

# Templating silver nanoparticle growth using phosphonated calixarenes

Karel J. Hartlieb,<sup>a,b</sup> Martin Saunders<sup>b</sup> and Colin L. Raston<sup>\*a</sup>

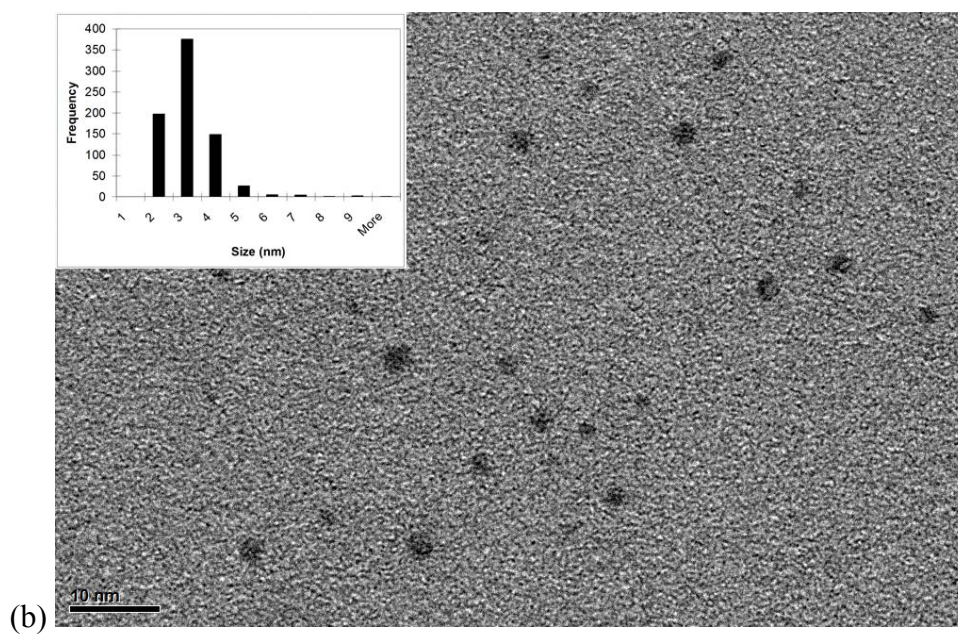
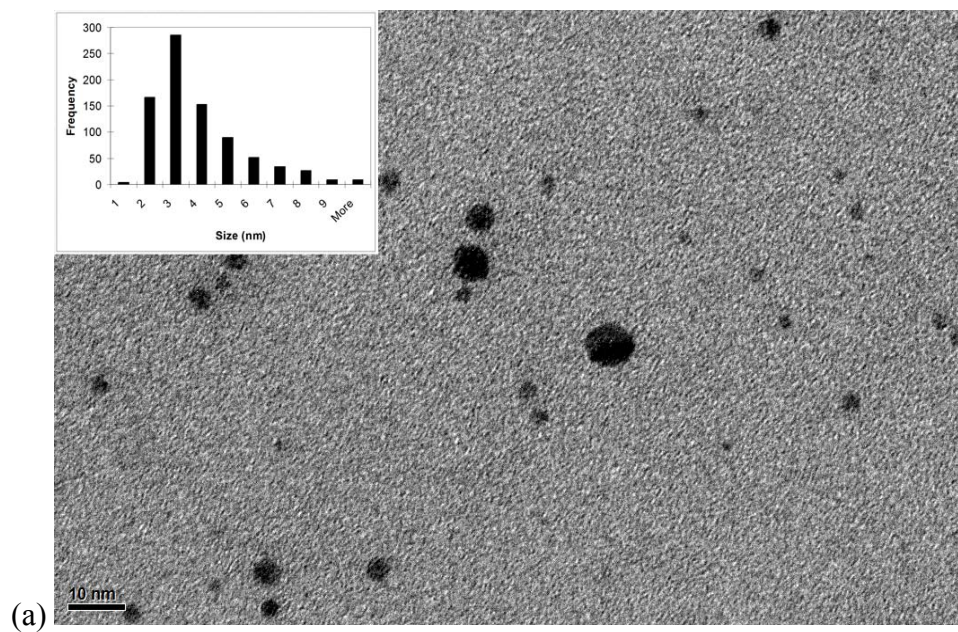
## Supporting Information

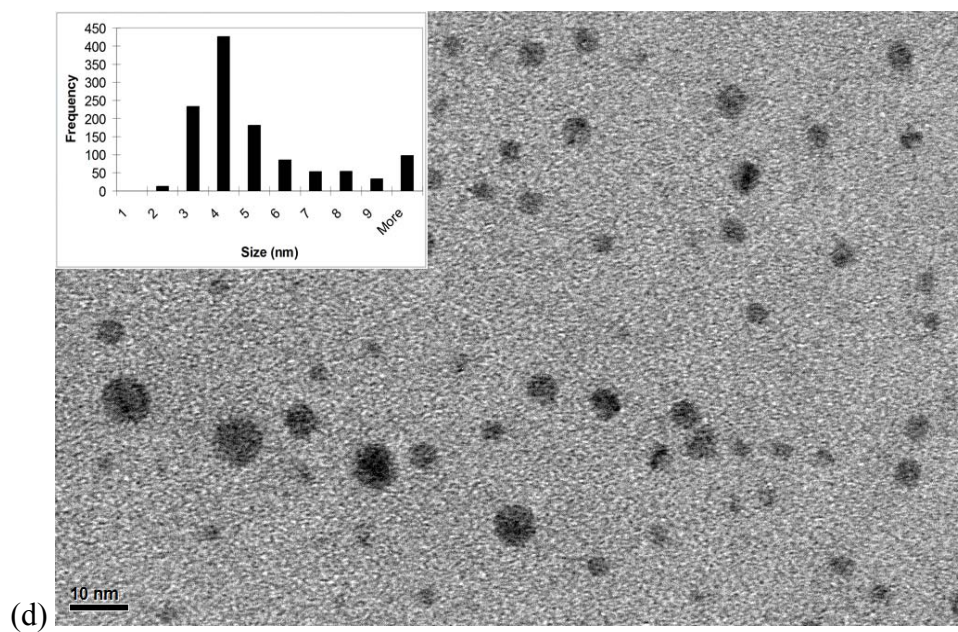
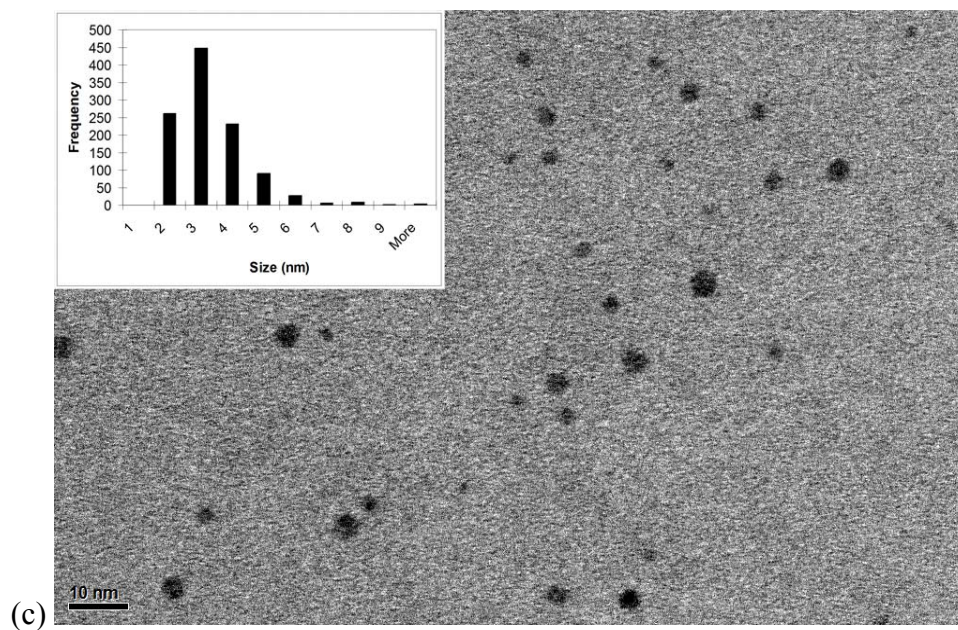
### Experimental

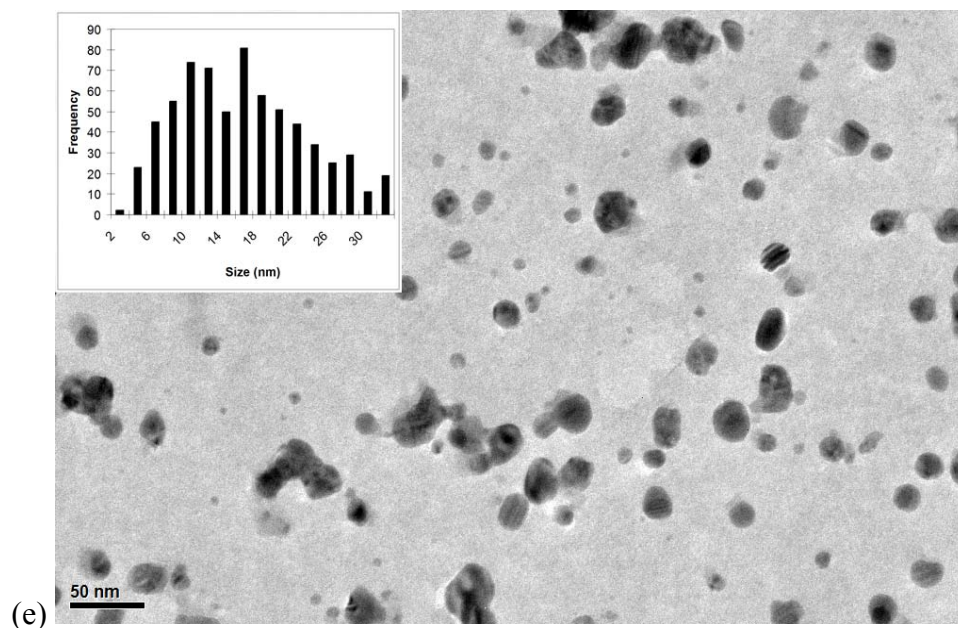
*Materials:* Silver nitrate (99.8%, Unilab), sodium hydroxide (Redox Chemicals), hydrogen (industrial grade, Air Liquide), sodium polyphosphate (Riedel-de Haën) were used as received. Phosphonated calix[n]arenes (n = 4, 5, 6, 8) were synthesised using established literature procedures,<sup>[1]</sup> and the O-alkylated phosphonated calix[4]arene, 5, 11, 17, 23-Tetrakis(dihydroxyphosphoryl)-25, 26, 27, 28-tetrapropoxycalix[4]arene – cone conformation was synthesised as previously reported.<sup>[2]</sup>

*Synthetic procedure:* A phosphonated calix[n]arene was dissolved in 200 mL of Millipore water (10 MΩ cm<sup>-1</sup>) in an Erlenmeyer flask in targeting a certain concentration (occasionally with the assistance of sonication, particularly for phosphonated calix[4]arene). The pH was then adjusted to 9 using NaOH solution, and heated to 70 °C with magnetic stirring. Hydrogen was then vigorously bubbled into the solution and once the temperature stabilized silver nitrate was added to afford a 1x10<sup>-3</sup> M solution.

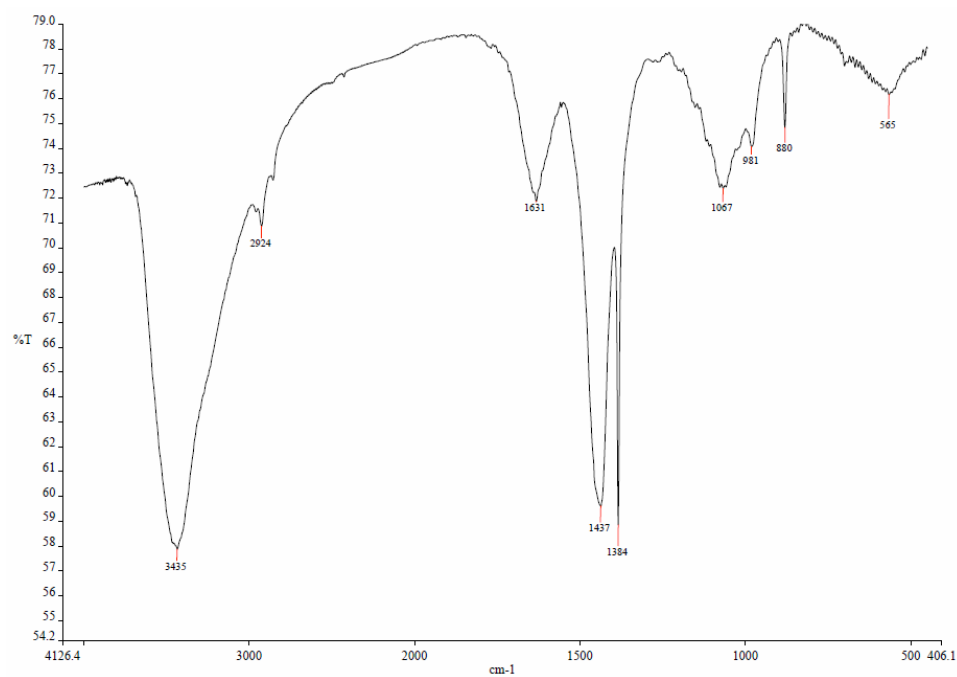
*Characterisation:* Transmission electron microscopy (TEM) was performed on a JEOL 2100 operating at an accelerating voltage of 200 kV and high-resolution TEM was performed on a JEOL 3000F operating at 300 kV. Samples for TEM were prepared by diluting the product with water in a ratio of product:water = 1:10 and placing a 6 μL drop onto a 200 mesh copper grid covered by a holey amorphous carbon film (SPI supplies). UV-Visible spectroscopy was performed on a Varian Cary 50 Tablet UV-Visible Spectrophotometer using quartz cuvettes with a path length of 1 cm and water as the reference material. Fourier Transform Infrared spectroscopy was performed on a PerkinElmer Spectrum 1 FT-IT spectrometer using KBr discs.

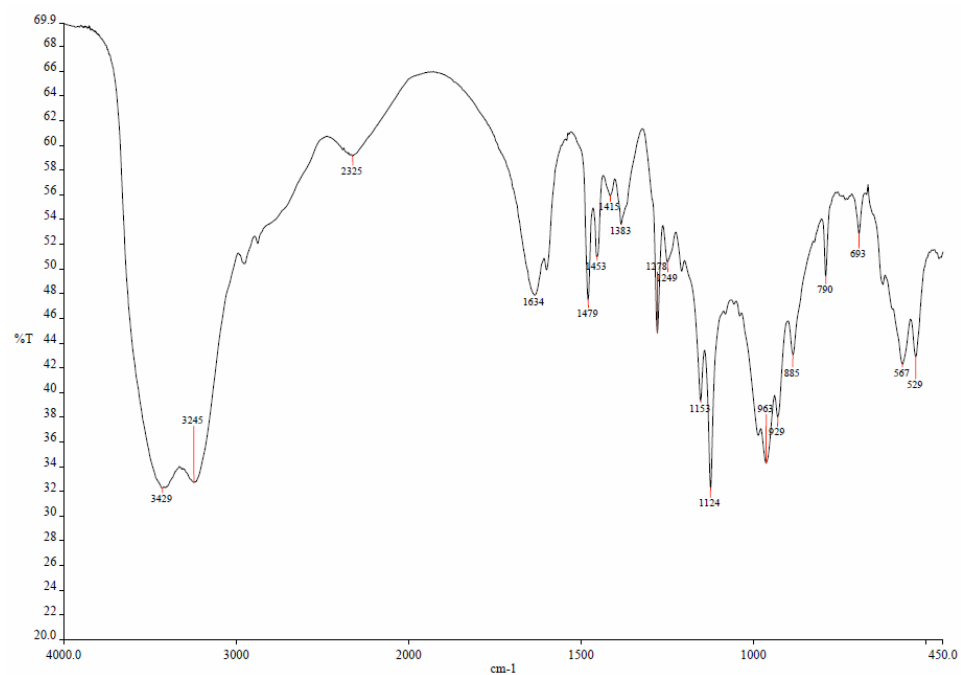




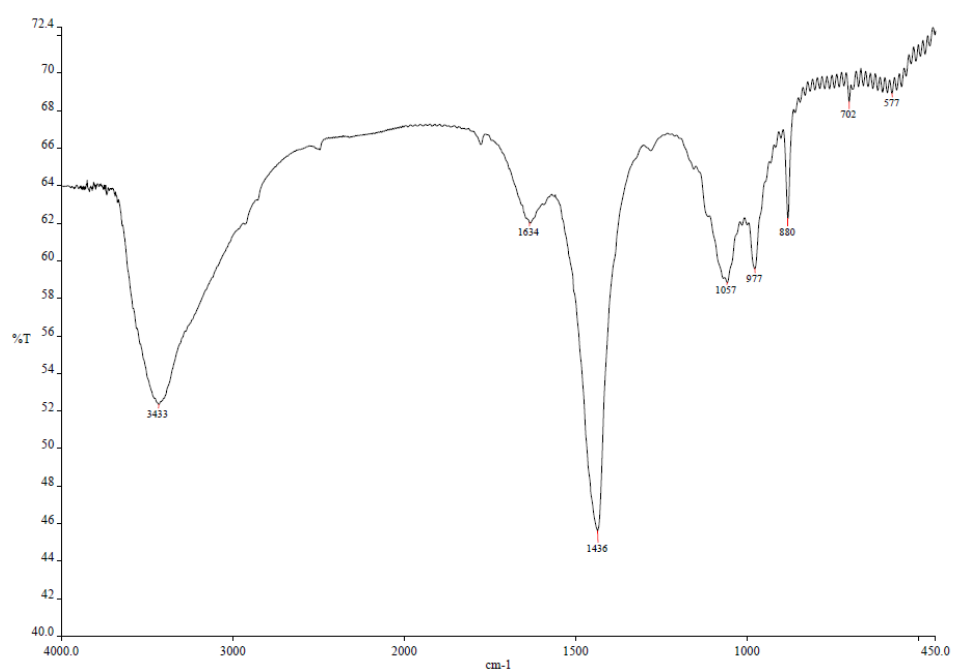


**Figure S1.** Typical transmission electron micrographs of silver nanoparticles with variation in size and concentration of phosphonated calix[n]arenes; (a)  $n = 4$ , 0.05 mM, (b)  $n = 4$ , 0.5 mM, (c)  $n = 5$ , 0.05 mM, (d)  $n = 6$ , 0.05 mM, (e)  $n = 8$ , 0.05 mM. Inset: Particle size distribution histogram based on measuring ~700 – 1000 particles.





(b)

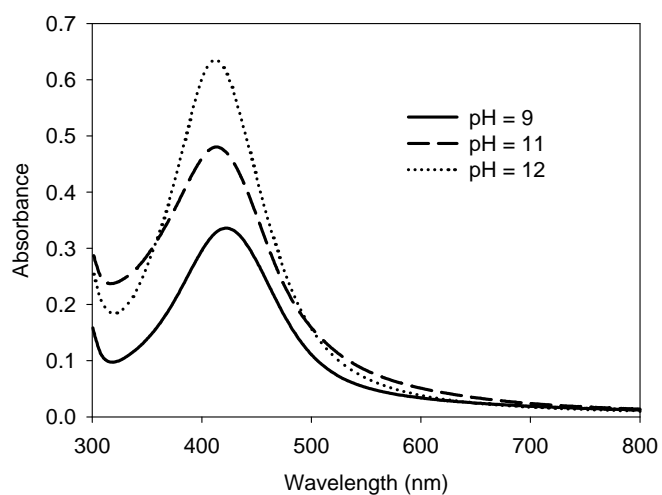


(c)

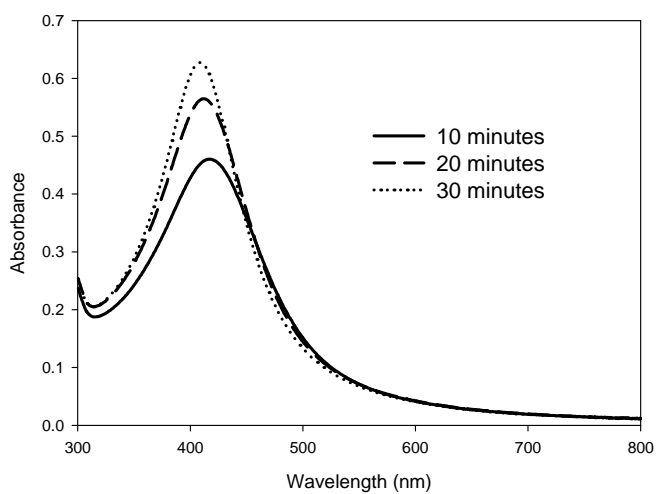
**Figure S2.** FTIR spectrum for (a) Ag nanoparticles with phosphonated calix[8]arene (from solution at pH = 12), (b) phosphonic acid calix[8]arene, (c) phosphonated calix[8]arene sodium salt.



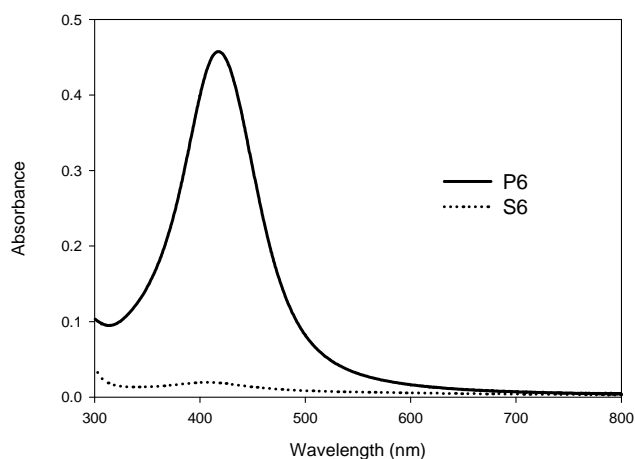
**Figure S3.** Silver nitrate solution at pH = 9 after bubbling with H<sub>2</sub> for 10 mins; left: without phosphonated calixarene, right: with 0.05 mM phosphonated calix[4]arene.



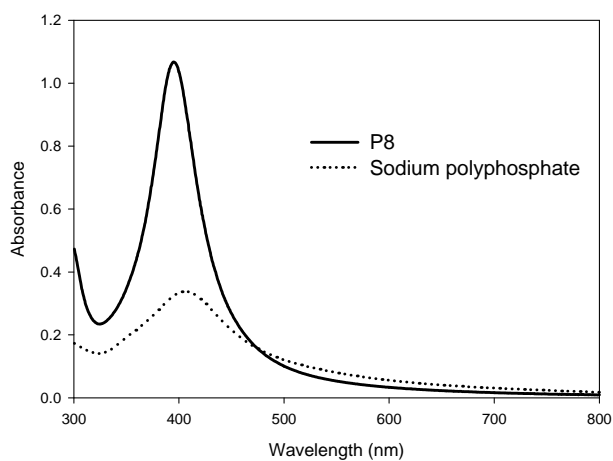
**Figure S4.** Influence of pH on the UV-Vis absorbance spectrum after 10 mins using 0.25 mM phosphonated calix[4]arene.



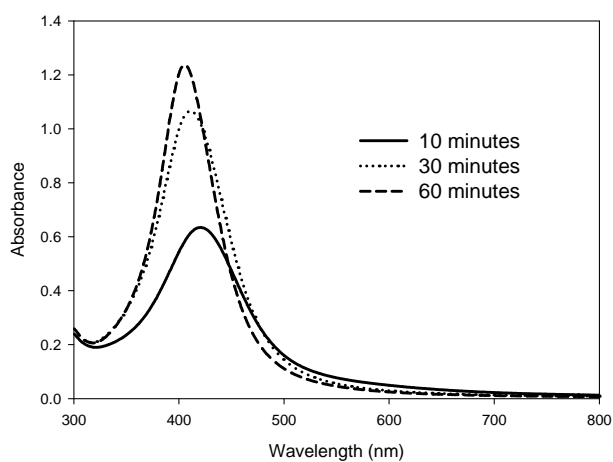
**Figure S5.** UV-Vis absorption after various reaction times using 0.25 mM phosphonated calix[4]arene at pH = 9.



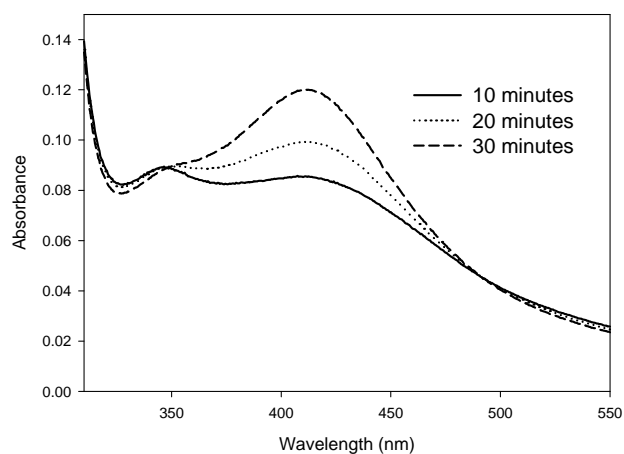
**Figure S6.** UV-Vis absorption after 10 mins 0.25 mM phosphonated calix[6]arene and sulfonated calix[6]arene at pH = 9.



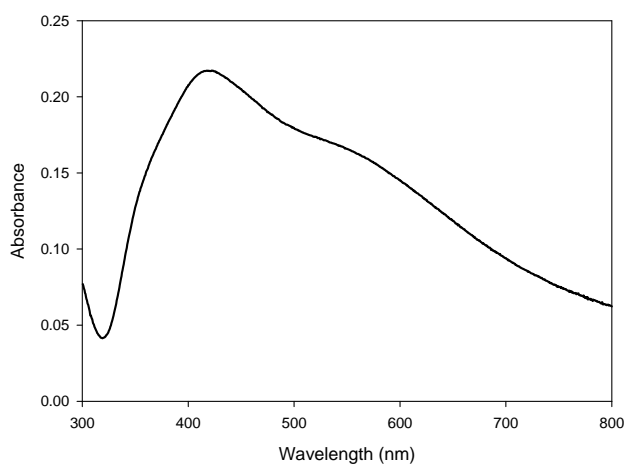
**Figure S7.** UV-Vis absorption after 10 mins 0.25 mM phosphonated calix[8]arene and 0.167 mM sodium polyphosphate at pH = 12.



**Figure S8.** UV-Vis absorption of Ag nanoparticles produced with 0.05 mM phosphonated calix[8]arene in 0.1M H<sub>3</sub>BO<sub>3</sub> buffer at pH = 9 over time.

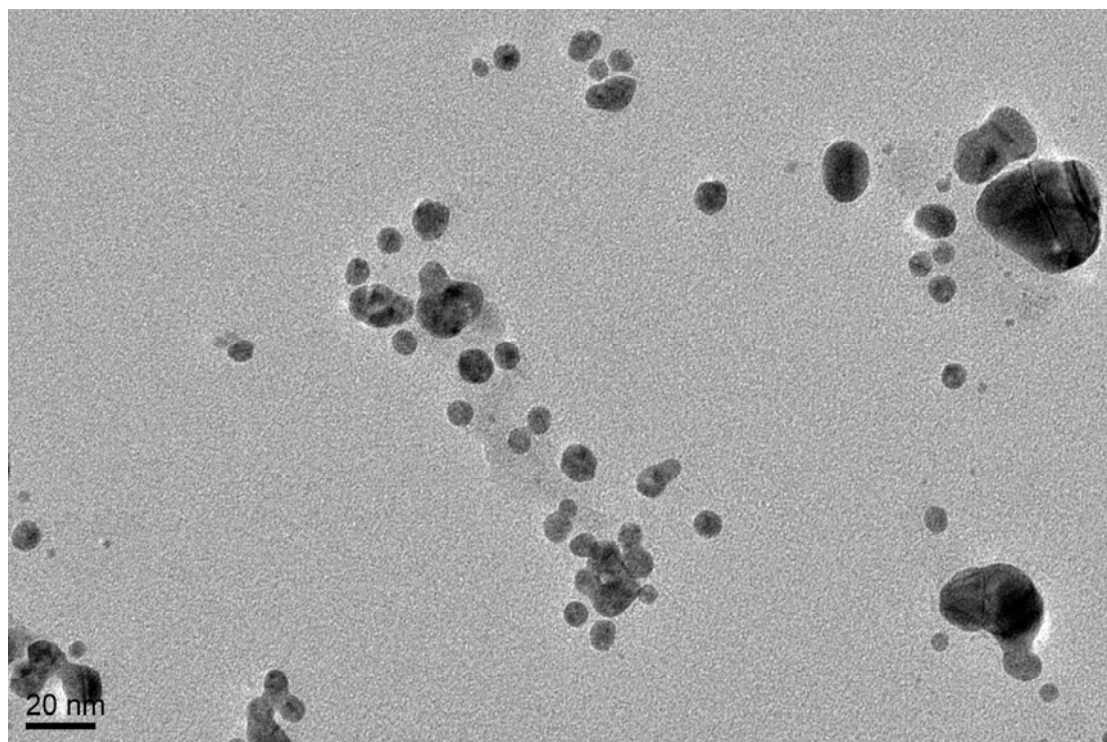


**Figure S9.** UV-Vis absorption of Ag nanoparticles produced with 0.25 mM phosphonated calix[8]arene and 0.25 mM AgNO<sub>3</sub> at pH = 11 over time.



**Figure S10.** UV-Vis absorption of Ag nanoparticles produced with 1 mM 5, 11, 17, 23-Tetrakis(dihydroxyphosphoryl)-25, 26, 27, 28-tetrapropoxycalix[4]arene – cone conformation and 0.25 mM AgNO<sub>3</sub> at pH = 12 after 10 mins.





**Figure S11.** TEM image of Ag nanoparticles produced with 0.167 mM sodium polyphosphate at pH = 12 after 90 minutes.

[1] T. E. Clark, M. Makha, A. N. Sobolev, H. Rohrs, J. L. Atwood, C. L. Raston, *Chemistry - A European Journal*, 2008, **14**, 3931.

[2] D. Witt, J. Dziemidowicz, J. Rachon, *Heteroatom Chemistry*, 2004, **15**, 155.