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Preparative Manipulation of Gold Nanoparticles by Reversible Binding to a Polymeric Solid Support

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Abstract: A preparative scheme is presented for controlled modification of gold nanoparticles (NPs) by using reversible binding to a polymeric solid support through boronic acid chemistry. Octanethiol-capped Au NPs were bound to a boronic acid functionalized resin by custom-synthesized bifunctional linker molecules. The NPs were chemically released from the resin to the solution, with one (or a few) linker molecules embedded in their capping layer. This was confirmed by rebinding the linker-derivatized NPs to a boronic resin, exploiting the reversibility of the boronic acid/diol chemistry. The same scheme was employed to demonstrate a new method for affinity separation of NPs by means of a solid-phase reaction. The use of boronic acid provides versatility and chemical reversibility, while the polymeric solid support affords the separation and preparative aspects. The method presented here may be useful in various facets of NP handling, manipulation, and separation.

Keywords: affinity separation · boronic acid · gold · nanostructures · reversible binding · surface chemistry

Introduction

Gold nanoparticles (NPs) have been the subject of numerous studies in recent years, representing particularly convenient building blocks for nanostructure fabrication, while displaying well-defined dimensions and geometry, as well as optical and electronic properties.[1–7] The capping layer of the nanoparticles can be varied and modified, thus providing a unique possibility to control their surface chemistry and certain properties.[8]

The ability to modify Au NPs by exploiting the NP surface chemistry is a basic requirement for their use as nanometric components and building blocks. Modification of the NP capping layer is commonly achieved by a place-exchange reaction, that is, exchange of capping molecules with other molecules dissolved in the colloid solution.[9] The degree of exchange, determined by the reaction time, concentration of the exchanging thiol, and other factors,[10] is not easily controlled and a certain average can only be estimated.

Au NP separation is essential for purification and selection. Several techniques for NP separation have been reported: 1) Size-selective precipitation, used for preparative separation of NPs of different sizes usually having the same capping layer;[11–13] 2) electrophoresis, commonly carried out on hydrophilic NPs having charged groups on their surfaces, for example, DNA molecules;[14] 3) chromatography, which is preparative and may be suitable for NP separation based on size and/or functional groups.[15–17]

Binding of NPs to polymeric solid supports was reported recently.[18–20] Here we present a preparative scheme for controlled modification of Au NPs by using reversible binding to a polymeric solid support by means of boronic acid chemistry. The solid-phase reaction ensures limited exchange of capping molecules due to the small number (as low as one) of resin functional groups interacting with each NP, while the use of boronic acid chemistry introduces the elements of reversibility and simplicity. The resultant modified Au NPs are used in an NP separation scheme based on the same solid-phase reaction. Application of boronic acid matrices to affinity separation of carbohydrates and oligonucteotides has been reported;[21–24] here we show for the first time preparative affinity separation of Au NPs by bor-

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onic acid chemistry. The process generally resembles the well-established affinity chromatography, applied here to NPs.

Results and Discussion

Figures 1 and 2a show the two kinds of Au NPs used in this work, distinguished by size (Figure 1) and color of their respective solutions in chloroform (Figure 2a). The transmission electron microscope (TEM) images in Figure 1 show

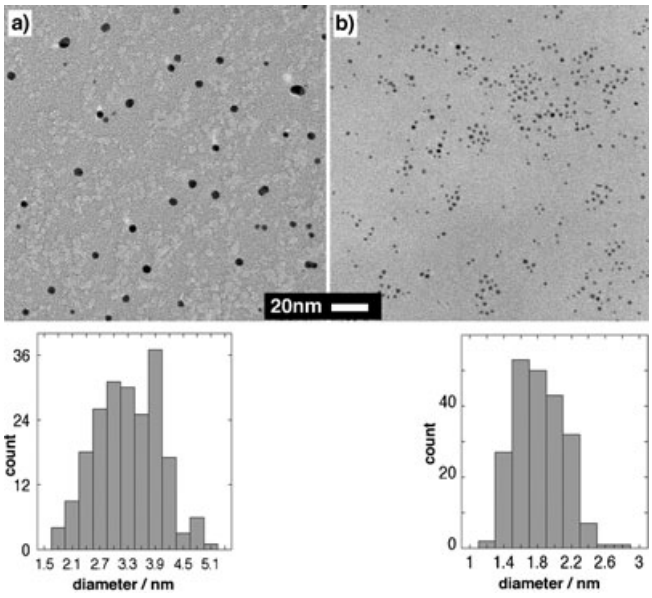


Figure 1. TEM images and size distribution histograms of a) red and b) brown NPs. Concentrations were approximately 0.1 mg mL^{-1}.

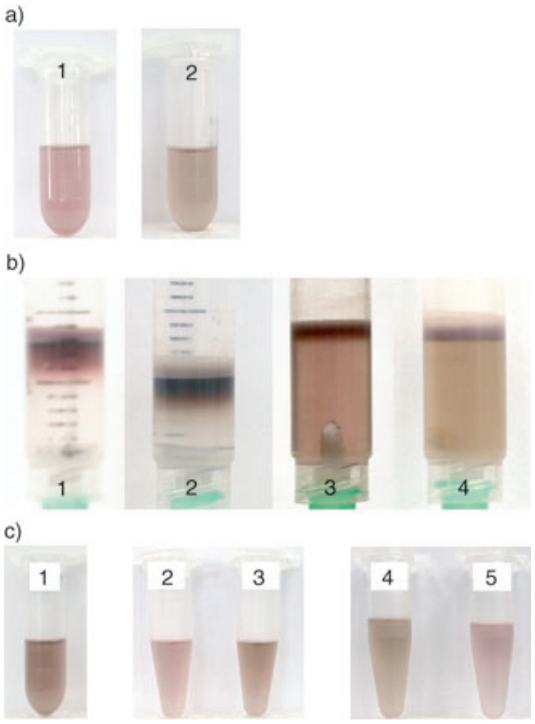
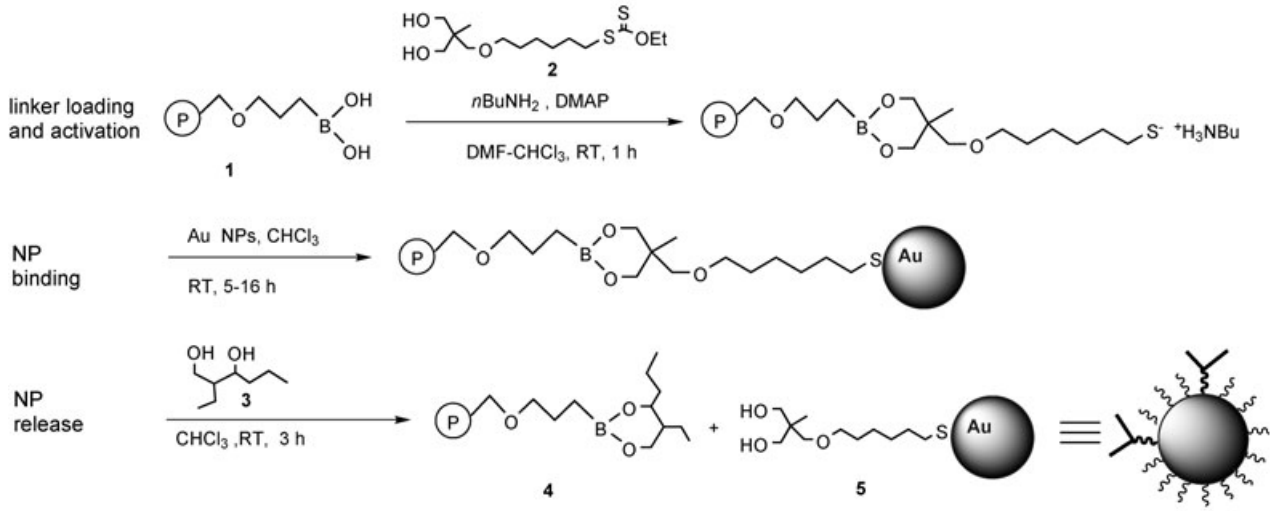


Figure 2. a) Photographs of red (1) and brown (2) NP solutions in chloroform. b) Red (1) and brown (2) NPs released from the resin by treatment with diol **3** (see Scheme 1). The released NPs are seen as a cloud desorbing from the resin beads (white layer floating on the chloroform). b3) Selective NP binding to resin **1** (see Scheme 2) from a mixed solution of linker-modified brown NPs and unmodified red NPs; the resin turns brown while the solution turns red. b4) Cross experiment in which the linker molecules are on the red NPs. 3) and 4) Initial concentrations: about 0.07 mg mL^{-1}. c) Results of selective binding experiments. c1) A mixed chloroform solution of red and brown NPs (concentration of ca. 0.07 mg mL^{-1}). c2), c3) Separation results with the linker molecules on the brown NPs, showing the unbound and bound fractions after separation and collection, respectively. c4), c5) Results of a cross experiment in which the linker molecules are on the red NPs, showing the unbound and bound fractions after separation and collection, respectively.

the red (left) and brown (right) Au NPs, both capped with a monolayer of octanethiol, as well as size-distribution histograms (from TEM images). The photographs of the respective solutions in chloroform (Figure 2a) show the different colors of NPs of different average diameter, that is, 3.5 nm (red NPs) and 1.8 nm (brown NPs).

Scheme 1 illustrates the NP modification scheme. Resin **1** consists of a macroporous polystyrene backbone (Merrifield resin) substituted with boronic acid moieties.[25] The resin is treated with the custom-synthesized bifunctional linker molecule **2** bearing a diol group on one end and a thiol group on the other end, the latter protected as a xanthogenate due to the instability of free thiols. The boronic acid on the resin binds to the linker molecule by forming a cyclic boronate ester, while the thiol group is deprotected in situ by the *n*-butylamine and dimethylaminopyridine (DMAP) present in the solution. Excess (unreacted) linker molecules are washed away. The resin is then treated with a solution of octanethiol-capped Au NPs in chloroform; binding of NPs to the resin occurs in less than an hour by a place-exchange reaction in which linker molecules displace octanethiol molecules on the NP surface. The process is easily viewed as deep coloration of the resin. Excess (unreacted) NPs are washed away leaving a boronic–thiolate resin with chemically immobilized Au NPs. Binding of the NPs to the resin is stable and unaffected by solvent washing. The NP-loaded resin can be dried and stored under ambient conditions for several weeks with no change in performance.

Release of the bound NPs from the resin (Scheme 1) is achieved by reacting the loaded resin with the diol **3** (2-ethyl-1,3-hexanediol) in chloroform; this reaction transesterifies the boronate ester of the linker molecule, cleaving the bond between the linker molecules and the resin, thus releasing the NPs to the solution. The released NPs are collected and cleaned by evaporation of the chloroform, addition of acetonitrile, and centrifugation. The NPs (insoluble in acetonitrile) aggregate leaving the impurities in solution to be discarded. This process is repeated three times, after

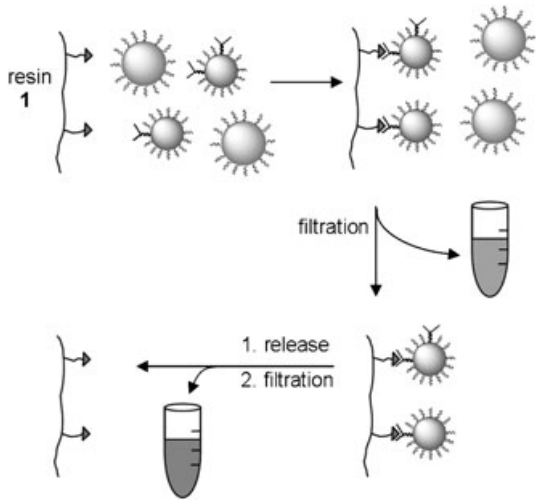


Scheme 1. Schematic presentation of the reversible binding of unmodified, octanethiol-capped gold NPs to boronic acid derivatized resin **1** and their release (octanethiol molecules not always shown).

which the NPs are redissolved in chloroform. The released and cleaned NPs **5** (Scheme 1) are now stabilized with octanethiol, in which one or possibly a few linker molecules are inserted. The boronate ester resin **4** can be hydrolyzed to regenerate resin **1**. A similar scheme for binding NPs to a solid support by using linker molecules was reported recently;[18,20] the boronic acid chemistry used here offers milder conditions and an additional degree of reversibility, because the linker-modified NPs are capable of rebinding to the resin by using the linker molecule, as detailed below.

Characterization of the product **5**, that is, establishing the presence of linker molecules in the released NP capping layer, is difficult, as the amount of exchanged linker molecules is below the detection limit of common techniques. This objective can, however, be achieved by exploiting the capability of the modified NPs **5** to rebind to resin **1** through the diol linker molecule (now present on their surface), while unmodified NPs will not bind to resin **1**. Moreover, this process demonstrates a new approach to preparative separation and recovery of NPs by using a polymeric solid support.

In a typical experiment NP modification is carried out as in Scheme 1, followed by affinity separation as shown in Scheme 2. NPs (e.g., brown NPs) are treated with a linker-modified resin, then released and cleaned (as in Scheme 1). The linker-carrying, brown NPs are then mixed with a stock solution of untreated red NPs, which are capped with octanethiol alone. The mixture is reacted with the boronic resin **1** for 5 h. The brown NPs are expected to bind selectively to resin **1**, leaving the red NPs in solution. The fraction not bound to the resin is filtered out and collected. The resin is then washed with chloroform and treated with a solution of the diol **3** in chloroform. The NPs on the resin are released to solution, filtered, and collected as shown schematically in Scheme 2. The same separation scheme can be employed to show the opposite selectivity by using a mixed solution of



Scheme 2. Schematic presentation of NP separation by selective binding of linker-bearing NPs to resin **1**, leaving the unmodified NPs in solution. Linker-bearing NPs are prepared according to the process shown in Scheme 1.

red and brown NPs, in which only the red NPs are modified with linker molecules.

Figure 2b illustrates several stages of the experiment. Frames b1 and b2 show the white resin floating on the chloroform, while "clouds" of red and brown NPs, respectively, are being released from the resin into the chloroform (corresponding to the NP release from the resin in Scheme 1). Frame b3 of Figure 2 shows selective binding from a mixed solution of brown NPs derivatized with linker molecules and red NPs without; the brown NPs are bound to the floating resin, leaving the red NPs in the chloroform. The cross experiment, that is, selective binding from a solution of red NPs derivatized with linker molecules and brown NPs without, is shown in frame b4. As detailed above, the NPs left in

solution are filtered out, the resin is then washed and exposed to a solution of the diol **3** in chloroform to release the NPs on the resin (Scheme 2).

Figure 2c shows the results of separation experiments. Frame c1 is a photograph of a reference solution of mixed red and brown NPs. Frames c2 and c3 represent results of an affinity separation experiment (as in Scheme 2) carried out with a mixed solution of linker-modified brown NPs (as in Scheme 1) and unmodified red NPs. Frames c2 (red) and c3 (brown) are the unbound and bound fractions, respectively, after separation and collection. Results of the cross experiment (mixed solution of linker-modified red NPs and unmodified brown NPs) are shown in frames c4 and c5, respectively. The expected results are visually apparent, that is, the unbound fractions are highly enriched with unmodified NPs, whereas the bound fractions are highly enriched with linker-modified NPs, indicating the effectiveness of the NP modification and affinity separation schemes. The qualitative results are not sensitive to variations in the initial fractions of modified and unmodified NPs in the mixed solution.

The efficiency of the affinity separation of Au NPs is evaluated quantitatively by using the Au NP optical absorbance. (TEM imaging cannot be used for this purpose due to extended size segregation of the NPs on the TEM grid.) The difference in the shape of the transmission UV-visible spectrum of the two types of NPs enables quantitative determination of the percentage of red and brown NPs in the separated fractions. The working hypothesis in the analysis is that the spectrum of a mixed (red+brown) NP solution can be analyzed as a linear combination of the spectra of the pure components. Hence, by using the experimental spectra of pure red and pure brown NPs as references, the spectra of mixed solutions can be deconvoluted to give the ratio of red-to-brown components. This working hypothesis is spectroscopically sound provided that the size distributions of red and brown NPs after separation are similar to those in the pure solutions. This condition is supported by the fact that the spectra of the pure NP solutions are unchanged after treatment with resin **1** and release (Scheme 1).

Figure 3 presents results of NP affinity separation experiments, shown as transmission UV-visible spectra measured before and after separation. The initial mixed (red+brown) solutions contain either brown NPs (a) or red NPs (b) with linker molecules. The three parts in each experiment (marked 1–3) show spectra of the initial mixture, the fraction bound to resin **1** and released, and the fraction that did not bind to the resin, respectively. Each plate contains four graphs. The solid line is the experimentally measured spectrum. The dashed–dotted line is a computer-generated, best-fit line constructed as a linear combination of the spectra of pure red and brown NP references, each multiplied by an appropriate factor to fit the experimental curve. The red and brown components of the best-fit curve are shown as the dashed line and the dotted line, respectively. The calculated spectra nearly coincide with the experimental lines in all cases.

The efficiency of the separation was determined quantitatively from the simulations by using the empirical observation that solutions of red or brown NPs of the same concen-

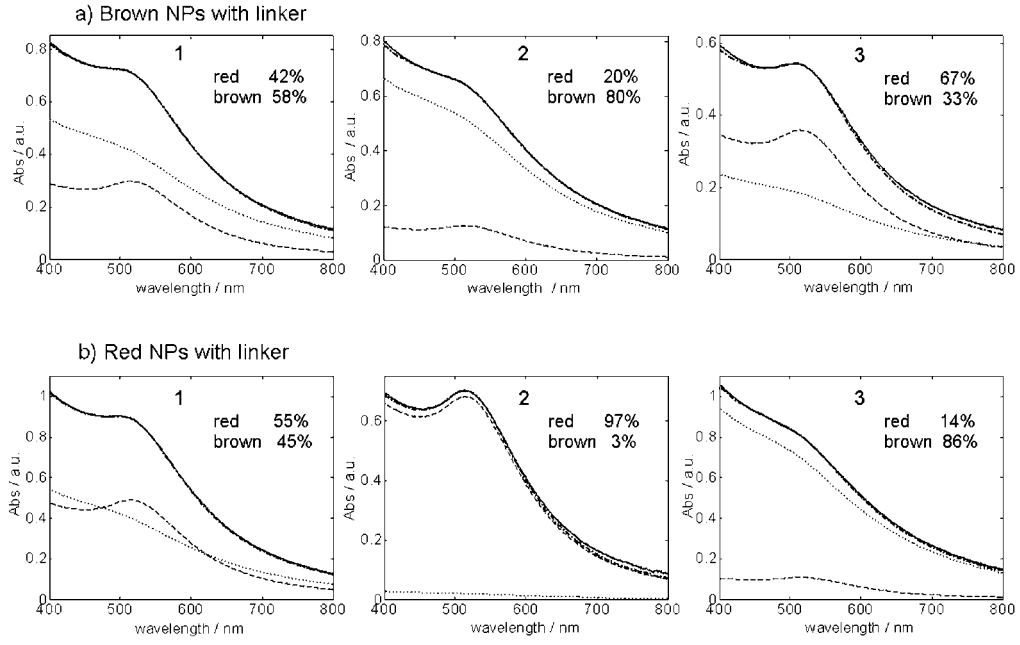


Figure 3. Experimental (solid lines) and calculated best-fit (dashed–dotted lines) UV-visible spectra representing results of NP affinity separation experiments (as in Scheme 2) on mixed NP solutions, in which the linker molecules are on a) the brown or b) the red NPs. The spectra (1–3) correspond to the initial mixture, the fraction of NPs that were bound to the resin (and released), and the fraction that remained unbound in solution, respectively. Results of the analysis, as percentages of the two components (weight%), extracted from the absorbance at 514 nm (see text) are also shown. Initial concentrations in a1) and b1) were 0.06 and 0.07 mg mL^{-1}, respectively. (See text for explanation of calculated spectrum.)

tration have the same absorbance at 514 nm. In this way the ratio of red to brown NPs in a test solution is given by the ratio of the absorbance at 514 nm in the two calculated spectra of its pure components,[26] thus eliminating the need to know the exact concentrations of the reference solutions.

The results are summarized in Table 1 and are also given in Figure 3. Evidently, the separation is efficient but not complete and can be described as effective enrichment, with

Table 1. Results of NP affinity separation experiments (as in Scheme 2). Material recovery was calculated by comparing the absorbance of the initial mixture with the combined absorbances of the recovered components. Volume changes were compensated for by normalizing the absorbances to a 1 mL solution.

Sample	Composition [wt% ±3%] red	brown	Enrichment factor	Material recovery [%]
brown NPs with linker molecules				
initial mixture	42	58		
bound	20	80	2.8	82
not bound	67	33	2.8	
red NPs with linker molecules				
initial mixture	55	45		
bound	97	3	28	85
not bound	14	86	7.8	

enrichment factors ranging from approximately 3 to 30. Better separation is attained when the linker molecules are on the red NPs, possibly the result of some nonspecific binding of red NPs to the resin. This effect, apparently related to the difference in NP size and certain properties of the resin, requires further study. The separation can be improved by a second enrichment (not shown) by means of the same scheme, exploiting the easy regeneration of resin **1** (see above). The total material recovery, determined from the absorbance values, is better than 80%, appropriate for preparative applications.

Conclusion

Reversible binding of Au NPs to a polymeric solid support was demonstrated by using boronic-derivatized resins and the specific reaction of diol molecules with boronic acid. The versatility of boronic acid chemistry offers a powerful tool for NP manipulation, while the polymer support provides the preparative element. In the present case the boronic acid/diol chemistry was exploited for controlled transfer of linker molecules from the resin to the capping layer of the NPs, to obtain free, linker-modified Au NPs. The reversibility of boronic acid chemistry was used for rebinding linker-bearing NPs to a boronic resin by means of the diol linker molecule, thereby establishing 1) the presence of linker molecules on the modified NPs and 2) an effective affinity separation scheme. This enabled selective extraction and separation of NPs from a mixed solution, as well as convenient NP recovery.

The affinity separation scheme was demonstrated here with an artificial mixture, that is, Au NPs were modified with diol linker molecules and mixed with unmodified NPs, to be separated again. However, the concept is quite general. One can envisage, for example, a case of NPs undergoing an exchange reaction in solution, after which unmodified NPs have to be separated from modified ones carrying just a few substituent molecules. Such a separation would be practically impossible by other means, as the NPs exhibit the same size and solubility properties determined by their nearly identical capping layers.

The preparative schemes presented here may be useful in various aspects of NP technology. These include specialized NP modification, controlled NP release, NP separation and purification, chemical reactions on immobilized NPs, and others. Some of these applications are currently under further study.

Experimental Section

Materials and reagents: Unless otherwise stated, chemicals and reagents were purchased from Sigma–Aldrich and were used as received. Chloroform (Biolab, Israel) stabilized with amylene was filtered through basic alumina. THF (Biolab, Israel) was distilled with sodium and benzophenone. Boronic acid derivatized resin **1** was synthesized from macroporous Merrifield resin (200–400 mesh, a gift from Dr. Andrew Coffee, Polymer Laboratories, UK). The detailed synthesis, as well as the synthesis of linker molecule **2**, will be reported elsewhere.[25]

Preparation of octanethiol-capped Au NPs

Brown Au NPs: Octanethiol-capped brown NPs were prepared according to the procedure of Brust et al.[27]

Red Au NPs: Octanethiol-capped red NPs were prepared in two steps: 1) synthesis of red NPs stabilized with tetraoctylammonium bromide (TOAB),[28] and 2) exchange of the TOAB stabilizer with octanethiol.

1) Red NPs stabilized with TOAB: Toluene (50 mL) and TOAB (600 mg) were added to a round-bottomed flask (100 mL) equipped with a magnetic stirrer. An aqueous solution of $HAuCl_4$ (20 mL, 10 mg mL^{-1}) was added, thus, transferring the chloroaurate to the toluene layer. The toluene was separated and added to the cleaned flask, and moderate-to-high-speed stirring was applied. A solution of $NaBH_4$ (200 mg in 15 mL water) was added dropwise to the toluene chloroaurate solution at a rate of about 2 drops per second; reduction began immediately. The initial brown color of the solution gradually changed to red, indicating growth of the NPs. After 2 h the red toluene layer was separated and washed twice with the following solutions (20 mL): NaOH (20 mM), water, saturated NaCl. The NP solution was diluted to 100 mL with toluene.

2) Red NPs stabilized with octanethiol: TOAB-stabilized NPs in toluene (20 mL) were added dropwise to a vigorously stirred solution of octanethiol (100 μL) in toluene (10 mL) in a round-bottomed flask (100 mL), at a rate of about 2 drops per second under a nitrogen stream. The flask was then capped and left to stir overnight. Methanol (20 mL) was added to induce aggregation of the NPs, and the aggregates were centrifuged at 8000 rpm for 5 min. The methanol was decanted, clean methanol was added, followed by short sonication and centrifugation. This process was repeated three times. The octanethiol-capped NP aggregates could be dissolved in chloroform, and to a lesser extent in toluene or THF. The toluene-soluble fraction, consisting of the smaller NPs, was collected, redissolved in chloroform, and used for the experiments.

Reversible binding of unmodified Au NPs to Resin 1: Resin **1** (5 mg) was placed in a syringe used as a reactor and washed with chloroform (1 mL). A solution of linker molecules **2** in chloroform (0.5 mL, 1 mg mL^{-1}), DMAP (4.6 mg), *n*-butylamine (60 μL), and DMF (0.7 mL) was mixed

with the resin and left for 1 h, stirring occasionally. The resin was washed with chloroform (4×1 mL), then treated with a solution of octanethiol-capped NPs (1.5 mL, 0.1 mg NPs mL^{-1}) and left overnight. The excess NPs were washed away with chloroform (3×1 mL).

To release the linker-modified NPs, the NP-loaded resin was treated with a solution of diol **3** in chloroform (1 mL, 0.15 M) for 3 h. The released NPs were filtered, and the chloroform was evaporated under a stream of nitrogen. Acetonitrile was added, and the aggregated NPs were centrifuged at 8000 rpm for 10 min. The acetonitrile was decanted, and the procedure was repeated three times. The cleaned NPs were dissolved in chloroform.

Selective binding of linker-modified Au NPs to resin 1: Cleaned Au NPs modified with linker molecules as described above were mixed with unmodified NPs of the other type to obtain a solution (1 mL, THF (10%) in chloroform). The NP solution was added to a reactor syringe containing cleaned (washed with THF (10%) in chloroform) resin **1** (5 mg) and left for 5 h, stirring occasionally. The fraction that did not bind to the resin was collected, and the resin was washed with chloroform (3×1 mL). The resin was then treated with a solution of diol **3** in chloroform (1 mL, 0.15 M) for 3 h. The released NPs were filtered and collected.

Analyses: UV/Vis spectra were obtained with a Varian CARY 50 UV/VIS/NIR spectrophotometer in a quartz cuvette with an optical path of 1 cm and width of 2 mm. TEM images were taken with a Philips CM 120 instrument by using 400 mesh copper grids coated with nitrocellulose followed by carbon evaporation. A drop of the NP solution was placed on the grid followed by solvent evaporation at room temperature.

Acknowledgements

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