Supplementary Information

Stabilisation of small mono- and bimetallic gold-silver nanoparticles by calix[8]arene derivatives

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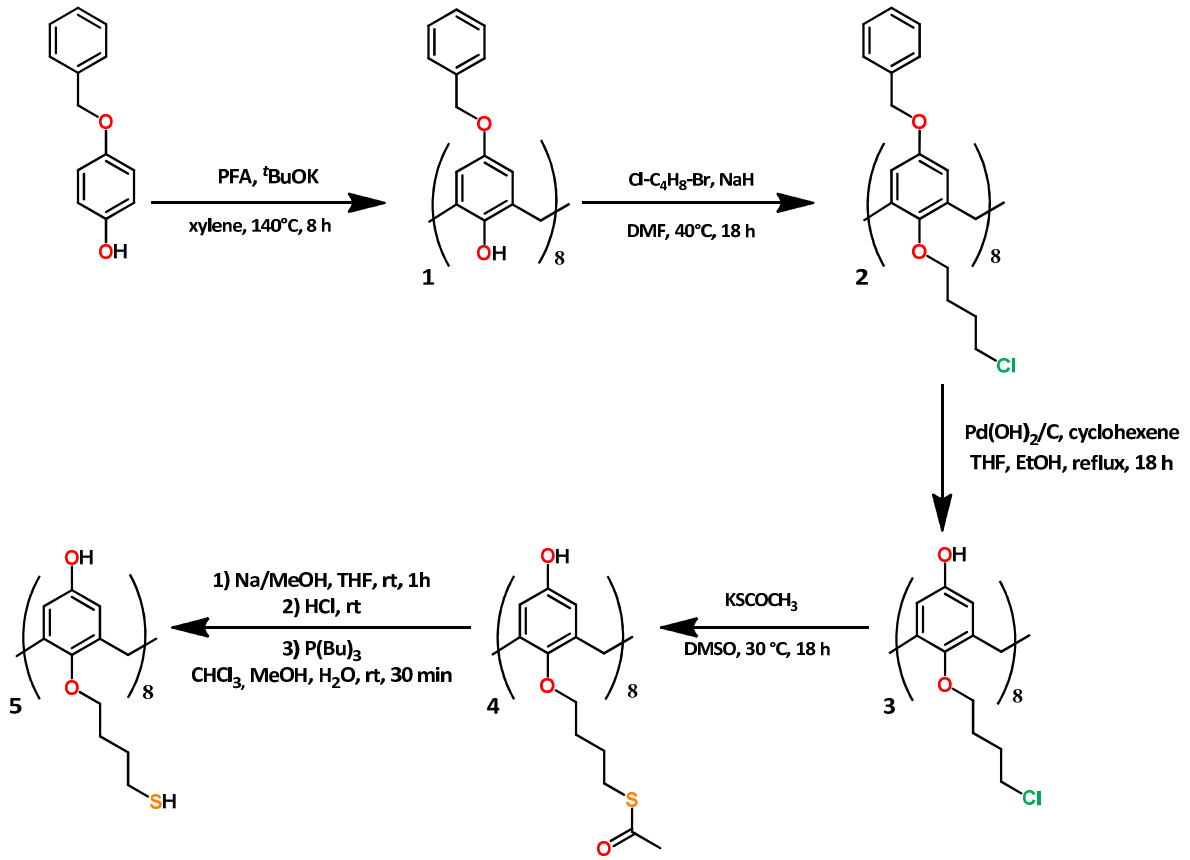
1. Synthesis of the octa(hydroxy)-octa(mercaptobutoxy)calix[8]arene 5



Scheme S1. Synthetic route toward the octa(hydroxy)-octa(mercapto)butoxycalix[8]arene **5**.

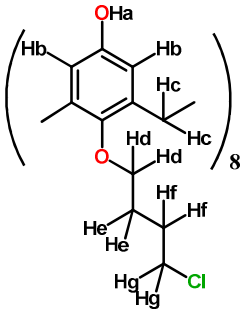
p-octa(benzyloxy)-octa(chlorobutoxy)calix[8]arène **2**:

To a solution of **1** (42.3 g, 24.9 mmol, 1 equiv.) in anhydrous DMF (64 mL) was added 1-bromo-4-chlorobutane (192.3 mL, 1.7 mol, 67 equiv.). The mixture was stirred and heated to 40 °C under argon. NaH (9.57 g, 0.4 mol, 16 equiv.) was **carefully** introduced in 3 times over 6 h and the reaction mixture was stirred for 18 h under argon at 40 °C. Then the mixture was cooled down and MeOH were added to the mixture to neutralize NaH excess (around 50 mL). The suspension was filtered through celite with CH_2Cl_2. The filtrate was stirred for 1 h with MeOH (500 mL). The suspension was filtered after one night and washed with MeOH. The residue was purified by column chromatography (SiO_2, toluene/CH_2Cl_2, gradient from 0 to 80 % CH_2Cl_2). The compound **2** was obtained as a white powder in 78.3 % yield (47.25 g, 19.5 mmol).

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.15 (*m*, 40H, **Ha**), 6.50 (*s*, 16H, **Hc**), 4.69 (*s*, 16H, **Hb**), 3.89 (*s*, 16H, **Hd**), 3.56 (*m*, 16H, **He**), 3.47 (*t*, 16H, $^3J(H_e,H_h)$=6.4 Hz, **Hh**), 1.74 (*m*, 16H, **Hf**), 1.64 (*m*, 16H, **Hg**).

^{13}C NMR (300 MHz, DMSO-d_6, ppm): δ 153.8, 148.5, 136.7, 134.3, 128.0, 127.4, 114.4, 72.0, 68.9, 44.9, 30.5, 29.5, 28.8, 27.0.

m/z (ESI, CH_2Cl_2-isopropanol, positive mode): 2439.85 $[M+Na]^+$ (calc. = 2416.36).



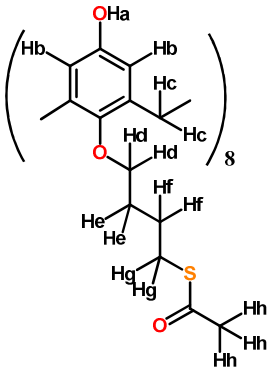
p-octa(hydroxy)-octa(chlorobutoxy)calix[8]arène **3**:

To a suspension of **2** (4 g, 1.65 mmol, 1 equiv.) in THF (70 mL) and EtOH (70 mL) in a two-necked flask equipped with a reflux condenser were added cyclohexene (45 mL, 0.44 mol, 300 equiv.) and Pearlman's catalyst $Pd(OH)_2/C$ (20 % Pd, 2.64 g, 18.80 mmol, 11 equiv.) at room temperature (rt). The mixture was stirred overnight under argon at 75°C. The mixture was cooled down and filtered through celite and washed with THF. The solvent was removed under reduced pressure at 40 °C. A yellowish oil was obtained and stirred in 200 mL pentane overnight. The mixture was filtered and the residual solid washed with pentane. The solid residue was washed with Et_2O for 2 h (2 x 100 mL). The solution was filtered and the residual solid was washed with Et_2O and dried under vacuum. The product **3** was obtained as a white powder in 98 % yield (2.75 g, 1.61 mmol).

^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 8.85 (*s*, 8H, **Ha**), 6.30 (*s*, 16H, **Hc**), 3.79 (*s*, 16H, **Hb**), 3.55 (*m*, 32H, **He**/**Hf**), 1.80 (*m*, 16H, **Hd**), 1.70 (*m*, 16H, **Hg**).

^{13}C NMR (300 MHz, DMSO-d_6, ppm): δ 153.72, 148.28, 135.20, 115.96, 73.16, 67.96, 46.17, 30.07, 28.13.

m/z ESI (THF-isopropanol, negative mode): 1695.48 $[M-H]^+$ (calc. = 1696.48).



p-octa(hydroxy)-octa(thioacetanobutoxy)calix[8]arène **4**:

To a solution of **3** (2 g, 1.18 mmol, 1 equiv.) in DMSO (40 mL) was added potassium thioacetate (1.34 g, 11.8 mmol, 10 equiv.) at rt. The mixture was stirred overnight at rt under argon. The solution was diluted with water (450 mL) and placed for 1 h at -15 °C. Then, the solution was stirred for 2 h at rt. The solution was filtered and the solid was washed with water and dried under vacuum. The crude residue was purified by column chromatography (SiO_2, $MeOH/CH_2Cl_2$ gradient from 2 to 3 % MeOH). The product **4** is obtained as white powder in 78 % yield (1.85 g, 0.92 mmol).

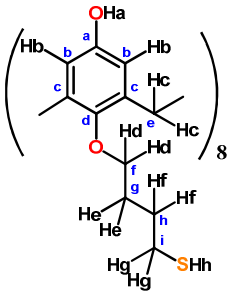
^{1}H NMR (250 MHz, DMSO-d_6, ppm): δ 8.75 (*s*, 8H, **Ha**), 6.26 (*s*, 16H, **Hb**), 3.79 (*s*, 16H, **Hc**), 3.57 (*t*, 16H, **Hd**), 2.84 (*t*, ^3J (**Hg**,**Hh**)=6.4 Hz, 16H, **Hg**), 2.27 (*s*, 24H, **Hh**), 1.67 (*m*, 32H, **He**/**Hf**).

^{13}C NMR (300 MHz, DMSO-d_6, ppm): δ 195.97, 153.64, 148.28, 135.17, 115.89, 73.40, 31.32, 29.77, 29.27, 26.97.

m/z (ESI, THF-isopropanol, positive mode): 2039.65 $[M+Na]^+$ (calc. = 2016.66).

m/z (ESI, THF-isopropanol, negative mode): 2015.65 $[M-H]^+$ (calc. = 2016.66).

IR (KBr, cm^{-1}): 3200 (vs, O-H stretching); 3024, 2938, 2867 (s, C-H stretching); 1689, 1665 (vs, C=O stretching); 1597, 1455 (vs, aromatic breathing); 1204 (vs, C-O stretching).



p-octa(hydroxy)-octa(mercaptobutoxy)calix[8]arène **5**:

To a degassed solution of compound **4** (0.40 g, 0.198 mmol, 1 equiv.) in dry THF (5 mL) was added a degassed solution of Na (0.274 g, 11.88 mmol, 60 equiv.) in dry MeOH (5 mL). The mixture was stirred for 1 h at rt. To the mixture was added dropwise an aqueous solution of HCl (1 M) until a pH of 1 was reached. The residue was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over $MgSO_4$ and filtered with CH_2Cl_2. The solvent was removed under vacuum. The residue was resolubilised under argon in a mixture of $CHCl_3$/MeOH/H_2O (30/4/0.5 mL) and tri-*n*-butylphosphine (586 µL, 2.38 mmol, 12 equiv.) was added. The mixture was stirred for 30 min at rt. Pentane (200 mL) was fed upon stirring for 15 min. The mixture was filtered and the solid was dried under vacuum. The product **5** was obtained as a white powder in 91 % yield (0.8 g, 0.475 mmol).

^{1}H NMR (360 MHz, $CDCl_3$/MeOD: 80:20, ppm): δ 6.16 (*s*, 16H, **Hb**), 3.80 (*s*, 16H, **Hc**), 3.58 (*bs*, 16H, **Hd**), 2.43 (*t*, 16H, **Hg**), 1.68 (*bs*, 32H, 16**He**/16**Hf**).

^{1}H NMR (360 MHz, DMSO-d_6, ppm): δ 8.82 (*s*, 8H, **Ha**), 6.28 (*s*, 16H, **Hb**), 3.79 (*s*, 16H, **Hc**), 3.55 (*brt*, 16H, **Hd**), 2.45 (*dt*, $^3J(Hg,Hh)$= 7.3 Hz, 16H, **Hg**), 2.06 (*s*, 8H, **Hh**), 1.67 (*bs*, 32H, **He**/**Hf**).

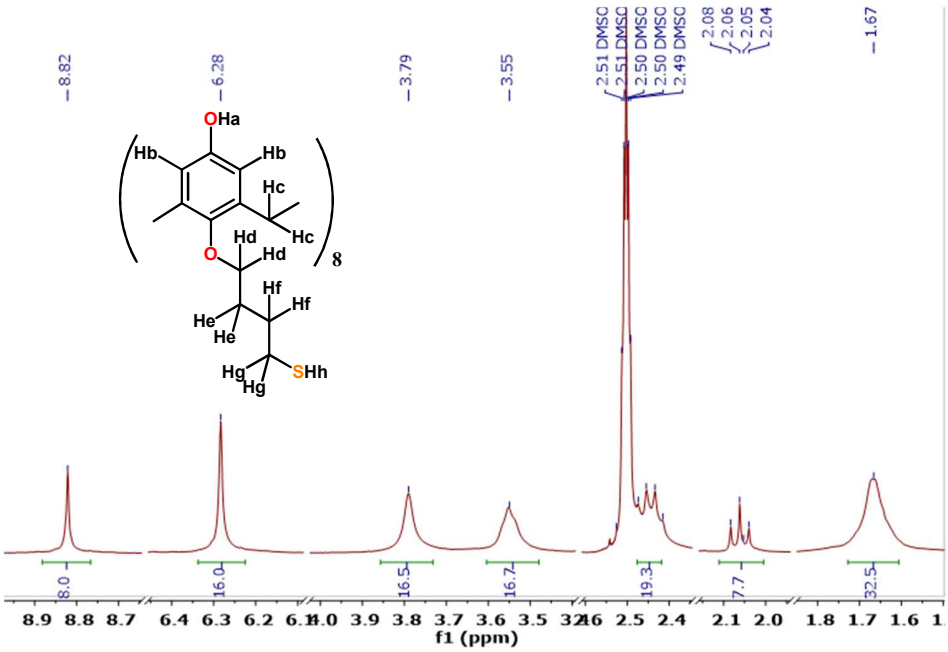
^{13}C NMR (300 MHz, $CDCl_3$/MeOD: 80/20, ppm): δ 152.26 (**Cd**), 148.39 (**Ca**), 135.17 (**Cc**), 115.30 (**Cb**), 73.19 (**Cf**), 30.85 (**Cg**), 29.93 (**Ce**), 29.17 (**Ch**), 24.52 (**Ci**).

m/z (ESI, THF-MeOH, positive mode): 1680.57 $[M+H]^+$, 1703.54 $[M+Na]^+$, 1718.54 $[M+K]^+$ (calc. = 1680.57).

m/z (ESI, THF-MeOH, negative mode): 1679.57 $[M-H]^+$ (calc. = 1680.57).

IR (KBr, cm^{-1}): 3293 (*vs*, O-H stretching); 2935, 2867 (*s*, C-H stretching); 2561 (*w*, S-H stretching); 1598, 1456 (*vs*, aromatic breathing); 1205, 1006 (*vs*, C-O stretching); 861 (*s*, aromatic C-H stretching).

2. ^{1}H-NMR spectrum of calix[8]arene 5

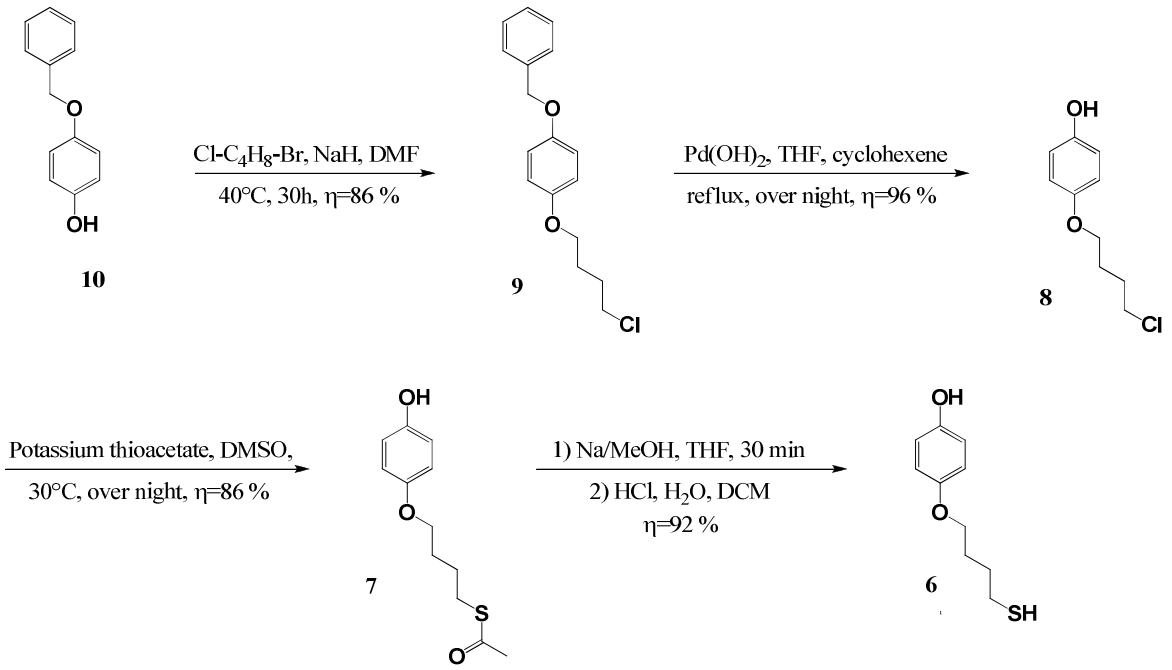


Protons	**Ha**	**Hb**	**Hc**	**Hd**	**He**	**Hf**	**Hg**	**Hh**
δ (ppm)	8.82	6.28	3.79	3.55	1.67	1.67	2.43	2.06

Figure S1. ^{1}H-RMN spectrum of calix[8]arene **5** in d_6-DMSO, recorded at 360 MHz and 25 °C..

The symmetry and high flexibility allow the recording of well-resolved, symmetrical and narrow signals. The integration of all signals gives a multiple of 8. It is to be noted that the signal at 2.43 ppm, attributed to the protons **Hg** located on carbon atom in α position of the sulfur atom, corresponds to a splitted triplet due to the coupling between these protons and the proton **Hh** on the sulfur atom ($^{3}J(Hg,Hh)$= 7,34 Hz).

3. Synthesis of the monomer 4-(4-mercaptobutoxy)phenol



Scheme 2. Synthetic route toward the monomer **6**

1-(benzyloxy)-4-(4-chlorobutoxy)benzene **9**

A solution of **10** (10 g, 50 mmol) in 1-Bromo-4-chlorobutane (37 mL) and anhydrous DMF (4 mL) was placed under argon and stirred at 40 °C. NaH (4 g, 100 mmol) was carefully introduced in small fractions over 6 h and the reaction mixture was heated overnight at 50 °C. The middle was condensed at 70 °C under reduced pressure and precipitated with pentane (500 mL). The suspension was placed overnight at 0 °C and filtered (12.46 g, η=86 %).

^{1}H NMR ($CDCl_3$, ppm): 7.45-7.31 (m, 5H), 6.92-6.80 (m, 4H), 5.02 (s, 2H), 3.94 (t, 2H), 3.62 (t, 2H), 1.94 (m, 4H).

m/z (ESI, THF-EtOH, positive mode): 313.09 [$M+Na^+$].

4-(4-chlorobutoxy)phenol **8**

A suspension of **9** (8 g, 27.5 mmol) and $Pd(OH)_2$/C (20 % Pd, 3 g) in cyclohexene (90 mL) and THF (300 mL) was placed under argon and refluxed overnight. The suspension was then filtered over celite, condensed under reduced pressure and precipitated in pentane (200 mL). The white powder was filtrated and dried under vacuum (5.32 g, 2.65 mmol, η=96 %).

^{1}H NMR ($CDCl_3$, ppm): 6.77 (s br, 4H), 5.29 (s vbr, 1H), 3.94 (t, 2H), 3.61 (t, 2H), 1.94 (m, 4H).

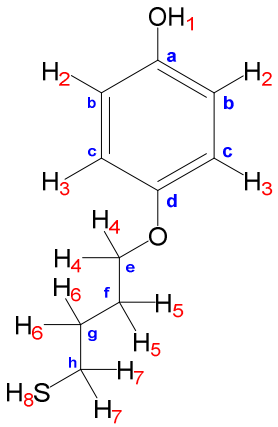
m/z (ESI, THF-EtOH, negative mode): 199.05 ([M-H$^+$].

S-4-(4-hydroxyphenoxy)butyl ethanethioate **7**

A solution of **8** (4 g, 19.9 mmol) and potassium thioacetate (2.5 g, 21.9 mmol) in DMSO (34 mL) was heated overnight at 30 °C. A solution of brine was added and the middle was extracted twice with DCM (50 mL). After evaporating DCM, the residue was recrystallized in heptane and filtered to afford a white powder (4.12 g, 17.1 mmol, η=86 %).

^{1}H NMR ($CDCl_3$, ppm): 6.75 (s, 4H), 3.89 (t, 2H), 2.93 (t, 2H), 2.33 (s, 3H), 1.79 (m, 4H).

m/z (ESI, THF-EtOH, negative mode): 239.07 ([M-H$^+$].



4-(4-mercaptobutoxy)phenol **6**

A suspension of MeONa in anhydrous MeOH (Na: 2.30 g, 100 mmol; MeOH: 5 mL) under argon was added to a solution of compound **2** (3 g, 12.5 mmol) in anhydrous THF (40 mL) under argon. The reaction mixture was stirred 30 min and treated with sonicated HCl 1M (100 mL), then extracted with DCM (3×50mL). The combined organic phases were dried over $MgSO_4$ and condensed under reduced pressure at room temperature. The product was recrystallized in heptane (300 mL) and filtrated to afford needles (2.25 g, 11.36 mmol, η=92 %).

^{1}H NMR ($CDCl_3$, ppm): 6.76 (s, $2H_2$+$2H_3$), 5.09 (s vbr, $1H_1$), 3.91 (t, $2H_4$), 2.60 (q, $2H_7$), 1.83 (m, $2H_5$ + $2H_6$), 1.39 (t, $1H_8$).

^{13}C NMR ($CDCl_3$, ppm): 153.35 (C_d), 149.85 (C_a), 116.42 (C_c), 116.06 (C_b), 68.46 (C_e), 30.90 (C_f), 28.37 (C_g), 24.71 (C_h).

m/z (ESI, THF-EtOH, negative mode): 197.07 [M-H$^+$].

4. Characterisation of silver nanoparticles stabilised by calix[8]arenes 5

Effect of Ag^+/calix ratio

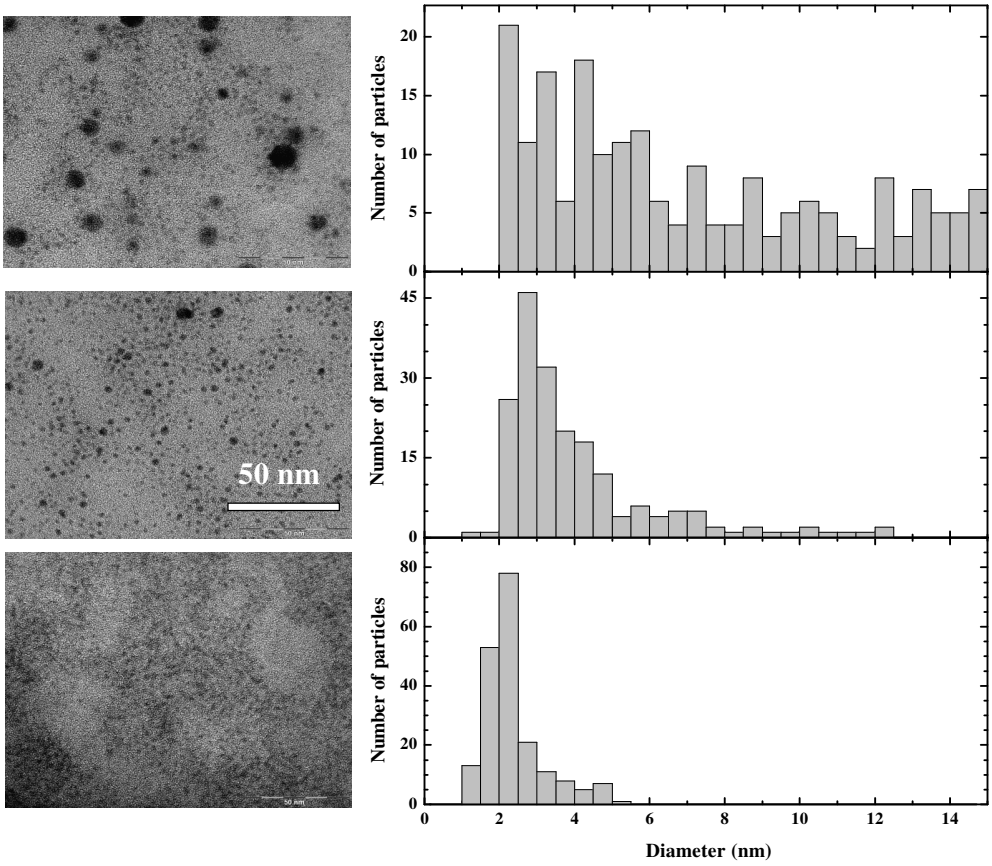


Figure S2. TEM micrographs and size distribution of silver nanoparticles obtained by total γ-reduction of ethanolic solutions containing 5×10^{-5} M calix[8]arene **5** and different concentrations of $AgClO_4$: **(top)** 1×10^{-3} M (dose 1440 Gy), **(middle)** 7.5×10^{-4} M (dose 1080 Gy), **(bottom)** 5×10^{-4} M (dose 720 Gy). The scale is the same for the three micrographs.

4. Characterisation of silver nanoparticles stabilised by calix[8]arenes 5

Effect of silver salts

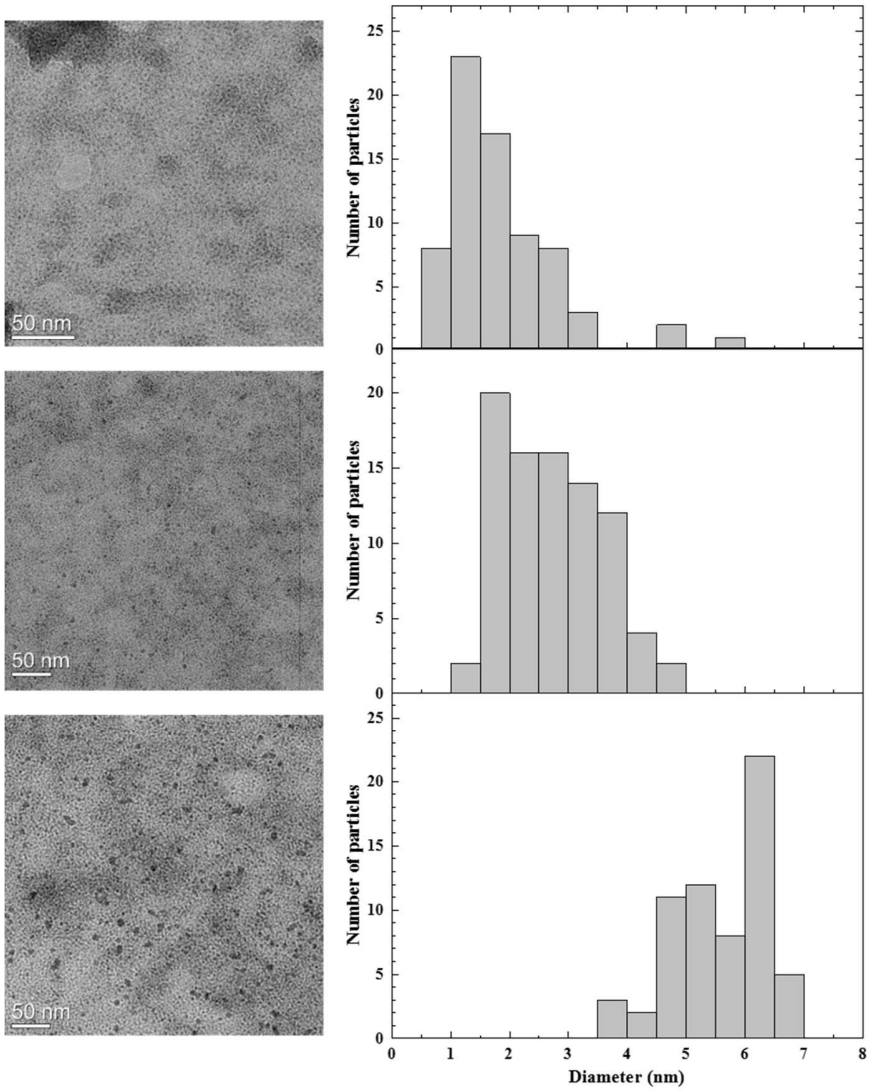


Figure S3. TEM micrographs and size distribution of silver nanoparticles obtained by total γ-reduction (dose 720 Gy) of ethanolic solutions containing 5×10^{-5} M calix[8]arene 5 and 5×10^{-4} M silver salt : **(top)** $AgPF_6$**, (middle)** AgOTf, **(bottom)** $AgBF_4$.

5. Characterisation of gold nanoparticles stabilised by calix[8]arenes 5

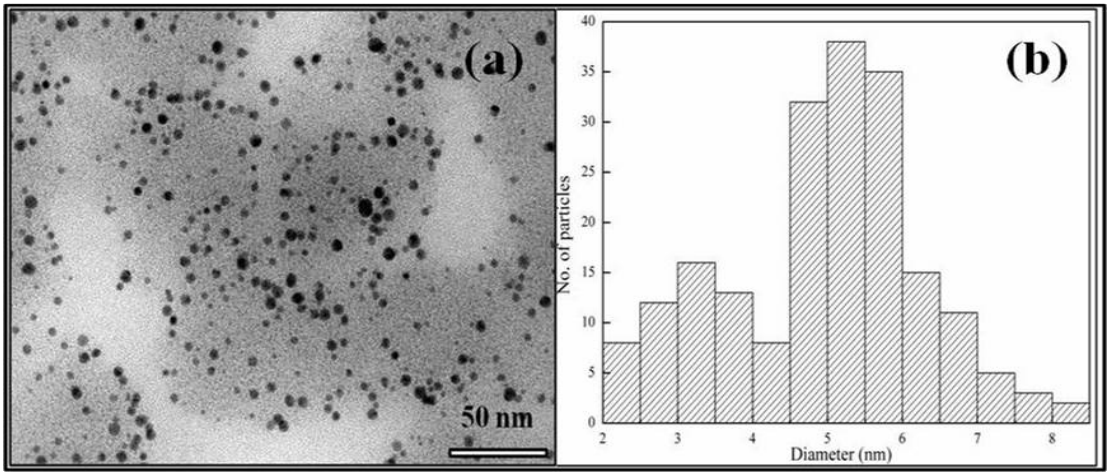


Figure S4. (a) TEM micrographs and **(b)** size distribution of gold nanoparticles obtained by total γ-reduction (dose 2160 Gy) of ethanolic solutions containing 5×10^{-5} M calix[8]arene **5** and 5×10^{-4} M $HAuCl_4$.

6. Characterisation of gold-silver nanoparticles stabilised by calix[8]arenes 5

Effect of silver salt

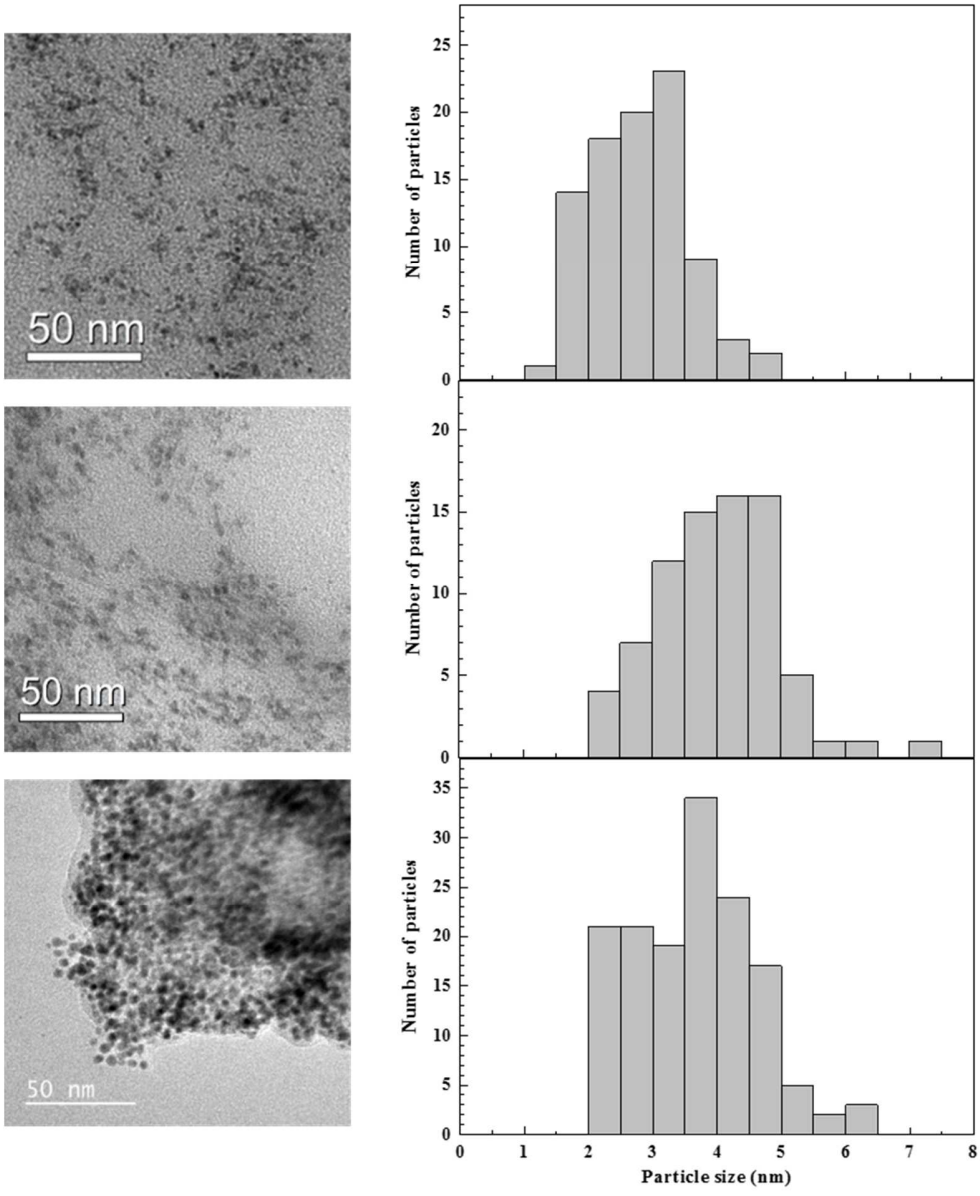


Figure S5. TEM micrographs and size distribution of gold-silver nanoparticles obtained by total γ-reduction (dose 1440 Gy) of ethanolic solutions containing 5×10^{-5} M calix[8]arene **5**, 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M silver salt: **(top)** $AgPF_6$**, (middle)** AgOTf, **(bottom)** $AgClO_4$.

6. Characterisation of gold-silver nanoparticles stabilised by calix[8]arenes 5

XPS analysis

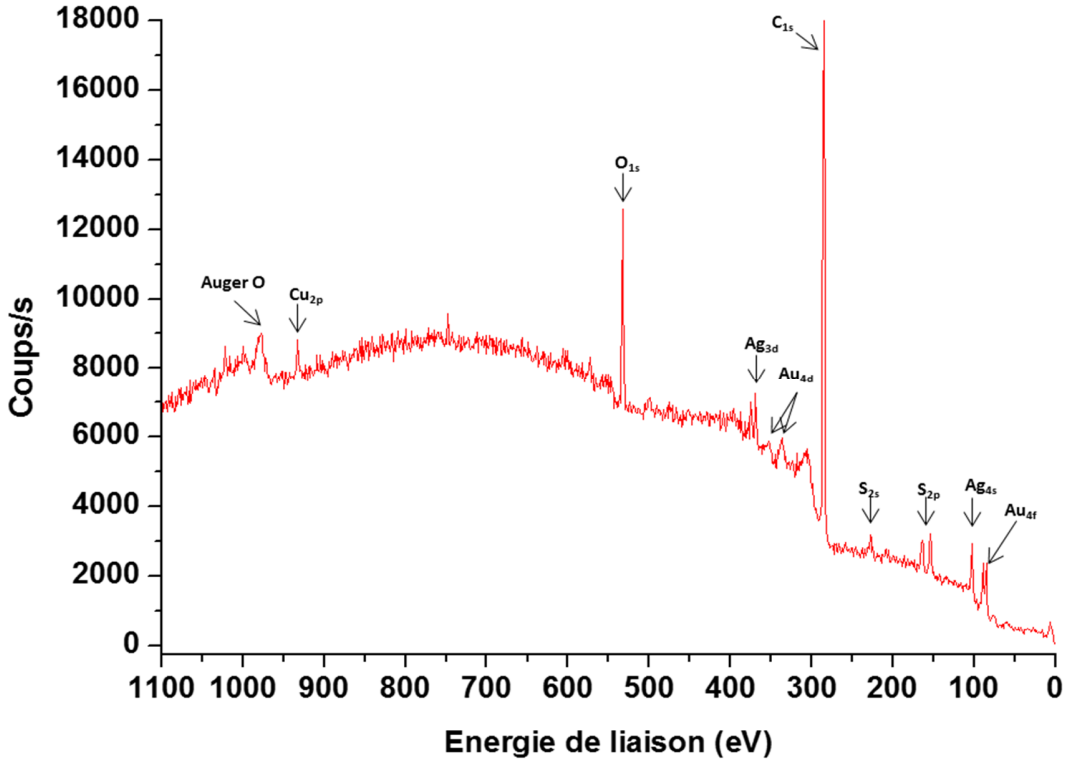


Figure S6. XPS spectrum of gold-silver nanoparticles obtained by total γ-reduction (dose 1440 Gy) of ethanolic solutions containing 5×10^{-5} M calix[8]arene **5**, 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M $AgClO_4$

6. Characterisation of gold-silver nanoparticles stabilised by calix[8]arenes 5

EDX analysis

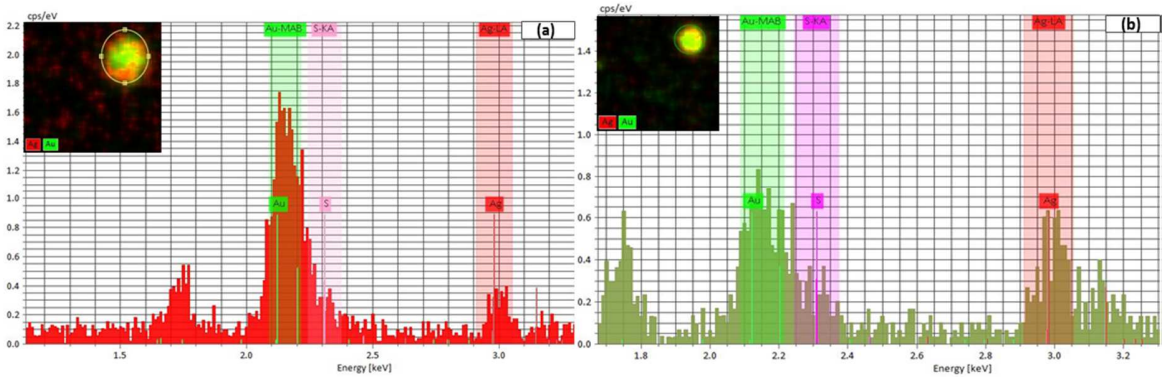


Figure S7. EDX spectra of gold-silver nanoparticles obtained by total γ-reduction (dose 1440 Gy) of ethanolic solutions containing 5×10^{-5} M calix[8]arene **5**, 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M $AgBF_4$

Table S1. Element quantification for the bimetallic nanoparticles in Figure S7

	(a)	(b)
Element	**Atomic percentage**	
Sulphur	22.08	29.41
Gold	57.18	22.02
Silver	20.74	48.57