Supplementary material (ESI) for Chemical Communications

Electronic Supporting Information

for

End-to-end assembly of gold nanorods by means of oligonucleotides-mercury (II) molecular recognition

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Experimental Details

Apparatus

The extinction spectra were measured with a UV-3600 UV-Visible-NIR spectrophotometer (Shimadzu, Japan). An S-4800 scanning electron microscope (Hitachi, Japan) was used to measure the scanning electron microscopy (SEM) images of gold NPs and the morphologies of their assemblies. Dynamic light scattering (DLS) measurements of the individual building blocks or their assemblies were performed by means of a N5 Submicron Particle Size Analyzer (Beckman, USA). The SZCL-3A magnetic stirrer (Henan, China) was used for the stirring reaction. A high-speed TGL-16M centrifuge (Hunan, China) was used for the centrifugation of solution.

Materials

All reagents including cetyltrimethylammonium bromide (CTAB) and hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) (both from Sinopharm Group Chemical Regent Co., Ltd., Shanghai, China), sodium borohydride ($NaBH_4$, Huanwei Fine Chemical Co., Ltd., Tianjin, China), L-ascorbic acid (L-AA, Chuandong Chemical Group Co., Ltd., Chongqing, China), silver nitrite ($AgNO_3$, Beijing

Chemical Co., Ltd., Beijng, China), trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) and $HgCl_2$ (both from Chemical Reagent Co., Shanghai, China) were commercially available. Tris (2-carboxyethyl) phosphine hydrochloride (TCEP) was supplied by Sigma-Aldrich, Inc. (Louisiana, USA). The sequence of DNA used is 5'-SH-$(CH_2)_6$-CCC CCC CCC CTT TTT TTT TTT TTT TT-3', which was prepared by Invitrogen Biotechnology Co., Ltd. (Shanghai, China).

All the reagents used were of analytical grade and without further purification. Acetate buffer (pH 5.2) was employed for acidity control and Mili-Q purified water (18.2 MΩ) was used throughout the experiment. The glass vials were cleaned by aqua regia solution (HCl/HNO_3 in volume = 3:1), and then soaked with 12 M NaOH for 1 h at room temperature. Copious amounts of Mili-Q purified water were used to rinse the vials subsequently before use.

Synthesis of Gold Nanospheres (GNSs)

GNSs were prepared according to previous references by reducing $HAuCl_4 \cdot 4H_2O$ with citrate which acts as both a reducing agent and a stabilizer. [1, 2] In detail, 48 mL of Mili-Q purified water and 2 mL of 1% (w/w) $HAuCl_4$ solution were mixed in a flask to make the final concentration of $HAuCl_4 \cdot 4H_2O$ 1 mM. The mixture was then heated under magnetic stirring until it began to boil, and 1 mL of 5% trisodium citrate was quickly added to the solution. The solution should change from pale yellow to deep red with about 3 min. After boiling for another 5 min, the solution was cooled to room temperature (25 °C) under vigorous magnetic stirring, and then stored in a refrigerator (4 °C) and kept from light. The approximate concentration of such GNSs was calculated according to previous reference. [3]

Synthesis of Gold Nanorods (GNRs)

GNRs were prepared by the seed-mediated method, [4] and it should have to get the gold seeds and growth solutions ready. Gold seeds were prepared by reducing $HAuCl_4 \cdot 4H_2O$ (2.5×10^{-4} M) with ice-cold $NaBH_4$ (9.0×10^{-4} M) in the presence of CTAB (7.5×10^{-2} M). The $NaBH_4$ solution was added at one time within 30s with vigorous mixing. The mixture rapidly became into a color of light brown. After aged

for 2 h and 24 h at 25 °C, the gold seeds could be applied for further use. Growth solution containing 5 mL 0.002 M $HAuCl_4 \cdot 4H_2O$ and 7.7 mL H_2O should be mixed with 11.9 mL 0.2 M CTAB before the synthesis of GNRs. The color of the mixture quickly developed from light yellow into orange. Followed by the addition of 0.15 mL 0.01 M $AgNO_3$ and 0.16 mL 0.1 M L-AA, the color of the mixture changed into colorless immediately. After the both solutions get ready, GNRs could be prepared by adding 0.11 mL 2-h aged Au seed solution into the growth solution and left undisturbed for 24 h, during which, the red color gradually changes. The approximate concentration of such GNRs was calculated according to previous reference. [5]

Functionalization of GNRs or GNSs with DNA

The thiol-modified T-rich DNA (10 μM) was firstly deprotected by l mM TCEP (freshly prepared) in 50 mM acetate buffer (pH 5.2) for 1 h at room temperature. Then the TCEP-treated DNA was added to the GNRs (4 mL) or GNSs (2 mL) solution under gentle shaking, respectively. The mixtures were incubated in dark at room temperature for 16 h, and purified by centrifugation to eliminate the superfluous DNA. The GNRs were redispersed by 1 mM CTAB (2 mL).

Preparation of GNR, GNS or Gold Nanorod-Sphere (GNRS) Assemblies

DNA-functionalized GNRs, GNSs or their mixture were added to 250 μL mercury (II) with the concentration of 1.0×10^{-5} M in 50 mM acetate buffer (pH 5.2) and incubated for 5 min at room temperature, respectively. The final volume of the solution is 500 μL.

References

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2. K. C. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.* , 1995, **67**, 735-743.
3. H. D. Hill and C. A. Mirkin, *Nature Protocols*, 2006, **1**, 324-336.
4. X. C. Jiang, A. Brioude and M. P. Pileni, *Colloids and Surfaces A*, 2006, **277**,

201-206.

5. C. J. Orendorff and C. J. Murphy, *J. Phys. Chem. B*, 2006, **110**, 3990-3994.

Figures

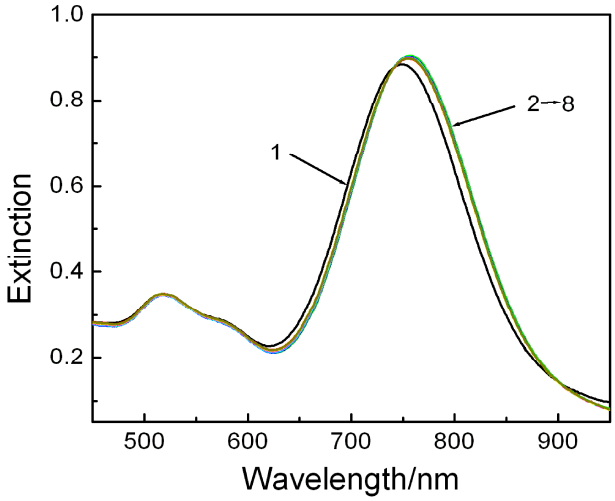

Fig. S1 The temporal evolution of extinction spectra for the end-to-end assembly of GNRs mediated by T-rich oligonucleotides-mercury (II) recognition system. 1, DNA-GNRs; 2-8, DNA-GNRs treated with Hg^{2+} (5.0 μM) and be incubated with different time. The incubation time: 2, 1 min; 3, 5 min; 4, 10 min; 5, 15 min; 6, 20 min; 7, 25 min; 8, 30 min.

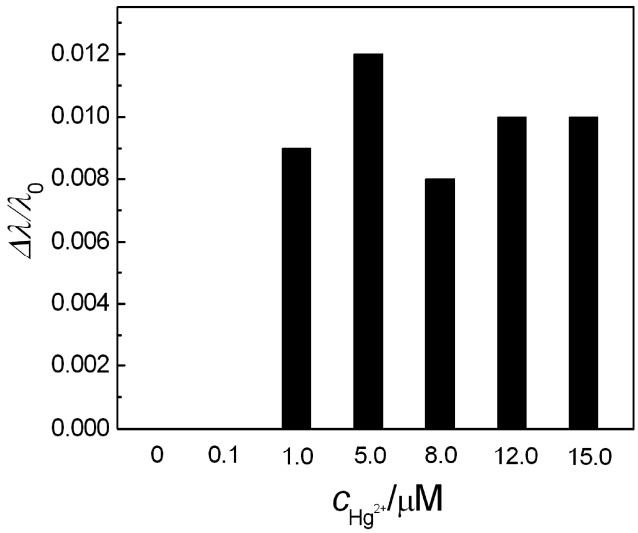

Fig. S2 Fractional red-shift of the longitudinal LSPR absorption bands of DNA-GNRs in extinction spectra mediated by various concentrations of Hg^{2+}. The concentrations of Hg^{2+} used were from 0 to 15.0 μM.

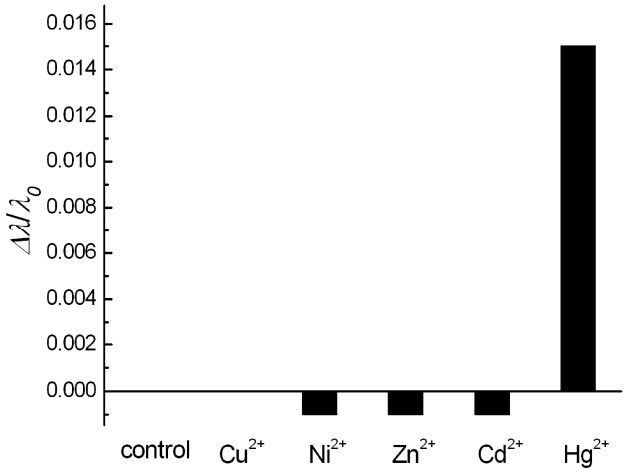

Fig. S3 Fractional red-shift of the longitudinal LSPR absorption bands of DNA-GNRs in the presence of various bivalent metal ions. The concentrations of all metal ions are 5.0 μM, and the pH is 5.2.

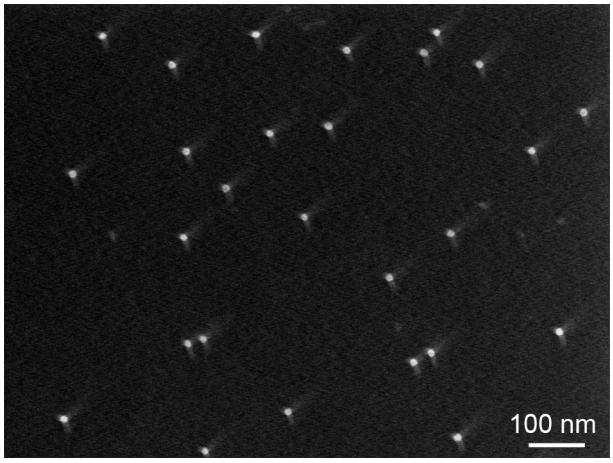

Fig. S4 SEM micrograph of citrate-capped gold nanospheres used in the preparation of GNS and GNRS assemblies.

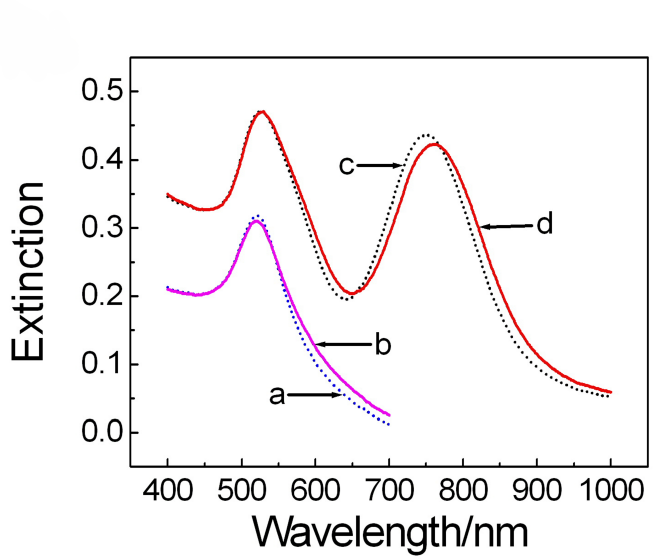

Fig. S5 Extinction spectra of the preparation of GNS and GNRS assemblies. (a) DNA-GNSs; (b) DNA-GNSs + Hg^{2+}; (c) the mixture of DNA-GNSs and DNA-GNRs; (d) DNA-GNSs + DNA-GNRs + Hg^{2+}. The concentrations of GNSs are 4.0 nM and 2.0 nM for GNS and GNRS assemblies, respectively. GNRs, 0.3 nM; Hg^{2+}, 5.0 μM; pH, 5.2.