

Rings of Nanorods**

Bishnu P. Khanal and Eugene R. Zubarev*

Finding new ways to assemble nano-objects^[1–6] into finite superstructures is an important task because their properties depend not only on their size and shape but also on the spatial arrangement and the degree of order among the individual building blocks. Ringlike assemblies are fairly common and have been documented for various polymers,^[7–10] small organic molecules,^[11] and spherical inorganic nanoparticles.^[12,13] Several mechanisms have been proposed to explain the formation of rings, including the Marangoni effect,^[14] the hole-nucleation mechanism,^[12] “2D gas bubbles”,^[11] and the “breath figures” method (BF).^[15] The latter mechanism takes advantage of the condensation of water microdroplets from moist air and uses them as templates. Thus, the BF method typically produces a honeycomb structure, which can be viewed as an array of air bubbles embedded into a continuous 2D matrix formed by polymer chains^[16] or spherical nanoparticles.^[17] One can see that if the concentration of solute is reduced, the perforated film should transform into a set of isolated rings, as was recently demonstrated in the case of linear polymers.^[18] However, rings composed of anisometric nanocrystals, especially inorganic rods, have never been observed. Nearly all reports on the self-assembly of nanorods describe their packing in a parallel fashion.^[19] Theoretical models also predict a side-by-side packing of rods regardless of their overall morphology.^[20] In stark contrast to that, we describe herein a spontaneous assembly of hybrid gold/polymer core-shell nanorods into ringlike arrays. A systematic investigation shows that the rings of rods described here are templated by water droplets that condense on the surface of nonpolar solvents from humid air, akin to the classical BF method. The high yield and the well-defined structure of rings are a result of the presence of polystyrene (PS) chains covalently attached to the surface of the gold nanorods. The polymer shell insures high solubility of the hybrid 1D nanostructures and keeps the AuNR(PS)_n rods in solution during the evaporation until they are concentrated around the circumferences of water droplets. This method is surprisingly simple and can be used for organizing nanorods into circular arrays in a nearly quantitative yield.

Our recent studies revealed that carboxyl-terminated polymers can be covalently attached to phenol-functionalized gold nanoparticles under mild esterification conditions.^[21] To test the versatility of such an approach, we attempted a synthesis of rodlike gold/polymer core-shell nanostructures. Unlike spherical nanoparticles, the functionalized nanorods cannot be directly prepared by reduction of gold ions in the presence of thiols. For that reason, we first prepared gold nanorods stabilized by cetyltrimethylammonium bromide (CTAB) surfactant using a modified seed-mediated growth method.^[22] However, a seemingly trivial step of exchanging CTAB for a functional thiol was found to be a serious challenge. For example, the removal of either water or CTAB surfactant causes an irreversible agglomeration of nanorods and the subsequent multiple attempts to attach thiols in organic media are completely unsuccessful. In addition, many functional thiols are not soluble in water and their dispersion in an aqueous solution of CTAB-stabilized nanorods does not result in ligand exchange. After many trials, we found that dropwise addition of a concentrated solution of 4-mercapto-phenol in THF directly into an aqueous growth solution of rods led to CTAB-thiol exchange and a slow precipitation of phenol-functionalized nanorods.

After centrifugal purification, AuNR(SC₆H₄OH)_n rods could be dispersed in dichloromethane and covalently coupled with carboxybiphenyl-terminated polystyrene ($M_w = 5000 \text{ g mol}^{-1}$; Figure 1). The reaction proceeded within several hours after the addition of 4-(*N,N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) and 1,3-diisopropyl carbodiimide (DIPC). Remarkably, the reaction could be monitored by TLC as the starting material AuNR(SC₆H₄OH)_n with a retention factor of $R_f = 0$ gradually transforms into AuNR(PS)_n product, which moves on a TLC plate as a single dark-red spot ($R_f = 0.6$ in 15% THF in CH₂Cl₂). The product was isolated by centrifugal ultrafiltration of the THF solution using a regenerated cellulose membrane (MWCO = 30 kDa). Importantly, the complete removal of linear polystyrene was confirmed by size-exclusion chromatography of the THF-soluble AuNR(PS)_n product, whereas the presence of covalently attached PS arms was confirmed by ¹H NMR spectroscopy (see the Supporting Information). The typical weight gain of such coupling reactions is about 40%, which allows us to estimate the grafting density of PS arms (5 kDa) on gold nanorods (10 nm × 45 nm as determined by transmission electron microscopy (TEM)). The grafting density is about 2.1 chains nm⁻², which means that approximately 3000 PS chains are covalently attached to a given nanorod (see the Supporting Information). The value of the grafting density is comparable to that reported for spherical Au nanoparticles (2.9 chains nm⁻²).^[21] The presence of a dense polymer shell ensures high solubility and stability of the nanorods in organic solvents.

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[**] This work was supported by a NSF CAREER Award (DMR-0547399) and the Robert A. Welch Foundation (L-C-0003). Partial support provided by the NSF NIRT grant (CBET-0506832) is also acknowledged.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

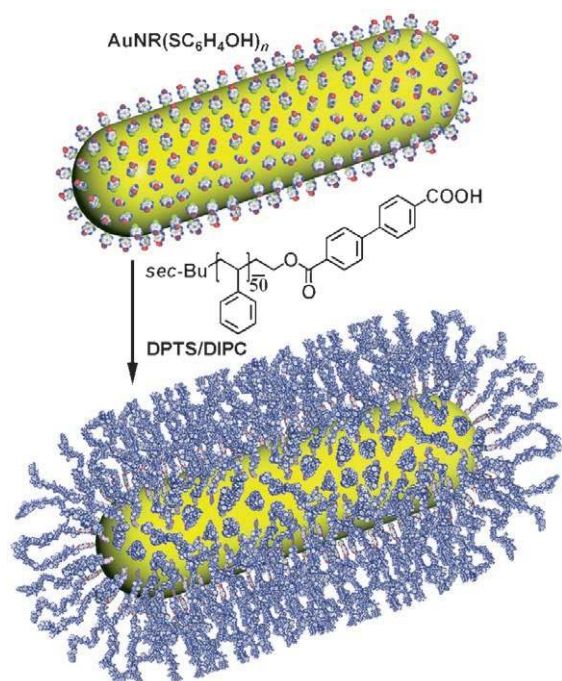


Figure 1. Synthesis of gold nanorods with covalently attached PS arms.

Examination of $\text{AuNR}(\text{PS})_n$ by TEM revealed their unexpected and counterintuitive properties. When a carbon-coated grid is dipped in a CH_2Cl_2 solution and the drop is allowed to dry in air at room temperature, the nanorods spontaneously organize into ring structures (Figure 2). The diameter of the rings varies from 300 nm to a few microns, and their typical width is about 50 nm. In most rings the orientation of rods is random (Figure 2c,d), but at low concentration they tend to line up in a head-to-tail fashion

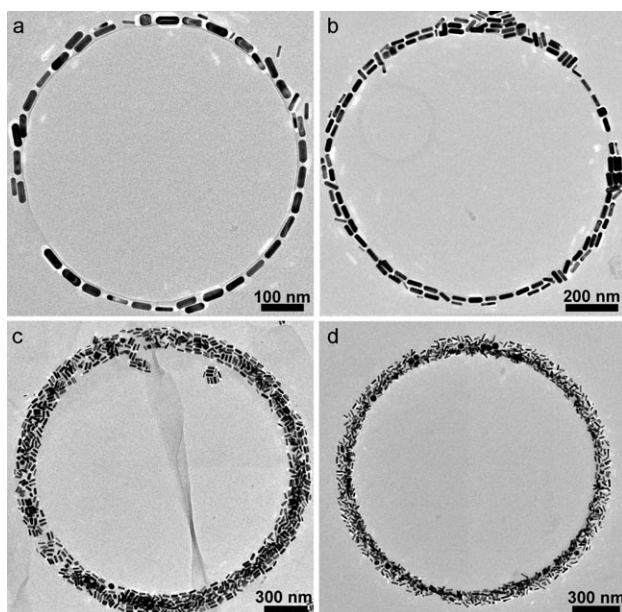


Figure 2. TEM images of rings formed by $\text{AuNR}(\text{PS})_n$ rods from a solution in CH_2Cl_2 (1 mg mL^{-1}). See text for details.

along the circumference (Figure 2a,b). Importantly, virtually all of the rings that were found have one common feature: there are very few, if any, rods inside the rings, which is indicative of a templated process. TEM imaging at low magnification (Figure 3) revealed the presence of rings

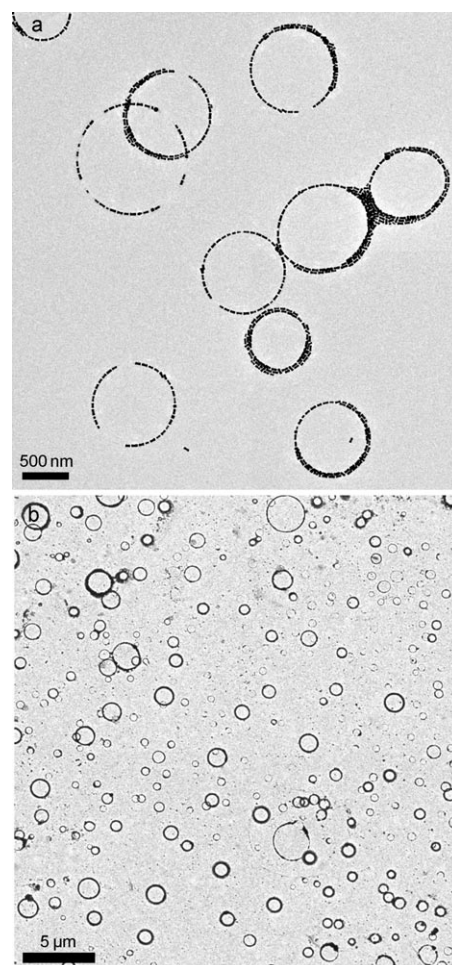


Figure 3. Representative low-magnification TEM images of rings formed by $\text{AuNR}(\text{PS})_n$ when a carbon-coated grid is dipped into a solution of the rods in CH_2Cl_2 (1 mg mL^{-1}).

throughout the entire substrate. The yield of rings is nearly quantitative as there are very few rods either inside the rings or in the areas between them. The average size of the rings is not influenced by the concentration, and similar results were obtained when the samples were also prepared from other nonpolar solvents, such as chloroform and benzene.

The aforementioned hole-nucleation mechanism^[12] cannot explain the assembly of $\text{AuNR}(\text{PS})_n$ rods because the rings form on very different substrates (wetting and non-wetting conditions), their size varies within a broad range, and it does not depend on the concentration. These initial data led us to hypothesize that the nanorods assemble around water droplets that can condense from the air when highly volatile CH_2Cl_2 evaporates and cools its surface below the dew point. It has been shown previously that the temperature on the surface of evaporating volatile solvents can be as low as

0 °C.^[15,16] In addition, it has been proposed that microdroplets of water retain their small and uniform size and pack into a 2D hexagonal superlattice on the liquid surface of organic solvents.^[23] We were able to confirm this phenomenon by direct visualization of water microdroplets condensed on the surface of a solution of AuNR(PS)_n in dichloromethane, as well as on pure CH₂Cl₂, deposited onto carbon-coated TEM grids (Figure 4). The droplets, however, are not stationary and

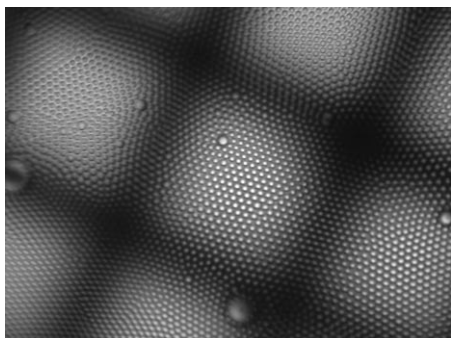


Figure 4. Optical micrograph of water droplets on the liquid surface of a dichloromethane solution of AuNR(PS)_n cast on the carbon-coated TEM grid. The square windows of the copper grid in the background measure 100 μm × 100 μm.

rapidly move in various directions as a result of convective flow. As observed in the optical microscope, the droplets retain their uniform size only for a limited amount of time and undergo coalescence as soon as the organic solvent is evaporated.

An important control experiment was carried out in the absence of moisture. When a sample is prepared in a glove box under ultradry nitrogen atmosphere, not a single ring can be found on the substrate (see the Supporting Information). This simple experiment also proves that the formation of rings is not driven by the Marangoni effect. We also found that rings do not form from nonvolatile solvents such as toluene owing to its insufficient evaporative cooling and inability to cause the condensation of water droplets. Moreover, rings form only if the solvent is not miscible with water (CH₂Cl₂ or CHCl₃) and they cannot be produced from water-miscible solvents like tetrahydrofuran or acetone even though their boiling points are very close to that of chloroform.

On the basis of these data, the following mechanism can be proposed. A fast evaporation of CH₂Cl₂ leads to a condensation of numerous water droplets (Figure 5a), which subsequently land on the carbon substrate and become surrounded by a thin continuous film of the dichloromethane solution of rods (Figure 5b). Because AuNR(PS)_n nanorods are highly soluble in CH₂Cl₂, they will remain in solution until its last portion is concentrated around the impervious walls of the water droplets (Figure 5c,d). At this point the temperature of the substrate will start rising back to room temperature, thus causing evaporation of the water templates and leaving behind ringlike arrays of the nanorods (Figure 5e).

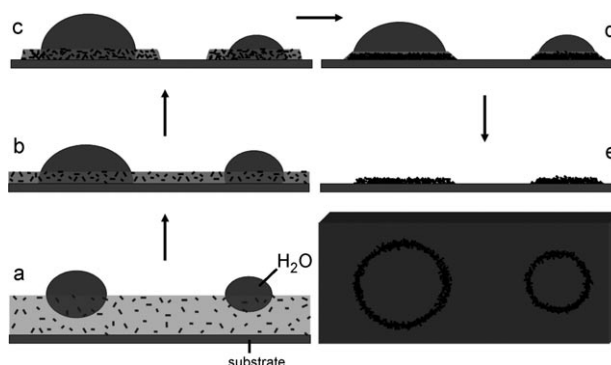


Figure 5. A schematic representation of the formation of rings templated by water droplets. See text for details.

One can directly observe in an optical microscope that the coalescence of microdroplets takes place when the majority of organic solvent is evaporated and results in a broad size distribution of rings (Figure 3b). However, the rings have well-defined structures and their overall yield is remarkably high. This is as a result of a combination of two important characteristics of the reported nanorods: The *hydrophobic nature* of PS arms prevents the nanorods from entering the interior of water templates, whereas their *high solubility* in CH₂Cl₂ ensures that they do not precipitate out of solution early and do not deposit themselves in the areas between the water droplets. The importance of the former characteristics was confirmed by examining analogous nanorods with a hydrophilic shell. We synthesized rods with covalently attached polyethylene glycol (PEG) arms (5 kDa) and found that they do not produce any rings (Supporting Information). This is because water droplets cannot stop water-soluble AuNR(PEG)_n nanorods at the interface. Finally, there are two more required elements for the successful formation of rings. The solvent should be water-immiscible and volatile enough to cause an evaporative cooling below the dew point.

In conclusion, we have described a new method for the synthesis of anisometric core-shell hybrid nanorods and found an efficient way to induce their spontaneous organization into ringlike superstructures. This highly efficient and simple technique may be used to manipulate the optical properties of gold nanorods.

Received: December 3, 2006

Keywords: electron microscopy · gold · nanostructures · organic-inorganic hybrid composites · self-assembly

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Supporting Information

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Rings of Nanorods

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General. Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. The ^1H NMR spectra were recorded in CDCl_3 on a Varian Unity 300 (300 MHz) spectrometer and Bruker 400 MHz spectrometer. Size Exclusion Chromatography (SEC) analysis was conducted on a Waters Breeze 1515 series liquid chromatograph equipped with a dual λ absorbance detector (Waters 2487), manual injector, and three styrogel columns (HR1, HR3, HR4) using linear polystyrene standards for calibration and tetrahydrofuran (THF) as the mobile phase. Centrifugal filters (2 mL capacity) Ultrafree[®]-CL containing regenerated cellulose membranes with a molecular weight cut-off 30,000 g/mol were purchased from Fisher Scientific (cat.# UFC4LTK25). 4-(*N,N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared by mixing saturated THF solutions of *N,N*-dimethylaminopyridine (DMAP) (1 equiv) and *p*-toluenesulfonic acid monohydrate (1 equiv) at room temperature. The precipitate was filtered, washed several times with THF, and dried under vacuum. The structure of DPTS was confirmed by ^1H NMR. TEM images were obtained on a JEOL 1200EX transmission electron microscope operating at 100 kV accelerating voltage and JEOL 2010 TEM microscope operating at 120 kV. Samples were prepared by dipping carbon-coated copper TEM grids (continuous carbon film, Electron Microscopy Sciences) in methylene chloride or

chloroform solutions of AuNR(PS)_n nanorods (c =0.5-1 mg mL⁻¹). Similar results are obtained if a drop is cast onto a carbon-coated grid.

Synthesis of Nanorods. As mentioned in the text, the direct synthesis of functionalized rods by reducing gold ions in the presence of a functional thiol is not possible. At least two steps are required for that purpose. First, non-functionalized nanorods have to be synthesized. Second, the non-functionalized rods have to be reacted with a functional thiol.

Preparation of bare gold nanorods AuNR. One of the best procedures for synthesizing gold nanorods was described by El-Sayed in 2003.^[22b] This procedure was highly reproducible in our hands and indeed gave Au nanorods in high yield (90 % of rods vs. spherical particles and other random shapes). This approach is known as a modified seed-mediated growth method,^[22a] which requires the preparation of a seed solution (4 nm Au NPs stabilized by CTAB surfactant) and a growth solution containing CTAB, Au (I) ions and silver nitrate. When a small amount of seed is introduced into the growth solution, the 1D growth ensues resulting in 10 x 45 nm Au nanorods stabilized by CTAB surfactant, which keeps them in the aqueous media. We slightly modified the original procedure described by El-Sayed in order to scale-up the reaction and obtain 20-30 mg of the nanorods in one experiment. Below is the detailed description of the modified procedure used in our lab.

Seed Solution. 364 mg of CTAB (hexadecyltrimethylammonium bromide, Aldrich) is dissolved in 5 mL of water upon a slight heating with a heat gun (up to 30-35 °C). In a separate vial, 1 mg of HAuCl₄ · 3 H₂O is dissolved in 5 mL of water at room temperature. These two solution are mixed together right after their preparation and 0.6 mL of 0.01M ice-cold aqueous solution of NaBH₄ is added at once upon vigorous stirring (1200 rpm). The color changes from greenish-yellow to brown and the mixture is stirred for 2 minutes. The stirring is then stopped and the seed solution containing 4 nm AuNPs

stabilized by CTAB surfactant is used 5 minutes after the stirring was stopped. This appears to be a critical element and therefore the growth solution has to be prepared in advance.

Growth Solution. 8.5 mg of AgNO_3 was dissolved in 12.5 mL of water. Next, 18.22 g (grams!) of CTAB was dissolved in a 250 ml of water in a 500 mL Erlenmeyer flask. In order to completely dissolve the CTAB a slight heating with a heat gun was used. The two solutions were mixed and the mixture was kept at 25 °C (oil bath) without any stirring. After 10 minutes, 250 mL of aqueous solution of $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ (prepared separately by dissolving 98.5 mg $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ in 250 mL of H_2O) was added to the mixture of CTAB and AgNO_3 . After additional 3 minutes, 3.5 mL of 0.0788 M aqueous solution of ascorbic acid was added to the above mixture. The flask was hand-stirred until the mixture became colorless (typically takes 3-5 seconds). The disappearance of color indicates the reduction of Au^{3+} into Au^+ ions caused by ascorbic acid which is a weak reducing agent. The obtained growth solution was typically used right after its preparation.

At this point, 0.8 mL of seed solution was added to the entire growth solution (~535 mL) and the mixture was stirred for 30 seconds. After that the flask containing the growth solution was placed into an oil bath at 27 °C and kept without stirring. A reddish-brown color slowly developed within the first 10 minutes. Investigation of the growth solution by TEM has shown that the growth of rods is complete within 30 minutes and no change in size of the rods occurs after that. The rods prepared under these conditions are typically 10 nm in diameter and 45 nm in length.

Preparation of functionalized gold nanorods $\text{AuNR}(-\text{S}-\text{C}_6\text{H}_4-\text{OH})_n$. Functionalization of the CTAB-stabilized nanorods posed a significant challenge and required many different trials under various conditions. Initially, we attempted the isolation of the nanorods from the aqueous growth solution. However, the excess of CTAB surfactant prevents the precipitation of nanorods and requires a very

powerful centrifuge. When the rods are finally collected and rinsed to remove the residual CTAB, they are not soluble in any organic solvent and all the attempts to react them with 4-mercaptophenol in DMF, or CH₂Cl₂/DMF mixture were unsuccessful. It appears that after the removal of CTAB the rods agglomerate and cannot be redispersed in order to react with a thiol. Another route was taken to avoid the centrifugation. We found that addition of excess THF to the aqueous growth solution of rods caused their slow precipitation. The rods were collected by decantation, rinsed several times and dried under vacuum. Once again, the reaction with thiol was not successful. These results lead us to hypothesize that the exchange of CTAB for a thiol could be attempted *in situ* by introducing the thiol directly into the growth solution of rods. However, 4-mercaptophenol is not a water-soluble compound. For that reason, we added a concentrated THF solution of 4-mercaptophenol (2.5 g of thiol in 30 mL of THF) into the growth solution of AuNRs. The addition is normally done dropwise upon vigorous stirring of the growth solution. This addition causes a change in color (from dark brown to black). The mixture is then allowed to stir at 27 °C for 12 h and the black precipitate can be collected after centrifugation (3750 rpm, 10 min). The residual CTAB and 4-mercaptophenol were removed by multiple rinsing with THF. The total weight of the dried product was typically 20-25 mg.

Synthesis of gold nanorods with covalently attached polystyrene arms AuNR(PS)_n.
Carboxybiphenyl-terminated polystyrene (5kDa) was prepared from a hydroxyl-terminated linear polystyrene (PDI=1.06; Polymer Source) using standard procedures described in our previous publications.^[21] Methylene chloride (2 mL) was added to 21 mg of mercaptophenol-functionalized gold nanorods in a glass vial and the mixture was stirred for several minutes before the addition of 100 mg of carboxybiphenyl-terminated polystyrene. DPTS (10 mg) was added next and the mixture was allowed to stir for 5 minutes at room temperature. DIPC was introduced dropwise (15 drops) followed by 0.3 mL of DMF. The reaction could be monitored by TLC because the R_f of the starting material is

significantly lower than that of the product (0 vs. 0.6 in 15 % THF in CH₂Cl₂). The product moves on a TLC plate as a dark-red spot, which can be visualized without a UV lamp. The coupling normally takes several hours (3-6 h). At this point 5 mL of THF are added to the reaction mixture and nitrogen is gently blown above the solution in order to evaporate most of the methylene chloride. The resulting THF solution is then split into three centrifugal filters (2 mL capacity) which are centrifuged at 5000 rpm. Within approximately 30 min the volume of the solution above the membrane of the filter is reduced to 0.2-0.3 mL. The colorless solution containing all the low molar mass components as well as unreacted polystyrene (5 kDa), penetrates through the membrane and is collected on the bottom of the filter. The dark purple/brown solution concentrated on the top of the membrane contains the hybrid nanorods. New portion of THF is then added into each filter bringing the volume back to ~2 mL and the centrifugation is repeated for another 2 or 3 times until GPC shows no trace of linear polystyrene. The resulting solution is evaporated under reduced pressure giving 30 mg of the pure product AuNR(PS)_n.

Estimation of the grafting density. The average number of PS arms attached to a given nanorod was estimated as follows. The volume of one nanorod assuming 45 nm for the length and 10 nm for diameter (based on TEM) is $V = 45 \text{ nm} \times 3.14 \times 25 \text{ nm} = 3532.5 \text{ nm}^3$, which means that the mass of an average rod is $6.82 \times 10^{-17} \text{ g}$ ($\rho_{\text{Au}}=19300 \text{ kg m}^{-3}$). Hence, the molecular weight is

$M = m \cdot N_A \cong 41,076,000 \text{ g mol}^{-1} = 4.11 \cdot \text{g mol}^{-1}$. The increase in mass after the coupling of polymer is about 40 % (from 21 mg of AuNR(-S-C₆H₄-OH)_n nanorods to 30 mg of AuNR(PS)_n). That means the molecular weight after coupling rose to $57,520,000 \text{ g mol}^{-1}$. So the mol. weight of the polymer shell is about $16,440,000 \text{ g mol}^{-1}$, which gives $16,440,000:5,000 = 3288$ PS chains per one nanorod. Simple estimation shows that the surface of a gold nanorod is about 1570 nm^2 (assuming a cylindrical shape).

Therefore, the grafting density is $3288/1570=2.094$ chains nm^{-2} . This number is comparable to the value reported for spherical 2 nm gold particles (2.91 chains nm^{-2}).^[21]

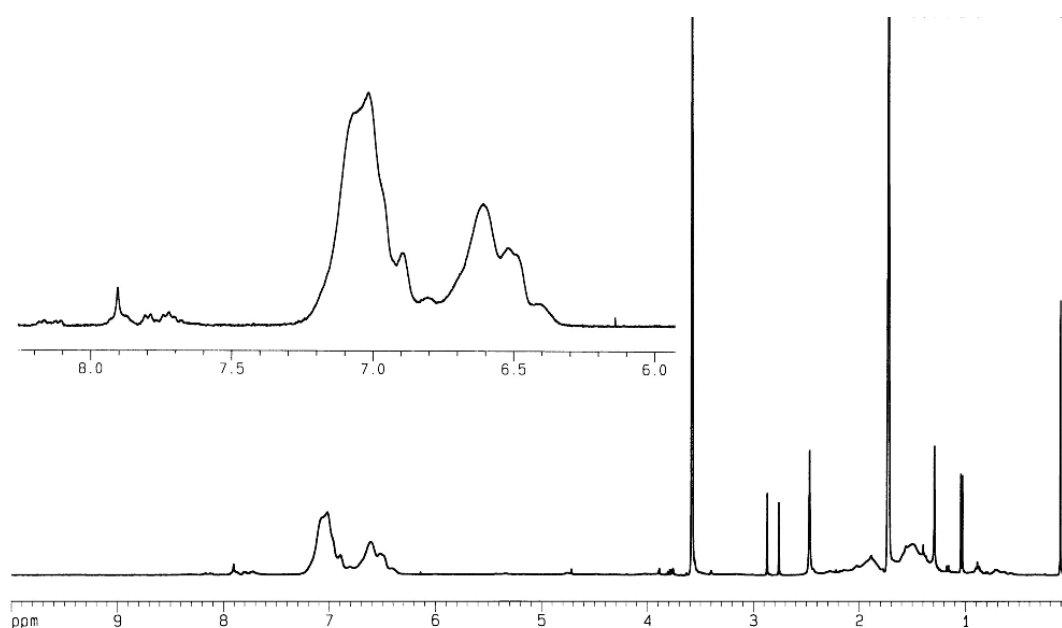


Figure S1. ¹H NMR of AuNR(PS)_n in CDCl₃.

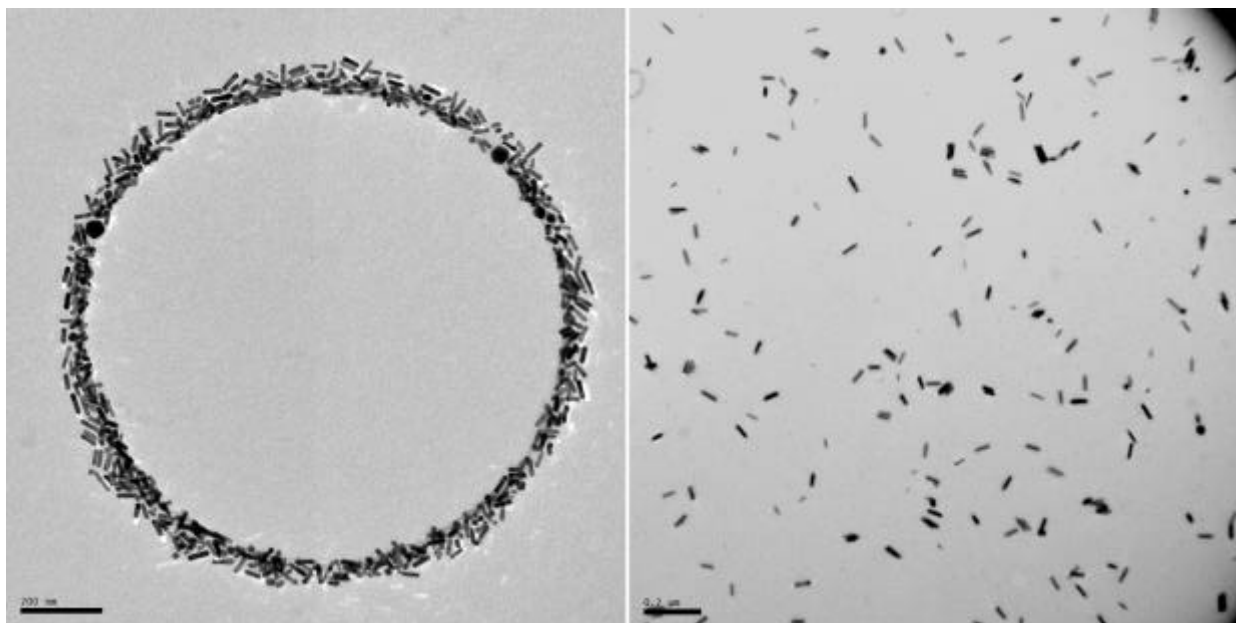


Figure S2. Control experiment: TEM images of samples prepared from CH_2Cl_2 solution of $\text{AuNR}(\text{PS})_n$ in air (left) and under dry nitrogen atmosphere (right).

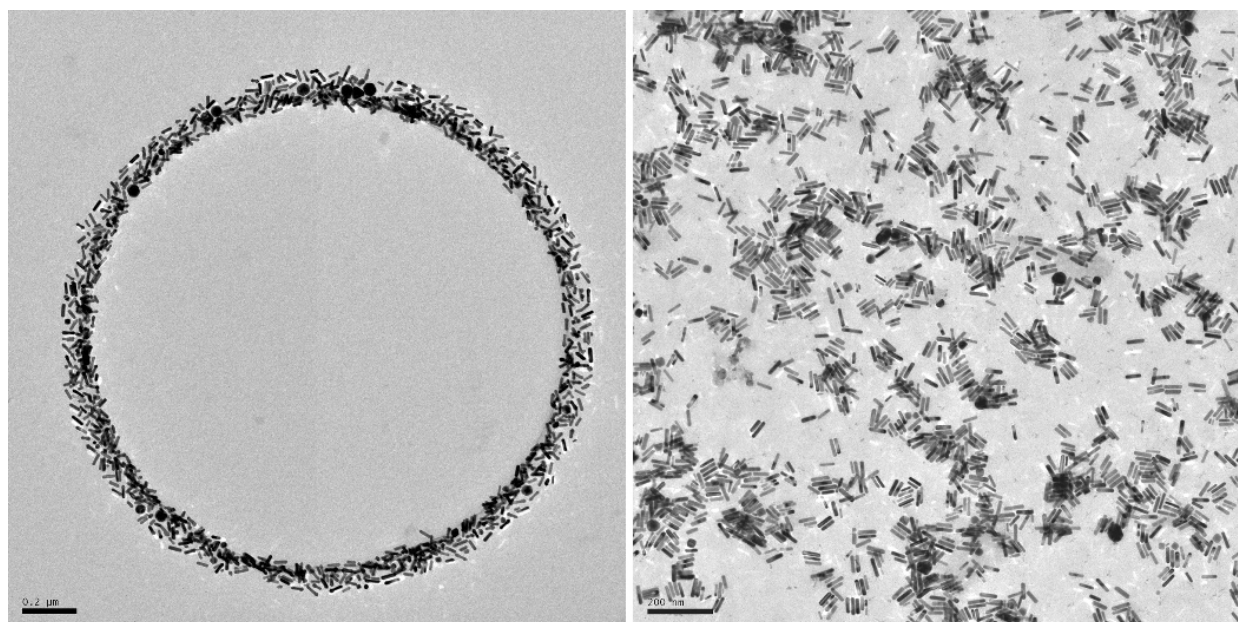


Figure S3. Control experiment: TEM images of samples prepared from CH_2Cl_2 solution of hydrophobic $\text{AuNR}(\text{PS})_n$ (left) and hydrophilic $\text{AuNR}(\text{PEG})_n$ (right) nanorods.