Synthesis of \( p \)-sulfonatocalix[4]arene modified silver nanoparticles as colorimetric histidine probes

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Experimental details

Synthesis of \( p \)-sulfonatocalix[4]arene: The procedure according to Shinkai’s method\(^1-3\) was slightly modified as follows. Calix[4]arene (1g) was mixed with 10 mL of concentrated \( \text{H}_2\text{SO}_4 \). Then the solution was heated at 70 °C for 3h. An aliquot was withdrawn from the solution and poured into water to determine the progress of the reaction. The reaction was completed when water-insoluble material was not detected. After cooling, the precipitate was recovered by filtration. The precipitate was dissolved in 4 mL water before addition of 20 mL brine. Finally, 1.3 g \( p \)-sulfonatocalix[4]arene was obtained after evaporation of water in yield of 66.3%;

Single spot on paper chromatography (water-2-propanol 1:1 v/v); IR (KBr) \( \nu_{\text{OH}} \) 3431,3188 cm\(^{-1}\), \( \nu_{\text{SO}_3} \) 1187, 1049 cm\(^{-1}\); \(^1\)H NMR (\( \text{D}_2\text{O} \)) \( \delta \) (ppm): 3. 45, 4. 25 (d, 8H, \( \text{ArCH}_2\text{Ar} \)), 7. 93 (Ar H, s ,8H ) .


2 mL of \( 10^{-2} \) M \( \text{AgNO}_3 \) solution was added to 96 mL of triply distilled water. To this solution, 2 mL of \( 10^{-2} \) M \( p \)-sulfonatocalix[4]arene aqueous solution was added as stabilizer with stirring for 20 min. And then, 8.8 mg of \( \text{NaBH}_4 \) was added to the
solution. The mixture was continually stirred for 5 min at room temperature. The silver colloids were finally obtained.

**Synthesis of mercaptoacetic acid modified silver nanoparticles**

To the solution of 2 mL of $10^{-2}$ M AgNO$_3$ solution and 96 mL of triply distilled water, 8.8 mg of NaBH$_4$ was added. And then, 2 mL of $10^{-2}$ M mercaptoacetic acid aqueous solution was added as stabilizer with stirring for 7 hours at room temperature.

**The stability of $p$SC$_4$-Ag NPs and MA-Ag NPs**

Fig. S1 shows the adsorption spectra of $p$SC$_4$-Ag NPs and MA-Ag NPs recorded on different times. For $p$SC$_4$-Ag NPs, there was no obvious change in the shape, position and symmetry of the absorption peak during the initial one month, except for a little decrease of the absorbance intensity. However, for MA-Ag NPs, it is shown that the obvious change in the shape, position and symmetry of the absorption peak and the dramatical decrease of the absorbance intensity. The results indicate $p$SC$_4$-Ag NPs are more stable than MA-Ag NPs.
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Fig. S1: The absorption spectra of \( \rho \text{SCBridge}-\text{AgNPs} \) recorded at: (a) 0, (b) 48 h, (c) 120 h, (d) 720 h (one month) and \( \text{MA-AgNPs} \) recorded at: (e) 0 (f) 24 h (g) 240 h

References