Supplementary information

Electrostatic interaction driven gold nanoparticle assembly on three-dimensional triangular pyramid DNA nanostructures

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Scheme S1. Schematic drawing of X-shaped DNA (X-DNA) structures and oligonucleotide sequences[#] of the X-DNA building blocks for the trigonal-pyramid DNA nanostructure.[##]

Building block	Strand	Segment 1	Segment 2
X_1	X_{11} X_{12} X_{13} X_{14}	5'-$(GT)_{20}$ **5'-Phos-TGA CCC TT** **5'-Phos-ATC GGT AT** **5'-Phos-GCA TCT GG**	CGA CCG ATG AAT AGC GGT CAG ATC CGT ACC TAC TCG CGA GTA GGT ACG GAT CTG CGT ATT GCG AAC GAC TCG CGA GTC GTT CGC AAT ACG GCT GTA CGT ATG GTC TCG CGA GAC CAT ACG TAC AGC ACC GCT ATT CAT CGG TCG
X_2	X_{21} X_{22} X_{23} X_{24}	5'-$(T)_{40}$ **5'-Phos-TTG CAC CT** **5'-Phos-GGA TCA TC** **5'-Phos-AAG GGT CA**	CGA CCG ATG AAT AGC GGT CAG ATC CGT ACC TAC TCG CGA GTA GGT ACG GAT CTG CGT ATT GCG AAC GAC TCG CGA GTC GTT CGC AAT ACG GCT GTA CGT ATG GTC TCG CGA GAC CAT ACG TAC AGC ACC GCT ATT CAT CGG TCG
X_3	X_{31} X_{32} X_{33} X_{34}	5'-$(AT)_{20}$ **5'-Phos-CTG TTG GA** **5'-Phos-ATA CCG AT** **5'-Phos-AGG TGC AA**	CGA CCG ATG AAT AGC GGT CAG ATC CGT ACC TAC TCG CGA GTA GGT ACG GAT CTG CGT ATT GCG AAC GAC TCG CGA GTC GTT CGC AAT ACG GCT GTA CGT ATG GTC TCG CGA GAC CAT ACG TAC AGC ACC GCT ATT CAT CGG TCG
X_4	X_{41} X_{42} X_{43} X_{44}	5'-$(GA)_{20}$ **5'-Phos-CCA GAT GC** **5'-Phos-GAT GAT CC** **5'-Phos-TCC AAC AG**	CGA CCG ATG AAT AGC GGT CAG ATC CGT ACC TAC TCG CGA GTA GGT ACG GAT CTG CGT ATT GCG AAC GAC TCG CGA GTC GTT CGC AAT ACG GCT GTA CGT ATG GTC TCG CGA GAC CAT ACG TAC AGC ACC GCT ATT CAT CGG TCG

[#] Same color sequences represents the complementary sequences between each other.

[##] 5'-Phos represents the phosphorylated 5' end of the oligonucleotide

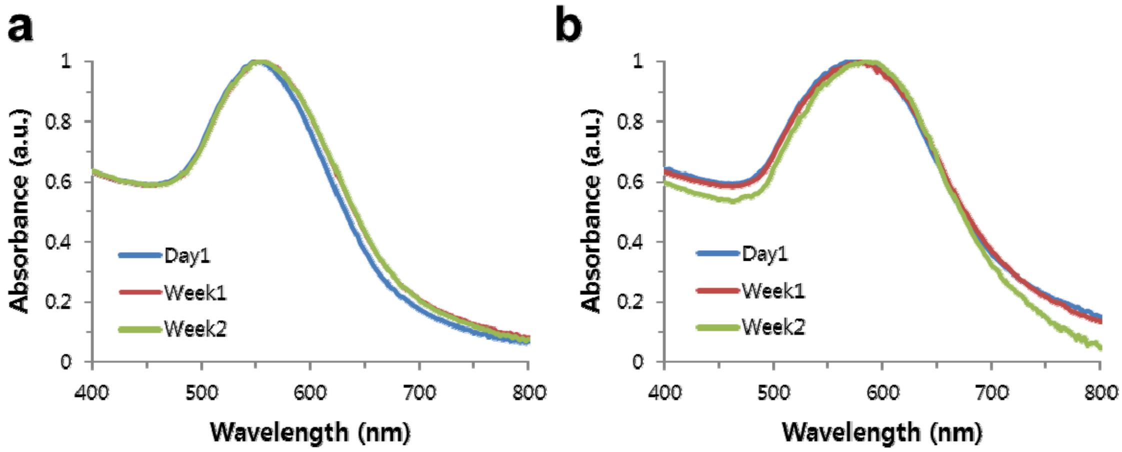
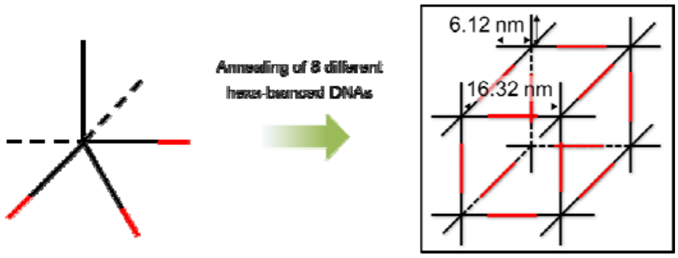


Figure s1. Colloidal stability of TANAs at a time of day 1, week 1 and week 2 after mixing the DNA structures and AuNPs. (a) Absorption spectrum of TANA obtained by mixing TP-DNA and AuNP in a ratio of 1:1, (b) Absorption spectrum of TANA obtained by mixing TP-DNA and AuNP in a ratio of 1:2.

Scheme S2. Schematic drawing of hexa-branched DNAs which have three partially complementary sticky ends (red letters) and other three non-complementary free ends (black letters) and oligonucleotide sequences of the hexa-DNA building blocks for the DNA cubic.



Building block	Strand	Segment 1	Segment 2
H_1	H_{11}	5'-CTA ATC CGC ACA	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{12}	5'-TAT CGA CCA TGC	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{13}	5'-ATG GCA ACT ATA	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{14}	5'-Phos-GCT AGA GTC GTT	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{15}	5'-Phos-ACC TTA GAC TCT	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{16}	5'-Phos-TTC GTA TGG ACA	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_2	H_{21}	5'-TTC CTC ATG CGA	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{22}	5'-AGC CTT GTA ACT	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{23}	5'-Phos-AGA GTC TAA GGT	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{24}	5'-Phos-GGT AAC ATT CCG	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{25}	5'-CGG TTA CGA TTC	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{26}	5'-Phos-ATT CGC TAC TCA	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_3	H_{31}	5'-GGT AAC TAC TGT	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{32}	5'-Phos-CGG AAT GTT ACC	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{33}	5'-Phos-ATT GCC AGT TAG	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{34}	5'-CTA TTC GGT CAA	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{35}	5'-AAT TGC CTA GGT	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{36}	5'-Phos-GTT AGC GAA ACT	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_4	H_{41}	5'-CGG TTT CTA ACG	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{42}	5'-Phos-AAC GAC TCT AGC	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{43}	5'-ATT GGC TAC TCA	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{44}	5'-CCT AAG TTT CGA	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{45}	5'-Phos-CTA ACT GGC AAT	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{46}	5'-Phos-TTG TCC TAA TCG	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_5	H_{51}	5'-Phos-TGT CCA TAC GAA	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{52}	5'-ATT GAC CAG ACG	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{53}	5'-AAG TGG ATT ACC	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{54}	5'-Phos-GGT AAT CTC AAG	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{55}	5'-Phos-TCT TGC ATG GCA	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{56}	5'-AGT AAC TGC GTT	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_6	H_{61}	5'-Phos-TGA GTA GCG AAT	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{62}	5'-CGT TGA ATC CTA	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{63}	5'-Phos-TGC CAT GCA AGA	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{64}	5'-Phos-ATT CGT AGA CTC	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{65}	5'-GTT ACC ATA ACG	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{66}	5'-TTT GCG ATC TAC	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_7	H_{71}	5'-Phos-AGT TTC GCT AAC	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{72}	5'-Phos-GAG TCT ACG AAT	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{73}	5'-Phos-CCT ATG AAC GTT	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{74}	5'-AAG GAT CGG TAT	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{75}	5'-CTA AGG TTT CAC	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{76}	5'-TTA GTT CCG ATC	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA
H_8	H_{81}	5'-Phos-CGA TTA GGA CAA	TCG CTG ACG TTG CAG ACA TCA CGT TGA CGC TGT CGA
	H_{82}	5'-Phos-CTT GAG ATT ACC	TCG ACA GCG TCA ACG TGA AAC GTG AAG CGT CTG CGA
	H_{83}	5'-AGC CAA ATG GTT	TCG CAG ACG CTT CAC GTT GAG CAC AGA CGT TGA CGA
	H_{84}	5'-GCT TTC CAT AGA	TCG TCA ACG TCT GTG CTC GCA GCG TCT TAA CGT CGA
	H_{85}	5'-Phos-AAC GTT CAT AGG	TCG ACG TTA AGA CGC TGC AGA CGT TCA GGA CTA CGA
	H_{86}	5'-TTG ACC TAA GGA	TCG TAG TCC TGA ACG TCT TGT CTG CAA CGT CAG CGA

Experimental details

General. DNA materials were purchased from IDT and used without further purification. Water was triply distilled using a Millipore filtration system. Solutions of $HAuCl_4$ and NaBH4 were freshly prepared in distilled water.

Synthesis of DNA nanostructures. Triangular DNA structure has been synthesized by hybridization of four X-shaped DNA followed by ligation. X-shaped DNAs have been fabricated by mixing equimolar amount of four partially complementary oligonucleotide sequences dispersed in pH 8.0, 1xTE buffer(see Table in Scheme S1) followed by annealing step. The detailed procedure followed previous report.[1] Four X-shaped DNAs fabricated in separate tubes were mixed in equimolar amount. The mixture was incubated in 35^{o}C for 10 minutes and the temperature has been decreased to 16^{o}C by 1^{o}C in stepwise for every 5 minute. After completing the annealing, the buffer has been exchanged to DI water using Amicon centrifugal filter (3kD Mw cutoff). The hybridized DNA structures have been tightened by ligating X-DNAs. The ligation has been performed by adding 3 units of T4 DNA ligase to 1 nmole of total X-DNA amount at 16^{o}C for 8 hrs. The synthesized triangular DNA nanostructures have been concentrated using Amicon centrifugal filter and resuspended in DI water to have an appropriate concentration.

Preparation of the citric acid-capped gold nanoparticle. An aqueous solution of 99.999% hydrogen tetrachloroaurate hydrate (12.5 ml, 10 mM) was added to 250 ml D.I. water on a stirring hot plate. To the rapidly-stirred boiling solution, 7.5 ml of 50 mM aqueous solution of sodium citrate tribasic dihydrate was quickly added. The color of the solution changed from yellow to purple and finally became red within 5 min. The mixture was removed from heat when the solution had turned deep red and then cooled for 30 min at room temperature. After cooling, the reaction solution was dialyzed using Amicon ultra 100 kDa Mw cutoff centrifugal filters for purification.

Ligand exchange to the positive-charged gold nanoparticle. AuNP surface was dispersed in aqueous solution that contains lipoic acid derivative molecules with quaternary ammonium, which was reported previously, to enhance the colloidal stability and change the surface charge of AuNPs.[2] Lipoic acid-derived quaternary ammonium ion (1 ml, 10 mM) solution was mixed to 1 ml of 100 nM AuNP solution and stirred at room temperature. After 10 h, the reaction solution was dialysed three times using Amicon ultra 100 kDa Mw cutoff centrifugal filters for purification.

Assembly of AuNPs on a DNA pyramid. The complex has been made by simple mixing and incubation of positive-charged AuNPs and triangular DNA pyramid in a specific molar ratio at room temperature. The assembled complex of AuNPs and DNA nanostructures have been confirmed by measuring the plasmonic absorption peak shift using Agilent Technologies 8453 UV-Vis Spectrophotometer G1103A.

AFM imaging. All the Atomic Force Microscope (AFM) experiments were performed by tapping-mode XE-100 Park AFM system (Korea) with a liquid cell at room temperature. Silicon cantilevers (NSC36, Ti / Pt, 1 N/m) were utilized for imaging. The sample (5 µl) was adsorbed on a freshly cleaved mica plate pretreated with 1x Tris-acetate-EDTA (TAE) buffer for 5 min at room temperature and then washed three times with a buffer solution containing 1x TAE and 10mM $MgCl_2$.

Reference

1. N. Park, J. S. Kahn, E. J. Rice, M. R. Hartman, H. Funabashi, J. Xu, S. H. Um and D. Luo, *Nature protocols*, 2009, **4**, 1759-1770.

2. H. Jin, J. Nam, J. Park, S. Jung, K. Im, J. Hur, J. Park, J. Kim and S. Kim, *Chemical Communications*, 2011, **47**, 1758-1760.