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Hydrophilic Cucurbit[7]uril-Pseudorotaxane-Anchored-Monolayer-Protected Gold Nanorods

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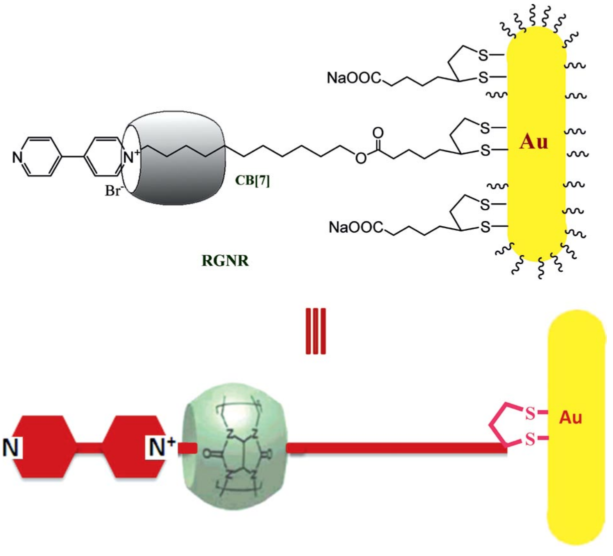
Cucurbit[*n*]uril-based rotaxane or pseudorotaxane devices connected to gold electrode surfaces and spherical gold nanoparticles have previously been developed. Herein, we report the preparation and characterization of gold nanorods (GNRs) protected by a hydrophilic cucurbit[7]uril-based-pseudorotaxane anchored monolayer. The resulting GNRs decorated with both cucurbit[7]uril-based pseudorotaxane disulfide and sodium thioctate on their entire surface through covalent S–Au linkages are water-soluble as well as stable in both solution and the solid state.

Introduction

Owing to their unusual behavior compared with isotropic spherical gold nanoparticles as well as the corresponding bulk materials, anisotropic gold nanorods (GNRs) provide many promising applications in optics, electronics, catalysis, biological detection, cellular imaging, and cancer photothermal therapy.[1–6] To date, GNRs have mainly been prepared in aqueous solution by a seed-mediated growth method, in which cetyltrimethylammonium bromide (CTAB) is widely used as a shape-directing surfactant to selectively form a densely packed dynamic layer around the sidewall of a growing GNR with its two ends free from CTAB for an anisotropic growth along the longitudinal axis. The resultant GNRs covered with a CTAB layer on their longitudinal surface (CTAB-GNRs) are water-soluble. However, the dynamic CTAB layer is unstable and easily yields to irreversible aggregation of GNRs into gold clusters when the excess free CTAB and other components in aqueous solution are removed by centrifugation to obtain CTAB-GNRs. Furthermore, the water solubility of CTAB-GNRs is favorable for their use in biotechnology. However, the CTAB molecules on the GNR surface are toxic to biological cells, proteins, and tissues. Therefore, the challenge is to stabilize and functionalize GNRs and disperse them well in aqueous solution to expand their functionality and potential use in biologically related applications. One solution is to employ a hydrophilic thiol-containing monolayer to protect GNRs on their entire surface through strong covalent Au–S linkages.

Pseudorotaxanes with rodlike dumbbell molecules threading into macrocycles can offer fascinating applications in nanostructured functional switches, logic gates, memory devices, sensors, and so on.[7] Cucurbit[*n*]uril (CB[*n*]), a multimeric macrocyclic compound prepared from an acid-catalyzed condensation reaction of glycoluril and formaldehyde, is an attractive building block for supramolecular pseudorotaxanes and rotaxanes owing to its rigid structure and its ability to form stable complexes with molecules and ions.[8] The development of supramolecular rotaxanes and pseudorotaxane devices, such as rotaxanes or pseudorotaxanes connected to silicon materials, gold elec-



Scheme 1. Schematic illustration of the CB[7] pseudo[2]rotaxane mixed monolayer-protected RGNRs.

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trode surfaces, and spherical gold nanoparticles, has revealed many significant effects.[9] Herein, we report the successful synthesis of GNRs protected by a CB[7]-based-pseudo[2]rotaxane anchored monolayer (RGNRs, Scheme 1). The resulting GNRs, which are covered with both CB[7]-based pseudo[2]rotaxane disulfide and sodium thioctate on their entire surface through strong covalent S–Au linkages were found to be water-soluble as well as stable in both solution and the solid state.[10] To the best of our knowledge, this is the first hydrophilic CB[7]-pseudorotaxane-monolayer-protected GNR hybrid to be reported. This hybrid system incorporates an organic supramolecular complex and an inorganic gold nanomaterial together and gives a new concept in the construction of multifunctional organic–inorganic hybrid materials.

Results and Discussion

Characterization of the Pseudo[2]rotaxane PAL@CB[7]

The dumbbell molecule PAL (a 4,4′-bipyridinyl unit connected to an alkyl chain with a disulfide unit at the other end, see Figure 6) was synthesized by a quarternization reaction between 4,4′-bipyridine and an alkyl bromide (AL) molecule containing a disulfide group at the other end. The CB[7] pseudo[2]rotaxane PAL@CB[7] was prepared by adding one equivalent of CB[7] to the aqueous PAL solution owing to the strong complex interaction between them.[11] The formation of the inclusion complex between the dumbbell PAL molecule and CB[7] was clearly confirmed by ^{1}H NMR spectroscopic experiments in D_2O (Figure 1). The resonance of the aromatic bipyridinium proton H_a shifts upfield from δ = 9.14 to 8.12 ppm (Δ = –1.02 ppm) because of the shielding effect of the CB[7] cavity as it is included inside the CB[7]. The resonances of the other bipyridinium protons H_b, H_c, and H_d shift downfield because of the deshielding effect of CB[7]. The resonance of H_b shifts from δ =8.54 to 8.91 ppm (Δ = 0.37 ppm), that of H_c shifts from δ = 7.99 to 8.28 ppm (Δ = 0.29 ppm), and that of H_d shifts from δ = 8.79 to 9.01 ppm (Δ = 0.22 ppm). It can be deduced that the CB[7] macrocycle includes the PAL molecule and interacts strongly with the positive charge of the 4,4′-bipyridine unit; the whole cavity body, including the part on the alkyl chain site, is only connected to the 4,4′-bipyridine motif, which is consistent with the report by Kaifer et al.[11]

To determine the exact stability constant of the resulting pseudorotaxane PAL@CB[7], we titrated the dumbbell PAL with CB[7] in H_2O at 298 K (Figure 2). After the addition of increasing amounts of CB[7] into an aqueous solution of PAL (4.0×10^{-5} M), the corresponding absorbance spectra changes were recorded. The binding constant *K* between the dumbbell PAL and CB[7] was found to be as high as ca. 1.7×10^4 M^{-1}. Therefore, the pseudorotaxane PAL@CB[7] is very stable and is not easy to dissociate into two components even during the centrifugation process to purify the RGNRs.

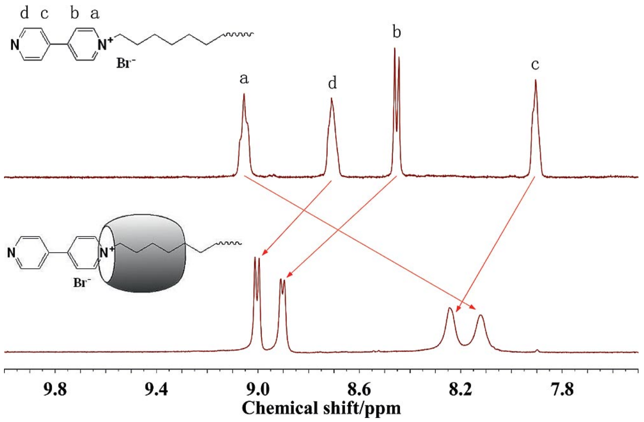

Figure 1. Partial ^{1}H NMR spectra of the dumbbell PAL (top) and the CB[7] pseudo[2]rotaxane PAL@CB[7] prepared by adding one equivalent of CB[7] to PAL (bottom) in D_2O at 298 K.

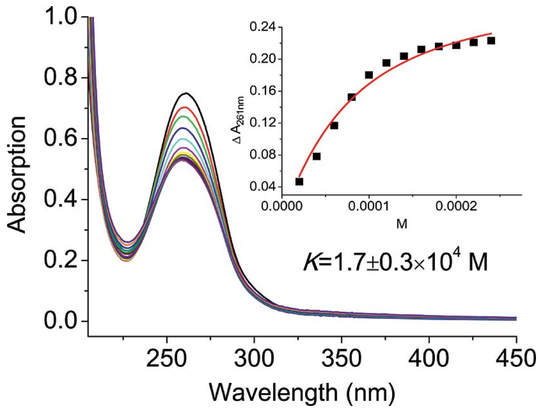

Figure 2. The UV/Vis absorption spectral changes observed upon the titration of PAL (4.0×10^{-5} M) with increasing quantities of aqueous CB[7] at 298 K (0.5, 1.0, 1.5, 2.0, ..., 6.5 equiv.). The inset shows the corresponding titration data obtained by monitoring the absorbance at 261 nm.

TEM Images of RGNRs and CTAB-GNRs

CTAB-GNRs were freshly prepared by the seed-mediated growth method.[12] The target RGNRs protected by a hydrophilic pseudo[2]rotaxane PAL@CB[7] mixed monolayer were synthesized by employing the disulfide-containing pseudo[2]rotaxane PAL@CB[7] to replace the CTAB on the surface of GNR in water, followed by the addition of sodium thioctate (SLA) to further connect some SLA molecules onto the GNR surface through strong covalent Au–S linkages. The shorter SLA molecule was used to fill in the unoccupied surface of the GNR as much as possible because the PAL@CB[7], with relatively large bulk, leaves part of GNR surface unoccupied, which increases the density of the surface protected-monolayer and makes it more water-soluble. By using this strategy, water-soluble and stable RGNRs were successfully constructed. Figure 3 shows the transmission electron microscopy (TEM) images of RGNRs and CTAB-GNRs, in which both the RGNRs and CTAB-GNRs exhibited good rod shape and distinct particles.

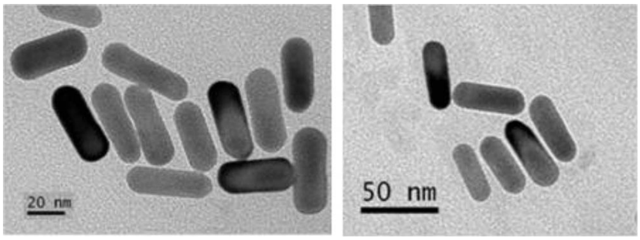

Figure 3. TEM images of RGNRs (left) and CTAB-GNRs (right).

Raman Spectra and UV/Vis/NIR Spectra

The successful attachment of the PAL@CB[7] to the surface of the GNRs through strong covalent S–Au linkages was confirmed by Raman spectroscopy. As shown in Figure 4 (top), CTAB-GNRs showed a characteristic Au–Br band at 172 cm^{-1} and a CH$_2$ band at ca. 759 cm^{-1}. As expected, the characteristic Au–Br bond from CTAB-GNRs disappeared in the Raman spectrum of RGNRs, accompanied by the appearance of new Raman peaks corresponding to $\nu_{\text{Au–S}}$ at ca. 266 cm^{-1} and $\delta_{\text{Au–S–C}}$ at ca. 117 cm^{-1}, which indicates that no CTAB remained on the surface of RGNRs and the covalent modification of the thiol molecules through S–Au linkages onto their entire surface was achieved.

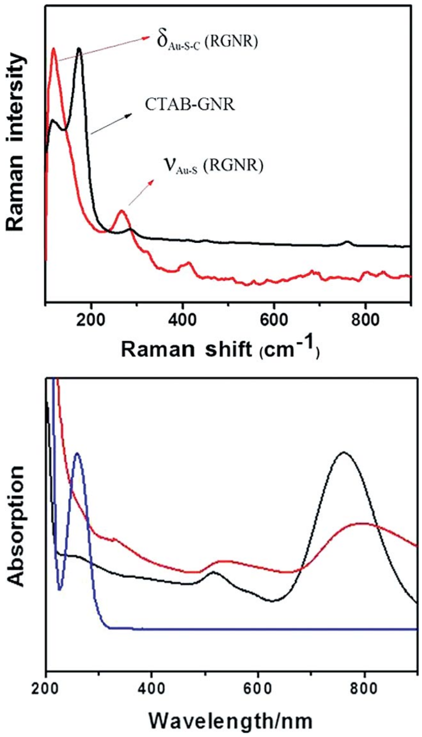

Figure 4. Top: Raman spectra of PAL@CB[7] and SLA protected RGNRs (red) and CTAB-GNRs (black). Bottom: UV/Vis/NIR spectra of pseudo[2]rotaxane PAL@CB[7] (blue), CTAB-GNRs (black), and PAL@CB[7]-monolayer-protected RGNRs (red) in water at 298 K.

UV/Vis/NIR spectra of CTAB-GNRs and RGNRs are shown in Figure 4 (bottom). The curve of CTAB-GNRs exhibited the two characteristic plasma absorption bands of GNRs: a strong longitudinal band at ca. 762 nm in the near-infrared region corresponding to electron oscillations along the long axis and a weaker transverse band at about 516 nm in the visible region corresponding to electron oscillations along the short axis. The curve of RGNRs still showed the two characteristic plasma absorption bands of GNRs but at 797 and 536 nm, respectively. Compared with the CTAB-GNR absorption bands, the broader shape of the RGNR absorption bands might be caused by size selection during the centrifugation or a change in the resonance owing to the different dielectric properties of the PAL@CB[7] monolayer.

The electrochemical properties of PAL, PAL@CB[7], and RGNRs were investigated by cyclic voltammetry. As shown in Figure 5, the free dumbbell compound PAL with one positive charge undergoes a single-electron reduction process to its neutral form and then a reversible reoxidation process. After adding CB[7] to PAL to form the pseudorotaxane PAL@CB[7], the reduction peak of PAL@CB[7] exhibits a negative shift (from –0.971 to –1.079 V, Δ = 108 mV), which indicates that the complexation of CB[7] makes the reoxidation of PAL more difficult.[13] Notably, the reduction and reoxidation peaks of PAL@CB[7] are not so centrosymmetrical, which means that the redox process of PAL@CB[7] is not fully reversible. The reduction makes the PAL molecule neutral, and the macrocycle CB[7] cannot as readily form a complex with the neutral reduced PAL^0. However, the CV curve of RGNR is much more centrosymmetrical, which indicates that the redox process of RGNR is much more reversible. This might result from the fact that the bulky GNR and the hydrophilicity of sodium thioctate modified on the GNR surface makes it more stable to some extent during the redox process.

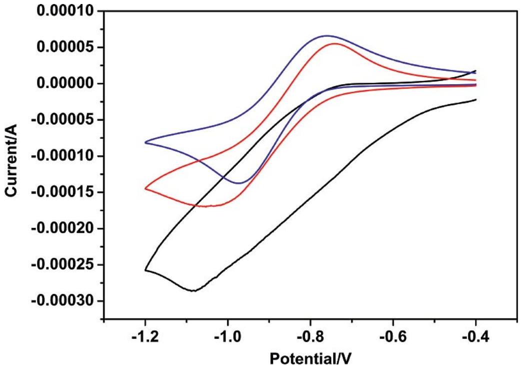

Figure 5. Cyclic voltammetry of PAL (blue), PAL@CB[7] (black), and RGNRs (red) recorded from a thin film coated onto glassy carbon electrodes in an electrolyte solution of Bu$_4$NPF$_6$ (0.10 M) in acetonitrile with an Ag/AgCl (0.10 M) reference electrode. Scan rate: 0.05 V/s.

Conclusions

GNRs protected by a hydrophilic CB[7]-based-pseudo-[2]rotaxane anchored monolayer were prepared and characterized by TEM, Raman spectroscopy, UV/Vis/NIR spectroscopy, and CV. The resulting RGNRs covered with both cucurbit[7]uril-based pseudo[2]rotaxane disulfide and sodium thioctate on their entire surface through strong covalent S–Au linkages were found to be water-soluble as well as very stable in both solution and the solid state. The shorter sodium thioctate, which fills up the potential space on the GNR surface between the pseudorotaxane molecules, not only acts as a stabilizer but also provides better water solubility. The hybrid system demonstrated here, which combines a supramolecular machine and GNR together, should open new and interesting research avenues for the construction of multifunctional organic–inorganic hybrid materials.

Experimental Section

Materials and Instruments: All chemicals and solvents were commercially available and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with 400 or 200 MHz instruments. Elemental analysis was performed by Robertson Microlit Inc. UV/Vis/NIR spectra were recorded with a PerkinElmer Lambda 25 UV/Vis spectrometer at a resolution of 1 nm. Raman spectra were measured with a Renishaw InVia Raman Spectrometer. Samples for Raman spectroscopy were deposited on a glass slide and left to dry before measurement. The wavelength of the laser used was 785 nm. TEM experiments were performed with an FEI Tecnai TF20 FEG TEM instrument. For the observation, the samples in aqueous solution were firstly dispersed on TEM Cu grids precoated with thin carbon films (Cu-400 CN) purchased from Pacific Grid Tech and then completely dried for analysis.

Synthesis of AL: AL was synthesized by an amidation reaction between commercial 11-bromoundecan-1-ol and lipoic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP, Figure 6). The detailed procedure was as follows: A solution of 11-bromoundecan-1-ol (2.0 g, 98%, 7.8 mmol) and lipoic acid (2.0 g, 9.7 mmol) in CH_2Cl_2 (60 mL) was cooled to 0 °C. DCC (2.0 g, 9.7 mmol) and a small amount of DMAP (95 mg, 0.78 mmol) were added to the solution. The solution was then allowed to stir at room temperature for 12 h. The reaction was then quenched by the addition of water, and the CH_2Cl_2 solution was firstly filtered and then washed with dilute sodium carbonate solution and water. The lower CH_2Cl_2 layer was collected and dried with anhydrous $MgSO_4$, and then the filtrate was collected. After evaporation of the CH_2Cl_2, the solid was dried under vacuum. The crude product AL was collected and used for the next reaction step without further purification.

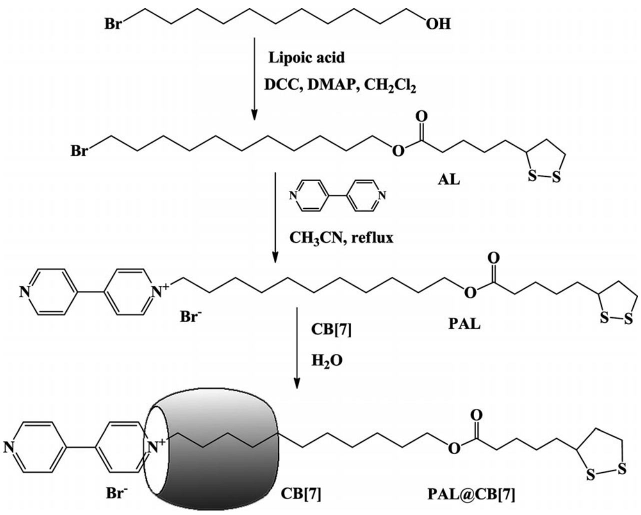

Figure 6. Synthesis of CB[7] based pseudorotaxane PAL@CB[7].

Dumbbell Molecule PAL: A solution of 4,4′-bipyridine (0.39 g, 2.5 mmol) and crude AL (ca. 1.1 g) in acetonitrile (20 mL) was stirred for 10 h at ca. 80 °C. Most of the acetonitrile was then removed and diethyl ether (50 mL) was added to engender precipitation. The precipitate was washed several times with ethyl ether (50 mL) to give the pure PAL as a yellow solid (0.85 g, yield 57%, Figure 6). ^{1}H NMR ([D$_6$]DMSO): δ = 9.23 (d, 2 H), 8.87 (d, 2 H), 8.63 (d, 2 H), 8.04 (d, 2 H), 4.63 (t, 2 H), 3.99 (t, 2 H), 3.60 (m, 1 H), 3.18–3.09 (m, 2 H), 2.40 (m, 1 H), 2.29 (t, 2 H), 1.96 (t, 2 H), 1.87 (m, 1 H), 1.66 (m, 1 H), 1.54 (m, 4 H) 1.40–1.25 (m, 17 H) ppm. ^{1}H NMR (D_2O): δ = 9.14 (d, 2 H), 8.79 (d, 2 H), 8.54 (d, 2 H), 7.99 (d, 2 H), 4.83 (t, 2 H), 3.94 (t, 2 H), 3.48 (m, 1 H), 3.07 (m, 2 H), 2.38 (m, 1 H), 2.22 (t, 2 H), 2.08 (t, 2 H), 1.82 (m, 1 H), 1.60–1.48 (m, 5 H), 1.31–1.13 (m, 17 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 172.9, 152.3, 151.0, 145.3, 140.9, 125.4, 122.0, 63.7, 60.4, 56.1, 38.1, 34.0, 33.4, 30.7, 28.9, 28.8, 28.6, 28.4, 28.1, 28.1, 25.4, 25.4, 24.3 ppm. HRMS: calcd. for $C_{29}H_{43}BrN_2NaO_2S_2$ [M + Na]$^+$ 617.1847; found 617.1876.

Preparation of CTAB-Bilayer-Coated Gold Nanorods (CTAB-GNRs): The CTAB-bilayer-coated GNRs were freshly prepared by the seed-mediated growth method. For seed preparation, an aqueous solution of $HAuCl_4$ (0.01 M, 0.50 mL) was added to an aqueous CTAB solution (0.10 M, 15 mL) in a vial. The solutions were gently mixed by inversion. The solution was bright brown-yellow. An ice-cold aqueous $NaBH_4$ solution (0.01 M, 1.20 mL) was then added, and the solution was mixed by rapid inversion for 2 min. Care should be taken to allow the escape of evolved gas during mixing. The solution became pale brown-yellow. The vial was kept in a water bath maintained at 25 °C for future use. This seed solution was used 2 h after its preparation.

An aqueous CTAB solution (0.1 M, 9.5 mL) was added to a tube, and solutions of $HAuCl_4$ (0.01 M, 0.40 mL) and $AgNO_3$ (0.01 M, 0.06 mL) were added in this order and mixed by inversion. An ascorbic acid solution (0.1 M, 0.06 mL) was added and the resulting mixture became colorless. The seed solution (0.02 mL) was added to the above mixture tube, and the tube was slowly mixed for 10 s and left to sit still in a water bath at 25–30 °C for 3 h. The final solution turned purple within minutes after the tube was left undisturbed.

Preparation of Pseudo[2]rotaxane PAL@CB[7] and SLA Monolayer Protected Gold Nanorods RGNRs: The solution of CTAB-GNRs prepared above was centrifuged (7500 rpm, 20 min) two times to remove the excess CTAB and other soluble components and then redispersed in water (4 mL). This aqueous solution of CTAB-GNRs was added dropwise to an aqueous solution of the PAL@CB[7] (ca. 100 mg) with stirring under the protection of nitrogen. The solution was purple. The reaction mixture was stirred at room temperature for 3 d. The mixture was then centrifuged (7500 rpm, 20 min) three times to remove the excess free PAL@CB[7] and CTAB. This entire procedure was repeated three times. The resulting GNRs were redispersed in water with the addition of excess sodium thioctate (SLA, ca. 100 mg). The mixture was stirred for another 24 h and then centrifuged. This procedure was employed to ensure that the GNRs were encapsulated with the PAL@CB[7] and SLA molecules over the entire surface through strong covalent Au–S linkages. The as-prepared hybrid gold nanorods RGNRs were centrifuged (7500 rpm, 20 min) and washed with water five times to remove the excess free PAL@CB[7] and SLA in the thiol-monolayer-protected RGNRs. The RGNRs are very stable in aqueous media (Figure 7).

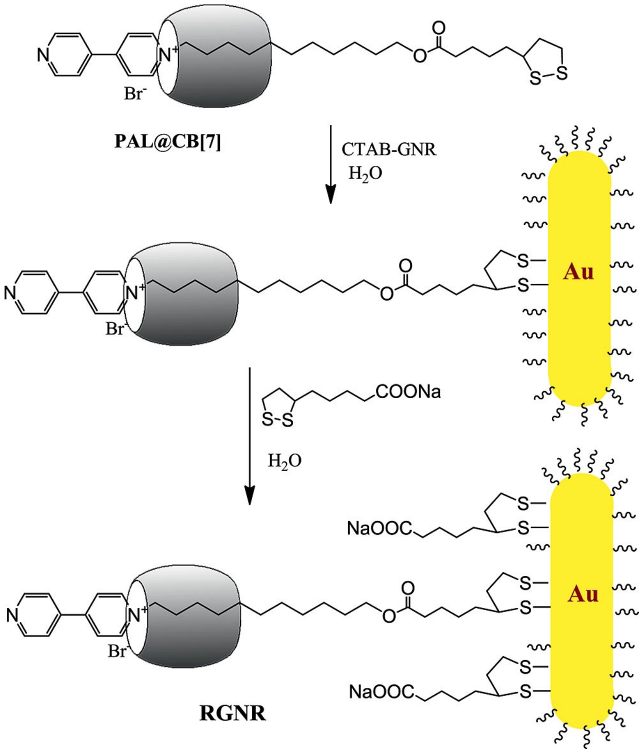

Figure 7. Synthesis of GNRs protected by PAL@CB[7] and SLA.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR and HRMS spectra for PAL.

Acknowledgments

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