Electronic Supplementary Information

Pt Supraparticles with Controllable DNA Valences for Programmed Nanoassembly

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Experimental details

Chemicals: Ascorbic acid (AA) was obtained from Bio Basic Inc. (BBI, Canada). $H_2PtCl_6 \cdot 6H_2O$, $NaBH_4$, citric acid, sodium acetate trihydrate, and magnesium acetate tetrahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium citrate tribasic dihydrate and Na_2PdCl_4 were purchased from Sigma. Bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP) was a product of Strem Chemicals, Inc. (Newburyport, MA, USA). All the reagents were used as received without further purification.

DNA sequences:

DNA oligonucleotides were custom-synthesized by Sangon Bioengineering Technology and Services Co., Ltd. (Shanghai, China) and purified by PAGE (unmodified DNA) or HPLC (thiolated DNA). The DNA oligos were subject to molecular weight verification by MALDI-TOF mass spectroscopy. Sequences of the DNA strands are listed as following. Underlined bases mark the hybridization parts during the assembly of nanoparticles.

(1) ssDNA (89 bases)

HS-5'GCAGTAACGCTATGTGACCGAGAAGGATTCGCATTTGTA***GTCTTGAGCCCGCACGAAACC TGGACACCCCTAAGCAACTCCGTATCAGA***3'

(2) ssDNAc (89 bases)

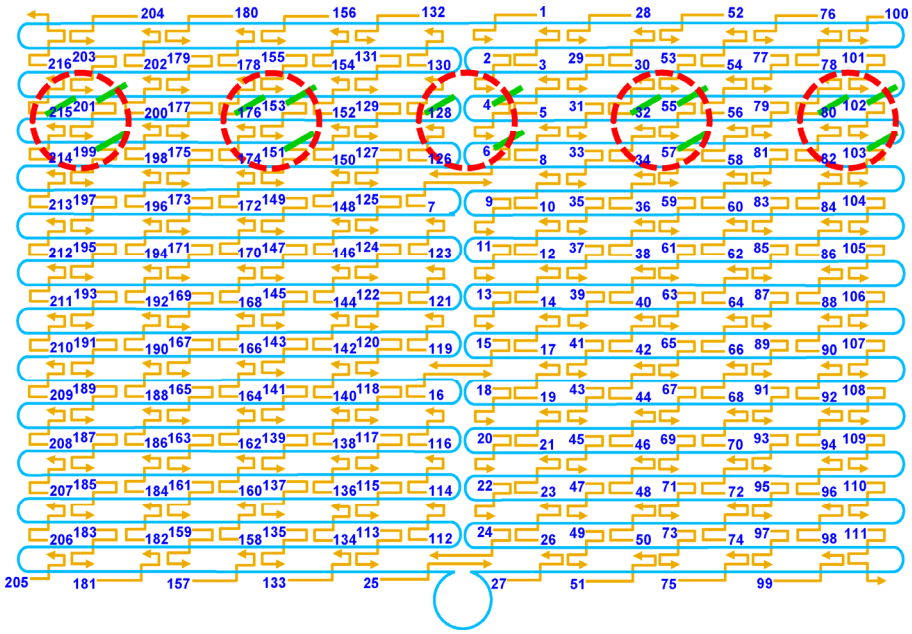
HS-5'GCAGTAACGCTATGTGACCGAGAAGGATTCGCATTTGTA***TCTGATACGGAGTTGCTTAGGG GTGTCCAGGTTTCGTGCGGGCTCAAGAC***3'

(3) LK-3s (the underlined polyT sequence will hybridize with the polyA tails on DNA origami):

5'***TTTTTTTTTTTTTT***GACCGAGAAGGATTCGCATTTGTATCTGATACGGAGTTGCTTAG3'SH

DNA origami:

Totally 216 helper strands were used to fold a circular single stranded M13 genome (New England Biolab) into a rectangular shape (shown below). These DNA oligonucleotides were custom-synthesized by Sangon Bioengineering Technology and Services Co., Ltd. (Shanghai, China). The red circles mark the positions of five PtSPs. The LK-3s strand used to functionalize the PtSPs has a polyT sequence complementary to the polyA tails (indicated as green bars) appended on selected helper strands. Each particle simultaneously hybridize with three polyA tails to achieve enhanced stability [*J. Am. Chem. Soc.*, 2010, **132**, 3248]. Sequences of the helper strands are available in literature [*Science*, 2008, **319**, 180].



The rectangular DNA origami was assembled following published procedures [*Science*, 2008, **319**, 180; *J. Am. Chem. Soc.*, 2013, **135**, 11441]. Briefly, 216 custom-synthesized staple strands were combined with a circular single-stranded M13mp18 genome in a 1×TAE/Mg^{2+} buffer containing 12.5 mM Mg^{2+}. 15 out of 216 staple strands in the origami structure (see the schematic drawing above) were appended with polyA tails for the capturing of PtSPs. Such a solution was first heated to 94°C and then slowly cooled to 20°C with the help of a PCR machine. The product was isolated by removing unassembled staple strands through ultrafiltration, with the resulting DNA origami stored at 4°C before use.

10/29/48/73 nm Pt supraparticles: The 10, 29, 48, and 73 nm (defined as the diameter of the external circular boundary of a particle, or the major axis of an ellipse boundary in the case of an elongated particle) Pt supraparticles were synthesized according to a published method [*Nano Lett.*, 2008, **8**, 4588]. Briefly, the stepwise syntheses of the PtSPs started with 3-4 nm PtNP seeds for the growth of 10 nm and 29 nm PtSPs. The 29 nm PtSPs were then used as seeds for the synthesis of 48 and 73 nm PtSPs. $NaBH_4$ was employed to reduce H_2PtCl_6 into the small PtNP seeds in the presence of citrate ligands. Ascorbic acid was the chemical reductant for the growth of PtSPs in various sizes. The concentrations of as obtained PtSPs were estimated based on the amounts of H_2PtCl_6 and the corresponding particle sizes measured by TEM. Such concentrations should be a little underestimated due to the lower apparent density of the porous supraparticles compared to a solid Pt metal.

Discrete DNA conjugation of 10 nm PtSPs: Thiolated single stranded DNA (i.e. ssDNA or ssDNAc) were combined with PtSPs at appropriate molar ratios in 0.5×TBE buffer (Tris, 44.5 mM; EDTA, 1 mM; boric acid, 44.5 mM; pH 8.0) supplemented with 40 mM NaCl. The conjugation reaction was conducted at 20°C for 3 hours. The products were loaded in a 3% agarose gel and run in 0.5×TBE buffer at 4°C with an electric field of 13 V/cm. Completely separated gel bands corresponding to PtSPs decorated with discrete numbers of DNA ligands were observed on the gel.

High density DNA modification of 29/ 48/ 73 nm PtSPs: ssDNAc was combined with 29, 48, and 73

nm PtSPs at 300:1, 400:1, and 500:1 molar ratios, respectively. NaCl was gradually introduced over 12 h to reach a final concentration of 140, 130, and 120 mM, respectively. The solutions were centrifuged twice at 6000, 4000, and 2000 rpm (for the 29-73 nm PtSPs, respectively) for 10 min to remove unbound DNA, and the precipitates of DNA-capped PtSPs were redispersed in 0.5×TBE plus 40 mM NaCl.

High density DNA modification of 10 nm PtSPs: DNA LK-3s was combined with 10 nm PtSPs at a 200:1 molar ratio. NaCl was gradually introduced over 12 h to reach a final concentration of 200 mM. The solution was centrifuged twice at 16200 g for 20 min to remove unbound DNA. The precipitates containing LK-3s-decorated Pt supraparticles were redispersed in 1×TAE/Mg^{2+} buffer (Tris, 40 mM; acetic acid, 20 mM; EDTA, 2 mM; and magnesium acetate, 12.5 mM; pH 8.0) for further use.

Dimeric assembly of 10 nm PtSPs: The as-obtained ssDNA- and ssDNAc-monoconjugated 10 nm PtSPs were mixed at a 1:1 molar ratio and incubated in 0.5×TBE plus 40 mM NaCl for 6 h. 3% agarose gel electrophoresis run at 4°C was employed to isolate the dimeric assemblies.

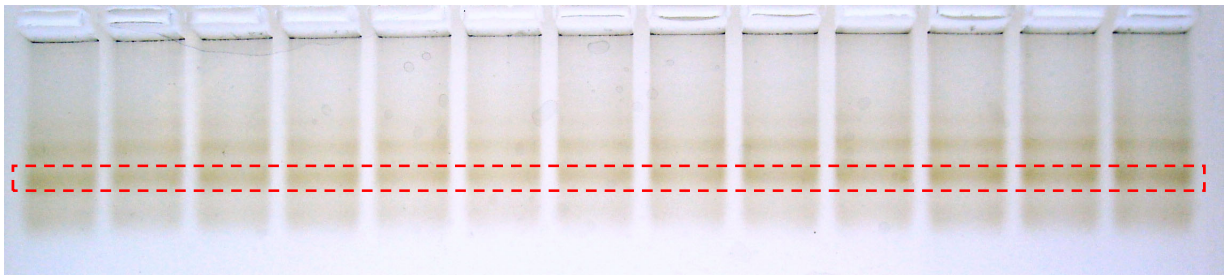
Core-satellite assembly: As-obtained ssDNA-monoconjugates of 10 nm PtSPs were mixed with 29, 48, and 73 nm PtSPs (decorated with a high density of ssDNAc) at appropriate ratios and incubated in 0.5×TBE plus 40 mM NaCl for 12 h, respectively. Agarose gel electrophoresis was used for the characterization and isolation of the assembled core-satellite structures.

10 nm PtSP linear arrays assembled on DNA origami: As-obtained 10 nm PtSPs bearing a high density of LK-3s DNA were mixed in a large excess with the DNA origami template in 1×TAE/Mg^{2+} buffer. The temperature of the sample was cycled between 45°C and 30°C in a PCR machine and finally decreased to 4°C by storing the sample in a fridge. During the cycling, the temperature decreased at a rate of 1°C per 10 min from 45°C to 30°C. Such a cycling was repeated four times before the final cooling to 4°C. 1% agarose gel electrophoresis was employed to isolate correctly assembled PtSP-origami hybrids.

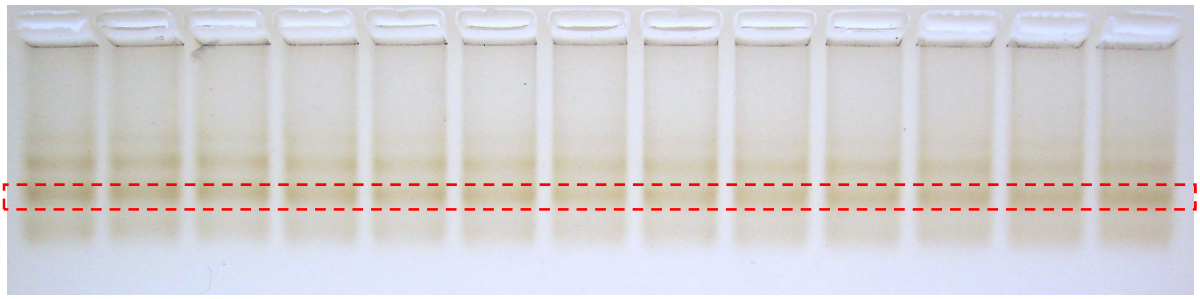
TEM imaging: TEM imaging was conducted on Hitachi H-7650 and JEOL-2010 transmission electron microscopes operated at an acceleration voltage of 100 kV and 200 kV, respectively. Samples were deposited on carbon coated copper grids for TEM observations.

AFM imaging: The DNA origami sample was imaged by a Nanofirst-3000 (Shanghai Haizisi Optical-Electronics Co., Ltd., China) atomic force microscope (AFM) operated in tapping mode using a MikroMasch NSC11 tip. The DNA sample was deposited on a freshly cleaved mica surface. The mica substrate was then washed by water to remove buffer salts and dried in air before AFM imaging.

Figure S1. 3% agarose gel electrophoretic isolations of ssDNA- and ssDNAc-monoconjugated 10 nm PtSPs (see marked bands). The samples were prepared in 0.5×TBE plus 0.04M NaCl, with a molar ratio of 15:1 between DNA and PtSPs. The lanes on the same gel represent different divided parts of the same sample.

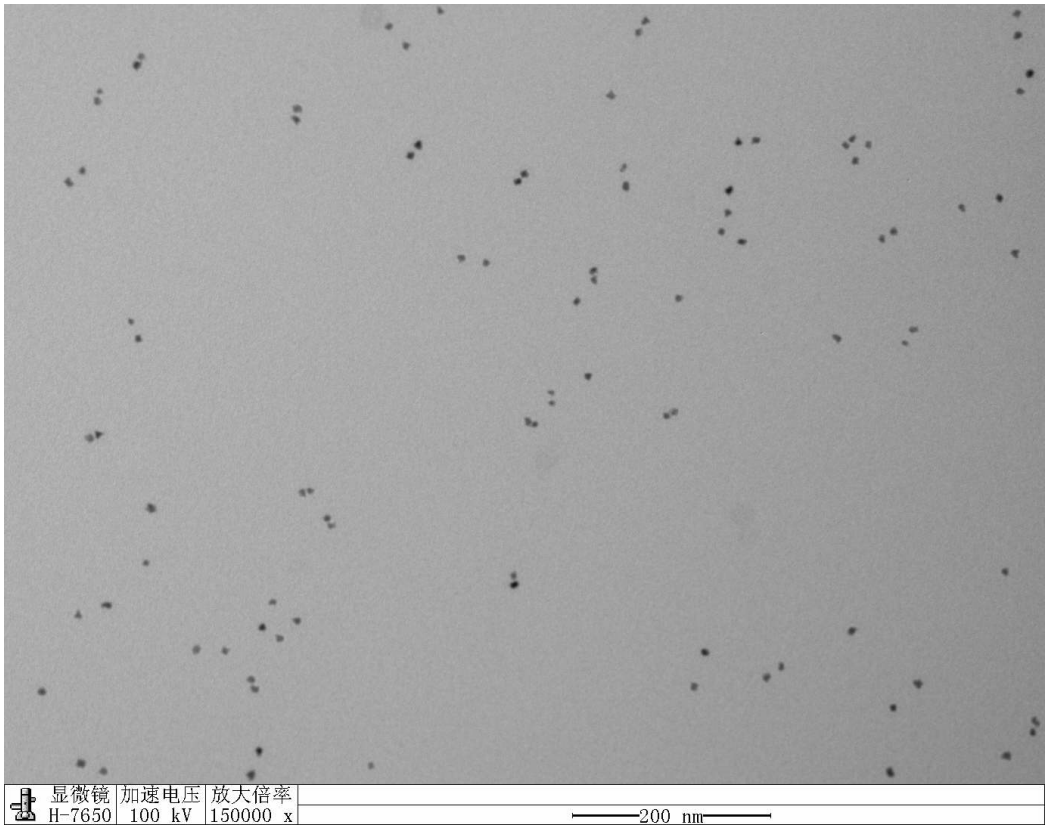


ssDNA-conjugated 10 nm PtSPs



ssDNAc-conjugated 10 nm PtSPs

Figure S2. Large area TEM images showing a high yield assembly of 10 nm PtSP dimers. About 86% of all observed particles are in the form of a dimer based on the TEM images.



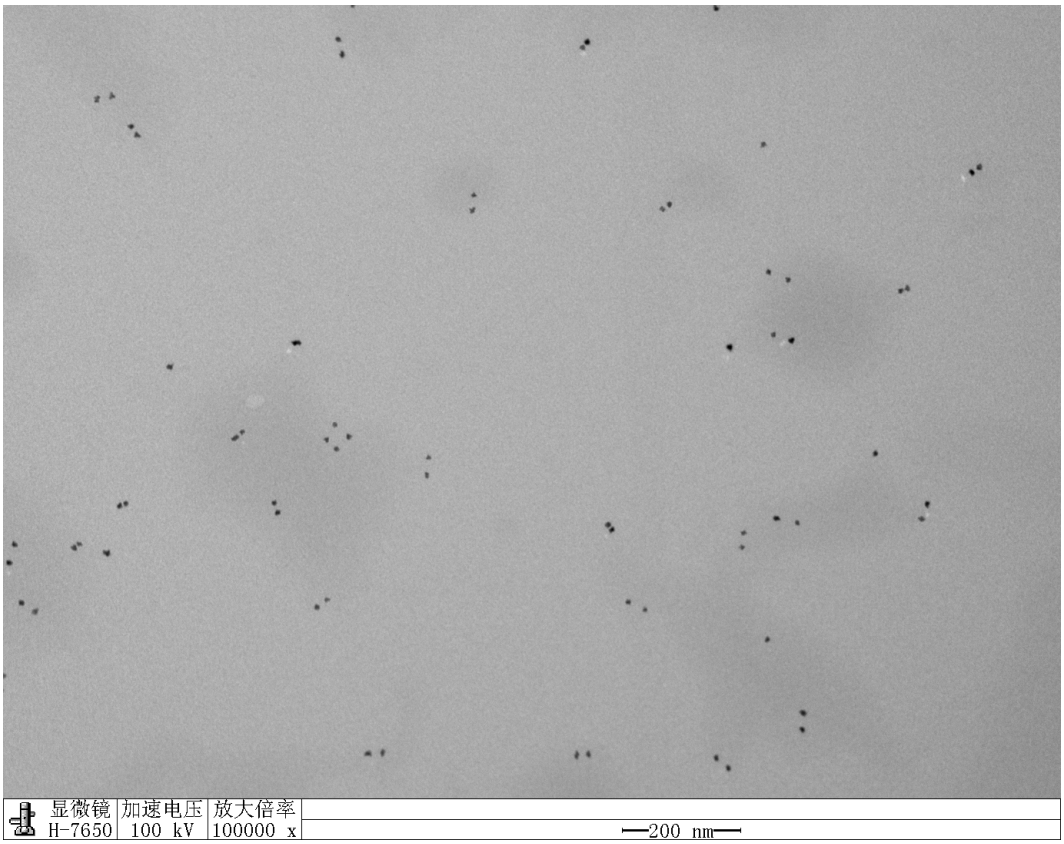


Figure S3-1. 1% Agarose gel electrophoresis showing the retarded mobilities of 29 nm PtSPs after DNA decoration and the assembly with DNA-monofunctionalized 10 nm PtSPs.

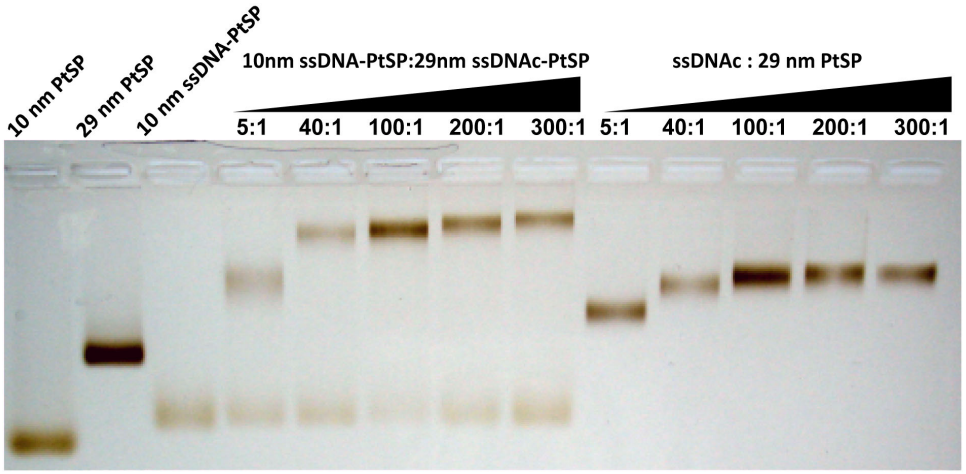


Figure S3-2. 0.8% Agarose gel electrophoresis showing the retarded mobilities of 48 nm PtSPs after DNA decoration and the assembly with DNA-monofunctionalized 10 nm PtSPs.

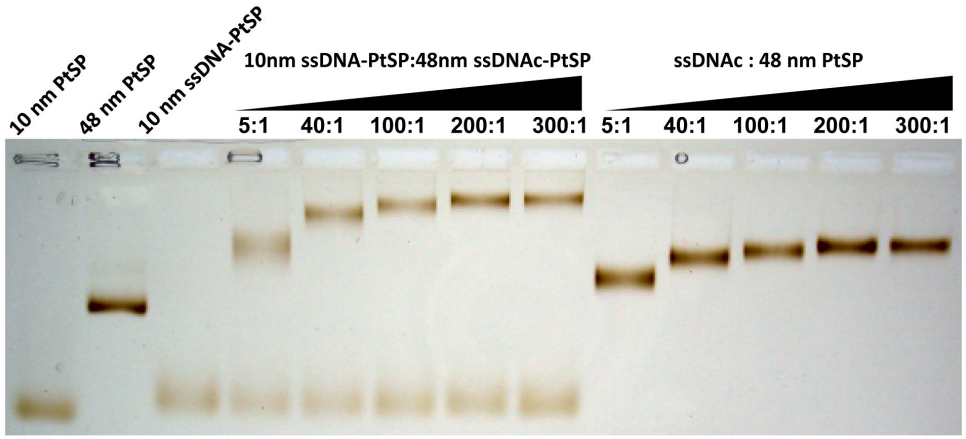


Figure S3-3. 0.6% Agarose gel electrophoresis showing the retarded mobilities of 73 nm PtSPs after DNA decoration and the assembly with DNA-monofunctionalized 10 nm PtSPs.

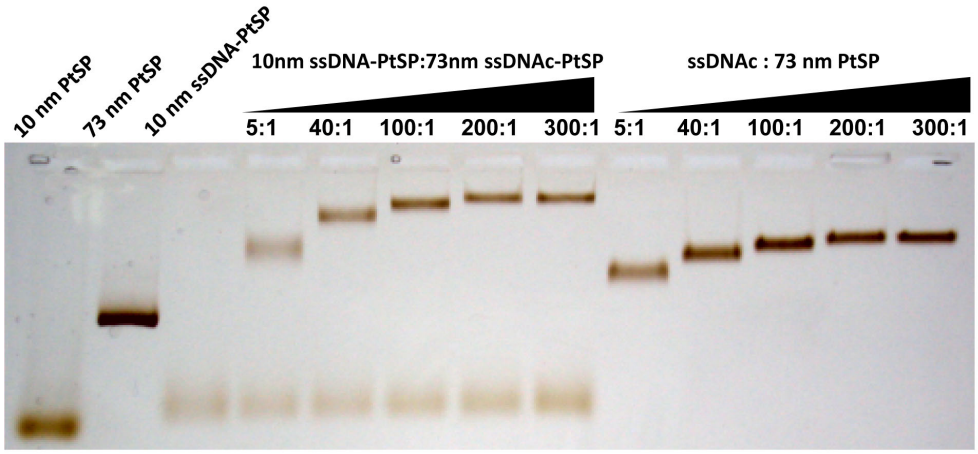


Figure S4-1. A large area TEM image showing as-assembled core-satellite structures each containing a 29 nm PtSP core and multiple 10 nm PtSP satellites.

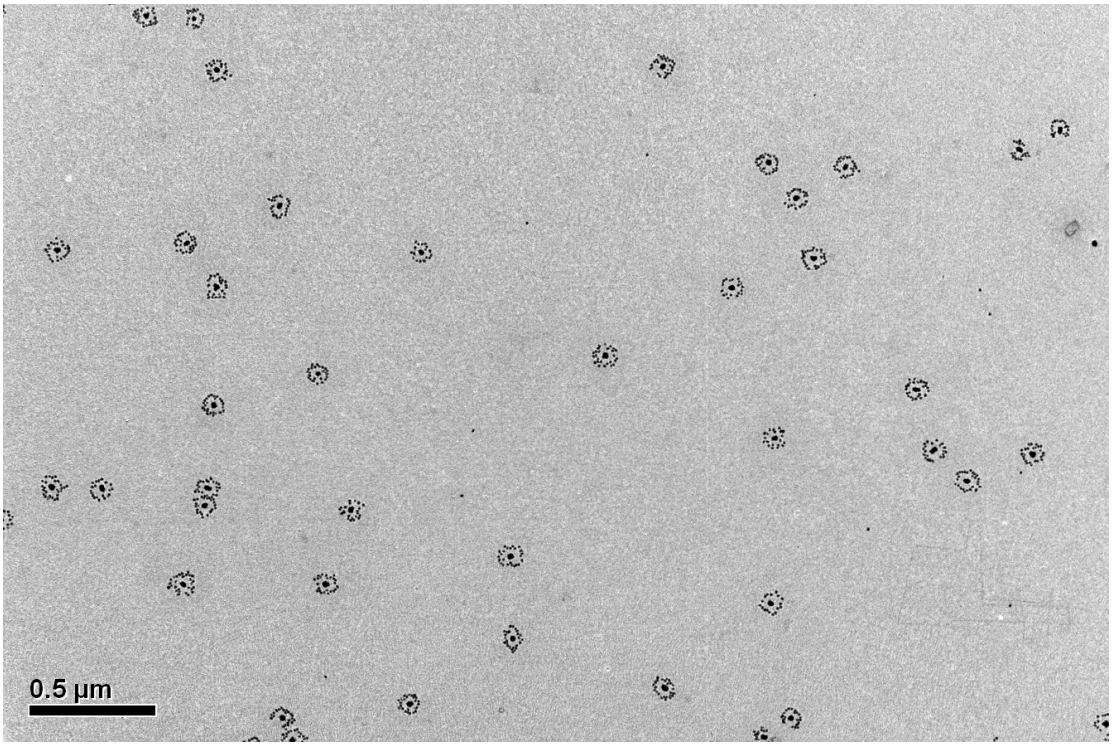


Figure S4-2. A large area TEM image showing as-assembled core-satellite structures each containing a 48 nm PtSP core and multiple 10 nm PtSP satellites.

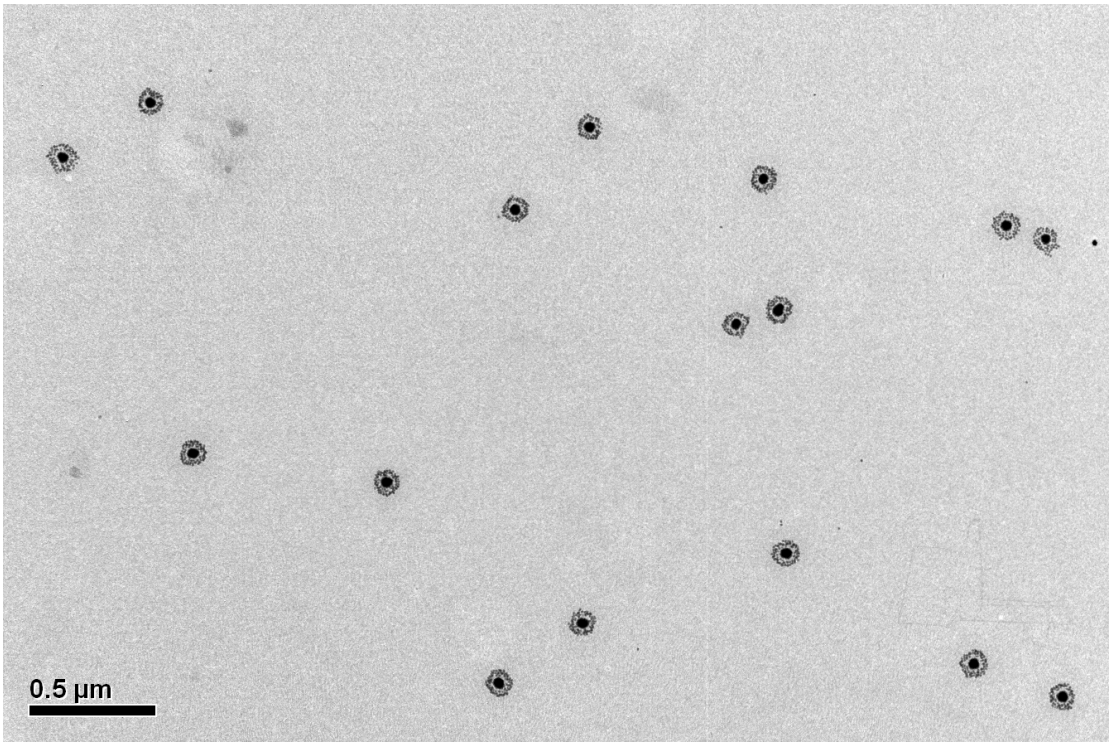


Figure S4-3. A large area TEM image showing as-assembled core-satellite structures each containing a 73 nm PtSP core and multiple 10 nm PtSP satellites.

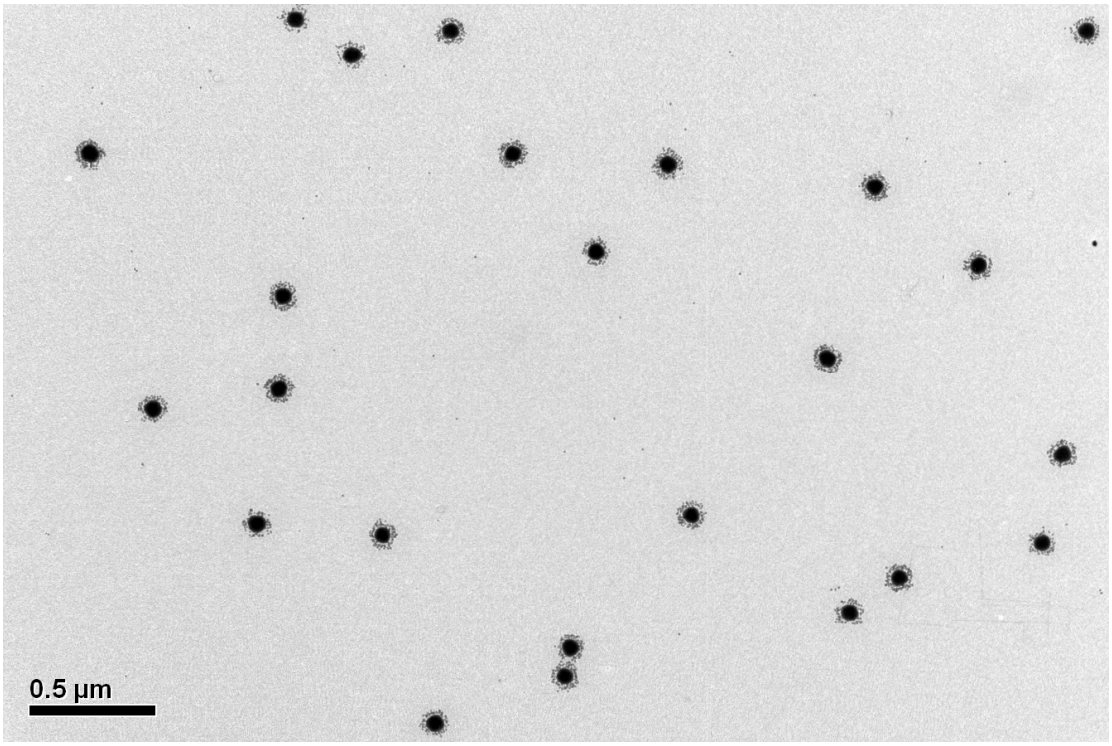


Figure S5. Atomic force microscopy (AFM) images of a rectangular DNA origami in low and high magnifications.

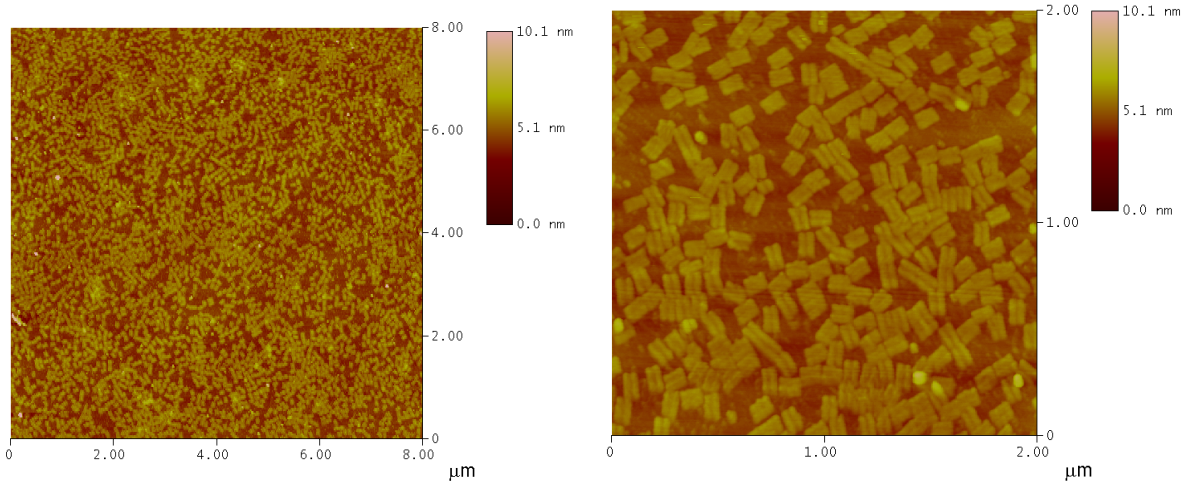


Figure S6. A large area TEM image showing 10 nm PtSP linear arrays assembled on rectangular DNA origami nanosheets. The origami structures are not visible under TEM due to their very low electron-scattering ability. Inset is a statistic chart reflecting the particle numbers in the assemblies. About 4.6 particles in average were found in each assembly.

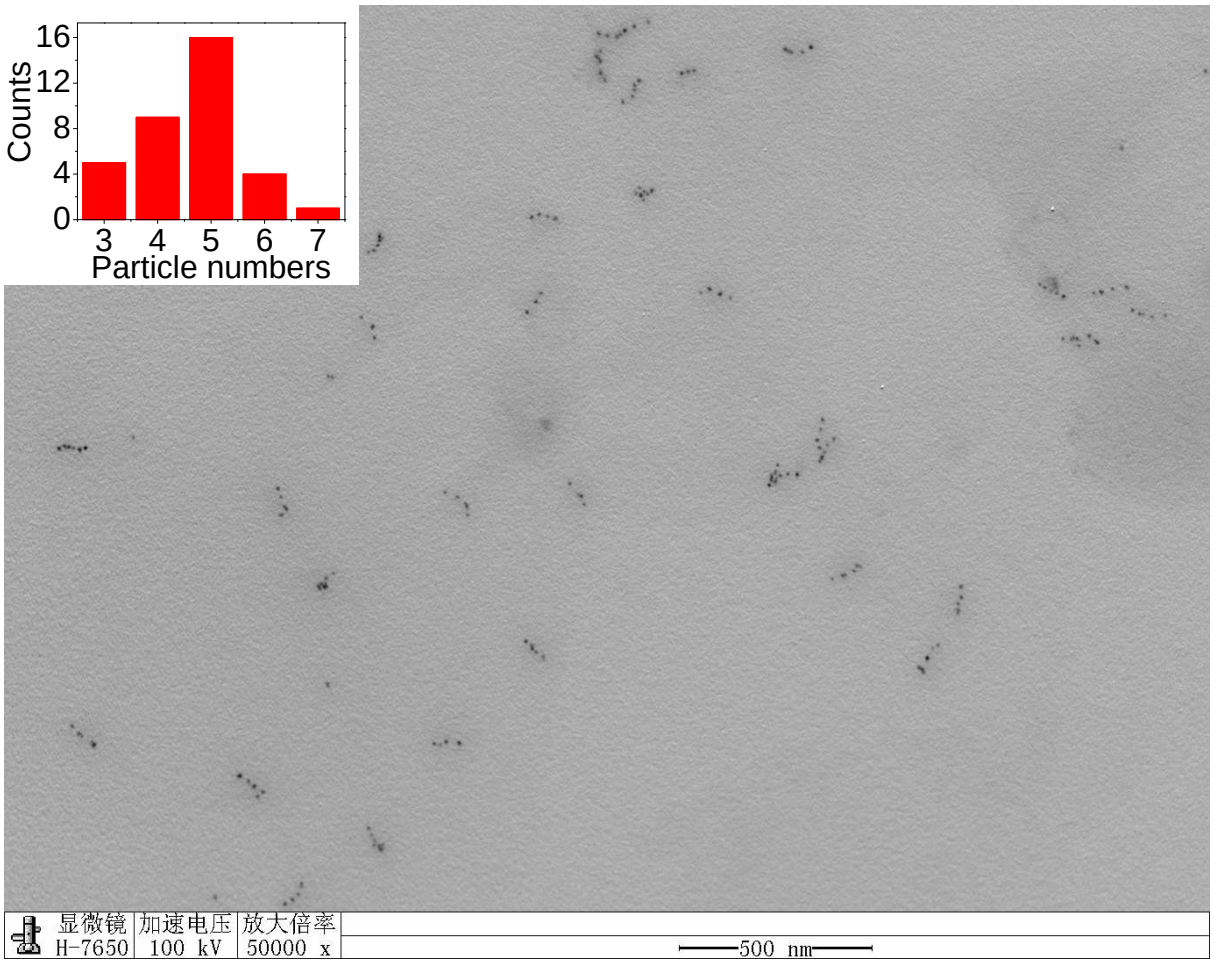
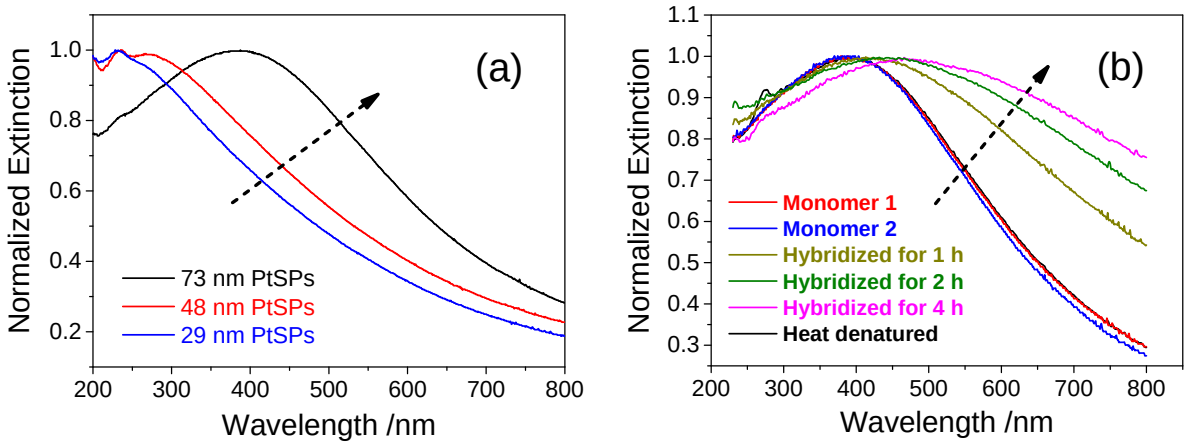


Figure S7. Plasmonic optical properties of PtSPs with different diameters and assembly sizes. The results show a clear size-dependence of plasmonic resonance wavelengths of the PtSPs (a) and their assembly-induced spectral shifts due to inter-particle plasmonic coupling (b). The formation of visible aggregates of 73 nm PtSPs by DNA hybridization and their reversible disruption by thermal denaturing are also observed (c). PtSP-1 (monomer 1) and PtSP-2 (monomer 2) represent 73 nm PtSPs decorated with complementary ssDNAc and ssDNA sequences, which are able to form DNA-directed PtSP aggregates upon hybridization.



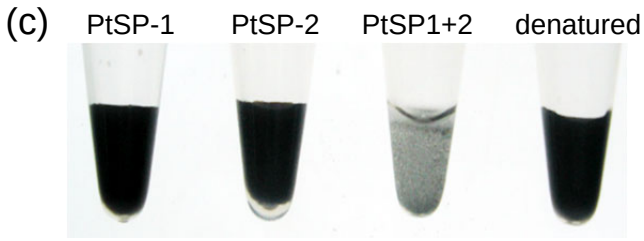


Figure S8. Catalytic characterizations of PtSPs with different surface functionalities through metal-catalyzed hydrogenation of 4-nitrophenol by $NaBH_4$. (a) 29 nm PtSPs capped by citrate, BSPP, and ssDNAc (the labelled DNA ratios are those used during DNA functionalization steps); (b) 26.5 nm AuNPs with different surface functionalities; (c) Absorbance spectra of nitrophenolate ion during its catalytic conversion to aminophenolate catalyzed by citrate-capped 29 nm PtSPs; (d) Kinetic analyses based on (a) and (b) showing much more dramatic decreases of catalytic activities (apparent rate constant, k_{app}) for the AuNPs after a surface stabilization by BSPP, indicating a much easier loss of their surface activity compared to PtSPs. DNA-L and DNA-H represent the Au and Pt particles with low and high DNA coverages, respectively. These data also indicate that a low DNA coverage is required to maximally maintain a catalytic activity where a monovalent DNA conjugate produced in this work will be most preferred.