Amphiphilicity-Driven Organization of Nanoparticles into Discrete Assemblies

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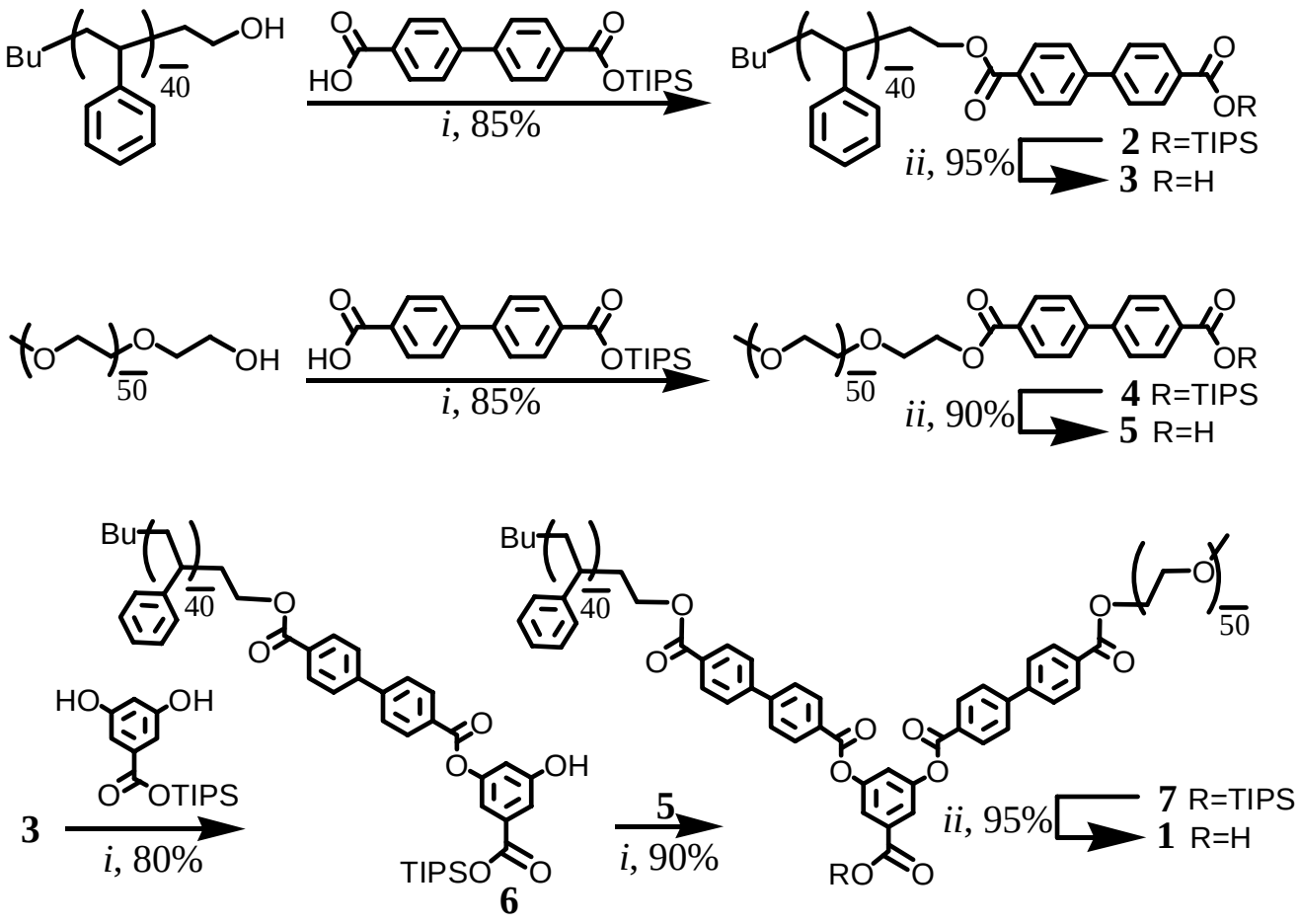
Supporting Information

General. Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on solutions in CD_2Cl_2 or $CDCl_3$ on a Varian Unity 300 (300 MHz) spectrometer. GPC analysis was conducted on a Waters Breeze 1515 series liquid chromatograph equipped with a dual λ absorbance detector (Waters 2487) and three styrogel columns (HR1, HR3, HR4) using linear polystyrene as calibration standards and THF as an eluent. Hydroxyl-terminated polystyrene (M_n=4000 g/mol, M_w/M_n=1.1) was purchased from Polymer Source, Inc. Hydroxyl-terminated poly(ethylene oxide) monomethyl ether with molecular weight (M_n=2,200, M_w/M_n=1.17) was also purchased from Polymer Source, Inc. and was used as received. 4-(N,N-dimethylamino)pyridinium-4-*p*-toluenesulfonate (DPTS) was prepared by mixing saturated THF solutions of DMAP (1 equiv) and *p*-toluenesulfonic acid monohydrate (1 equiv) at room temperature. The precipitate was filtered, washed several times with THF, and dried under vacuum. The structure of DPTS was confirmed by ^{1}H NMR. Materials Studio Program (version 2.1.5) was used to estimate the contour length of the arms, and the size of hybrid micelles upon force field energy minimization in the absence of solvent. Size distribution analysis was carried out with Brookhaven ZetaPALS dynamic light scattering (DLS) instrument with BI-9000AT digital autocorrelator at 656 nm wavelength. All studies were done at a 90° scattering angle and temperature controlled at 25 °C in standard 4 ml cuvettes. Measurements were made using "9KDLSW" software package and the results were averaged over a 10 min time period. TEM images were obtained on a JEOL 1200EX scanning/transmission electron microscope operating at 100 kV accelerating voltage. Samples were prepared by casting one droplet (5 μL) of a dilute aqueous solution (0.1 mg/mL) onto carbon-coated TEM grids followed by immediate blotting of the droplet with filter paper. AFM

imaging was performed using a SOLVERP 47-H Scanning Probe Microscope, equipped with a type EV scanner, operating in tapping mode. The samples were prepared by casting a drop of dilute aqueous solution of Au(PS-PEO)$_n$ NPs onto silicon substrate. The drop was immediately blotted with a filter paper, and the sample was dried in air for several hours before the AFM imaging.

Scheme S1. Synthesis of polystyrene-*b*-poly(ethylene oxide) amphiphile **1**.



Reaction Conditions: *i* DPTS/DIPC, CH_2Cl_2, 2-6 h, rt; *ii* TBAF, THF, -78 ^oC 3h

General procedure for esterification coupling reactions. The acid (1 equiv), phehol (1 equiv), DPTS (1.6 equiv), and CH_2Cl_2 were combined in a round-bottom flask charged with a stir bar at room temperature. 1,3-Diisopropyl carbodiimide (DIPC, 5 equiv) was added after 1 minutes and the

solution was allowed to stir for several hours. The coupling reactions were monitored by TLC, GPC, and ^{1}H NMR. Most of the esterification reactions reported here proceeded very rapidly at room temperature and nearly complete disappearance of starting materials was typically observed within 1-3 h. The reaction mixture was then diluted with dichloromethane and 2-4 extractions with DI water were used to quench the reaction and to remove DPTS. The crude product was purified by column chromatography on silica gel and/or dialysis against DI water for several days as outlined below.

General procedure for the deprotection reactions using tetrabutyl ammonium fluoride (TBAF). Triisopropylsilyl (TIPS) protected compound (1 equiv) was dissolved in THF and cooled to -78 ^{o}C using dry ice-acetone bath. The solution was allowed to stir for 5 min and 10 equiv of TBAF (1.0 M solution in THF) was quickly injected via syringe upon rigorous stirring. Addition of TBAF immediately resulted in appearance of a characteristic yellow-greenish color which remained unchanged throughout the entire reaction. Acetic acid (11 equiv) was added to reaction mixture after 2 h and the stirring proceeded for additional 5 min to ensure that all residual TBAF was quenched before the mixture was allowed to warm to room temperature. The mixture was then diluted with CH_2Cl_2 and washed several times with DI water. The organic layer was collected and concentrated *in vacuo*. The crude product was purified by column chromatography as outlined in the following text.

Biphenyl-4,4'-dicarboxylic acid 4'-triisopropylsilyl ester. Biphenyl-4,4'-dicarboxylic acid (1 equiv) was dissolved in DMSO and 0.3 equiv. of triisopropylsilyl chloride (TIPSCl) was added via syringe. The mixture was stirred for 5 min and 0.33 equiv. of triethyl amine was added dropwise. The reaction was monitored by TLC and was complete after 2 h. The reaction mixture was diluted with 5 fold volume of dichloromethane/THF mixture (70:30 vol.) and DMSO was removed upon several extractions with DI water. The product was purified by flash chromatography on silica gel eluting with THF/CH_2Cl_2 (7:93 vol.) mixture (R_f=0.55) to give the product as white solid. Yield 60 %. ^{1}H

NMR (300 MHz, CD_2Cl_2 /THF-d_8 (9:1 vol.)): δ 1.16 (d, 18 H, *J*= 8.3 Hz), 7.74 (dd, 4H, *J*= 8.3 Hz), 8.13 (d, 2H, *J*= 8.4 Hz), 8.16 (d, 2H, *J*= 8.4 Hz).

TIPS-protected carboxybiphenyl terminated polystyrene (2). Hydroxyl-terminated polystyrene (Polymer Source, Inc. M_n=4000 g/mol, M_w/M_n=1.1) (1 equiv), biphenyl-4,4'-dicarboxylic acid 4'-triisopropylsilyl ester **2** (1.4 equiv), and DPTS (1.5 equiv) were dissolved in CH_2Cl_2 and the mixture was allowed to stir for 5 min before 5 equiv of DIPC was added dropwise. The reaction was monitored by TLC using CH_2Cl_2 as an eluent. Complete disappearance of polystyrene spot (R_f=0.3 in methylene chloride) occurred after 3 h and the reaction mixture was evaporated and the product was isolated by column chromatography eluting with a mixture of hexane and dichloromethane (30:70 vol.) to give the product as a white glassy powder (R_f=0.7). Yield 85 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.85 (br, 6H, C*H*$_3$ of *sec*-Bu), 1.20 (d, 18 H, *J* = 8.2 Hz, C*H*$_3$ of TIPS), 2.3-1.3 (br, 120H, Ar'*H* polystyrene aliphatic protons and C*H* protons of TIPS), 4.03 (br t, 2H, PS-CH_2-C*H*$_2$-O-CO-), 7.4-6.3 (br, 200H, Ar'*H* polystyrene aromatic protons), 7.68 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2' and C-6' protons of biphenyl), 7.77 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2 and C-6 protons of biphenyl), 7.93 (d, 2H, Ar*H*, *J* = 8.3 Hz, C-3' and C-5' protons of biphenyl), 8.21 (d, 2H, Ar*H*, *J* = 8.1 Hz, C-3 and C-5 protons of biphenyl). GPC (254 nm, THF), M_w=4310, PDI=1.08.

Carboxybiphenyl terminated polystyrene (3). This compound was prepared from **2** following the standard TBAF deprotection procedure described above. The crude product was purified by column chromatography on silica gel eluting with 5 % THF in CH_2Cl_2 as an eluent (R_f=0.55) to give **3** as a white glassy powder. Yield 95 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.85 (br, 6H, C*H*$_3$ of *sec*-Bu), 2.3-1.3 (br, 118H, Ar'*H* polystyrene aliphatic protons), 4.03 (br t, 2H, PS-CH_2-C*H*$_2$-O-CO-), 7.4-6.3 (br, 200H, Ar'*H* polystyrene aromatic protons), 7.67 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2' and C-6' protons of biphenyl), 7.75 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2 and C-6 protons of biphenyl), 7.95 (d, 2H, Ar*H*, *J* = 8.3

Hz, C-3' and C-5' protons of biphenyl), 8.22 (d, 2H, Ar*H*, *J* = 8.1 Hz, C-3 and C-5 protons of biphenyl). GPC (254 nm, THF), M_w=4211, PDI=1.1.

TIPS-protected carboxybiphenyl terminated poly(ethylene oxide) (4). Biphenyl-4,4'-dicarboxylic acid 4'-triisopropylsilyl ester (4.0 equiv), hydroxyl-terminated PEO (1.0 equiv), and DPTS (1.6 equiv) were dissolved in dichloromethane. DIPC (5 equiv) was added after 1 min and the reaction was stirred for 4 h. The reaction mixture was washed 3 times with DI water and the product was purified by column chromatography using 9 % MeOH/CH_2Cl_2 mixture as an eluent. Yield 85 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.16 (d, 18 H, *J* = 8.2 Hz, C*H*$_3$ of TIPS), 1.45 (m, 3H, C*H* of TIPS), 3.38 (s, 3H, terminal C*H*$_3$ of PEO), 3.7-3.55 (br, 200H, C*H*$_2$ of PEO), 4.09 (t, 2H, PEO-C*H*$_2$-CH$_2$-O-CO-), 4.49 (t, 2H, PEO-CH$_2$-C*H*$_2$-O-CO-), 7.70 (d, 4H, Ar*H*, *J* = 8.2 Hz, C-2', C-6', C-2, and C-6 protons of biphenyl), 8.16 (d, 4H, Ar*H*, *J* = 8.2 Hz, C-3', C-5', C-3, and C-5 protons of biphenyl). GPC (254 nm, THF), M_w=2770, PDI=1.12.

Carboxybiphenyl terminated poly(ethylene oxide) (5). This compound was prepared from **4** following the standard TBAF deprotection procedure described above. The product was purified by column chromatography using 10 % MeOH/CH_2Cl_2 mixture as an eluent to give **6** as tacky solid.. Yield 90 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.37 (s, 3H, terminal C*H*$_3$ of PEO), 3.75-3.55 (br, 200H, C*H*$_2$ of PEO), 4.26 (t, 2H, PEO-C*H*$_2$-CH$_2$-O-CO-), 4.49 (t, 2H, PEO-CH$_2$-C*H*$_2$-O-CO-), 7.68 (dd, 4H, Ar*H*, *J* = 8.2 Hz, C-2', C-6', C-2, and C-6 protons of biphenyl), 8.16 (dd, 4H, Ar*H*, *J* = 8.2 Hz, C-3', C-5', C-3, and C-5 protons of biphenyl). GPC (254 nm, THF), M_w=2620, PDI=1.12.

3,5-Dihydroxy-triisopropylsilyl benzoate. Morpholine (1.3 equiv) was added to a homogeneous solution of 3,5-dihydroxybenzoic acid (1 equiv) in DMF. Triisopropylsilyl chloride (1.1 equiv) was added via syringe upon rigorous stirring. The reaction mixture was allowed to stir for 5 minutes at room temperature and then diluted with CH_2Cl_2 and washed several times with DI water. The organic

layer was evaporated and the crude product was purified by column chromatography on silica gel (5% THF in CH_2Cl_2) to yield the product as a colorless liquid (R_f = 0.4). Yield: 75 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.13 (d, 18 H, *J*= 8.2 Hz, C*H*$_3$ of TIPS), 1.43 (m, 3H, C*H* of TIPS), 6.59 (t, 1H, Ar''*H*, *J* = 2.0 Hz, DHBA C-4 proton), 7.16 (d, 2H, Ar''*H*, *J* = 2.2 Hz, DHBA C-2 and C-6 protons).

Compound 6. Carboxybiphenyl terminated polystyrene **3** (1 equiv), was added to a 10 wt. % CH_2Cl_2 solution of 3,5-dihydroxy-triisoprorylsilyl benzoate (10 equiv). DPTS (1.2 equiv) was added to the resulting solution and the mixture was stirred for 1 minutes before DIPC (5 equiv) was added via syringe. The reaction proceeded for 4 h. The mixture was diluted with CH_2Cl_2 and washed with water 3 times. The product was purified by flash chromatography eluting with 3 % THF/CH_2Cl_2 mixture (R_f=0.6) to give **6** as a white fluffy solid. Yield: 80 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.88 (br, 6H, C*H*$_3$ of *sec*-Bu), 1.21 (d, 18 H, *J* = 8.2 Hz, C*H*$_3$ of TIPS), 2.3-1.3 (br, 118H, Ar'*H* polystyrene aliphatic protons), 4.03 (br t, 2H, PS-CH_2-C*H*$_2$-O-CO-), 7.4-6.3 (br, 200H, Ar'*H* polystyrene aromatic protons), 7.46 (s, 1H, Ar''*H*, C-2 proton of DHBA), 7.54 (s, 1H, Ar''*H*, C-6 proton of DHBA), 7.69 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2' and C-6' protons of biphenyl), 7.79 (d, 2H, Ar*H*, *J* = 8.2 Hz, C-2 and C-6 protons of biphenyl), 7.96 (d, 2H, Ar*H*, *J* = 8.3 Hz, C-3' and C-5' protons of biphenyl), 8.31 (d, 2H, Ar*H*, *J* = 8.1 Hz, C-3 and C-5 protons of biphenyl). GPC (254 nm, THF), M_w=4489, PDI=1.1.

Compound 7. Compound **6** (1.1 equiv), compound **5** (1.0 equiv), and DPTS (1.6 equiv) were dissolved in dichloromethane. DIPC was added after 1 min and the reaction was stirred for 3 h. The reaction was monitored by TLC and GPC because the molecular weight of the product is much higher than that of both starting materials. The reaction mixture was directly placed onto silica gel column running in 11:89 (vol.) mixture of chloroform and methanol. Collected solution of the product was dried by blowing air through the flask at room temperature. Please note that if solution is heated above 60 ^{o}C under reduced pressure to remove MeOH and $CHCl_3$, partial reesterification of silyl ester

occurs. This is highly undesirable side reaction which must be avoided since selective deblocking of methyl ester cannot be done in the presence of other esters (i.e. esters connecting the arms and biphenyls). After removal of methanol, the product was put on vacuum line and dried for additional 1 h. Yield 90 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (br, 6H, C*H*$_3$ of *sec*-Bu of PS), 1.18 (d, 18 H, *J* = 8.2 Hz, C*H*$_3$ of TIPS), 2.3-1.3 (br, 120H, Ar'*H* polystyrene aliphatic protons and C*H* protons of TIPS), 3.39 (s, 3H, terminal C*H*$_3$ of PEO), 3.7-3.6 (br, 200H, C*H*$_2$ of PEO), 4.05 (br, 2H, PS-CH_2-C*H*$_2$-O-), 4.51 (t, 2H, PEO-CH_2-C*H*$_2$-O-), 7.4-6.3 (br, 200H, Ar'*H* polystyrene aromatic protons), 7.51 (s, 1H, Ar''*H*, C-4 proton of DHBA), 7.71 (br, 2H, Ar''*H*, C-2 and C-6 protons of DHBA), 7.85-7.74 (m, 6H, Ar*H*, C-2 and C-6 protons of PS biphenyl, C-2' and C-6' protons of PS and PEO), 7.96 (d, 4H, Ar*H*, *J* = 8.3 Hz, C-3' and C-5' protons of PS and PEO biphenyl), 8.21 (d, 2H, Ar*H*, *J* = 8.1 Hz *J* = 8.3 Hz, C-2 and C-6 protons of PEO biphenyl), 8.32 (d, 4H, Ar*H*, *J* = 8.1 Hz, C-3 and C-5 protons of PS and PEO biphenyls). GPC (254 nm, THF), M_w=8320, PDI=1.11.

Compound 1 (PS_{40}-*b*-PEO_{50} amphiphile). 10 wt. % solution of **7** in THF was placed into a plastic container and excess (~50 equiv) hydrofluoric acid (49 % aq. solution of HF) was added via syringe upon rigorous stirring. The reaction was allowed to stir for 12 h at room temperature. The mixture was then diluted with dichloromethane and quenched with aqueous saturated solution of sodium bicarbonate while in the plastic bottle. The organic layer was additionally washed 3 times with water and the product was purified by column chromatography (10 % MeOH in CH_2Cl_2) to give **1** as a colorless tacky solid. Yield 95 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.86 (br, 6H, C*H*$_3$ of *sec*-Bu of PS), 2.3-1.3 (br, 120H, Ar'*H* polystyrene aliphatic protons), 3.39 (s, 3H, terminal C*H*$_3$ of PEO), 3.7-3.6 (br, 200H, C*H*$_2$ of PEO), 4.02 (br, 2H, PS-CH_2-C*H*$_2$-O-), 4.52 (t, 2H, PEO-CH_2-C*H*$_2$-O-), 7.4-6.3 (br, 200H, Ar'*H* polystyrene aromatic protons), 7.51 (s, 1H, Ar''*H*, C-4 proton of DHBA), 7.74 (br, 2H, Ar''*H*, C-2 and C-6 protons of DHBA), 7.90-7.78 (m, 6H, Ar*H*, C-2 and C-6 protons of PS biphenyl, C-2' and C-6' protons of PS and PEO), 7.95 (d, 4H, Ar*H*, *J* = 8.3 Hz, C-3' and C-5' protons

of PS and PEO biphenyl), 8.23 (d, 2H, Ar*H*, *J* = 8.1 Hz *J* = 8.3 Hz, C-2 and C-6 protons of PEO biphenyl), 8.33 (d, 4H, Ar*H*, *J* = 8.1 Hz, C-3 and C-5 protons of PS and PEO biphenyls). GPC (254 nm, THF), M_w=8160, PDI=1.1.

Synthesis of Au(PS_{40}-PEO_{50})$_n$ nanoparticles. 50 mg of amphiphile **1**, 6 mg of mercaptophenol-functionalized 2 nm gold particles (Brust et al. method), and 10 mg of DPTS were dissolved in 1 mL of methylene chloride in a small glass vial at room temperature. The mixture was allowed to stir for 2-3 min before 10 drops of DIPC were added. After additional 5 minutes, 0.3 mL of DMF was introduced and the reaction continued for 2-3 h. Methylene chloride was removed under reduced pressure and the mixture was diluted with 6 mL of THF and split into 3 membrane filters (regenerated cellulose, MWCO 30 kDa, Millipore). Centrifugation was repeated 3 times until the complete removal of all low molar mass products and the excess of amphiphile **1** was confirmed by GPC (254 nm, THF), M_w=46700, PDI=1.12. The mass of isolated dark brown tacky solid was 42 mg. The reaction mixture did not contain any appreciable amount of unreacted gold nanoparticles.

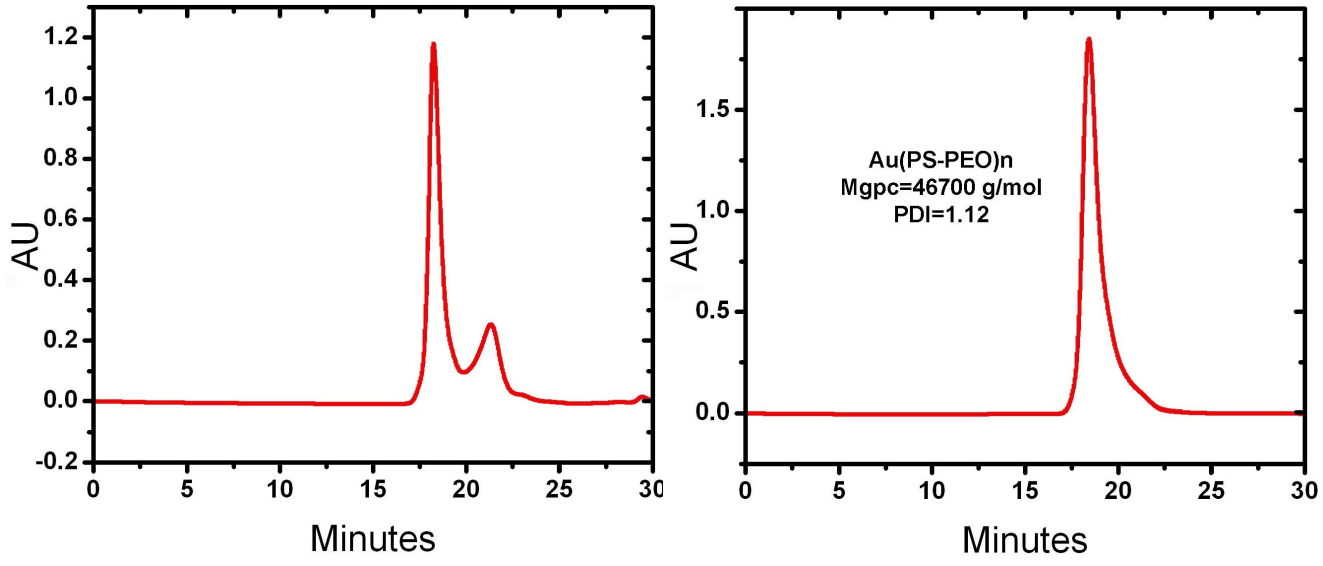


Figure S1. GPC trace of Au(PS_{40}-PEO_{50})$_n$ nanoparticles. Left trace is taken from the reaction mixture before purification (small low molar mass peak corresponds to excess PS_{40}-*b*-PEO_{50} amphiphile **1**). Right GPC trace is taken after 3 rounds of centrifugal ultrafiltration (THF, 30 kDa MWCO membrane).

Silver nanoparticles. These were prepared by the same Brust method (one-phase synthesis) using silver acetate. The average diameter of the particles was found to be approximately 2 nm by TEM. Amphiphile **1** was coupled with Ag NPs under the same conditions as described above for gold particles.

Au(PS_{30}-PEO_{50})$_n$ nanoparticles. These were prepared using the same procedure starting from analogous PS_{30}-*b*-PEO_{50} V-shaped amphiphile (MW_{PS}=3,000 g/mol).

Au(PB_{100}-PEO_{115})$_n$ nanoparticles. These were prepared using the same procedure starting from PB_{100}-*b*-PEO_{115} V-shaped amphiphile (MW_{PB}=5,000 g/mol (1,4-addition), MW_{PEO}=5,000 g/mol,) which was synthesized according to procedures described in reference 12.

Preparation of aqueous solutions of cylindrical assemblies. The Au(PS_{40}-PEO_{50})$_n$ nanoparticles (10 mg) were dissolved in 1 mL of tetrahydrofuran (THF) and 3 mL of DI water were added drop-wise (1 drop per 5 sec) upon stirring. The resulting mixture was transferred into dialysis bag (10,000 MWCO, Fischer Scientific) and dialyzed against DI water for 3 days. Samples for TEM were prepared by dipping a carbon-coated copper grid into dilute aqueous solution (0.1 mg/mL). In order to obtain long micellar arrays of NPs, a DMF solution (10mg/mL) was used. The contrast in the TEM images shown in the text and supporting material is due to the presence of gold particles, and no staining agents were used.

Preparation of aqueous solutions of vesicular assemblies. The Au(PS_{40}-PEO_{50})$_n$ nanoparticles (40 mg) were dissolved in 1 mL of DMF and 3 mL of DI water were added drop-wise (1 drop per 5 sec) upon stirring. The resulting mixture was transferred into dialysis bag (10,000 MWCO, Fischer Scientific) and dialyzed against DI water for 3 days. Samples for TEM were prepared by dipping a carbon-coated copper grid into dilute aqueous solution (0.1 mg/mL).

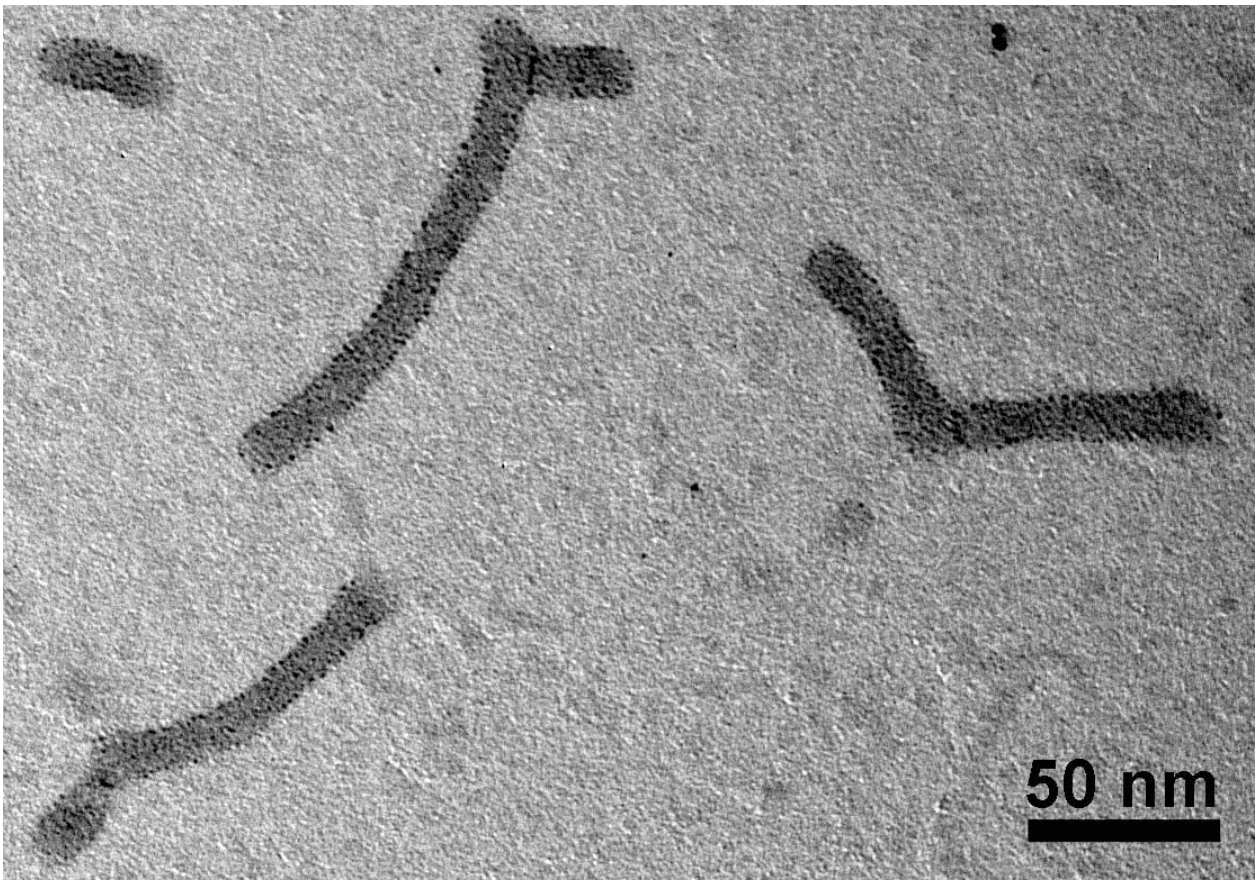


Figure S2. Unstained TEM image of structures from the aqueous solution of $Ag(PS_{40}\text{-}PEO_{50})_n$ particles. A solution of $Ag(PS_{40}\text{-}PEO_{50})_n$ in THF/H_2O mixture was dialyzed against DI water for 3 days.

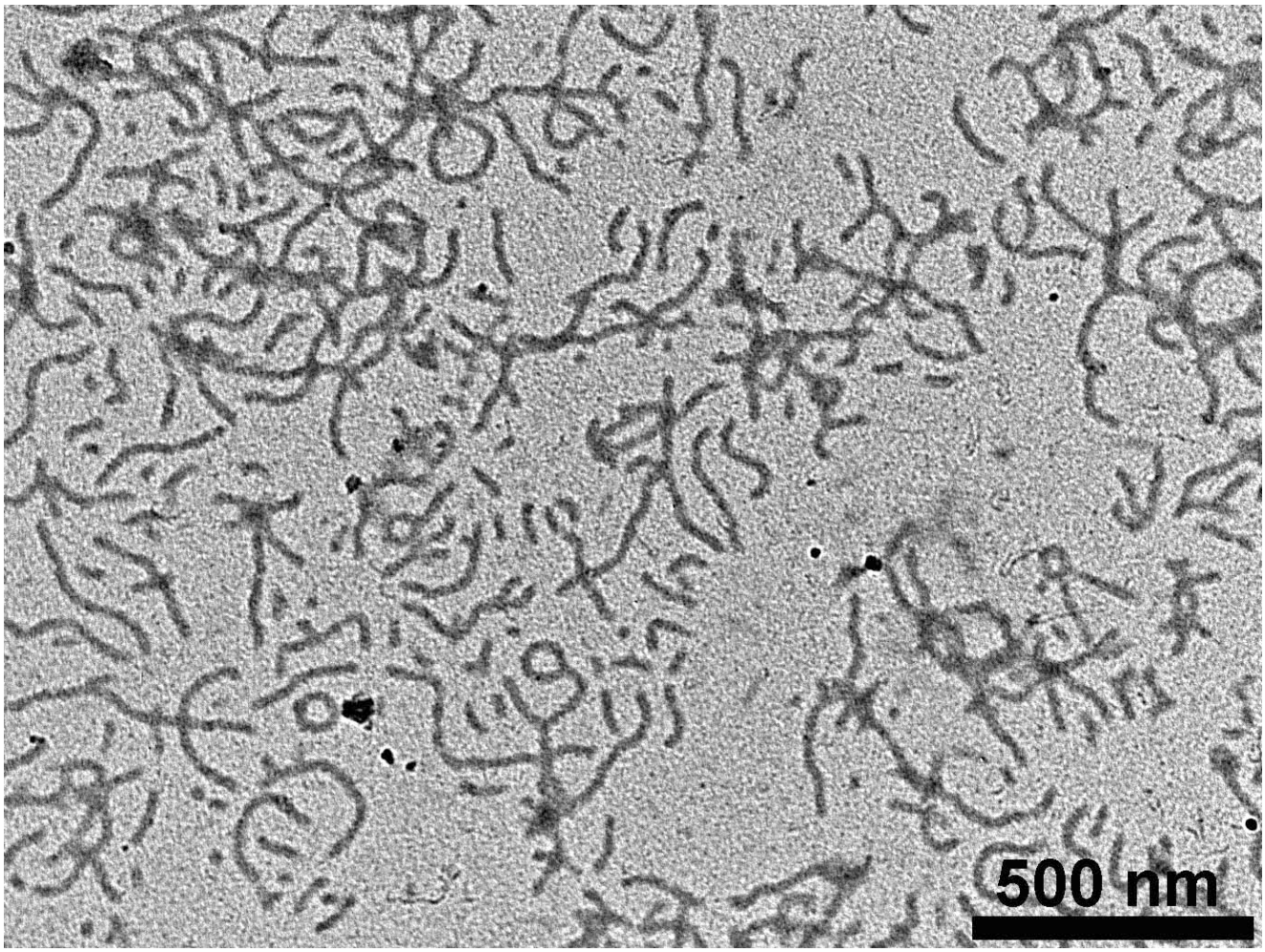


Figure S3. Unstained TEM image of structures from the aqueous solution of $Ag(PS_{40}\text{-}PEO_{50})_n$ particles. A solution of $Ag(PS_{40}\text{-}PEO_{50})_n$ in DMF/H_2O mixture was dialyzed against DI water for 3 days.

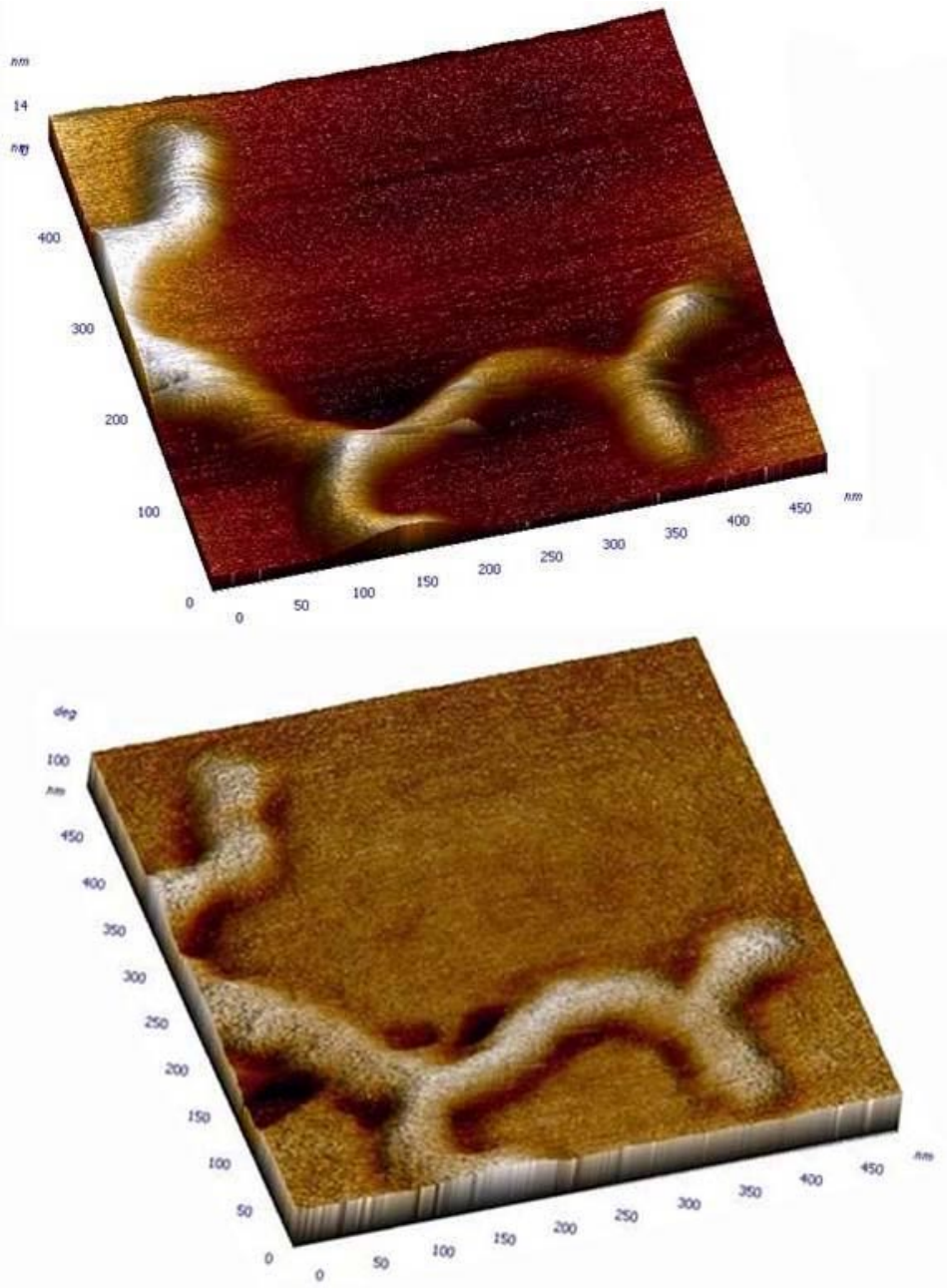
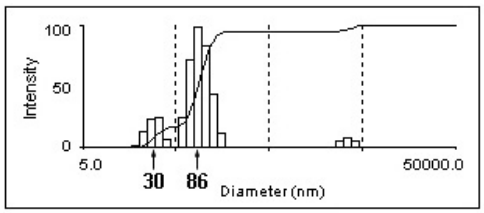


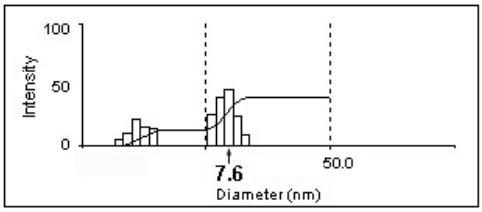
Figure S4. Topography (top) and phase contrast tapping mode AFM 3D images (500 × 500 nm) of structures formed by $Au(PS_{40}\text{-}PEO_{50})_n$ in water (dialysis from DMF/H_2O mixture). Please note that the diameter appears to be ~ 50 nm, which is significantly larger than that observed in TEM (18 nm). This is due to the tip dilation effect and the presence of PEO corona that is not visible in TEM images.

A



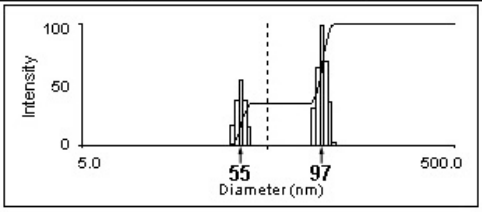
d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
12.47	0	0	104.54	85	82	876.62	0	95
15.13	0	0	126.83	44	93	1063.58	0	95
18.35	2	1	153.89	12	95	1290.41	0	95
22.26	14	4	186.70	0	95	1565.61	0	95
27.01	24	9	226.52	0	95	1899.51	0	95
32.77	25	15	274.83	0	95	2304.62	0	95
39.76	8	17	333.45	0	95	2796.13	6	97
48.24	0	17	404.56	0	95	3392.46	8	99
58.53	26	23	490.84	0	95	4115.97	6	100
71.02	73	40	595.52	0	95	4993.78	0	100
86.16	100	63	722.53	0	95	6058.80	0	100

B



d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
1.00	6	1	5.54	26	18			
1.17	11	3	6.47	41	25			
1.36	22	7	7.56	47	34			
1.59	17	10	8.83	25	39			
1.86	15	13	10.31	9	40			
2.18	0	13	12.05	0	40			
2.54	0	13	14.08	0	40			
2.97	0	13	16.45	0	40			
3.47	0	13	19.22	0	40			
4.06	0	13	22.45	0	40			
4.74	0	13	26.23	0	40			

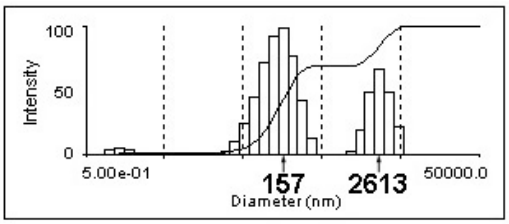
C



d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
26.38	0	0	45.70	0	35	79.16	0	35
27.73	0	0	48.04	0	35	83.21	0	35
29.15	0	0	50.50	0	35	87.47	32	42
30.65	0	0	53.09	0	35	91.95	66	56
32.22	18	4	55.80	0	35	96.66	100	77
33.87	39	12	58.66	0	35	101.61	71	92
35.60	55	23	61.67	0	35	106.82	36	99
37.42	38	31	64.82	0	35	112.29	3	100
39.34	17	35	68.14	0	35	118.04	0	100
41.35	0	35	71.63	0	35	124.08	0	100
43.47	0	35	75.30	0	35	130.44	0	100

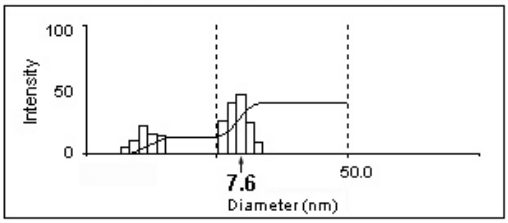
Figure S5. Reversibility of the assembly-disassembly process: (A) DLS data of the aqueous solution obtained after first dialysis from THF solution of $Au(PS_{40}\text{-}PEO_{50})_n$ NPs. (B) DLS data after the disassembly of nanoparticulate arrays by adding a non-selective solvent (95 % vol. of THF). (C) DLS data of the aqueous solution obtained after dialysis of the THF solution shown in panel B. Please note the correlation between the DLS (~90 nm) and the TEM data shown in Fig. 1B (short cylindrical arrays that measure ~100 nm in length).

A



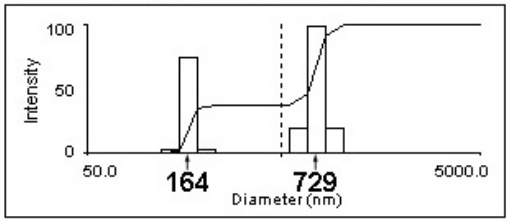
d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
1.00	5	1	22.00	0	2	484.01	0	70
1.32	5	1	29.14	4	3	641.05	0	70
1.75	5	2	38.59	10	4	849.05	0	70
2.32	0	2	51.11	25	8	1124.53	3	70
3.08	0	2	67.70	46	14	1489.40	21	73
4.08	0	2	89.66	73	24	1972.65	49	80
5.40	0	2	118.76	95	37	2612.70	69	90
7.15	0	2	157.29	100	51	3460.41	50	97
9.47	0	2	208.32	79	62	4583.18	23	100
12.54	0	2	275.92	44	68	6070.24	0	100
16.61	0	2	365.44	13	70	8039.79	0	100

B



d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
1.00	6	1	5.54	26	18			
1.17	11	3	6.47	41	25			
1.36	22	7	7.56	47	34			
1.59	17	10	8.83	25	39			
1.86	15	13	10.31	9	40			
2.18	0	13	12.05	0	40			
2.54	0	13	14.08	0	40			
2.97	0	13	16.45	0	40			
3.47	0	13	19.22	0	40			
4.06	0	13	22.45	0	40			
4.74	0	13	26.23	0	40			

C



d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
56.68	0	0	589.32	19	46			
70.13	0	0	729.11	100	91			
86.77	0	0	902.07	19	100			
107.35	0	0	1116.05	0	100			
132.81	4	2	1380.80	0	100			
164.32	76	36	1708.34	0	100			
203.29	4	38						
251.52	0	38						
311.18	0	38						
385.00	0	38						
476.33	0	38						

Figure S6. Reversibility of the assembly-disassembly process: (A) DLS data of the aqueous solution obtained after first dialysis from DMF solution of $Au(PS_{40}\text{-}PEO_{50})_n$ NPs. (B) DLS data after the disassembly of nanoparticulate arrays by adding a non-selective solvent (95 % vol. of THF). (C) DLS data of the aqueous solution obtained after dialysis of the DMF solution prepared from the sample shown in panel B. Please note the correlation between the DLS (0.7-2.6 μm) and the TEM data shown in Fig. 2A (long cylindrical arrays that measure up to several microns in length).

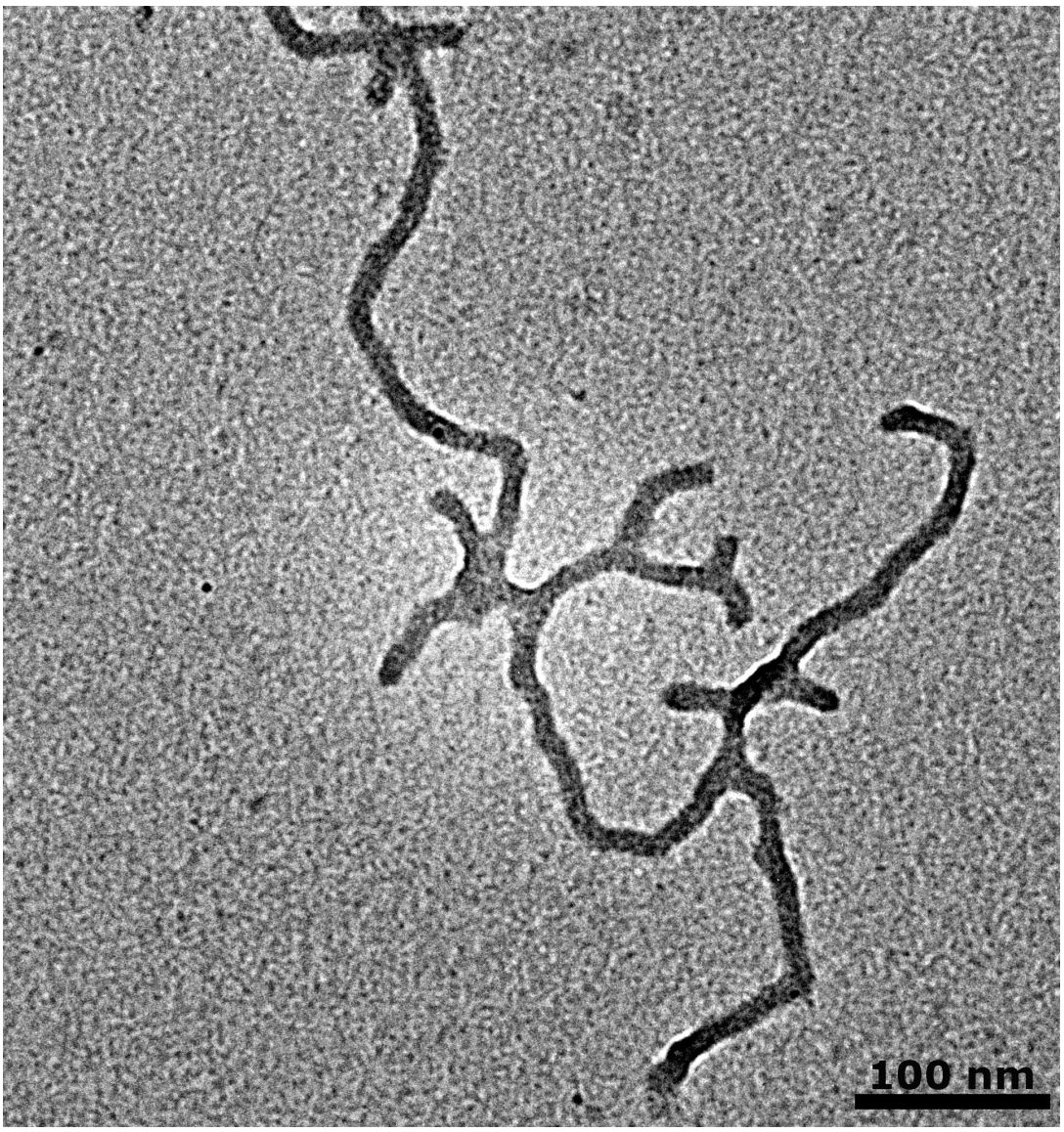


Figure S7. TEM images of worm-like assemblies of amphiphilic Au-$(PS_{30}\text{-}PEO_{50})_n$ NPs from an aqueous solution after dialysis from a DMF/H_2O (1:3 vol.) mixture. Please note the reduction in the diameter of the hydrophobic PS core from 18 ± 2 nm (Fig. 1B in the text) to 14 ± 2 nm as the molecular weight of the PS arms is decreased from 4,000 to 3,000 g/mol, respectively.

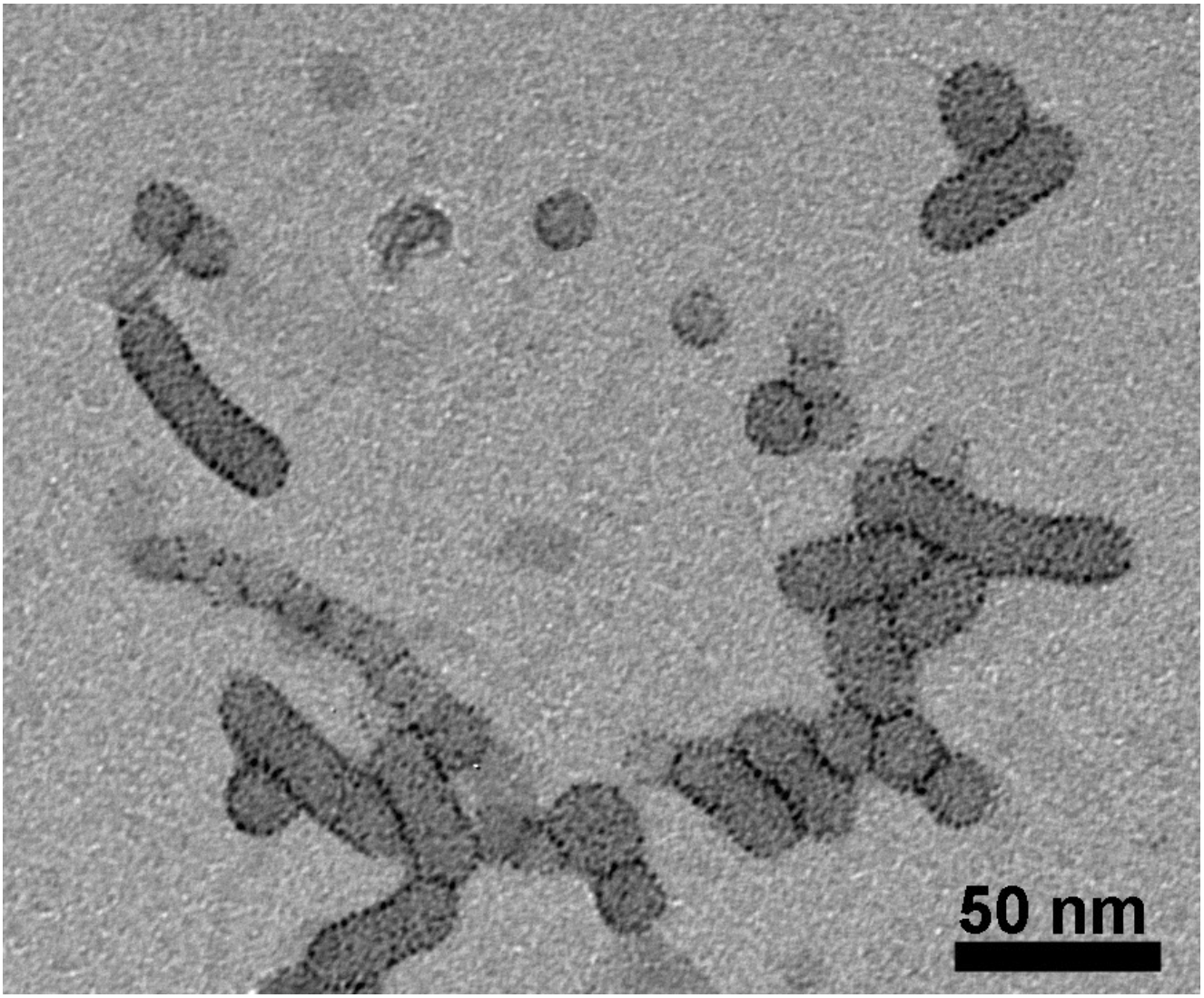


Figure S8. TEM images of short cylindrical and spherical assemblies of amphiphilic Au-(PS_{40}-PEO_{50})$_n$ NPs from an aqueous solution containing 10 % (vol.) methanol. The sample was not stained, and the contrast was due to the gold core of the amphiphilic Au-(PS_{40}-PEO_{50})$_n$ structures.

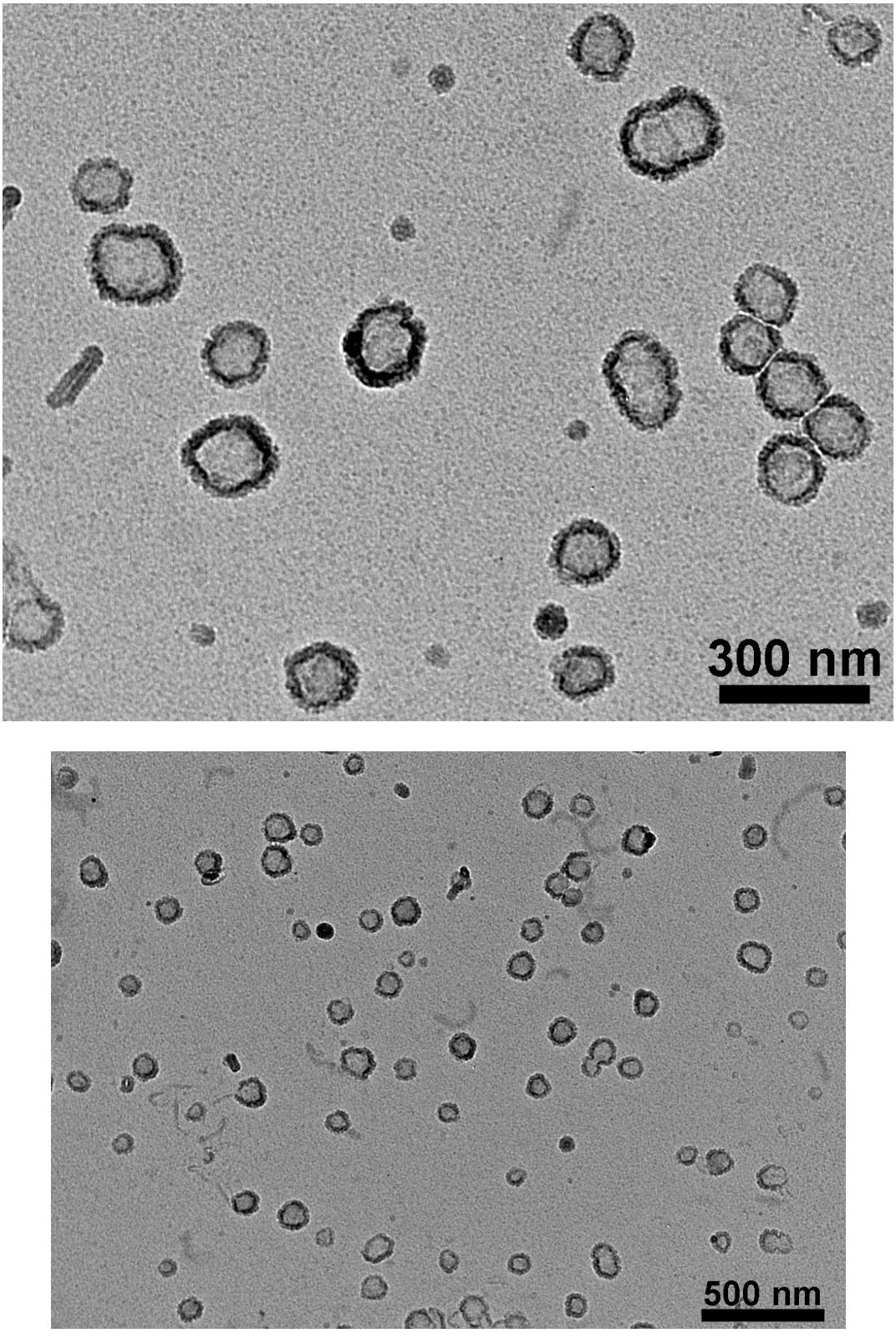


Figure S9. High (top) and low magnification TEM images of vesicular assemblies of amphiphilic $Au(PS_{40}\text{-}PEO_{50})_n$ NPs from an aqueous solution prepared after dialysis from a concentrated solution (40 mg/mL) of $Au(PS_{40}\text{-}PEO_{50})_n$ NPs in DMF.

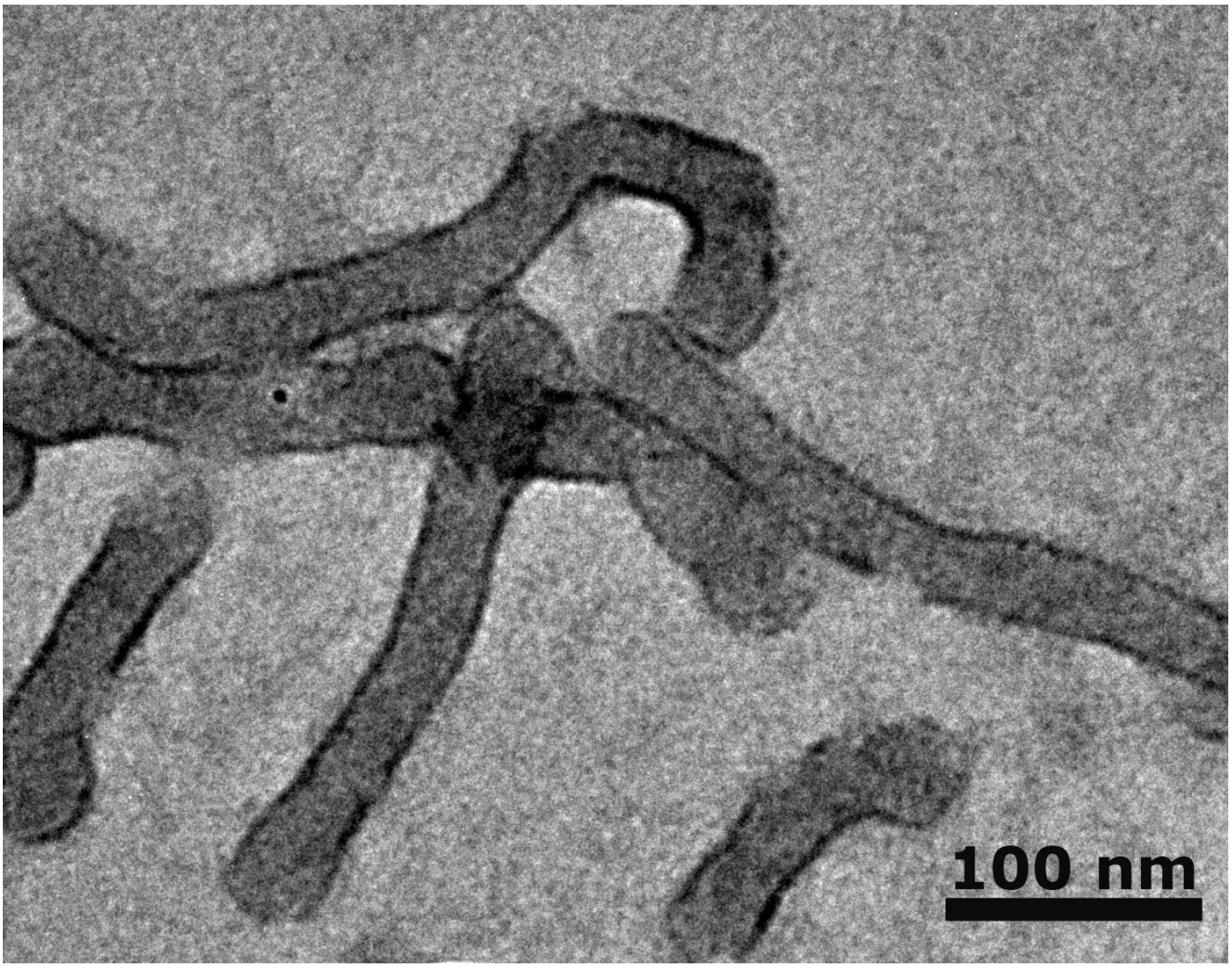


Figure S10. TEM images of worm-like assemblies of the amphiphilic Au-$(PB_{100}$-$PEO_{115})_n$ NPs from an aqueous solution after the dialysis from a DMF/H_2O (1:3 vol.) mixture. Please note the increase in the diameter of the hydrophobic core from 18 ± 2 nm (Fig. 1B in the text) to 32 ± 3 nm as the contour length of the hydrophobic arms is increased from ~10 nm to ~50 nm, respectively.