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Supporting Information

Monodisperse Fiber-Like Micelles of Controlled Length and Composition with an Oligo(*p*-phenylenevinylene) Core via “Living” Crystallization-Driven Self-Assembly

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SUPPORTING EXPERIMENTAL DETAILS

Materials

N-isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized from a mixture of benzene and *n*-hexane (v:v = 1:3). 2-(Diethylamino)ethyl methacrylate (DEAEMA, Aldrich, 97%) was passed through a basic alumina column and distilled under reduced pressure from CaH₂ prior to use. Copper(I) chloride (CuCl, Aldrich, 99%) was purified by stirring overnight over CH₃CO₂H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying *in vacuo* at 40°C overnight. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN, Aldrich, 97%) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%) were used as received without further purification. All organic solvents such as tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were distilled prior to use. Other reagents that were not specially mentioned were purchased from Aldrich and used as received without further purification.

Instrumentation

¹H (400 MHz) NMR analyses were performed on a JEOL JNM-ECZ400 Varian spectrometer in CDCl₃ and CD₂Cl₂, tetramethylsilane was used as an internal standard. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) using a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, a Waters 2487 dual λ absorbance detector, and a set of Waters Styragel columns (HR3

(500-30,000), HR4 (5,000-600,000) and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 µm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) Small aliquots of sample solutions (2 µL, 1.0 mg/mL) in dichloromethane were added to a sample plate for MALDI-TOF. After drying in air at room temperature (~10 min), an aliquot of α -cyano-4-hydroxy cinnamic acid (2 µL, 5.0 mg/mL) dispersed in a mixture of acetonitrile and water (acetonitrile/water = 1/1) was added and allowed to dry in air at room temperature. MALDI-TOF spectra were obtained on a Waters MICROMASS MALDI micro MX Mass Spectrometer.

Transmission electron microscopy (TEM). TEM images were obtained by a JEOL JEM-2100 instrument operated at 80 kV. A 10 µL drop of micellar solution was placed on a Formvar and carbon-coated copper grid for 30 s and then a filter paper touched the edge of the drop to absorb most of the liquid on the grid. The grid was allowed to dry at room temperature. For the samples stained by phosphotungstic acid, after the grid was dried (*ca.* 1 min after touching it with the filter paper), a drop of phosphotungstic acid aqueous solution (10 µL, 1.0 mg/mL) was added onto the surface. After 1 min, most of the solution on the grid was absorbed by touching the edge of the drop with a filter paper, and then the grid was allowed to dry at room temperature. For each sample, length distributions of micelles were determined by tracing more than 100 individual micelles, and width distributions were determined by

making measurements at least 100 different positions on several micelles and analysis using the software program ImageJ from National Institutes of Health. Values of the number-average length (L_n) and weight-average length (L_w) of micelles were calculated as follows:

$$L_n = \frac{\sum_{i=1}^N N_i L_i}{\sum_{i=1}^N N_i} \quad (1)$$

$$L_w = \frac{\sum_{i=1}^N N_i L_i^2}{\sum_{i=1}^N N_i L_i} \quad (2)$$

where N_i is the number of micelles of length L_i , and N is the number of calculated micelles in each sample. The distribution of micellar length is characterized by both L_w/L_n and the standard deviation of the length distribution σ .

Atomic force microscopy (AFM). AFM images were acquired in air in tapping mode using a JPK NanoWizard Sense system. Aliquots (10 μ L) of micellar solutions prepared as described were deposited on a mica substrate and dried at room temperature in air.

Wide-angle X-ray scattering (WAXS). WAXS measurements were conducted using a Philips X'Pert PRO X-ray powder diffractometer with $\text{CuK}\alpha$ (1.541 $\text{\AA}$) radiation (40 kV, 40 mA) and the samples were exposed at a scan rate of $2\theta = 0.0334^\circ/\text{s}$ in the range between 3° and 30° . Samples of $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ for WAXS experiments were prepared by casting micellar solution (1 mg/mL) of the polymer onto a silicon wafer and allowing the solvent to evaporate at room temperature. The

sample of PNIPAM₄₉ for WAXS analysis was prepared by casting an ethanol solution of PNIPAM onto a silicon wafer, and allowing it to dry at room temperature.

Dynamic light scattering (DLS). DLS measurements were performed at room temperature (23°C) on a Malvern Nano-ZS90 Zetasizer at a scattering angle of 173°. Apparent hydrodynamic diameters (D_h) were calculated via a cumulant analysis using software associated with the instrument. Intensity distribution profiles were also calculated with instrument software. For tracking the self-assembly of OPV₅-*b*-PNIPAM₄₉ in ethanol, DLS measurements were performed on the hot solution after an ethanol solution of OPV₅-*b*-PNIPAM₄₉ (0.05 mg/mL) was heated at 80°C for 30 min, and DLS measurements were conducted again after the solution had cooled to room temperature followed by aging at room for 24 h. DLS measurements of the fiber-like micelles obtained by self-seeding were carried out at room temperature.

UV/vis and fluorescence spectroscopy. UV/vis absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. Fluorescence spectra were measured using a Hitachi F-2700 fluorescence spectrophotometer with a band width of 5 nm. The temperature of the cell housing (1 cm path cell) was controlled with a Neslab RTE-110 bath. For the kinetics study, an ethanol solution of OPV₅-*b*-PNIPAM₄₉ (0.05 mg/mL) was firstly heated at 80°C for 30 min, and then UV/vis and fluorescence measurements were performed under room temperature at different time intervals over the cooling and aging process (room temperature).

Monomer and Polymer Synthesis

Synthesis of aldehyde-terminated OPV₅. Aldehyde-terminated OPV₅ was synthesized via a modified procedure similar to previous reports as shown in Scheme S1.^{1,2}

Scheme S1. Synthetic route for the preparation of aldehyde-terminated OPV₅.

Synthesis of 2,5-dihexyloxytoluene 1. Methylhydroquinone (21.6 g, 0.17 mol), KOH (28 g, 0.50 mol), and 1 mL of phase transfer catalyst (Aliquat 336) was dissolved in 350 mL of anhydrous ethanol under N_2 . After the reaction mixture was stirred under reflux for 1 h, 1-bromohexane (87 g, 0.53 mol) was added dropwise, and the mixture was refluxed at 80°C for 24 h. The reaction mixture was poured into water followed by extraction with ethyl acetate. The crude product was purified by silica column chromatography (eluent: hexane) to give 2,5-dihexyloxytoluene **1** (45.6 g,

90%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm): 0.92 (t, 6H, CH_2CH_3), 1.18-1.54 (m, 12H, $(\text{CH}_2)_3$), 1.68-1.90 (m, 4H, OCH_2CH_2), 2.20 (s, 3H, ArCH_3), 3.95 (t, 2H, OCH_2), 4.02 (t, 2H, OCH_2), 6.64 (dd, 1H, ArH), 6.70 (d, 1H, ArH), 6.72 (s, 1H, ArH).

Synthesis of 1,4-dihexyloxybenzene 2. 1,4-Dihexyloxybenzene **2** was achieved similarly with **1**, using hydroquinone as starting material. ^1H NMR (400 MHz, CDCl_3): δ (ppm): 0.92 (t, 6H, CH_2CH_3), 1.18-1.54 (m, 12H, $(\text{CH}_2)_3$), 1.68-1.90 (m, 4H, OCH_2CH_2), 4.02 (m, 4H, OCH_2), 6.79 (s, 2H, ArH), 7.22 (s, 2H, ArH).

Synthesis of 2,5-dihexyloxy-4-methylbenzaldehyde 3. To a solution of **1** (15 g, 0.05 mol) in 150 mL of dry CH_2Cl_2 , TiCl_4 (14.6 g, 0.077 mol) was added. The reaction mixture was cooled to 0°C and stirred for 1 h. Dichloromethyl methyl ether (13.0 g, 0.11 mol) was then added slowly. After stirring for further 30 min at 0°C and 1 h at room temperature, the mixture was poured onto 200 g of crushed ice and stirred for 1 h. The aqueous phase was extracted several times with CH_2Cl_2 . The combined organic layers were washed with water, NaHCO_3 aqueous solution, and again water. After the organic phase was dried over Na_2SO_4 and the solvent was evaporated *in vacuo*, the crude product was purified by silica column chromatography (eluent: ethyl acetate/hexane = 1/30). Recrystallization from hexane yielded 2,5-dihexyloxy-4-methylbenzaldehyde **3** (7.6 g, 46%) as a white crystalline solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm): 0.92 (t, 6H, CH_2CH_3), 1.18-1.54 (m, 12H, $(\text{CH}_2)_3$), 1.68-1.90 (m, 4H, OCH_2CH_2), 2.27 (s, 3H, ArCH_3), 3.95 (t, 2H, OCH_2), 4.02 (t, 2H, OCH_2), 6.79 (s, 1H, ArH), 7.22 (s, 1H, ArH), 10.42 (s, 1H, CHO).

Synthesis of 2,5-dihexyloxybenzaldehyde 4. 2,5-Dihexyloxybenzaldehyde **4**

was achieved similarly with **3**, using 1,4- dihexyloxybenzene **2** as starting material.

^1H NMR (400 MHz, CDCl_3): 0.92 (t, 6H, CH_2CH_3), 1.18-1.54 (m, 12H, $(\text{CH}_2)_3$), 1.68-1.90 (m, 4H, OCH_2CH_2), 3.95 (t, 2H, OCH_2), 4.02 (t, 2H, OCH_2), 6.91(d, 1H, ArH), 7.11 (dd, 1H, ArH), 7.31 (d, 1H, ArH), 10.42 (s, 1H, CHO).

Synthesis of 1-bromo-2,5-dihexyloxy-4-bromomethylbenzene 5. NBS (15.6 g, 87.6 mmol) and AIBN (3.54 g, 21.6 mmol) were added to a solution of **1** (21.3 g, 72.9 mmol) in dry CCl_4 (80 mL) in two equal portions under N_2 within 30 min. After the reaction mixture was stirred for 2 h under reflux, it was subsequently allowed to cool to room temperature and filtered. After the evaporation of solvent, hexane (50 mL) was added to the residue and the resulting suspension was filtered and evaporated to dryness. The remaining residue was dissolved in dry THF (40 mL). NBS (15.6 g, 87.6 mmol) was added in two equal portions, and the reaction mixture was stirred at reflux temperature for 1 h. After the evaporation of solvent, hexane (50 mL) was added. The solution was filtered and the solvent was removed *in vacuo*, the crude product was purified by silica column chromatography (eluent: $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/20$). Recrystallization from ethanol gave 1-bromo-2,5- dihexyloxy-4-bromomethylbenzene **5** (8.85 g, 27%) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm): 0.92 (m, 6H, CH_2CH_3), 1.18-1.54 (m, 12H, $(\text{CH}_2)_3$), 1.68-1.90 (m, 4H, OCH_2CH_2), 3.96 (m, 4H, OCH_2), 4.50 (s, 2H, CH_2Br), 6.89 (d, 1H, ArH), 7.06 (s, 1H, ArH).

Synthesis of diethyl(2,5-dihexyloxy-4-bromobenzyl)phosphonate 6. Triethyl phosphite (3.0 g, 18.1 mmol) and **5** (5.5 g, 12.2 mmol) were stirred at 160°C for 2 h

while the liberated ethyl bromide was distilled off. The reaction mixture was cooled to room temperature and the crude product was purified by silica column chromatography (eluent: ethyl acetate /hexane = 1/5) to give 4.20 g (68%) of diethyl(2,5-dihexyloxy-4-bromobenzyl)phosphonate **6** as a light yellow oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 12H, CH₂CH₃), 1.18-1.54 (m, 12H, (CH₂)₃), 1.68-1.90 (m, 4H, OCH₂CH₂), 3.20 (d, 2H, ArCH₂), 3.96 (m, 8H, OCH₂), 6.95(s, 1H, ArH), 7.02 (s, 1H, ArH).

Synthesis of of (E)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybromobenzene 7. A solution of **3** (6.7 g, 20.9 mmol) in 50 mL of dry DMF was added dropwise to a solution of **6** (12.4 g, 24.5 mmol) and *t*-BuOK (2.9 g, 25.9 mmol) in 40 mL of dry DMF under N₂. The reaction mixture was stirred overnight at room temperature and subsequently poured onto 200 g of crushed ice. HCl (3 M, 100 mL) was added, and the aqueous phase was extracted with diethyl ether. The organic phase was dried over Na₂SO₄, then the solvent was evaporated *in vacuo*. Recrystallization of the residue from ethanol yielded 6.52 g (46%) of (E)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybromobenzene **7** as a light yellow crystal. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 12H, CH₂CH₃), 1.18-1.54 (m, 24H, (CH₂)₃), 1.68-1.90 (m, 8H, OCH₂CH₂), 2.22 (s, 3H, ArCH₃), 3.96 (m, 8H, OCH₂), 6.72 (s, 1H, ArH), 7.02 (s, 1H, ArH), 7.06 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.31(d, 1H, ArCH=), 7.43 (d, 1H, ArCH=).

Synthesis of (E)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybenzaldehyde 8. **7** (7.85 g, 11.7 mmol) was dissolved in a mixture of 130 mL of dry diethyl

ether and 65 mL of dry THF under N₂. The solution was cooled to 0°C, and 22 mL of *n*-butyllithium in hexane (1.6 M in hexane) was added slowly. The cooling bath was removed after the mixture was stirred for 30 min, and dry DMF (13.5 mL, 175 mmol) was added dropwise. The mixture was stirred for another 2 h at room temperature followed by adding HCl (3 M, 100 mL). The product was extracted with CH₂Cl₂ followed by washing with water and a saturated NaHCO₃ solution, and drying with Na₂SO₄. After the solvent was evaporated, the residue was purified by silica column chromatography (eluent, CH₂Cl₂/hexane = 1/5), followed by recrystallization from methanol to yield 3.44 g (47%) of (*E*)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybenzaldehyde **8** as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 12H, CH₂CH₃), 1.18-1.54 (m, 24H, (CH₂)₃), 1.68-1.90 (m, 8H, OCH₂CH₂), 2.22 (s, 3H, ArCH₃), 3.96 (m, 8H, OCH₂), 6.72 (s, 1H, ArH), 7.04 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.29 (s, 1H, ArH), 7.40 (d, 1H, ArCH=), 7.55 (d, 1H, ArCH=), 10.47 (s, 1H, CHO).

Synthesis of 2,5-dihexyloxy-*N*-benzylideneaniline **9.** **4** (1.0 g, 3.3 mmol) was added to aniline (0.61 g, 6.6 mmol). The mixture was reacted at 60°C under ~10 Torr vacuum for 3 h. The product of 2,5-dihexyloxy-*N*-benzylideneaniline **9** was used directly without further purification.

Synthesis of (*E*)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybenzaldehyde dimethyl acetal **10.** Amberlite IR120 (2.0 g), trimethyl orthoformate (20 mL), and **8** (2.7 g, 4.3 mmol) were added to 80 mL of dry methanol under N₂. The mixture was stirred at 70°C for 3 h, then cooled to room temperature followed by adding 1.5 g

of Na₂CO₃. The suspension was filtered and the solvent was removed *in vacuo* to yield the product of (*E*)-4-(4-methyl-2,5-dihexyloxystyryl)-2,5-dihexyloxybenzaldehyde dimethyl acetal **10** quantitatively, which was used directly without further purification.

Synthesis of (*E,E*)-4-[4-(2,5-dihexyloxystyryl)-2,5-dihexyloxystyryl]-2,5--dihexyloxybenzaldehyde **11.** **10** (2.1 g, 3.1 mmol) and **9** (1.3 g, 3.4 mmol) were dissolved in 30 mL of anhydrous DMF. *t*-BuOK (2.0 g, 17.9 mmol) was added to the solution, and the reaction mixture was heated to 80°C and stirred for 2 h under N₂. The reaction mixture was cooled to room temperature and poured onto a mixture of 100 g of crushed ice and 50 mL of 3 M HCl. The mixture was extracted three times with diethyl ether. The combined organic layers were washed with water and dried over Na₂SO₄. After the evaporation of solvent, the crude product was purified by silica column chromatography (eluent: ethyl acetate/hexane = 1/20), followed by recrystallization from methanol to yield 1.49 g (51%) of (*E,E*)-4-[4-(2,5-dihexyloxystyryl)-2,5-dihexyloxystyryl]-2,5-dihexyloxybenzaldehyde **11** as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 18H, CH₂CH₃), 1.18-1.54 (m, 36H, (CH₂)₃), 1.68-1.90 (m, 12H, OCH₂CH₂), 3.96 (m, 12H, OCH₂), 6.72 (dd, 1H, ArH), 6.82 (d, 1H, ArH), 7.12 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.17 (d, 1H, ArH), 7.20 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.46 (s, 1H, ArCH=), 7.47 (s, 1H, ArCH=), 7.48 (d, 1H, ArCH=), 7.62(d, 1H, ArCH=), 10.47 (s, 1H, CHO). MALDI-TOF: 910.4 [M-H]⁺.

Synthesis of *N*-(4-((*E*)-4-((*E*)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)-styryl)-2,5-bis(hexyloxy)benzylidene)benzenamine **12.** The reaction between **11** and aniline was carried out under the same synthetic conditions for **9**, and the product of *N*-(4-((*E*)-4-((*E*)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)benzylidene)benzenamine **12** was used directly without further purification.

Synthesis of 2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)-styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)benzaldehyde **13.** The reaction between **12** and **10** was run under the same synthetic conditions for **11**. The crude product was purified by silica column chromatography (eluent: CH₂Cl₂/hexane = 1/2), followed by recrystallization from methanol to yield 1.02 g (78%) of 2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)benzaldehyde **13** as a red solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 30H, CH₂CH₃), 1.18-1.54 (m, 60H, (CH₂)₃), 1.68-1.90 (m, 20H, OCH₂CH₂), 3.96 (m, 20H, OCH₂), 6.72 (dd, 1H, ArH), 6.82 (d, 1H, ArH), 7.17 (m, 8H, ArH), 7.33 (s, 1H, ArH), 7.48 (m, 7H, ArCH=), 7.58 (d, 1H, ArCH=), 10.47 (s, 1H, CHO). MALDI-TOF: 1516.3 [M-H]⁺.

Synthesis of alkyne-terminated OPV₅. Alkyne-terminated OPV₅ was synthesized from **13** as shown in Scheme S2.^{1,2}

Scheme S2. Synthesis of alkyne-terminated OPV₅.

Synthesis of 2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)-styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)phenyl)methanol 14. 13 (2.0 g, 1.32 mmol) was dissolved in the mixture of 75 mL of CH₂Cl₂ and 25 mL of ethanol. Acetic acid (30 μ L) and NaBH₄ (0.25 g, 6.6 mmol) were added and the reaction mixture was stirred at room temperature overnight. The mixture was washed with water and dried with Na₂SO₄, and the solvent was evaporated. The residue was purified by silica column chromatography (eluent: CH₂Cl₂) to yield 1.72 g (86%) of 2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)phenyl)methanol 14 as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 30H, CH₂CH₃), 1.18-1.54 (m, 60H, (CH₂)₃), 1.68-1.90 (m, 20H, OCH₂CH₂), 3.96 (m, 20H, OCH₂), 4.69 (s, 1H, CH₂OH), 6.72 (dd, 1H, ArH), 6.83 (d, 1H, ArH), 6.88 (s, 1H, ArH), 7.17 (m, 8H, ArH), 7.49 (m, 8H, ArCH=). MALDI-TOF: 1518.3 [M-H]⁺.

Synthesis of alkyne-terminated OPV 16. 4-Pentynoic acid (1.0 g, 10.2 mmol) was dissolved in 25 mL of CH₂Cl₂. Oxalyl chloride (2.55 g, 20.0 mmol) and two drops of anhydrous DMF were added and the reaction mixture was stirred at room

temperature overnight. The solvent was evaporated to give pent-4-ynoyl chloride **15** without future purification.

14 (1.0 g, 0.66 mmol) was dissolved in 100 mL of CH₂Cl₂ followed by adding freshly prepared **15** (0.38 g, 3.3 mmol) and pyridine (0.26 g, 3.3 mmol). The reaction mixture was stirred at room temperature overnight. The mixture was washed with water and dried with Na₂SO₄. After the evaporation of solvent, the crude product was purified by silica column chromatography (eluent: CH₂Cl₂/hexane = 1/1) to yield 0.72 g (69%) of alkyne-terminated OPV₅ **16** as a yellow solid (Scheme S2). The product was subjected to ¹H NMR (Figure S1) and GPC analysis (Figure S3), and the “absolute” molecular weight was determined by MALDI-TOF (Figure S2). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 0.92 (m, 30H, CH₂CH₃), 1.18-1.54 (m, 60H, (CH₂)₃), 1.68-1.90 (m, 20H, OCH₂CH₂), 1.98 (m, 1H, alkyne H), 2.55 (m, 2H, CH₂CH₂CO₂), 2.63 (m, 2H, CH₂CH₂CO₂), 3.96 (m, 20H, OCH₂), 5.20 (s, 2H, COOCH₂), 6.72 (dd, 1H, ArH), 6.82 (d, 1H, ArH), 6.91 (s, 1H, ArH), 7.16 (m, 8H, ArH), 7.48 (m, 8H, ArCH=). MALDI-TOF: 1598.7 [M-H]⁺.

Synthesis of azide-terminated poly(*N*-isopropylacrylamide). The azide-functionalized initiator of 2-(2-azidoethoxy) ethylbromoisobutyrate **17** was first synthesized through two steps according to a previous report,³ using 2-(2-chloroethoxy)ethanol as starting material.

Solution ATRP of NIPAM was then performed in water/DMF at 25°C using **17** as initiator (Scheme S3). NIPAM (1.5 g, 13.3 mmol), CuCl (30 mg, 0.3 mmol), Me₆TREN (69 mg, 0.30 mmol), and DMF/water (6 mL, v:v = 1:1) were introduced

into a Schlenk tube. The flask was degassed by three freeze-pump-thaw cycles and the azide-functionalized initiator **17** (83 mg, 0.30 mmol) was injected into the Schlenk tube to initiate the polymerization. The polymerization lasted 10 h at room temperature and it was terminated by putting the flask into liquid N₂. The sample was passed through a short Al₂O₃ column to remove residual catalyst. The mixture was precipitated into hexane. The crude product was purified by repeated dissolution in THF and precipitation in hexane followed by drying *in vacuo* overnight to give 0.70 g of white solid, PNIPAM-N₃ **18**, which was subjected to GPC analysis (Figure S3, ¹H NMR, Figure S4). The “absolute” molecular weight was determined by ¹H NMR after coupling to OPV₅, see below.

Scheme S3. Synthesis of azide terminated PNIPAM.

Synthesis of OPV-*b*-PNIPAM diblock copolymer. Cu-catalyzed alkyne azide cycloaddition (CuAAC) reaction was used to synthesize OPV-*b*-PNIPAM diblock copolymers between alkyne-terminated OPV₅ **16** and PNIPAM-N₃ **18** (Scheme S4). **16** (40 mg, 25 μmol), **18** (250mg, 50 μmol), CuCl (7.5 mg, 0.075 mmol), and HMTETA (20 μL, 0.075 mmol) were added into a 25 mL Schlenk flask (flame-dried under vacuum prior to use). 5 mL of dry THF was charged via a gastight syringe. The flask was degassed by three freeze-pump-thaw cycles followed by immersing the flask into an oil bath set at 40°C. The reaction mixture was allowed to stir for 2 days. Aliquots of the mixture were removed to monitor the reaction progressed by GPC

(Figure S3). The solvent was evaporated and the residue was purified by silica column chromatography (eluent, CH₂Cl₂/methanol = 10/1) to remove the unreacted alkyne-terminated OPV₅ **16** and CuCl. To remove the excess PNIPAM-N₃ **18**, the crude product was purified by repeated dissolution in THF and precipitation in cold water three times, followed by drying *in vacuo* overnight to give 110 mg (62%) of yellow solid, OPV₅-*b*-PNIPAM₄₉ **19** diblock copolymer. The polymer was subjected to GPC analysis (Figure S3), and the number average degree of polymerization of the PNIPAM block $DP_n = 49$ was determined by ¹H NMR on the basis of the known DP_n of OPV₅ (Figure S5).

Scheme S4. Synthesis of OPV₅-*b*-PNIPAM₄₉ diblock copolymer.

Synthesis of azide-terminated poly(2-(diethylamino)ethyl methacrylate).

DEAEMA (2 g, 10.80 mmol), CuCl (54 mg, 0.54 mmol), HMTETA (124 mg, 0.54 mmol), and 2 mL of anhydrous THF were introduced into a Schlenk tube. The flask was degassed by three freeze-pump-thaw cycles, then initiator **17** (75 mg, 0.27 mmol) was injected into the Schlenk tube to initiate the polymerization. The polymerization lasted 10 h at room temperature and it was terminated by putting the flask into liquid N₂. The sample was passed through a short Al₂O₃ column to remove the residual

catalyst. The reaction mixture was precipitated into cold hexane. The crude product was purified by repeated dissolution in THF and precipitation in hexane followed by drying *in vacuo* overnight to give 0.62 g of white solid, azide-terminated PDEAEMA-N₃ **20**, which was subjected to GPC analysis (Figure S19), and the number average degree of polymerization $DP_n = 60$ was determined by ¹H NMR after coupling to OPV₅ on the basis of the known DP_n of OPV₅ (Figure S16). GPC: $M_n^{GPC} = 5,800$ g/mol, $M_w/M_n = 1.16$.

Synthesis of OPV-*b*-PDEAEMA diblock copolymer. The Cu-catalyzed alkyne azide cycloaddition (CuAAC) reaction between alkyne-terminated OPV₅ **16** and PDEAEMA-N₃ **20** was used to synthesize OPV-*b*-PDEAEMA diblock copolymers (Scheme S5).

Scheme S5. Synthesis of OPV₅-*b*-PDEAEMA₆₀ diblock copolymer.

16 (60 mg, 37.5 μmol), **20** (325 mg, 56.25 μmol), CuCl (7.5 mg, 0.075 mmol), and HMTETA (20 μL, 0.075 mmol) were added into a 25 mL Schlenk flask (flame-dried under vacuum prior to use). 5 mL of dry THF was charged via a gastight syringe. The flask was degassed by three freeze-pump-thaw cycles of, followed by immersing the

flask into an oil bath set at 40°C. Then the reaction was allowed to stir for 2 days. Aliquots of the mixture were removed to monitor the reaction progress by GPC. The solvent was evaporated and the residue was purified by silica column chromatography (eluent, CH₂Cl₂/methanol = 10:1) to remove the unreacted alkyne terminated OPV₅ **16** and CuCl/HMTETA. To remove the excess PDEAEMA-N₃ **20**, the crude product was purified by repeated dissolution in THF and precipitation in cold water three times, followed by drying *in vacuo* overnight to give 70 mg (26%) of yellow solid, OPV₅-*b*-PDEAEMA₆₀ **21** diblock copolymer. The polymer was subjected to GPC analysis (Figure S17), and the number average degree of polymerization of PDEAEMA block $DP_n = 60$ was determined by ¹H NMR on the basis of the known DP_n of OPV₅ (Figure S16).

Self-assembly Experiments

Self-assembly of OPV₅-*b*-PNIPAM₄₉ diblock copolymer in ethanol.

OPV₅-*b*-PNIPAM₄₉ **19** diblock copolymer was directly suspended in ethanol (0.05 mg/mL). Then, the mixture was heated at 80°C for 30 min, followed by aging at room temperature (23°C) for 24 h. A drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 1A and S6). AFM height images of these structures are presented in Figures 1D and 1E.

Preparation of seed cylindrical micelles of OPV₅-*b*-PNIPAM₄₉. Seed micelles were prepared by sonicating (BRANSON model 1510 70 W ultrasonic cleaning bath) the original long cylindrical micelles (0.05 mg/mL) formed by OPV₅-*b*-PNIPAM₄₉ **19**

diblock copolymer at 0°C for 30 min. After aging at room temperature (23°C), a drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 2A, S11A, and Table S1).

Self-seeding of seed cylindrical micelles of OPV₅-*b*-PNIPAM₄₉. The self-seeding of seed cylindrical micelles formed by OPV₅-*b*-PNIPAM₄₉ was conducted by thermal annealing at different annealing temperatures ranging from 30°C to 65°C. Aliquots of the seed solutions (0.05 mg/mL) were placed in several vials (2 mL for each vial) and put into preset oil baths at different temperatures. After heating for 0.5 h, the vials were removed from the heating bath and then cooled to 23°C. After these samples were aged for 24 h at room temperature, a drop of each solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 2, S10, S11, and S20). Characterization details are summarized in Table S1. CONTIN plots from the DLS measurements on these micellar solutions obtained by self-seeding are presented in Figure S12.

Seeded growth to prepare uniform cylindrical micelle of OPV₅-*b*-PNIPAM₄₉
Different aliquots (6.3, 12.5, 18.8, 25, 37.5, and 50 µL) of a concentrated THF solution of OPV₅-*b*-PNIPAM₄₉ (6.0 mg/mL) were added into a diluted seed solution of OPV₅-*b*-PNIPAM₄₉ (3 mL, 0.01 mg/mL in ethanol, $L_n = 51$ nm, $L_w = 53$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.24$) at 30°C under stirring, respectively. Subsequently, the samples were stirred for another 10 s and then aged at 30°C for 24 h. TEM images of the micelles obtained are shown in Figures 3, S14, and S15. Characterization details are summarized in Table S2.

Self-assembly of OPV₅-*b*-PDEAEMA₆₀ diblock copolymers in ethanol. Vials containing OPV₅-*b*-PDEAEMA₆₀ **21** diblock copolymer directly suspended in ethanol (0.05 mg/mL) were heated at 80°C for 30 min and then cooled to room temperature (23°C) by removing the vials from the heating bath. After these samples were aged for 24 h at 23°C, a drop of each solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures S18A and S18B).

Preparation of seed cylindrical micelles of OPV₅-*b*-PDEAEMA₆₀. Seed micelles were prepared by sonicating (0°C for 30 min, BRANSON model 1510 70 W ultrasonic cleaning bath) a solution in ethanol containing the original long cylindrical micelles (0.05 mg/mL) formed by OPV₅-*b*-PDEAEMA₆₀ **21** diblock copolymer. After aging at room temperature (23°C), a drop of the solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures S18C and S18D).

Preparation of seed cylindrical micelles of OPV₅-*b*-PDEAEMA₆₀ for seeded growth by self-seeding. The self-seeding of seed cylindrical micelles of OPV₅-*b*-PDEAEMA₆₀ ($L_n = 41$ nm, $L_w/L_n = 1.10$) was conducted by thermal annealing at 53°C to prepare seed micelles for further epitaxial growth. A solution of OPV₅-*b*-PDEAEMA₆₀ micelle fragments (5 mL, 0.05 mg/mL) was heated at 53°C for 0.5 h and then cooled to 23°C. After the sample was aged for 24 h at room temperature, a drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM. (Figures 4A and 4D).

Preparation of A-B-A triblock co-micelles by seeded growth. 12.5 μ L of a concentrated THF solution of OPV₅-*b*-PNIPAM₄₉ (6.0 mg/mL) was added into 3 mL

of a diluted seed solution of OPV₅-*b*-PDEAEMA₆₀ (0.01 mg/mL in ethanol, $L_n = 126$ nm, $L_w/L_n = 1.04$) at 30°C under stirring. Subsequently, the sample was stirred for another 10 s and then aged at 30°C for 24 h. TEM images of the micelles obtained are shown in Figures 4B, 4C and S19.

ADDITIONAL RESULTS AND DISCUSSION

The synthesis of OPV₅-b-PNIPAM₄₉.

The synthesis started with the preparation of an alkyne-terminated OPV₅, which was characterized by ¹H NMR, MALDI-TOF, and GPC (Schemes S1 and S2, Figures S1, S2, and S3). The M_n of OPV₅ (1598.7 g/mol by MALDI-TOF) is consistent with the theoretical M_n of the targeted OPV₅ with an alkyne chain end (1598.3 g/mol). Subsequently, the alkyne-terminated OPV₅ was coupled with azide-terminated PNIPAM ($DP_n = 49$ repeat units), which was prepared by ATRP of NIPAM monomer using an azide-containing initiator (Scheme S3, Figures S3, and S4), through the copper-catalyzed azide-alkyne cycloaddition click reaction (Scheme S4). The product was purified by silica chromatography and washing with water to remove unreacted OPV₅ and PNIPAM₄₉, respectively, to give an orange powder. The chemical structure of OPV₅-*b*-PNIPAM₄₉ diblock copolymer was confirmed by ¹H NMR (Figure S5) and M_n of OPV₅-*b*-PNIPAM₄₉ was obtained by ¹H NMR based on the known DP_n of OPV₅. By gel permeation chromatography (GPC), OPV₅-*b*-PNIPAM₄₉ showed a unimodal and symmetrical eluent peak with a low dispersity ($\mathcal{D} = 1.10$, Figure S3), suggesting that all of the unreacted PNIPAM and OPV₅ were completely removed,

and the possible intermolecular coupling reaction of PNIPAM with its Cl chain end could be neglected.

Self-seeding of OPV₅-b-PNIPAM₄₉ at a higher temperature

At higher annealing temperatures (63°C and 65°C), we observed the formation of long fiber-like micelles (L up to 2 μm), suggesting that the block copolymer had completely dissolved and self-nucleated upon cooling. These were accompanied by shorter micelles ($L < 200$ nm, Figure S20). This phenomenon is similar to observations of self-seeding of P3HT-based block copolymers⁴ and may reflect thermally induced fracture during the cooling step.⁵

Seeded growth of OPV₅-b-PNIPAM₄₉

In order to check the living seeded growth of OPV₅-b-PNIPAM₄₉ micelles, we conducted a control experiment, in which different aliquots of a concentrated THF solution of OPV₅-b-PNIPAM₄₉ (6 mg/mL) were added under stirring to 3 mL of ethanol without seed micelles, followed by stirring for another 10 s and aging for 24 h at 30°C. Although fiber-like micelles were formed with a uniform width, the lengths were not dependent on the amount of added OPV₅-b-PNIPAM₄₉. The micelles formed were long ($L > 1$ μm) accompanied by shorter fiber-like micelles with $L < 100$ nm, and the overall length distributions were very broad (Figure S21). This observation demonstrates the important role of pre-formed seeds as nucleation sites for the living seeded growth process.

SUPPORTING FIGURES

Figure S1. ¹H NMR spectrum of alkyne-terminated OPV₅ **16** in CDCl₃.

Figure S2. MALDI-TOF spectrum of alkyne-terminated OPV₅ **16**.

Figure S3. GPC curves of OPV₅, PNIPAM₄₉, OPV₅-*b*-PNIPAM₄₉, and reaction solutions before purification.

Figure S4. ¹H NMR spectrum of azide-terminated PNIPAM-N₃ 18 in CDCl₃.

Figure S5. ^1H NMR spectrum of $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ **19** in CD_2Cl_2 .

Figure S6. (A) TEM image and (B) width distribution of micelles formed by $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ **19** diblock copolymer.

Figure S7. Hydrodynamic diameter distribution of ethanol solution of $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ after heating at 80°C for 30 min and after aging at 23°C for 24h.

Figure S8. WAXS spectra of dried PNIPAM and fiber-like micelles formed by $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ **19** diblock copolymer.

Figure S9. GPC curves of OPV_5 and $\text{OPV}_5\text{-}b\text{-PNIPAM}_{49}$ before and after sonication treatment.

Figure S10. TEM images and contour length distribution histograms of the micelles obtained after annealing at (A) 35°C, (B) 37°C, (C) 44°C, (D) 47°C, (E) 50°C, and (F) 53°C, followed by aging at room temperature for 24 h.

Figure S11. Contour length distribution histograms of seeds (A) and the micelles obtained after annealing at (B) 40°C, (C) 57°C, and (D) 60°C, followed by aging at room temperature for 24 h.

Figure S12. Apparent hydrodynamic diameters of micellar solutions obtained by annealing of seed micelle solution at different temperature for 30 min, followed by aging at 23°C for 24 h.

Figure S13. TEM images of fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by adding (A) 1.25, (B) 2.5 (C) 5.0, and (D) 10.0 equivalent amount of unimers (as 6 mg/mL solution in THF) to ethanol solutions of seed micelles (3.0 mL, 0.01 mg/mL) at 23°C and aging at 23°C for 24 h.

Figure S14. TEM images and contour length distribution histograms of the micelles obtained by addition of (A) 2.5, (B) 5.0, and (C) 10.0 equivalent amount of unimers (6 mg/mL in THF) to 3.0 mL ethanol solution of seed micelles (0.01 mg/mL) at 30°C, followed by aging at 30°C for 24 h.

Figure S15. Contour length distribution histograms of the micelles obtained by adding (A) 1.25, (B) 3.75, and (C) 7.5 equivalent amount of unimers (6 mg/mL solution in THF) to 3.0 mL ethanol solution of seed micelles (0.01 mg/mL) at 30°C, followed by aging at 23°C for 24 h.

Figure S16. ^1H NMR spectrum of $\text{OPV}_5\text{-}b\text{-PDEAEMA}_{60}$ in CDCl_3 .

Figure S17. GPC curves of OPV_5 , PDEAEMA_{60} , $\text{OPV}_5\text{-}b\text{-PDEAEMA}_{60}$, and reaction solutions before purification.

Figure S18. TEM images (A and B) of fiber-like micelles of OPV₅-*b*-PDEAEMA₆₀ prepared by heating the ethanol solution of OPV₅-*b*-PDEAEMA₆₀ (0.05 mg/mL), followed by aging at 23°C for 24 h. TEM image (C) and contour length distribution histograms (D) of seed micelles generated by sonication of sample in (A) at 0°C for 30 min.

Figure S19. TEM image of A-B-A triblock fiber-like co-micelles obtained by the addition of a THF solution of OPV₅-*b*-PNIPAM₄₉ (12.5 μ L, 6.0 mg/mL) into a seed micelle solution of OPV₅-*b*-PDEAEMA₆₀ (0.01 mg/mL, 3.0 mL). The short micelles highlighted with red circles appear to be fiber-like micelles of OPV₅-*b*-PNIPAM₄₉, since these micelles are not stained with phosphotungstic acid as much as the central block of OPV₅-*b*-PDEAEMA₆₀.

Figure S20. TEM images of micelles of OPV₅-*b*-PNIPAM₄₉ after annealing at (A) 63°C and (B) 65°C, followed by aging at 23°C for 24 h.

Figure S21. TEM images of fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by adding (A) 1.25, (B) 2.5 (C) 5.0, and (D) 10.0 equivalent amounts of unimers (6 mg/mL solution in THF) to 3.0 mL ethanol without seed micelles at 30°C, followed by aging at 30°C for 24 h.

SUPPORTING TABLES

Table S1. Characteristics of seed micelles and elongated fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by self-seeding.^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	51	53	1.05	12	0.24
35	55	58	1.06	16	0.29
37	63	66	1.05	16	0.25
40	143	153	1.07	39	0.27
44	169	180	1.07	42	0.24
47	186	191	1.03	38	0.20
50	311	330	1.06	77	0.25
53	513	543	1.06	131	0.25
57	556	595	1.07	148	0.27
60	871	958	1.10	271	0.31

^a: The mean lengths of the micelles were calculated from measurements of over 100 individual micelles in multiple TEM images.

^b: L_n , L_w , and σ are the number-average micelle length, weight-average micelle length, and the standard deviation of micelle length distribution, respectively, as calculated from the histograms of the length distributions.

Table S2. Characteristics of seed micelles and elongated fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by seeded growth.^a

ratio of unimer-to-seed	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	51	53	1.05	12	0.24
1.25	114	120	1.05	26	0.23
2.5	175	184	1.05	39	0.22
3.75	234	243	1.04	46	0.20
5.0	290	302	1.04	55	0.19
7.5	476	505	1.06	113	0.24
10.0	557	602	1.08	158	0.28

^a: The mean lengths of the micelles were calculated from measurements of over 100 individual micelles in multiple TEM images.

^b: L_n , L_w , and σ are the number-average micelle length, weight-average micelle length, and the standard deviation of micelle length distribution, respectively, as calculated from the histograms of the length distributions.

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