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# Reversible assembly of silver nanoparticles driven by host−guest interactions based on water-soluble pillar[*n*]arenes†

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**Silver nanoparticles can reversibly self-assemble driven by host−guest interactions based on water-soluble pillar[*n*]arenes.**

In the past decades, great efforts have been made to control assembly of metal nanoparticles because the resultant assemblies show different optical, electronic, magnetic and biological properties from the individual nanoparticles.[1] Among various metal particles, silver nanoparticles (AgNPs) are particularly attractive due to their stability, uniformity and biocompatibility etc.[2] Different approaches to produce AgNP assemblies via hydrogen bonding,[3a] ion pairing,[3b] and metal–ligand interactions[3c] have been reported.[3] In comparison with assembly of metal NPs, the reverse process, i.e. disassembly of the assembled particles, which is very important for the repeated usage of metal NPs in various applications is generally difficult to perform and control as the assembled NPs tend to collapse and precipitate, and in many cases the linkages between the particles could not be broken and recovered repeatedly.[4] However, host−guest interaction is an efficient way to prepare reversible assembly of metal NPs.

As a new type of host molecules after cyclodextrins,[5] crown ethers,[6] calixarenes,[7] and cucurbiturils,[8] pillar[*n*]arenes,[9] which consist of hydroquinone units linked by methylene (-CH$_2$-) bridges at their 2,5-positions, were first reported in 2008.[9a] Due to their high solubility, low toxicity and specific recognition towards many model substrates, pillar[*n*]arenes were most appreciated to functionalize metal nanoparticles for particle assembly. The first pillar[*n*]arene modified metal nanoparticles was reported by our group in 2012,[9h] then Yang and *co*-workers investigated some other pillar[5]arene modified nanoparticles.[1f]

Herein, we report the controllable self-assembly and disassembly of AgNPs with water-soluble pillar[5]arene (**WP5**) anchoring on their surfaces. The formation of silver assemblies is driven by the host−guest interactions between **WP5** and water soluble guest (**G**) which have two paraquat units and glue the individual particles together. This causes a significant shift in the absorption spectrum accompanied by visible color changes from bright-yellow to brown. Furthermore, the formed assemblies can be disassembled through the introduction of excess competitive host water-soluble pillar[6]arene (**WP6**), which forms complexes with **G** more favorably than **WP5** does. In addition, the recovered discrete **WP5** modified AgNPs can be separated from the solution by centrifugation and redispersed in water. Thus, this process of assembly–disassembly of **WP5** modified AgNPs can be performed repeatedly with concomitant color changes (bright-yellow−brown−bright-yellow) as described in Scheme 1.
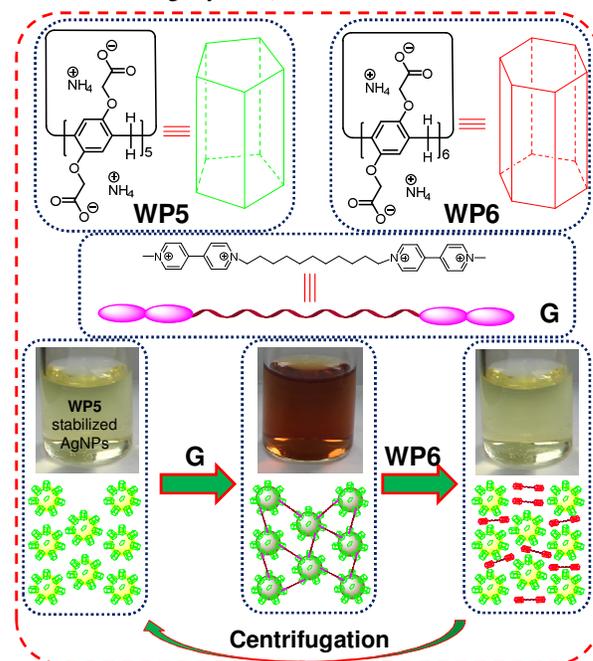


**Scheme 1**. Chemical structures and cartoon representations of **WP5**, **WP6** and **G**, and the illustration of the reversible assembly–disassembly of **WP5** stabilized AgNPs by sequential addition of **G** and **WP6**.

We first synthesized **WP5**-stabilized AgNPs by reducing AgNO$_3$ (10 mM, 100 μL) with NaBH$_4$ (50 mM, 100 μL) in the presence of the selected concentrations of **WP5** (5.00 mL). The corresponding UV−Vis spectra are shown in Fig. S1. The well-known surface plasmon resonance (SPR) of AgNPs was observed at ~400 nm, suggesting the formation of stable **WP5**-stabilized silver nanoparticles.[10] Due to the increasing concentration of **WP5**, the SPR peak gradually underwent a blue shift from 430 to 400 nm, indicating smaller average silver nanoparticles diameters (Fig. S1, lines a-f, ESI†).[11] However, upon increasing the concentration of **WP5** from 0.400 mM to 0.800 mM, the SPR peak maximum ($\lambda_{max}$) remained the same in wavelength (Fig. S1, lines g-h, ESI†), indicating that the continuous addition of excess **WP5** has

little influence on the sizes of AgNPs after a certain amount of **WP5** was added to cover the surfaces of the silver nanoparticles completely. Then we used the AgNPs where the concentration of **WP5** was 0.400 mM for further studies.

The host–guest molecular interaction between pillar[5]arenes and paraquat derivatives is proverbial.[12] It is reasonable to speculate that bis-paraquat derivative (**G**) can act as a bridge to link the individual AgNPs together to induce self-assembly of **WP5** stabilized AgNPs.

Representative UV–Vis spectra of **WP5** stabilized AgNPs with **G** at different concentrations present clear evidence of the assembly. As shown in Fig. 1, the SPR absorption of AgNPs shows clear trends of red shift and intensity decrease with the increasing molar ratio of guest to host ([**G**]/[**WP5**]). When [**G**]/[**WP5**] is 0.100, the SPR peak ($\lambda_{max}$) is at 404 nm, only 2 nm red shift appeared compared with that of the initial individual AgNPs without any guest molecules. In this case, the concentration of the guest seems too low to induce particle assembly. As [**G**]/[**WP5**] increases to 0.300, $\lambda_{max}$ shifts to 416 nm accompanied by a visible color change from bright-yellow to light brown, indicating the formation of silver assemblies. When [**G**]/[**WP5**] increases to 0.700, $\lambda_{max}$ increases to 447 nm showing an obvious change of the solution color. Finally $\lambda_{max}$ reaches 458 nm when [**G**]/[**WP5**] increases to 1.00, and then it almost keeps constant even when more guest molecules are added. This means that the linkage of the silver nanoparticles gets saturated. The results are summarized in the inset in Fig. 1 showing that $\lambda_{max}$ increases sharply with [**G**]/[**WP5**] when the value of [**G**]/[**WP5**] is lower than 1.00 and hardly changes afterwards even when [**G**]/[**WP5**] reaches 10.0. In fact, for the samples with [**G**]/[**WP5**] over 1.00, precipitates could be seen at the bottom of the bottle after standing overnight (Fig. S2, ESI†).
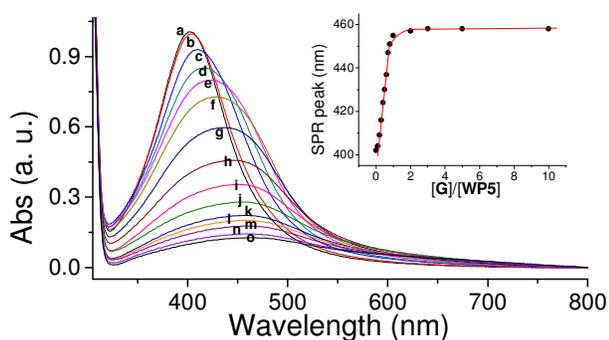


**Fig. 1** UV–Vis spectra of the **WP5** stabilized AgNPs with different ratios of [**G**]/[**WP5**]: (a) 0; (b) 0.100; (c) 0.200, (d) 0.300, (e) 0.400, (f) 0.500, (g) 0.600, (h) 0.700; (i) 0.800; (j) 0.900; (k) 1.00; (l) 2.00; (m) 3.00; (n) 5.00; (o) 10.0. The insert is the dependence of $\lambda_{max}$ on the value of [**G**]/[**WP5**].

Transmission electron microscopy (TEM) experiments assisted in the visualization of the assemblies of **WP5** stabilized AgNPs and **G**. Fig. 2a is for the sample with [**G**]/[**WP5**] as low as 0.100. Obviously, all the particles existed separately and no assembly could be seen, which is the same as that of the pure **WP5** stabilized AgNPs without any **G** (Fig. S3, ESI†). Such result is in agreement with the

conclusion drawn from the UV–Vis spectra. Small assemblies composed of several separated silver particles are obtained (Fig. 2b) when [**G**]/[**WP5**] reaches 0.300. Even larger assemblies containing thousands of particles sticking together were obtained when excess guest molecules were added ([**G**]/[**WP5**] = 1.00, Fig. 2c). Therefore, the conclusion could be drawn that the assembly degree of **WP5** stabilized AgNPs strongly depends on [**G**]/[**WP5**]. The number of AgNPs in each silver assembly increases with increasing [**G**]/[**WP5**].
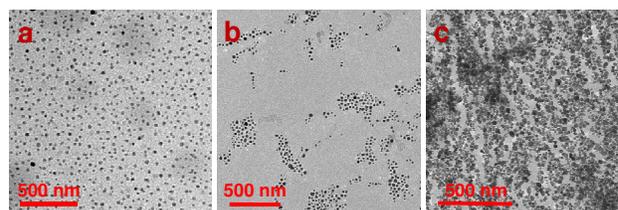


**Fig. 2** TEM images of the **WP5** stabilized AgNPs with different ratios of [**G**]/[**WP5**]: (a) 0.100; (b) 0.300; (c) 1.00.

It is known that the association constant of **WP5** with paraquat is $(8.20 \pm 1.70) \times 10^4$ M$^{-1}$,[12a] while for **WP6**⊃paraquat, it is about $(1.02 \pm 0.10) \times 10^8$ M$^{-1}$.[12b] Therefore, **WP6** could act as a strong competitor with **WP5** in complexation with **G**. As a result, the guest molecules which linked the **WP5** stabilized AgNPs together could be captured from the cavity of **WP5** by excess **WP6**, leading to disassembly of the silver assemblies (Scheme 1). Here we just investigate the results for the case of [**G**]/[**WP5**] = 1.00 as an example. After addition of excess **WP6** into the solution of the **WP5** stabilized AgNP assemblies and sonication for 1 hour, the color of the solution turned from brown to bright-yellow, suggesting disassembly of the silver assemblies (Fig. S4, ESI†). Accordingly, in the UV–Vis spectra, $\lambda_{max}$ decreases to 404 nm (Fig. S5, ESI†), which does not change any more even when prolonging the sonication periods (Fig. S5, ESI†). After centrifugation and subsequently immediate redispersion in water, $\lambda_{max}$ of the redispersed AgNPs is slightly broadened compared with that of the disassembled nanoparticles before centrifugation (Fig. S6, ESI†). This probably indicates subtle changes happening to the particles during the precipitation/dispersion process. However, the TEM image (Fig. S7, ESI†) of the redispersed silver nanoparticles presents clear proof for the completely discrete particles as a result of the successful disassembly.

This supramolecular replacement reaction of **WP5** by **WP6** was found really powerful in making complete disassembly of the other silver assemblies with different aggregation degrees. Discrete particles were successfully obtained by addition of excess **WP6** into the silver assemble solutions with different [**G**]/[**WP5**] values even when [**G**]/[**WP5**] was as high as 10.0, where the assemblies were in the form of precipitates (Fig. S8, ESI†). It should be pointed out that excess **WP6** is needed in making the complete disassembly and vigorous sonication is essential. In our control experiment, sonication could not make the silver assemblies disassembly without **WP6** (Fig. S9, ESI†). Furthermore, the disassembled **WP5** stabilized AgNPs could be separated from the solution by centrifugation and then redispersed in water. The assembly of the recovered AgNPs

was realized again by re-addition of **G** accompanied by a $\lambda_{max}$ shift from 404 nm to 456 nm. This reversible process was confirmed to be repeatable through several cycles (Fig. 3). Fig. 3 also reveals a slight tendency of the decrease of $\lambda_{max}$ for the re-assembled AgNPs. It was probably due to the fact that repeated precipitation and redispersion process makes a certain loss of the AgNPs, thus decreasing the concentration and then the degree of assembly.[13]
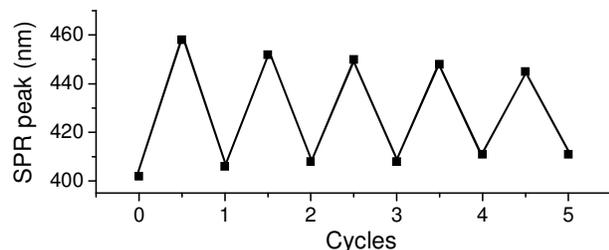


**Fig. 3** SPR peak of the silver assemblies or nanoparticles after sequential addition of **WP6** and re-addition of **G**.

In conclusion, **WP5** stabilized AgNPs could self-assemble into assemblies via the host–guest complex between **WP5** and **G** producing significant changes in the absorption spectrum with concomitant visible color change. The degree of the particle aggregation is dependent on the addition concentration of **G**. The silver assemblies could be disassembled into discrete silver particles by addition of a competitive host **WP6**, which captured the guest molecules from the cavity of the **WP5** on the AgNP surface. The recovered **WP5** stabilized AgNPs self-assembled again once the guest molecules were added. So the assembly and disassembly of the AgNPs are completely reversible and controllable. This simple and efficient strategy to control self-assembly of AgNPs is expected to increase the utility of the silver nanoparticles in diverse technologies including colorimetric sensors and provides a way of repeating usage of the particles. In principle, this self-assembly and disassembly approach based on the host–guest interactions[14] can also be applied into the studies of other metal particles.

## Notes and references

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