- Electronic Supplementary Information -

Controllable synthesis of gold nanoparticle dimers via a site-selected growth

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Chemicals:

All chemical reagents were used without further purification. Ascorbic acid (AA, 99%), hexadecyltrimethylammonium bromide (CTAB, 99%), sodium borohydride (NaBH$_4$, 99%), silver nitrate (AgNO$_3$, 99.9%), and 2-naphthalenethiol (99%) were purchased from Sigma-Aldrich. Gold (III) chloride trihydrate (HAuCl$_4$·3H$_2$O, 99.9%) was purchased from Alfa Aesar. Sodium hydroxide (NaOH, 98%), *N, N'*-dimethylformamide (DMF, 99.8%), and hydrochloric acid (HCl, 37% by weight in water) were purchased from Sinopharm Chemical Reagent. Sodium oleate (NaOL, 99%) was purchased from TCL. Amphiphilic diblock copolymer polystyrene-*block*-poly(acrylic acid) (Mn = 16,000 for the PS block and Mn = 3700 for the PAA block, Mw/Mn = 1.14) was purchased from Polymer Source Inc.

Deionized water (resistance > 18.2 MΩ/cm) was used in reactions.

Preparation of AuNRs@PSPAA and transformation of polymer shell:

The AuNRs (length = 200-300 nm; diameter = 20-30 nm) were prepared according to the literatures.[1] The synthesized AuNRs were purified by centrifugation and washed by water twice to remove the excess CTAB (Figure S1a).

The short AuNRs were prepared by a binary surfactant seed-mediated method.[2] The prepared AuNRs were purified by centrifugation and washed by water twice to remove the excess CTAB and NaOL (Figure S4a).

The encapsulation and transformation methods are according to our previous work.[3] 200 μL of purified long AuNRs were added into the mixture containing DMF (670 μL), PSPAA (80 μL, 8 mg/mL in DMF), and 2-naphthalenethiol (150 μL, 3 mg/mL in DMF). Then, the mixture was heated at 110 °C for 2 h, and slowly cooled down till room temperature. For the short AuNRs, the amounts of PSPAA and DMF were changed to 50 μL and 700 μL, respectively. The solvent ratio of DMF/H$_2$O is 4.5.

The synthesized AuNR@PSPAA were centrifuged for 15 min. The speed was 8500 rpm for the long rods, and 9500 rpm for the short ones. The nanorods were purified again via centrifugation at 7000 rpm, 15 min. Finally, the concentrated nanorods were diluted by 1 mL water and heated at 115 ℃ for 2 h. After that, the mixture was cooled to room temperature. The AuNR@PSPAA were concentrated via centrifugation to remove the excess ligand and polymer. The concentrated AuNRs@PSPAA were dispersed in 500 μL water for the further growth.

Preparation of nanoparticle dimers:

In a typical synthesis, NaOH (6 μL, 0.1 M) and $HAuCl_4$ (0.38 mM in final solution) were added in to 1 mL CTAB (25 mM) aqueous solution. Then, AA (0.57 mM in final solution) was added into the above mixture under vortex. The mixture color was changed from yellow to colorless. Finally, 15 μL of AuNR@PSPAA were added, and the reaction was carried out at room temperature for 2 h.

Colloidal SERS measurement:

The synthesized nanoparticle dimers were purified via centrifugation two times to remove the residual CTAB, and dispersed into water (495 μL). Then, the Raman molecules 2-naphthalenethiol (5 μL, 18.8 mM, in DMF) was added into the dimer solution. The mixture was incubated at 60 ℃ for 2 h, and cooled to room temperature for the SERS measurement.

Calculations of the Raman enhancement factor:

We use the following Equation 1 to calculate the Raman enhancement factor:

$$EF = (I_{SERS} \times C_{bulk})/(C_{SERS} \times I_{bulk}) \qquad\qquad 1$$

Where I_{SERS} and I_{bulk} are the Raman intensities of the 1620 cm^{-1} peak for gold dimers and the 1627 cm^{-1} peak for pure 2-naphthalenethiol solution. C_{SERS} and C_{bulk} are the concentrations of 2-naphthalenethiol on gold dimers and in pure solution, respectively.

In order to select the I_{bulk}, we used 1.5 M 2-naphthalenethiol nearly saturated DMF solution for Raman characterization. Since DMF has a strong Raman signal that would affect the signal of 2-naphthalenethiol, we performed Raman characterization of the pure DMF solution. We choose the peak at 1627 cm^{-1} for calculation, where 2-naphthalenethiol does not overlap with DMF and has the highest peak intensity.
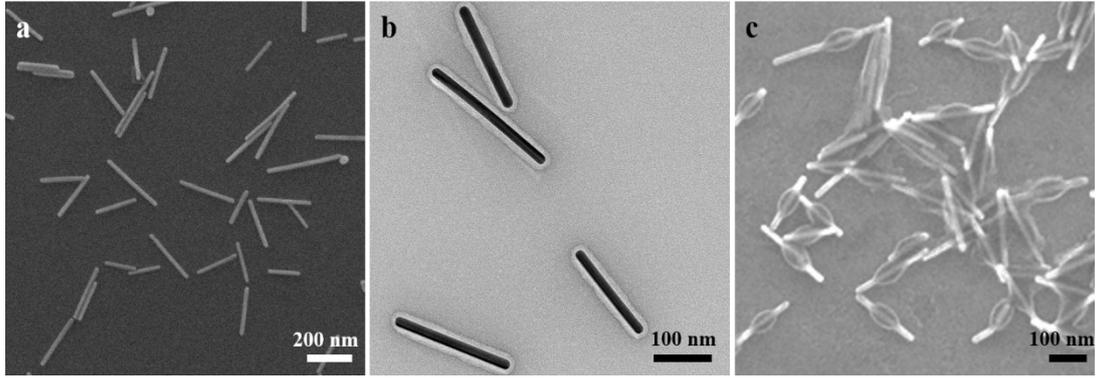
Figure S1. (a) SEM image of long AuNRs; (b) TEM image of long AuNR@PSPAA; (c) SEM image of AuNR@PSPAA after polymer shell contraction.
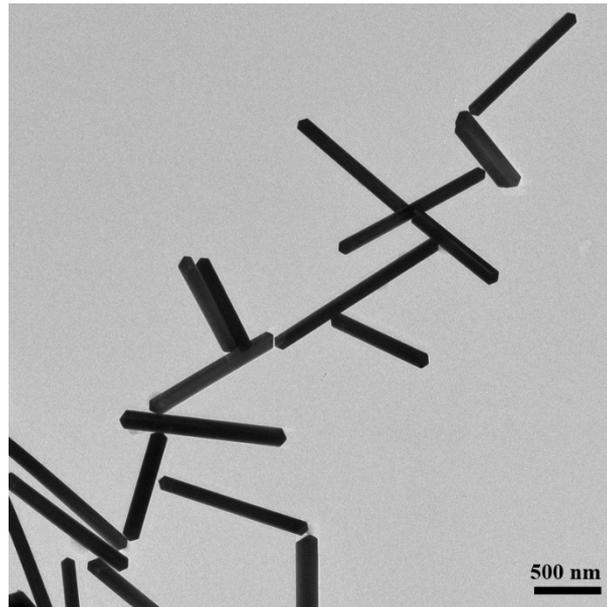
Figure S2. TEM image of the nanostructure directly grew on AuNRs.
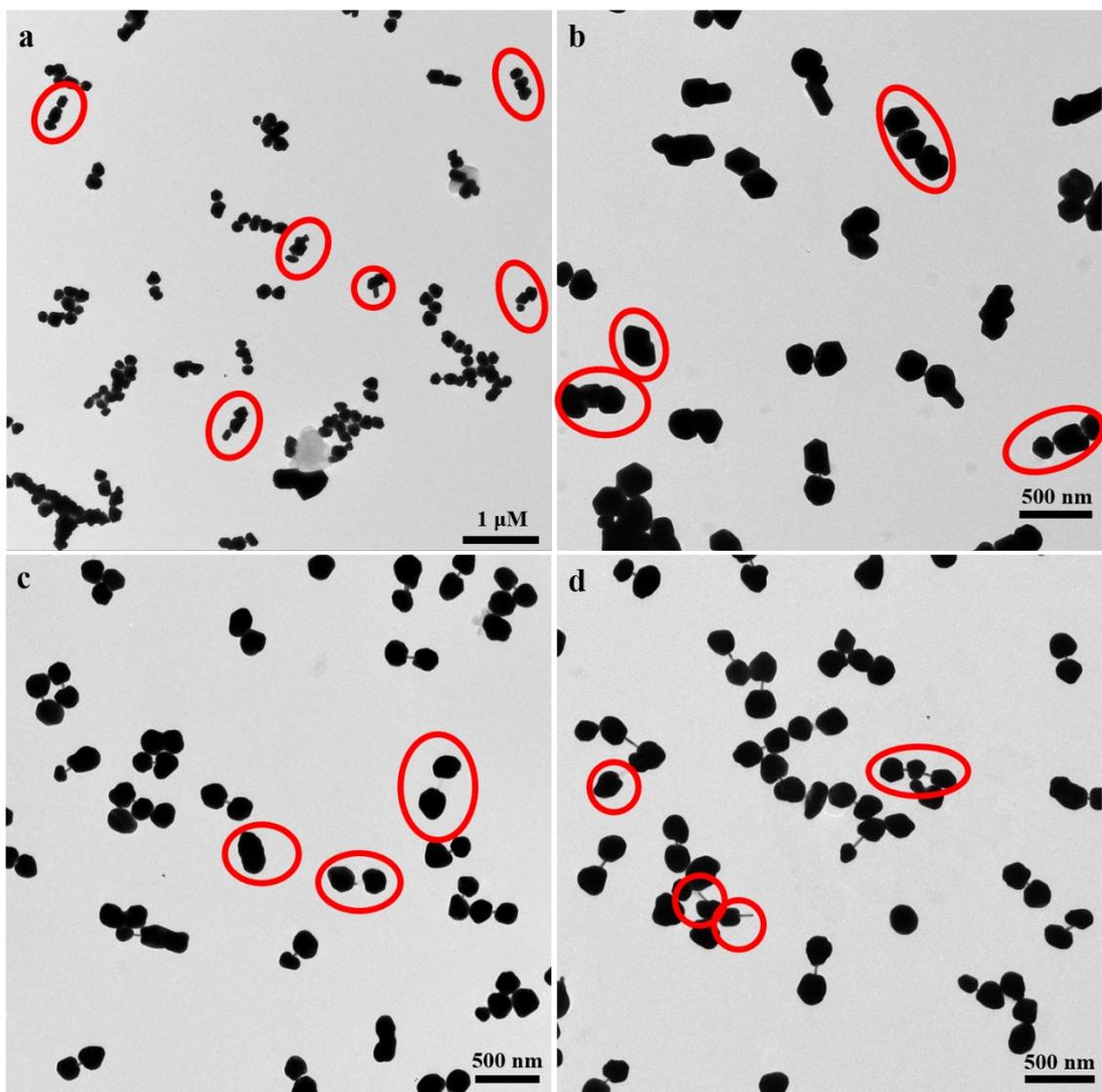
Figure S3. TEM images of the synthesized dimers containing 19% monomer and 10% trimer labeled in red circles.
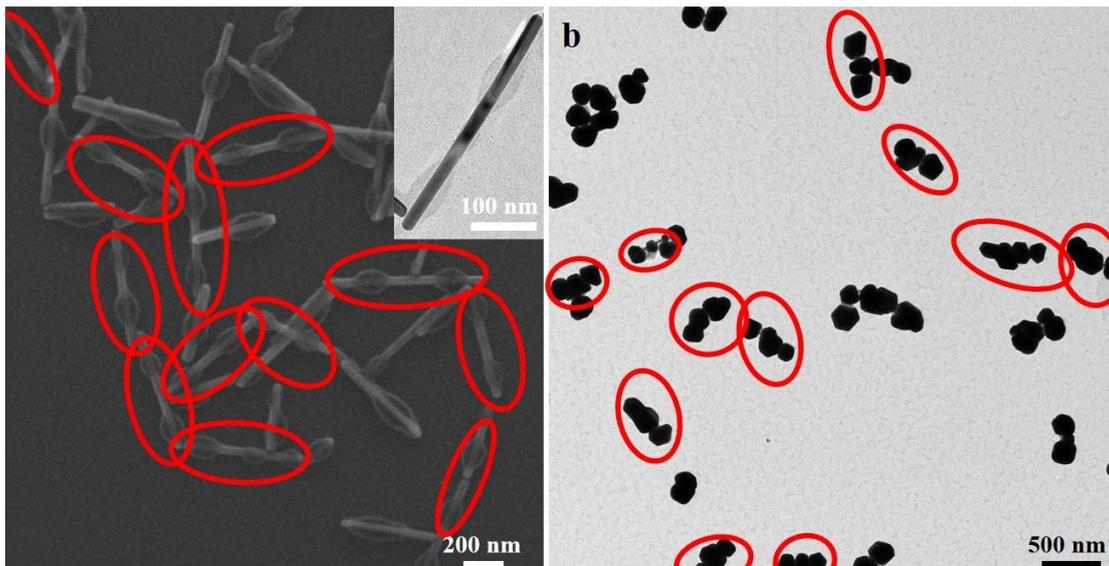
Figure S4. (a) SEM image of the bimodal contraction mode of polymer shell. Inset: TEM image of the bimodal contraction of polymer shell. (b) TEM image of the nanoparticle trimers.
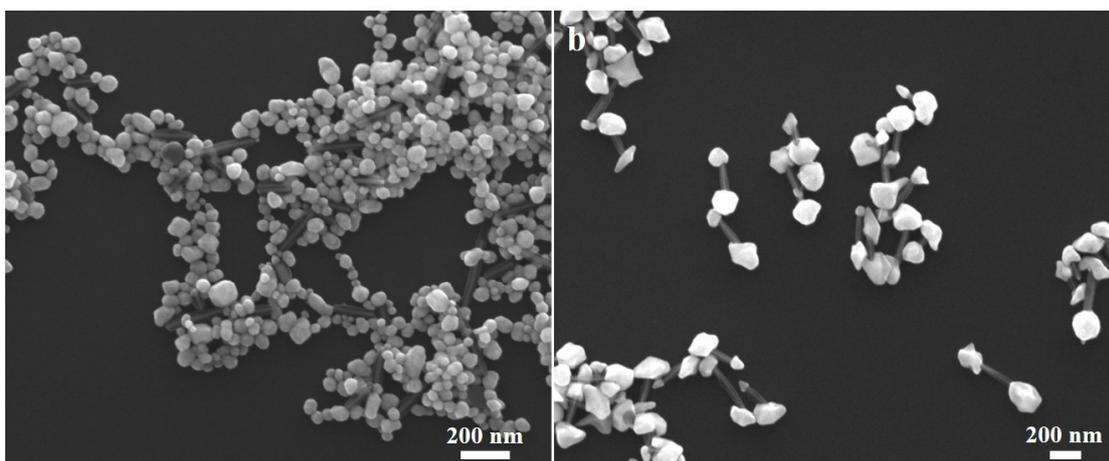
Figure S5. SEM images of the nanoparticle dimers prepared with different concentration of CTAB: (a) 0, and (b) 0.1 M.
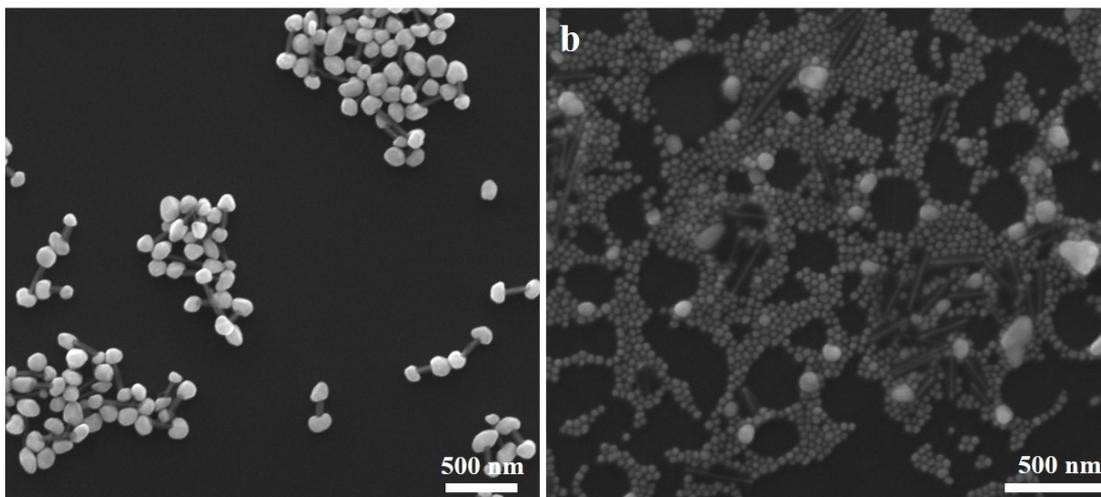
Figure S6. SEM images of the nanoparticle dimers prepared with different concentration of NaOH: (a) 0, and (b) 2.6 mM.
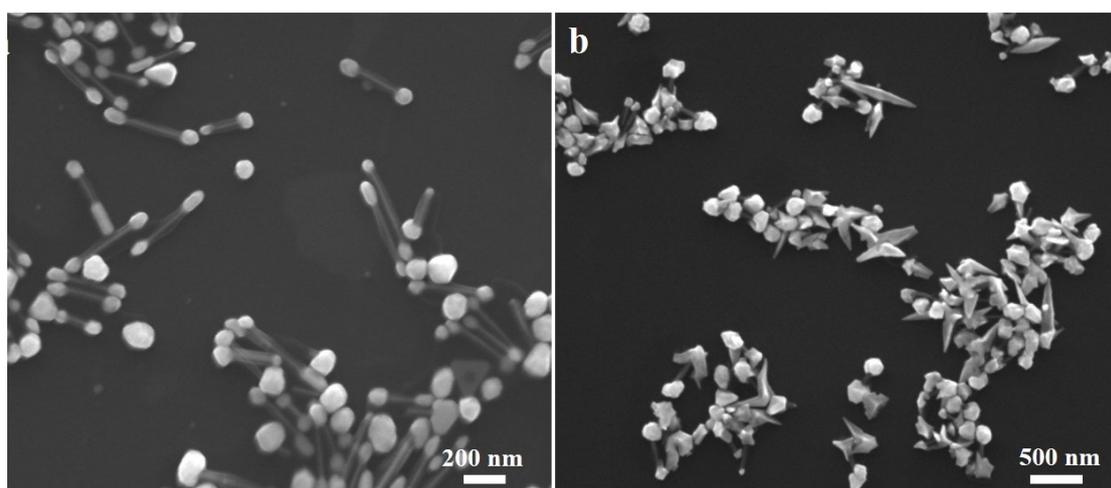
Figure S7. SEM images of the nanoparticle dimers prepared with different concentration of AA: (a) 0.27, and (b) 4.1 mM.
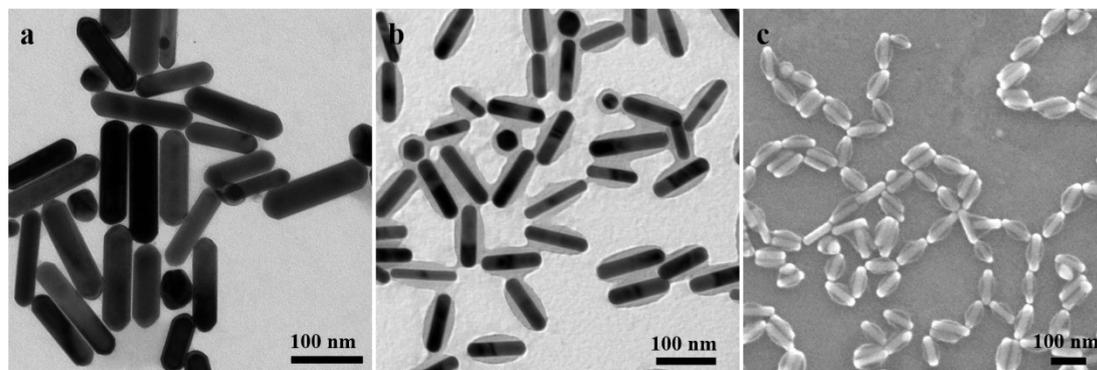
Figure S8. TEM images of (a) short AuNRs, and (b) AuNR@PSPAA; (c) SEM image of AuNR@PSPAA after polymer shell contraction.
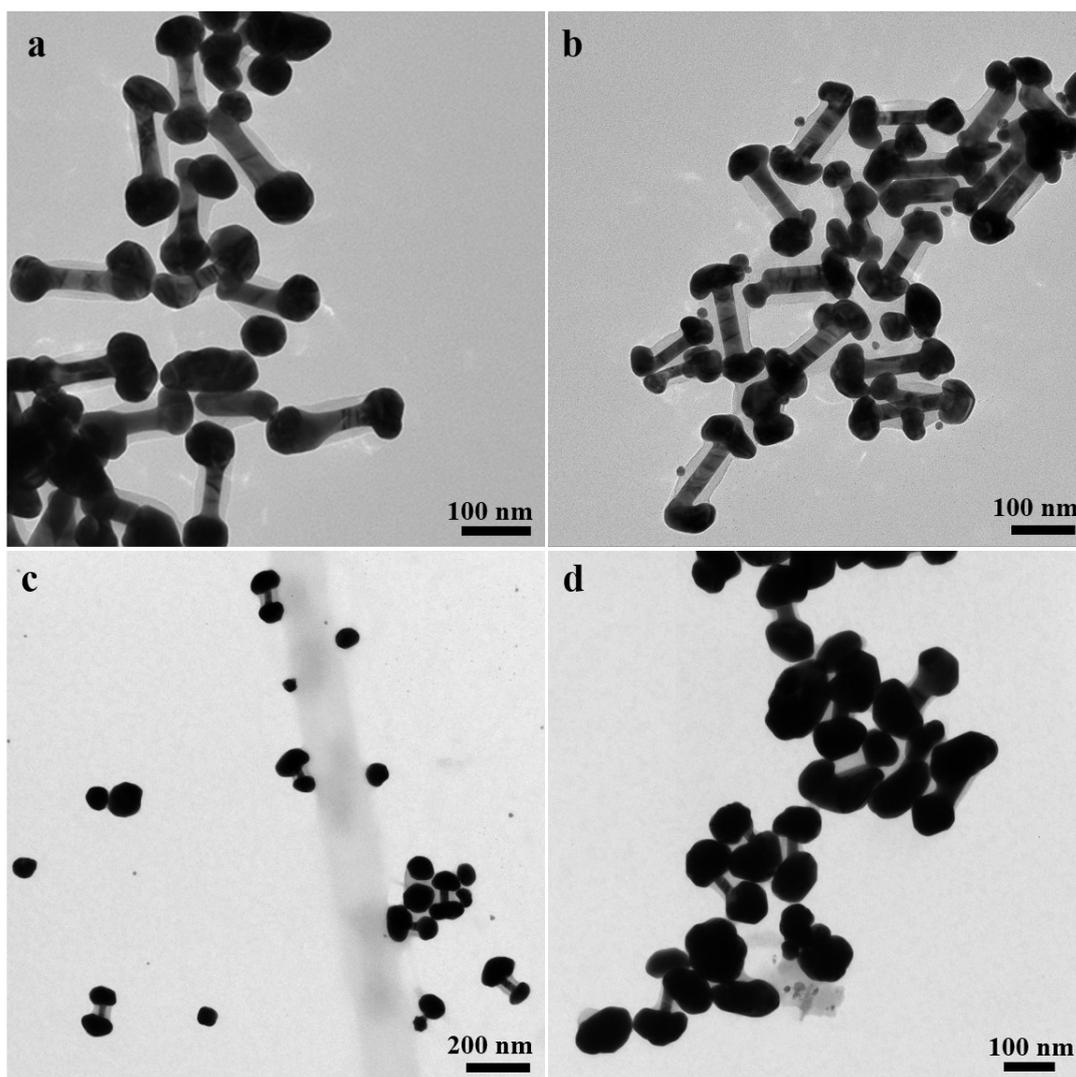
Figure S9. TEM images of dimers growing from short nanorods with different gaps: (a-b) 69 nm, and (c-d) 24 nm.
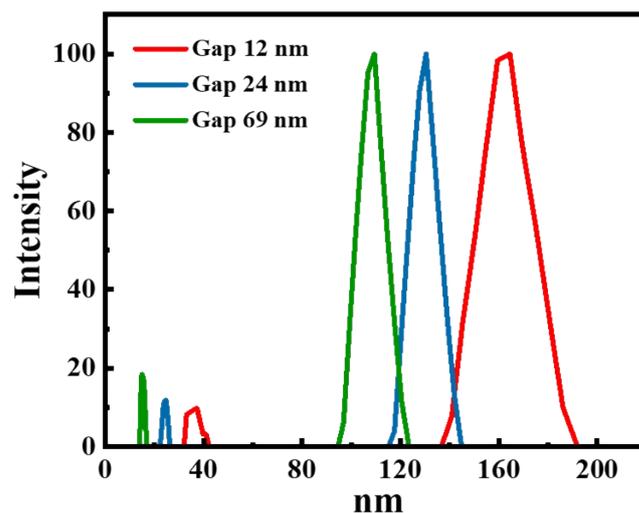
Figure S10. Dynamic light scattering (DLS) of nanoparticle dimers with different interparticle spacing: 12 nm (red curve), 24 nm (blue curve), and 69 nm (green curve).
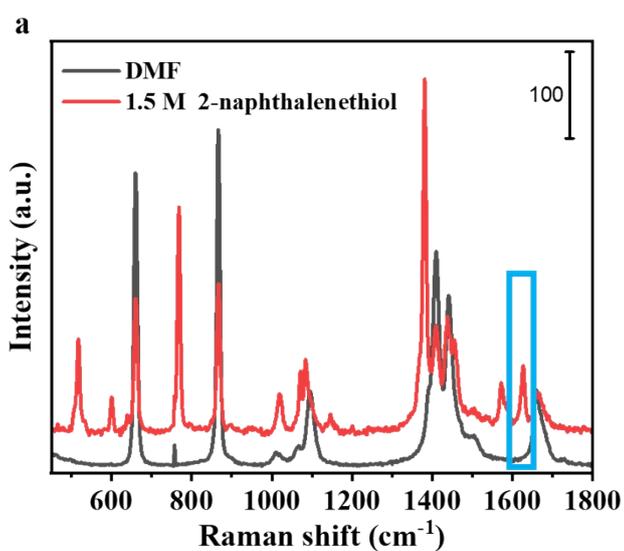
Figure S11. Raman spectra of pure DMF and 2-naphthalenethiol in DMF (1.5 M).

References:

1. A. Gole and C. J. Murphy, Chem. Mater., 2004, 16, 3633-3640.

2. X. Ye, C. Zheng, J. Chen, Y. Gao and C. B. Murray, Nano Lett., 2013, 13, 765-771.

3. Z. Wang, B. He, G. Xu, G. Wang, J. Wang, Y. Feng, D. Su, B. Chen, H. Li, Z. Wu, H. Zhang, L. Shao and H. Chen, Nat. Commun., 2018, 9, 563.