Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Pt Nanoparticles Decorated with a Discrete Number of DNA Molecules for Programmable Assembly of Au/Pt Bimetallic Superstructures

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Experimental section

1. Materials and Chemicals

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). All DNA oligos were subject to a molecular weight verification by MALDI-TOF mass spectroscopy. The purities of the DNA oligos were checked by PAGE before use.

Following are the sequences (5'-3') of the DNA oligonucleotides used in this work.

S strand (24 bases):

HS-$(CH_2)_6$-TTTTTTTTTTGCGCGAACCGTATA

ss55 strand:(55 bases):

HS-$(CH_2)_6$-TTACTGACATGAAGCCGGATATAGATTCTGGAGCGATCGTCCTCCTTGAAGCTAG

L1 strand (48 bases):

CTATATCCGGCTTCATGTCAGTAATATACGGTTCGCGCAAAAAAAAAA-$(CH_2)_3$-SH

L2 strand (48 bases):

TTACTGACATGAAGCCGGATATAGTATACGGTTCGCGCAAAAAAAAAA

L3 strand (37 bases):

TCTATCCTACGCTTATACGGTTCGCGCAAAAAAAAAA

L4 strand (31 bases):

CTACGCTTATACGGTTCGCGCAAAAAAAAAA

L5 strand (24 bases):

TATACGGTTCGCGCAAAAAAAAAA

Chemicals: Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), hexachloroplatinic(IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), sodium borohydride ($NaBH_4$), sodium acetate (NaAc, anhydrous), tannic acid ($C_{76}H_{52}O_{46}$) and potassium carbonate (K_2CO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethylenediamine tetraacetic acid disodium salt ($EDTA \cdot Na_2$) was obtained from Sangon Bioengineering Technology and Services Co., Ltd. (Shanghai, China). Agarose, sodium chloride, boric acid, and tris(hydroxymethyl) aminomethane (Tris) were from Bio Basic Inc. (BBI, Canada). Sodium citrate tribasic dihydrate was purchased from Sigma. Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP) was a product of Strem Chemical (Newburyport, MA, USA).

2. Synthesis of AuNPs and PtNPs

5 nm AuNPs: 5 nm AuNPs were synthesized by a citrate-tannic acid method following published procedures.[S1,S2] Ligand exchange with bis(*p*-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP) was performed after the synthesis to increase the stability of as-synthesized gold nanoparticles (see references 6a and 6b in the main text for a detailed process).

13 nm AuNPs: 13 nm AuNPs were synthesized by a citrate method following the literature.[S1,S3] Ligand exchange with BSPP was similarly conducted as the 5 nm AuNPs.

3 nm PtNPs: PtNPs with a diameter of 3 nm were synthesized on the basis of a previously reported method with slight modifications.[S4,S5] Briefly, 100 μL of 200 mM aqueous H_2PtCl_6 solution was added to 10 mL of 1.2 mM trisodium citrate solution. 360 μL of 200 mM aqueous $NaBH_4$ solution was added dropwise to the above solution in an ice-water bath under vigorous stirring. After a further stirring for 30 min, 20 mg BSPP was introduced to start an

overnight ligand-exchange reaction with the citrate-capped PtNPs. The resulting solution was centrifuged at 21500 g for 3~5 hr. The PtNP precipitates were redispersed in doubly distilled H_2O (ddH_2O) containing 2 mg/mL BSPP to get concentrated PtNPs capped by BSPP.

Determination of the molar extinction coefficient of PtNPs

The molar extinction coefficient of PtNPs was determined following a literature work.[S6] The as-prepared PtNPs were centrifuged at 21500 g for 3 hours to remove unreacted H_2PtCl_6. The resulting pellet containing PtNPs was redispersed in ddH_2O. The resulting solution was divided into two parts. One part was measured for its optical absorbance spectrum, and the other part was subject to ICP-AES quantitation of platinum. The mass concentration of the PtNPs determined by ICP-AES was converted to a molar concentration according to the average size (3 nm) of the PtNPs (see Figure S4) and the density of bulk Pt metal. Since PtNPs did not show an absorption peak in the range of 400-800 nm, we tentatively used their absorbance value at 500 nm to calculate the molar extinction coefficient of as-synthesized PtNPs ($\varepsilon_{500nm} = 1.6\times10^6\ M^{-1}cm^{-1}$). The 500 nm wavelength was chosen to avoid any UV absorbance from DNA and other capping molecules such as BSPP.

DNA conjugation of 5 nm AuNPs and 3 nm PtNPs

To prepare an AuNP-DNA or Pt-DNA conjugate, thiolated single or double stranded DNA was combined with AuNPs or PtNPs at appropriate molar ratios in 0.5×TBE buffer supplemented with 50 mM NaCl (Tris, 44.5 mM; EDTA, 1 mM; boric acid, 44.5 mM, NaCl, 50 mM; pH 8.0). The double stranded DNA was pre-formed via a thermal annealing process in the same buffer. The resulting sample was incubated at 4°C for 5-10 hours, loaded in a 3% agarose gel, and then run in 0.5×TBE buffer at 4 ºC for a suitable time period at 16 V/cm.

High density DNA modification of 13nm AuNPs

5'-thiolated **S** strand and thiol-free **L2** strand (see sequence information in Materials and Chemicals section) were hybridized in 0.5×TBE plus 50 mM NaCl. Subsequently, the DNA hybrid was combined with 13 nm AuNPs at 200:1 molar ratio with a final concentrations of 0.072 μM for the AuNPs. NaCl concentration was gradually increased during a 48 h period to reach a final concentration of 0.2 M. The solution was centrifuged at 9560 g for 10 min , and the resulting precipitates were collected and redispersed in 0.5×TBE plus 0.1 M NaAc. The purified AuNP-DNA conjugate was quantified by measuring its optical absorbance at 520 nm. The product was then stored at 4 ºC in 0.5×TBE plus 0.1 M NaAc for further use.

Agarose gel based isolation of individual product bands

To recover a desired product from the gel, the corresponding gel band was cut out and inserted into a dialysis tubing (MWCO of 3500 Da). The dialysis tubing was sealed at both ends and immersed in 0.5×TBE buffer (containing 25 mM NaAc) for an electroelution of the AuNPs or PtNPs under an applied electric field. The AuNP-DNA or PtNP-DNA conjugate was collected from the dialysis tubing and quantified on the basis of its absorption at 520 nm (for AuNPs) or 500 nm (for PtNPs). The recovered Nanoparticle/DNA conjugates were stored at 4 ºC in 0.5×TBE plus 0.1M NaAc.

Assembly of Au/Pt discrete heteronanostructures or AuNP(13 nm)-PtNP core-satellites

As-obtained AuNP-DNA and PtNP-DNA conjugates were mixed at appropriate molar ratios and incubated in 0.5×TBE buffer plus 0.1 M sodium acetate for 5-10 h. 3% (1.5% for the core-satellite structures) agarose gel electrophoresis was used for the characterization and isolation of assembled products. All the experiments were

carried out at 4 ºC.

TEM characterizations

Transmission electron microscopy (TEM) imaging was conducted on a JEM-2100F field emission transmission electron microscope with an acceleration voltage of 200 kV. Samples were prepared on carbon coated copper grids at 4 ºC.

References

S1. G. Frens, *Nat. Phys. Sci.* **1973**, *241*, 20-24.

S2. J. W. Slot, H. J. Geuze, *Eur. J. Cell. Biol.* **1985**, *38*, 87-93.

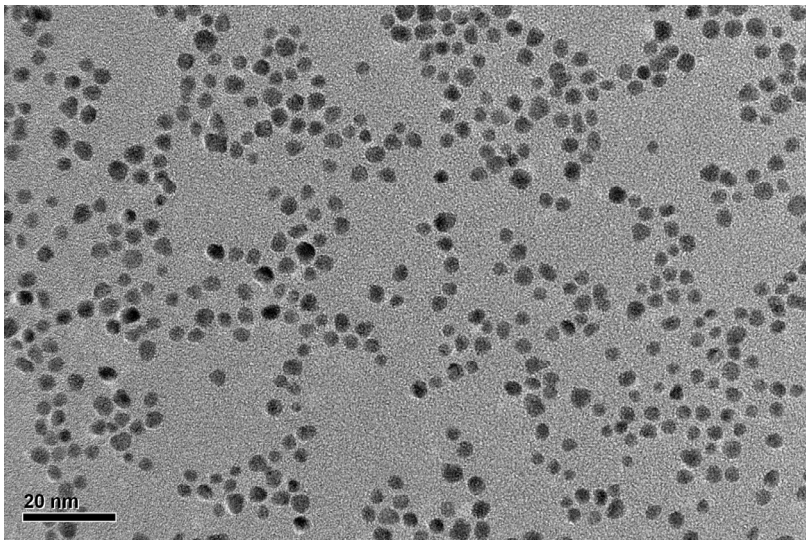
S3. K. C. Grabar, R. G. Freeman, M. B. Hommer, M. J. Natan, *Anal. Chem.* **1995**, *67*, 735-743.

S4. J. Yang, J. Y. Lee, H. P. Too, *Anal. Chim. Acta.* **2006**, *571*, 206-210.

S5. X. Y. Xiao, F. R. F. Fan, J. P. Zhou, A. J. Bard, *J. Am. Chem. Soc.* **2008**, *130*, 16669-16677.

S6. R. C. Mucic, J. J. Storhoff, C. A. Mirkin, R. L. Letsinger, *J. Am. Chem. Soc.* **1998**, *120*, 12674-12675.

Figure S1. A typical TEM image of as-synthesized BSPP-protected PtNPs (upper panel) and a statistical analysis (lower panel) of the size distribution of the PtNPs. A total of 493 particles were counted.



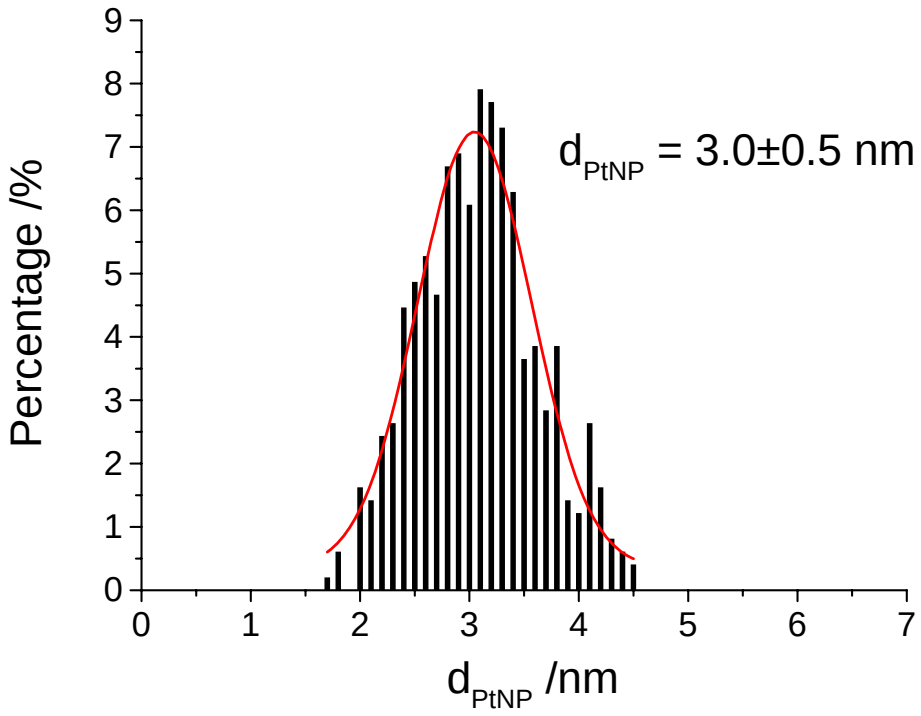
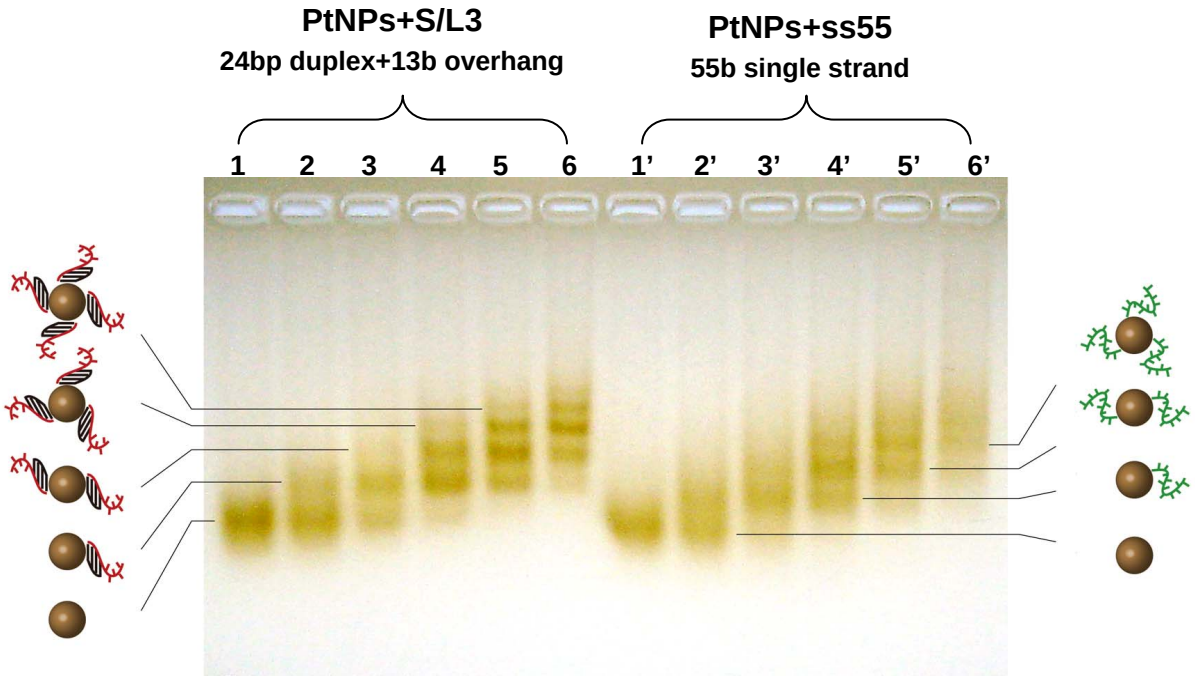


Figure S2. 3% agarose gel electrophoresis data showed that both double-stranded and single stranded DNA could be employed to achieve discrete modifications of PtNPs (upper panel), and a minimum of 24bp duplex was enough to produce a ladder of resolvable gel bands (lower panel). Lanes 1-6 and 1'-6' in the upper panel, and lanes 1-5, 1'-5' and 1''-5'' in the lower panel corresponded to increased amount of DNA relative to PtNPs (no DNA was added for lanes 1, 1' and 1''). See experimental section for the DNA sequences.



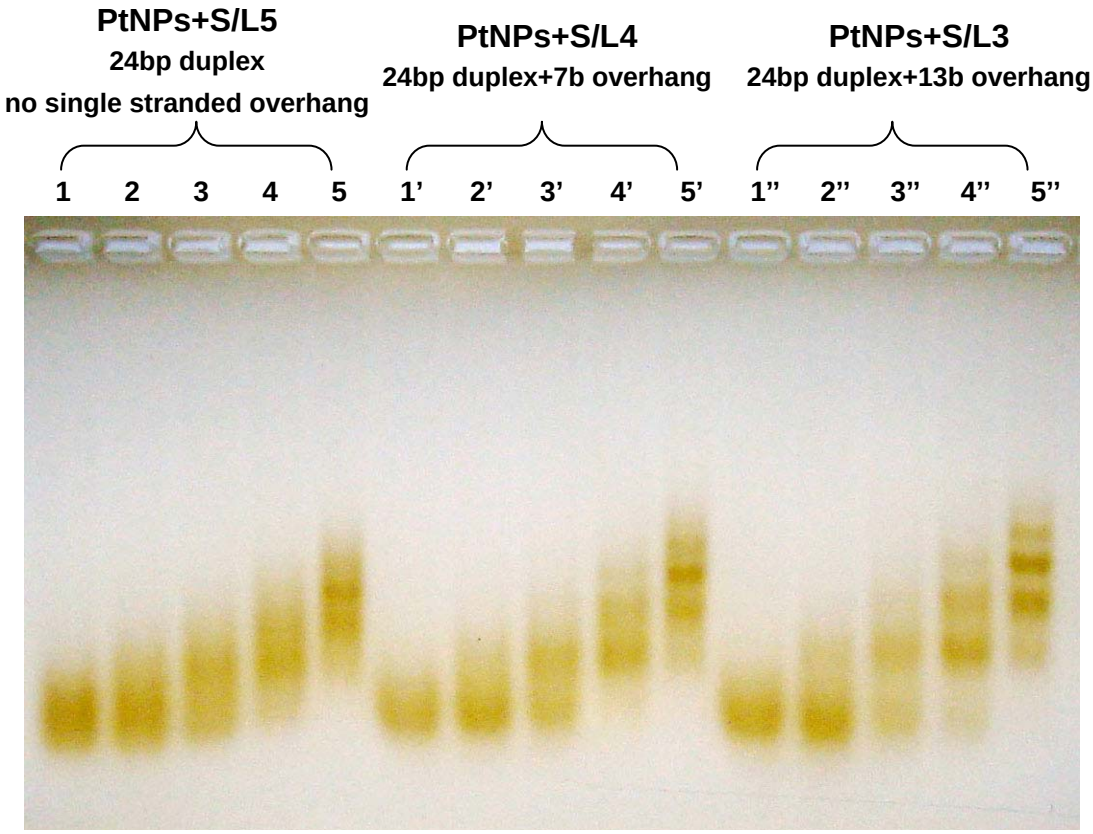
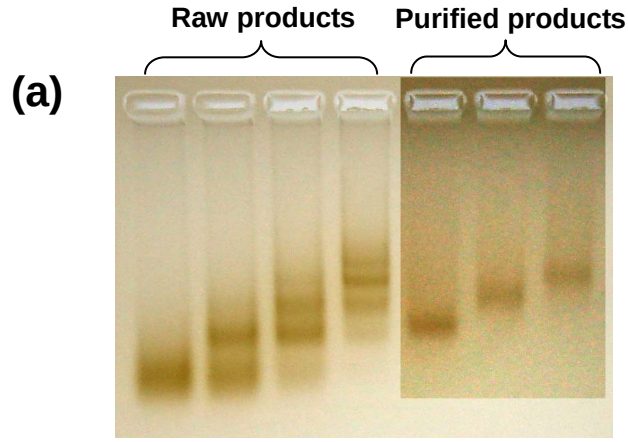
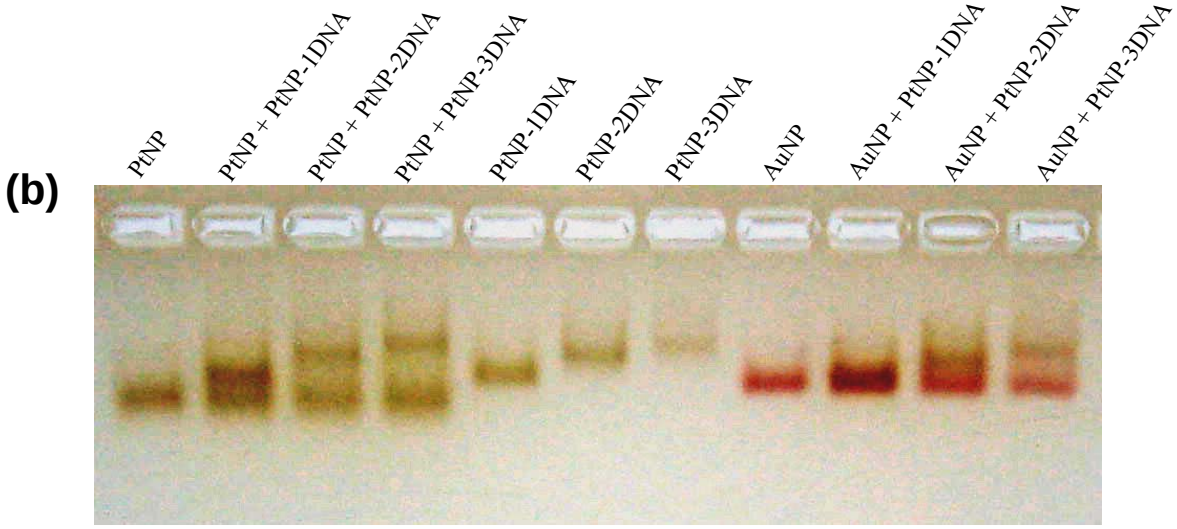
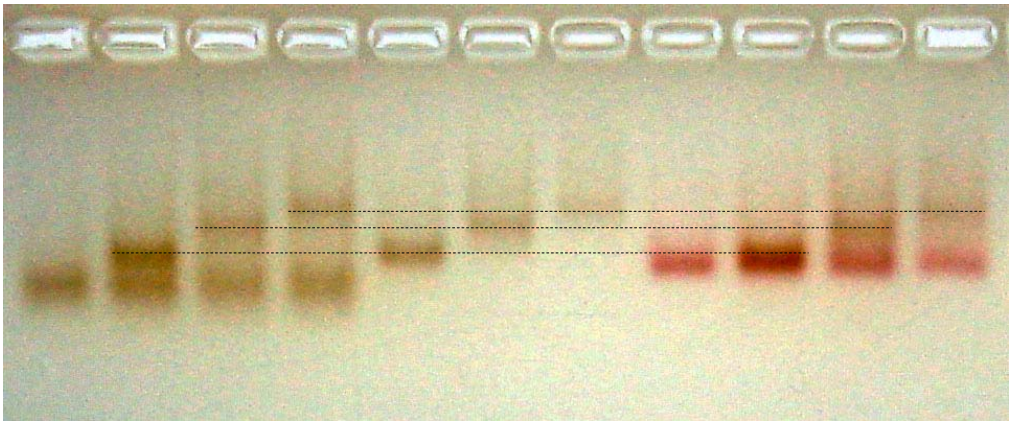


Figure S3. Stability tests of the isolated mono-, di- and trivalent PtNPs in the absence and presence of purposely added DNA-free AuNPs and PtNPs. (a) The purified products maintained their original mobility as in the raw products. (b) No interactions between the purified PtNPs and DNA-free Au or Pt nanoparticles were observed after a 3 h incubation.





Run at 16 V/cm for 40 min



Run at 16 V/cm for 60 min

Figure S4. Gel electrophoresis based titrations revealing the stepwise assembly of discrete Au/Pt bimetallic superstructures. Lanes 1 and 5 corresponded to AuNP-DNA (or PtNP-DNA) with suitable valences of DNA ligands. Lanes 2, 3 and 4 represented mixtures between AuNP-DNA and PtNP-DNA (as shown in lanes 1 and 5) with increased molar ratios of the AuNP-DNA or PtNP-DNA. See Figure 3 for TEM images of the assembled products.

Au_3Pt_1

Lanes	2	3	4
PtNPs (pmol)	7.0	4.9	2.4
AuNPs(pmol)	4.2	6.1	8.0
PtNPs/AuNPs	1:0.6	1:1.25	1:3.3

Au_2Pt_1

Lanes	2	3	4
PtNPs (pmol)	4.4	4.0	2.5
AuNPs(pmol)	2.1	3.5	4.6
PtNPs/AuNPs	1:0.5	1:0.9	1:1.8

Au_1Pt_1

Lanes	2	3	4
PtNPs (pmol)	1.6	3.4	6.8
AuNPs(pmol)	3.4	3.4	3.4
PtNPs/AuNPs	0.5:1	1:1	2:1

Au_1Pt_2

Lanes	2	3	4
PtNPs (pmol)	1.4	3.0	6.8
AuNPs(pmol)	3.5	3.0	2.2
PtNPs/AuNPs	0.4:1	1:1	3.1:1

Au_1Pt_3

Lanes	2	3	4
PtNPs (pmol)	3.4	5.8	8.8
AuNPs(pmol)	3.3	2.8	2.2
PtNPs/AuNPs	1:1	2:1	4:1

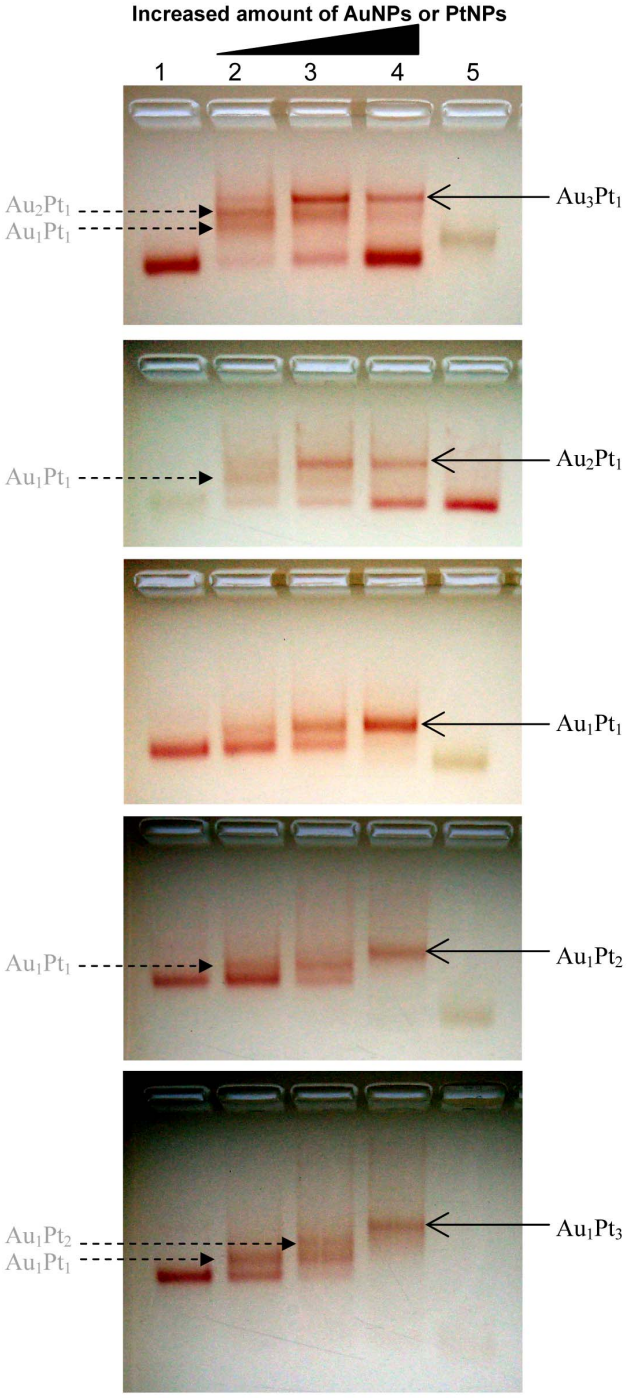


Figure S5. Visible absorbance spectra of gel-isolated Au_1Pt_1 heterodimer along with DNA mono-functionalized Pt and Au nanoparticles. A plasmonic absorbance peak at around 515 nm could be seen for the dimer structure, which was attributed to the Au nanoparticle component within the dimer. Absorbance spectra of AuNP-1DNA and PtNP-1DNA were normalized to a particle concentration of about 0.015 μM.

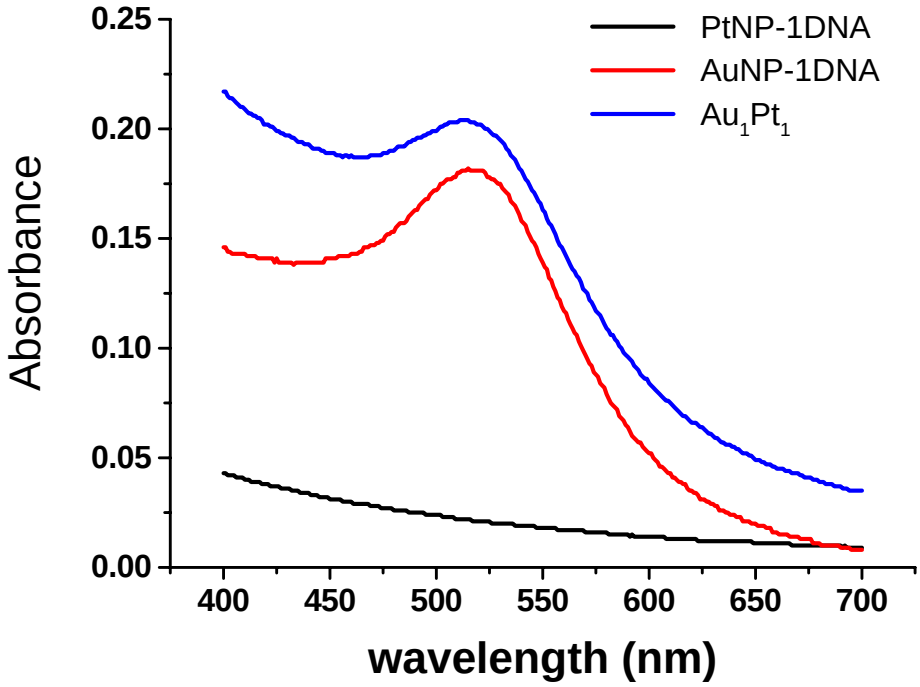


Figure S6. Agarose gel electrophoresis verified that the assembly of Au_1Pt_1 could be reversed upon addition of 50% (V/V) formamide to the sample solution followed by a brief heating at 50 °C for 10 min to disrupt DNA basepairing. **It could be seen from the gel that the dissociated product migrated at an increased rate than the intact Au_1Pt_1 dimer.**

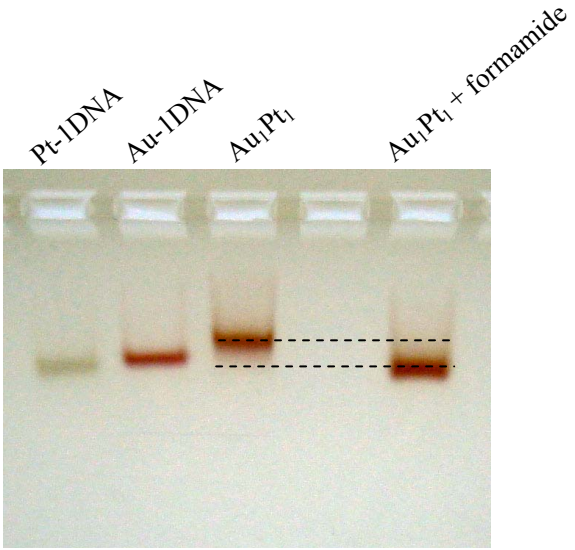


Figure S7. TEM images showing gradually increased densities of the surrounding DNA-monofunctionalized PtNPs in the Au/Pt core-satellite structures (a-d, corresponding to lanes 1-4 in Figure 4c.), **and the formation of dualcore-satellite structures when a mixed-valence PtNP-DNA conjugate was used for the assembly (e).** Note: panels (a1) and (a2) were images from the same sample.

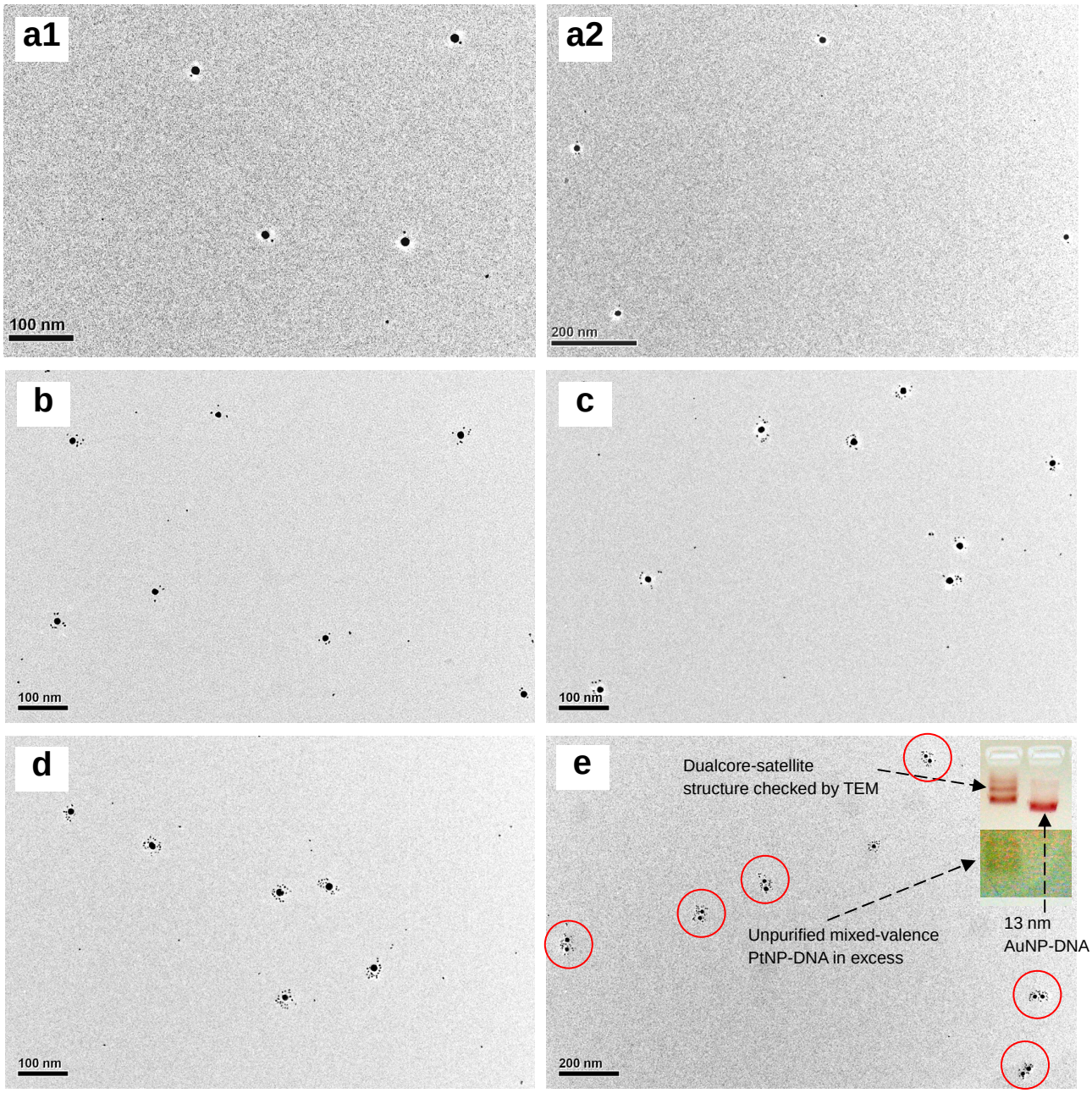


Table S1. TEM-based yield analysis of as-formed Au/Pt heterostructures.

Sample	Correctly assembled particles	Particles counted	Percentage
Au_3Pt_1	608	1131	53.7%
Au_2Pt_1	909	1463	62.1%
Au_1Pt_1	1100	1563	70.4%
Au_1Pt_2	474	768	61.7%
Au_1Pt_3	472	871	54.2%