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A new water-soluble pillar[5]arene: synthesis and application in the preparation of gold nanoparticles†

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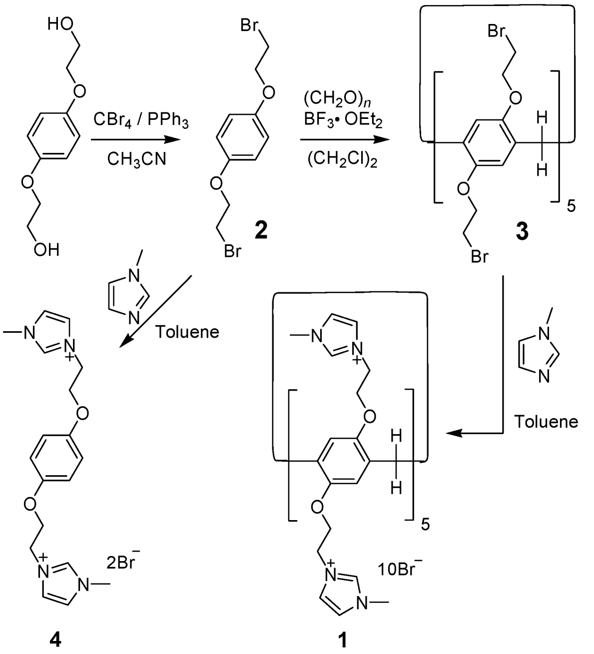
A new water-soluble pillar[5]arene containing ten imidazolium groups was prepared. It can be used as a stabilizer to fabricate gold nanoparticles smaller than 6 nm in water.

Over the past decade, there has been widespread interest in nanomaterials' syntheses and applications.[1] Among various nanomaterials, gold nanoparticles (GNPs) have made significant progress in different scientific areas due to their unique properties and applications in electronics, photonics and catalysis.[2] However, like other metal nanoparticles, small GNPs are only kinetically stable and easily aggregate to form larger particles owing to the large surface area and high surface energy, which decreases their activity.[3] Therefore, the controlled preparation of gold materials in the nanometer range is attracting increasing research efforts.[4] For the fabrication of GNPs, stabilizers play an essential role in controlling the formation of nanoparticles as well as their dispersion stability.[5–7]

On the other hand, as a new class of supramolecular hosts, pillar[*n*]arenes are versatile macrocyclic compounds that present a hydrophobic core sandwiched between two functionalizable rims.[8] They can be easily modified chemically and such modification is of interest for promising applications in nanomaterials and molecular recognition.[9]

Here we designed and synthesized a new water-soluble pillar[5]arene stabilizer **1** (Scheme 1) with ten imidazolium groups for the preparation of GNPs, in which the pillar[5]arene framework was used as the platform, and the imidazolium groups contain weakly coordinating cations and anions that bind feebly to the gold surface.[6b] This new type of stabilizer is less deactivating than the commonly employed capping or protective ligands, and thus can enhance the catalytic activity (Table S1, ESI†). The fabrication of GNPs in the presence of trace pillar[5]arene in aqueous media was investigated in detail by ultraviolet visible (UV/Vis) spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). Hence, their catalytic activity for the reduction of 4-nitroaniline in the presence of $NaBH_4$ was also studied (Fig. 2).



Scheme 1 Syntheses of pillar[5]arene **1** and noncyclic monomeric analog **4**.

The synthetic route to the stabilizer pillar[5]arene **1** in three steps is shown in Scheme 1. Condensation of **2** with boron trifluoride etherate as the catalyst in CH_2ClCH_2Cl yielded **3** (52%).[9j] Then compound **1** was obtained by refluxing a solution of **3** and *N*-methylimidazole in toluene (91%).

The structure of **1** was characterized by ^{1}H NMR, ^{13}C NMR and HRESIMS (ESI†). HRESIMS of **1** revealed peaks at *m*/*z* 1170.65, 754.13, 545.37, 420.51, 336.93 and 277.53, corresponding to $[M - 2Br]^{2+}$, $[M - 3Br]^{3+}$, $[M - 4Br]^{4+}$, $[M - 5Br]^{5+}$, $[M - 6Br]^{6+}$ and $[M - 7Br]^{7+}$, respectively (Fig. S8, ESI†). It is shown that **1** can lose different numbers of bromide anions to form a series of fragments containing different numbers of positive charges.

Because of the presence of ten imidazolium groups on the macrocyclic ring, pillar[5]arene **1** can be considered as a cluster

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of imidazolium groups and bromide anions, which could provide a shell of anions and cations around the gold nanoparticles, so gold nanoparticles can be stabilized in aqueous solution. For comparison, noncyclic monomeric analog **4** (Scheme 1) was also prepared and used to stabilize gold particles under the same experimental conditions. Unfortunately, with **4** as the stabilizer, we obtained dark purple particles instead of wine red nanoparticles with **1** as the stabilizer (Fig. 1). Therefore, it was indicated that the pillar[5]arene framework played an important role in stabilizing the gold nanoparticles.

Representative UV/Vis spectra of gold colloids stabilized by **1** at different concentrations revealed that all of the pillar[5]arene-protected GNPs displayed the characteristic optical signal of gold colloids: a surface-plasmon resonance in the visible region within the 500 nm to 560 nm range (Fig. S10, ESI†).[10] When the concentration of **1** was 2 μM, 4 μM, 10 μM, 50 μM and 200 μM, the corresponding maximum absorption wavelength of the gold hydrosols was 560 nm, 545 nm, 534 nm, 519 nm and 512 nm, respectively. The surface-plasmon absorption band undergoes a slight blue shift from 560 to 512 nm with increasing concentration of **1**. This shift might be due to the decreasing size of the GNPs formed. Additionally, the intensity of GNPs' absorption peak decreased with the decreasing concentration of pillar[5]arene, which suggested that larger-sized GNPs were obtained at lower concentrations of **1**.

When the concentration of **1** was 200 μM, a typical transmission electron microscopy (TEM) image and histogram of size distribution of GNPs were obtained (Fig. S11, ESI†). The average diameter and standard deviation determined from the histogram were 1.88 ± 0.58 nm. The TEM images revealed that the nanoparticles were spherical in shape. As anticipated from the absorption data, spherical GNPs with a relatively narrow particle size distribution were also observed. With decreasing concentration of the stabilizer, spherical GNPs together with a few triangular GNPs appeared. In addition, when **1** was used as a dispersing agent at a very low concentration (10^{-6} mol L^{-1}), although some polydisperse GNPs were observed, the average particle size was still smaller than 6 nm (Fig. S12–S14, ESI†).

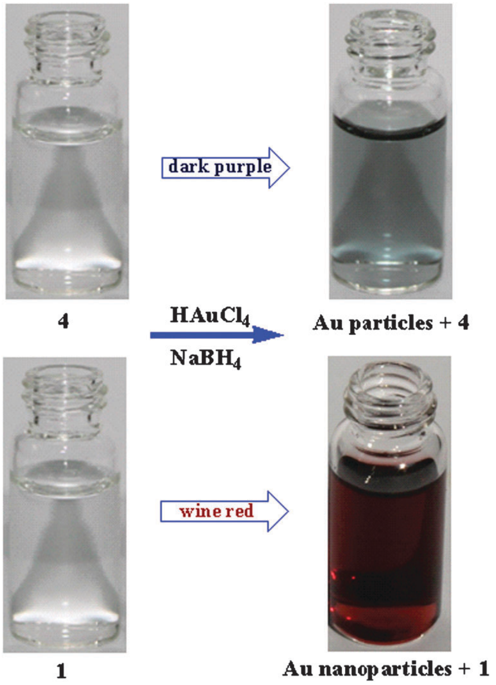

Fig. 1 Gold particles stabilized by **1** and **4**.

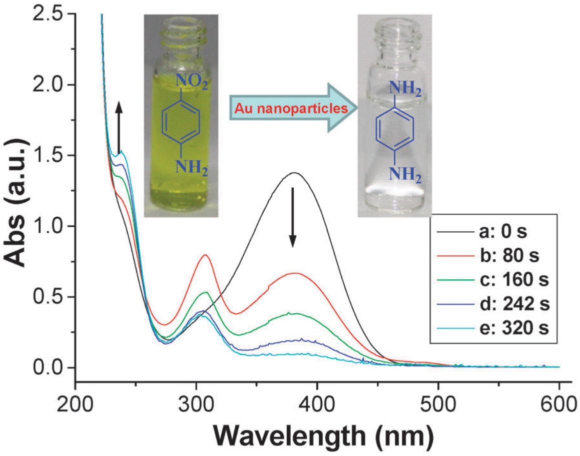

Fig. 2 Successive UV/Vis absorption of the reduction of 4-nitroaniline by excess $NaBH_4$ using the pillar[5]arene-stabilized gold nanoparticles (0.08 mol%, 1.88 ± 0.58 nm) as the catalyst.

The high resolution TEM image revealed that the GNPs had well-defined crystalline planes (Fig. S16, ESI†). The marked inter-planar *d* spacings are 0.235 nm and 0.203 nm, which are consistent with the inter-planar distance of (111) and (200) planes, respectively, for face-centered-cubic (fcc) gold.[11] The powder XRD pattern of GNPs shows that five diffraction peaks positioned at Bragg angles (2θ) between 30° and 90° can be attributed to the diffractions from five different gold lattice planes [(111), (200), (220), (311) and (222)] (Fig. S15, ESI†).

One of the important applications of GNPs is to catalyze some reactions that are otherwise not feasible. Hence, in the present study, we have examined the performance of these pillar[5]arene stabilized GNPs as catalysts for the borohydride reduction of 4-nitroaniline as a model reaction. In the absence of GNPs, the mixture of 4-nitroaniline and $NaBH_4$ shows an absorption peak at 400 nm (Fig. 2). This peak remains unaltered for a long duration suggesting the inability of the reducing agent $NaBH_4$ itself to reduce 4-nitroaniline. However, the addition of a very small amount of **1**-stabilized GNPs to the reaction system caused fading and ultimate bleaching of the yellow colour of the reaction mixture in quick succession, suggesting the occurrence of the reduction reaction. This discoloration was quantitatively monitored spectrophotometrically with time and noted visually as well; this was due to the reduction of 4-nitroaniline to 1,4-diaminobenzene. Fig. 2 shows that the absorption band of 4-nitroaniline at 400 nm decreases and disappears within six minutes after the addition of the GNPs, with the concomitant appearance of new peaks at 300 nm and 240 nm, which are attributed to 1,4-diaminobenzene.

In our reaction system, the concentration of BH_4^- greatly exceeded that of 4-nitroaniline, so it is reasonable to consider its concentration to be constant during the reaction.[12] As expected, a good linear correlation of ln(A) *versus* time was obtained (Fig. S17, ESI†), and the kinetic reaction rate constant was estimated to be $8.34 \times 10^{-3}\ s^{-1}$. The catalytic activity of the GNPs is possibly due to efficient electron transfer from the BH_4^- anion to nitro compounds mediated by the large Fermi level shift of nanoparticles.[13] As shown in Fig. S21 (ESI†), the catalytic reduction is carried out on the surface of the GNPs: the nanoparticles react with the borohydride ions to form the metal hydride. Subsequently, nitroaniline molecules adsorb onto the metal surface. The adsorption/desorption of both reagents on the surface is fast and can be modelled in terms of a Langmuir isotherm.[14] When the same experiment was conducted with GNPs of 3.09 ± 0.79 nm, 3.86 ± 0.91 nm and 5.95 ± 1.64 nm, the rate constants were estimated to be $5.73 \times 10^{-3}\ s^{-1}$, $2.72 \times 10^{-3}\ s^{-1}$ and $8.17 \times 10^{-4}\ s^{-1}$, respectively, indicating that the smaller GNPs were more efficient in catalyzing the reaction (Fig. S18–S20, ESI†).

In conclusion, we have successfully synthesized a new water-soluble pillar[5]arene **1** with ten imidazolium groups at its two rims. When **1** was used as the stabilizer at very low concentrations, GNPs smaller than 6 nm were prepared in aqueous solution. It was found that the average particle size of the AuNPs stabilized by **1** decreased with increasing molar ratio of [pillar[5]arene]/[Au^{3+}], and their standard deviations also became smaller. Since this water-soluble pillar[5]arene contains only weakly coordinating cations and anions that bind feebly to the gold surface, the plasmon resonance of the gold nanoparticles stabilized by it shows greater sensitivity than that of the gold nanoparticles stabilized by the commonly employed capping or protective ligands, and thus the obtained gold nanoparticle catalysts are of superior activity (Table S1, ESI†). The present study provided a potential application of pillar[*n*]arenes in the catalysis industry.

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