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# Number-controlled spatial arrangement of gold nanoparticles with DNA dendrimers

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# Supporting Information

## Materials and methods

All DNA strands were purchased from Invitrogen Biotech (Beijing, China) and PAGE purified. Lipoic acid was obtained from Alfa Aesar (Shanghai, China). Bis(*p*-sulfonatophenyl)-phenylphosphine dehydrate dipotassium salt (BSPP) was purchased from Sigma-Aldrich (Shanghai, China). All other chemicals were of reagent grade or better and used as received. Water used in all experiments was Millipore Milli-Q deionized (resistance >18 MΩ.cm).

Agarose gel electrophoresis was run at 5 V/cm in 0.5 × TBE buffer. 3% and 0.5% agarose gels were used for purification of DNA monofunctionalized AuNPs and characterization of DNA dendrimers, respectively.

Transmission electron microscopy (TEM) was carried out on FEI T20 electron microscope operated at 200 kV. Samples were prepared by placing a drop of the AuNPs onto TEM copper grids, which were air-dried for 12 h.

Dynamic light scattering (DLS) measurements were performed using LLS spectrometer equipped with a multi-τ digital time correlator and a He-Ne Laser (λ=632.8 nm) at an angle of 90°.

Atomic force microscopy (AFM) measurements were performed on a Veeco MultiMode 8 Scanning Probe Microscope. The DNA nanostructures were deposited on mica and imaged by tapping mode AFM under buffer.

UV/Vis spectra were recorded on a Varian Cary 100 spectrophotometer equipped with a programmable temperature-control unit.

**Table S1** DNA sequences used in experiments to construct DNA dendrimers

| | |
|---|---|
| $Y_{0a}$ | 5'-AGT GTT AGT GGA CCG ATG GAT GAC CTG TCT GCC TAA TGT GCG TCG TAA G-3' |
| $Y_{0b}$ | 5'-AGT GTT AGT GGA CCG ATG GAT GAC TTA CGA CGC ACA AGG AGA TCA TGA G-3' |
| $Y_{0c}$ | 5'-AGT GTT AGT GGA CCG ATG GAT GAC TCA TGA TCT CCT TTA GGC AGA CAG G-3' |

| | |
|---|---|
| $Y_{1a}$ | 5’-GAA GCC ACT CTG ACC TGT CTG CCT AAT GTG CGT CGT AAG-3’ |
| $Y_{1b}$ | 5’-GAA GCC ACT CTG ACT TAC GAC GCA CAA GGA GAT CAT GAG GTG TTA GTG TT-3’ |
| $Y_{1c}$ | 5’-TCA TCC ATC GGT CCC CTA ACC CTA ACC CTA ACC CCT CAT GAT CTC CTT TAG GCA GAC AGG-3’ |
| $Y_{2a}$ | 5’-CTG TCA TCG GTC AC CTG TCT GCC TAA TGT GCG TCG TAA G-3’ |
| $Y_{2b}$ | 5’-CTG TCA TCG GTC AC TTA CGA CGC ACA AGG AGA TCA TGA G-3’ |
| $Y_{2c}$ | 5’-TCA GAG TGG CTT CC TCA TGA TCT CCT TTA GGC AGA CAG G-3’ |
| $Y_{3a}$ | 5’-TGC TGT CTG TCC AC CTG TCT GCC TAA TGT GCG TCG TAA G-3’ |
| $Y_{3b}$ | 5’-GAC ACA CTG AGG TC TTA CGA CGC ACA AGG AGA TCA TGA G-3’ |
| $Y_{3c}$ | 5’-TGA CCG ATG ACA GC TCA TGA TCT CCT TTA GGC AGA CAG G-3’ |
| $Y_{4a}$ | 5’-TGC TGT CTG TCC AC CTG TCT GCC TAA TGT GCG TCG TAA G-3’ |
| $Y_{4b}$ | 5’-TGC TGT CTG TCC AC TTA CGA CGC ACA AGG AGA TCA TGA G-3’ |
| $Y_{4c}$ | 5’-ACC TCA GTG TGT CC TCA TGA TCT CCT TTA GGC AGA CAG G-3’ |

**Table S2** DNA sequences used in experiments to prepare DNA monofunctionalized AuNPs

| | |
|---|---|
| $cY_0$ | 5’-TCA TCC ATC GGT CCA CTA ACA CTT T-3’$NH_2$ |
| EXT-$Y_0$ | 5’-AGT GTT AGT GGA CCG ATG GAT GAT AGG ACG ACT TCT TGT TGT AGC ACG ACT TGG ACG CA-3’ |
| cEXT-$Y_0$ | 5’-TGC GTC CAA GTC GTG CTA CAA CAA GAA GTC GTC CTA TCA TCC ATC GGT CCA CTA ACA CT-3’ |
| $cY_1$ | 5’-TCA GAG TGG CTT CTT-3’$NH_2$ |
| EXT-$Y_1$ | 5’-GAA GCC ACT CTG AGG AGC AAG AAC GCA TAG ACG GAC ACT GAA GTA GAC GGT ATT AGT AT-3’ |

| | |
|---|---|
| cEXT-$Y_1$ | 5’-ATA CTA ATA CCG TCT ACT TCA GTG TCC GTC TAT GCG TTC TTG CTC CTC AGA GTG GCT TC-3’ |
| c$Y_2$ | 5’-TCC AAC AGC ATC CTT-3’$NH_2$ |
| EXT-$Y_2$ | 5’-GGA TGC TGT TGG ACG AGA GAC GAA TGG TAG TGT AAG AGG TAG ACG AAG ATG GTG ATG GT-3’ |
| cEXT-$Y_2$ | 5’-ACC ATC ACC ATC TTC GTC TAC CTC TTA CAC TAC CAT TCG TCT CTC GTC CAA CAG CAT CC-3’ |
| c$Y_3$ | 5’-ACC TCA GTG TGT CTT-3’$NH_2$ |
| EXT-$Y_3$ | 5’-GAC ACA CTG AGG TTA CGA TGC CAC TAT GAG AAC TCT ATC CAA TCA AGA ATC TAC GAA TG-3’ |
| cEXT-$Y_3$ | 5’-CAT TCG TAG ATT CTT GAT TGG ATA GAG TTC TCA TAG TGG CAT CGT AAC CTC AGT GTG TC-3’ |
| c$Y_4$ | 5’-TGG ACA GAC AGC ATT-3’$NH_2$ |
| EXT-$Y_4$ | 5’-TGC TGT CTG TCC AGT GAG TTC CAG GTA TCT TGA ATC CAT CAT CTA TCT ATC CGA CGA AT-3’ |
| cEXT-$Y_4$ | 5’-CAT TCG TAG ATT CTT GAT TGG ATA GAG TTC TCA TAG TGG CAT CGT AAC CTC AGT GTG TC-3’ |

## Preparation of Y-shaped DNA (Y-DNA)

Stoichiometric amounts of three DNA strands ($Y_{na}$, $Y_{nb}$ and $Y_{nc}$) were mixed together in a PBS (phosphate buffer saline, 100 mM NaCl, 50 mM phosphate, pH 8.0) to give a final concentration of 20 mM for each strand. Then the mixtures were heated to 95°C for 5 min and cooled to 4°C at a rate of 1°C per minute to form the desired structures.

The thermal stabilities of Y-DNA were measured by UV-vis spectroscopy (Fig. S1). The melting temperatures ($T_m$) of all Y-scaffolds were above 60°C, which means that these dendrimer monomers (Y-DNAs) were stable at room temperature.

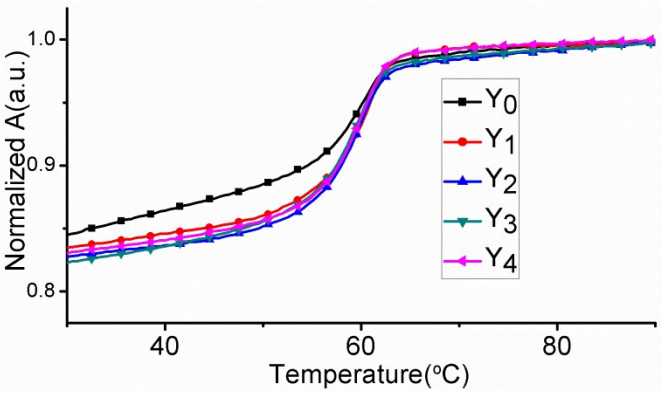


**Fig. S1 $T_m$ measurements of Y-DNA. UV melting experiments were carried out by monitoring the absorbance at 260 nm. The concentration of Y-DNA was 1.3 μM each.**

## Preparation of DNA dendrimers

In a typical experiment, $3\times2^{n-1}$ molar ratio $Y_n$ and 1 molar ratio $G_{n-1}$ ($n \geq 1$) were mixed together in phosphate buffer, after which the mixtures were kept at room temperature for one hour to prepare $G_n$. All assembled DNA dendrimers were characterized by gel electrophoresis and dynamic light scattering. Thermal denaturation curve of the prepared $G_4$ measured by UV indicated that the $T_m$ of $G_4$ was about 65°C (Fig. S2).

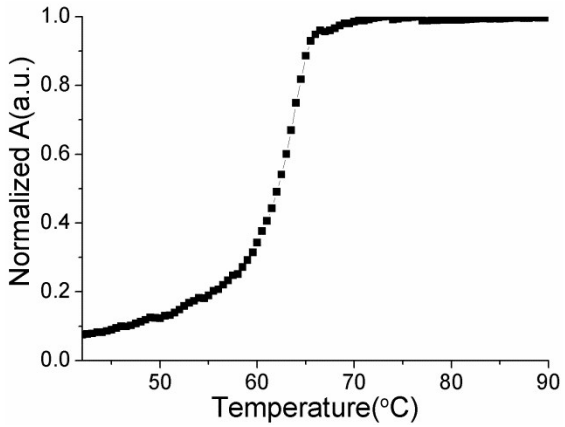


**Fig. S2 $T_m$ measurements of DNA dendrimer ($G_4$)**

## Synthesis of lipoic acid modified DNA

3'-lipoic acid modified single strand DNA (ssDNA) were prepared and purified according to the published method.[1] In brief, 3'-amine modified DNA ($cY_n$) and lipoic acid ester were

mixed at a molar ratio of more than 200:1 in acetic acid-triethylamine (TEAA) buffer. Then the solution was incubated at room temperature over 10 hrs. The resulting product (lipoic acid modified $cY_n$, named LA-$cY_n$) was purified using reverse-phase HPLC (ACN/TEAA, 20:1 → ACN/TEAA, 4:1).

## Preparation of DNA monofunctionalized AuNPs

First, lipoic acid modified DNA ($cY_n$-LA) were conjugated with extension strands (EXT-$Y_n$) to increase the length of DNA. Then these partially complementary DNA were added to 5 nm gold nanoparticles stabilized by BSPP, and the mixtures were incubated at room temperature for 2 hrs. The desired DNA/gold conjugates were isolated from agarose gels, after which the EXT strands were removed by adding excessive complementary strands cEXT-$Y_n$.[2]

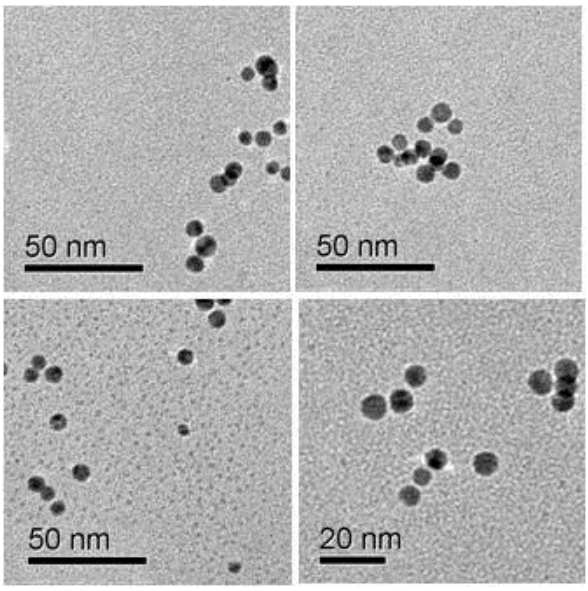


**Fig. S3 TEM images of AuNPs assemblies directed by $G_0$**

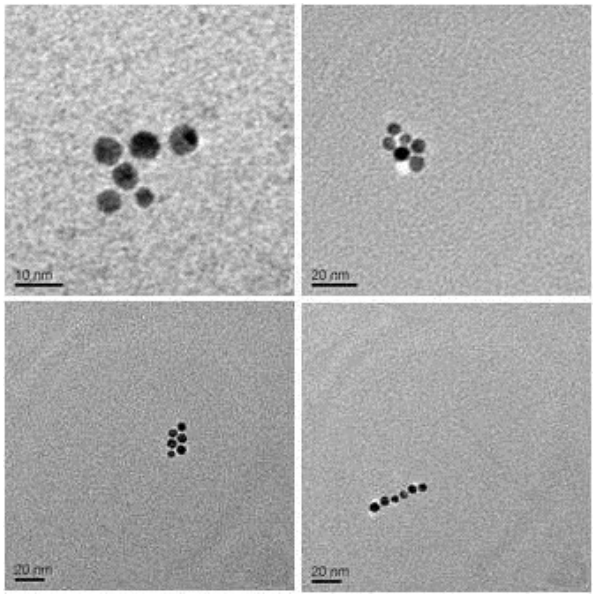


**Fig. S4 TEM images of AuNPs assemblies directed by $G_1$**

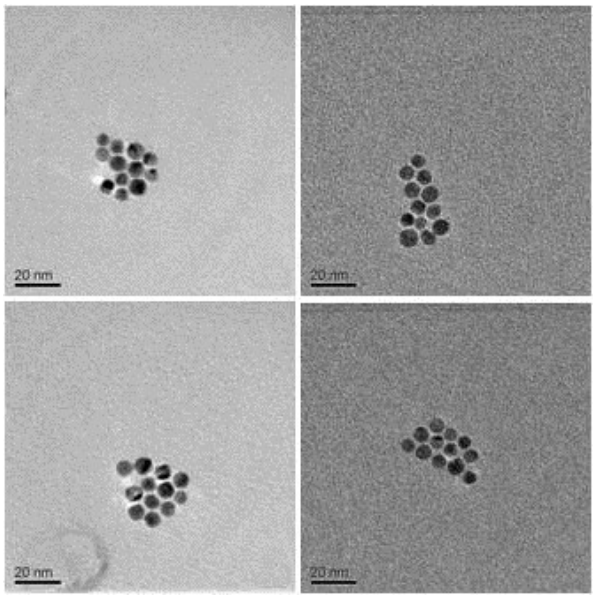


**Fig. S5 TEM images of AuNPs assemblies directed by $G_2$**

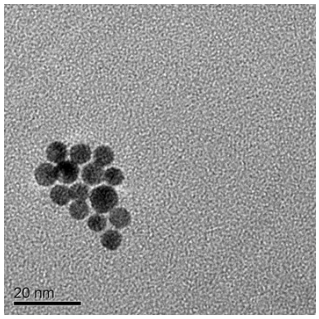


**Fig. S6 TEM images of AuNPs assemblies directed by $G_3$**

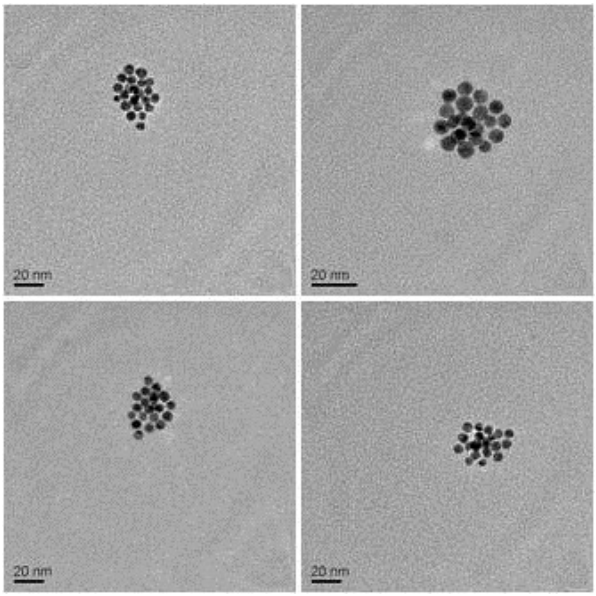


**Fig. S7 TEM images of AuNPs assemblies directed by $G_4$**

## References

[1] Zhang, T., et al. A New Strategy Improves Assembly Efficiency of DNA Mono-Modified Gold Nanoparticles. *Chem. Commun.*, **2011**(20): 5774-5776.

[2] Aldaye, F.A., et al. Dynamic DNA Templates for Discrete Gold Nanoparticle Assemblies: Control of Geometry, Modularity, Write/Erase and Structural Switching. *J. Am. Chem. Soc.*, **2007**(14): 4130-4131.