Sensors

Pillar[5]arene-Mediated Synthesis of Gold Nanoparticles: Size Control and Sensing Capabilities

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Abstract: We present a simple procedure for the synthesis of quasi-spherical Au nanoparticles in a wide size range mediated by macrocyclic host molecules, ammonium pillar[5]arene (AP[5]A). The strategy is based on a seeded growth process in which the water-soluble pillar[5]arene undergoes complexation of the Au salt through the ammonium groups, thereby avoiding Au nucleation, while acting as a stabilizer. The presence of the pillar[5]arene onto the Au nanoparticle particle surface is demonstrated by surface-enhanced Raman scattering (SERS) spectroscopy, and the most

Introduction

The development of supramolecular chemistry relies on the design and synthesis of macrocyclic host molecules. A number of successful examples have been reported in the literature including crown ethers,^[1] cyclodextrins,^[2] cucurbit[*n*]urils,^[3] calixarenes,^[4] and more recently, pillar[*n*]arenes.^[5,6] These macrocycles allowed not only the development of new materials based on the theory of self-assembly at the molecular level, but also the binding of chemical moieties through host–guest noncovalent interactions.^[7] Pillar[*n*]arenes present several advantages as

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probable conformation of the molecule when adsorbed on the Au nanoparticles surface is suggested on the basis of theoretical calculations. In addition, we analyze the host– guest interactions of the AP[5]A with 2-naphthoic acid (2NA) by using ¹H NMR spectroscopy and the results are compared with theoretical calculations. Finally, the promising synergetic effects of combining supramolecular chemistry and metal nanoparticles are demonstrated through SERS detection in water of 2NA and a polycyclic aromatic hydrocarbon, pyrene (PYR).

compared with the most traditional macrocyclic hosts: High selectivity toward guests (provided by their high symmetry and rigidity), easy functionalization, and solubility in organic solvents. Therefore, this new type of macrocyclic compounds has become very popular since their invention in 2008.^[8]

On the other hand, there has been common interest in the synthesis and development of new applications based on nanomaterials. For instance, there has been tremendous progress over the past two decades in the synthesis of gold and silver nanoparticles of various sizes and shapes and with good yield and monodispersity,^[9–11] which led to significant progress in different areas due to their unique properties and applications in electronics, photonics, catalysis, sensing, and medicine. However, a prerequisite for every possible application is the proper functionalization of the nanoparticles surface, because this may determine the stability (against aggregation or degradation), biocompatibility, the assembly into extended nanostructures and functional systems, targeting, sensing capabilities, and so on.

A very attractive application of macrocyclic host molecules is their combination with nanoparticles, since they can be used to enhance the colloidal stability while providing molecular selectivity toward binding of guest molecules. In the case of metal nanoparticles, this can be exploited for improving plasmonic sensing applications, such as those related to surface enhanced Raman scattering (SERS). Several approaches toward nanoparticle–macrocycle hybrids involve the surface modification of preformed particles. For instance, Kaifer et al. reported the surface modification of gold nanoparticles with cyclodextrins and studied their assembly and phase-transfer possibilities.^[12,13] Metal nanoparticles have also been modified with calixarenes, thereby enhancing their dispersion and self-assembly

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into well-defined structures,^[14] but also acting as effective supramolecular hosts for detection based on SERS. Guerrini et al. have functionalized Ag nanoparticles with calixarenes for detection of polycyclic aromatic hydrocarbons SERS (PAHs).^[15,16] Manahan and Scherman et al. employed cucurbit-[n]urils to functionalize gold nanoparticles^[17] and evaluated their self-assembly capabilities for quantitative SERS analysis, although no control over the self-assembly process was shown.^[18] Few reports can also be found regarding the synthesis of small gold nanoparticles stabilized by either pillar[5]arenes^[19,20] or cucurbit[n]urils^[21] but no size or shape control have been described so far. Nevertheless, the synthesis of metal nanoparticles mediated by supramolecular chemistry with size and shape control can be considered as a quite promising approach to take advantage of synergetic effects.

Here, we show for first time the use of macrocyclic host molecules as capping agents for the synthesis of quasi-spherical Au nanoparticles in a wide size range (see Scheme 1), through



Scheme 1. Schematic representation of the synthesis of quasi-spherical Au nanoparticles through the AP[5]A-mediated seeded growth process and their sensing capabilities based on host–guest interactions.

a seeded growth method. The strategy is based on a watersoluble pillar[5]arene bearing ammonium groups (hereafter ammonium pillar[5]arene or AP[5]A), which form a complex with the Au salt, thereby avoiding Au nucleation, while acting as a stabilizer. The presence of the pillar[5]arene onto the particle surface can easily be demonstrated by SERS spectroscopy. The most probable conformation of the molecule when adsorbed on the Au nanoparticles surface was suggested by theoretical calculations. The host–guest interactions of the AP[5]A with 2-naphthoic acid (2NA) were studied by ¹H NMR spectroscopic titrations and the results were compared with theoretical calculations. Finally, the sensing capability of the AP[5]Astabilized Au nanoparticles was demonstrated through the SERS detection in water of 2NA and a polycyclic aromatic hydrocarbon, pyrene (PYR).

Results and Discussion

Synthesis of gold nanoparticles with size control

The growth of spherical gold nanoparticles requires a good control over the nucleation and growth processes. The seeded growth method has been demonstrated to be the most reliable method to achieve size control with rather low polydispersity. Among the existing approaches, the seeded growth method based on using ascorbic acid as a mild reducing agent and quaternary ammonium surfactants (usually cetyl trimethyl-ammonium bromide, CTAB) as stabilizers,^[22,23] additionally provides shape control (spheres, rods, plates, concave cubes, etc.).^[24] A key element in this method is the complexation of the gold salt precursor with the quaternary ammonium group of the surfactant, which increases its redox potential.^[25] Therefore, upon addition of ascorbic acid, $[AuCl_4]^-$ is selectively reduced to $[AuCl_2]^-$ and just after seed addition further reduction into Au⁰ proceeds catalytically on the seed surfaces.

We selected for this work a cationic water-soluble pillar[5]arene, which has guaternary ammonium groups at both rims (hereafter is named ammonium pillar[5]arene or AP[5]A; see Scheme 1), to act as stabilizer.^[26] As in the case of CTAB, addition of [AuCl₄]⁻ ions is expected to yield formation of an ion pair with the quaternary ammonium groups of the macrocycle. Indirect evidence of such complexation is provided by the absence of nucleation upon addition of ascorbic acid, meaning that it is only able to reduce Au^{III} into Au^I (see Figure S6, the Supporting Information). The final reduction of Au¹ into Au⁰ occurs only after the addition of gold seeds, in a similar fashion to the CTAB-mediated growth. Thus, quasi-spherical Au nanoparticles with a narrow size distribution can be readily prepared (see Figure 1), whereas a second population of plates and rods was also obtained through the CTAB-mediated growth.^[23] Although the process is similar to that with CTAB, the catalytic reduction of Au¹ into Au⁰ is faster (20-30 min for CTAB, but 3-5 min for AP[5]A). Therefore, to obtain monodisperse samples or avoid free nucleation, careful temperature control (around 25 °C) and stepwise ascorbic acid addition are required (see the Experimental Section in the Supporting Information). This protocol can also be used to grow larger Au particles by simply varying the Au^{III}/Au⁰ molar ratio. Figure 1 shows representative TEM images of Au spheres with sizes of 33, 78, and 95 nm (see histograms in Figure S7, the Supporting Information), all of which were obtained by seeded growth of 20 nm seeds (Figure S8, the Supporting Information) in one step, with Au^{III}/Au⁰ molar ratios of 2.3, 52, and 88.8, respectively. The obtained diameters, which closely match the calculated diameters,^[27] together with the relatively low polydispersity (around 10%) suggest that no nuclei are formed and only seeded growth occurs. Although the spherical shape is preserved for sizes up to 95 nm, larger spherical particles can only be obtained through two or three growth steps. As mentioned above, the catalytic reduction of Au¹ to Au⁰ in the presence of

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Figure 1. A–C) Representative TEM images of AP[5]A-stabilized Au nanoparticles prepared by a seeded growth method, with average sizes of (33.6 ± 4.0) (A), (77.5 ± 7.0) (B), and (94.8 ± 8.5) nm (C). All scale bars correspond to 200 nm. (D) Extinction spectra of the Au nanoparticles shown in images A–C: (—) (A), (–––) (B), and (–•–•) (C). All spectra were normalized to 1 at 400 nm to facilitate comparison.

AP[5]A is rather fast (several minutes), which leads to the growth of tips when using large molar ratios of Au salt to Au seeds (>106), due to fast overgrowth (leading, eventually, to star-shaped nanoparticles). Figure 2 shows representative TEM images of nanoparticles of about 120 nm in diameter prepared in a single growth step (A) and in two sequential growth steps (B; 20 to 60 to 120 nm). The formation of spikes is clearly seen for the one-step growth, whereas spherical nanoparticles form when the growth is performed in two sequential steps. As expected, such morphological changes are reflected in the optical response of the colloids, see Figure 2C. The presence of tips and spikes produces a strong redshift and broadening of the extinction spectrum in contrast with the narrow band for quasi-spherical particles ($\lambda_{max} = 700$ vs. 600 nm).^[28,29] However, the spiky Au nanoparticles are not stable and evolve toward more rounded shapes after several days (see Figure S9, the Supporting Information).



Figure 2. Representative TEM images of about 120 nm Au nanoparticles prepared in A) a single growth step, or B) in two growth steps; C) Vis-NIR extinction spectra of the particles prepared in a single step (---) or after sequential growth (---).

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The adsorption of AP[5]A was characterized by Zeta potential measurements, which revealed a positive value of $+(19.5\pm$ 1.7) mV. Since the starting Au seeds presented negative charge (around -30 mV) due to the presence of citrate ions on the metal surface, the positive charge of the resulting particles indicates that the adsorption of AP[5]A onto the metal surface is likely to be mediated by the bromide ions.^[30] Additional evidence for the adsorption of pillar[5]arene was provided by SERS data. Figure 3 shows the Raman spectrum of a pillar[5]arene solution and the corresponding SERS spectrum of the colloid. Assignment of the bands was performed on the basis of DFT calculations (see more details in Figure 3 A and in the Supporting Information: the Experimental Section and Table S1). Thus, the measured Raman spectrum of AP[5]A (Figure 3B) is mainly dominated by the aromatic ring stretching (1613 cm^{-1}), ring breathing (1267 cm⁻¹), ring deformation (956 and 541 cm⁻¹), CH bending (1449 and 793 cm⁻¹) and CN stretching (877 and 722 cm⁻¹). As shown in Figure 3 C, the SERS spectrum for AP[5]A-stabilized Au nanoparticles (NPs) displays additional signals mainly associated with CH bending of the chain bearing the ammonium groups (1537, 1443, 1394 1335, 1311, 1207, 1137, and 1073 cm⁻¹) and ring vibrations (1588, 758, 700, 661, 622, 573, 509, and 424 cm⁻¹; a detailed description of the vibrational assignments can be found in the Supporting Information, Table S1). Thus, SERS enhancement of the vibrations associated with the ammonium side chains is indeed related to adsorption through the vicinal bromide atoms. On the other hand, the SERS enhancement is especially significant for the ring out-of-plane deformation at 700 cm⁻¹, ring breathing at 1266 cm⁻¹ and for the CH bending of the lateral chain at 1394 and 1537 cm⁻¹. This indicates that the central aromatic rings of the AP[5]A are perpendicularly oriented on the Au surface as a preferential configuration.[31]

Assuming that the molecules are adsorbed to the gold surface through the bromide ions, in principle it is possible to identify up to three different conformations; two of which would have the pillar[5]arene cavity oriented parallel to the gold surface, whereas the other one features the cavity perpendicular to the gold surface, as schematically depicted in



Figure 3. A) Calculated Raman, B) measured Raman, and C) SERS spectra of ammonium pillar[5]arene.

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Figure 4. A–C) Proposed configurations for the ammonium pillar[5]arene when it is adsorbed on a gold monolayer: one perpendicular (A) and parallel (B,C) to a gold surface; D) Variation of the adsorption energy for the different AP[5]A configurations A–C (as indicated in the labels) with the number of gold layers. The distance of the molecule to the metal surface was 2.5 Å.

Figure 4. The most probable conformation was identified by theoretical determination of the adsorption energy of an AP[5]A molecule on a gold monolayer as a function of the distance between the molecule and the metal surface, r (Figure S10, the Supporting Information). All possible conformations show a minimum in the adsorption energy at a distance of 2.5 Å, but the adsorption energy is more negative when the pillar[5]arene cavity is perpendicularly adsorbed to the gold surface. Analysis of the influence of the number of gold layers on the adsorption energy for the three configurations (Figure S10, the Supporting Information) shows a decrease of the adsorption energy with increasing the number of gold layers (Figure 4). Thus, these theoretical calculations suggest the perpendicular adsorption of pillar[5]arene configuration as the most probable configuration, in agreement with the results obtained by SERS.

Host-guest chemistry and sensing capabilities

Within supramolecular chemistry, the macrocyclic host-quest chemistry can be used to bind two chemical moieties to each other, through noncovalent interactions. The host-guest complex formation involving the above-mentioned macrocycles takes place usually in aqueous media.^[32] In particular, the presence of ten positive charges on the AP[5]A macrocycle render its host-guest chemistry to be mainly driven by hydrophobic and electrostatic interactions.^[20,26] Therefore, prior to evaluating the sensing capabilities of the AP[5]A-stabilized gold nanoparticles, we studied the inclusion properties of this pillar[5]arene with a guest of interest. We selected 2-naphthoic acid (2NA, see Figure 5Top) as a model guest, not only because it presents a low adsorption capability on citrate-stabilized metal colloids, but also because it contains a negatively charged functional group (a carboxyl that is deprotonated at pH above its pK_{a}).^[33] The host-quest interactions of AP[5]A with 2NA



Figure 5. Top: Chemical structure of 2-naphthoic acid. Bottom: ¹H NMR spectra (D_2O , 293 K, 400 MHz) of 2-naphthoic acid (2 mm) with different concentrations of ammonium pillar[5]arene: a) 0.0, b) 0.3, c) 0.5, d) 0.7, e) 1.0, f) 2.0, and g) 3.0 mm.

were investigated by using ¹H NMR spectroscopy. Figure 5 shows the ¹H NMR spectroscopic titration spectra of pillar[5]arene in a 2 mm solution of 2NA in water. Whereas the increase of AP[5]A concentration barely affects (ca., $\Delta \delta = 0.1$ ppm) the proton NMR spectroscopic signals corresponding to H_a , H_b , and H_c, thus suggesting that they are located outside of the macrocyclic cavity, the NMR spectroscopic signals of H_d and H_e are shifted upfield considerably ($\Delta \delta = 0.8$ and 1.75 ppm, respectively). These upfield chemical shifts are a consequence of the interaction between the C-H bonds of 2NA and the large fraction of π surfaces offered by the pillar[5]arene cavity. Besides the more pronounced shift for H_e than for H_d protons, this also suggests that the host-guest complex is located close to the aromatic ring region, that is, forming a [2]pseudorotaxane. This conformation might also favor the electrostatic interaction between the cationic ammonium group from pillar[5]arene and the carboxylic group from 2NA. Finally, it is remarkable that the chemical shifts of H_e and H_d barely changed ($\Delta \delta$ \approx 0.1 ppm) when the molar ratio of pillar[5]arene to 2NA increased to 3:2 (see Figure 5). This indicates that the stoichiometry of the complex between the AP[5]A and 2NA has an 1:1 stoichiometry and, more importantly, that more than 90% of the guest molecules were already encapsulated at equimolar concentrations, meaning that they have a relatively high binding constant.

To further confirm the proposed conformation, we performed B3LYP/6-31G* geometrical optimizations for the two possible orientations of the 2-naphthoate anion within the AP[5]A cavity, that is, with the carboxylate group oriented towards both inside and outside the cavity (see Figure S11, the Supporting Information). We also computed theoretical values of the ¹H isotropic magnetic shielding for both orientations and the results obtained were compared with those for the isolated 2-naphoate anion (see Table S2, the Supporting Information). Interestingly, the theoretical ¹H magnetic shielding

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values show an agreement with the experimental observations only if the carboxylate group is oriented to the outside of the pillar[5]arene cavity. In this situation the nuclei (H_d and H_e) that are close to the aromatic rings are more shielded, that is, they appear at smaller chemical shifts than in the isolated 2-naph-thoate anion (around $\delta = 2-3$ ppm). However, for the opposite orientation with the carboxylate group clearly inside the cavity, the theoretical values of the ¹H magnetic shieldings for the nuclei closer to the carboxylate group would be larger than in the isolated 2-naphthoate anion (around $\delta = 4$ ppm).

So far we have proven that the AP[5]A is adsorbed onto the quasi-spherical Au nanoparticles with the pillar[5] arene cavity perpendicularly oriented to the metal surface. In addition, we have also confirmed the ability of this water-soluble pillar[5]arene to bind 2NA, forming a [2]pseudorotaxane. With this information at hand, we are ready to analyze the sensing ability of the pillar[5]arene-stabilized gold nanoparticles towards 2NA by SERS. On one hand, it is important to note that 2NA cannot be detected by SERS spectroscopy using citrate-stabilized Au (or Ag) nanoparticles, as reported in the literature,^[33] because of its low affinity to metallic surfaces, as well as electrostatic repulsions. On the other hand, 2NA presents several characteristic Raman signals that do not overlap with those from AP[5]A (see the calculated Raman spectra for 2NA and AP[5]A in Figure S12, the Supporting Information). In agreement with previous assignments,^[33, 34] the Raman spectrum for the 2-naphthoic acid (Figure 6A) is characterized by ring stretching (1633, 1391, and 1022 cm⁻¹), CH bending (1470 cm⁻¹), ring breathing (772 cm⁻¹), and ring deformation (519 cm⁻¹). Additional vibrational assignments for CH bending based on theoretical DFT calculations can be found in the Supporting Information (see Table S3). As shown in Figure 6, a well-defined SERS spectrum was obtained when 2NA was added to AP[5]A-stabilized 80 nm Au nanoparticles in water at pH above the pK_a (4.17) of 2NA. It also confirms the complexation between 2NA and pillar[5]arene. To facilitate the analysis, Figure 6 shows the SERS spectra after subtracting the SERS signals from AP[5]A (the SERS spectra including AP[5]A contributions are shown in Figure S13, the



Figure 6. A) Raman spectrum of 2NA; B–D) SERS spectra of 2NA at 10^{-4} (B), 10^{-5} (C), and 10^{-6} M (D). The excitation laser line was 785 nm. In spectra B–D, the SERS contributions from AP[5]A were subtracted.

Chem. Eur. J. 2014, 20, 1–7 www.chemeurj.org These are not the final page numbers! 77 Supporting Information). Significantly, only the bands associated with in-plane ring vibrations at 1391, 1022, 772, and 519 cm⁻¹ are enhanced in the SERS spectra. This suggests a perpendicular orientation of the 2-naphthoate anion relative to the gold surface, which is in agreement with the proposed perpendicular adsorption preference of AP[5]A over the gold surface. Finally, SERS signals at 770 and 1388 cm⁻¹ are perfectly recognized down to 1 μ M. It should be pointed out as an important advantage that the detection can be performed directly in the colloidal suspension in water, which contributes to the reliability and reproducibility of the detection.

Finally, we analyzed the possibility of detecting a polycyclic aromatic hydrocarbon, such as pyrene, again using the AP[5]Astabilized Au nanoparticles in solution. PYR belongs to a family of hazardous pollutants with a condensed benzene ring structure, which confers a very low affinity by metals.^[16] Therefore, its detection by SERS requires the presence of an appropriate host, that is, with strong affinity towards plasmonic surfaces and a high selectivity for interaction with a molecule containing four benzene rings. In agreement with previous assignments,^[16] the Raman spectrum of PYR (Figure 7 A) is dominated by ring C=C stretching (1407 and 1242 cm⁻¹), ring deformation (409 cm⁻¹), ring breathing (594 cm⁻¹), ring C=C stretching (1594 and 1628 cm⁻¹), and CH bending (1067 and 1143 cm⁻¹). Most of the signals do not overlap with those from AP[5]A (see the calculated Raman spectra for PYR and AP[5]A in Figure S14, the Supporting Information), therefore PYR can in principle be detected by SERS using AP[5]A as the host molecule. Figure 7B-D shows the SERS spectra of PYR after subtracting the AP[5]A peaks (the SERS spectra including AP[5]A contributions are shown in Figure S15, the Supporting Information). Remarkably, the most intense signals in the SERS spectra correspond to ring vibrational modes of a_g symmetry (see Table S4, the Supporting Information). Again, this can be explained if pyrene is oriented perpendicularly to the metal surface because for the a_a modes the Raman polarizability change would be large along the molecular axis normal to the surface (see Figure S16, the Supporting Information).^[35] Finally, SERS signals at 594 and



Figure 7. A) Raman spectrum of solid pyrene; B–D) SERS spectra of pyrene at 10^{-6} (B), 10^{-7} (C), and 10^{-8} M (D). The excitation laser line was 785 nm. In spectra B–D, the SERS contributions from AP[5]A were subtracted.

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1242 cm⁻¹ are perfectly recognized down to 10^{-8} M, which is a limit of detection similar to those reported for calix[4]arenestabilized silver nanoparticles^[16] (more sensitive) or using chromatographic techniques.^[36]

Conclusion

Ammonium pillar[5]arene-stabilized Au nanoparticles with quasi-spherical morphology and size control (up to 120 nm) were successfully synthesized by using seeded growth. Apart from acting as stabilizer, which was demonstrated by SERS, AP[5]A plays an important role during synthesis through complexation of the Au salt and avoiding further nucleation. Theoretical calculations of the adsorption energy demonstrate that AP[5]A is perpendicularly adsorbed onto the Au nanoparticle surface as the most probable conformation. After identifying the strong host–guest interaction of the AP[5]A with 2NA by using ¹H NMR spectroscopy, the AP[5]A-stabilized Au nanoparticles were successfully tested for SERS detection of guest molecules such as 2NA or polycyclic aromatic hydrocarbons (such as PYR), directly in water and achieving detection limits of 10^{-6} and 10^{-8} m, respectively.

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FULL PAPER

Sensing platform: Ammonium pillar[5]arene (AP[5]A)-stabilized Au nanoparticles with quasi-spherical morphology and size control (up to 120 nm) were successfully synthesized by a seeded growth method (see figure). The presence of AP[5]A onto the Au nanoparticle surface allows the detection based on surface-enhanced Raman scattering (SERS) of guest molecules, such as 2naphthoic acid (2NA) or polycyclic aromatic hydrocarbons (pyrene), directly in water achieving limits of detection of 10^{-6} and 10^{-8} M, respectively.



Sensors

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Pillar[5]arene-Mediated Synthesis of Gold Nanoparticles: Size Control and Sensing Capabilities