48	0,086
Ag_NP_SC4c + CPB 5x CMC	146,56 ± 0,74	0,099
Ag_NP_SC4c + CPB 1x CMC	105,9 ± 0,2	0,236
Ag_NP_SC4c + CPB 0,1x CMC	42,02 ± 13,98	0,323
Ag_NP_SC4c + CTAB 5x CMC	160,1 ± 2,4	0,176
Ag_NP_SC4c + CTAB 1x CMC	88,89 ± 0,5	0,233
Ag_NP_SC4c + CTAB 0,1x CMC	49,43 ± 36,88	0,34

Table S1 Z average of calix[4]arene capped silver nanoparticles (Ag_NP_SC4a, Ag_NP_SC4b and Ag_NP_SC4c) mixed with CTAB or CPB at different concentration ratio.

Sample	Diameter (nm)	PdI
Ag_NP_SC4a	32,99 ± 6,2	0,28
Ag_NP_SC4a + CPB / NOG 5x C^M	140,6 ± 0,5	0,37
Ag_NP_SC4a + CPB / NOG 1x C^M	77,6 ± 1,25	0,42
Ag_NP_SC4a + CPB / NOG 0,1x C^M	47,1 ± 1,2	0,08
Ag_NP_SC4a + CTAB / NOG 5x C^M	200,1 ± 8,2	0,21
Ag_NP_SC4a + CTAB / NOG 1x C^M	128,2 ± 1,2	0,34
Ag_NP_SC4a + CTAB / NOG 0,1x C^M	44,45 ± 2,1	0,1

Sample	Diameter (nm)	PdI
Ag_NP_SC4b	56,98 ± 0,92	0,099
Ag_NP_SC4b + CPB / NOG 5x C^M	80,38 ± 3,05	0,469
Ag_NP_SC4b + CPB / NOG 1x C^M	55,48 ± 1,53	0,475
Ag_NP_SC4b + CPB / NOG 0,1x C^M	44,13 ± 0,7	0,339
Ag_NP_SC4b + CTAB / NOG 5x C^M	74,55 ± 1,24	0,363
Ag_NP_SC4b + CTAB / NOG 1x C^M	62,1 ± 0,32	0,276
Ag_NP_SC4b + CTAB / NOG 0,1x C^M	64,43 ± 1,2	0,419

Sample	Diameter (nm)	PdI
Ag_NP_SC4c	62,25 ± 15,48	0,086
Ag_NP_SC4c + CPB / NOG 5x C^M	215,36 ± 4,83	0,266
Ag_NP_SC4c + CPB / NOG 1x C^M	142,43 ± 3,66	0,479
Ag_NP_SC4c + CPB / NOG 0,1x C^M	112,5 ± 0,7	0,312
Ag_NP_SC4c + CTAB / NOG 5x C^M	1444 ± 55	0,492
Ag_NP_SC4c + CTAB / NOG 1x C^M	191,26 ± 1,74	0,24
Ag_NP_SC4c + CTAB / NOG 0,1x C^M	130,23 ± 4,93	0,357

Table S2 Z average of calix[4]arene capped silver nanoparticles (Ag_NP_SC4a, Ag_NP_SC4b and Ag_NP_SC4c) mixed with NOG and CTAB (or CPB) at different concentration ratio.

Sample	Diameter (nm)	PdI
Ag_NP_SC4a	32,99 ± 6,2	0,28
Ag_NP_SC4a + CPB / Triton 5x C^M	159,8 ± 1,2	0,25
Ag_NP_SC4a + CPB / Triton 1x C^M	46,16 ± 0,3	0,43
Ag_NP_SC4a + CPB / Triton 0,1x C^M	39,22 ± 12,7	0,26
Ag_NP_SC4a + CTAB / Triton 5x C^M	217,1 ± 2,1	0,24
Ag_NP_SC4a + CTAB / Triton 1x C^M	140,4 ± 0,6	0,56
Ag_NP_SC4a + CTAB / Triton 0,1x C^M	30,48 ± 0,8	0,5

Sample	Diameter (nm)	PdI
Ag_NP_SC4b	56,98 ± 0,92	0,099
Ag_NP_SC4b + CPB / Triton 5x C^M	48,94 ± 3,65	0,46
Ag_NP_SC4b + CPB / Triton 1x C^M	51,61 ± 16,76	0,34
Ag_NP_SC4b + CPB / Triton 0,1x C^M	79,5 ± 0,66	0,247
Ag_NP_SC4b + CTAB / Triton 5x C^M	54,02 ± 8,91	0,436
Ag_NP_SC4b + CTAB / Triton 1x C^M	41,7 ± 1,95	0,448
Ag_NP_SC4b + CTAB / Triton 0,1x C^M	69,03 ± 1,41	0,46

Sample	Diameter (nm)	PdI
Ag_NP_SC4c	62,25 ± 15,48	0,086
Ag_NP_SC4c + CPB / Triton 5x C^M	368,8 ± 9,6	0,446
Ag_NP_SC4c + CPB / Triton 1x C^M	64,88 ± 0,86	0,274
Ag_NP_SC4c + CPB / Triton 0,1x C^M	69,21 ± 0,15	0,255
Ag_NP_SC4c + CTAB / Triton 5x C^M	266,23 ± 0,53	0,499
Ag_NP_SC4c + CTAB / Triton 1x C^M	90,91 ± 0,55	0,248
Ag_NP_SC4c + CTAB / Triton 0,1x C^M	81,84 ± 54,86	0,257

Table S3 Z average of calix[4]arene capped silver nanoparticles (Ag_NP_SC4a, Ag_NP_SC4b and Ag_NP_SC4c) mixed with Triton and CTAB (or CPB) at different concentration ratio.

Sample	Molar fraction Triton	C^M (M)
CTAB	0,19	0,000215
CPB	0,16	0,000258

Table S4 Exemple of calculation of C^M. The determination of the Critical Micellar Concentration Mixture (or C^M) was done from the molar ration of Triton used in all experiments. To obtain these values, we reported on the results obtained by Kharitonova [7]

Sample	Total concentration of CTAB / Triton (M)	C^M (M)
5x C^M	0,00615	28,6
1 x C^M	0,00123	5,7
0,1 xC^M	0,000123	0,6

Sample	Total concentration of CPB / Triton (M)	C^M (M)
5x C^M	0,00735	28,5
1 x C^M	0,00147	5,7
0,1 xC^M	0,000147	0,6

Table S5 Exemple of calculation of C^M. The Critical Micellar Concentration Mixture (or C^M) is then calculated proportionally to the C^M previously

determined according to the total concentration of surfactant mixture used in our experiments.