In Situ Gold Nanoparticle Synthesis Mediated by a Water-Soluble Leaning Pillar[6]arene for Self-Assembly, Detection, and Catalysis

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Supporting Information

ABSTRACT: An anionic water-soluble leaning pillar[6]arene (AWLP6) has been synthesized and utilized as both the reductant and stabilizer for the one-pot synthesis of gold nanoparticles (AWLP6-AuNPs). Interestingly, AWLP6-AuNPs show not only optimal performance in self-assembly and label-free detection of methyl viologen, one of the most widely used herbicides, but also efficient catalytic activity for the hydrogenation of p-nitrophenol. The synthetic route to AWLP6 is shown in Scheme 2. First, a facile two-step ring-forming reaction was carried out to synthesize the permethylated LP6 (MeLP6), which was used to synthesize ethoxy carbonyl-substituted LP6 (EtLP6) through demethylation (OHLp6) and etherification. The carboxylated LP6, abbreviated as CLP6, was obtained from EtLP6 through hydrolysis and acidification, followed by further deprotonation to give carboxylated LP6 salt, that is, AWLP6. According to our previous report, in the high-quality single crystal of the OHLP6, the dihedral angles between the

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Scheme 1. Schematic Illustration of AWLP6-AuNPs and Their Self-Assembly, Label-Free Detection of Cationic Methyl Viologen (MV), and Efficient Catalysis for the Hydrogenation of \( p \)-Nitrophenol

Figure 1. (a) UV−vis absorption spectrum and (b) transmission electron microscopy (TEM) image and high-resolution TEM image (inset) of AWLP6-AuNPs, and (c) the histogram of size distribution based on TEM images (based on 300 particles). (d) Fourier transform infrared (FT-IR) spectra of AWLP6 and AWLP6-AuNPs.

Scheme 2. Synthetic Route to AWLP6

phenylene rings and the plane of methylene bridges are decreased to 54.48° and 77°. In addition, the dihedral angles are self-tunable with different substituents, indicating the excellent flexible rotation of LP6, which can adopt a favorable leaning conformation for binding guest within the cavity. On the other hand, the conformation in solution should be highly flexible, as indicated by our previous work using DFT calculations, thus it is difficult to predict what kind of conformation this macrocycle may adopt on the AuNP surface, which is a dynamic situation. The structures and purity of AWLP6 were confirmed by \(^1\)H and \(^{13}\)C NMR spectroscopy and mass spectroscopy (Figures S1–S6). The AWLP6 sodium salts were used in all experiments unless otherwise noted.

Since the carboxylate moiety can be used not only as a reductant for Au(III) of HAuCl₄ to prepare AuNPs but also as a stabilizer based on the strong affinity with the gold surface via an O−Au coordination bond, the monodisperse AWLP6-AuNPs were fabricated in situ by a facile one-pot hydrothermal method without the presence of any other reductants such as NaBH₄ or ascorbic acid. The procedure is as follows: the boiled HAuCl₄ aqueous solution (100 mL, 0.1 mmol/L) was reduced by AWLP6 aqueous solution (1.0 mL, 24 mmol/L) under vigorous stirring for 1.5 h. Then AWLP6-AuNPs were collected by centrifugation followed by redispersion in deionized water for further studies.

Furthermore, the characteristics of AWLP6-AuNPs were investigated in detail by UV−vis spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS), powder X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. As shown in the UV−vis spectrum (Figure 1a), the surface plasmon resonance (SPR) of AWLP6-AuNPs was observed at 520.5 nm. TEM image revealed that the fraction of spherical nanoparticles was almost 100% (Figure 1b), and their average diameter was 11.1 ± 1.7 nm (Figure 1c). The average hydrodynamic diameter was 15.7 nm (Figure S7), with some enlargement compared to TEM measurements because of the hydration layer of AWLP6. As determined by the high-resolution TEM image, AWLP6-AuNPs had well-defined crystalline planes with an interplanar spacing of 0.235 nm (Figure 1b, inset), in agreement with the (111) plane of face-centered cubic (fcc) Au. Moreover, the crystalline structures of AWLP6-AuNPs were further identified by their XRD pattern (JCPDS No. 04-0784) in which five diffraction peaks could be assigned exclusively to the (111), (200), (220), (311), and (222) planes of fcc Au (Figure S8).

Furthermore, the similar characteristic peaks in the FT-IR spectra of AWLP6 and AWLP6-AuNPs verified the modification of AWLP6 on the surface of AuNP (Figure 1d). In the FT-IR spectrum of AWLP6-AuNPs, the typical peaks at ~1601 and ~1508 cm\(^{-1}\) were attributed to the C=C stretching vibrations of the benzene ring in the backbone of AWLP6. The peaks at ~1657 and ~1412 cm\(^{-1}\) resulted from −COO− stretching vibrations. The peaks at ~1063 and ~1201 cm\(^{-1}\) corresponded to the Ar−O−C group. Significantly, AWLP6-AuNPs could remain stable for several months, which is consistent with the sufficiently negative ζ-potential of −5.4 mV (Table S1). In sharp contrast, the use of an onycyclic monomer of AWLP6 could not lead to uniform and stable AuNP colloids under identical conditions.

As indicated above, the carboxylate substituents and skeleton structure of AWLP6 rings are essential for the preparation of AuNPs. First, those −COO− groups in AWLP6 serve as a reductant for producing Au\(^0\) from HAuCl₄ for the nucleation and growth of AuNPs. Second, AWLP6 attached on the surface of AuNP by O−Au coordination bond, endowing AuNPs with optimal stability. Third, the electrostatic repulsion and skeleton structure of AWLP6 can regulate the growth of AuNP with uniform morphology and particle size.

To confirm the host−guest recognition property endowed by AWLP6 rings on AWLP6-AuNP surface, the assembly of AWLP6-AuNPs modulated by different amounts of cationic guest was investigated. 1,1,2,2-Tetrakis[(1-(trimethylammonium)butoxy)phenyl]tetraphenylenethene (TPE-4Q) was synthesized as a mediator for the assembly of AWLP6-AuNPs...
Because four quaternary ammonium salt substituents of TPE-4Q could not only play the role of host–guest recognition sites for AWLP6 but also weaken the electrostatic repulsion between AWLP6-AuNPs by neutralizing the electronegativity on AuNP surfaces, when a small amount of TPE-4Q mediator was introduced, AWLP6-AuNPs could assemble in one-dimension (1D) with the broadening and decrease of SPR peak at 520.5 nm (Figure 2a,d). Interestingly, these results further validated the host–guest property of AWLP6-AuNPs inherited from AWLP6.

On the basis of the fact that the SPR peak of AWLP6-AuNPs was closely dependent on their self-assembly state, we envisioned that AWLP6-AuNPs could be used as a fast and simple optical probe for the sensitive label-free detection of trace cationic guests. Methyl viologen (MV), one of the most widely used herbicides, possesses positive charge and molecular size matching the cavity size of AWLP6. Therefore, MV was chosen as the model cationic guest. The host–guest interaction between AWLP6 and MV was first investigated by \(^1\)H NMR spectroscopic analysis of the 1:1 host–guest mixture (Figure S9). Compared with the free MV, all protons of MV shifted upfield upon mixed with AWLP6, suggesting the strong host–guest affinity between AWLP6 and MV. The complexation of AWLP6 and MV would destroy the original electrostatic balance and promote the aggregation of AWLP6-AuNPs by neutralizing their negative surface charge. Since the assembly state of AWLP6-AuNPs can be analyzed by calculating the ratio of the integrated intensity of ranges for the aggregated (A, ranging from 550 to 750 nm) and dispersed (D, ranging from 450 to 540 nm) AWLP6-AuNPs (Figure 3a), a four times higher sensitivity for MV was achieved with a detection limit of 0.02 ppm (0.05 \(\mu\)M) as compared with traditional caboxylatopillar[5]arenes (0.2 \(\mu\)M),\(^{13}\) which fulfills the demands on the residue amount of MV according to The National Standard GB 2763–2016 (0.03 and 0.05 ppm in grains and vegetables, respectively). Moreover, compared with nitrophenolate ions obeys the Lambert–Beer law, the linear correlation between \(\ln(C_0/C_f)\) and reaction time is consistent with that between \(\ln(Abs/Abs_0)\) and reaction time (Figure 4b).\(^{16}\) The apparent rate constant \(k_{\text{app}}\) (with \(k = k_{\text{app}} N_{\text{Au}}\)) and intrinsic rate constant \(k\) (with \(k_{\text{app}} = kC\)) and

\[ y = -0.001 + 0.88 x \]
\[ R^2 = 0.993 \]

\[ y = -0.001 + 0.131 x \]
\[ R^2 = 0.996 \]

The catalysis based on AWLP6-AuNPs has three advantages: First, AWLP6 regulated the growth of AuNP with more suitable particle size (11.1 ± 1.7 nm) and uniform morphology for enhanced catalytic activity. As Rademann et al. revealed,\(^{17}\)
AuNPs with size of 10–13 nm exhibited better catalytic activities than that with the size of 3.5, 28, or 56 nm because of their more appropriate specific surface areas for the adsorption of p-nitrophenol molecules. Second, the electrostatic repulsion and skeleton structures of AWLP6 endowed AuNPs with stable catalytic activity. Third, the flexible skeleton structures of AWLP6 provided convenience for p-nitrophenol to attack on the gold surface by slightly adjusting the conformations.

In summary, we synthesized a new version of an anionic water-soluble leaning pillar[6]arene (AWLP6) with good cavity adaptability and four carboxylate groups on each rim, which is less but more efficient than traditional five- or six-membered rings of carboxylatopillar[n]arenes. AWLP6-AuNPs were prepared in situ by a facile one-pot hydrothermal method using AWLP6 as an efficient reductant and an optimal stabilizer. Thanks to the host–guest properties of AWLP6, the degree of AWLP6-AuNPs assembly was modulated by varying the concentration of cationic guest TPE-4Q, accompanied by significant changes in SPR signal and visible color. We further demonstrated the optimal performance in label-free detection of methyl viologen (MV) and its derivative via UV–vis spectral analysis. An appreciable lower detection limit for MV compared with traditional carboxylatopillar[n]arenes was achieved that reached the demands on the residue amount of MV in national standard. The enhanced catalytic activity of the newly obtained AWLP6-AuNPs for the reduction of p-nitrophenol was also investigated and analyzed. The functionalization and combination strategy of AWLP6 macrocycles and AuNPs is easily amenable to the fabrication of other organic–inorganic hybrid nanosystems with promising potential for applications in sensors, catalysis, and biomedicine.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01827.

Synthesis, 1H and 13C NMR spectroscopy, and mass spectroscopy of AWLP6; preparation and characterization of AWLP6-AuNPs; host–guest interaction between AWLP6 and MV (PDF)

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**Notes**

The authors declare no competing financial interest.

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