β-Cyclodextrin-Functionalized Silver Nanoparticles for the Naked Eye Detection of Aromatic Isomers

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romatic compounds are found in disinfectants and antiseptics and are widely used as intermediates of dyes in organic synthesis processes and, as a result, are potentially hazardous to the environment. The environmental concern results from the high level of toxicity of phenols and anilines to mammals, fish, and other aquatic organisms. According to the integrated wastewater discharge standard of China, the concentration of aromatic amine compounds and phenolic aromatic compounds in discharged wastewater should be less than 1.0 and 0.3 mg/L, respectively. Hence, the detection and discrimination of trace amounts of different aromatic compounds is very important for evaluating the total toxicity of an environmental water sample. Several methods, such as liquid chromatography,^{1,2} gas chromatography,^{3,4} and capillary electrophoresis,⁵ have been used for the detection of aromatic compounds in water. However, these techniques usually require complicated sample pretreatment, rendering them as unsuitable methods for continuous onsite monitoring. The simplistic sample preparation of naked eye colorimetric detection overcomes these limitations and is therefore a desirable method for onsite analyses of these toxic substances.

A class of materials that have been investigated for their potential use as colorimeter probes are silver and gold nanoparticles. These materials have been explored because of their differing levels of aggregation due to interactions with various compounds, leading to a visual change in color.^{6–8} Further, these nanoparticle-based sensors have the distinct advantage over macroscopic sensors in that they can penetrate into environments normal sensors **ABSTRACT** We report herein the development of a highly robust, quantitative, sensitive, and naked eye colorimetric detection method for different isomers of aromatic compounds using β -CD-modified silver nanoparticle (AgNPs) probes. This assay relies on the distance-dependent optical properties of Ag nanoparticles and the different inclusion binding strength of the aromatic guests to β -CD host. In the presence of different isomers of aromatic compounds, AgNPs could be rapidly induced to aggregate, thereby resulting in apricot-to-red color change. The variety and concentration of different isomers of aromatic compounds could be determined by monitoring with the naked eye or a UV—vis spectrometer. The present detection limit for different isomers of aromatic compounds is 5×10^{-5} M. We believe that the surface architectures of AgNPs after the introduction of the CD-based host—guest recognition would be applicable for a range of chemical and bioanalytical molecular sensing systems in aqueous media.

KEYWORDS: silver nanoparticle $\cdot \beta$ -cyclodextrin \cdot aromatic isomers \cdot naked eye colorimetric detection \cdot host-guest interactions

cannot reach, and an ensemble of nanoparticle sensors can be located throughout an entire sample, leading to increased sensitivity and shorter response times.^{9–12} Among these, the attachment of functional groups capable of engaging in well-defined host-quest interactions is receiving considerable attention. For instance, Mirkin and co-workers have prepared gold colloidal particles with oligonucleotides and used their recognition properties to form nanoparticle assemblies, as well as for the detection of specific nucleotide sequences,^{13,14} the Thomas group has done extensive work on gold and silver nanoparticles modified by gallic acid as a sensing unit toward Pb²⁺ in aqueous solution.¹⁵ Li and co-workers synthesized calixarene-modified silver nanoparticles that enabled a highly sensitive determination of histidine¹⁶ and pesticides.17

Cyclodextrins (CDs) are cyclic oligosaccharides that consist of six, seven, or eight glucopyranose units in α , β , and γ forms, respectively. They are well-known for *Address correspondence to gangzou@ustc.edu.cn.

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forming an inclusion complex with various guest molecules because of their special molecular structures-hydrophobic internal cavity and hydrophilic external surface.^{18,19} As reported in the literature,²⁰ CDs showed different association constants with the isomers of aromatic compounds. In this sense, the difference in association abilities and sharp selectivity of CDs could be used for identifying isomers of aromatic compounds. Herein, we attempted to synthesize β-cyclodextrin (β-CD)-functionalized silver nanoparticles (AgNPs) via a thiol attachment according to the intriguing reactivity between the thiol group of β-SH-CD and AgNPs,²¹ as a colorimetric probe for the isomers of aromatic compounds (I, pyrocatechin, hydroquinone, and resorcinol; II, o-phenylenediamine, p-phenylenediamine, and

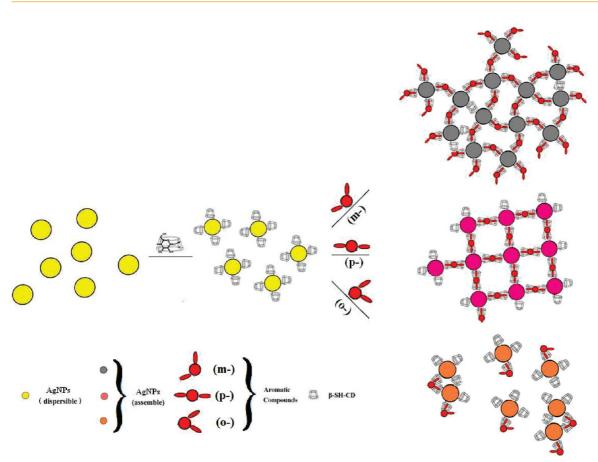
o-phenylenediamine, p-phenylenediamine, and m-phenylenediamine) that form complexes with the β -CD. While the AgNPs provided colorimetric optical properties, β -CD showed different association abilities with the isomers of aromatic compounds, which allowed for the adjustment of the relative spatial distances between neighboring AgNPs, further inducing the colorimetric change of the system.

In order to prove the above idea, β -CD-modified AgNPs were synthesized in analogy to the previous procedure.²² The preparation of β -CD, β -SH-CD, and β -CD-modified AgNPs was monitored by infrared spectrum (Supporting Information Figure S1), which demonstrated the successful formation of β -CD-modified AgNPs. As shown in Figure S1, the stretching vibration peak of S–H for β -SH-CD was located at 2569 cm⁻¹ and the stretching vibration peak of S–H disappeared when β -CD modified with AgNPs, which showed the apparent evidence of the successful formation of β -CD and anchoring β -SH-CD on AgNPs. This is consistent with the results reported in the literature.²²

AgNPs were prepared by sodium borohydride reduction of silver nitrate with a citrate stabilizer. The method ensured that the nanoparticles provided an intense surface plasmon band that could be used in the colorimetric assay. The negative citrate ions surrounding the AgNPs (~10 nm) provided enough electrostatic repulsion to overcome the attractive hydrophobic and van der Waals forces and, in doing so, caused the AgNPs to remain stable and dispersive in an aqueous solution.²³ These dispersive AgNPs had a surface plasmon resonance absorption peak at about 388 nm, which corresponded to an apricot-like color. However, the aggregation of the AgNPs, as a result of different complexes forming between the aromatic compounds and β -CD, led to a rapid apricot-to-red (or brown) color change. The schematic of host–guest recognition for β -CDmodified AgNPs with different aromatic compounds is shown in Scheme 1.

RESULTS AND DISCUSSION

To verify if our system could be used to identify the isomers of aromatic compounds, several different aromatic compounds were respectively added into the solution of β-CD-modified AgNPs or unmodified AgNPs with a concentration of 10^{-4} M. The concentration of β-CD-modified and unmodified AgNP aqueous solutions was always maintained at 9.85 mg/L in all tests. Figure 1a is a typical colorimetric detection of phenolic aromatic compounds with $\beta\text{-CD-modified}$ AgNP (${\sim}10$ nm) probes. Before the aromatic compounds were added, the β -CD-modified AgNP colloidal solution was apricot-colored. After being mixing with phenol for 2 h, no significant color change could be observed for the β-CD-modified AgNP colloidal solution. However, with the addition of equivalent diphenols, pyrocatechin, resorcinol, or hydroquinone, the β-CD-modified AqNP solutions turned to a bright yellow color, dark-brown, and red, respectively. These color changes could be attributed to the different aggregation degree of the AgNPs caused by the shape selectivity of the β -CD cavity and the different inclusion binding strengths of the aromatic guests to the β -CD host: resorcinol > hydroquinone > pyrocatechin > phenol,²⁴ which could also be demonstrated by ¹H NMR results of β-CD-modified AgNPs mixing with various aromatic compounds. The ¹H NMR spectrum of β-CD-modified AqNPs with phenol, pyrocatechin, hydroquinone, and resorcinol is shown in Figure S2 (Supporting Information). The signals for H-1 were upfield shifted by about 0.03, 0.05, 0.065, and 0.075 ppm, respectively. The signal for H-3 was upfield shifted by about 0.04, 0.05, 0.06, and 0.075 ppm, while the band for H-5 and H-6 protons had a maximum upfield shift by about 0.05, 0.07, 0.09, and 0.11 ppm, respectively. The observed chemical shifts for H-1, H-3, H-5, and H-6 protons crowning the primary hydroxyl edge of the cavity suggested that phenol, pyrocatechin, hydroquinone, and resorcinol had different interaction with the internal protons near the smaller opening of the cavity. For resorcinol, the size of this aromatic molecule compared very well with the pore size of β -CD and the steric effect was relatively weak. Thus, the inclusion binding strength between resorcinol and β-CD was stronger than those between β-CD and other aromatic compounds. This meant that the stronger inclusion interaction between resorcinol and β -CD would induce severe AgNPs aggregation, and the relative spatial distances between neighboring Ag-NPs would be significantly reduced, causing the resulting color change of the solution. However, the matching between the size of hydroquinone and the pore size of β -CD was poorer than that between resorcinol and β -CD, leading to low amounts of hydroquinone/ β -CDmodified AgNP interactions, and therefore, the AgNPs were less inclined to aggregate. Pyrocatechin had the poorest size similarity with the β-CD pores of the compounds along with its large steric effects and caused



Scheme 1. Schematic of host-guest recognition for β -CD-modified AgNPs with different aromatic compounds.

minute levels of β -CD-modified AgNP interaction, and therefore the AgNPs were even less inclined to aggregate. Similar experiments have been done to identify *o*-phenylenediamine, *p*-phenylenediamine, and *m*-phenylenediamine. More obvious color changes were observed, which should be ascribed to the greater aggregation of β -CD-modified AgNPs caused by the addition of aniline aromatic compounds (as shown in Figure 1b). This might be attributed to strong Coulombic interaction between AgNPs and amino group and the inclusion interaction between β -CD and anilines (Supporting Information Figure S3). The combination of Coulombic interaction and inclusion interaction induced the more dramatic aggregation and the sedi-

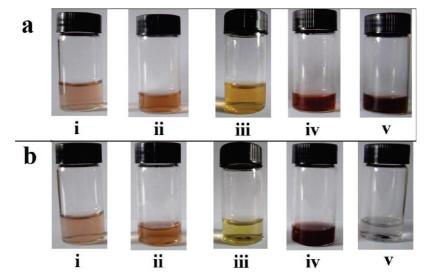


Figure 1. Color photographs of β -CD-modified AgNP aqueous solution before (a,i and b,i) and after mixing with different isomers of aromatic compounds (10⁻⁴ M) for 2 h. The aromatic compounds are phenol (a,ii), pyrocatechin (a,iii), hydro-quinone (a,iv), resorcinol (a,v), aniline (b,ii), *o*-phenylenediamine (b,iii), *p*-phenylenediamine (b,iv), and *m*-phenylenediamine (b,v).

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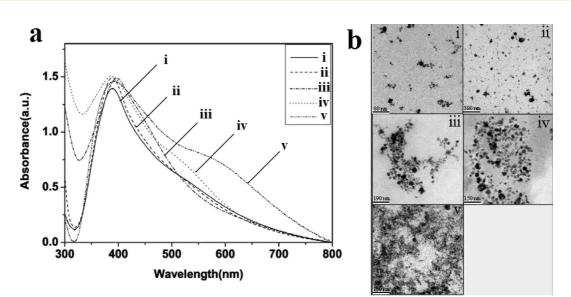


Figure 2. UV-vis absorption spectra (a) and transmission electron microscopy (b) of β -CD-modified AgNPs before (i) and after mixing with different isomers of aromatic compounds (10⁻⁴ M) for 2 h: (ii) phenol, (iii) pyrocatechin, (iv) hydroquinone, and (v) resorcinol.

mentation of the AgNPs. As a blank sample, the unmodified AgNPs only showed a very weak color change after 2 h of mixing with *o*-phenylenediamine, *p*-phenylenediamine, or *m*-phenylenediamine caused by Coulomb interaction between positive and negative charges and no obvious color change after 2 h mixing with pyrocatechin, hydroquinone, or resorcinol, which could not be used as the naked eye colorimetric detection to different isomers of aromatic compounds (Figure S4 and Figure S5). All of the above results indicate that the stronger colorimetric responses of β -CDmodified AgNPs with different aromatic compounds are mainly related to specific association of the isomers of aromatic compounds with β -CD, instead of AgNPs themselves.

In order to prove the above idea, UV-vis absorption spectra, transmission electron microscopy (TEM), and dynamic light scattering (DLS) were performed (as shown in Figure 2 and Figure S6). As shown in Figure 2a, the plasmon absorption band of AgNPs at 388.0 nm shifted to the longer wavelength with the addition of phenolic aromatic compounds (10^{-4} M) . The maximum absorption band could reach 600.0 nm depending on the species of phenolic aromatic compounds, which was due to the electric dipole-dipole interaction and coupling between the neighboring particles in the aggregates. It was obvious that the new plasmon absorption band of AgNPs occurred at 600, 520, and 460 nm after mixing with resorcinol, hydroguinone, and pyrocatechin for 2 h, respectively. TEM and DLS gave other evidence of the different inclusion interactions between β-CD-modified AgNPs and the isomers of aromatic compounds. As shown in Figure 2b and Figure S6, β-CD-modified AgNPs were dispersed in an aqueous solution and had only slight aggregation with a maxi-

mum aggregate size of about 100 nm. After mixing with phenol for 2 h, there was still no apparent aggregation; the size of the aggregates had no significant change. However, the introduction of pyrocatechin, resorcinol, and hydroquinone for 2 h caused the relative spatial distances between neighboring AgNPs to be reduced significantly due to the strong inclusion interaction between β -CD and phenolic aromatic compounds. The aggregate sizes were up to 300, 600, and 1000 nm, respectively. The change of color and aggregation degree, as judged from the UV spectra, TEM, and DLS analysis, implies the different inclusion binding strength of the aromatic guests to β -CD host: resorcinol > hydroquinone > pyrocatechin > phenol. Similar results could also be observed for the samples with the addition of different aromatic amine compounds (as shown in Figure 3 and Figure S7); however, there was limited plasmon absorption for AgNPs after mixing with *m*-phenylenediamine for 2 h, due to AgNP precipitation caused by strong inclusion interaction between β-CD and *m*-phenylenediamine. All of the above results indicated that the colorimetric detection technology for isomers of aromatic compounds based on β-CDmodified AgNPs should be ascribed to the aggregation of AgNPs caused by varying degree of host-guest interaction between β -CD and the isomers of aromatic compounds, rather than the redox reactions of the aromatic analytes caused by oxygen in the air. For example, phenol could be oxidized to p-benzoguinone and *o*-benzoquinone; *p*-phenylenediamine could be oxidized to p-benzoquinone, azobenzene, oxidation of azobenzene, and nitroazobenzene. Although these redox reactions of the aromatic analytes could produce colored oxides which might also cause the changes of the color and UV-vis absorption spectra of the solu-

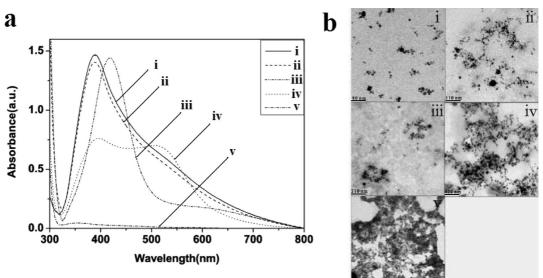


Figure 3. UV-vis absorption spectra (a) and transmission electron microscopy (b) of β -CD-modified AqNPs before (i) and after mixing with different isomers of aromatic compounds (10⁻⁴ M) for 2 h: (ii) aniline, (iii) o-phenylenediamine, (iv) *p*-phenylenediamine, and (v) *m*-phenylenediamine.

tion, the redox reactions of the aromatic analytes would not cause the significant aggregation of AgNPs, which was proved by TEM and DLS analysis.

Since the β -CD-modified AgNPs were used as the naked eye detection of the isomers of aromatic compounds, it is worth noting that the β -CD-modified AgNP sensor for the isomers of aromatic compounds should be nonresponsive to other substituted phenol and aniline compounds. Figure S8 shows the UV-vis absorption spectra and photos of β-CD-modified AgNPs before and after mixing with different substituted phenol and aniline compounds (m-cresol, m-nitrophenol, *m*-nitrobenzenamine, and *m*-methylaniline, 10^{-4} M) for 2 h. The plasmon absorption bands of β -CD-modified AgNPs mixing with different substituted phenol and aniline compounds were all located near 390 nm, and there was no apparent extra peak in the long wavelength region, which indicated that the addition of different substituted phenol and aniline did not have any

obvious effect on the identification of the isomers of aromatic compounds using β-CD-modified AgNPs. The selectivity of this method for different isomers of aromatic compounds (pyrocatechin, hydroquinone, resorcinol, o-phenylenediamine, p-phenylenediamine, and *m*-phenylenediamine) was evaluated by testing the response of the assay to different substituted phenol and aniline compounds (including phenols, m-cresol, m-nitrophenol, aniline, m-nitrobenzenamine, and *m*-methylaniline). The histogram according to the location of the new plasmon absorption band of AgNP responses of various compounds is shown in Figure 4. It was clear that only isomers of aromatic compounds caused significant discrepancies between the new plasmon absorption band and the original plasmon band of β -CD-modified AgNPs ($\Delta\lambda$). Importantly, different isomers of aromatic compounds showed different discrepancy values, and other substituted phenol and aniline compounds could not interfere in the detection

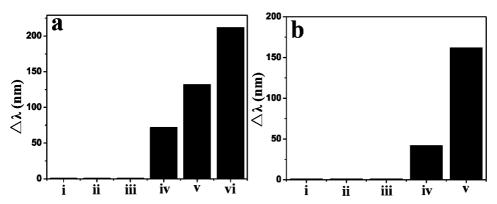


Figure 4. Discrepancy between the plasmon band position ($\Delta\lambda$) of the AgNPs before and after mixing with different aromatic compounds at a concentration of 10^{-4} M. a: (i) phenol, (ii) *m*-cresol, (iii) *m*-nitrophenol, (iv) pyrocatechin, (v) hydroquinone, (vi) resorcinol. b: (i) aniline, (ii) m-nitrobenzenamine, (iii) m-methylaniline, (iv) o-phenylenediamine, and (v) p-phenylenediamine.

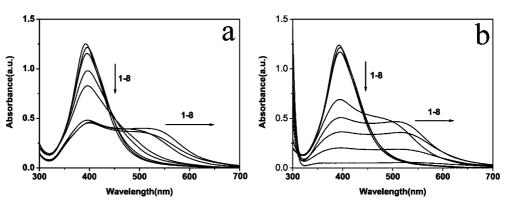


Figure 5. UV-vis absorption spectra of β -CD-modified AgNP solutions obtained after mixing with different concentrations of hydroquinone (a) and *p*-phenylenediamine (b). The concentration of different isomers of aromatic compounds was (1) 10⁻⁶ M, (2) 5 × 10⁻⁶ M, (3) 10⁻⁵ M, (4) 5 × 10⁻⁵ M, (5) 10⁻⁴ M, (6) 5 × 10⁻⁴ M, (7) 10⁻³ M, and (8) 5 × 10⁻³ M.

of the isomers of aromatic compounds. Compared to the other compounds, the high selectivity and tight binding of different isomers of aromatic compounds (pyrocatechin, hydroquinone, resorcinol, *o*-phenylenediamine, *p*-phenylenediamine, and *m*-phenylenediamine) for β -CD-modified AgNPs under the proposed experimental conditions led to an assay of different isomers of aromatic compounds with high specificity. All of the above results indicated that the β -CD-modified AgNPs were highly applicable for the fabrication of robust, quantitative, sensitive, and naked eye colorimetric detection for the isomers of aromatic phenolic and aromatic phenolic and aromatic amine compounds.

Quantitative analysis results of the aromatic phenolic and aromatic amine compounds are shown in Figure 5, which displays the UV-vis absorption spectra regularly changing with an increase concentration of hydroquinone (Figure 5a) and *p*-phenylenediamine (Figure 5b). It clearly indicated that the plasmon band of the β-CD-modified AgNPs was influenced by the concentration of aromatic compounds. At lower concentrations of hydroquinone $(10^{-6} \text{ M}, \text{ trace 1 in Figure 5a})$, the solution possessed an intense plasmon band at 388 nm. The absorption band at 388 nm became weak and broad after increasing the hydroquinone concentration $(5 \times 10^{-5} \text{ M})$, and the emergence of a new plasmon resonance peak at a longer wavelength (520 nm at 10⁻⁴ M) was evident. At higher concentrations of hydroguinone (traces 7 and 8 in Figure 5a), the absorption band became weaker and the new plasmon resonance peak further red-shifted. Similar results were also observed from the UV-vis absorption spectra of β-CDmodified AgNPs mixing with p-phenylenediamine (as shown in Figure 5b). It is worth mentioning that the drop of plasmon resonance peak of AgNPs (388 nm) and the red shift degree of new plasmon resonance peak of AgNPs were different, even when the aromatic amine compounds and phenolic aromatic compounds had the same concentration. These results meant that the detection limit for each aromatic compound using

this method was different depending on the isomers of the aromatic compound because of the different inclusion interaction between β-CD and the isomers of aromatic compounds. As to display the detection sensitivity and limit more clearly, we prepared a histogram according to the absorbance of AgNPs at about 400 nm versus the concentration of various aromatic compounds (as shown in Figure S9). It was obvious that the plasmon absorption band of AgNPs at 388 nm dramaticly decreased when the concentration of hydroquinone droped to 5×10^{-4} mM or the concentration of *p*-phenylenediamine droped to 5×10^{-5} mM. Thus, the present detection limit for hydroquinone (phenolic aromatic compound) was 5 imes 10⁻⁴, while for *p*-phenylenediamine (amine aromatic compound), it appeared to be 5×10^{-5} . The quantitative colorimetric response kinetics behavior of the β-CD-modified AgNPs with *p*-phenylenediamine was also measured to analyze the response time of our system (as shown in Figure 6). With the extension of the mixing time, the absorption band at 388 nm became weak and the emergence of a new plasmon resonance peak at a longer wavelength, which continuously red-shifted until 88 min, was evident. To obtain the detection limit for different isomers of aromatic compounds, several different aromatic compounds were added into the solution of β-CD-modified AgNPs with the concentration ranging from 10^{-4} to 10^{-6} M. When the concentration of different aromatic compounds was as low as 10^{-6} M, the β-CD-modified AgNPs were not able to distinguish pyrocatechin, hydroquinone or o-phenylenediamine, *p*-phenylenediamine by the naked eye or UV-vis absorption (Supporting Information Figure S10 and Figure S11), and it was concluded that the present limit of detection for different isomers of aromatic compounds was 5 \times 10⁻⁵ M. This sensor's advantages lie in the detection simplicity (naked eye analysis), the low cost to carry out analysis, and accurately distinguishing these isomers of aromatic compounds during detection process, not its ability to detect trace amounts of the analyte. However, the insufficient detection limit could be

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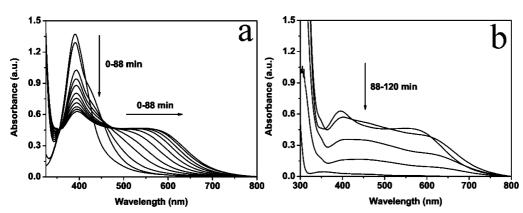


Figure 6. Quantitative colorimetric response kinetics behavior of AgNP sensors with phenylenediamine. UV absorption spectra of β -CD-modified AgNPs recorded at 25 °C and after the addition of 10^{-4} M *m*-phenylenediamine for different times: (a) 0–88 min and (b) 88–120 min.

improved after further optimization and more detailed investigations are being carried out.

CONCLUSIONS

We have presented a simple and convenient chemical method for the preparation of water-soluble and stable AgNPs using CDs as surface-coating agents. The β -CD-modified AgNPs have a sensitive naked eye colorimetric detection to different aromatic compounds, even to the isomers. We believe that the surface architectures of AgNPs after introducing the CD-based host—guest recognition would generate a variety of molecular sensing systems for chemical and bioanalytical sensing in aqueous media.

METHODS

Materials. AgNO₃, KHSO₄, P₂O₅, *N*,*N*-dimethylformamide, methanol, sodium borohydride, trisodium citrate dehydrate, triphenylphosphine dibromide, I₂, sodium methoxide, thiourea, sodium hydroxide, and β -CD were obtained from Beijing Chemical Reagent Ltd. and used without further purification.

Synthesis of Per-6-iodo- β -cyclodextrin (1). This compound was prepared from β -CD as described by Defaye and Gadelle.²⁵ However, instead of precipitating the products with iced water, the reaction mixture was poured into 800 mL of methanol to form a precipitate, which was washed with methanol, dried superficially, and Soxhlet extracted with methanol for 20 h. After rigorous drying, compound **1** was recovered as a white powder in 90% yield.

Synthesis of Per-6-thio-β-cyclodextrin (β-CD). Compound **1** (0.965 g) was dissolved in DMF (10 mL); thiourea (0.301 g) was then added and the reaction mixture heated to 70 °C under a nitrogen atmosphere. After 19 h, the DMF was removed under reduced pressure to give a yellow oil, which was dissolved in water (50 mL). Sodium hydroxide (0.26 g) was added and the reaction mixture heated to a gentle reflux under a nitrogen atmosphere. After 1 h, the resulting suspension was acidified with aqueous KHSO₄ and the precipitate filtered off, washed thoroughly with distilled water, and dried. To remove the last traces of DMF, the product was suspended in water (50 mL) and the minimum amount of potassium hydroxide added to give a clear solution; the product was then reprecipitated by acidifying with aqueous KHSO₄. The resulting fine precipitate was carefully filtered off and dried under vacuum over P_2O_5 to yield β -CD (0.536 g, 85%) as an off-white powder.

Preparation of CD-Capped Silver Nanopartides. AgNO₃ aqueous solution (1 mL, 0.01 M) and trisodium citrate dehydrate aqueous solution (1 mL, 0.03 M) were added to ultrapure water (97 mL), and sodium borohydride aqueous solution (1 mL, 1.79 mg/mL) was dropped into the solution with stirring. The formation of the AgNPs was confirmed by the solution changing to a yellow color after about 20 min, and this AgNP aqueous dispersion was used without further purification in the following procedure. β -CD and AgNPs were mixed in a 1:2 molar ratio, and the reaction mixture developed a buff color immediately, but we allowed the reaction to proceed for 24 h with continuous stirring. At this point,

a precipitate was collected by centrifugation and washed with DMF (4 \times 50 mL) to remove free thiolated CD. The solid product was further washed (4 \times 50 mL) with ethanol/water (90:10 v/v), collected by centrifugation, and dried at 60 °C under vacuum for 24 h. After this, the resulting powder was resuspended in distilled water to achieve a concentration of 9.85 mg/L.

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Supporting Information Available: Characterization, FTIR, ¹H NMR spectra, UV-vis absorption spectra, DLS measurement of β -CD-modified AgNPs with different aromatic compounds. This material is available free of charge *via* the Internet at http:// pubs.acs.org.

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