Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

One-step formation of responsive "dumbbell" nanoparticle dimers via quasi-two-dimensional polymer single crystals

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Experimental Section

Materials.

Dihydroxyl-terminated polycaprolactone ($PCL(OH)_2$, M_n ~ 2k g/mol), 3-mercaptopropionic acid (MPA) (99%), Candida antarctica lipase B (CALB) (≥10,000U/g), 3-(triethoxysilyl)propyl isocyanate (95%), $AuCl_3$ (99%), didecyldimethylammonium bromide (DDAB) (98%), tetrabutylammonium bromide (TBAB) (98%), decanoic acid (98%), hydrazine (anhydrous, 98%), iron(III) chloride hexahydrate (97%), 1-octadecene (90%), oleic acid (99%), 1-butanol (≥99.5%), pentyl acetate (99%) were purchased from Sigma Aldrich. Sodium oleate (97%) was bought from Pfaltz & Bauer and used as received. Silica sol (IPA-ST, 10-15 nm, 30-31 wt.% in isopropanol) was a sample provided by Nissan Chemical America Corporation. All other chemicals were obtained from Sigma Aldrich and used without further purification.

Synthesis of dithiol- and dialkoxysilane terminated polycaprolactone ($PCL(SH)_2$ & $PCL(SiOR)_2$). $PCL(SH)_2$ was synthesized following Martinelle's method.[1] Typically, 300 mg $PCL(OH)_2$ was mixed with 20 mg CALB and 2 mL 3-mercaptopropionic acid at 60 ˚*C*. The reaction was stopped after 72 h by cooling the system to room temperature followed by addition of 1 mL dichloromethane. $PCL(SH)_2$ was precipitated from the dichloromethane solution in ice-cold methanol followed by vacuum filtration. For $PCL(SiOR)_2$, 300 mg $PCL(OH)_2$ was dissolved in 20 mL dichloromethane followed by dropwise addition of 5 mL 3-(triethoxysilyl)propyl isocyanate. The reaction was allowed to proceed at room temperature for 24 h. Upon completion,

the solution was concentrated and precipitated in ice-cold methanol. $PCL(SiOR)_2$ was collected by filtration and washed thoroughly with methanol before use.

Growth of $PCL(SH)_2$ and $PCL(SiOR)_2$ single crystals using self-seeding. 3 mg of either $PCL(SH)_2$ or $PCL(SiOR)_2$ was dissolved in 10 g 1-butanol at 60 ˚C. The solution was quenched to -10 ˚C for 3 h. The crystal suspension was then heated at 42 ˚C for 10 min to obtain crystal seeds. Finally, the single crystals were allowed to grow at 35 ˚C for 7 days. Uncrystallized polymer was removed via isothermal filtration followed by a multiple centrifugation process. The $PCL(SH)_2$ and $PCL(SiOR)_2$ single crystals were redispersed in pentyl acetate and 1-butanol, respectively, for further experiments.

Immobilization of nanoparticles and formation of nanoparticle dimers. Gold nanoparticles (AuNPs, average diameter ~ 9 nm) were synthesized according to Peng's method.[2] Iron oxide nanoparticles (Fe_3O_4NPs, average diameter ~ 12 nm) were synthesized following Hyeon's approach.[3] For the immobilizations of both AuNPs and Fe_3O_4NPs, the $PCL(SH)_2$, *a* single crystal suspension in pentyl acetate was mixed with a AuNPs or Fe_3O_4NPs solution for chemisorption. The weight ratio between the crystal suspension and nanoparticle solution was kept at 5:1. After immobilization, free particles were removed via multiple centrifugation, and the crystals with nanoparticles on the surface ($PCL(SH)_2$@AuNPs & $PCL(SH)_2$@Fe_3O_4NPs) were redispersed in pentyl acetate. For the immobilization of silica nanoparticles (SiNPs), $PCL(SiOR)_2$ a single crystal suspension in 1-butanol was mixed with IPA-ST at weight ratio of 10:1. After stirring

overnight, PCL(SiOR)$_2$ crystals with SiNPs immobilized onto the surface (PCL(SiOR)$_2$@SiNPs) were purified via multiple centrifugation and redispersed in 1-butanol. Multiple immobilizations were applied when necessary. Nanoparticle dimers were obtained directly after single crystals with nanoparticles on the surface were dissolved in toluene without further purification.

Characterizations. ^{1}H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Atomic force microscopy (AFM) images were obtained in tapping mode with a Veeco diNanoScope 3D instrument. Images of 512 × 512 points were acquired at a scanning rate of ~ 1.0 Hz per line. Transmission electron microscopy (TEM) experiments were carried out using a JEM2100 TEM operated at an acceleration voltage of 200 kV. To prepare the TEM specimens, one drop (5 μL) of diluted sample suspension, either crystals or nanoparticles, was drop cast on a carbon-coated nickel TEM grid. A piece of filter paper was used to quickly blot the grid and minimize particle aggregation. When necessary, the TEM grid was stained with ruthenium tetraoxide (RuO_4) vapor for 30 min before observation. UV-Vis absorption spectra of AuNP and AuNP dimer solution were acquired at a wavelength of 400 ~ 800 nm on an Ocean Optics USB4000 miniature fiber optic spectrometer using a quartz cuvette. Dynamic light scattering (DLS) experiments of gold nanoparticle dimer solutions were carried out on Zetasizer Nano ZS90 (Malvern Instruments, Ltd.) using a quartz cuvette at 20 ˚C.

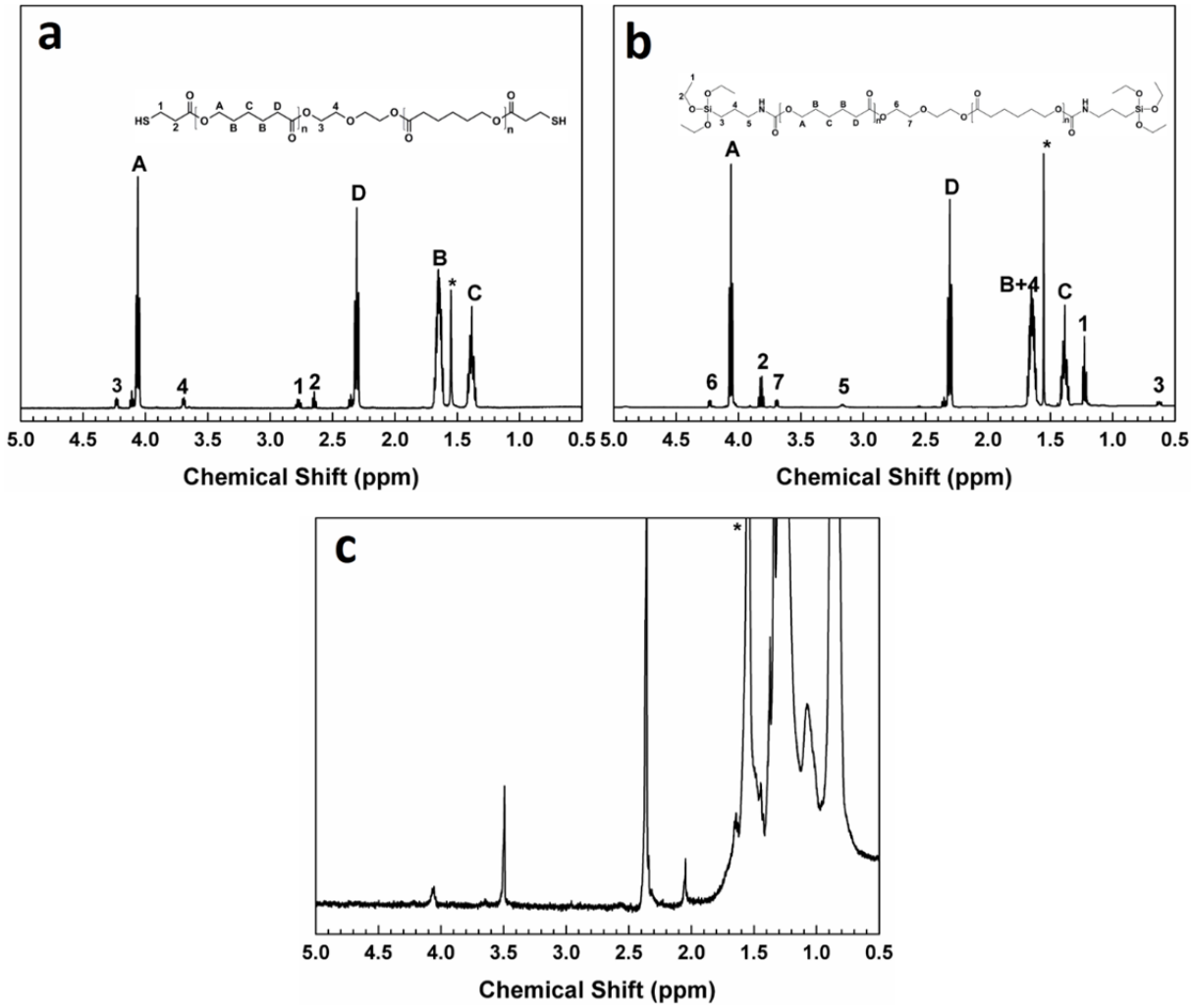

Figure S1. ^{1}H Nuclear Magnetic Resonance (NMR) spectra of PCL-2SH (a), PCL-2SiOR (b) and Au-dimer (c) in $CDCl_3$. *: solvent.

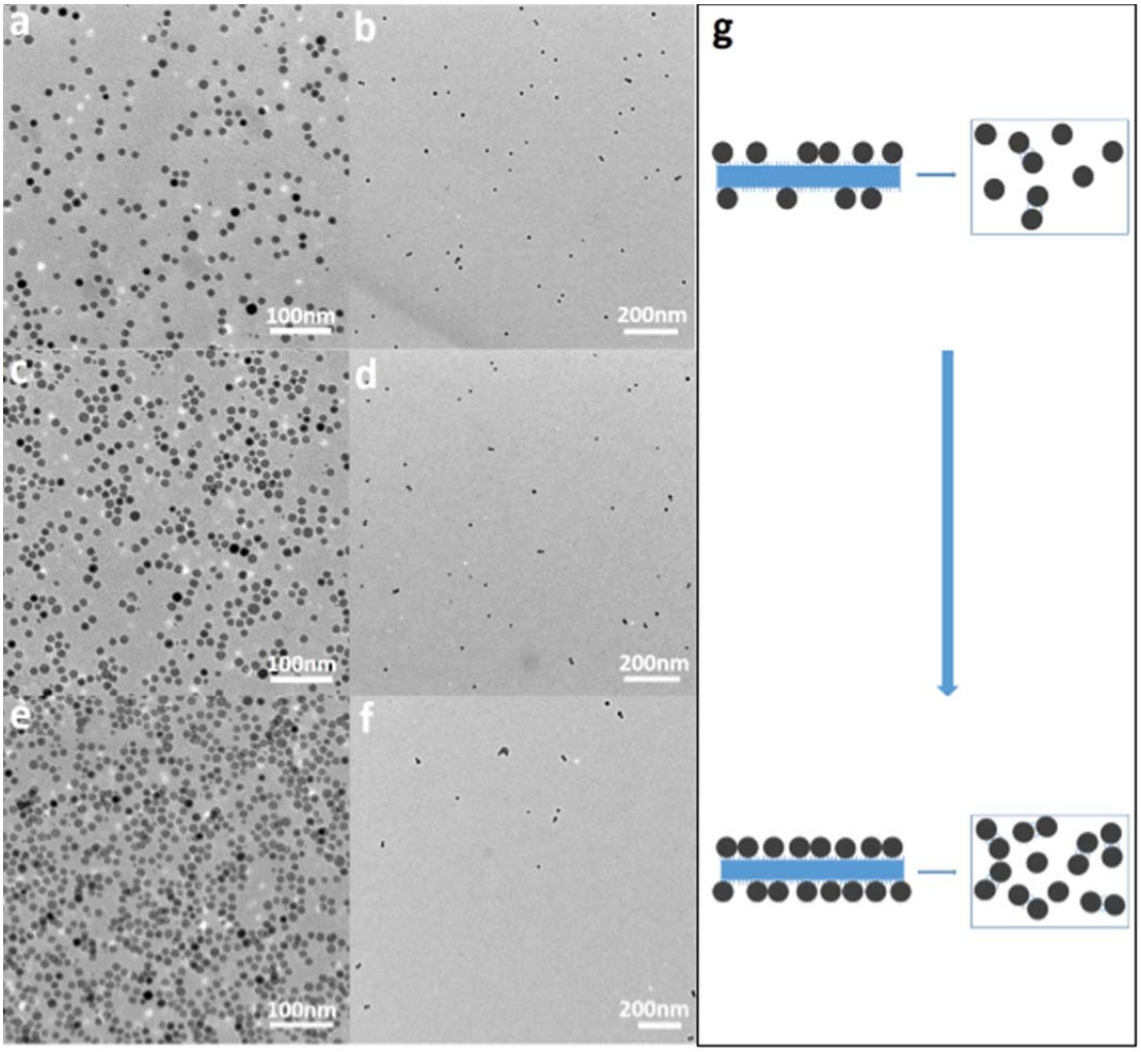

Figure S2. Transmission electron microscopy images of PCL-2SH single crystal templated iron oxide nanoparticles after multiple immobilization process and corresponding dimer nanoparticles formed immediately after dissolving the nanosandwiches: a & b, first immobilization; c & d, second immobilization; e & f, third immobilization; g, illustration of how nanoparticle density on single crystal lamellar affects dimer yield.

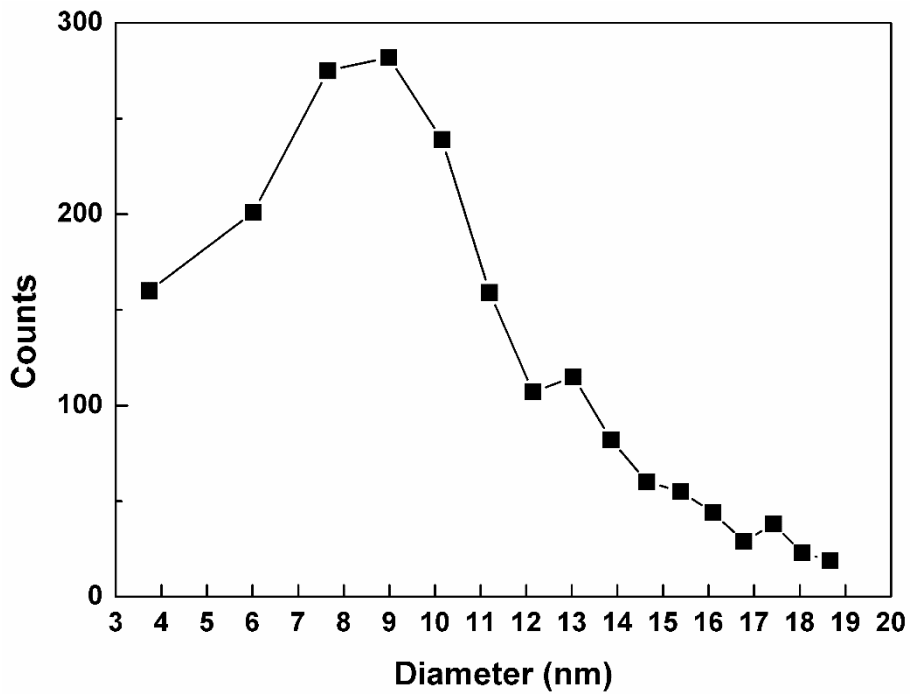

Figure S3. Particle size distribution of AuNPs after being immobilized on $PCL(SH)_2$ single crystals as shown in Figure 2e.

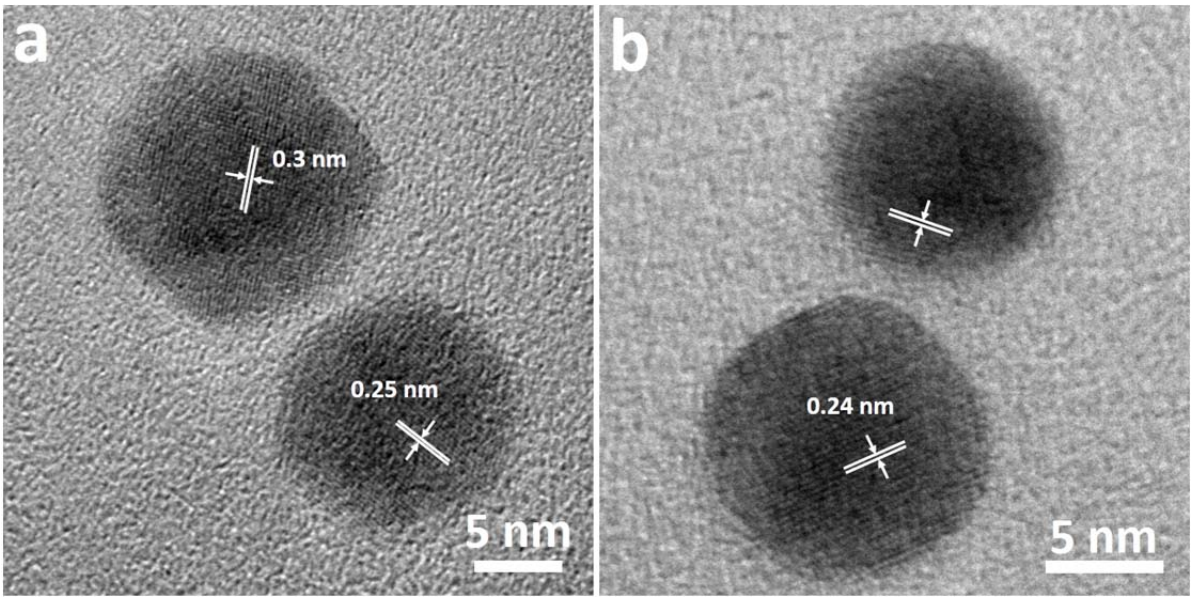

Figure S4. High-resolution transmission electron microscopy (HRTEM) images of Fe_3O_4-dimer nanoparticle (a) and Au-dimer nanoparticle (b) highlighting their lattice structures: (311) (d=0.25 nm) and (220) (d=0.3 nm) of Fe_3O_4NPs; (111) (d=0.24 nm) of AuNPs.

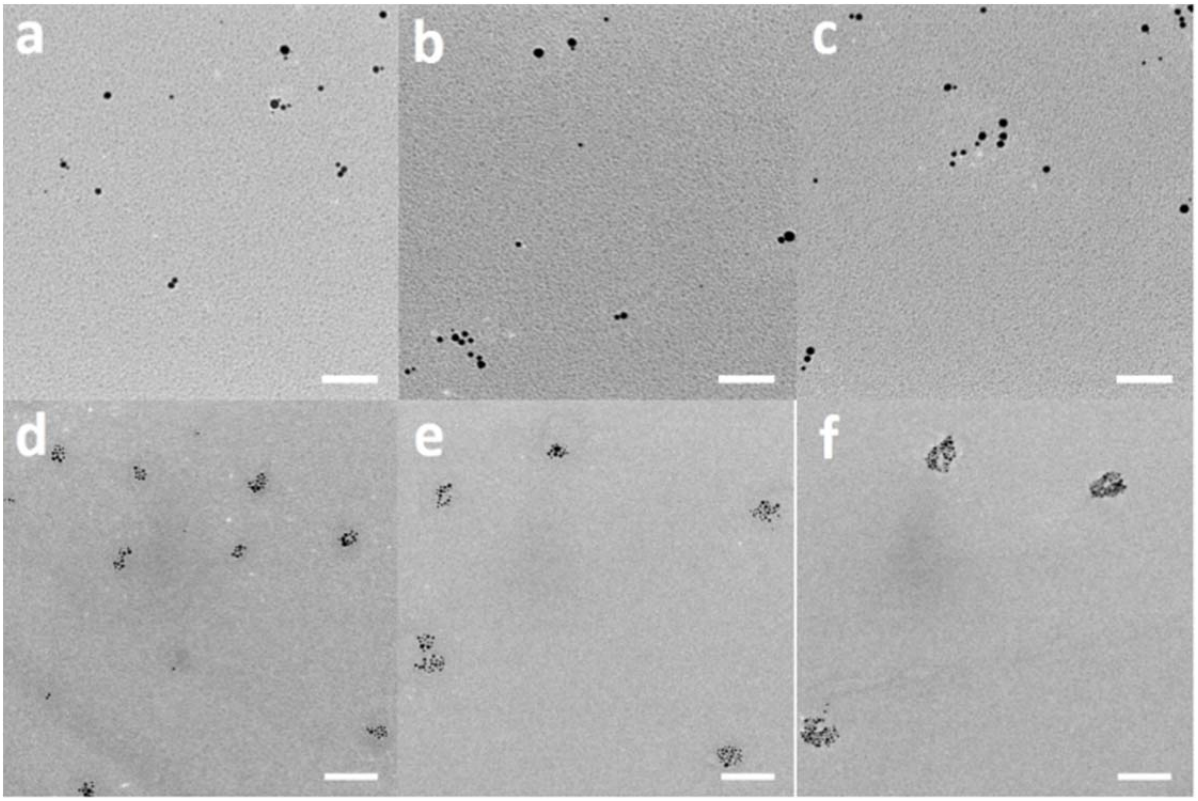

Figure S5. Transmission electron microscopy (TEM) images of Au-dimer nanoparticles in mixed solvent of toluene (TOL) and hexane (HEX) with different volume ratio: a. pure TOL; b. TOL/HEX=5/1; c. TOL/HEX=5/2; d. TOL/HEX=5/3; e. TOL/HEX=5/4; f. TOL/HEX=5/5. The scale bars are 200 nm.

References

1. Hedfors, C.; Ostmark, E.; Malmstrom, E.; Hult, K.; Martinelle, M., Thiol end-functionalization of poly(epsilon-caprolactone), catalyzed by Candida antarctica lipase B. *Macromolecules* **2005,** *38* (3), 647-649.

2. Jana, N. R.; Peng, X. G., Single-phase and gram-scale routes toward nearly monodisperse Au and other noble metal nanocrystals. *J Am Chem Soc* **2003,** *125* (47), 14280-14281.

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