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Supporting information:

Janus Nanoparticle Dimers and Chains via Polymer Single Crystals†

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Experimental

Alpha-thio-omega-carboxy poly(ethylene glycol) (MW 3,000 Dalton, COOH-PEG-SH) and alpha-t-butyloxycarbonylamino-omega-mercapto poly(ethylene glycol) (MW 3,000 Dalton, BOC-NH-PEG-SH) were purchased from Iris biotech GMBH. (N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), polyacrylic acid (PAA, 450k), trifluoroacetic acid and iron oxide nanoparticles was obtained from Sigma Aldrich Company. AuNPs were synthesized following literature method (*J. Am. Chem. Soc.* 2003, **125**, 14280).

Polymer single crystals were prepared using self-seeding method: for COOH-PEG-SH single crystals, 12 mg of COOH-PEG-SH was dissolved in 30 g pentyl acetate at 60 °C for 10 mins. Then the solution was brought to 5 °C for 2 hours. The crystal solution was then heated at 40 °C for 10mins to obtain the crystal seeds. Finally, the solution was allowed to crystallize at 22 °C for 24 hours. The suspension of the single crystals was isothermally filtered to remove uncrystallized polymers. For BOC-NH-PEG-SH single crystals, 24 mg of BOC-NH-PEG-SH was dissolved in 30 g pentyl acetate at 60 °C for 10 mins. Then the solution was brought to 5 °C for 2 hours. The crystal solution was then heated at 33 °C for 10mins to obtain the crystal seeds. Finally, the solution was allowed to crystallize at 17 °C for 24 hours. The suspension of the single crystals was isothermally filtered to remove uncrystallized polymers.

To attach nanoparticles onto the single crystals, a suspension of the single crystal in pentyl acetate was mixed with Au or Fe_3O_4 NP's toluene solution with 5:1 volume ratio and stirred for 24 hours. Free ligands and nanoparticles were then removed by centrifugation. 1 wt% of DDT was then added to this solution and stirred for 12 hours. Multiple centrifugation process was used to remove free DDT. The product was then precipitated in methanol for three times. The final precipitate was

collected and dried in vacuum for 24 hours. Before dimerization reaction, BOC protection group was deprotected using trifluoroacetic acid following the literature method (*Org. Lett.* 2004, **6**, 3675.). Dimerization was achieved by mixing functionalized Janus NPs at the presence of EDC and NHS. In a typical experiment, 1ml dichloromethane solution of COOH-PEG-Au-DDT (0.3mg) was mixed with 1ml of NH_2-PEG-Au-DDT (0.3mg), then 7.6 mg of EDC (20mM) and 4.6 mg of NHS (20mM) were added. The solution was allowed for reaction for 16 hours. The solution was then directly used for TEM analysis. NP chains were synthesized by mixing PAA with amine functionalized Janus NP at the presence of EDC and NHS. For example, 1ml dimethylformamide (DMF) solution of PAA (1mg) was mixed with 1ml dichloromethane solution of NH_2-PEG-Au-DDT (0.3mg), then 7.6 mg of EDC (20mM) and 4.6 mg of NHS (20mM) were added. After reacting for 16 hrs, precipitate formed at the bottom of the reaction vial. The precipitate was rinsed with dichloromethane 3 times, dissolved in DMF and then subject to TEM analysis. TEM experiments were carried out using a JEOL JEM2100 TEM operated at an acceleration voltage of 200 kV. To prepare the TEM sample, one drop of single crystal or nanoparticle suspension was cast on a carbon-coated nickel grid. After solvent evaporation, the sample was used for TEM observation without further treatment. UV-Vis spectra were collected using an Ocean Optics USB4000 Miniature Fiber Optic Spectrometer at room temperature.

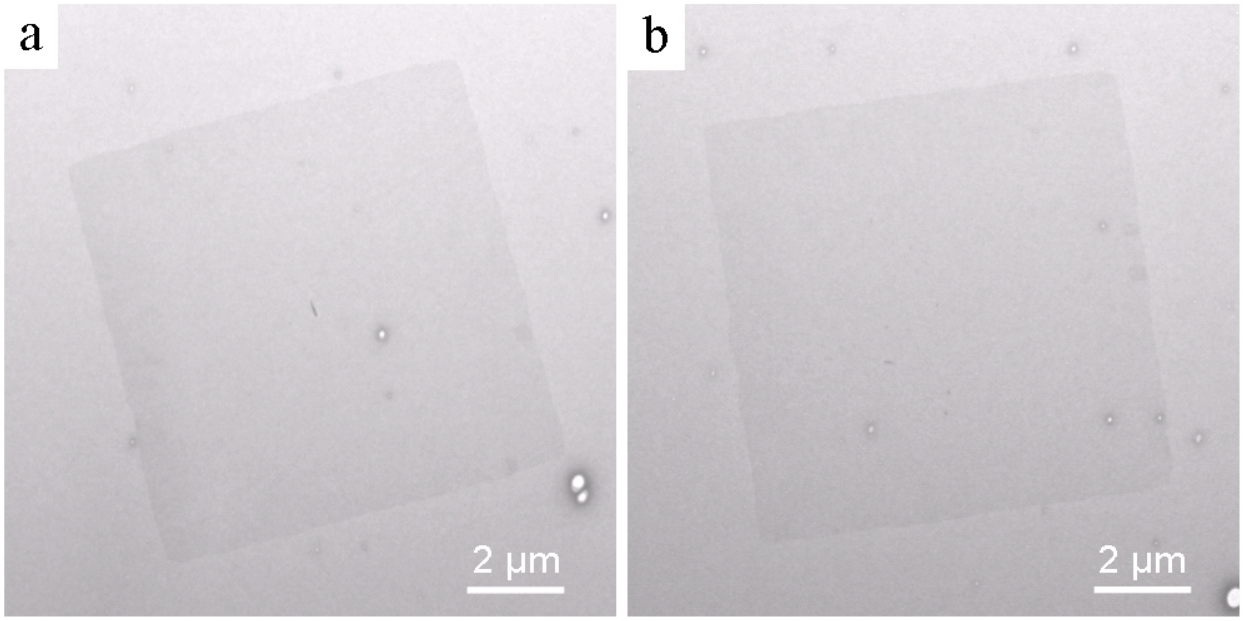

Fig. S1 TEM images of polymer single crystals formed by solution crystallization. (a) COOH-PEG-SH and (b) BOC-NH-PEG-SH.

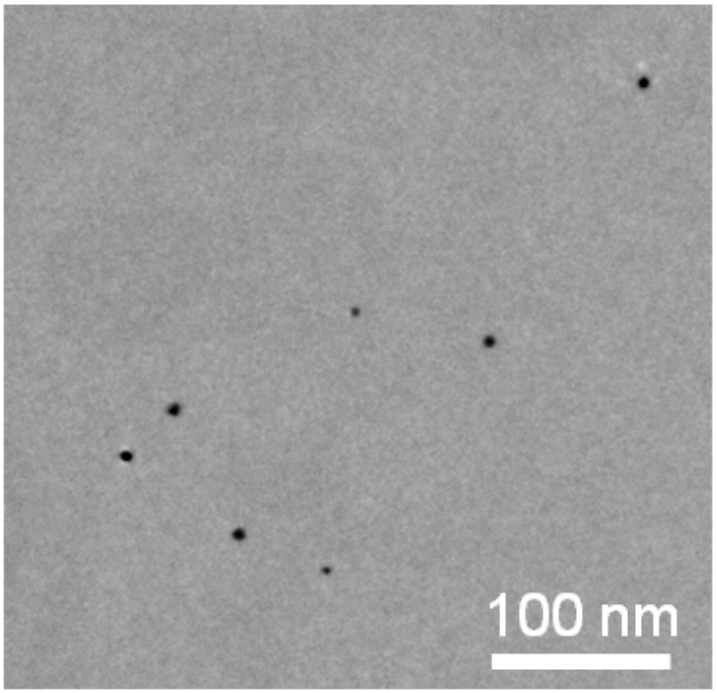

Fig. S2 TEM image of control experiment of mixing COOH-PEG-Au-DDT and NH_2-PEG-Au-DDT at the absence of EDC/NHS.

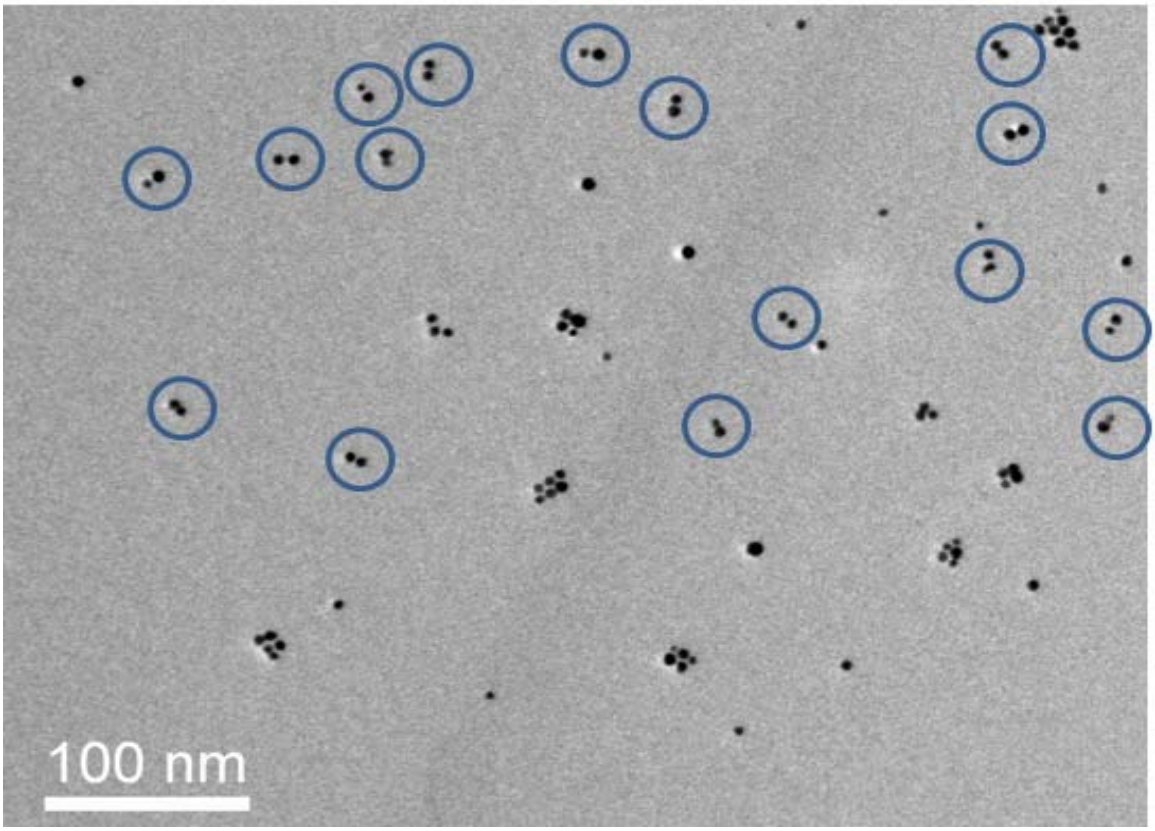

Fig. S3 Low magnification TEM image of 6-6nm Au-Au dimer.

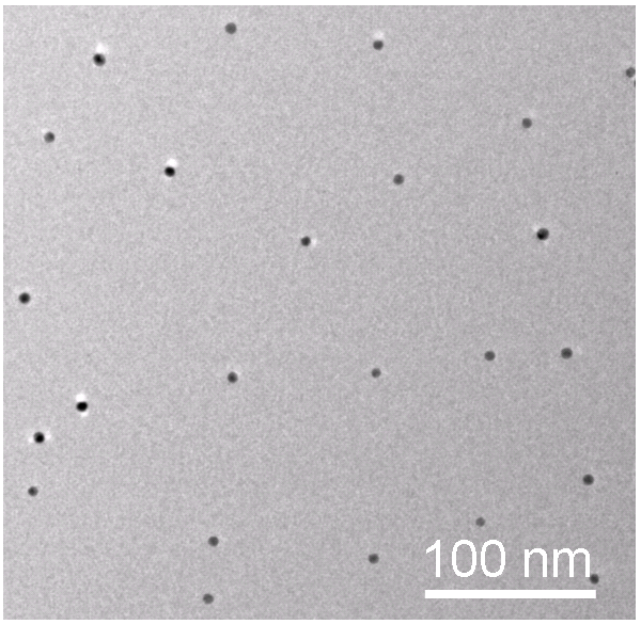

Fig. S4 TEM image of control experiment of mixing NH_2-PEG-Au-DDT and PAA at the absence of EDC/NHS.