Supporting Information

for

Orthogonally dual-clickable Janus nanoparticles *via* a cyclic templating strategy

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Experimental Section

Materials. Poly(acrylic acid)-block-polystyrene (PAA_{105}-*b*-PS_{135}) copolymers were synthesized by acidolysis of P*t*BA_{105}-*b*-PS_{135} (PDI<1.16) precursors, which were prepared by sequential polymerization of *tert*-butyl acrylate and styrene *via* nitroxide mediated radical polymerization (NMP), followed by trifluoroacetic acid (TFA) deprotection, as reported in the literature [1]. Citrate stabilized 40 nm gold nanoparticles were purchased from Nanopartz Inc., and 2 nm gold nanoparticles stabilized in citrate solution were obtained from Strem Chemicals, Inc. Tetrahydrofuran (THF), copper sulfate pentahydrate, sodium ascorbate, propargyl alcohol, 11-azido-3,6,9-trioxaundecan-1-amine, 4-(dimethylamino)pyridine (DMAP), 2,2'-(ethylenedioxy)bis(ethylamine), N,N'-dicyclohexylcarbodiimide (DCC), 1-[3'-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDCI) and 4,7,10,13,16,19,22,25,32,35,38,41,44,47,50,53-hexadecaoxa-28,29-dithiahexapentacontanedioic acid were used as received from Sigma-Aldrich Company (St. Louis, MO).

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Inova 300 MHz or Varian Mercury 300 MHz spectrometers interfaced to a UNIX computer using VnmrJ software. Chemical shifts were referred to the solvent resonance signals.

Gel permeation chromatography was performed on a Waters Chromatography, Inc., 1515 isocratic HPLC pump equipped with an inline degasser, a model PD2020 dual-angle, light scattering detector (Precision Detectors, Inc.), a model 2414 differential

refractometer (Waters, Inc.), and four PL_{gel} polystyrene-*co*-divinylbenzene gel columns (Polymer Laboratories, Inc.) connected in series: 5 μm Guard (50 × 7.5 mm), 5 μm Mixed C (300 × 7.5 mm), 5 μm 10^4 (300 × 7.5 mm), and 5 μm 500 Å (300 × 7.5 mm) using the Breeze (version 3.30, Waters, Inc.) software. The instrument was operated at 35 °C with THF as eluent (flow rate set to 1.0 mL/min). Polymer solutions were prepared at a known concentration (*ca*. 3 mg/mL) and an injection volume of 200 μL was used. Data collection was performed with Precision Acquire 32 Acquisition program (Precision Detectors, Inc.) and analyses were carried out using Discovery32 software (Precision Detectors, Inc.) with a system calibration curve generated from plotting molecular weight as a function of retention time for a series of broad polydispersity poly(styrene) standards.

IR spectra were recorded on an IR Prestige 21 system (Shimadzu Corp., Japan) and analyzed using IRsolution v. 1.40 software.

Ultraviolet-visible spectroscopy (UV-vis) absorption measurements were made using a UV-2550 system (Shimadzu Corp., Japan) using PMMA cuvettes. Spectra were analyzed with UV-Probe v. 2.33 software.

Fluorescence spectra were obtained using a RF-5301 PC system (Shimadzu Corp., Japan) and analyzed with Panaroma Fluorescence v. 2.1 software.

Glass transition temperatures (T_g) were measured by differential scanning calorimetry on a Mettler-Toledo DSC822® (Mettler-Toledo, Inc., Columbus, OH), with a heating rate of 10 °C /min. Measurements were analyzed using Mettler-Toledo Star^e v. 7.01 software. The T_g was taken as the midpoint of the inflection tangent, upon the third

heating scan. Thermogravimetric analysis was performed under N_2 atmosphere using a Mettler-Toledo model TGA/SDTA851[e], with a heating rate of 5 °C /min. Measurements were analyzed using Mettler-Toledo Star[e] v. 7.01 software.

Dynamic light scattering measurements were conducted with a Brookhaven Instruments, Co. (Holtsville, NY) DLS system equipped with a model BI-200SM goniometer, BI-9000AT digital correlator, and a model EMI-9865 photomultiplier, and a model Innova 300 Ar ion laser operated at 514.5 nm (Coherent Inc., Santa Clara, CA). Measurements were made at 25 ± 1 °C. Prior to analysis, solutions were filtered through a 0.45 μm Millex®-GV PVDF membrane filter (Millipore Corp., Medford, MA) to remove dust particles. Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 ratio spaced channels, and initial delay of 5 μs, a final delay of 50 ms, and a duration of 8 minutes. A photomultiplier aperture of 400 μm was used, and the incident laser intensity was adjusted to obtain a photon counting of between, 200 and 300 kcps. The calculations of the particle size distributions and distribution averages were performed with the ISDA software package (Brookhaven Instruments Company), which employed single-exponential fitting, Cumulants analysis, and CONTIN particle size distribution analysis routines. All determinations were average values from ten measurements.

Transmission electron microscopy (TEM) bright-field imaging was conducted on a Hitachi H-7500 microscope, operating at 100 kV. The TEM imaging at high magnification was carried out on a FEI Tecnai G2 F20 microscope, operating at 200 kV. The samples were prepared as following: 4 μL of the dilute solution (with a polymer concentration of *ca.* 0.2 ─ 0.5 mg/mL) were deposited onto a carbon-coated copper grid,

which was pre-treated with absolute ethanol or oxygen plasma to increase the surface hydrophilicity. After 1 min, the excess of the solution was quickly wicked away by a piece of filter paper. The samples were then negatively stained with 4 μL of 1 wt% phosphotungstic acid (PTA) aqueous solution. After 30 seconds, the excess PTA solution was quickly wicked away by a piece of filter paper and the samples were left to dry under room temperature overnight.

Atomic force microscopy (AFM) imaging was performed using a MFP-3D system (Asylum Research, Santa Barbara, CA) in tapping mode using standard silicon tips (AC160TS, 160 μM, spring constant 42 N m^{-1}). Samples were prepared by direct deposition onto freshly cleaved mica or AP-mica substrates and allowed to stand for 30 s after which the excess solution was wicked off using a filter paper and air-dried.

Preparation of PAA_{105}-*b*-PS_{135} micelle. A round-bottom flask equipped with a stir bar was charged with PAA_{105}-*b*-PS_{135}, (M_n^{NMR} = 21000 g/mol; 0.60 g, 3.0 mmol of acrylic acid groups), THF (300 mL) was added and the solution was allowed to stir at room temperature for 2 hours to ensure the mixture was homogeneous. Nanopure water (300 mL) was added *via* a metering pump at the rate of 15 mL/h. After all the water had been added and further stirred for 12 hours, the micelle solution was transferred to presoaked dialysis membrane tubes (MWCO *ca*. 6-8 kDa), and dialyzed against nanopure water for 4 days, to remove all THF. The final concentration of micelle solution was 0.67 mg/mL. D_h (DLS, number) = 25 ± 7 nm; D_h (DLS, volume) = 31 ± 13 nm; D_h (DLS, intensity) = 55 ± 22 nm; D_{av} (TEM) = 21 ± 2 nm; D_{av} (AFM) = 84 ± 14 nm; H_{av}

(AFM) = 5 ± 1 nm. Lyophilization of an aliquot of this solution gave a white solid for characterization. DSC: $(T_g)_{PAA}$ = 133 °C, $(T_g)_{PS}$ = 101 °C. TGA in N_2: 200–300 °C, 16% mass loss; 380–450 °C, 71% mass loss, 10% mass remaining above 450 °C. IR: 3550-2900, 1895, 1721, 1603, 1584, 1491, 1456, 1232, 1177, 1026, 912, 878, 758, 703 cm^{-1}.

Preparation of azide-functionalized [PAA_{84}-*co*-$PAA(N_3)_{21}$]-*b*-PS_{135} micelle. To a stirred solution of micelle (100 mL, 0.67 mg/mL, 0.34 mmol of acrylic acid) in a round-bottom flask was added a solution of 11-azido-3,6,9-trioxaundecan-1-amine (14.8 mg, 0.068 mmol) in nanopure water (1.5 mL). The solution was allowed to stir for two hours at room temperature. To this reaction mixture was added dropwise, *via* a metering pump at the rate of 6 mL/h, a solution of EDCI (22.1 mg, 0.075 mmol) dissolved in nanopure water (6 mL). The reaction mixture was allowed to stir overnight at room temperature and was then transferred to presoaked dialysis membrane tubes (MWCO *ca*. 6-8 kDa), and dialyzed against nanopure water for 4 days to remove small molecule contaminants. Final concentration of azide-functionalized micelle solution was 0.54 mg/mL. D_h (DLS, number) = 30 ± 8 nm; D_h (DLS, volume) = 35 ± 19 nm; D_h (DLS, intensity) = 49 ± 20 nm; D_{av} (TEM) = 22 ± 3 nm; D_{av} (AFM) = 92 ± 18 nm; H_{av} (AFM) = 6 ± 2 nm. Lyophilization of an aliquot of this solution gave a white solid for characterization. DSC: $(T_g)_{PAA}$ = 138 °C, $(T_g)_{PS}$ = 105 °C. TGA in N_2: 200–300 °C, 10% mass loss; 380–450 °C, 80% mass loss, 10% mass remaining above 450 °C. IR: 3500-3100, 3080, 3026, 2921, 2100, 1721, 1658, 1565, 1493, 1452, 1387, 1263, 1146, 761, 700, 621 cm^{-1}.

Preparation of azide-functionalized shell crosslinked (SCK) nanoparticle. To a stirred solution of azide-functionalized micelle (100 mL, 0.54 mg/mL, 0.18 mmol of acrylic acid, 0.04 mmol of azide groups) in a round-bottom flask equipped with a stir bar was added, dropwise over 10 minutes, a solution of 2,2'-(ethylenedioxy)bis(ethylamine) (5.2 mg, 0.034 mmol) in nanopure water (1.0 mL). The solution was allowed to stir for 3 h at room temperature. To this reaction mixture was added dropwise, *via* a metering pump at the rate of 2 mL/h, a solution of EDCI (12.1 mg, 0.041 mmol) dissolved in nanopure water (2 mL). The reaction mixture was allowed to stir overnight at room temperature and was then transferred to presoaked dialysis membrane tubes (MWCO *ca*. 6-8 kDa), and dialyzed against nanopure water for 4 days to remove small molecule contaminants. Final concentration of SCK solution was 0.46 mg/mL. D_h (DLS, number) = 28 ± 10 nm; D_h (DLS, volume) = 51 ± 17 nm; D_h (DLS, intensity) = 73 ± 29 nm; D_{av} (TEM) = 22 ± 3 nm; D_{av} (AFM) = 98 ± 17 nm; H_{av} (AFM) = 5 ± 2 nm. Lyophilization of an aliquot of this solution gave a white solid for characterization. DSC: $(T_g)_{PS}$ = 105 °C. TGA in N_2: 200–300 °C, 12% mass loss; 380–450 °C, 73% mass loss, 10% mass remaining above 450 °C. IR: 3400-3140, 3027, 2972, 2921, 2100, 1720, 1655, 1635, 1561, 1493, 1452, 1397, 1164, 1009, 808, 764, 692 cm^{-1}.

Synthesis of alkyne-OEO-disulfide. To a solution of 4,7,10,13,16,19,22,25,32,35,38,41,44,47,50,53-hexadecaoxa-28,29-dithiahexapentacontanedioic acid (azide-OEO-disulfide, 243 mg, 0.27 mmol) in 4 mL of dry CH_2Cl_2 at room temperature were added DMAP (17.7 mg, 0.15 mmol) and DCC (0.123 g, 0.60 mmol), and the reaction mixture was stirred for 10 minutes. After the

addition of propargyl alcohol (60.0 mg, 0.50 mmol), the reaction mixture was further stirred 20 hours at room temperature. Then the reaction mixture was filtered with Celite and the filtrate was concentrated to *ca*. 0.3 mL. The crude product obtained was further purified by flash column chromatography (8-9% MeOH/CH_2Cl_2, v/v) to afford alkyne-OEO-disulfide as a light yellow solid (0.289 g, 98% yield). Alkyne-OEO-disulfide was stored under nitrogen atmosphere at -15 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 4.65 (s, 4H, OC*H*$_2$C≡CH), 3.75-3.57 (m, 64H, OC*H*$_2$CH$_2$, C*H*$_2$CH$_2$C(O)O, and C*H*$_2$CH$_2$S), 2.84 (t, *J* = 6.9 Hz, 4H, CH$_2$C*H*$_2$C(O)O), 2.61 (t, *J* = 6.9 Hz, 4H, CH$_2$C*H*$_2$S), 2.48 (s, C≡C*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 170.7, 77.1, 75.0, 70.6-70.3, 69.6, 66.3, 51.9, 38.4, 34.8.

Preparation of alkyne-functionalized gold nanoparticles (GNPs). To a stirred solution of 40 nm GNPs colloid solution (0.05 mg/mL, 70000 Au surface atoms per particle, particle concentration = 8.7×10^{10} per mL, surface Au concentration = 1.0×10^{-5} mmol/mL, 100 mL) at pH 9 in a round-bottom flask, a solution of alkyne-OEO-disulfide in ethanol (10 mg/mL, 0.8 mL, 16 times excess than needed) was added. After being stirred for 24 hours at room temperature, alkyne-functionalized GNPs solution was ultracentrifuged for 5 min (at 13 krpm, 20 °C), followed by decantation of supernatants and subsequent dispersal into same volume of nanopure water. Ultracentrifugation and re-dispersal were repeated three times to remove all unreacted small molecules. Alkyne-functionalized GNPs solution was stored at – 4 °C. D_h (DLS, number) = 55 ± 5 nm; D_h (DLS, volume) = 56 ± 7 nm; D_h (DLS, intensity) = 57 ± 10 nm; D_{av} (TEM) = 46 ± 6 nm; D_{av} (AFM) = 230 ± 40 nm; H_{av} (AFM) = 45 ± 7 nm. UV-vis: (H_2O) λ_{max} = 529 nm (ε = 7

$\times 10^9$ $M^{-1}cm^{-1}$). 40 nm GNPs: D_h (DLS, intensity) = 49 ± 5 nm; D_h (DLS, volume) = 50 ± 5 nm; D_h (DLS, number) = 51 ± 7 nm; D_{av} (TEM) = 46 ± 4 nm.

Cu-catalyzed azide/alkyne cycloaddition (CuAAC) reaction between nanoparticles. To a stirred solution of alkyne-functionalized GNPs (30 mL) in a round-bottom flask, was added a solution of azide-functionalized micelles or SCKs (15 mL), a solution of sodium ascorbate (250 mM, 0.90 mL) and a solution of CuSO4•5H_2O (50 mM, 0.90mL). Once all reagents were added, one to five minutes sonication was applied to the reaction mixture to avoid aggregation at the beginning of the click reaction. After being stirred for 10 hours at room temperature, the reaction mixture was ultracentrifuged for 5 min (at 13 krpm, 20 °C), followed by decantation of supernatants and subsequent dispersal into same volume of nanopure water. Ultracentrifugation and re-dispersal were repeated three times to ensure complete separation. The supernatant solutions were combined, dialyzed against nanopure water for 4 days to remove small molecule contaminants, and ultracentrifuged for 10 minutes to precipitate remaining dense species, to yield a solution of recovered azide-functionalized micelles or SCKs. The precipitate was re-dispersed into 30 mL nanopure water to yield a solution of hybrid nanoclusters. The final concentration of hybrid nanoclusters in the solution was 8.7×10^{10} particles per mL, as estimated from the concentration of GNPs. The solution of hybrid nanoclusters was stored at – 4 °C. Hybrid nanoclusters containing GNPs and SCKs: D_h (DLS, number) = 81 ± 19 nm; D_h (DLS, volume) = 117 ± 38 nm; D_h (DLS, intensity) = 136 ± 36 nm; D_{av} (TEM, GNPs) = 45 ± 7 nm; D_{av} (TEM, SCKs) = 20 ± 2 nm; D_{av} (AFM) = 240 ± 40 nm; H_{av} (AFM) = 53 ± 7 nm. UV-vis: (H_2O) λ_{max} = 536 nm ($\varepsilon = 7 \times 10^9$ $M^{-1}cm^{-1}$).

Recovered azide-functionalized SCKs: D_h (DLS, intensity) = 28 ± 7 nm; D_h (DLS, volume) = 33 ± 12 nm; D_h (DLS, number) = 48 ± 23 nm; D_{av} (TEM) = 22 ± 3 nm; D_{av} (AFM) = 91 ± 15 nm; H_{av} (AFM) = 5 ± 2 nm.

Formation of Janus-faced thiol-modified SCKs (JSCKs) by ligand exchange reaction. To a solution of hybrid nanoclusters containing GNPs and SCKs (30 mL), was added a solution of alkyne-OEO-disulfide in ethanol (8.0 mg/mL, 1.2 mL, 100 times excess than needed) and a solution of sodium ascorbate (250 mM, 0.60 mL) [2]. The reaction mixture was stirred at room temperature for 3 days, with application of sonication intermittently for 30 minutes four times per day. Afterwards, the reaction mixture was ultracentrifuged for 5 min (at 13 krpm, 20 °C), followed by decantation of supernatants and subsequent dispersal into same volume of nanopure water. Ultracentrifugation and re-dispersal were repeated three times to ensure complete separation. The supernatant solutions were combined, dialyzed against nanopure water for 4 days to remove small molecule contaminants, and ultracentrifuged for 10 minutes to precipitate remaining dense species, to yield a solution of Janus-faced thiol-modified SCKs (JSCKs). The precipitate was re-dispersed into 30 mL nanopure water to yield a solution of recovered alkyne-functionalized GNPs. The recovered alkyne-functionalized GNPs solution was stored at – 4 °C. JSCKs: D_h (DLS, intensity) = 29 ± 15 nm; D_h (DLS, volume) = 34 ± 19 nm; D_h (DLS, number) = 46 ± 27 nm; D_{av} (TEM) = 23 ± 2 nm; D_{av} (AFM) = 89 ± 12 nm; H_{av} (AFM) = 4 ± 2 nm. Recovered alkyne-functionalized GNPs: D_h (DLS, intensity) = 62 ± 13 nm; D_h (DLS, volume) = 60 ± 15 nm; D_h (DLS, number) =

58 ± 10 nm; D_{av} (TEM) = 46 ± 7 nm. UV-vis: (H_2O) λ_{max} = 529 nm ($\varepsilon = 7 \times 10^9$ $M^{-1}cm^{-1}$).

Fluorescein labeling by Cu-catalyzed azide/alkyne cycloaddition (CuAAC) reaction. To an aqueous solution of the JSCKs (10 mL) was added a solution of alkyne-functionalized fluorescein (2 mg/mL, 0.5 mL, large excess) in methanol, a solution of sodium ascorbate (50 mM, 0.5 mL) and solution of CuSO4•5H_2O (50 mM, 0.50 mL). The reaction mixture was allowed to stir for 2 days and was then transferred to presoaked dialysis tubing (MWCO *ca*. 6000-8000 Da) and extensively dialyzed against nanopure water for 5 days to remove excess dye and copper catalyst. UV-vis: (H_2O) λ_{max} = 490.5 nm.

BODIPY 577/618 maleimide labeling by thiol-maleimide Michael addition. To an aqueous solution of the JSCKs (10 mL) or fluorescein labeled JSCKs (10 mL) was added a solution of thiol-reactive BODIPY 577/618 maleimide in a pH=10 sodium carbonate buffered solution (2 mg/mL, 1.5 mL, large excess). The reaction mixture was allowed to stir for 2 days under a nitrogen atmosphere in the presence of tris(2-carboxyethyl)phosphine and was then transferred to presoaked dialysis tubing (MWCO *ca*. 6000-8000 Da) and extensively dialyzed against nanopure water for 5 days to remove excess dye. UV-vis: (H_2O) λ_{max} = 599.5 nm.

Preparation of thiol-functionalized shell crosslinked (SCK) nanoparticles. To an aqueous solution of azide-functionalized SCKs (10 mL) was added a solution of alkyne-OEO-disulfide in ethanol (10 mg/mL, 2.0 mL, large excess), sodium ascorbate (250 mM, 0.040 mL) and solution of $CuSO4•5H_2O$ (50 mM, 0.040 mL). The reaction mixture was allowed to stir for 2 days and was then transferred to presoaked dialysis tubing (MWCO *ca*. 6000-8000 Da) and dialyzed against nanopure water for 5 days to remove excess alkyne-OEO-thiol.

Studies of the association of 2 nm GNPs with JSCKs, thiol-functionalized SCKs and azide-functionalized SCKs. To an aqueous solution of the JSCKs (1 mL) was added a solution of citrate stabilized 2 nm GNPs (several drops). To an aqueous solution of the thiol-functionalized SCKs (1 mL) was added a solution of citrate stabilized 2 nm GNPs (several drops). To an aqueous solution of the azide-functionalized SCKs (1 mL) was added a solution of citrate stabilized 2 nm GNPs (several drops). Three reaction mixtures were allowed to stir for 2 days and were then transferred to presoaked dialysis tubings (MWCO *ca*. 6000-8000 Da) and dialyzed against nanopure water for 5 days to remove most unbound 2 nm GNPs [3].

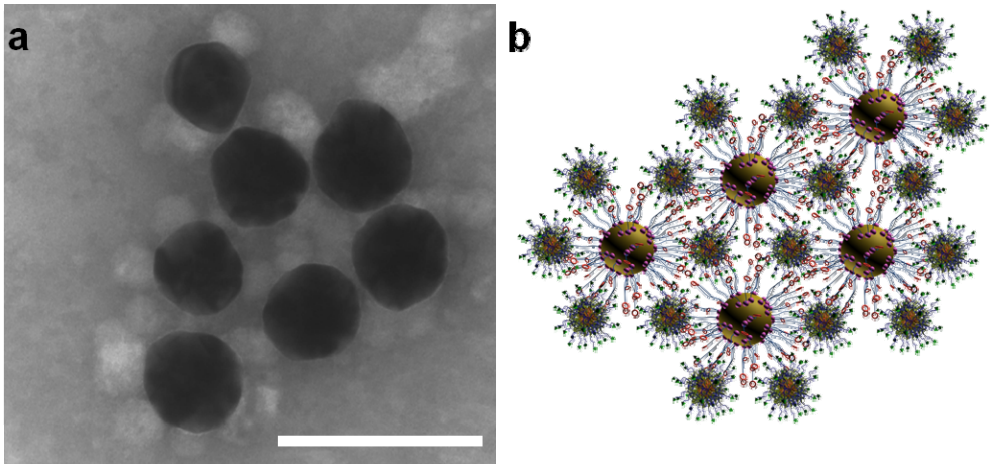

Figure S1. Hybrid crosslinked network. a, TEM image of hybrid crosslinked network made from azide-functionalized SCKs and alkyne-functionalized GNPs in near 1:1 ratio. Scale bar: 100 nm. b, Schematic representation of hybrid crosslinked network of GNPs and SCKs.

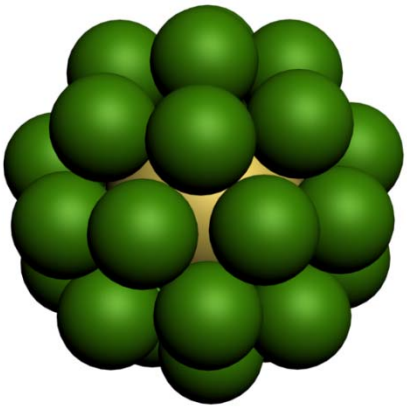

Figure S2. Schematic illustration of 27 SCKs (with a diameter of 28 nm) packing at the surface of one GNP (with a diameter of 53 nm) based on "hard sphere" surface contacts. Using the angle (40.4°) between two adjacent circles of radius 28 on the surface of a circle radius 53, the maximum number of smaller spheres that can be packed on the surface of the larger sphere is 27. Sloane, N. J. A.; Hardin, R. H.; Smith, W. D., and others. Spherical Codes. http://www2.research.att.com/~njas/packings/ (accessed January 2011).

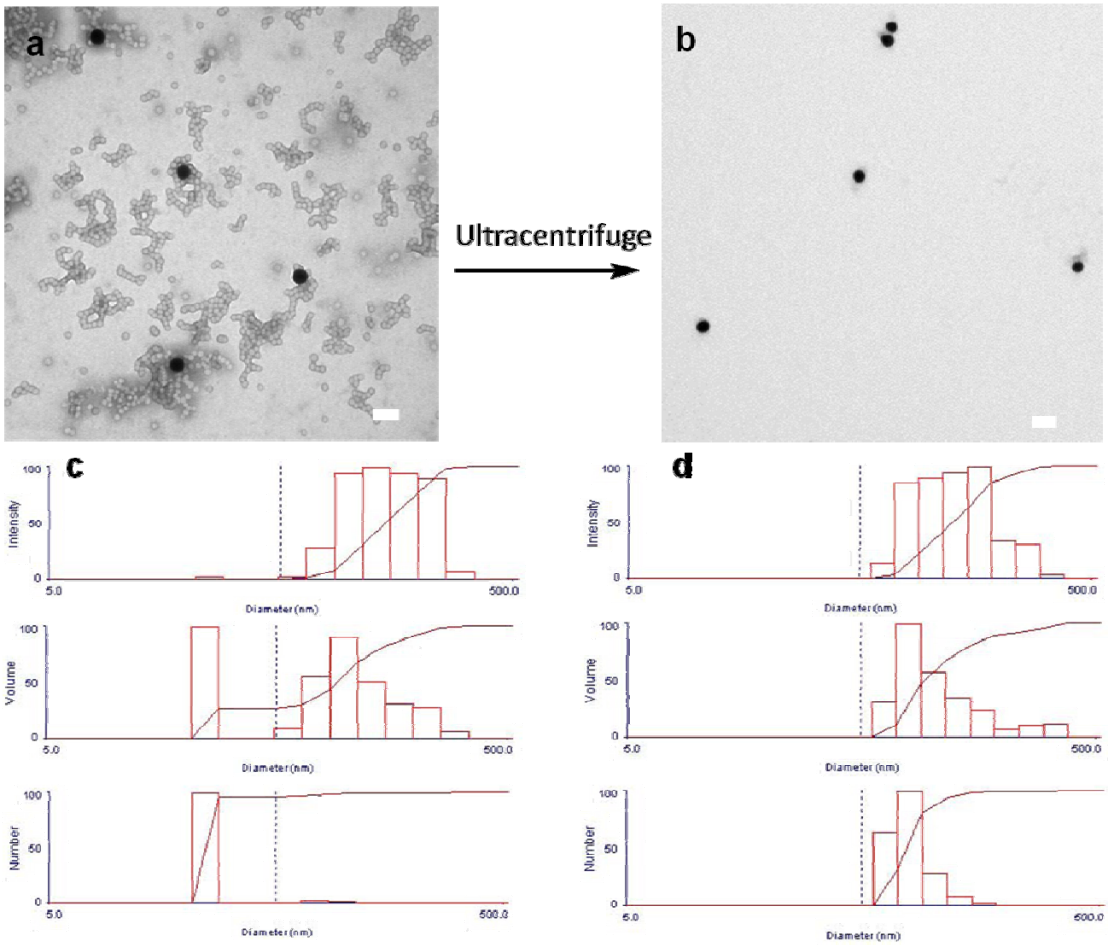

Figure S3. a, TEM image of hybrid nanoclusters, consisting of one GNP surrounded by several SCKs, and an excess of SCKs. b, TEM image of isolated hybrid nanoclusters after ultracentrifuge. Scale bars: 100 nm. c, DLS results of hybrid nanoclusters formed after click reaction. The number distribution plot shows that there is only a small portion of hybrid nanoclusters. d, DLS results of hybrid nanoclusters isolated by ultracentrifugation. The number distribution plot confirms successful removal of unbound SCKs.

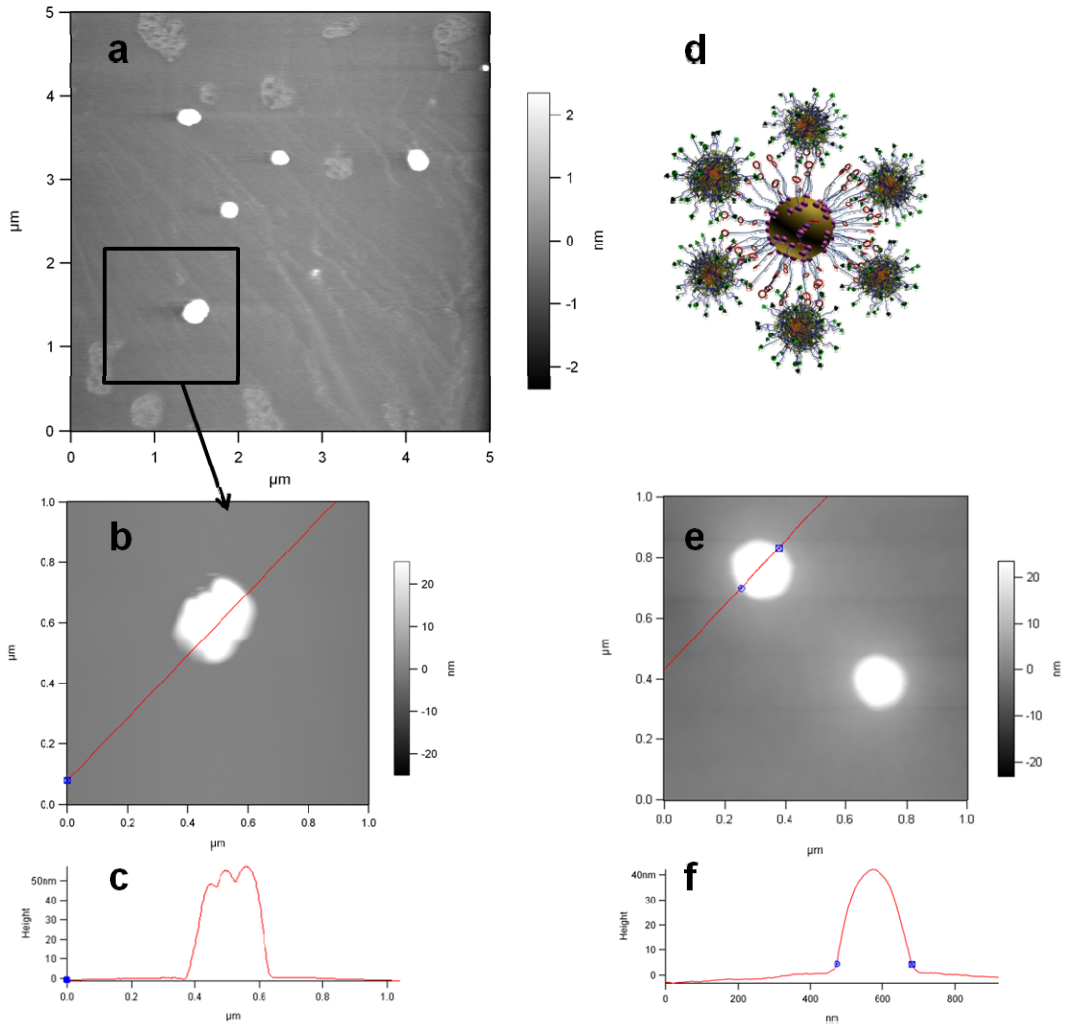

Figure S4. a, AFM height image of hybrid nanoclusters on AP-mica. b, Height image of an enlarged part of image a, showing a single hybrid nanocluster. c, Section analyses corresponding to the lines in image d. The height of the hybrid nanocluster is in agreement with the average height of a GNP plus two-fold the average height of an SCK. The wave-like shape of the pattern indicates that several SCKs are on the top of the GNP. d, Schematic representation of hybrid nanoclusters. e, Height image of two alkyne-functionalized GNPs. f Section analyses corresponding to the lines in image e.

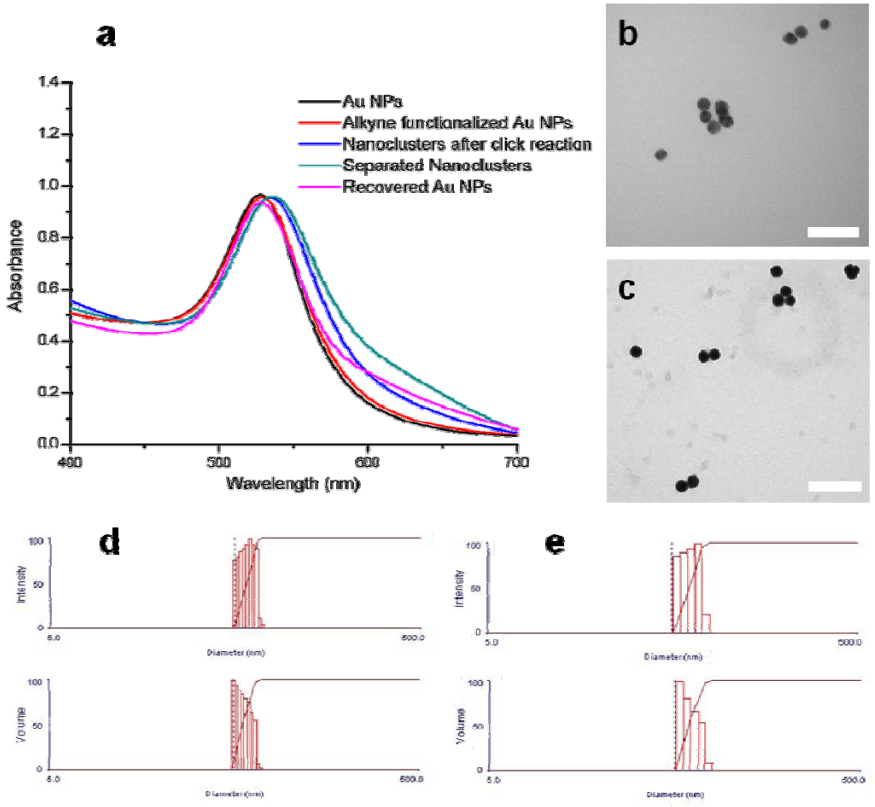

Figure S5. a, Monitoring the desymmetrization cycle by UV-vis of the gold surface plasmon resonance band in the solution, reflecting the surface functionality of the GNPs. At the beginning, 40 nm GNPs have a strong absorption at 527 nm, due to the characteristic surface plasmon resonance. After alkyne functionalization, the absorption peak slightly red shifted to 529 nm. In the next step, the absorption peak of hybrid nanoclusters largely shifted to 536 nm because of a change of refractive index caused by SCKs that attached on the GNPs surfaces. Finally, the absorbance band blue shifted back to 529 nm after the GNPs were recovered by ligand exchange reactions. b, TEM image of initial alkyne-functionalized GNPs; average diameter is 46 ± 6 nm. c, TEM image of recovered alkyne-functionalized GNPs; average diameter is 46 ± 7 nm, after counting more than 100 particles. Scale bars: 200 nm. d, DLS results of initial alkyne-functionalized GNPs. e, DLS results of recovered alkyne-functionalized GNPs.

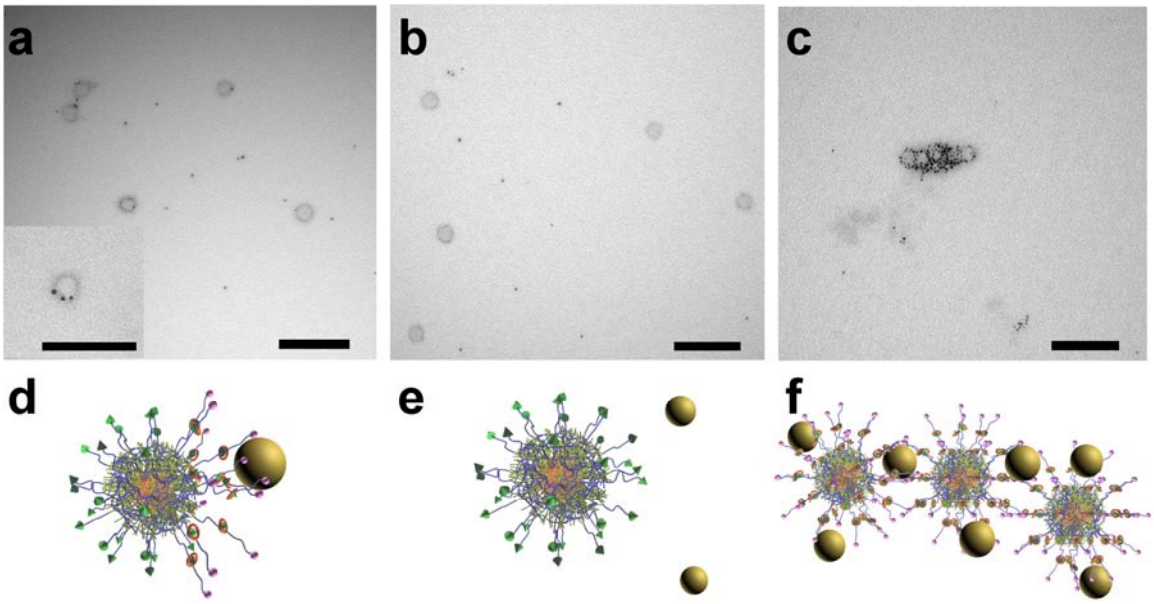

Fig. S6. a, TEM image of JSCKs labeled with 2 nm GNPs. b, TEM image of azide-functionalized SCKs mixed with 2 nm GNPs as negative control. c, TEM image of thiol-functionalized SCKs labeled with 2 nm GNPs as positive control. d, Schematic representation of JSCKs labeled with GNPs. e, Schematic representation of negative control. f, Schematic representation of positive control. Scale bars: 100 nm.

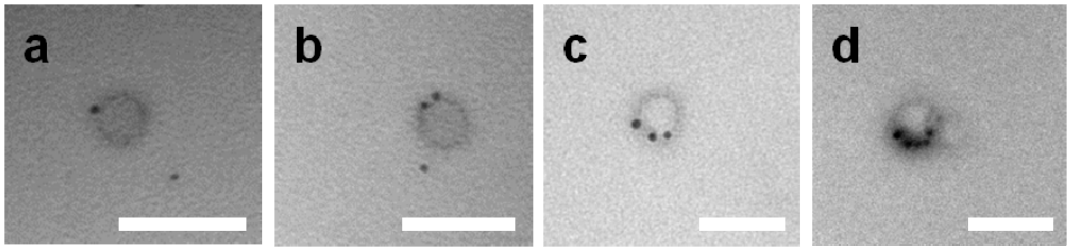

Figure S7. Selective TEM images of JSCKs labeled with 2 nm GNPs. Scale bars: 50 nm.

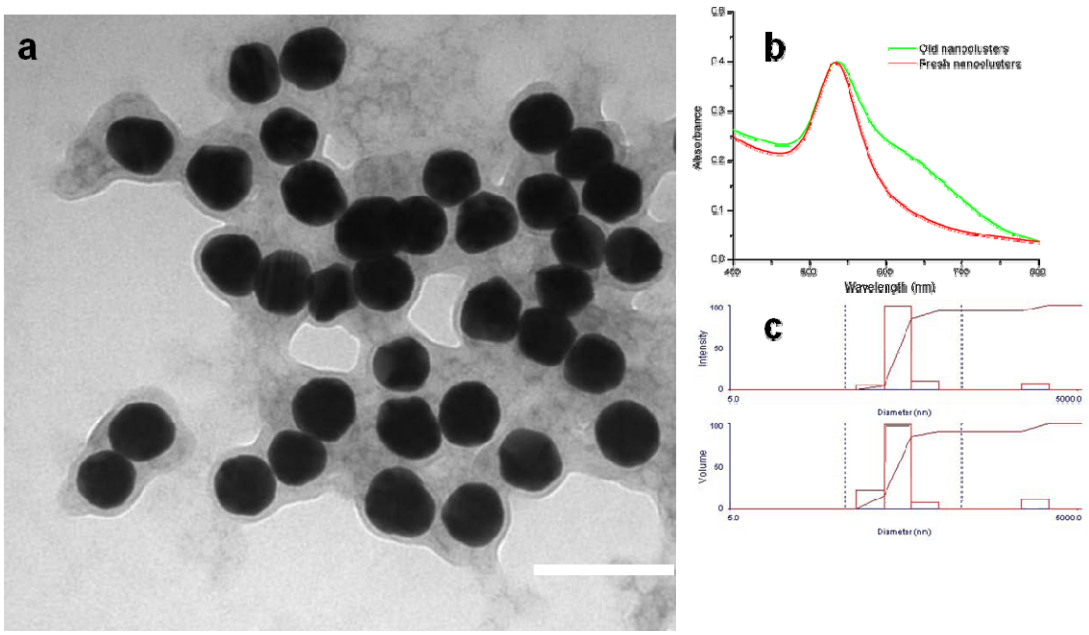

Figure S8. a, TEM image of hybrid nanoclusters five days after micelles were attached onto GNPs by CuAAC. Scale bar: 100 nm. b, UV-vis spectra of fresh hybrid nanoclusters and after five days. c, DLS of hybrid nanoclusters five days after CuAAC. Micron-sized species had been detected by DLS, which is in agreement with the TEM results.

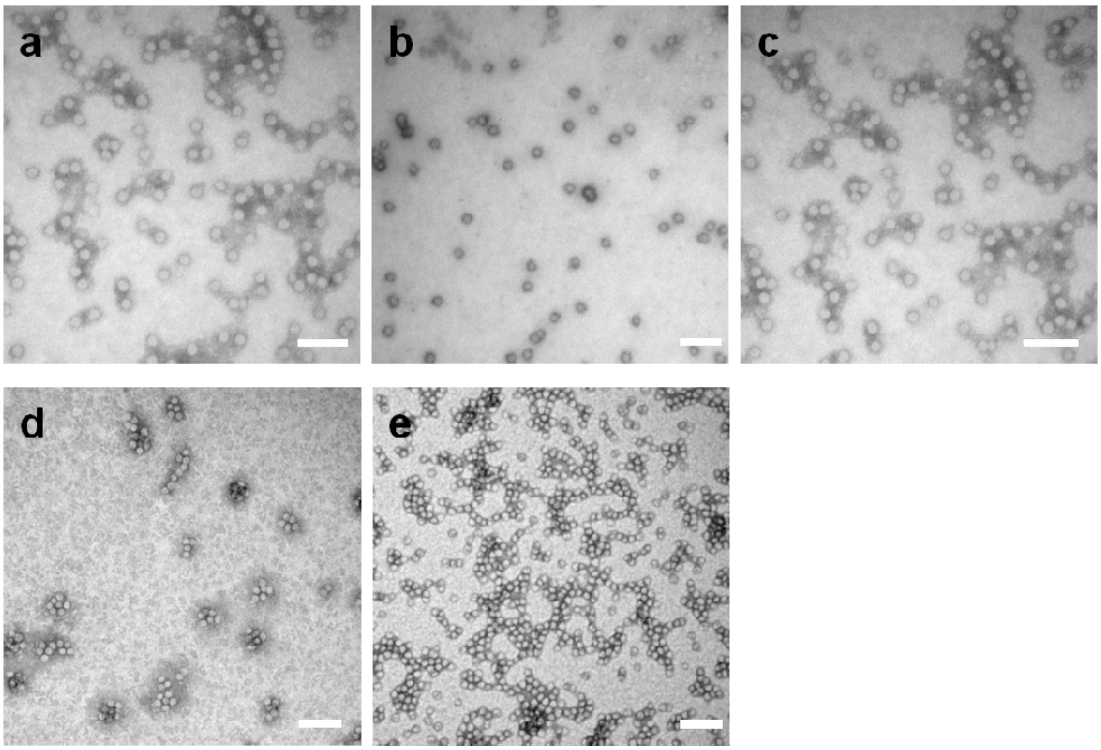

Figure S9. TEM images of all polymer nanoparticles. a, PAA_{105}-*b*-PS_{135} micelles. b, Azide-functionalized micelles. c, Azide-functionalized SCKs. d, Janus-faced thiol-functionalized SCKs. e, Recovered azide-functionalized SCKs. Scale bars: 100 nm.

References:

1. O'Reilly, R. K.; Joralemon, M. J.; Wooley, K. L.; Hawker, C. J. *Chem. Mater.* **2005**, *17*, 5976-5988.

2. Latham, A. H.; Williams, M. E. *Langmuir* **2006**, *22*, 4319-4326.

3. He, T.; Adams, D. J.; Butler, M. F.; Cooper, A. I.; Rannard, S. P. *J. Am. Chem. Soc.* **2009**, *131*, 1495-1501.

Complete list of authors and the full citation of Reference 2 (f):

Percec, V.; Wilson, D. A.; Leowanawat, P.; Wilson, C. J.; Hughes, A. D.; Kaucher, M. S.; Hammer, D. A.; Levine, D. H.; Kim, A. J.; Bates, F. S.; Davis, K. P.; Lodge, T. P.; Klein, M. K.; DeVane, H.; Aqad, E.; Rosen, B. M.; Argintaru, A. O.; Sienkowska, M. J.; Rissanen, K.; Nummelin, S.; Ropponen, J. *Science* **2010**, *328*, 1009-1014.