

Supporting Information

Size-controlled Preparation of Gold Nanoparticles with Novel pH Responsive Gemini Amphiphiles

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1. X-ray diffraction (XRD)

X-ray diffraction was used to confirm the crystalline nature of the particles. Fig. S1 shows a representative XRD pattern of the gold nanoparticles after the complete reduction of Au^{3+} to Au^0 . A number of Bragg reflections were present which can be indexed on the basis of the face centered cubic fcc structure of gold. The diffraction peaks at $2\theta = 38.31^\circ$ (1 1 1), 44.46° (2 0 0), 64.67° (2 2 0), 77.45° (3 1 1) and 81.76° (2 2 2) obtained are identical with those reported for the standard gold metal (Au^0) (Joint Committee on Powder Diffraction Standards-JCPDS no. 04-0784, USA) Thus, the XRD pattern suggests that the gold nanoparticles were essentially crystalline. The average crystallite size according to Scherrer equation calculated using the width of the (1 1 1) peak is found to be 5 nm and 2 nm at pH=2.0 and 7.0, respectively, which are in good agreement with the particle size obtained from the TEM images in Fig. S1

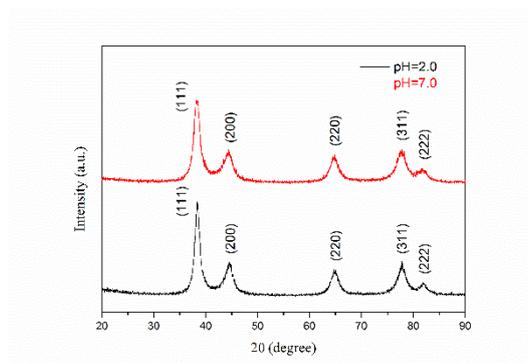


Figure S1. XRD patterns of Au NPs at pH=2.0 and 7.0, respectively.

2. Effect of pH without excess gemini surfactant

The molar ratio between ligand and Au ions R ($R = [\text{Di-C}_{12}\text{Ph}]/[\text{HAuCl}_4]$) was varied at constant $[\text{HAuCl}_4]$ of 1.6 mM by adjusting $[\text{Di-C}_{12}\text{Ph}]$ to 0.8 mM at pH =2.0 and to 1.6 mM at pH =7.0, respectively. Theoretically, Di- C_{12}Ph could transfer all the AuCl_4^- from the aqueous phase into the toluene phase without excess. Also, to check the level of AuCl_4^- transferred to the organic phase, NaBH_4 was added to the separated aqueous phase and it was found that the solution color maintained colorless at the both pH values. The corresponding appearance and absorbance UV-V spectra of organic phase samples were shown in Figure S2.

It was observed that the color of Au NPs in toluene (Figure S2) was changed from darker wine-red to wine-red upon increasing R and pH at constant $[\text{HAuCl}_4]$. Simultaneously, evident blue shifts of the typical plasmon resonance absorption were observed when R and pH were increased, suggesting the size of Au NPs was reduced.^{1,2} This result implicates that single charged amine

group is better than double charges ones in stabilizing Au ions. Since the electrostatic interaction between Di-C₁₂Ph and AuCl₄⁻ became weakened with the increase of solution pH and resulted in smaller particles.

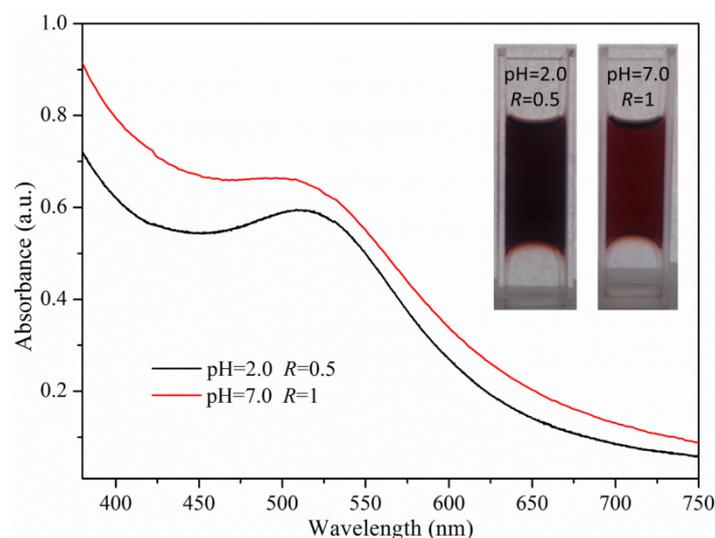


Figure S2. UV-Vis absorption spectra of Au NPs in toluene prepared by Di-C₁₂Ph at pH=2.0 with $R=0.5$ and pH= 7.0 with $R=1$, respectively. The insert images represent the corresponding optical appearance of Au NPs prepared in water/toluene binary systems.

3. Effect of Di-C₁₂Ph concentration on Au NPs formation

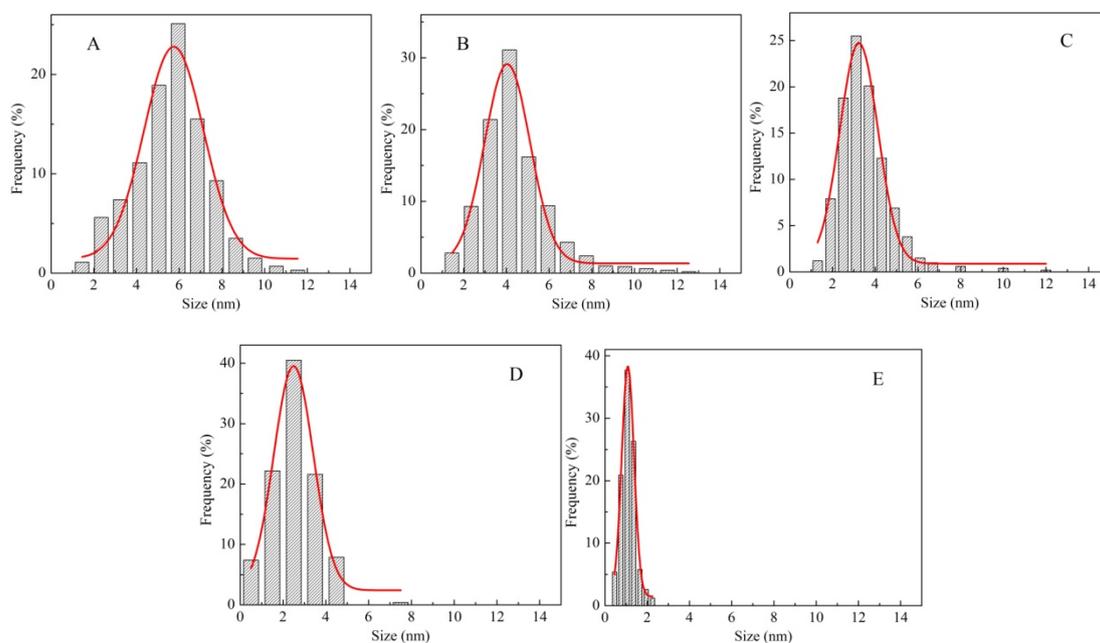


Figure S3. Size distribution histograms of more than 200 Au NPs synthesized at $R = 1.2$ (A), 1.5 (B), 2.0 (C) and 4.0 (D) at constant $[\text{Di-C}_{12}\text{Ph}] = 9.6 \text{ mM}$, and at $[\text{Di-C}_{12}\text{Ph}] = 1.8 \text{ mM}$ with constant $R = 6.0$ (E), respectively.

4. Effect of R on the particle size of Au NPs

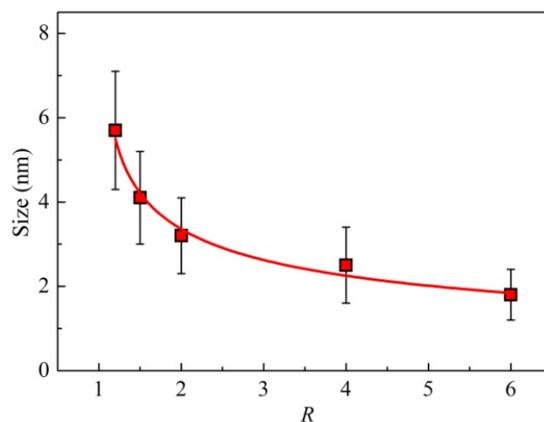


Figure S4. Effect of R on the particle size of Au NPs using Di-C₁₂Ph at pH = 7.0.

5. Effect of the hydrophobic chain length on the size of Au NPs

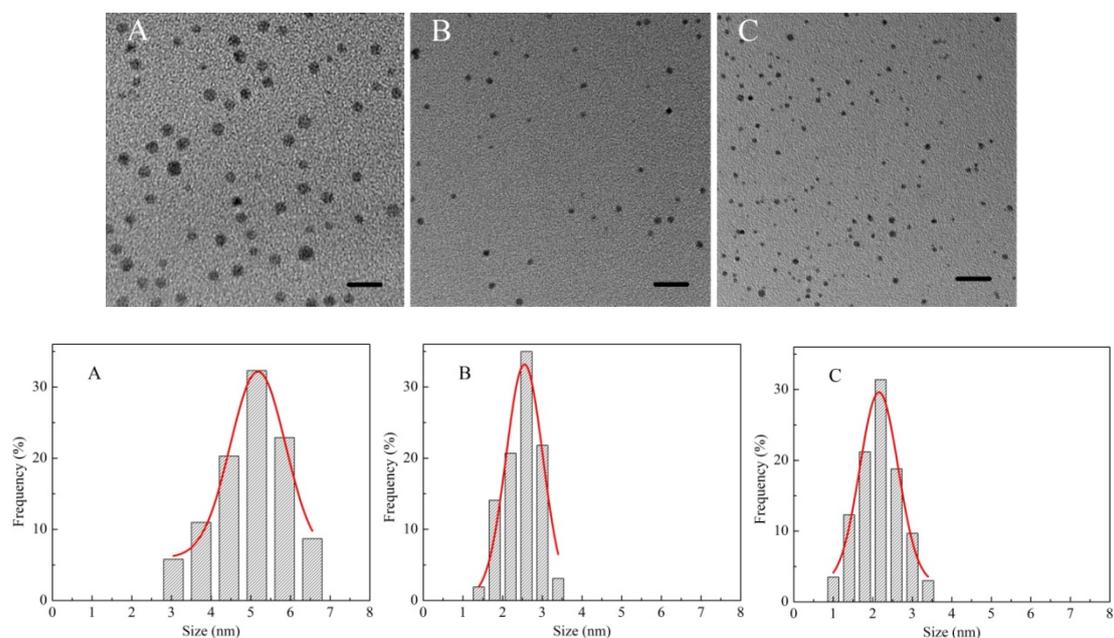


Figure S5. TEM images and corresponding size distribution histograms of more than 200 Au NPs synthesized using Di-C₆Ph (A), Di-C₈Ph (B) and Di-C₁₀Ph (C), respectively. Bar represents 20 nm.

References:

- [1] W. Cheng and E. Wang, *J. Phys. Chem. B*, 2004, **108**, 24.
- [2] N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir*, 2001, **17**, 6782.