Heterogeneous nanoclusters assembled by PNA-templated double-stranded DNA

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Supporting Information

Experimental Methods

AuNPs were purchased from Nanopartz Inc.. DNA oligonucleotides were purchased from Integrated DNA Technologies, Inc. as lyophilized powders. Unmodified DNA sequences were purified with standard desalting and thiol- and amino-modified DNA sequences were purified with HPLC. PNA-DNA chimera's were purchased from Bio-Synthesis Inc. as lyophilized powders. The chimeras were purified by HPLC. The sequences of all the strands used are listed in the supporting information.

AuNPs and QDs were functionalized with ssDNA as described in the literature.[3] For the fabrication of T-scaffolds, equal molar concentration of complementary ssDNA strands were first mixed in 0.1 M PBS with a finial DNA concentration of 1 μM. The mixture was then annealed at 80 ºC for overnight to make dsDNA, followed by adding equal molar of PNA-DNA chimera. The invasion was allowed at 50 ºC for at least overnight. For T-scaffold I, equal molar of two linker DNA strands were added and annealed at 50 ºC for 10 min and cooled to room temperature. Nanoparticle trimers and heterogeneous nanoclusters were synthesized by using diluted scaffold

solution (10 nM). After adding nanoparticles stoichiometrically, the solution was annealed at room temperature for at least 2 hr. All the samples were analyzed without further purification.

DLS measurements were performed on a Malvern Zetasizer ZS instrument. Samples for TEM images were prepared by placing drops of the aqueous solution containing DNA-functionalized AuNPs or assembled nanoclusters onto 400-mesh carbon-coated copper grids, followed by drying at room temperature for overnight before imaging. LR-TEM micrographs were collected using a JEOL 1300 transmission electron microscope operated at 120 kV. HR-TEM images were taken by a FEI Titan 80-300 environmental transmission electron microscope. Samples for SEM images were prepared on silicon wafers pre-treated in Piranha solution. The treated silicon wafers were dipped in 1 wt. % Poly(diallydimethylammonium chloride) solution with 0.5 M NaCl for 20 min, followed by washing with D.I. water. The samples were dried at room temperature for overnight before imaging. SEM images were taken using a Hitachi 4800 scanning electron microscope.

Sequences for the DNA (5‘ to 3‘) and PNA strands used in this study:

1.T-scaffold I:

100-b ssDNA A: CCA CCT ACC GTA GAC ACG GAC TCT CTA CGC GTT ATG CCT CAG CAT ATT GTT ATT ACT GCG GGA CAT ACG ATA GAG CTT TGC TAA AAT AAG TCC CTG CCT T.

200-b ssDNA B: ACG TAC CAA ATA CGT CGA TTG GCT ACG TAA TAA CAA TTT CTA TTG GTG GAA AGG CAG GGA CTT ATT TTA GCA AAG CTC TAT CGT ATG TCC CGC AGT AAT AAC AAT ATG CTG AGG CAT AAC GCG TAG AGA GTC CGT GTC TAC GGT

AGG TGG CCC ATT GGA AGA TTA ATA ACA ATG CGT TGA AGT GAG GGC CAG CTT GCG GA.

DNA Linker1: ACG TAT TTG GTA CGT TTT ATG AAG GTT AGG TTA.

DNA Linker2: ATG AAG GTT AGG TTA TTT TCC GCA AGC TGG CCC.

2.T-scaffold II:

200b ssDNA A: TCC GCA AGC TGG CCC TCA CTT CAA CGC TAC ACA TAC GAT CTT CCA ATG GGC CAC CTA CCG TAG ACA CGG ACT CTC TAC GCG TTA TGC CTC AGC ATA TTG TTA TTA CTG CGG GAC ATA CGA TAG AGC TTT GCT AAA ATA AGT CCC TGC CTT TCC ACC AAT AGA ATA CAC ATA CGC GTA GCC AAT CGA CGT ATT TGG TAC GT.

200b ssDNA B: ACG TAC CAA ATA CGT CGA TTG GCT ACG CGT ATG TGT ATT CTA TTG GTG GAA AGG CAG GGA CTT ATT TTA GCA AAG CTC TAT CGT ATG TCC CGC AGT AAT AAC AAT ATG CTG AGG CAT AAC GCG TAG AGA GTC CGT GTC TAC GGT AGG TGG CCC ATT GGA AGA TCG TAT GTG TAG CGT TGA AGT GAG GGC CAG CTT GCG GA.

3.PNA:

The PNA binding position in DNA is underlined above.

Sequence of the chimera for the middle site invasion on T-scaffold I and II: TAA TAA CAA T – linker –T_{15}-CAC ATC TCT TCT GAA.

Sequence of the chimera for the end site invasion on T-scaffold II: CGT ATG TGT A – linker – T_{15}-AGA ATG TCT AGC TGC.

The PNA is underlined and is written from N-C and the DNA is written from 5'-3'. The linker is: cysteine-SMCC-C6 amino.

4.Thiol-ssDNA on 30nm AuNPs: HS-T_{15}-TTC AGA AGA GAT GTG.

5.Thiol-ssDNA on 10nm AuNPs for T-scaffold I: HS-T_{15}-TAA CCT AAC CTT CAT.

6.Thiol-ssDNA on 10nm AuNPs for T-scaffold II: HS-T_{15}-GCA GCT AGA CAT TCT.

7.Amino-ssDNA on QDs: NH_2-T_{15}-TAA CCT AAC CTT CAT.

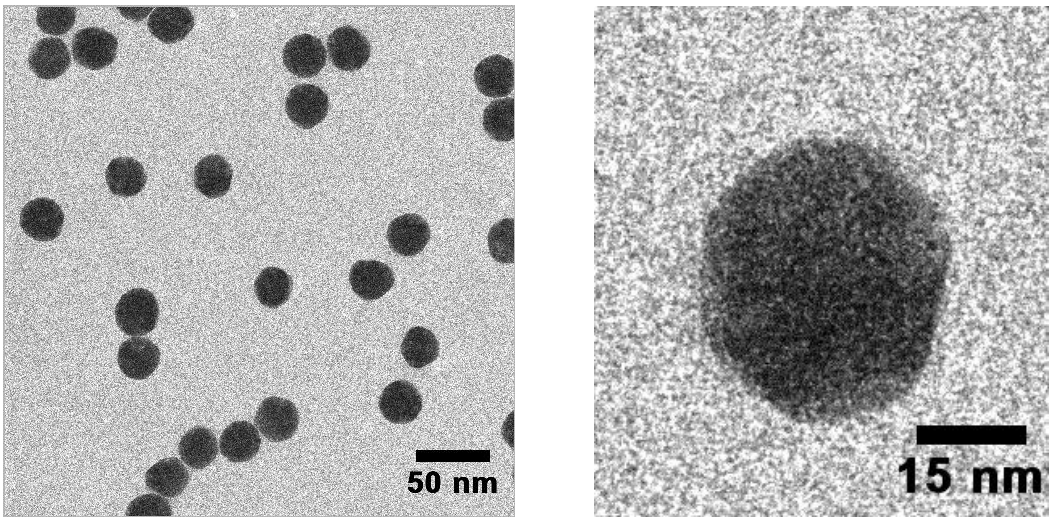

Fig. S1. LR-TEM images of the mixture of AuNPs and QDs without T scaffolds. There is no sign of the formation of core-shell structure as compared to Figure 5Ca and 5Cb. The LR-TEM images in Figure S1 and Figure 5Ca-b were taken under the same focusing condition.

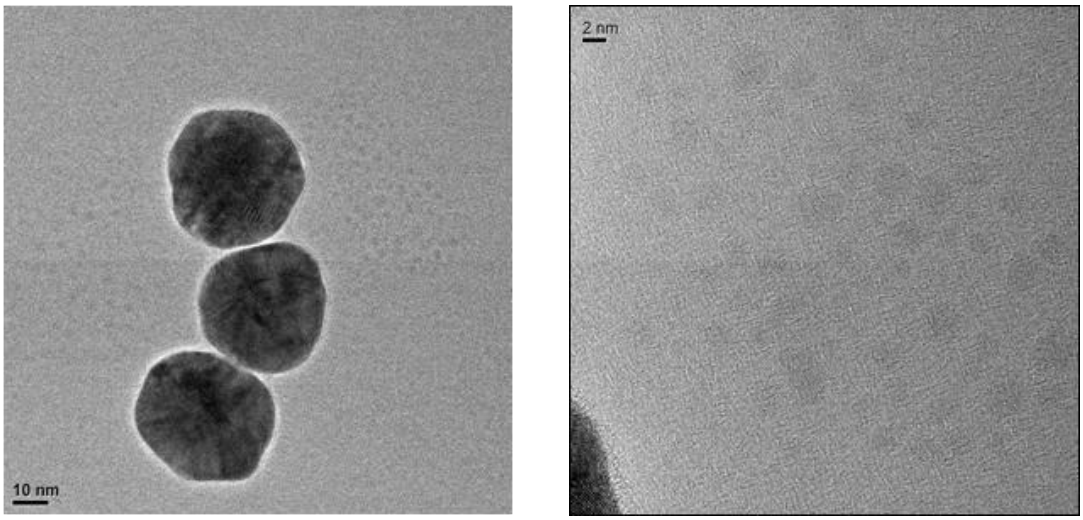

Fig. S2. HR-TEM images of the mixture of AuNPs and QDs without T scaffolds. There is no sign of the formation of core-shell structure as compared to Figure 5Cc and 5Cd.