Host–guest recognition-induced color change of water-soluble pillar[5]arene modified silver nanoparticles for visual detection of spermine analogues

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Electronic Supplementary Information (7 pages)

1. Materials and methods

1,4-Dimethoxybenzene, boron trifluoride etherate, BBr_3, $ClCH_2COOCH_3$, NaOH, HCl, $NH_3·H_2O$, spermine, 1,6-hexamethylenediamine, 1,12-dodecylamine, ethanediamine, tetraethylenepentamine, triethylenetetramine, and ursol were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literatures. The water-soluble pillar[5]arene **WP5** was prepared according to a method previously reported.[S1, S2] The TEM images were obtained using a JEM-1200EX instrument with an accelerating voltage of 80 kV. EDX was examined by TEM (JEM-1200EX) instrument. XRD data were obtained with a graphite monochromatic device and Cu Kα radiation (λ = 0.15406 nm) on the D8 Advance superspeed powder diffractometer (Bruker), operated in the θ:2θ mode primarily in the 20–85° (2θ) range and step-scan of 2θ = 0.04°. UV−Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV−Vis spectrometer. The fluorescence titration experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

*2. Synthesis of **WP5**-stabilized silver nanoparticles*

WP5-stabilized silver nanoparticles were synthesized by the reduction of $AgNO_3$ in the presence of **WP5**. In a typical synthesis, $AgNO_3$ (20.0 μL, 10.0 mM) was added to deionized water (20.0 mL), followed by the addition of an aqueous solution of **WP5** (1.00 mL, 0.100 mM). $NaBH_4$ (20.0 μL, 0.100 M) was freshly prepared with deionized ice water and added to the above reaction mixture while stirring. The solution immediately turned yellow and **WP5**-stabilized silver nanoparticles were thus obtained. This concentration of **WP5**-stabilized silver nanoparticles was used in all experiments unless otherwise noted.

*3. Characterization of **WP5**-stabilized silver nanoparticles*

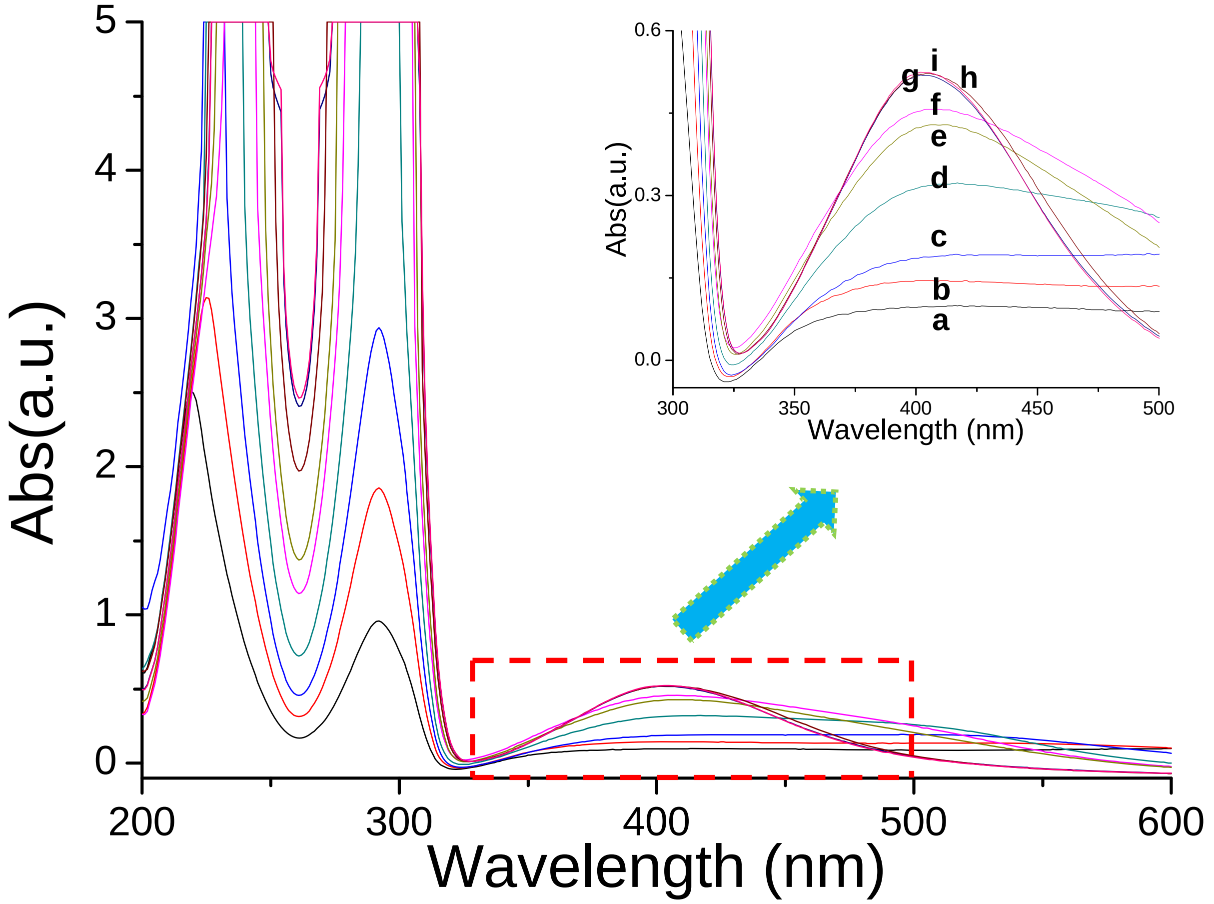

Fig. S1. UV–Vis spectra of silver nanoparticles with different concentration of **WP5** as stabilizer: (a) 3.33 × 10^{-5} M; (b) 6.67 × 10^{-5} M; (c) 1.00 × 10^{-4} M; (d) 1.67 × 10^{-4} M; (e) 2.67 × 10^{-4} M; (f) 3.33 × 10^{-4} M; (g) 4.00 × 10^{-4} M; (h) 5.00 × 10^{-4} M; (i) 6.67 × 10^{-4} M.

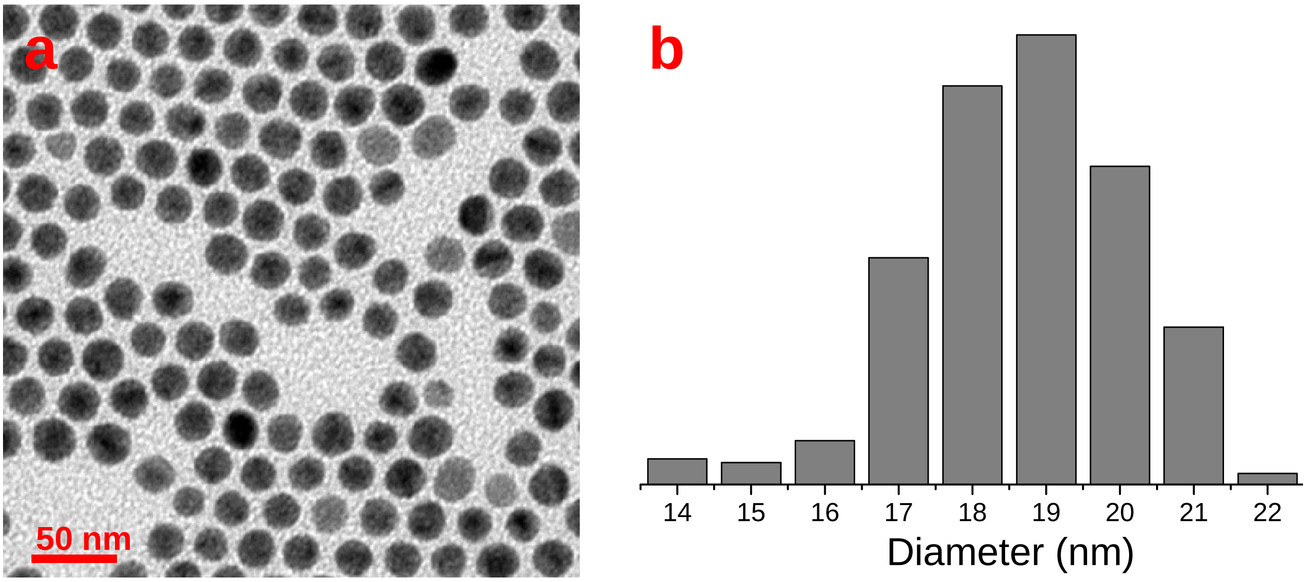

Fig. S2. TEM image of **WP5**-stabilized silver nanoparticles (a) and the histogram (b) of its size distribution when the concentration of **WP5** was 4.00 × 10^{-4} M.

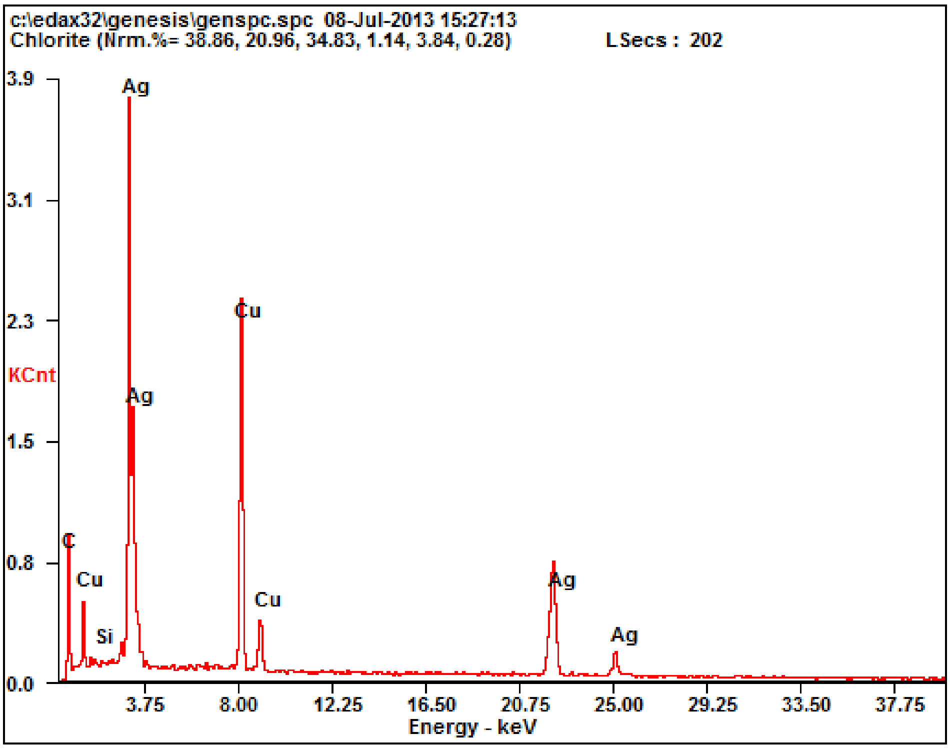

Fig. S3. EDX study of **WP5**-stabilized silver nanoparticles when the concentration of **WP5** was 4.00 × 10^{-4} M.

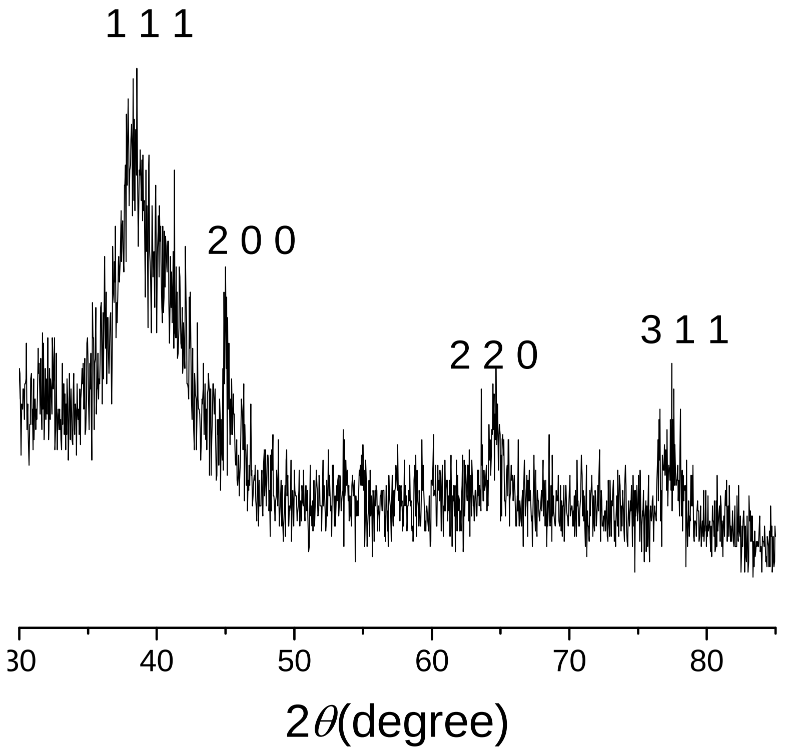

Fig. S4. XRD analysis of **WP5**-stabilized silver nanoparticles when the concentration of **WP5** was 4.00×10^{-4} M.

4. Visual detection of spermine analogues

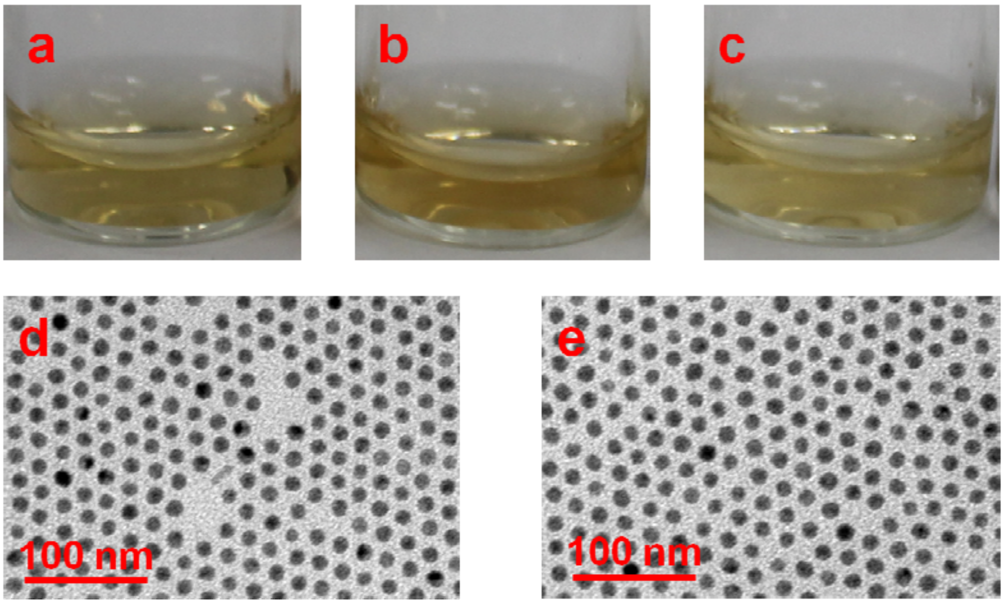

Fig. S5. Optical pictures of **WP5**-stabilized silver nanoparticles: (a) fresh prepared; (b) treated with elevated temperature (100 °C); (c) storage after 2 weeks. TEM images of **WP5**-stabilized silver nanoparticles: (d) treated with elevated temperature; (e) storage after 2 weeks.

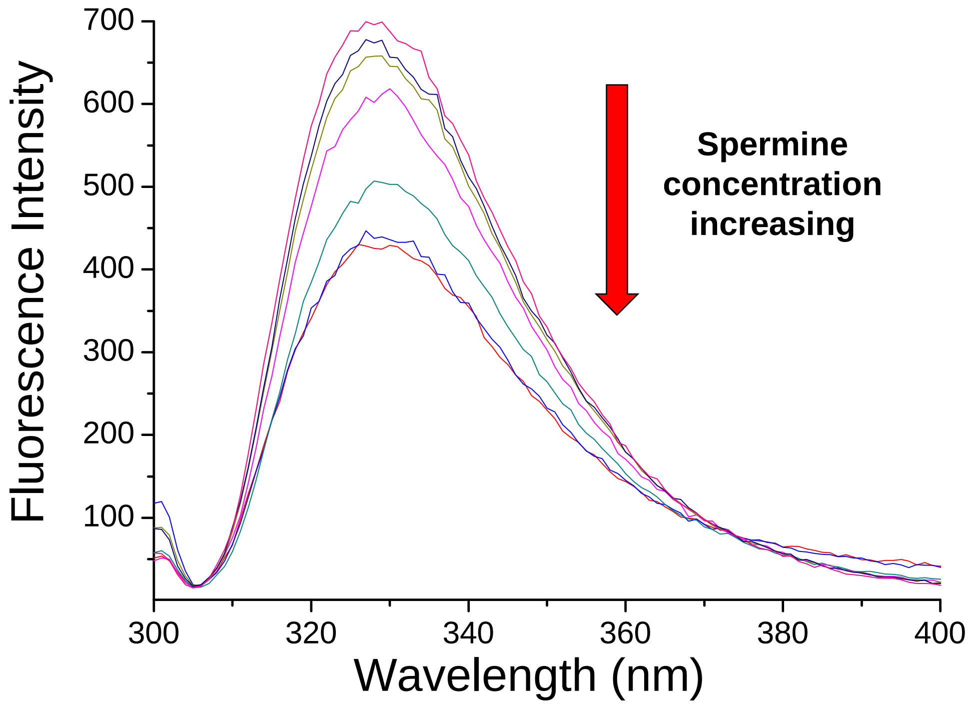

Fig. S6. Fluorescence emission spectra (λ_{exc} = 300 nm) of **WP5** (5.00×10^{-6} M) in aqueous solution at room temperature with different concentrations of spermine: 0.200, 0.497, 1.96, 6.54, 10.7, 14.5, and 20.5 $\times 10^{-6}$ M^{-1}.

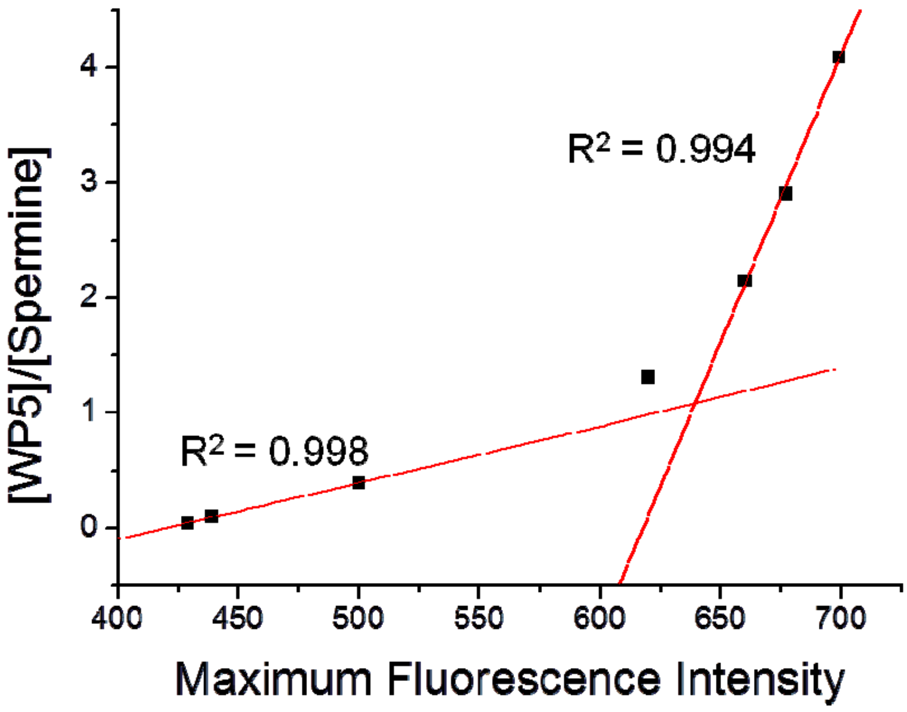

Fig. S7. Mole ratio plot for **WP5** and spermine, indicating a 1:1 stoichiometry.

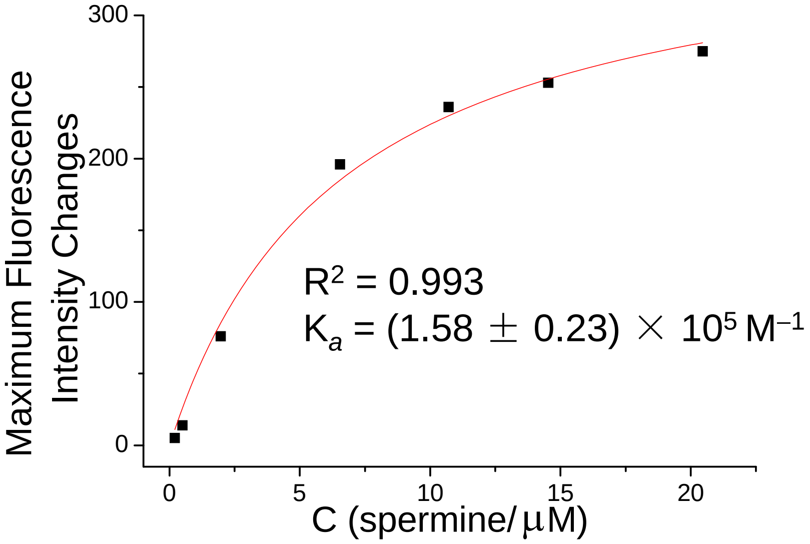

Fig. S8. The maximum fluorescence intensity changes of **WP5** upon addition of spermine. The red solid line was obtained from the non-linear curve-fitting.

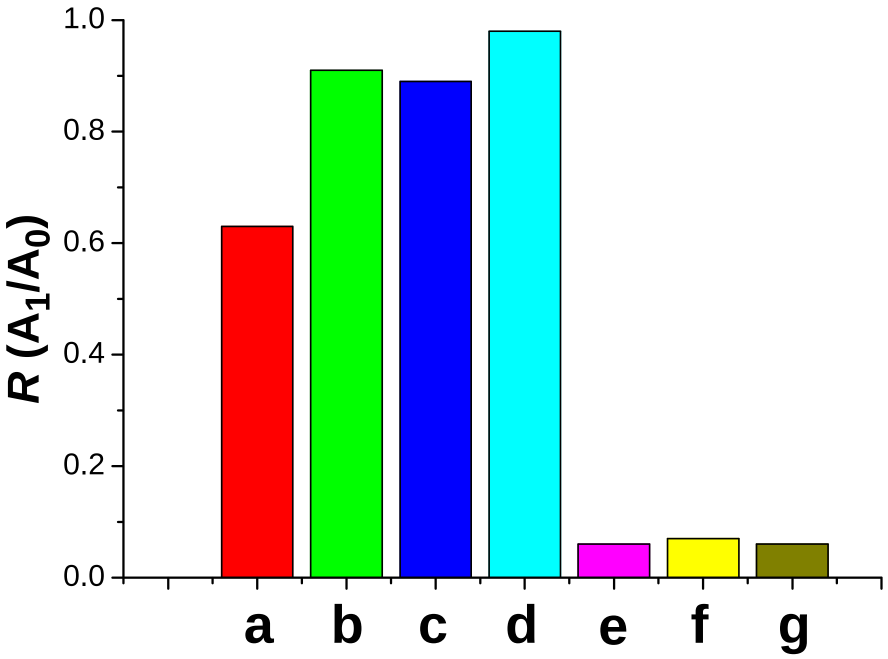

Fig. S9. The decrease in the absorbance peak at 400 nm after adding different diamine compounds: (a) 1,12-dodecylamine; (b) 1,6-hexamethylenediamine; (c) ursol; (d) ethanediamine; (e) spermine; (f) triethylenetetramine; (g) tetraethylenepentamine.

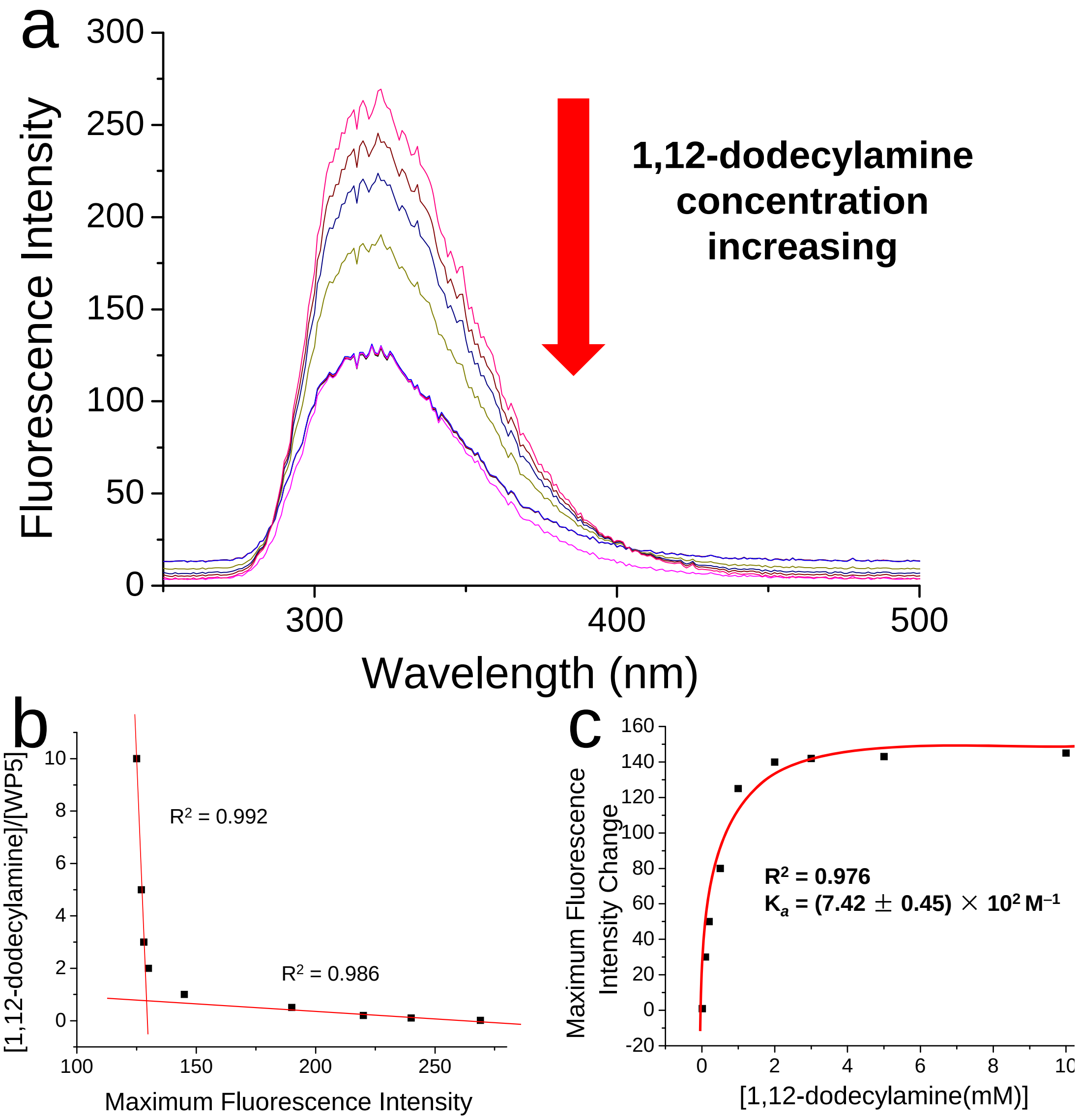

Fig. S10 (a) Fluorescence emission spectra (λ_{exc} = 300 nm) of **WP5** (2.00×10^{-6} M) in aqueous solution at room temperature with different concentrations of 1, 12-dodecylamine, (b) Mole ratio plot for **WP5** and 1, 12-dodecylamine, and (c) the maximum fluorescence intensity changes of **WP5** upon addition of 1, 12-dodecylamine.

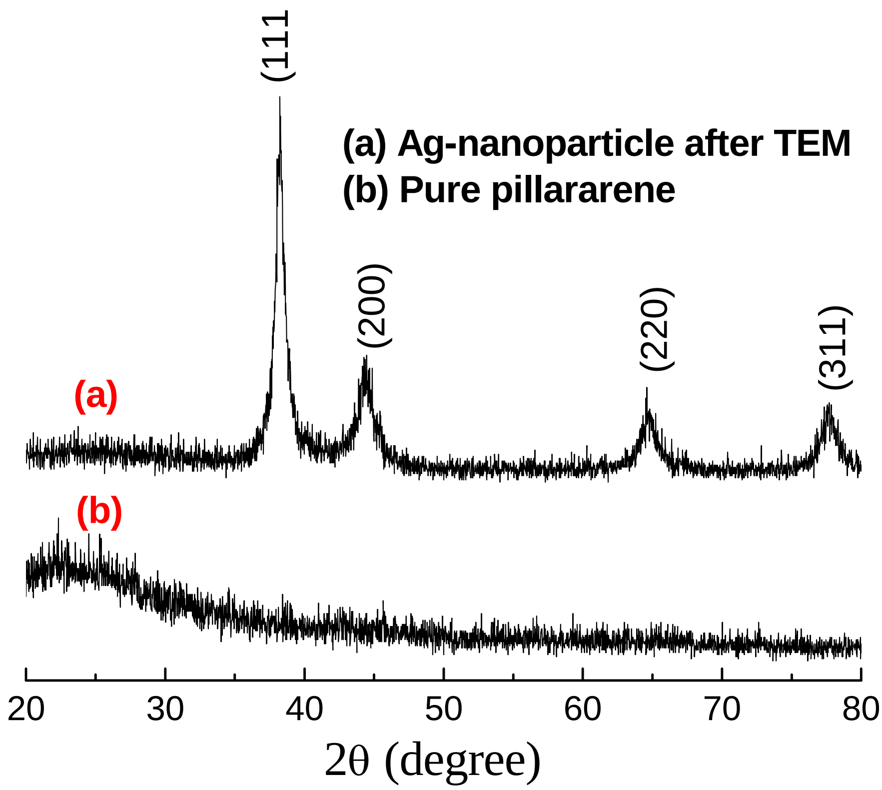

Fig. S11 XRD analysis: (a) **WP5**-stabilized silver nanoparticles after TEM studies; (b) pure pillararene.

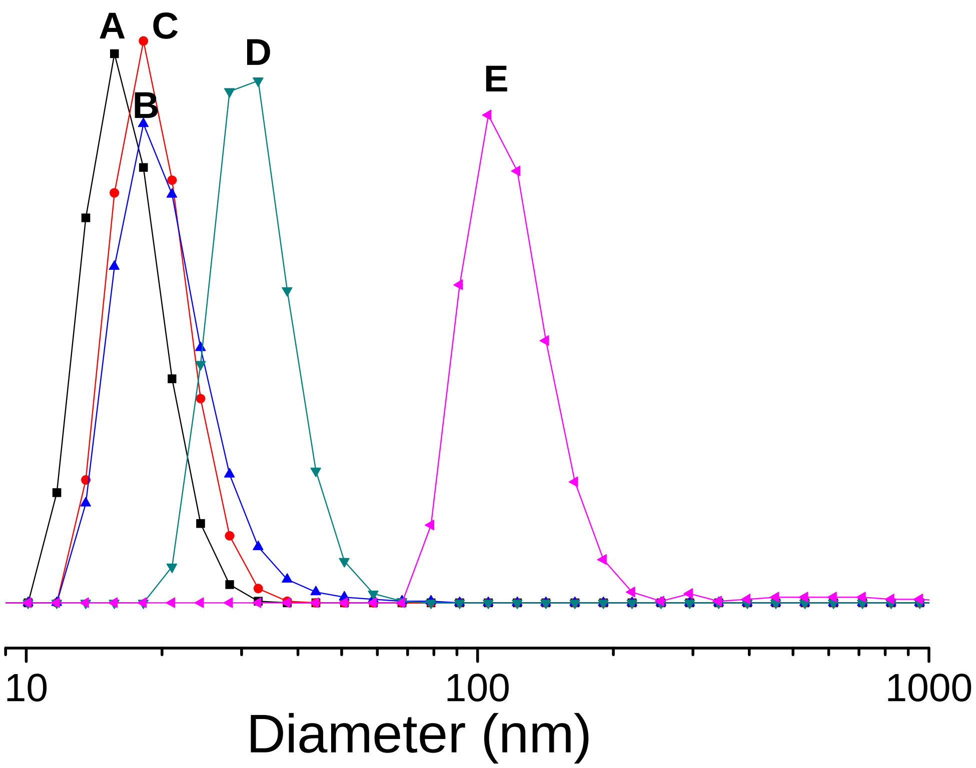

Fig. S12 DLS studies: An original WP5-stabilized silver nanoparticles; B after adding ethanediamine; C after adding ursol; D after adding 1,12-dodecylamine and E after adding spermine.

5. References:

S1. T. Ogoshi, M. Hashizume, T. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2010, **46**, 3708–3710.

S2. C. Li, X. Shu, J. Li, S. Chen, K. Han, M. Xu, B. Hu, Y. Yu and X. Jia, *J. Org. Chem.*, 2011, **76**, 8458–8465.