Supplementary Information (SI) for Materials Chemistry Frontiers.

Supplementary Information

Diblock Copolymer Micelles with Patches in Polyhedral Configurations Mimicking Atomic Valence Structures

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Experimental Section

Materials

All commercially available reagents were used as received unless specified otherwise. 2-Phenyl-2-propyl benzodithioate (99%), styrene (>99%), and 1,4-dibromobutane (99%) were purchased from Aldrich. 2-vinylpyridine (97%), 4-vinylpyridine (95%), and 1,3,5-tris(bromomethyl)benzene (>98%) were obtained from Acros Organic, Thermo Fisher Scientific, and Tokyo Chemical Industry, respectively. To remove impurities, styrene, 2-vinylpyridine, and 4-vinylpyridine were dried over CaH_2 while stirring overnight. The monomers underwent additional purification through vacuum distillation prior to the polymerization process. 2,2'-Azoisobutyronitrile (AIBN) (95%) was purchased from Merck and recrystallized from diethyl ether to remove impurities.

Synthesis of PS-b-P2VP diblock copolymers

The P2VP block was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization and served as a macro chain transfer agent (CTA) for the subsequent synthesis of the PS block. The following procedure describes a representative polymerization method for the synthesis of S2VP-2 in Table 1. In a 200 mL Schlenk tube, a mixture of 2-vinylpyridine (44.0 g), 2-phenyl-2-propyl benzodithioate (60 mg), AIBN (7 mg), and DMF (18.9 g) was added. The solution was degassed through three freeze-vacuum-thaw cycles and maintained under reduced pressure. The polymerization was carried out in an oil bath at 70 °C for 24 h and was then quenched by cooling the mixture in an ice bath. The resulting solution was diluted with chloroform (50 g), and the polymer was slowly precipitated in n-hexane (4 kg) under stirring. The polymer was separated through filtration and subsequently dried under vacuum at 25 °C for 24 h, yielding P2VP (20.0 g), which was used as a macro-CTA for the second polymerization step to synthesize the PS block. For S2VP-2, a mixture of styrene (17.5 g), P2VP macro-CTA (1.0 g), AIBN (0.3 mg), and DMF (18.5 g) was prepared in a Schlenk tube. After degassing, the polymerization was conducted at 90 °C for 36 h. The product was diluted with chloroform (20.0 g) and precipitated in n-hexane. The precipitated polymer was separated by filtration and then dried in a vacuum oven at 25 °C, and S2VP-2 was obtained as a light pink solid.

Synthesis of PS-b-P4VP diblock copolymers

The synthesis of PS-*b*-P4VP was carried out following a process similar to the PS-*b*-P2VP polymerization. The procedure below describes representative details of the synthesis for preparing PS(266k)-*b*-P4VP(58k). First, 4-vinylpyridine (49.8 g), 2-phenyl-2-propyl benzodithioate (106 mg), AIBN (12.9 mg), and DMF (12.3 g) were loaded into a 200 mL Schlenk tube. The solution underwent three freeze-vacuum-thaw cycles, and the tube was maintained under vacuum. Polymerization proceeded in an oil bath at 80 °C for 24 h and was then quenched in an ice bath. After diluting the product solution with chloroform (50 g), the product was slowly precipitated in excess n-hexane (4 kg) under stirring. The polymer was separated by filtration and then dried in a vacuum oven at 25 °C for 24 h. The resulting P4VP (25.0 g) was employed as a macro-CTA for the second PS block polymerization. A mixture of styrene (140 g), P4VP macro-CTA (7.0 g), AIBN (6.6 mg), and DMF (147 g) was loaded into a 500 mL Schlenk tube, degassed, and polymerized at 90 °C for 40 h. The final polymer was isolated and obtained as a light pink solid.

Formation of PS-b-P2VP micelles

To prepare S2VP micelles, 10.0 mg of the copolymer was dissolved in 1.0 g of chloroform, a solvent compatible with both PS and P2VP blocks, to form a 1.0 wt% solution. A syringe pump was used to add 5.0 g of *n*-butyl acetate, a selective solvent for the PS block, at a rate of 6 mL/h. Chloroform was then completely evaporated at 50 °C, yielding a 0.2 wt% *n*-butyl acetate solution of PS-*b*-P2VP micelles. To cross-link the cores, 1,3,5-tris(bromomethyl)benzene (3.5 mg) was added to the *n*-butyl acetate solution (5.0 g) containing 0.01 g of the copolymer, corresponding to a molar ratio of 1,3,5-tris(bromomethyl)benzene to 2VP of 0.33, which can fully quaternize the 2VP units. The solution was stirred at 90 °C for 24 h to complete cross-linking. The values described here are specific to S2VP-2.

Formation of PS-b-P4VP micelles

PS-*b*-P4VP micelles were prepared following a similar procedure to the PS-*b*-P2VP micelles. A 0.5 wt% solution was obtained by dissolving 10.0 mg of the copolymer in 2.0 g of chloroform. A syringe pump was used to add 1.0 g of *n*-butyl acetate at a rate of 1 mL/h. Chloroform was then completely evaporated at 50 °C, yielding a 1.0 wt% solution of PS-*b*-

P4VP micelles. To cross-link the cores, 1,4-dibromobutane (2.7 mg) was added to 1.0 g of the micelle solution containing 0.01 g of the copolymer, maintaining a molar ratio of 1,4-dibromobutane to 4VP of 0.5. The mixture was continuously stirred at 50 °C for 24 h to ensure complete cross-linking. The values described here are specific to PS(266k)-*b*-P4VP(58k).

Preparation of patchy micelles

By adding DMF (9.9 g) to a 0.2 wt% *n*-butyl acetate solution (0.1 g) of cross-linked PS-*b*-P2VP micelles, a 0.002 wt% solution of patchy micelles was prepared. This procedure was applied to both PS-*b*-P2VP and PS-*b*-P4VP.

Preparation of colloidal molecules

To assemble colloidal molecules, a 1 mL solution of multi-patch micelles of PS-*b*-P2VP was blended with a 1 mL solution of single-patch micelles of PS-*b*-P4VP. A mixture of DI water and DMF (25:75 w/w) was gradually introduced to the blended solution, adjusting the final water content to 12.5 wt%. The resulting mixture was then maintained at 30 °C without agitation for 12 h, enabling the formation of colloidal molecules.

Characterizations

Gel permeation chromatography (GPC) was performed using an Agilent 1260 Infinity system equipped with a PL gel 5 μm mixed D column and a differential refractive index detector. DMF served as the eluent at a flow rate of 1.0 mL/min, with the column temperature maintained at 50 °C. Molecular weights (M_n) and polydispersity indexes (PDI) were calculated based on calibration with polystyrene standards. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired using a Varian NMR spectrometer operating at 500 MHz, and block ratios of PS and P2VP were determined by integrating characteristic peaks. Transmission electron microscopy (TEM) images were captured with a Hitachi 7600 microscope set at an accelerating voltage of 100 kV. For sample preparation, 3 μL of the micelle solution was dropped onto carbon-coated grids, followed by solvent evaporation. To enhance contrast, staining was achieved using I_2 for P2VP cores or RuO_4 for PS coronas. Dynamic light scattering (DLS) measurements were conducted on a DLS-8000 (Otsuka Electronics), utilizing a He–Ne laser (632 nm) at a fixed scattering angle of 90°.

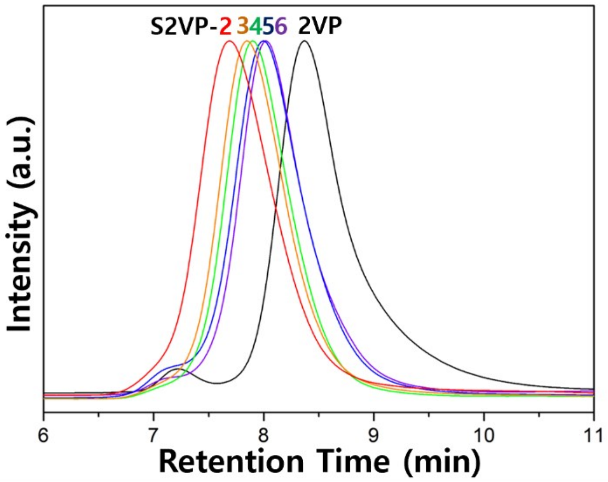

Figure S1. GPC profiles for PS-*b*-P2VP (S2VP).

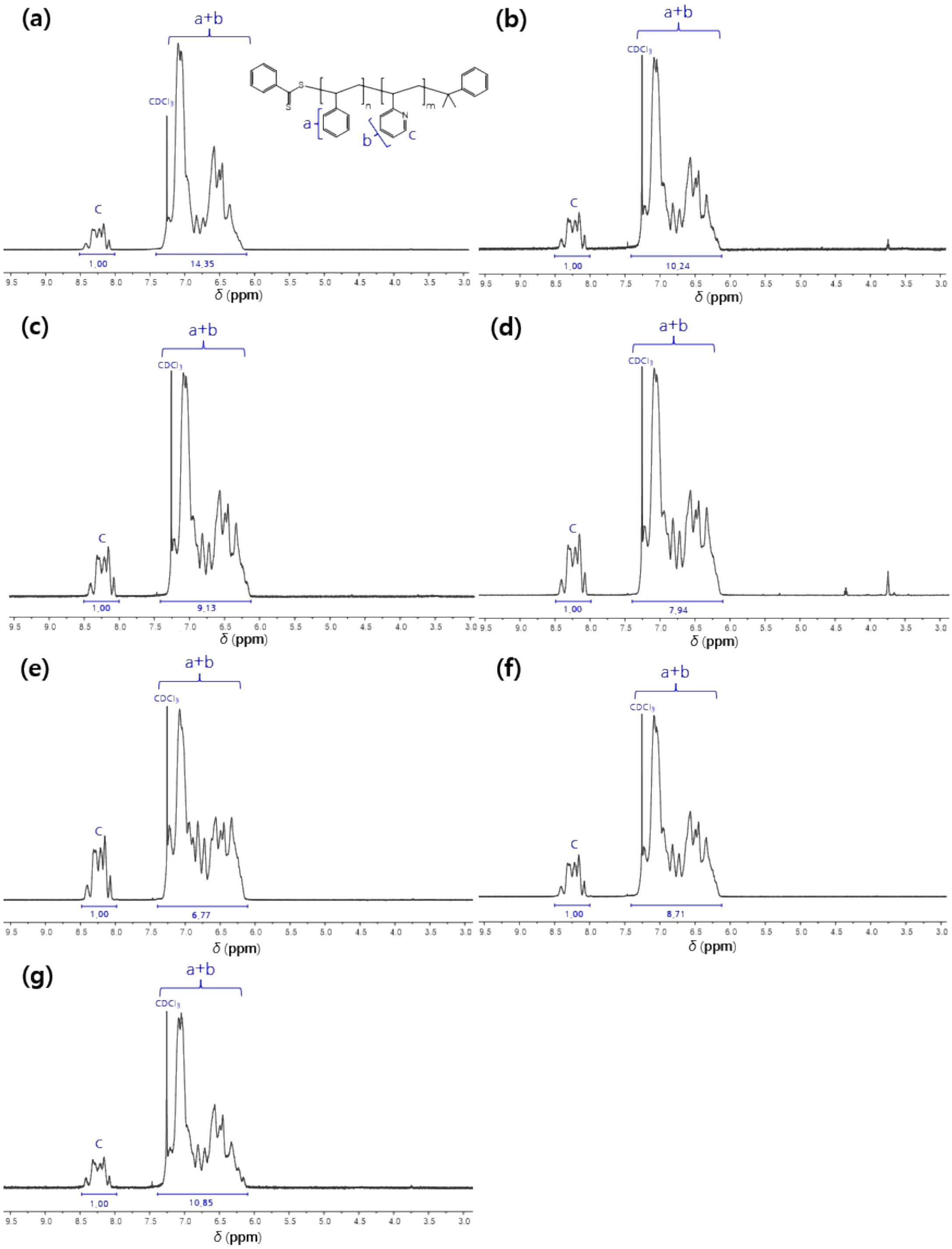

Figure S2. NMR spectra of PS-*b*-P2VP (S2VP): (a) S2VP-2; (b) S2VP-3; (c) S2VP-4; (d) S2VP-5; (e) S2VP-6; (f) S2VP-4s; (g) S2VP-4ss.

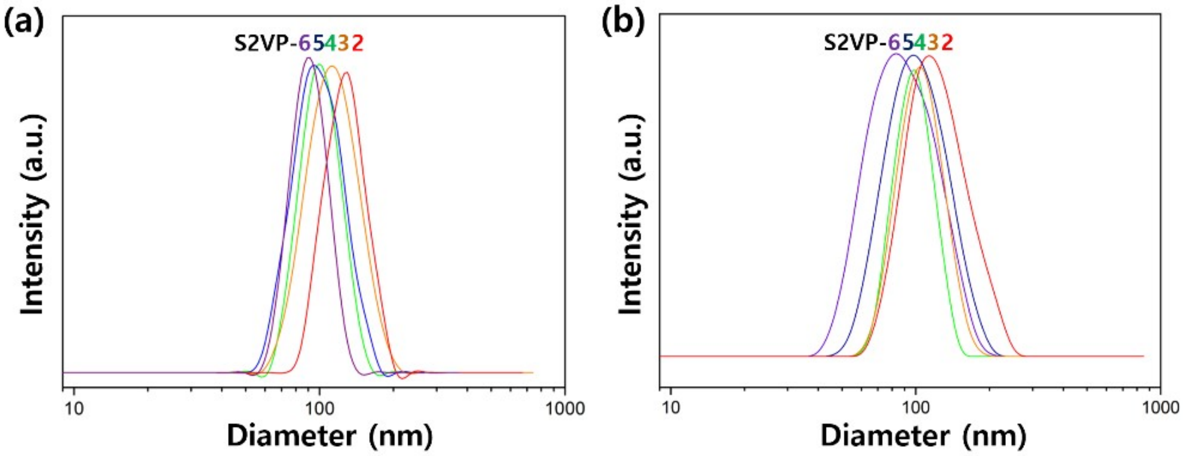

Figure S3. DLS results: (a) spherical micelles; (b) micelles with patches in polyhedral configurations.

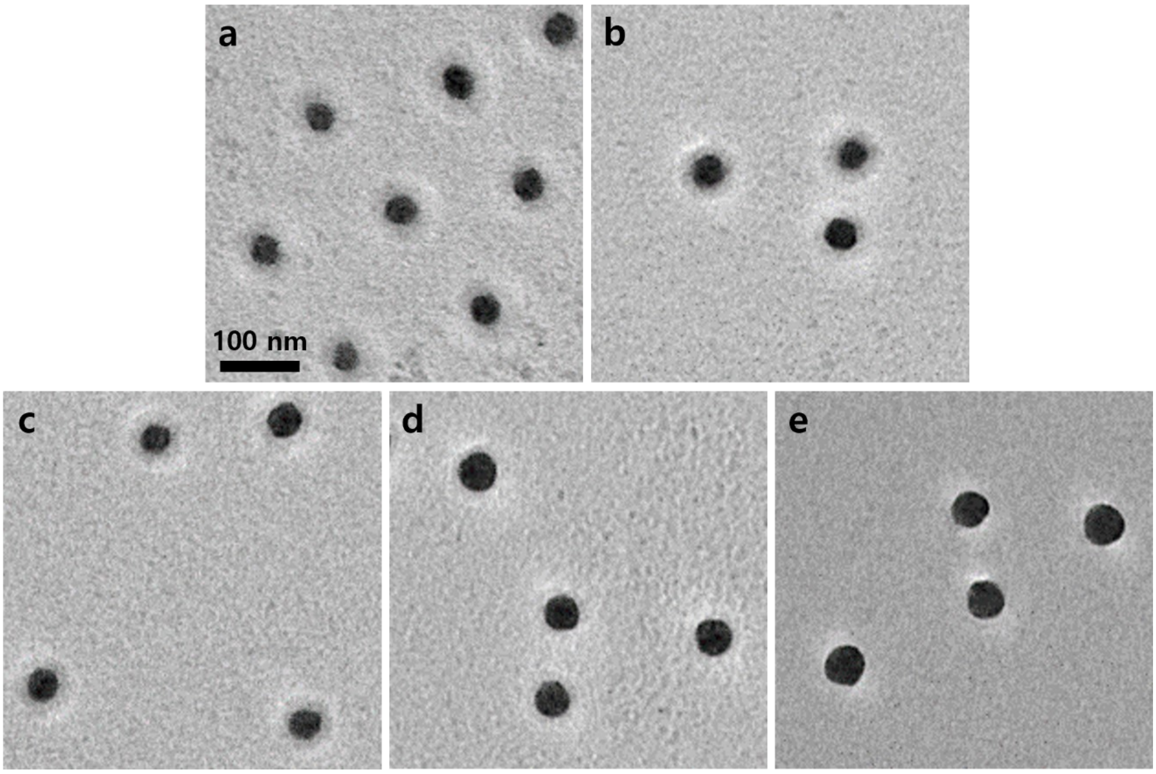

Figure S4. TEM images of S2VP micelles after staining the cores with I_2: (a) S2VP-2; (b) S2VP-3; (c) S2VP-4; (d) S2VP-5; (e) S2VP-6.

	M_n^{4VP} (g/mol)[a]	M_n^{S} (g/mol)[b]	M_n^{S}/M_n^{4VP}	PDI[a]
PS(266k)-*b*-P4VP(58k)	58,000	266,000	4.59	1.17
PS(80k)-*b*-P4VP(16k)	16,000	80,000	5.00	1.08

[a] Determined by GPC, Calibrated by PS standard. [b] Calculated from ^{1}H NMR.

Table S1. Characteristics of PS-*b*-P4VP.

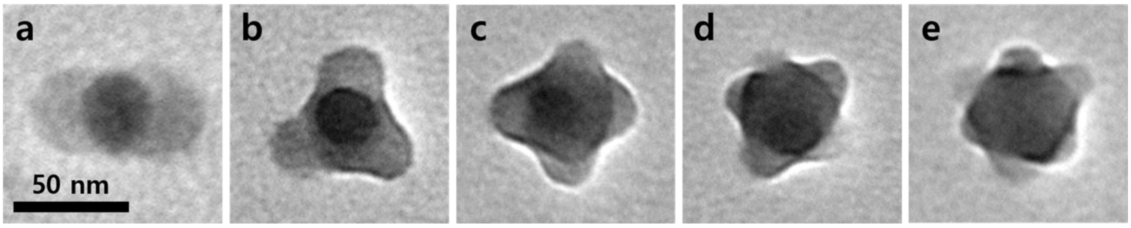

Figure S5. TEM images of patchy micelles after selective core staining with I_2: (a) S2VP-2; (b) S2VP-3; (c) S2VP-4; (d) S2VP-5; (e) S2VP-6.

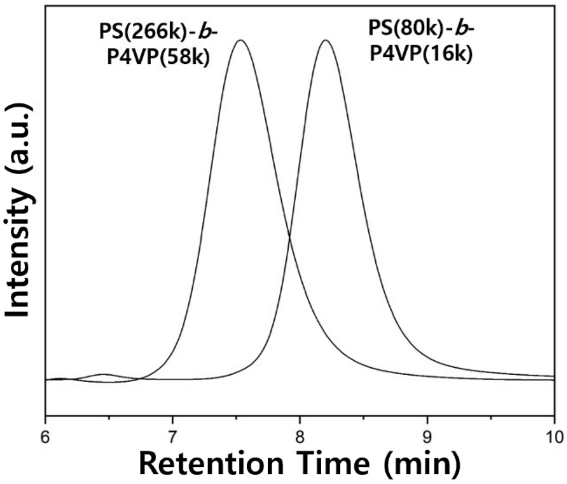

Figure S6. GPC profiles for PS-*b*-P4VP.

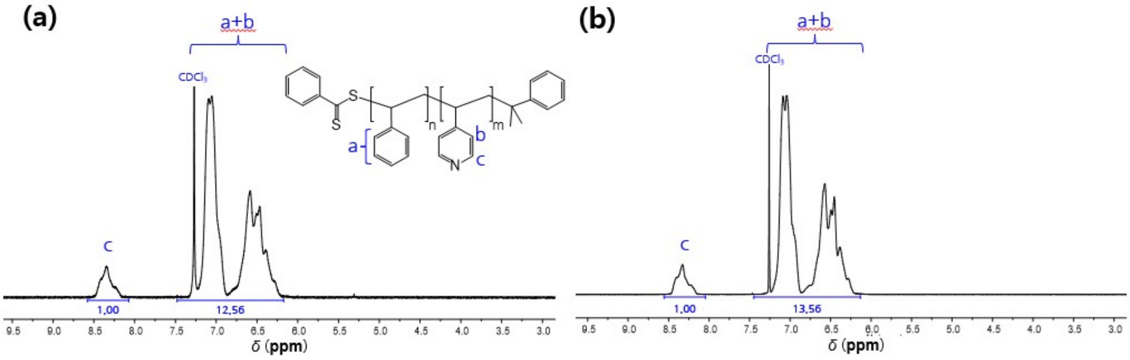

Figure S7. NMR spectra: (a) PS(266k)-*b*-P4VP(58k); (b) PS(80k)-*b*-P4VP(16k).

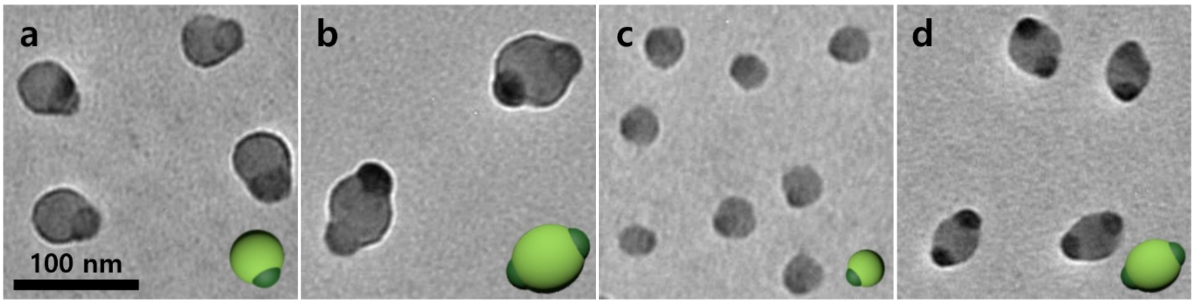

Figure S8. TEM images: (a) single-patch micelles of PS(266k)-*b*-P4VP(58k); (b) dimers of single-patch micelles of PS(266k)-*b*-P4VP(58k); (c) single-patch micelles of PS(80k)-*b*-P4VP(16k); (d) dimers of single-patch micelles of PS(80k)-*b*-P4VP(16k).

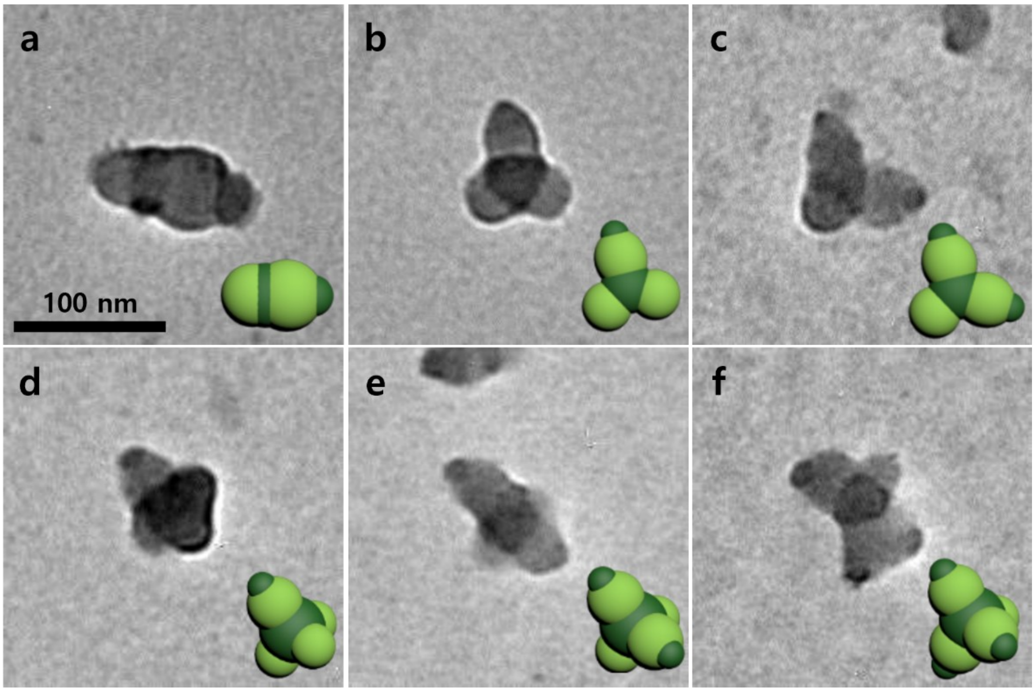

Figure S9. TEM images of patchy micelles partially assembled with single-patch micelles: (a) a two-patch micelle with one single-patch micelle; (b) a three-patch micelle with one single-patch micelle; (c) a three-patch micelle with two single-patch micelles; (d) a four-patch micelle with one single-patch micelle; (e) a four-patch micelle with two single-patch micelles; (f) a four-patch micelle with three single-patch micelles.

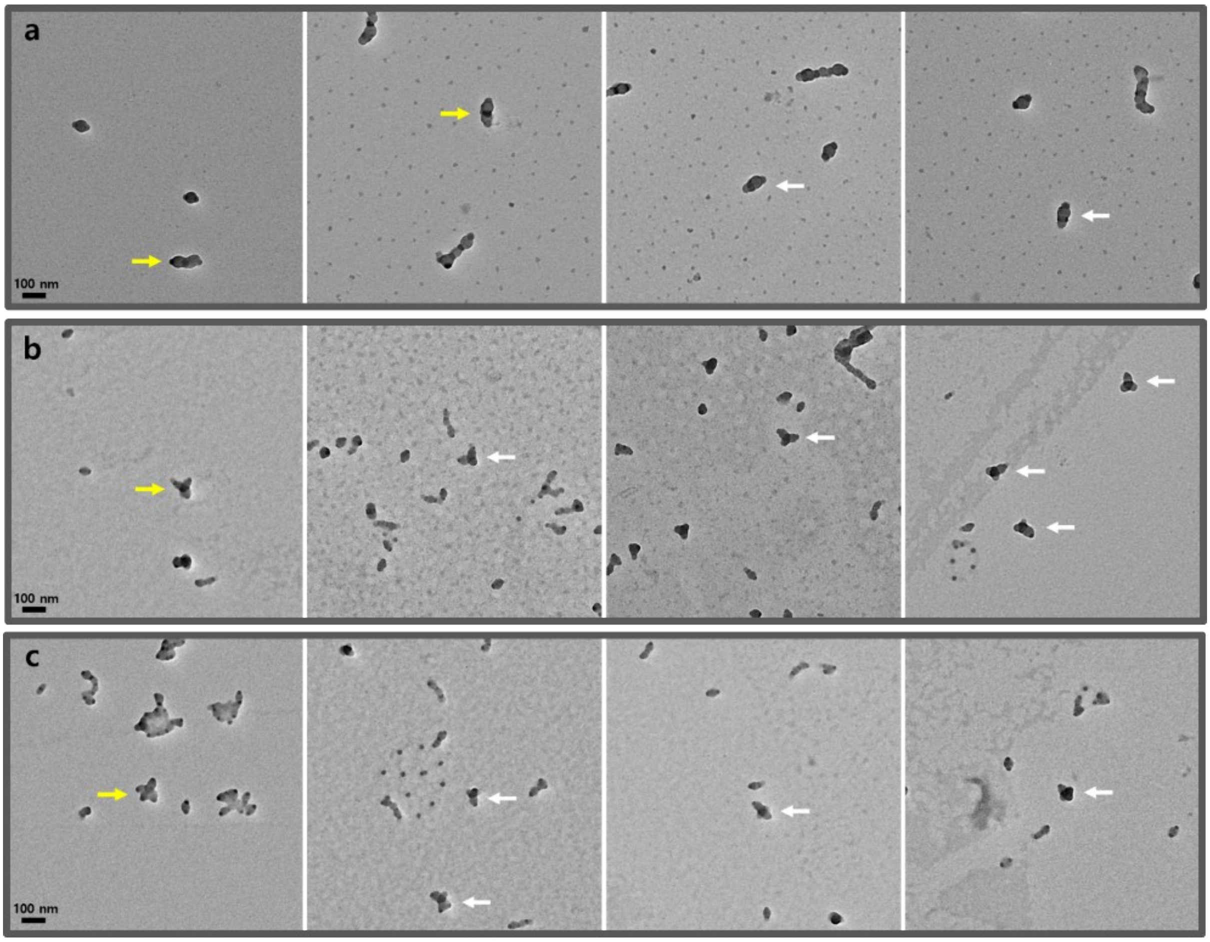

Figure S10. TEM images of patchy micelles assembled with single-patch micelles: (a) two-patch micelle; (b) three-patch micelle; (c) four-patch micelle. Yellow arrows indicate assemblies in which all patches are fully attached with single-patch micelles. White arrows indicate patchy micelles with only a subset of their patches connected to single-patch micelles. Many assemblies remain difficult to unambiguously identify.