Supporting Information for

Crystallization-Driven Co-self-seeding Strategy Toward Controlled Preparation of Heterojunction Nanofibers

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SUPPORTING EXPERIMENTAL DETAILS

Materials

All organic solvents such as tetrahydrofuran (THF) and ethanol (EtOH) were distilled prior to use. OPE_9-*b*-$P2VP_{56}$, BT-OPE_7-BT-*b*-$PNIPAM_{36}$ were prepared according to previous reports. [1,2]

Instrumentation

Transmission electron microscopy (TEM)

TEM images were obtained from a JEOL JEM-2100 instrument operated at 80 kV. A drop of micellar solution (10 μL) was placed on a Formvar and carbon-coated copper grid for 30 s and 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. The length, width and diameter distribution of micelles was determined by tracing more than 100 individual micelles and analysis using Image J software program from National Institutes of Health. Values of number-average length (L_n) , weight-average length (L_w), number-average width (W_n) and weight-average width (W_w) of micelles were calculated as follows:

$$L_n = \frac{\sum_{i=1}^{N} N_i L_i}{\sum_{i=1}^{N} N_i} \qquad \text{(S1)}$$

$$L_w = \frac{\sum_{i=1}^{N} N_i L_i^2}{\sum_{i=1}^{N} N_i L_i} \quad \text{(S2)}$$

$$W_n = \frac{\sum_{i=1}^{N} N_i W_i}{\sum_{i=1}^{N} N_i} \quad \text{(S3)}$$

$$W_w = \frac{\sum_{i=1}^{N} N_i W_i^2}{\sum_{i=1}^{N} N_i W_i} \quad \text{(S4)}$$

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

UV/vis and fluorescence spectroscopy

UV/vis absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. Fluorescence spectra were measured by using a Hitachi F-2700 fluorescence spectrophotometer with a 10 nm band width. UV/vis and fluorescence measurements were performed at room temperature.

Photoluminescence excitation and emission spectrometry

The photoluminescence excitation and emission spectra were obtained on an

Edinburgh FLS1000 steady-state transient fluorescence spectrometer with a Xenon lamp. Micellar solutions of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (2×10^{-6} mol/L in ethanol), OPE$_9$-*b*-P2VP$_{56}$ (2×10^{-6} mol/L in ethanol) and heterojunction comicelles (2×10^{-6} mol/L in ethanol) were subjected to photoluminescence analysis. For each sample, measurements were performed on deoxygenated solution (degassed by Ar bubbling). Photoluminescence excitation spectra were obtained with λ_{em} = 615 nm for BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$, λ_{em} = 534 nm for OPE$_9$-*b*-P2VP$_{56}$ and λ_{em} = 463 nm for heterojunction comicelles, respectively. The following settings were used for the spectra acquisition: step 1.0 nm, dwell 0.2 s, repeat 1. Photoluminescence emission spectra were obtained with λ_{ex} = 423 nm for BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$, λ_{ex} = 419 nm for OPE$_9$-*b*-P2VP$_{56}$ and λ_{ex} = 409 nm for heterojunction comicelles, respectively.

Time-correlated single photon counting (TCSPC)

The time-resolved fluorescence spectroscopy (photoluminescence decay profile) was measured by using time-correlated single photon counting (TCSPC) mode. Micellar solutions of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (2×10^{-6} mol/L in ethanol), OPE$_9$-*b*-P2VP$_{56}$ (2×10^{-6} mol/L in ethanol)and heterojunction comicelles (2×10^{-6} mol/L in ethanol) were subjected to TCSPC analysis. For each sample, measurements were performed on deoxygenated solution (degassed by Ar bubbling). Photoluminescence decay profiles were obtained on an Edinburgh FLS1000 steady-state transient fluorescence spectrometer with a picosecond pulsed diode (EPL) laser (λ_{ex} = 375 nm) operating at 5 MHz and emission peak as detection wavelength (λ_{em} = 615 nm for BT-

OPE_7-BT-*b*-$PNIPAM_{36}$, λ_{em} = 534 nm for OPE_9-*b*-$P2VP_{56}$ and λ_{em} = 463 nm for heterojunction comicelles, respectively). The decay curves were fitted using a nonlinear method with a multiexponential decay law given by

$$I(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} \quad \text{(S5)}$$

Where I is the fluorescence intensity at time, t is time, B_i is amplitude and τ_i is one component fluorescence lifetime. And the "intensity-weighted" mean decay times $<\tau>$ were obtained by

$$\langle\tau\rangle = B_1\tau_1 + B_2\tau_2 + B_3\tau_3 \ (B_1 + B_2 + B_3 = 1) \quad \text{(S6)}$$

Self-assembly Experiments

Preparation of comicelles of OPE_9-*b*-$P2VP_{56}$ and BT-OPE_7-BT-*b*-$PNIPAM_{36}$ by direct heating-cooling protocol

Concentrated THF solutions of BT-OPE_7-BT-*b*-$PNIPAM_{36}$ (5 mg/mL) and OPE_9-*b*-$P2VP_{56}$ (5 mg/mL) with mass ratio of $M_{BT\text{-}OPE7\text{-}BT/OPE9}$ = 1/1 were added into hot ethanol(80°C). Subsequently, the mixture were heated at 80°C for 1 h, followed by cooling/aging at 25°C for 24 h. A drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM.

Preparation of co-seed micelles of BT-OPE_7-BT-*b*-$PNIPAM_{36}$/OPE_9-*b*-$P2VP_{56}$

Co-seed micelles of BT-OPE_7-BT-*b*-$PNIPAM_{36}$/OPE_9-*b*-$P2VP_{56}$ were prepared by sonicating (SONICS VC 750 ultrasonic processor, 30% power) the as-prepared polydisperse fiber-like comicelles obtained with $M_{BT\text{-}OPE7\text{-}BT/OPE9}$ = 1/1 at 0°C for 30 min, followed by aging at room temperature (25°C). A drop of solution was placed on

a Formvar and carbon-coated copper grid and examined by TEM.

Preparation of seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$

Seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$ were prepared by sonicating the corresponding polydisperse fiber-like micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (0.05 mg/mL) and OPE$_9$-*b*-P2VP$_{56}$ (0.05 mg/mL) at 0^{o}C for 30 min, followed by aging at room temperature (25^{o}C), a drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM.

Co-self-seeding of co-seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$/OPE$_9$-*b*-P2VP$_{56}$

Aliquots of co-seed micelles (0.05 mg/mL in ethanol) obtained from polydisperse comicelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$/OPE$_9$-*b*-P2VP$_{56}$ with $M_{\text{BT-OPE7-BT/OPE9}}$ = 1/1 were annealed at different temperatures for 1 h, followed by cooling/aging at 25^{o}C for 24 h. Characterization details are summarized in **Table S1**.

Co-self-seeding of mixture of individual seed micelles formed separately from BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$

Individual seed micelles (0.05 mg/mL in ethanol) of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (**Fig. S5A**, L_n = 40 nm, L_w/L_n = 1.12) and OPE$_9$-*b*-P2VP$_{56}$ (**Fig. S5B**, L_n = 37 nm, L_w/L_n = 1.08) were firstly mixed together with $M_{\text{BT-OPE7-BT/OPE9}}$ = 1/1 to give mixture of seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$ (total concentration of 0.05 mg/mL in ethanol). Aliquots of resulting mixture were annealed at different temperatures for 1 h, followed by cooling/aging at 25^{o}C for 24 h. A drop of solution

was placed on a Formvar and carbon-coated copper grid and examined by TEM. Characterization details are summarized in **Table S2**.

Photocatalysis Experiments

Photocatalytic selective oxidation of 4-methoxyphenyl methyl sulfide to 4-methoxyphenyl methyl sulfoxide

4-methoxyphenyl methyl sulfide (0.05 mmol), heterojunction comicelles (0.00002 mmol), dodecane (0.00005 mmol) and d_6-EtOH (1 mL) were added to a 30 mL photo-reactor. Then the reaction mixture was stirred at 500 rpm for 1 h, followed by illuminating with a 300 W Xe lamp with a 420 nm cut-off filter (I = 10 A, 780 nm > λ > 420 nm, E = 135 mW/cm^2) for different time. A circulating cold bath outside the reactor kept the reaction temperature at 25°C. An oxygen ballon was used to charge the flask with oxygen at 1 atm. Conversion and selectively of 4-methoxyphenyl methyl sulfoxide were confirmed by ^{1}H NMR with dodecane as the internal standard. The 4-methoxyphenyl methyl sulfide conversion and 4-methoxyphenyl methyl sulfoxide yield were calculated with the following equation:

$$Conversion(\%) = \frac{S_0 - S_{Sulfide}}{S_0} \times 100\% \quad \text{(S7)}$$

Here, S_0 is the initial integral area of -SCH_3 in ^{1}H NMR spectra, $S_{sulfide}$ and $S_{sulfoxide}$ are the particularly reaction time integral area of -SCH_3 and -OSCH_3 in ^{1}H NMR spectra, respectively. The integral area of -CH_3 in dodecane is defined as 1.

Supporting Figures

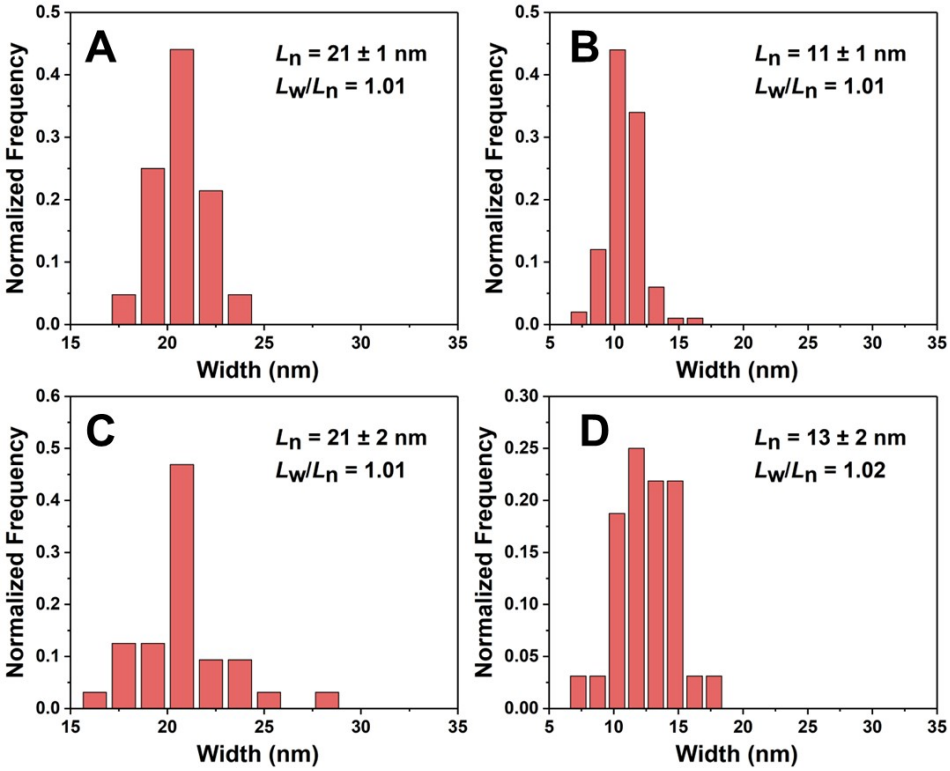


Fig. S1 Contour width distribution histogram of individual fiber-like micelles of OPE_9-*b*-$P2VP_{56}$ (A), individual fiber-like micelles of BT-OPE_7-BT-*b*-$PNIPAM_{36}$ (B), end blocks (C) and central blocks (D) of comicelles of BT-OPE_7-BT-*b*-$PNIPAM_{36}$/ OPE_9-*b*-$P2VP_{56}$.

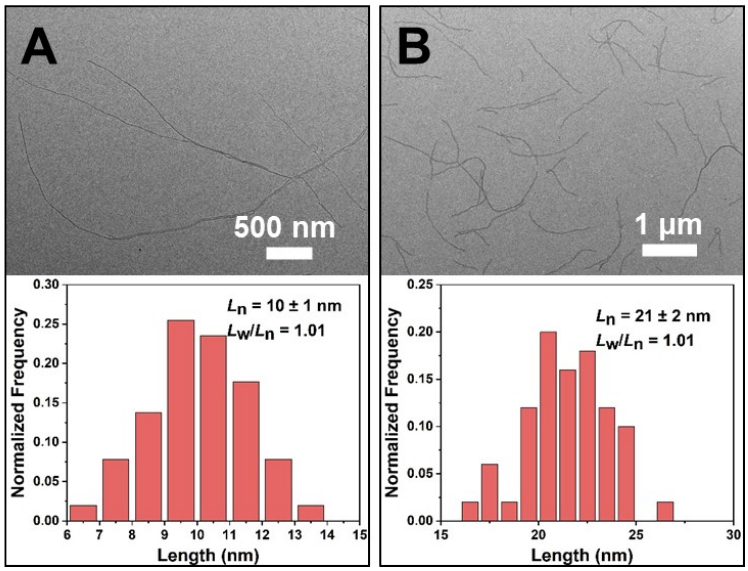


Fig. S2 Contour width distribution histogram of fiber-like micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (A), individual fiber-like micelles of OPE$_9$-*b*-P2VP$_{56}$ (B).

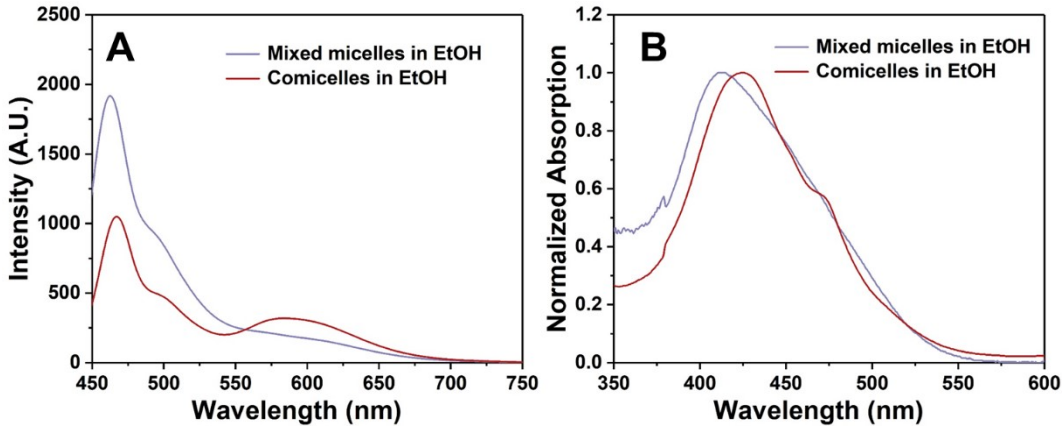


Fig. S3 UV/vis (A) and FL (B) spectra of mixed micelles and comicelles in ethanol.

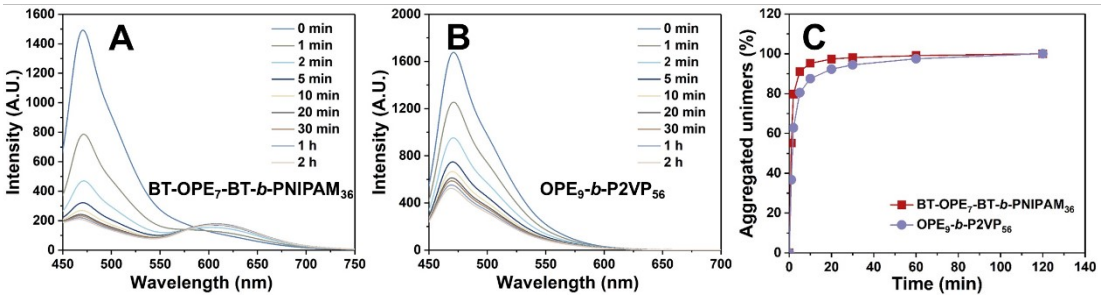


Fig. S4 Fluorescence emission spectra of ethanol solutions of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (A) and OPE$_9$-*b*-P2VP$_{56}$ (B) as they were cooled/aged at 25°C after heating at 80°C for 1 h (0.05 mg/mL).

(C) Dependence of calculated contents of aggregated unimers on cooling/aging time obtained on the basis of fluorescence results shown in Fig. S4A-B.

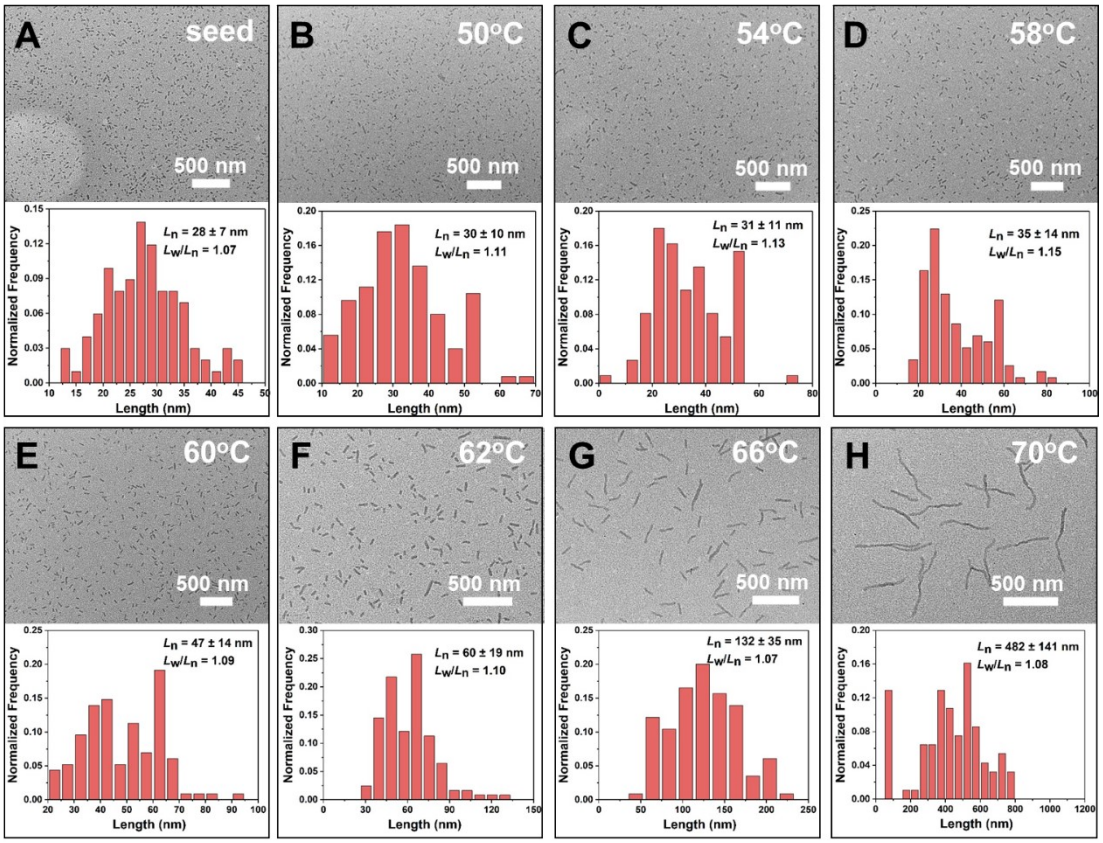


Fig. S5 TEM images and contour length distribution histogram of co-seeds of BT-OPE_7-BT-*b*-$PNIPAM_{36}$/OPE_9-*b*-$P2VP_{56}$ (A) and comicelles obtained by annealing the co-seeds at 50°C (B), 54°C (C), 58°C (D), 60°C (E), 62°C (F), 66°C (G) and 70°C (H).

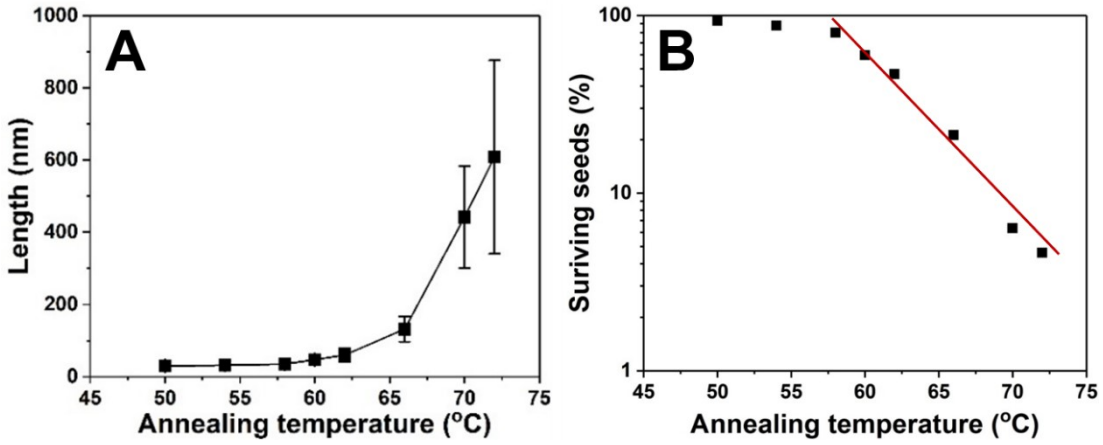


Fig. S6 L_n of obtained comicelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$/OPE$_9$-*b*-P2VP$_{56}$ (A) and semilogarithmic plot of fraction of surviving co-seeds (B) versus annealing temperature.

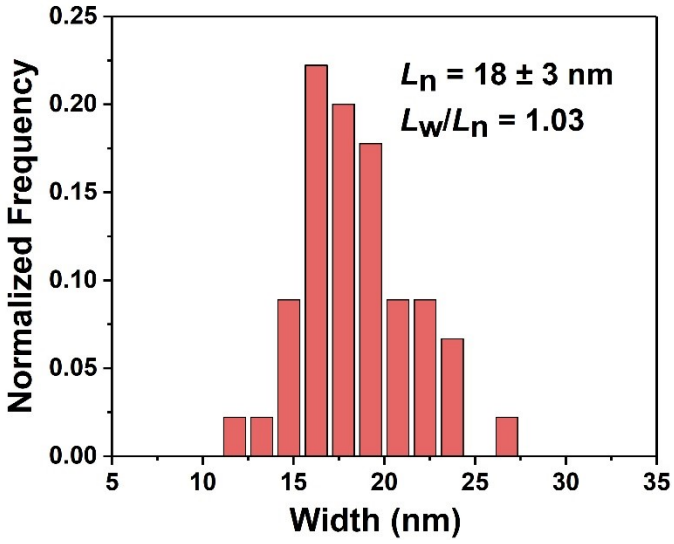


Fig. S7 Contour width distribution histogram of comicelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$/OPE$_9$-*b*-P2VP$_{56}$.

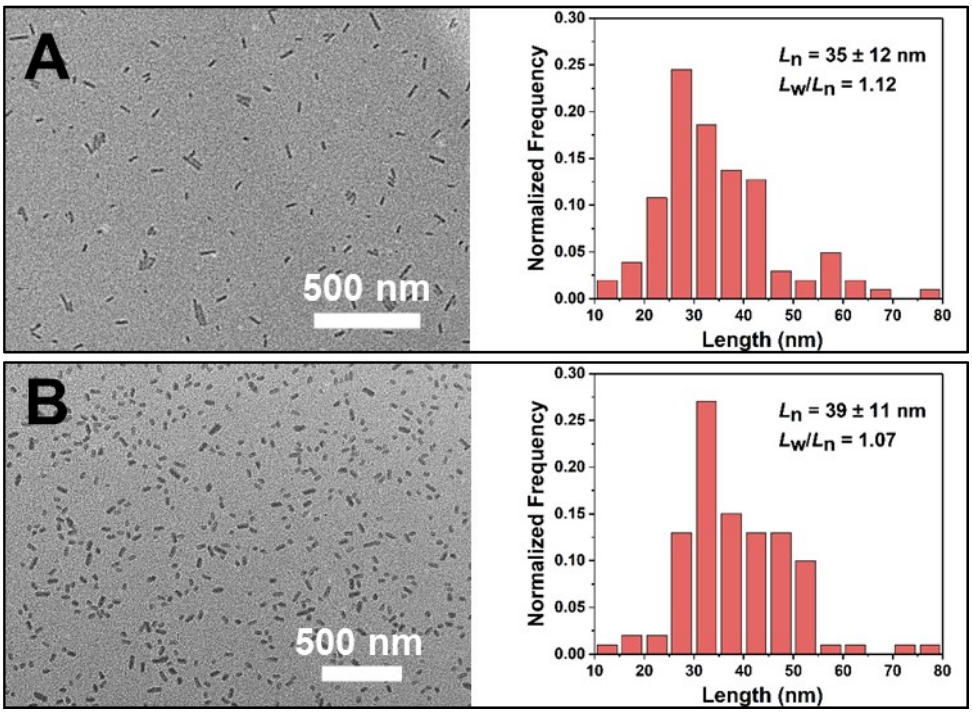


Fig. S8 TEM images and length distribution historgrams of individual seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ (A) and OPE$_9$-*b*-P2VP$_{56}$ (B).

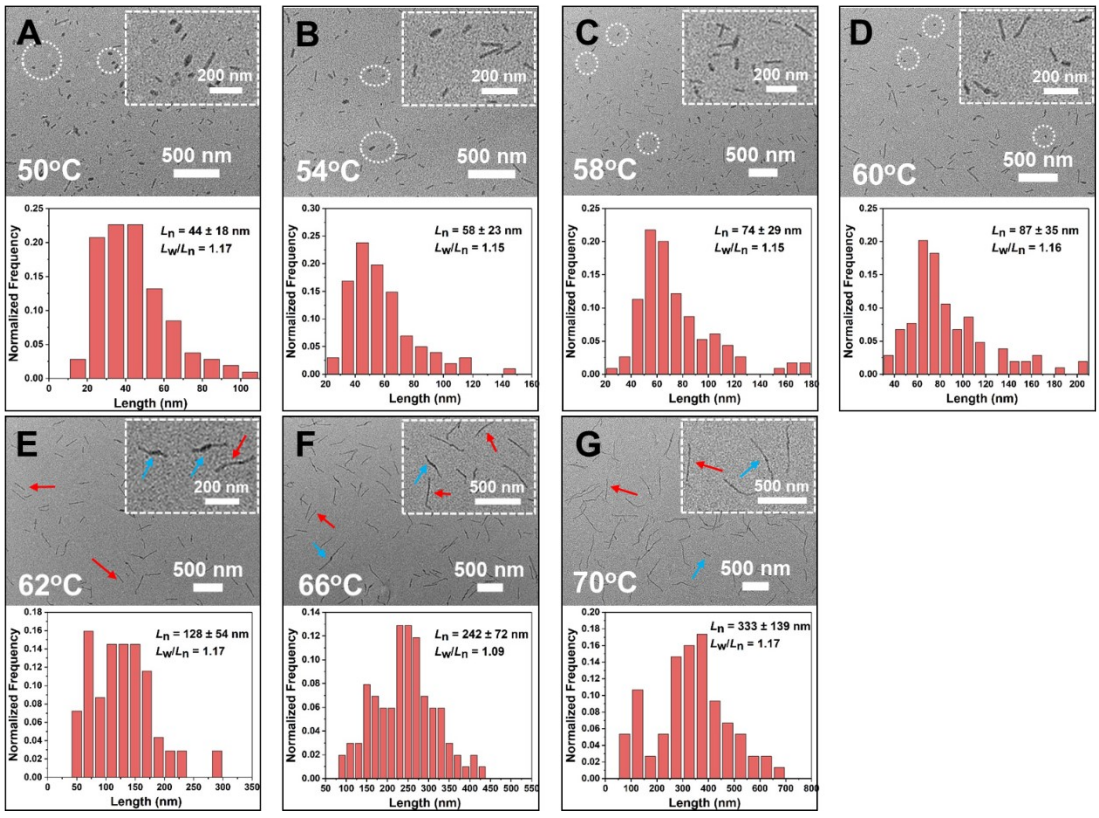


Fig. S9 TEM images and contour length distribution histogram of comicelles obtained by

annealing mixed seed micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$ at 50°C (A), 54°C (B), 58°C (C), 60°C (D), 62°C (E), 66°C (F) and 70°C (G).

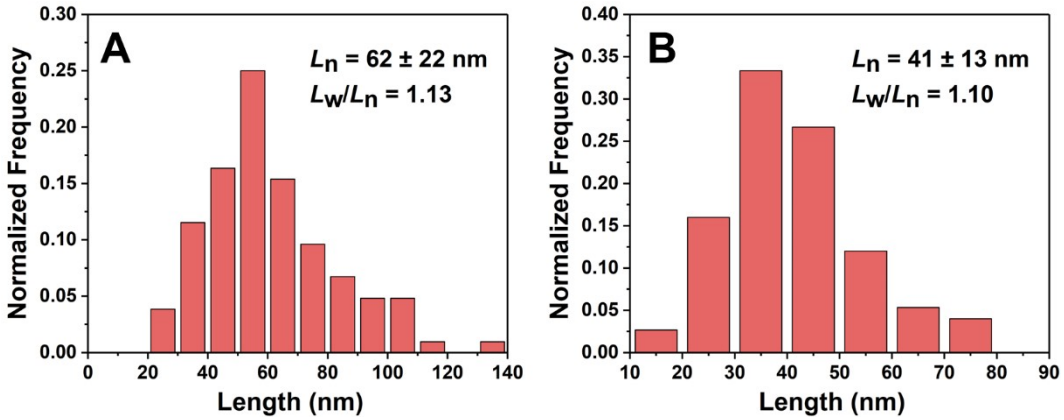


Fig. S10 Contour length distribution histograms of micelles with width of 11 nm (A) and 21 nm (B) obtained by annealing the mixed-seeds at 50°C.

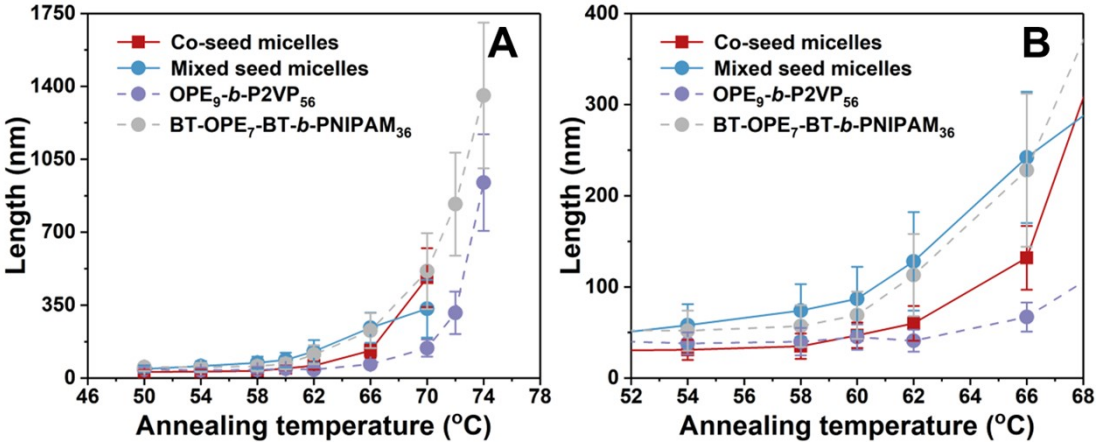


Fig. S11 (A-B) L_n of obtained comicelles of co-self-seeding of co-seed micelles and mixed seed micelles, elongated micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ and OPE$_9$-*b*-P2VP$_{56}$ versus annealing temperature.

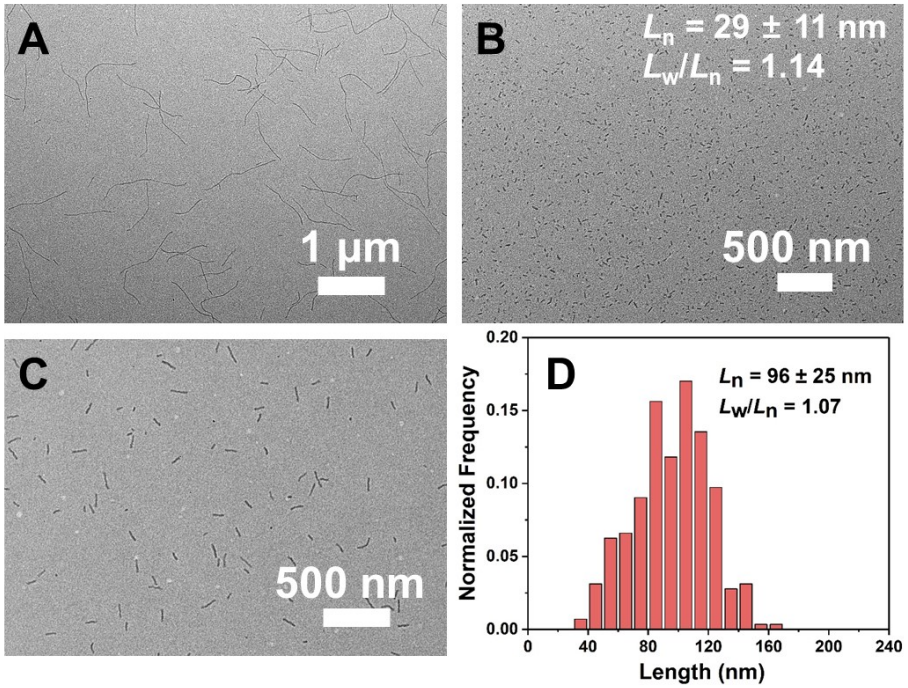


Fig. S12 TEM images of heterojunction comicelles (A), co-seed micelles (B), co-self-seeding micelles (C) and length distribution histogram (D).

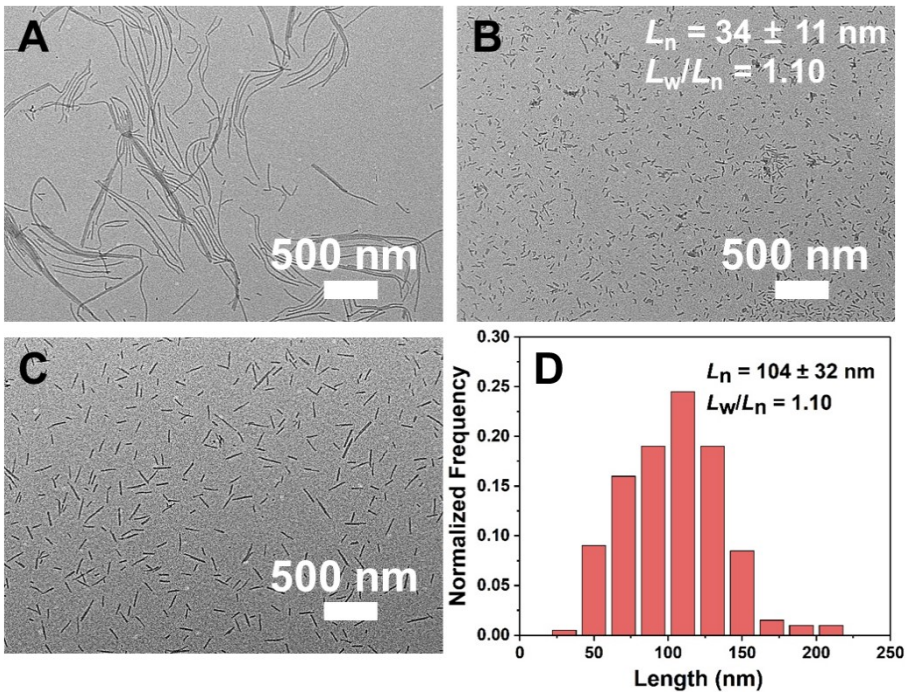


Fig. S13 TEM images of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$ long fiber-like micelles (A), seed micelles (B), self-seeding micelles (C) and length distribution histogram (D).

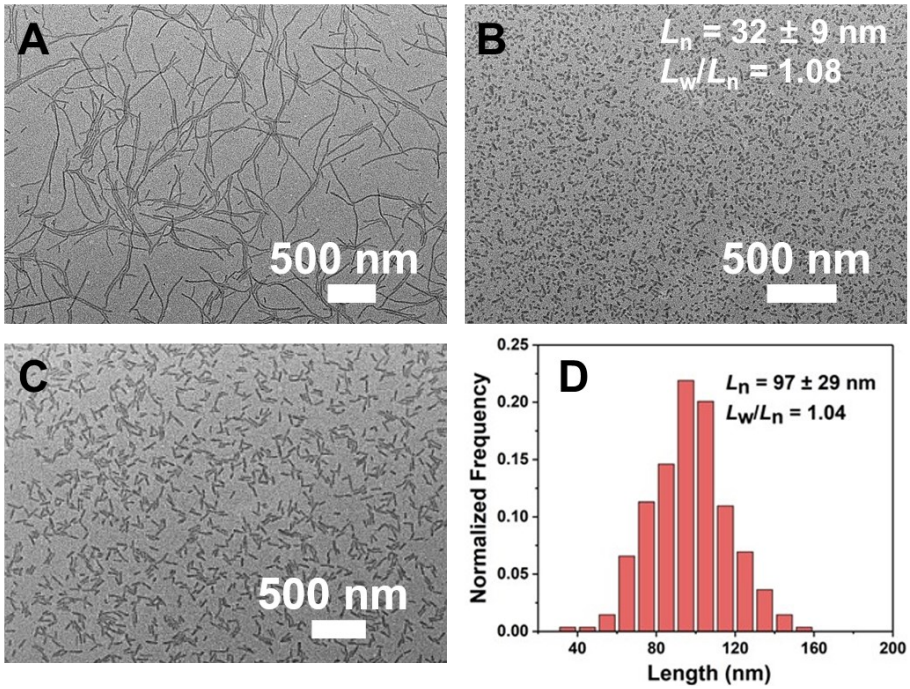


Fig. S14 TEM images of OPE_9-*b*-$P2VP_{56}$ long fiber-like micelles (A), seed micelles (B), self-seeding micelles (C) and length distribution histogram (D).

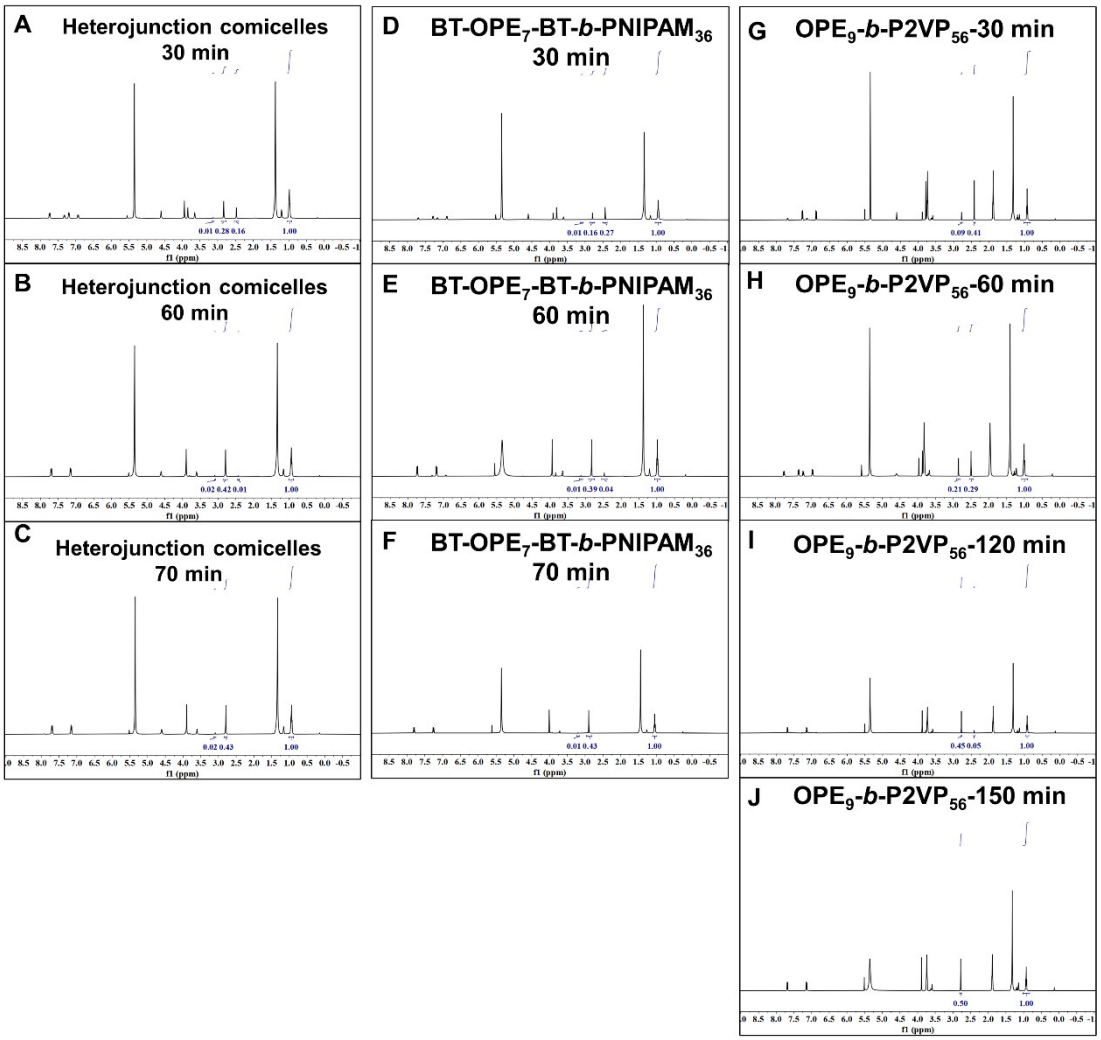


Fig. S15 ^{1}H NMR spectra (dodecane, 298 K, 400 MHz) of 4-methoxyphenyl methyl sulfide photooxidation in the presence of heterojunction comicelles, BT-OPE_7-BT-*b*-$PNIPAM_{36}$ fiber-like micelles and OPE_9-*b*-$P2VP_{56}$ fiber-like micelles as photocatalysts after irradiation at different time in d_6-ethanol.

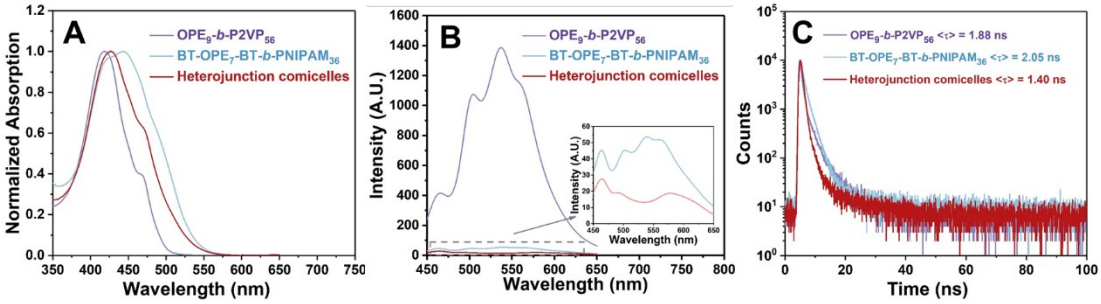


Fig. S16 UV/vis spectra (A), FL spectra (B) and time-resolved fluorescence decay (C) of micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$, OPE$_9$-*b*-P2VP$_{56}$ and heterojunction comicelles.

Supporting tables

Table S1. Characteristic of co-seed micelles and elongated comicelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$/OPE$_9$-*b*-P2VP$_{56}$ obtained by co-self-seeding strategy ($M_{\text{BT-OPE7-BT/OPE9}}$ = 1/1, 0.05 mg/mL).

T/^{o}C	L_n (nm)	L_w (nm)	L_w/L_n [b]	σ [b] (nm)	σ/L_n [b]
seed	28	30	1.07	7	0.26
50	30	34	1.11	10	0.33
54	31	35	1.13	11	0.36
58	35	41	1.15	14	0.39
60	47	51	1.09	14	0.30
62	60	66	1.10	19	0.31
66	132	141	1.07	35	0.27
70	482	523	1.08	141	0.29

[a] The mean length of micelles was calculated from measurements of over 200 individual micelles in multiple TEM images.

[b] L_n, L_w and σ are the number-average micelle length, weight-average micelle length and standard deviation of micelle length distribution, respectively, as calculated from the histogram of the length distribution.

Table S2. Characteristic of separate seed micelles of BT-OPE_7-BT-*b*-$PNIPAM_{36}$ and OPE_9-*b*-$P2VP_{56}$ and elongated comicelles obtained by annealing the mixed-seeds ($M_{BT\text{-}OPE7\text{-}BT/OPE9}$ = 1/1, 0.05 mg/mL).

T/°C	L_n (nm)	L_w (nm)	L_w/L_n [b]	σ [b] (nm)	σ/L_n [b]
BT-OPE_7-BT-*b*-$PNIPAM_{36}$ seed	35	39	1.12	12	0.34
OPE_9-*b*-$P2VP_{56}$ seed	39	42	1.07	11	0.27
50	44	52	1.17	18	0.42
54	58	67	1.15	23	0.39
58	74	86	1.15	29	0.39
60	87	101	1.16	35	0.40
62	128	151	1.17	54	0.42
66	242	263	1.09	72	0.30
70	333	390	1.17	139	0.42

[a] The mean length of micelles was calculated from measurements of over 200 individual micelles in multiple TEM images.

[b] L_n, L_w and σ are the number-average micelle length, weight-average micelle length and standard deviation of micelle length distribution, respectively, as calculated from the histogram of the length distribution.

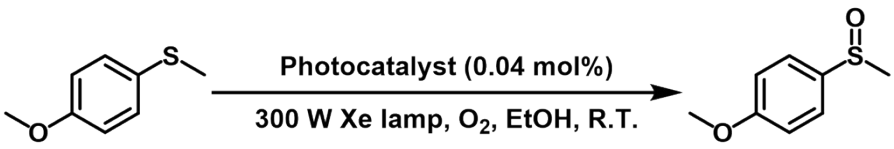
Table S3. Characteristic of micelles of BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$, OPE$_9$-*b*-P2VP$_{56}$ and heterojunction comicelles used for photocatalytic selective oxidation reactions.

Samples	L_n (nm)	L_w (nm)	L_w/L_n [b]	σ[b] (nm)	σ/L_n [b]
BT-OPE$_7$-BT-*b*-PNIPAM$_{36}$	104	114	1.10	32	0.31
OPE$_9$-*b*-P2VP$_{56}$	97	101	1.04	20	0.20
heterojunction comicelles	96	103	1.07	25	0.26

[a] The mean length of micelles was calculated from measurements of over 200 individual micelles in multiple TEM images.

[b] L_n, L_w and σ are the number-average micelle length, weight-average micelle length and standard deviation of micelle length distribution, respectively, as calculated from the histogram of the length distribution.

Table S4. Photocatalytic oxidation of 4-methyloxyphenyl methyl sulfide [a]



Entry	Photocatalyst	Time (min)	Conv. (%) [b]	Select. (%) [b]
1	OPE_9-*b*-$P2VP_{56}$ nanofibers	150	>99	99
2	BT-OPE_7-BT-*b*-$PNIPAM_{36}$ nanofibers	70	>99	99
3	heterojunction-micelles	70	>99	99

[a] Reaction conditions: 4-methoxyphenyl methyl sulfide (0.05 mmol), photocatalyst (0.00002 mmol), d_6-EtOH (1 mL), 1 atm O_2, irradiation with a 300 W Xe lamp ($780 > \lambda > 420$ nm, E = 135 mW/cm^2) at room temperature unless otherwise noted.

[b] Determined by ^{1}H NMR with dodecane as the internal standard.

Table S5. Comparison of selective oxidation of 4-methoxyphenyl methyl sulfide catalytic performance of heterojunction comicelles, BT-OPE_7-BT-b-$PNIPAM_{36}$ and OPE_9-b-$P2VP_{56}$ fiber-like micelles as photocatalysts.

Samples	Time (min)	$S_{sulfide}$ [a]	$S_{sulfoxide}$ [a]	$S_{sulfone}$ [a]	Conversion (%) [b]
Heterojunction comicelles	30	0.16	0.28	0.01	64
	60	0.01	0.42	0.02	98
	70	0	0.42	0.02	>99
BT-OPE_7-BT-b-$PNIPAM_{36}$	30	0.27	0.16	0.01	39
	60	0.04	0.39	0.01	91
	70	0	0.43	0.01	>99
OPE_9-b-$P2VP_{56}$	30	0.41	0.09	0	18
	60	0.29	0.21	0	42
	120	0.05	0.45	0	90
	150	0	0.50	0	>99

[a] $S_{sulfide}$, $S_{sulfoxide}$ and $S_{sulfone}$ are the particularly reaction time integral area of -SCH_3, -OSCH_3 and -O_2SCH_3 in ^{1}H NMR spectra, respectively. The integral area of -CH_3 in dodecane is defined as 1.

[b] $Conversion(\%) = \frac{S_0 - S_{sulfide}}{S_0} \times 100\%$, $S_0 = S_{sulfide} + S_{sulfoxide} + S_{sulfone}$

Table S6. Raw data corresponding particularly to photophysical properties of photocatalysts.

Photocatalyst	λ_{max} (nm) [a]	I_{530} [b]	$<\tau>$ (ns) [c]
OPE_9-*b*-$P2VP_{56}$ nanofibers	418	1305	1.88
BT-OPE_7-BT-*b*-$PNIPAM_{36}$ nanofibers	443	50.6	2.05
heterojunction-micelles	427	13.3	1.40

[a] λ_{max} is the maximum of absorption peak in UV/vis spectra.

[b] I_{530} is the fluorescence intensity at 530 nm in FL spectra.

[c] $<\tau>$ is the mean excited state lifetimes obtained by time-resolved fluorescence decay analysis.

Table S7. Fitting parameters from fluorescence decay measurements and calculated mean lifetimes for micellar solutions of heterojunction comicelles (2×10^{-6} mol/L in ethanol), BT-OPE_7-BT-*b*-$PNIPAM_{36}$ fiber-like micelles (2×10^{-6} mol/L in ethanol) and OPE_9-*b*-$P2VP_{56}$ (2×10^{-6} mol/L in ethanol)under Ar. [a]

Samples	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$<\tau>$ (ns)	χ^2
Heterojunction comicelles	0.76 (B_1 = 86.61%)	2.62 (B_2 = 10.35%)	14.87 (B_3 = 3.04%)	1.40	1.29
BT-OPE_7-BT-*b*-$PNIPAM_{36}$	0.91 (B_1 =37.14%)	2.16 (B_2 = 60.87%)	20.12 (B_3 = 2.00%)	2.05	1.21
OPE_9-*b*-$P2VP_{56}$	0.61 (B_1 = 52.25%)	2.36 (B_2 = 40.00%)	7.98 (B_3 = 7.75%)	1.88	1.24

[a] The "intensity-weighted" mean decay times $<\tau>$ were obtained by $<\tau> = B_1\tau_1 + B_2\tau_2 + B_3\tau_3$ ($B_1 + B_2 + B_3 = 1$).

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