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Viologen-Mediated Assembly of and Sensing with Carboxylatopillar[5]arene-Modified Gold Nanoparticles

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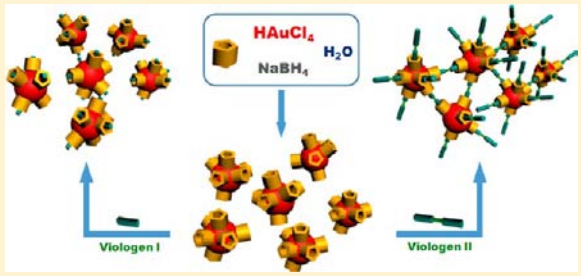
Supporting Information

ABSTRACT: Carboxylatopillar[5]arene (CP[5]A), a new water-soluble macrocyclic synthetic receptor, has been employed as a stabilizing ligand for *in situ* preparation of gold nanoparticles (AuNPs) to gain new insights into supramolecular host−AuNP interactions. CP[5]A-modified AuNPs with good dispersion and narrow size distributions (3.1 ± 0.5 nm) were successfully produced in aqueous solution, suggesting a green synthetic pathway for the application of AuNPs in biological systems. Supramolecular self-assembly of CP[5]A-modified AuNPs mediated by suitable guest molecules was also investigated, indicating that the new hybrid material is useful for sensing and detection of the herbicide paraquat.



INTRODUCTION

Gold nanoparticles (AuNPs) play important roles in the fields of nanomaterials and nanotechnology due to their importance in sensors,[1] nanoelectronics,[2−4] biomedicine,[5] catalysis,[6] and surface-enhanced Raman scattering (SERS) spectroscopy.[7] Their high chemical stability, facile synthesis, and surface functionalization make them important building blocks for novel hybrid nanomaterials.[8,9] Macrocycles, such as cyclodextrins, calixarenes, and cucurbiturils, continue to be central to supramolecular chemistry.[10−12] Recently, progress has been made in the synthesis and assembly of metal nanoparticles modified with cyclodextrins,[13,14] calixarenes,[15] and cucurbiturils.[16,17] Conjugation of AuNPs and supramolecular macrocycles significantly combines and enhances the characteristics of the two entities, such as the electronic, thermal, and catalytic properties of AuNPs and molecular recognition of the macrocyclic hosts, expanding potential applications as nanosensors, drug delivery vehicles, and recycling extraction agents.[18−20]

Pillar[*n*]arenes (P[*n*]A) are a relatively new class of supramolecular hosts and have received considerable attention for their novel symmetric pillar-shaped architectures, unique host−guest properties, and highly tunable functionality.[21] Based on these unique properties, we anticipated that P[*n*]As can be used as building blocks for the construction of supramolecular architectures (including catenanes, pseudorotaxanes, and polyrotaxanes)[22−25] and supramolecular sensors.[26−28] Their potential applications in hybrid nanomaterials, molecular machines, and nanoelectronic mechanical systems (NEMS) remain to be explored. Much research has focused on the synthesis of P[5]A and its derivatives, their host−guest chemistry, and their supramolecular self-assembly,[29,30] but the conjugation of P[*n*]A with AuNPs and the application of the resulting hybrid nanomaterials remain largely unexplored.[31]

Stabilizing ligands possessing amine (−NH_2), carboxyl (−COOH), or sulfhydryl (−SH) groups are essential to the synthesis and stabilization of AuNPs.[32−36] We envision that carboxylatopillar[5]arene sodium salts (CP[5]A), with five carboxyl groups on each rim, can be used as stabilizers for AuNPs. Furthermore, the water-soluble nature of CP[5]A opens the possibility of the preparation of AuNPs in aqueous phases, which is important from environmental protection and biomedical engineering perspectives.[37] Here, CP[5]A sodium salts were synthesized according to a procedure modified from the synthesis of CP[5]A ammonium salts[38,39] (Supporting Information) and then used as stabilizers for *in situ* preparation of Au nanospheres to result in AuNPs with narrow size distributions (3.1 ± 0.5 nm). Supramolecular self-assembly of CP[5]A-modified AuNPs mediated by viologens I and II was also investigated (Figure 1). Significantly, the guest-mediated assembly processes indicate that CP[5]A-functionalized AuNPs can be further used as optical probes for the detection of 1,1′-dimethyl-4,4′-bipyridinium salt (viologen I), i.e., paraquat (PQ), one of the world's most widely used herbicides.

EXPERIMENTAL SECTION

Materials. $HAuCl_4$ and $NaBH_4$ were purchased from Sinopharm Chemical Reagent Co., and NaOH was obtained from Beijing Chemical

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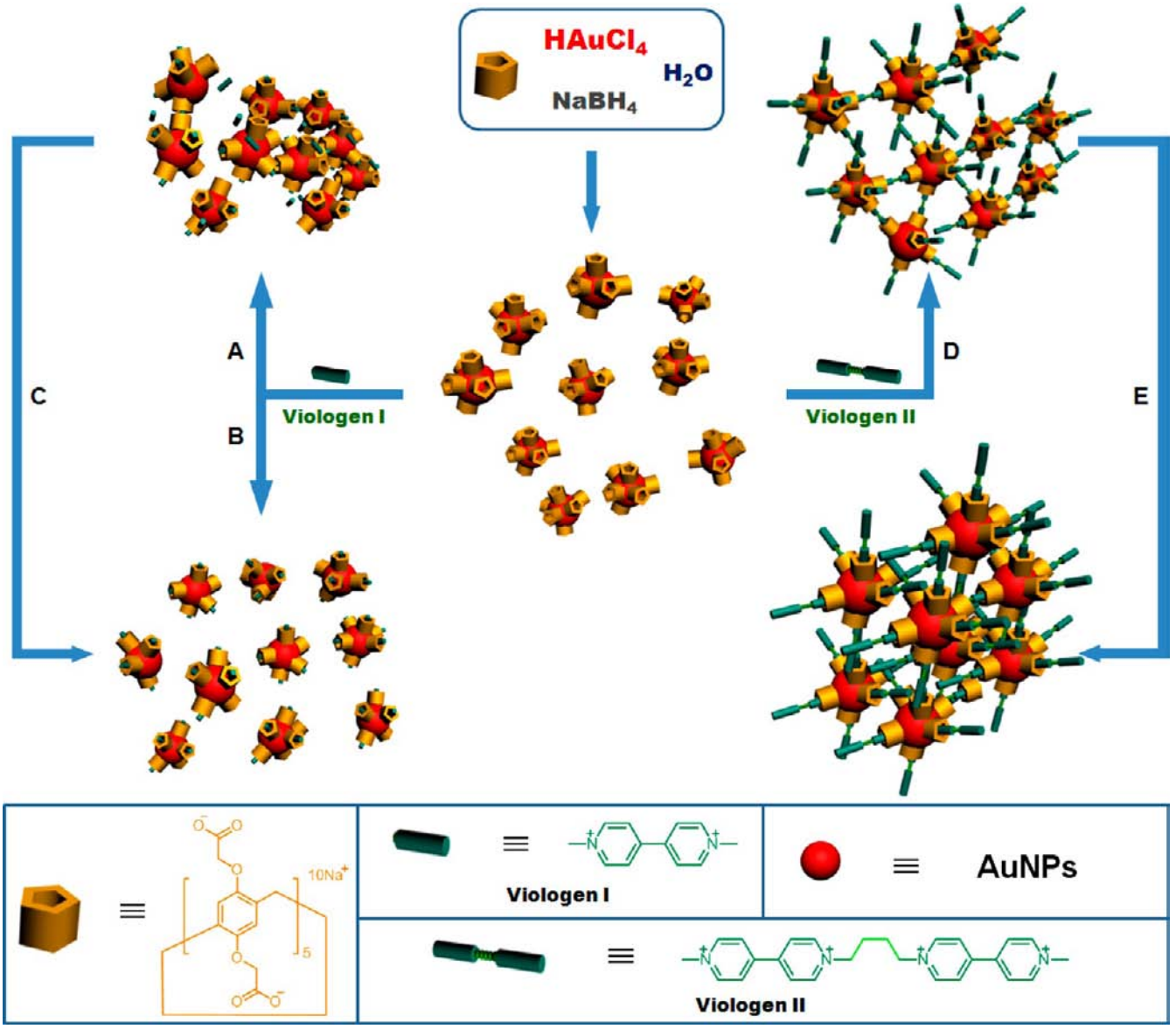

Figure 1. Schematic representation of the formation of CP[5]A-modified AuNPs and their supramolecular self-assembly upon addition of guest viologen molecules (I and II): (A) 5 min and (C) 24 h after the addition of viologen I (10 mM) into a solution of CP[5]A-stabilized AuNPs; (B) 5 min after the addition of viologen I (75 mM) into the solution of CP[5]A-stabilized AuNPs; (D) 5 min and (E) 24 h after the addition of viologen II (3.8 mM) into a solution of CP[5]A-stabilized AuNPs.

Reagents Co. All the chemicals involved in our experiments were of analytical grade and used as received. Deionized water was used in all relevant experiments. CP[5]A sodium salts and its noncyclic monomer were synthesized according to a modified procedure (see the Supporting Information); 1,1′-dimethyl-4,4′-bipyridinium salt (viologen I) and 1′,1″-(butane-1,4-diyl)-bis(1-methyl-4,4′-bipyridine-1,1′-diium) dibromide diiodide (viologen II) were synthesized according to literature procedures.[40,41] The aqueous solution of CP[5]A (4 mM) was prepared as follows: 47.6 mg of CP[5]A was dissolved in 9.6 mL of deionized water, and then 400 μL of 1.0 M NaOH was added under sonication to generate a clear solution of CP[5]A sodium salts (molar ratio of CP[5]A/NaOH = 1:10).

Synthesis of AuNPs. CP[5]A-modified AuNPs were synthesized by the reduction of $HAuCl_4$ in the presence of CP[5]A. In a typical synthesis, $HAuCl_4$ (165 μL, 24.3 mM) was added to deionized water (20 mL), followed by the addition of an alkaline aqueous solution of CP[5]A (75 μL, 4 mM, [CP[5]A]/[$HAuCl_4$] = 0.075). $NaBH_4$ (200 μL, 0.1 M) was freshly prepared with deionized ice water and added to the above reaction mixture while stirring. The solution immediately turned red, and CP[5]A-modified AuNPs were thus obtained. This concentration of CP[5]A-modified AuNPs was used in all experiments unless otherwise noted. In control experiments, AuNPs were synthesized in the absence of stabilizing ligands and in the presence of noncyclic monomer of CP[5]A (75 μL, 4 mM), respectively, under otherwise identical experimental conditions.

Guest-Mediated Self-Assembly of CP[5]A-Modified AuNPs. An aqueous solution of CP[5]A-modified AuNPs (3 mL, [CP[5]A]/[$HAuCl_4$] = 0.075) was mixed with different concentrations of viologen I (10 μL): 0, 1.5, 3, 4.5, and 22.5 mM, respectively.

Sensing and Detection of Paraquat. The experimental setup for PQ detection experiments is shown in Figure S11 of the Supporting Information. Different concentrations of PQ (10 μL) were added to aqueous solutions of CP[5]A-modified AuNPs (3 mL, [CP[5]A]/[$HAuCl_4$] = 0.075). After the reaction mixtures were stirred for 10 min, the solution UV−vis absorption spectra were recorded.

Characterization. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were collected on a FEI Tecnai F20 instrument at an accelerating voltage of 200 kV.

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X-ray photoelectron spectroscopy (XPS) measurements were carried out at 15 kV and 17 mA, using a Thermo ESCALAB 250 spectrometer with a twin anode Al Kα (1486.6 eV) X-ray source. Fourier transform infrared (FTIR) spectra were recorded on a Vertex 80 V spectrometer. Ultraviolet−visible (UV−vis) spectra were recorded on a Shimadzu UV-2550 instrument. Zeta-potential measurements were performed on a Zetasizer Nano-ZS90 instrument.

RESULTS AND DISCUSSION

CP[5]A-modified AuNPs were synthesized by reducing $HAuCl_4$ (0.2 mM) with $NaBH_4$ (1 mM) in the presence of the selected concentrations of CP[5]A. Corresponding UV−vis spectra are shown in Figure 2 (left). The well-known surface plasmon

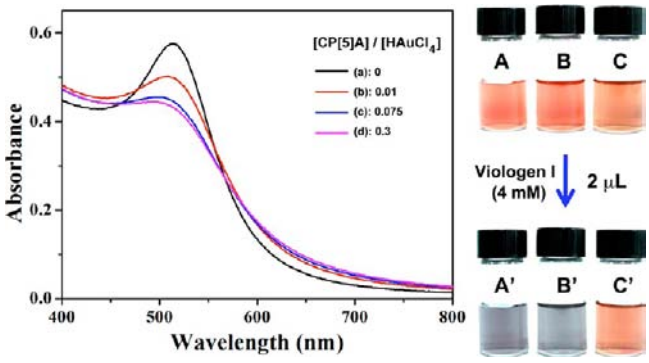

Figure 2. Left: Ultraviolet−visible spectra of CP[5]A-modified AuNPs synthesized with different [CP[5]A]/[$HAuCl_4$] ratios: (a) 0, (b) 0.01, (c) 0.075, (d) 0.3. Right: Photographs of solutions of (A and A′) bare AuNPs, (B and B′) noncyclic monomer of CP[5]A-modified AuNPs, (C and C′) CP[5]A-modified AuNPs before and after the addition of viologen I, respectively.

resonance (SPR) of AuNPs was observed at ∼500 nm, suggesting the formation of stable CP[5]A-modified AuNPs. Due to the presence of CP[5]A, the SPR peak gradually underwent a blue shift from 516 to 487 nm, indicating smaller average AuNP diameters. Upon increasing [CP[5]A]/[$HAuCl_4$] from 0.075 to 0.3, the SPR peak maximum changed only slightly in wavelength and intensity (Figure 2, curves c and d), indicating that the continuous addition of excess CP[5]A has little influence on the sizes of AuNPs after a certain amount of CP[5]A was added to cover the surfaces of the AuNPs completely.

CP[5]A-modified AuNPs are stable and resistant to surrounding condition changes as verified by the following control experiments. AuNPs were prepared in the absence of stabilizing ligands or in the presence of noncyclic monomers of CP[5]A under the same experimental conditions (Figure 2, right). Upon addition of a small amount of viologen I (Figure 2, right), which can form a 1:1 host−guest complex with CP[5]A,[38] samples A and B became dark gray in seconds and precipitation occurred after a few hours, while the color of sample C had almost no change and no precipitation was observed. Corresponding UV−vis spectra are shown in Figure S9 in the Supporting Information. The change of the SPR absorption further revealed that, after the addition of viologen I, bare AuNPs and noncyclic monomer-modified AuNPs aggregated and precipitated out from the solutions (curves A′ and B′). Thus, we learned that the macrocyclic framework of CP[5]A plays an important role in the stabilization of AuNPs, while AuNPs cannot be effectively protected in the absence of stabilizing ligands or in the presence of noncyclic monomers of CP[5]A.

In addition to UV−vis spectroscopy, TEM was employed to visualize and to explore the above spectral changes. In Figure 3a, AuNPs with no stabilizing ligands were metastable and aggregated into large networks with diameters of 7.7 ± 1.9 nm. In contrast, AuNPs that were synthesized in the presence of CP[5]A had better dispersibility, smaller sizes, and narrow size distributions (3.1 ± 0.5 nm) as compared with those synthesized in the absence of stabilizing ligands (Figure 3b). These observations suggest that CP[5]A can be used as a stabilizer in the preparation of AuNPs, in which the interactions between carboxylate groups and surface atoms of AuNPs play important roles: (a) the presence of CP[5]A stabilized the initially formed AuNPs by strong carboxyl−Au binding interactions, and (b) the rigid macrocyclic ring backbone structure of CP[5]A suppressed further growth of the AuNPs during the reduction step. In Figure 3c, a higher resolution detail of Figure 3b, narrow size distributions of CP[5]A-modified spherical AuNPs were observed, consistent with the high surface zeta potential (see Supporting Information, Table S1A). Furthermore, HRTEM images (Figure 3d) indicate that CP[5]A-stabilized AuNPs had well-defined crystalline planes with interplanar d spacings of 0.235 nm, corresponding to the (111) planes of face-centered-cubic Au.[42]

Fourier transform IR spectroscopy was used to test if AuNPs were indeed capped by CP[5]A macrocyles. From the FTIR spectra of CP[5]A-modified AuNPs (Figure 4), as compared to those of bare AuNPs, a typical absorption peak at 1600 cm^{-1} was observed arising from the C═C stretching of the benzene ring in the backbone of CP[5]A. The presence of CP[5]A on the Au surface and the interactions between the carboxylate groups of CP[5]A and Au were further confirmed by comparing the XPS spectra of pure CP[5]A and those of CP[5]A-stabilized AuNPs (see the Supporting Information). For pure CP[5]A, two peaks were identified at 531.5 and 533.2 eV, attributed to the carbonyl and hydroxyl oxygen atoms in the carboxylic acid (−COOH) moieties of CP[5]A, respectively (Figure S10a). However, for CP[5]A-stabilized AuNPs, only a single peak was identified at 532.1 eV in the O 1s spectral region (Figure S10b). This peak can be ascribed to the interaction of carboxylate groups with AuNP surfaces that results in the electronic environments of the two kinds of oxygen atoms in the carboxylate groups being more similar, or even identical.[43]

Cationic viologen I can form a stable 1:1 host−guest complex with CP[5]A.[38] So, in order to examine the interactions and assembly between viologen I and CP[5]A-modified AuNPs, different amounts of viologen I were added into the solutions of CP[5]A-modified AuNPs, showing solution color changes in 5 min (Figure 5, left-bottom). Compared to that in the absence of viologen I (A), the color of CP[5]A-modified AuNP solutions in turn became darker (B, C), purplish red (D), and clear red (E) upon the addition of different amounts of viologen I, which can be understood via the UV−vis spectra (Figure 5) and further verified by TEM experiments (Figure 6). In Figure 5a, SPR peaks of traces B and C were broadened with a slight red shift from 494 to 508 nm compared to trace A, representing AuNP aggregation (Figure 6a). However, for traces D and E, the shapes of the absorption peaks sharpened, suggesting a dispersed state (Figure 6c). After 24 h, samples C and D also became clear red (Figure 5 right bottom, C′ and D′). Correspondingly, their SPR main peaks (Figure 5b) became sharp. Thus, we concluded that monodisperse AuNPs were obtained as shown in Figure 6b. In addition, sample B had almost no change after 24 h (Figure 5B′) and was still in an aggregated state because the amount of

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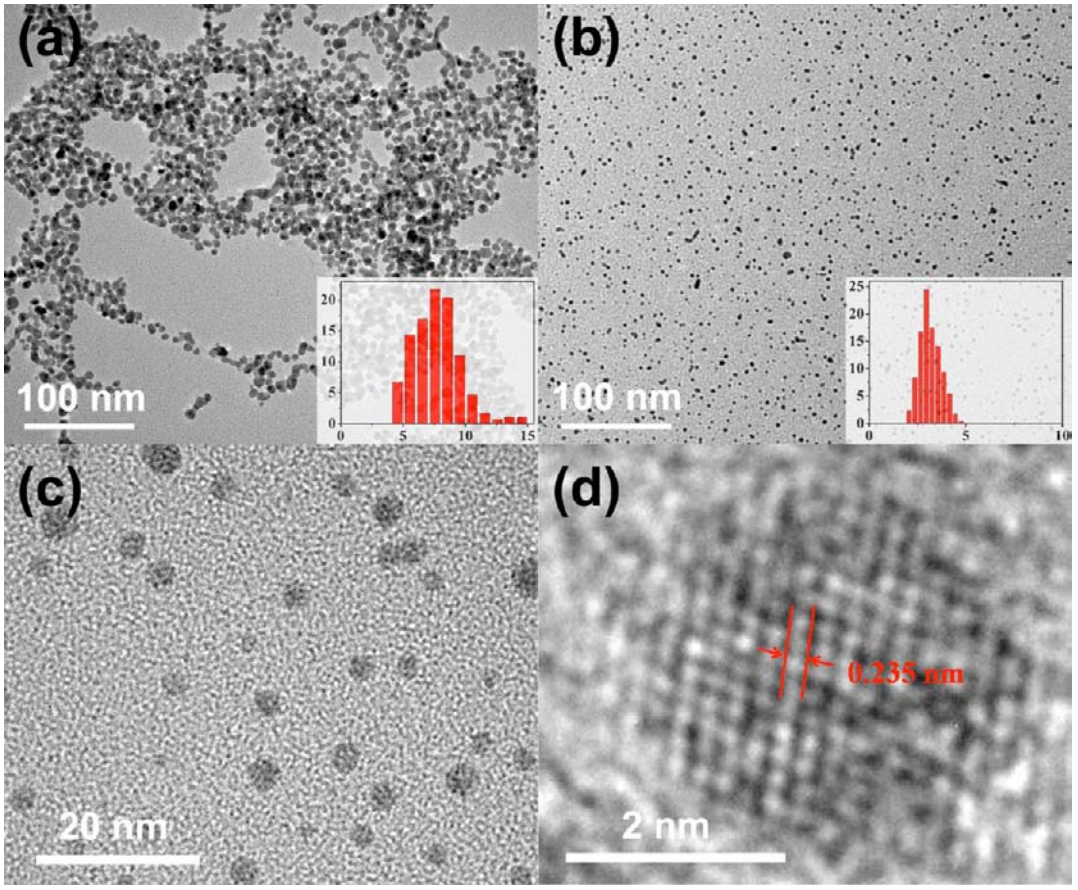

Figure 3. Transmission electron microscopy images of (a) bare AuNPs ([CP[5]A]/[$HAuCl_4$] = 0) and (b) CP[5]A-modified AuNPs ([CP[5]A]/[$HAuCl_4$] = 0.075). Insets show the corresponding histograms of the AuNP sizes based on 300 particles (*x*-axis, diameter/nm; *y*-axis, number counts). (c) Higher resolution image of parts of (b), and (d) HRTEM images of CP[5]A-modified AuNPs.

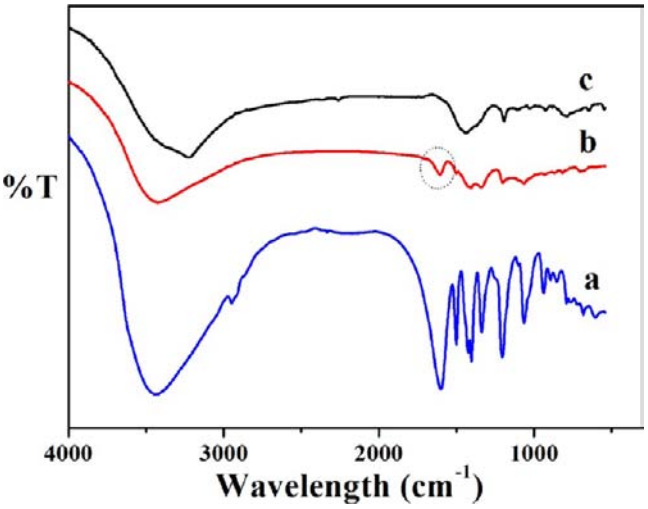

Figure 4. Fourier transform IR spectra of (a) pure CP[5]A sodium salts, (b) CP[5]A-stabilized AuNPs, and (c) bare AuNPs. The circle indicates the C═C stretching mode of the benzene ring.

viologen I was insufficient to result in CP[5]A-modified AuNP macroscopic changes. Meanwhile, sample E yielded a small amount of precipitate (Figure 5E′) because of the relatively high zeta potential of −29.87 mV (Table S1).

The experimental results and analyses were consistent in terms of photographs, UV−vis spectra, and TEM images of CP[5]A-stabilized AuNP samples upon addition of viologen I. We inferred that the assembly of CP[5]A-modified AuNPs mediated by viologen I is based on a dynamic equilibrium relying on the amount of viologen I added (Figure 1). First, we observed that a small amount of viologen I (in a typical system, [viologen I]/[CP[5]A] = 0.5) can cause the aggregation of CP[5]A-modified AuNPs in a short time (Figure 1, processes A and B). We concluded that (a) viologen I can form a stable 1:1 host−guest complex with CP[5]A, and (b) CP[5]A is negatively charged due to carboxylate anions on both rims, while viologen I is positively charged (the charge absolute value ratio of a CP[5]A molecule and a viologen I molecule was 5:1). Thus, AuNPs modified with CP[5]A exhibited negatively charged surfaces. Cationic viologen I combined with particle-immobilized CP[5]A through host−guest interactions and also reduced the surface potential of CP[5]A-modified AuNPs. In a short time, a small amount of viologen I caused the aggregation of CP[5]A-modified AuNPs, which was likely related to charge variations on the surfaces of AuNPs (Table S1). Interestingly, with increased incubation time, AuNPs exhibited good monodispersity, reaching a stable equilibrium.[44,45] The diameters of the AuNPs were slightly larger and their shapes became smoother and rounder, due to Ostwald ripening, where smaller particles shrink and larger particles grow.[44,45] Spherical particles can minimize total surface area, and larger particles are more energetically favored than smaller particles. In addition, when viologen I (in a typical system, [viologen I]/[CP[5]A] = 5) was in excess, the above processes (Figure 1, processes A and B) were accelerated. In a

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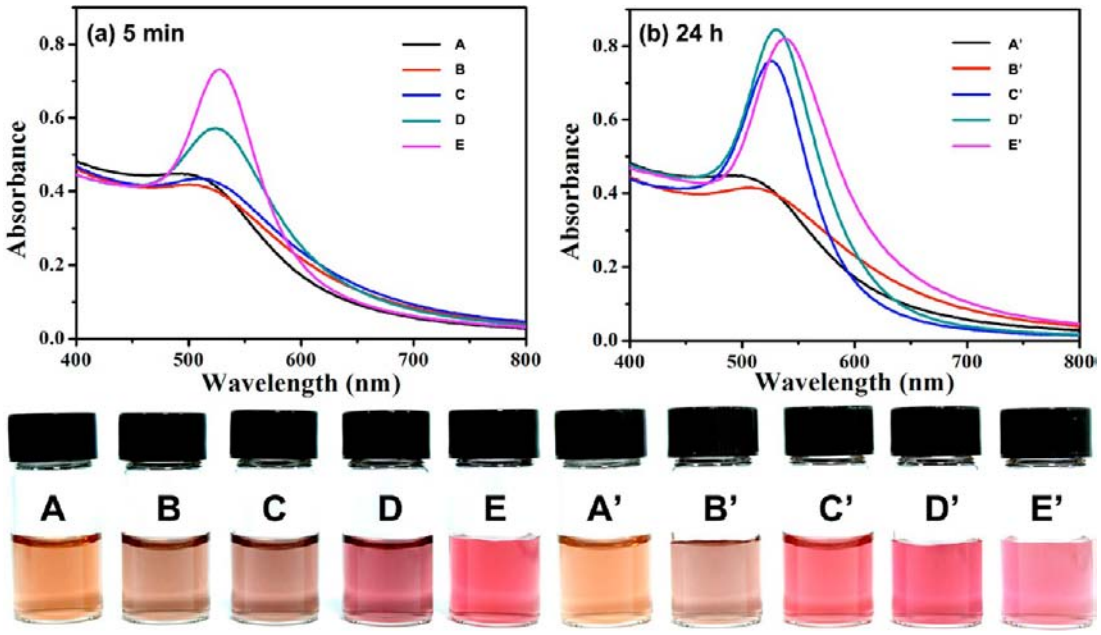

Figure 5. Ultraviolet−visible spectra of CP[5]A-stabilized AuNPs (a) 5 min and (b) 24 h after putting CP[5]A-stabilized AuNPs (57 μg/mL) with different concentrations of viologen I: (A and A′) 0 μM, (B and B′) 5 μM, (C and C′) 10 μM, (D and D′) 15 μM, and (E and E′) 75 μM. Corresponding photographs are shown below.

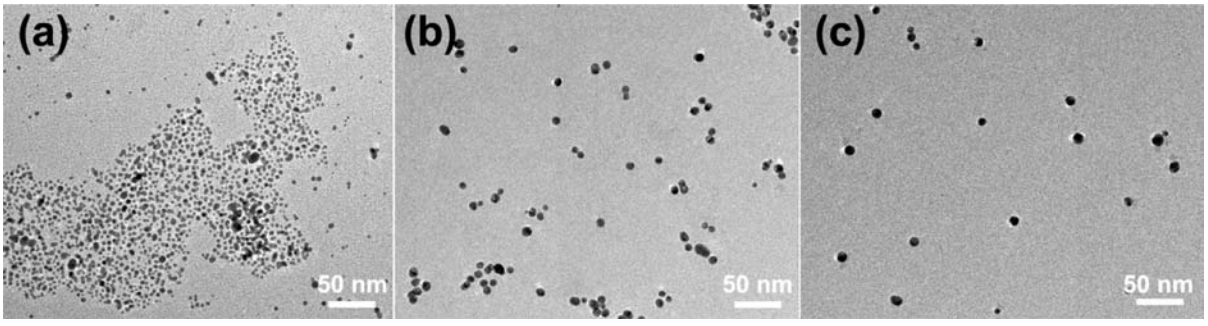

Figure 6. Transmission electron microscopy images of CP[5]A-stabilized AuNPs upon addition of viologen I: (a) samples C, (b) C′, and (c) E from Figure 5.

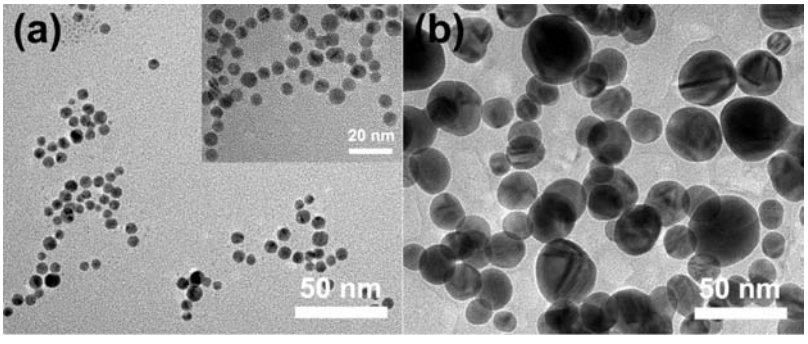

Figure 7. Transmission electron microscopy images of CP[5]A-stabilized AuNPs (a) 5 min and (b) 24 h after putting CP[5]A-stabilized AuNPs with viologen II (3.8 μM).

short time, monodisperse AuNPs with larger diameters and rounder appearance were obtained (Figure 1, process C).

In order to study the guest-controlled self-assembly of CP[5]A-modified AuNPs, we synthesized dimeric viologen I, i.e., viologen II, and envisioned that viologen II could bridge CP[5]A-modified AuNPs together to achieve patterned AuNPs (Figure 1, process D).[46−49] Indeed, when viologen II was added (Figure 7), one-dimensional (1D) chain-like and two-dimensional network-like self-assembled architectures, rather than simply mass aggregation, were observed as shown in Figure 7a,[13] owing to the 1:2 complexation between one dimeric viologen guest molecule (viologen II) and two CP[5]A supramolecular host molecules modified on two different AuNPs (see Figure 1, process D). We also observed the appearance of AuNPs with

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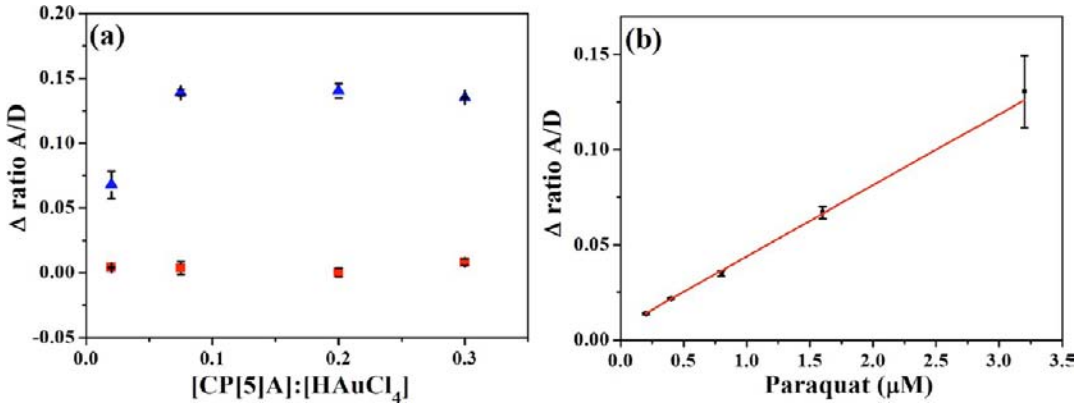

Figure 8. Sensing of CP[5]A-modified AuNPs for PQ. (a) Changes in Δ ratio A/D when 10 μL of pure water (red squares) or PQ (10 μL, 0.96 mM) was added into CP[5]A-modified AuNPs (3 mL; concentrations: 42, 57, 87, and 110 μg/mL, respectively; [CP[5]A]/[$HAuCl_4$] = 0.01, 0.075, 0.2, and 0.3, respectively, blue triangles). (b) Quantitative detection of PQ: 0.2, 0.4, 0.8, 1.6, and 3.2 μM. Linear fit: $y = 0.007 + 0.037x$, $r^2 = 0.996$.

larger spherical structures due to Ostwald ripening.[44,45] Later, AuNPs continued growing, and larger three-dimensional (3D) aggregates were formed in about 24 h (Figure 7b).

Since the addition of trace amounts of viologen I caused the aggregation of CP[5]A-modified AuNPs in a short time, we anticipated CP[5]A-modified AuNPs had potential applications as optical probes for the real-time detection of paraquat, PQ, the common name of viologen I when it is used as a herbicide. To test this idea, we introduced the Δ ratio A/D for the high-sensitivity detection of PQ,[50−52] where A stands for the integral of the UV−vis spectra ranging from 550 to 700 nm (aggregated area), and D stands for the integral of the UV−vis spectra ranging from 490 to 540 nm (dispersed area). Quantitative detection of PQ can be achieved by calculating the change of the ratio A/D for the area under the plasmon resonance peak after ultralow amounts of PQ were added. From the blank experiment (Figure S12a), pure water does not cause changes in Δ ratio A/D. Meanwhile, for different CP[5]A-modified AuNPs synthesized under different AuNP preparation conditions ([CP[5]A]:[$HAuCl_4$] = 0.01, 0.075, 0.2, 0.3), the change in Δ ratio A/D caused by the addition of PQ (3.2 μM) was significant (Figure 8a). So, it appears feasible that CP[5]A-modified AuNPs could be used as nanosensors for the detection of the herbicide PQ. As shown in Figure 8b, this method realized real-time quantitative detection of PQ with a detection limit of 0.2 μM (r^2 = 0.996). When the concentration of PQ was below 0.2 μM (correspondingly, Δ ratio A/D < 0.01), limited by the sensitivity of the UV−vis spectra, the change of the plasmon resonance peak cannot be faithfully reflected, and thus Δ ratio A/D gave relatively large errors. As shown in Figure S12b of the Supporting Information, nonlinearity was observed when the concentration of PQ was below 0.2 μM. Nevertheless, this new hybrid material can be used for qualitative determination of PQ due to changes in Δ ratio A/D. This method is more convenient and sufficiently fast for real-time measurements compared to traditional testing methods for PQ detection and quantification.[53−55]

CONCLUSIONS AND PROSPECTS

CP[5]A-modified AuNPs were successfully synthesized in aqueous solution with narrow size distributions (3.1 ± 0.5 nm), where CP[5]A with five carboxylate groups on each rim served as stabilizers. The interactions and assembly between guest molecules and CP[5]A-modified AuNPs have also been investigated and demonstrated. Interestingly, we found that viologen I could mediate the assembly of structures of CP[5]A-modified AuNPs by controlling the amount added and incubation time. Furthermore, viologen II (viologen I dimer) can induce 1D and 3D assembly of CP[5]A-modified AuNPs. Based on the effects of viologen I on CP[5]A-modified AuNPs, a small amount of viologen I can cause the CP[5]A-modified AuNPs to aggregate in a short time; CP[5]A-modified AuNPs can also be used as optical probes for herbicide detection. We anticipate that surface-enhanced Raman spectroscopy-based selective assays can be used to leverage the selective binding ability of CP[5]A toward guest molecules for ultrasensitive detection.[56,57] Further studies along these lines are currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of host molecules and guest molecules (Figures S1−S8); UV−vis spectra of bare AuNP solution and CP[5]A-modified AuNP solutions before and after the addition of viologen I (Figure S9); high-resolution XPS spectra for O 1s photoelectrons of pure CP[5]A sodium salts and the AuNP-immobilized CP[5]A sodium salts (Figure S10); dynamic light scattering of AuNPs (Table S1); setup for the detection of PQ and control experiments of PQ detection (Figures S11 and S12); and ^{1}H NMR spectra of host−guest interaction of CP[5]A with viologen salts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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