ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Synthesis, Self-assembly and Photophysical Properties of Oligo(2,5-dihexyloxy-1,4-phenylene vinylene)-*block*-Poly(ethylene glycol)

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ADDITIONAL EXPERIMENTAL DETAILS

Materials

All reagents were used as received, including methylhydroquinone (Aldrich, ≥ 99%), 1-bromohexane (Aldrich, 98%), potassium hydroxide (KOH, Aldrich, ≥ 85%), phosphorus oxychloride ($POCl_3$, Aldrich, 99%), aniline (Aldrich, 99%), potassium *tert*-butoxide (KO*t*Bu, Aldrich, 95%), Sodium triacetoxyborohydride ($NaBH(CH_3COO)_3$, Aldrich, 95%), anhydrous chloroform ($CHCl_3$, Aldrich, ≥ 99.9%), anhydrous dichloromethane (CH_2Cl_2, Aldrich, ≥ 99.8%), acetic acid (AcOH, Fisher Scientific, ≥ 99.5%), anhydrous *N*,*N*-dimethylformamide (DMF, Aldrich, 99.8%), α-cyano-4-hydroxy cinnamic acid (Aldrich, ≥ 99.9%), phosphotungstic acid hydrate ($H_3[P(W_3O_{10})_4]\cdot xH_2O$). The polymers MeO-PEG-$NH_2$ (M_n = 2 KDa and 5 KDa) were purchased from JenKem. mPEG550-OH was purchased from Aldrich. MeO-PEG-NH_2 (M_n = ~550) was prepared as described in the literarture.[1]

Synthesis of 2,5-Dihexyloxytoluene, 1.

Conversion of methylhydroquinone to its dihexyl ether was achieved by dissolving 24.83 g of methylhydroquinone (0.20 mol) and of KOH (39.61 g, 0.60 mol) in absolute ethanol (200 mL) and refluxing the mixture at 80 °C for 2 h. Subsequently, 1-bromohexane (99.02 g, 84.2 mL, 0.60 mol) was added dropwise, and mixture was refluxed at 80 °C for two days. The reaction mixture was poured into water, and the product was extracted with diethyl ether. The product was purified by silica column chromatography using a mixture of *n*-hexanes and ethyl acetate (v/v:100/3) to give a yellow oil of 2,5-dihexyloxytoluene (47.96 g, 82%).

^{1}H NMR ($CDCl_3$, 25 °C), δ: 0.90 (t, 6H, -C*H*$_3$), 1.33 (m, 8H, -C*H*$_2$C*H*$_2$CH$_3$), 1.44 (m, 4H, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.74 (m, 4H, -OCH$_2$C*H*$_2$-), 2.20 (s, 3H, Ar-C*H*$_3$), 3.88 (t, 4H, -O-C*H*$_2$-, 6.70 (m, 3H, Ar-*H*).

^{13}C NMR ($CDCl_3$, 25 °C), δ (ppm): 14.02 (-CH$_2$*C*H$_3$), 16.38 (Ar-*C*H$_3$), 22.62 (-*C*H$_2$CH$_3$), 25.76 (-*C*H$_2$CH$_2$CH$_3$), 29.41 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.61 (-*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 68.52 (-O*C*H$_2$CH$_2$-), 111.56, 112.26, 117.61, 123.11, 151.43 and 152.80 (carbons in Ar).

MS-ESI: m/z calculated for $C_{19}H_{33}O_2$ $(M + H)^+$ 293.2, found: 293.2.

Synthesis of 2,5-Dihexyloxy-4-methylbenzaldehyde, 2.

2,5-Dihexyloxy-4-methylbenzaldehyde was synthesized following the procedure described as described in a by Tanaka.[2]2,5-Dihexyloxytoluene (29.25 g, 0.10 mol) was dissolved in a mixture of anhydrous $CHCl_3$ (100 mL) and anhydrous DMF (31.0 mL, 29.26 g, 0.40 mol). $POCl_3$ (46.6 mL, 76.66 g, 0.50 mol) was added dropwise via a dropping funnel at room temperature. The reaction was stirred for 3 h and then refluxed at 80 °C for three days. The product was poured out onto ice, extracted into dichloromethane, and neutralized. The product was purified by column chromatography over silica gel using a mixture of *n*-hexanes and ethyl acetate (v/v:1/4) to give a white solid of 2,5-dihexyloxy-4-methylbenzaldehyde, **2**, (25.32 g, 79%).

^{1}H NMR ($CDCl_3$, 25 °C), δ (ppm): 0.99 (t, 6H, -C*H*$_3$), 1.33 (m, 8H, -C*H*$_2$C*H*$_2$CH$_3$), 1.45 (m, 4H, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.77 (m, 4H, -OCH$_2$C*H*$_2$-), 2.27 (s, 3H, Ar-C*H*$_3$), 3.95 (t, 2H, -O-C*H*$_2$- meta to aldehyde), 4.02 (t, 2H, -O-C*H*$_2$- ortho to aldehyde), 6.79 (s, H, Ar-*H* meta to aldehyde), 7.22 (s, H, Ar-*H* ortho to aldehyde), 10.42 (s, H, -C*H*=O)

^{13}C NMR ($CDCl_3$, 25 °C), δ (ppm): 13.77 (-CH$_2$*C*H$_3$), 17.39 (Ar-*C*H$_3$), 22.59 (-*C*H$_2$CH$_3$), 25.51 (-*C*H$_2$CH$_2$CH$_3$), 29.36 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.34 (-*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 68.46 (-OCH$_2$CH$_2$-), 108.08, 115.57, 123.04, 137.07, 151.01 and 156.22 (carbons in Ar) 189.47 (-*C*HO).

MS-ESI: m/z calculated for $C_{20}H_{32}O_3$ $(M + H)^+$ 321.2, found: 321.2.

Synthesis of 2',5'-Dihexyloxy-4'-methy-N-benzylideneaniline, 3.

To produce the imine, 2,5-dihexyloxy-4-methylbenzaldehyde, **2**, (3.20 g, 0.01 mol) was combined with aniline (1.8 mL, 1.84 g, 0.02 mol). The mixture was reacted at 60 °C under ~ 10 Torr vacuum for 2 h. The product was used directly without further purification.

Synthesis of Oligo(2,5-dihexyloxy-1,4-phenylene vinylene) (OHPV-CH=O), 4.

OHPV was synthesized by Seigrist polycondensation.[2] KO*t*Bu (3.37 g) was added to DMF (400 mL) and warmed to 30 °C. Then the 2',5'-dihexyloxy-4'-methy-*N*-benzylideneaniline **(3)**

solution dissolved in DMF (50 mL) was added dropwise into the KO*t*Bu solution over ~30 min, and the reaction was allowed to continue for another 45 min. The mixture was poured into acidified water (1% HCl) and stirred for two days to hydrolyze unreacted imines. The product was collected, neutralized, and fractionated by column chromatography over silica using a mixture of *n*-hexanes and DCM (v/v:3/4) to obtain a red solid (1.28 g, 42 %).

^{1}H NMR ($CDCl_3$, 25 ^{o}C) δ (ppm, integrated peak areas reported are based on methyl protons of the OHPV as a reference) (Figure S1): 0.91 (m, 6H/HPV, -C*H*$_3$, integration = 10.40), 1.37 (b, 8H/HPV, -C*H*$_2$C*H*$_2$CH$_3$, integration = 13.19), 1.54 (m, 4H/HPV, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.85 (b, 4H/HPV, -OCH$_2$C*H*$_2$-, integration = 6.66), 2.24 (s, 3H/HPV, Ar-C*H*$_3$, integration = 1.00), 4.04 (b, 4H/HPV, -O-C*H*$_2$-, integration = 7.06), 6.67-7.69 (b, 2H/HPV, -CH= and 2H/HPV, Ar-*H* integration = 8.08), 10.45 (s, H/HPV, -C*H*=O, integration = 0.31). The degree of polymerization (DP = 5) was calculated by comparing the integration of the ^{1}H NMR signals at 2.24 ppm (methyl end group of PHPV) to that at 0.91 ppm (methyl group on the hexyl side chain of PHPV).

GPC: M_n = 2300, M_w/M_n = 1.02. MS-MALDI: m/z = 1529.9 [M^+] (calcd 1530.3, DP = 5).

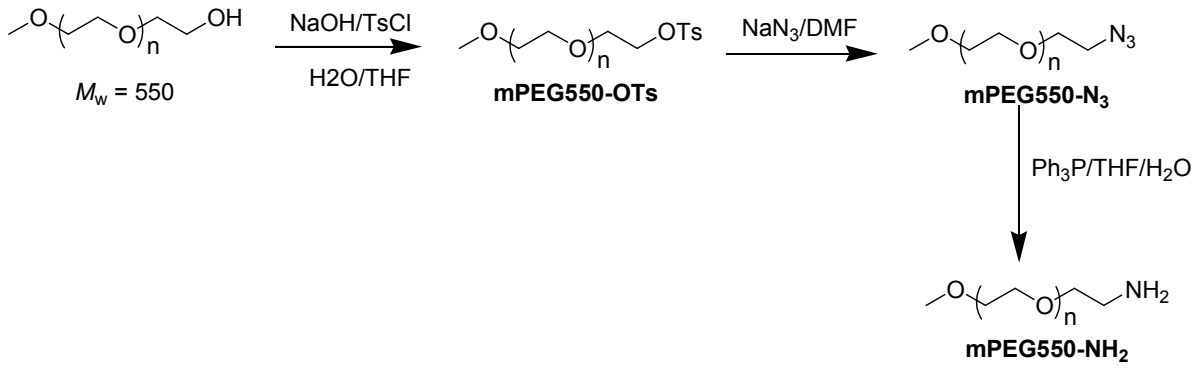
Synthesis of mPEG550-OTs.[1]

To a THF solution (40 mL) of mPEG550-OH (11.0g, 20.0 mmol), an aqueous solution (5 mL) of NaOH (1.25 g, 31.3 mmol) was added and the mixture was cooled to 0 °C. Then a solution of *p*-TsCl (4.77 g, 25.0 mmol) in anhydrous THF (7.5 mL) was added dropwise to the cold mixture. After the addition was finished, the resulting mixture was stirred at 4 – 8 °C in a cold water bath for 3 h. The organic phase was separated and dried over $MgSO_4$, then the solution was filtered and the filtrate was concentrated in *vacuo* to obtain a colourless oil. Yield: 11.9 g (85%).

^{1}H NMR (δ, ppm, $CDCl_3$): 2.43 (s, 3H, Ar-C*H*$_3$); 3.35 (s, 3H, OC*H*$_3$); 3.53-3.69 (m, 26H, glycol protons); 4.16 (s, 2H, SO_2-OC*H*$_2$); 7.35 (d, 2H, Ar-*H*, o-CH3); 7.81 (d, 2H, Ar-*H*, m-CH3).

Synthesis of mPEG550-N$_3$.[1]

mPEG550-OTs (5.72 g, 8.00 mmol) was dissolved in 30 mL of anhydrous DMF, then NaN_3 (2.60 g, 40.0 mmol) was added to the solution (see Scheme S1) . The solution was stirred at 50 °C for 5 h. After the reaction was complete, 10 mL of H_2O was added to the solution and the solution was extracted with 40 mL of CH_2Cl_2. The CH_2Cl_2 extract was separated and washed with 20 mL of brine, dried over $MgSO_4$ and concentrated in *vacuo* to obtain a colourless oil. Yield: 4.21 g (90%). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.31 (s, 3H, OC*H*$_3$); 3.32-3.7 (m, 28H, glycol protons).



Scheme S1. Synthesis of mPEG550-NH_2.

Synthesis of mPEG550-NH_2.[1]

mPEG550-N_3 (3.51 g, 6.00 mmol) was dissolved in 50 mL of THF, then PPh_3 (2.36 g, 9.00 mmol) was added to the solution. The mixture was stirred at rt for 4 h, then 0.5 mL of H_2O was added and the reaction was continued at rt for 20 h. Then the THF was evaporated in vacuo and 30 mL of H_2O was added to the residue. The insoluble by-product triphenylphosphine oxide was removed by vacuum filtration and the filtrate was washed with toluene (3 × 15 mL). The water was evaporated in *vacuo* to obtain a pale-yellow oil. Yield: 3.29 g (98%).

^{1}H NMR (δ, ppm, $CDCl_3$) (Figure S2): 2.84 (s, 2H, N-C*H*$_2$); 3.37 (s, 3H, OC*H*$_3$); 3.53-3.69 (m, 26H, glycol protons).

Synthesis and characterization of Oligo(2,5-dihexyloxy-1,4-phenylene vinylene)-block-poly(ethylene glycol) (OHPV-b- PEG).

In a typical procedure, 25 mg of OHPV (0.016 mmol aldehyde groups) and 240 mg of PEG-NH_2 (M_n = 5.0 K, 0.048 mmol amino group) and 50 mL toluene were added into 100 mL round bottom flask equipped with a Dean-Stark trap. After the solution was refluxed for 2 days, toluene was removed and 20 mL anhydrous dichloromethane (DCM), 36 mg of sodium triacetoxyborohydride (0.161 mmol) and 9 μL of glacial acetic acid (AcOH) (0.157 mmol) were added. After the mixture was stirred at room temperature for 3 days, it was washed with saturated sodium carbonate aqueous solution three times and water three times to remove most of free PEG-NH_2. Unreacted OHPV was removed by precipitation twice in hexanes and free PEG-NH_2 was removed by ultrafiltration four times using a membrane with a molecular weight cutoff of 50 K in water. Finally, the aqueous solution of the product was freeze-dried to give a red yellow powder (49 mg, 46 %). Details of sample characterization are provided below.

$OHPV_5$-*b*-PEG_{115}, ^{1}H NMR δ (ppm): δ (ppm, integrated peak areas reported are based on methyl protons of the hexyl group in OHPV as a reference): 0.91 (m, 30H/OHPV, -C*H*$_3$, integration = 30.00), 1.37 (b, 40H/OHPV, -C*H*$_2$C*H*$_2$CH$_3$, integration = 44.19), 1.54 (m, 20H/OHPV, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.85 (b, 20H/OHPV, -OCH$_2$C*H*$_2$-, integration = 19.60), 2.24 (s, 3H/OHPV, Ar-C*H*$_3$, integration = 2.23), 3.33-4.02 (b, 4(n+1)H, -OC*H*$_2$C*H*$_2$-, integration = 440.9), 4.04 (t, 20H/OHPV, -OC*H*$_2$CH$_2$CH$_2$-, integration = 18.37), 6.67-7.69 (b, 8H/OHPV, -CH= and 10H/OHPV, Ar-*H*). GPC: M_n = 7700 K, M_w/M_n = 1.05.

$OHPV_5$-*b*-PEG_{45}, ^{1}H NMR δ (ppm): δ (ppm, integrated peak areas reported are based on methyl protons of the hexyl group in OHPV as a reference): 0.91 (m, 30H/OHPV, -C*H*$_3$, integration = 30.00), 1.37 (b, 40H/OHPV, -C*H*$_2$C*H*$_2$CH$_3$, integration = 40.72), 1.55 (m, 20H/OHPV, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.85 (b, 20H/OHPV, -OCH$_2$C*H*$_2$-, integration = 20.93), 2.24 (s, 3H/OHPV, Ar-C*H*$_3$, integration = 2.51), 3.33-4.02 (b, 4(n+1)H, -OC*H*$_2$C*H*$_2$-, integration = 173.1), 4.04 (t, 20H/OHPV, -OC*H*$_2$CH$_2$CH$_2$-, integration = 19.29), 6.67-7.69 (b, 8H/OHPV, -CH= and 10H/OHPV, Ar-*H*). GPC: M_n = 3700 K, M_w/M_n = 1.06.

$OHPV_5$-*b*-PEG_{12}, ^{1}H NMR δ (ppm): δ (ppm, integrated peak areas reported are based on methyl protons of the hexyl group in PHPV as a reference): 0.91 (m, 30H/OHPV, -C*H*$_3$, integration = 30.00), 1.38 (b, 40H/OHPV, -C*H*$_2$C*H*$_2$CH$_3$, integration = 42.38), 1.55 (m, 20H/OHPV, -C*H*$_2$CH$_2$ CH$_2$CH$_3$), 1.85 (b, 20H/OHPV, -OCH$_2$C*H*$_2$-, integration = 21.57), 2.24 (s, 3H/OHPV, Ar-C*H*$_3$, integration = 2.90), 3.33-4.02 (b, 4(n+1)H, -OC*H*$_2$C*H*$_2$-, integration = 35.67), 4.04 (t, 20H/OHPV, -OC*H*$_2$CH$_2$CH$_2$-, integration = 21.14), 6.67-7.69 (b, 8H/OHPV, -CH= and 10H/OHPV, Ar-*H*).GPC: M_n = 1900, M_w/M_n = 1.04. MALDI-TOF: m/z = 2008.8 $[M+Na]^+$ (calc 2008.4, DP = 10 for PEG)

ADDITIONAL RESULTS AND DISCUSSION

Synthesis of OHPV.

In this work, Seigrist polycondensation was employed to prepare the OHPV oligomer, since this reaction allows for the synthesis of phenylenevinylene-based oligomers with an aldehyde end group, a narrow molecular weight distribution and only trans-linked repeat units. We began with the base catalyzed condensation of 2,5'-dihexyloxy-4'-methyl-*N*-benzylideneaniline in DMF solution. In contrast to the previously reported syntheses in which the oligomerization was carried out in refluxing THF[8] or in DMF at 80 °C,[2] we carried out the reaction at 30 °C, which led to a shorter oligomer product. The OHPV oligomer was then purified by silica gel column chromatography. The ^{1}H NMR spectrum of the product obtained is presented in Figure S1A. Characteristic resonances of the protons on the hexyl side group appear at 0.91 ('e'), 1.37, 1.54, 1.85 ('d'), and 4.06 ppm ('c'); the signal from the protons on the methyl and aldehyde group of OHPV backbone appear at 2.24 ('a') and 10.45 ppm ('g'). The number of dihexyloxy-phenylenevinylene (HPV) repeat units can be determined by the ratio of the integral area of peak 'e' (the CH_3 groups of the side chains) to 'a' (the 4-methyl group of the terminal HPV unit). This ratio is 10. Further information is available from the MALDI-TOF spectrum, shown in Figure S1B. The predominant peak appears at m/z 1529.9, which is very close to the theoretical

molecular weight of OHPV with 5 HPV units ($M+H^+$: 1530.1). No peaks were detected that could be attributed to $OHPV_6$ (m/z 1832.4) or $OHPV_4$ (m/z 1227.9).

Synthesis of OHPV-b-PEG

Attachment of the PEG chains took advantage of the aldehyde group on the OHPV chain end. Methoxy-PEG-NH_2 samples of different lengths were coupled to $OHPV_5$ through Schiff base formation between the aldehyde group of $OHPV_5$ and the amine group on the PEG chain end, followed by the reduction of the imine with sodium triacetoxyborohydride. This approach is similar to that reported by Mori et al.[2] Following the reaction, the unreacted OHPV was removed by precipitation twice in hexane. Excess unreacted PEG was removed by suspending the product in water and then subjecting the sample to ultrafiltration using a membrane with a molecular weight cutoff of 50 K. Figure S3 shows results for the reaction involving the highest molecular weight PEG sample, presenting GPC traces of the filtrate solution for successive steps in removing of excess PEG (M_n = 5 kDa).

The ^1H NMR spectrum of $OHPV_5$-*b*-PEG_{45} is presented in Figure 2 and the spectra of $OHPV_5$-*b*-PEG_{12} and $OHPV_5$-*b*-PEG_{115} are in Figure S4.

We measured the MADLI-TOF spectrum of $OHPV_5$-*b*-PEG_{12}, as shown in Figure S5. The peaks are separated by 44 mass units, indicative of the PEG block in the copolymer. The maximum peak appears at 2008.9, consistent with the theoretical molecular weight of $OHPV_5$-*b*-PEG_{10} + Na^+, that is close to the value expected for $OHPV_5$-*b*-PEG_{12}.

SUPPLEMENTAL FIGURES

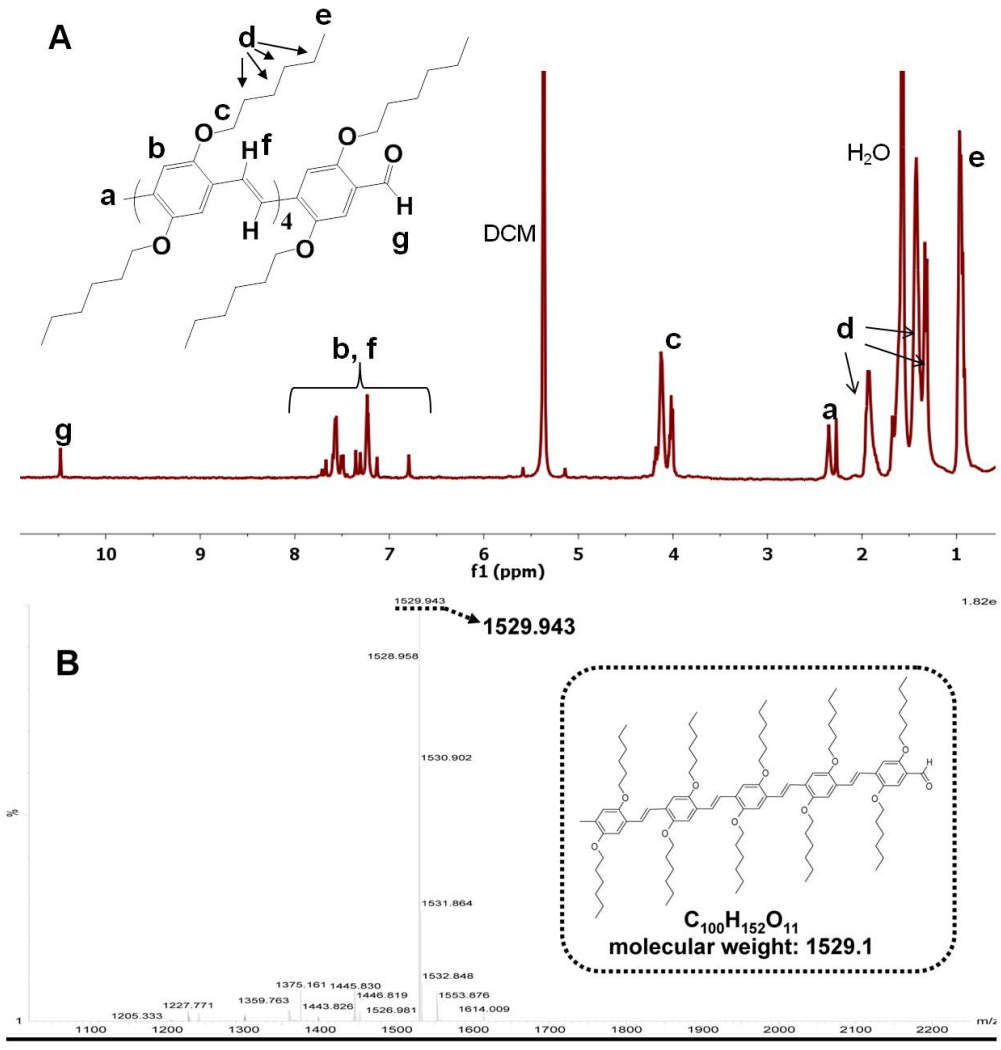


Figure S1. (A) ^{1}H NMR in CD_2Cl_2 and (B) MALDI-TOF mass spectra of $OHPV_5$, providing evidence supporting the assigned structure of the pentamer bearing a terminal aldehyde group.

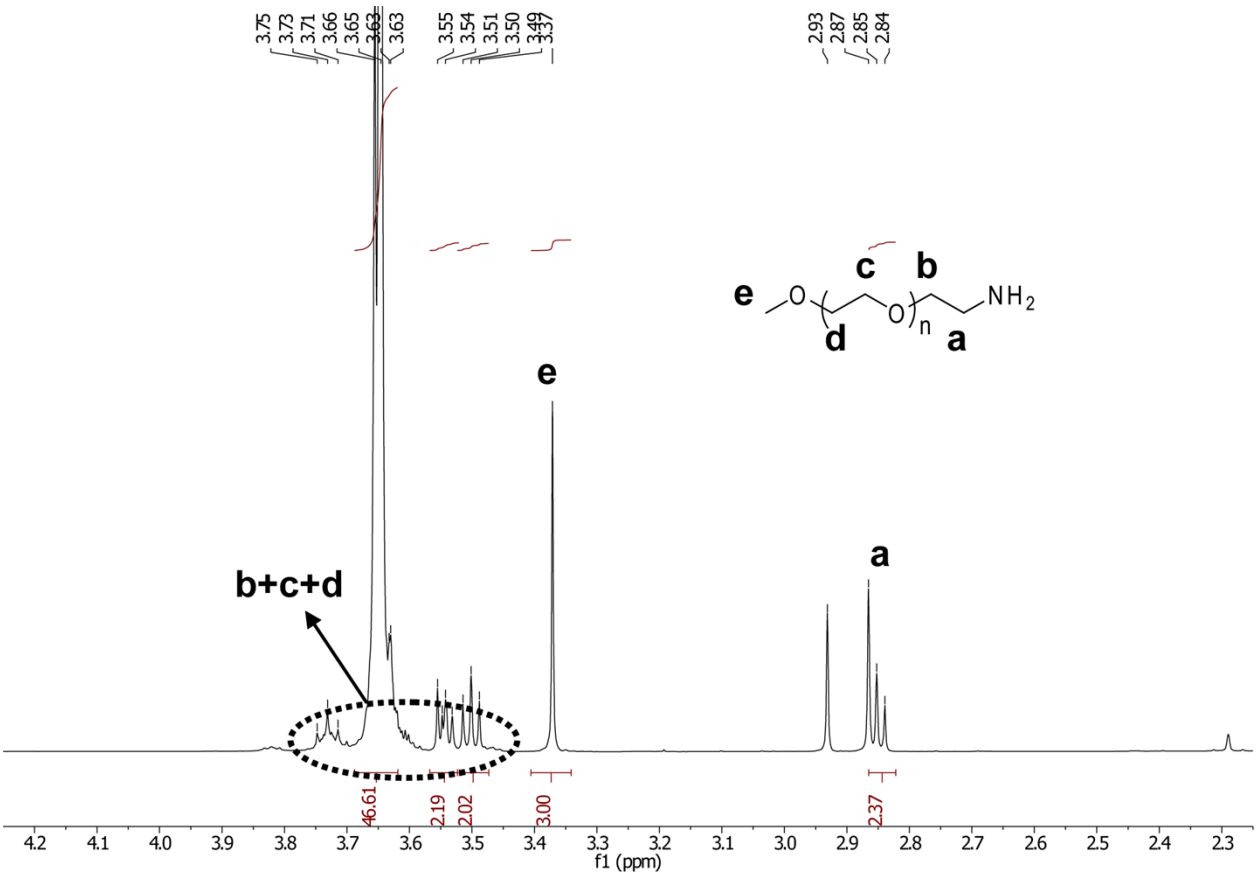


Figure S2. ^{1}H NMR of MeO-PEG550-NH_2.

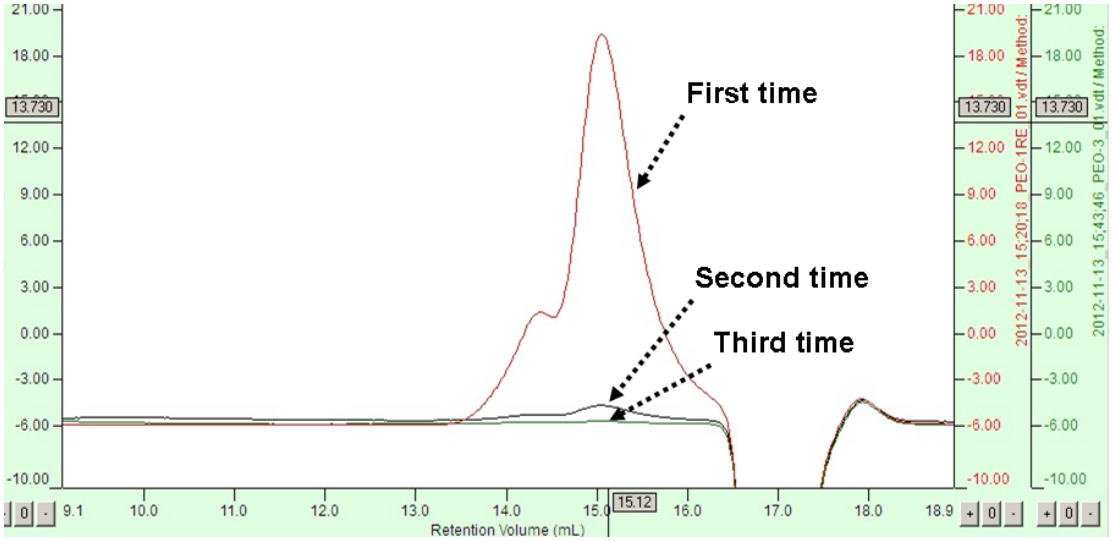


Figure S3. ^{1}H NMR of MeO-PEG550-NH_2. of filtrate solution at each ultrafiltration for removing excess PEG-NH_2 (M = 5 kDa) from the reaction with OHPV-CH=O. Eluent 0.2 M $NaNO_3$, 200 ppm NaN_3 and 25 mM, pH 8.5 phosphate buffer at a flow rate of 1.0 mL/min, R.I. detector, 25 °C.

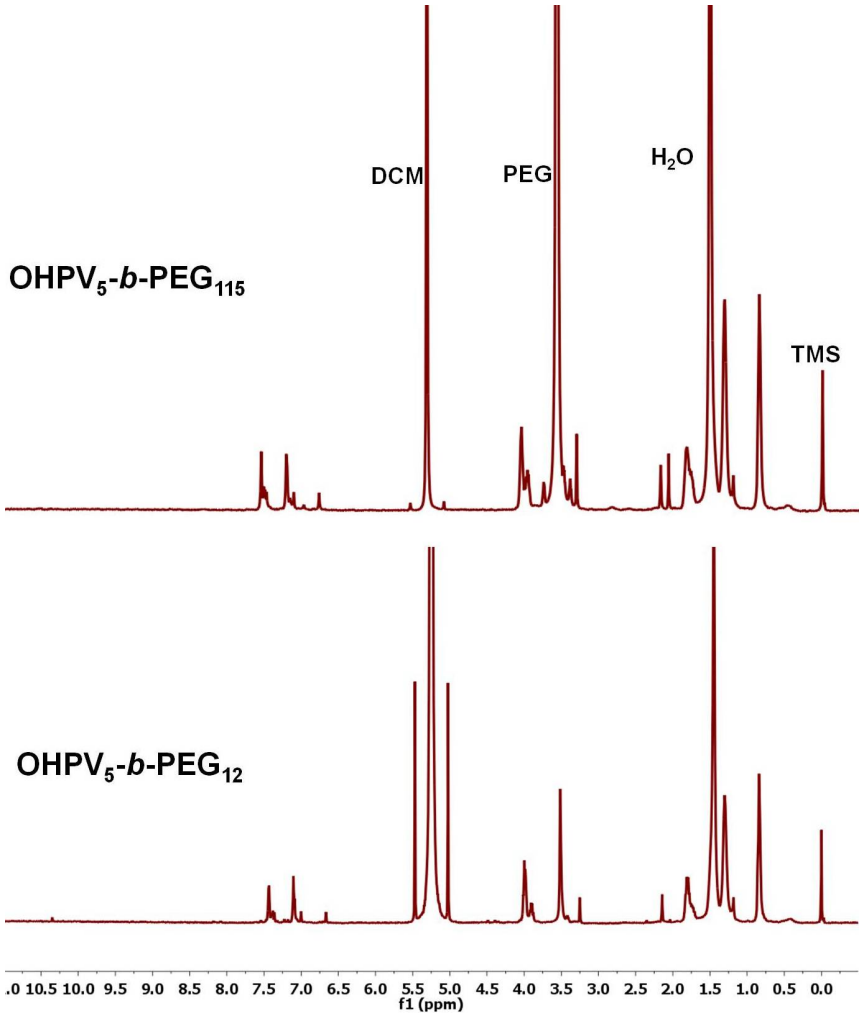


Figure S4. ^{1}H NMR spectrum in CD_2Cl_2 (DCM) of $OHPV_5$-*b*-PEG_{12} and $OHPV_5$-*b*-PEG_{115}.

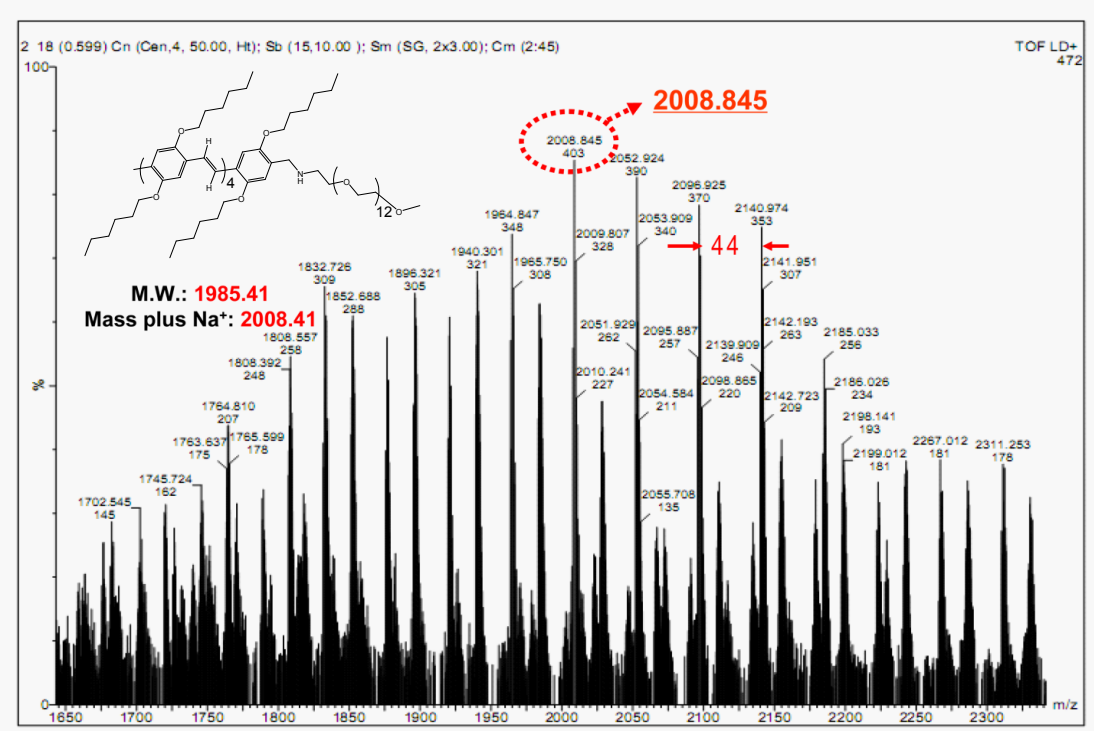


Figure S5. MADLI-TOF spectrum of $OHPV_5$-*b*-PEG_{12}.

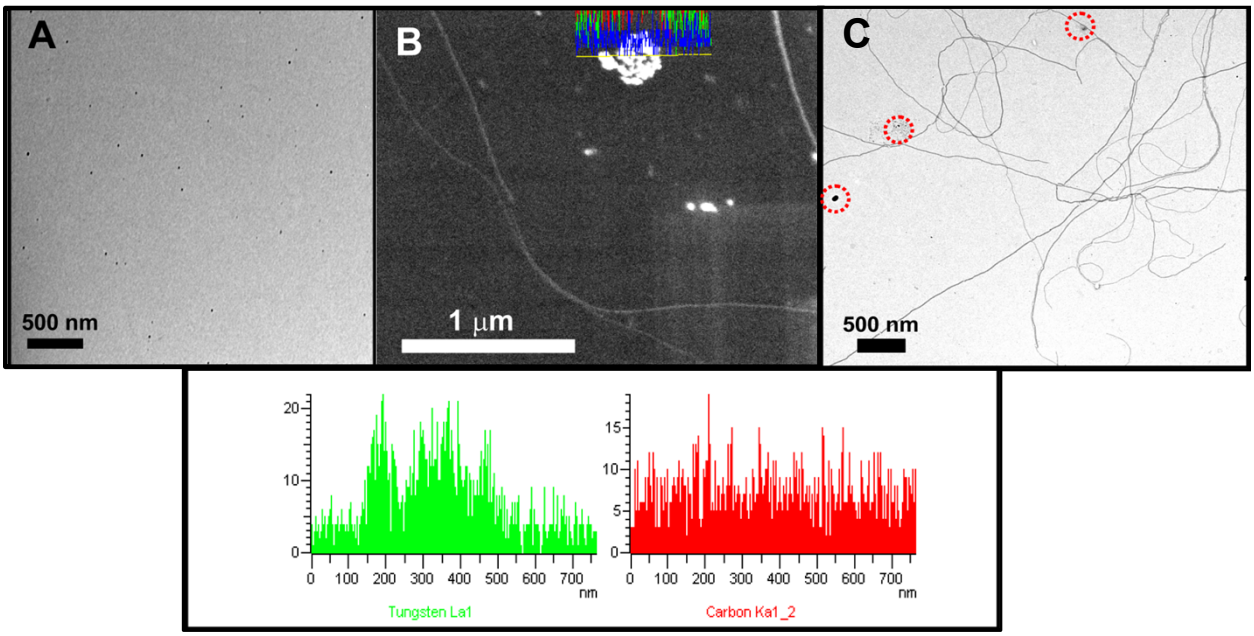


Figure S6. (A) Control experiment: TEM image of a grid prepared using pure ethanol instead of a micelle solution; (B) dark-field TEM image of phosphotungstic acid-stained micelles of $OHPV_5$-*b*-PEG_{115} and its EDX profile shown below. (Green, tungsten; red, carbon) (C) A bright-field TEM image of phosphotungstic acid-stained micelles of $OHPV_5$-*b*-PEG_{115} showing similar black spots to those identified in (B).

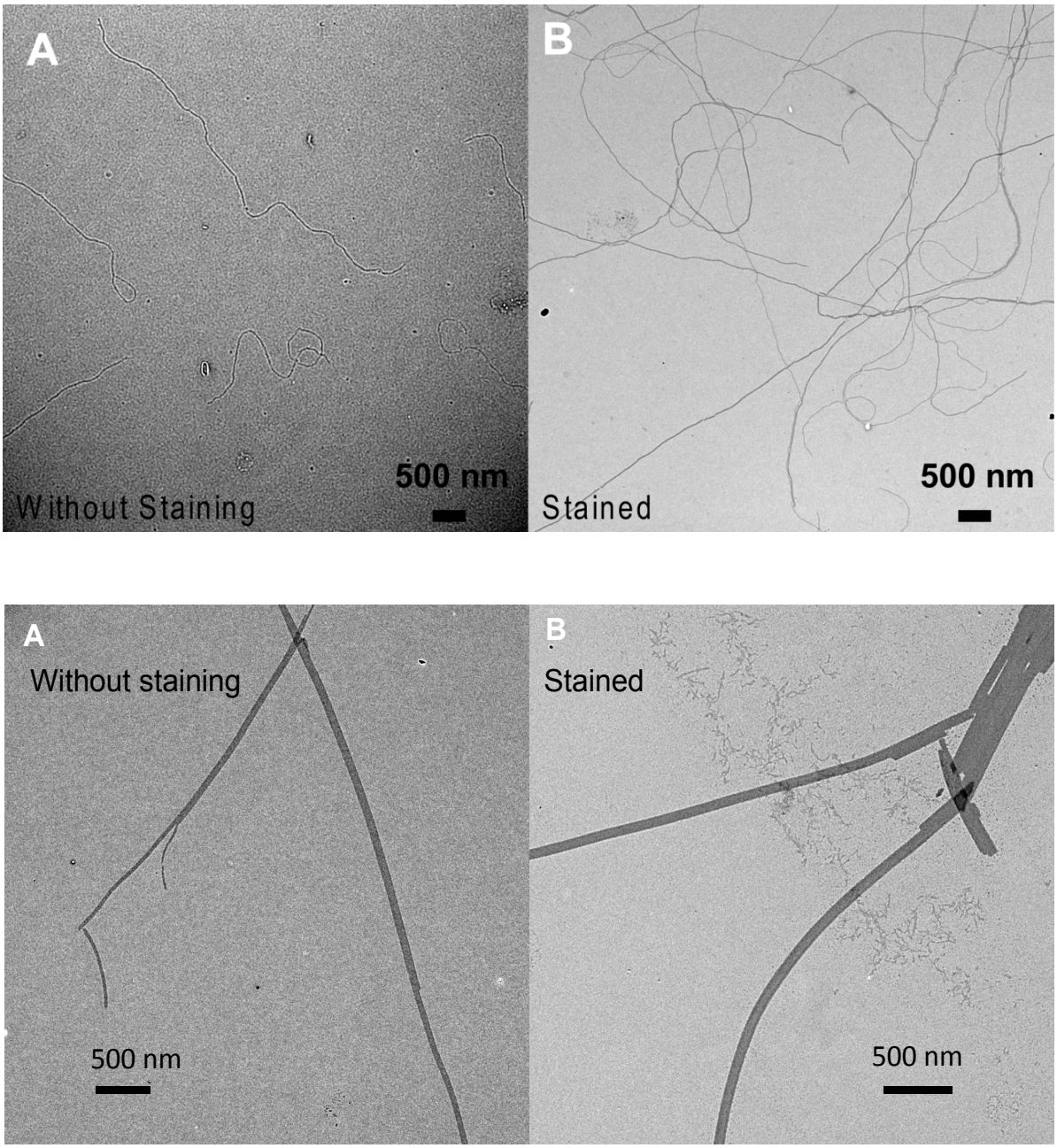


Figure S7. TEM images of micelles formed by $OHPV_5$-*b*-PEG_{115} (upper pair of images) and $OHPV_5$-*b*-PEG_{45} (lower pair of images) (A) without staining and (B) stained with phosphotungstic acid (1.0 mg/mL in water).

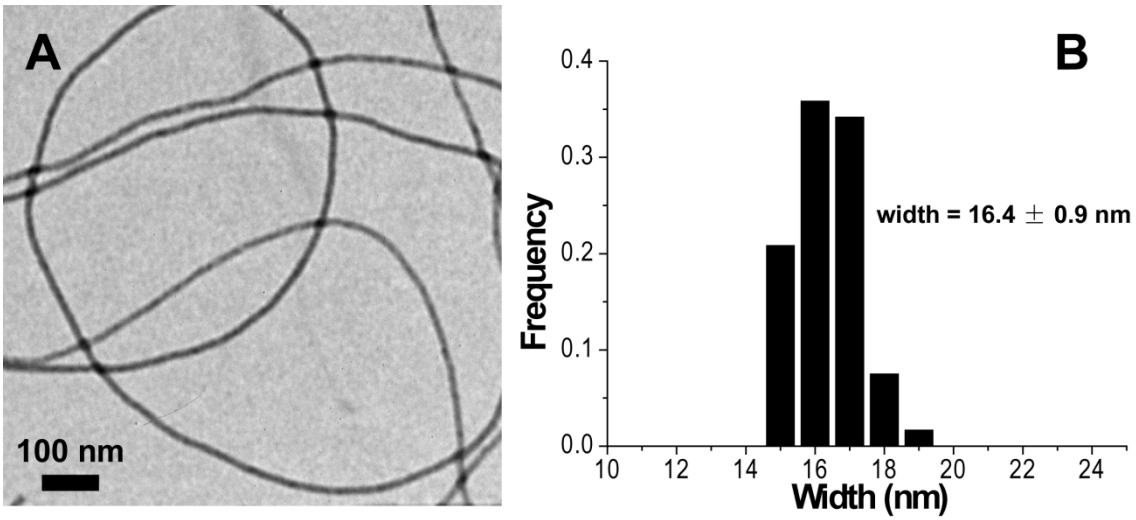


Figure S8. (A) TEM image and (B) a histogram of the width distribution of micelles of $OHPV_5$-*b*-PEG_{115}.

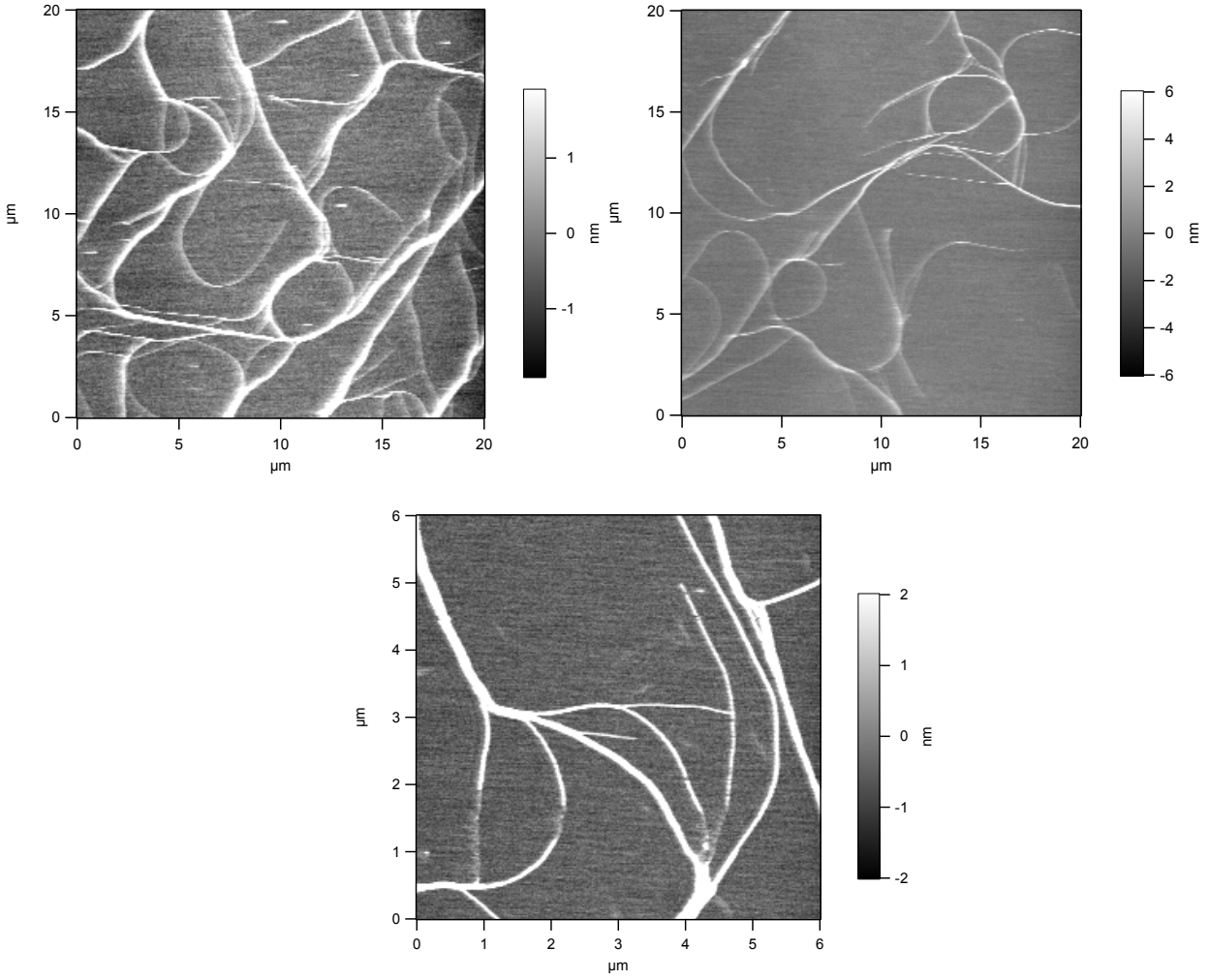


Figure S9. AFM phase images of bundles of fiber-like micelles formed by $OHPV_5$-*b*-PEG_{115} in ethanol c = 0.1 mg/mL.

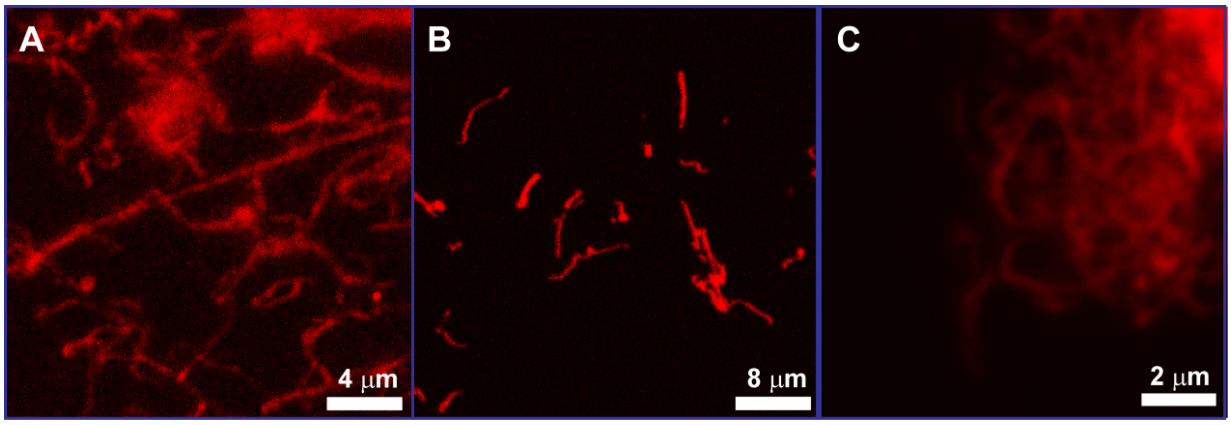


Figure S10. Laser confocal fluorescence microscopy images of micelles formed by (A) OHPV$_5$-*b*-PEG$_{115}$, (B) OHPV$_5$-*b*-PEG$_{45}$ and (C) OHPV$_5$-*b*-PEG$_{12}$ in ethanol at concentrations of 0.01 mg/mL.

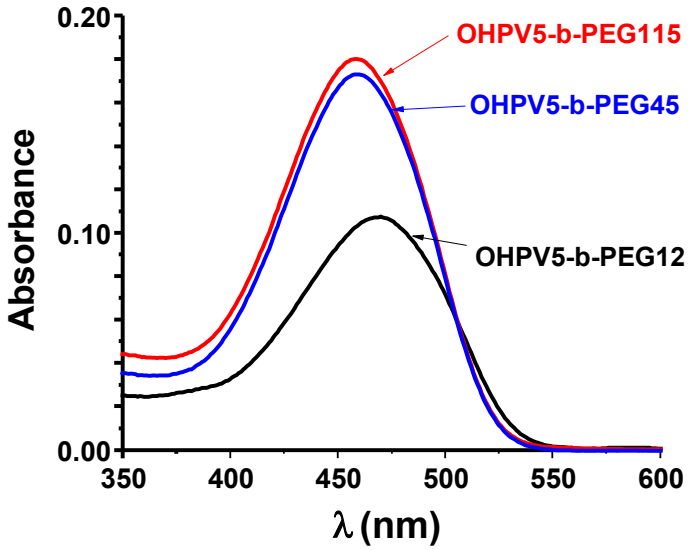


Figure S11. Absorbance spectra for the different OHPV$_5$-*b*-PEG samples in DCM. The spectra are recorded at 25 ^{o}C and the concentration for each polymer was 2.1 μM.

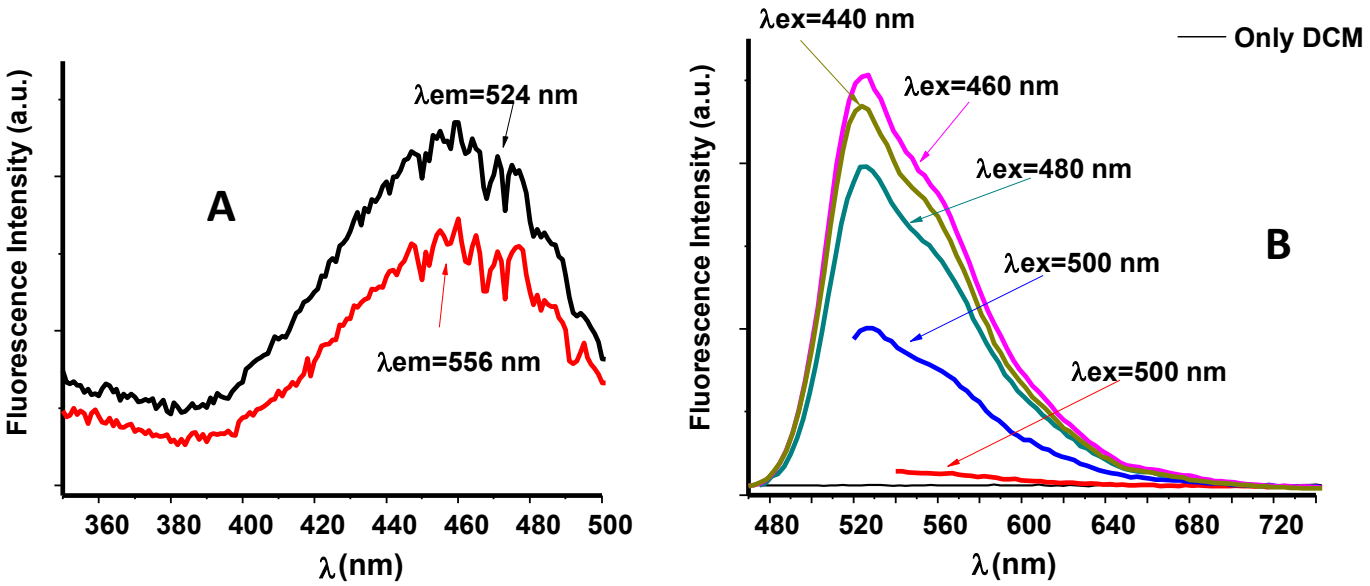


Figure S12. (A) Excitation spectra of $OHPV_5$-*b*-PEG_{45} in DCM at different emission wavelengths. (B) Emission spectra $OHPV_5$-*b*-PEG_{45} in DCM at different excitation wavelengths. The spectra are recorded at 25C and the concentration was 2.1 μM.

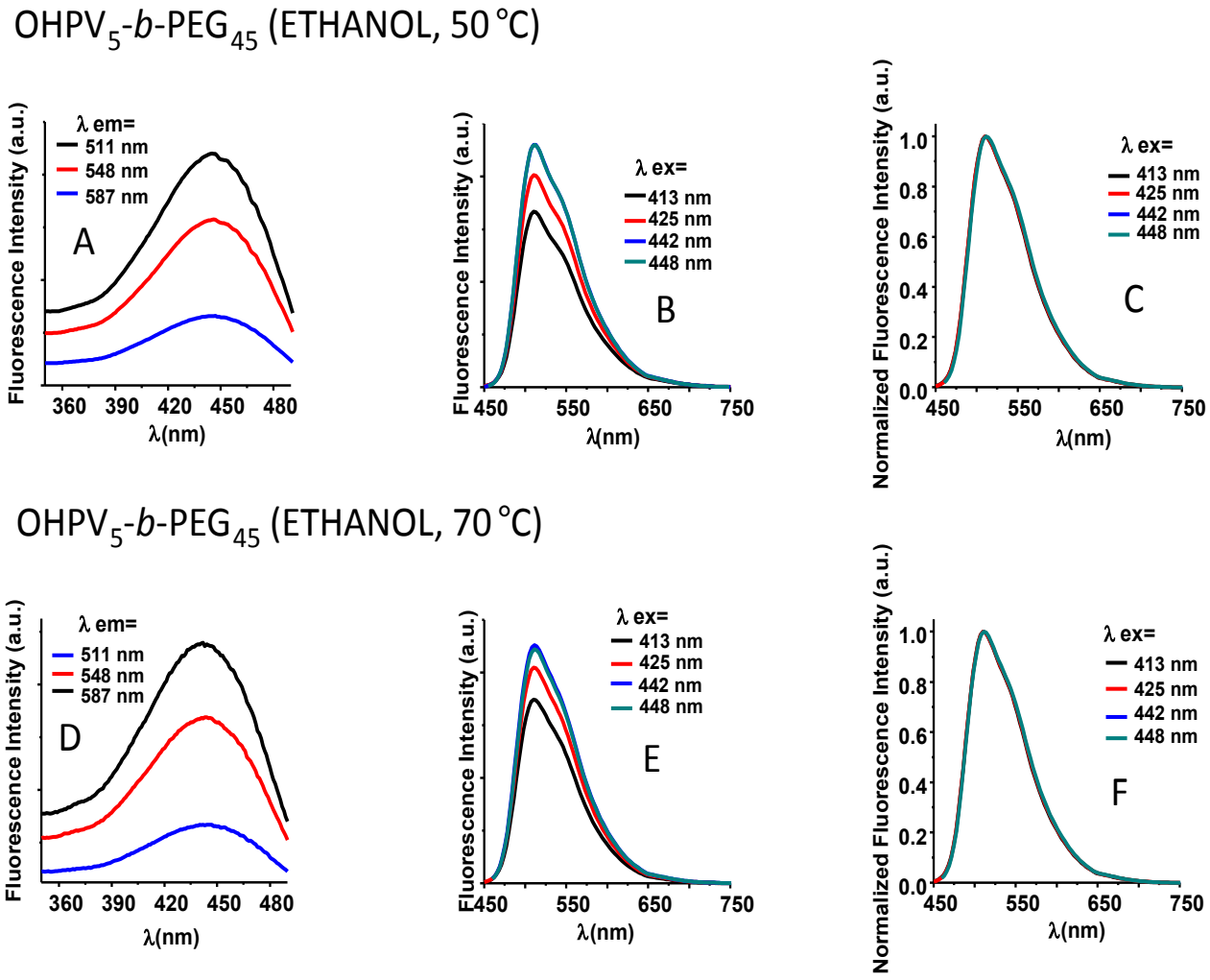


Figure S13. (A, D) Excitation spectra at different emission wavelengths (B, E) Emission spectra and (C, F) Normalized emission at different excitation wavelengths of $OHPV_5$-*b*-PEG_{45} in ethanol at 50°C (top) and 70°C (bottom). The sample concentration for each experiment was 2.1 μM.

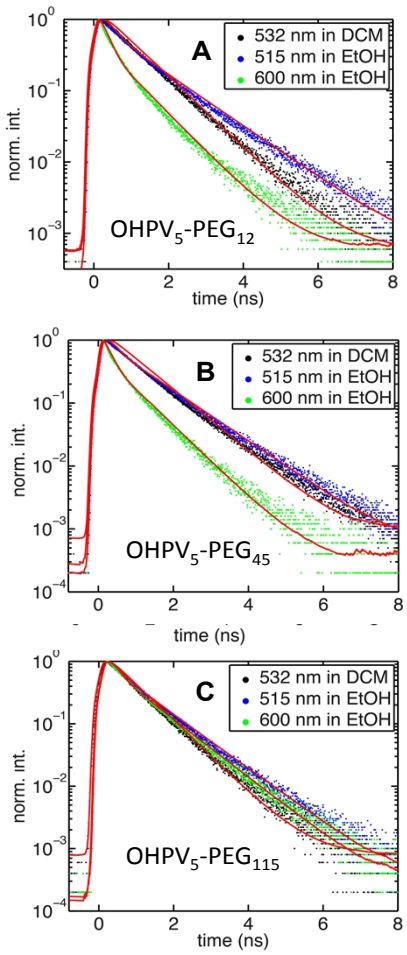


Figure S14. Fluorescence decays for the different block copolymers $OHPV_5$-*b*-PEG_{12} (A), $OHPV_5$-*b*-PEG_{45} (B) and $OHPV_5$-*b*-PEG_{115} (C) in DCM and ethanol. The excitation wavelength was 418 nm and the different emission wavelengths are indicated in each graph. The measurements were carried out at room temperature, and the concentrations were 2.1 μM.

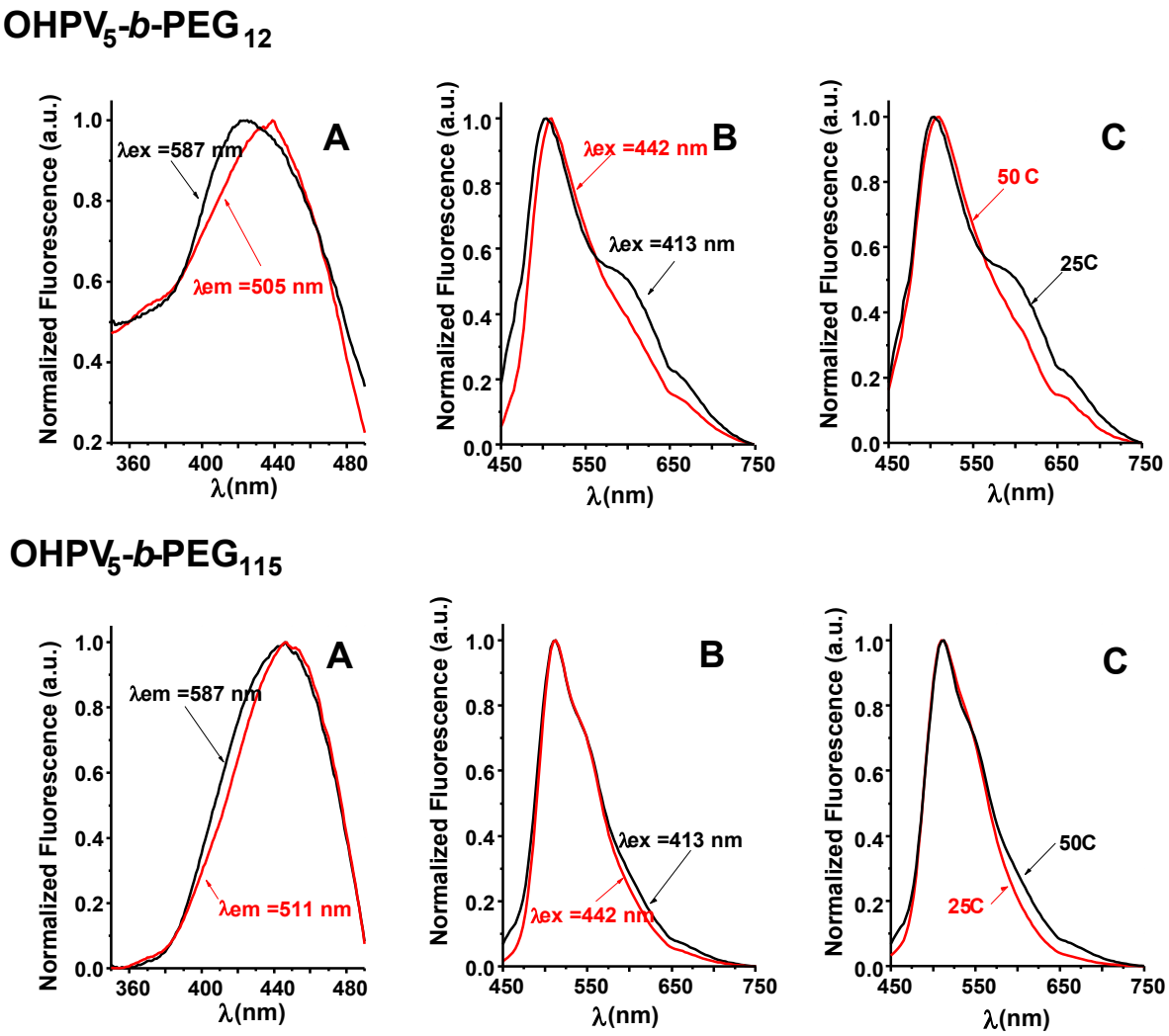


Figure S15. (A) Normalized excitation spectra at different emission wavelengths (B) Normalized emission spectra at different excitation wavelengths C) Normalized emission spectra (λ_{ex}= 413 nm) at different temperatures for OHPV$_5$-*b*-PEG$_{12}$ (up) and OHPV$_5$-*b*-PEG$_{115}$ (bottom) in ethanol. The spectra are recorded at 25C and the concentrations used in the experiments were 2.1 μM.

SUPPLEMENTAL TABLE

Table S1. Fluorescence lifetime values and contributions for $OHPV_5$-*b*-PEG_{12}, $OHPV_5$-*b*-PEG_{45} and $OHPV_5$-*b*-PEG_{115} in DCM and ethanol solutions (23 °C, λ_{ex} = 418 nm).

$OHPV_5$-PEG_{12}

Solvent	λ/nm	A_1 [a]	τ_1/ns	A_2 [a]	τ_2/ns	τ [b] /ns	$<\tau>$ [b] /ns
DCM	532	--	0.86	--	--	--	0.86
EtOH	515	0.55	0.26	0.45	1.21	0.69	1.00
	600	0.82	0.13	0.18	0.81	0.25	0.53

$OHPV_5$-PEG_{45}

Solvent	λ/nm	A_1 [a]	τ_1/ns	A_2 [a]	τ_2/ns	τ [b] /ns	$<\tau>$ [b] /ns
DCM	532	--	0.87	--	--	0.87	0.87
EtOH	515	0.55	0.26	0.45	1.21	0.69	1.00
	600	0.83	0.10	0.17	0.76	0.21	0.50

$OHPV_5$-PEG_{115}

Solvent	λ/nm	A_1 [a]	τ_1/ns	A_2 [a]	τ_2/ns	τ [b] /ns	$<\tau>$ [b] /ns
DCM	532	--	0.74	--	--	0.74	0.74
EtOH	515	0.50	0.25	0.50	1.00	0.63	0.85
	600	0.58	0.19	0.42	0.93	0.50	0.77

a. A_1 and A_2 are the normalized pre-exponential terms

b. The intensity-weighted mean decay time $\overline{\tau} = (\Sigma A_i \tau_i / \Sigma A_i)$; the lifetime-weighted mean decay time $<\tau> = (\Sigma A_i \tau_i^2 / \Sigma A_i \tau_i)$

REFERENCES

(1) Liu, W.; Greytak, A. B.; Lee, J.; Wong, C. R.; Park, J.; Marshall, L. F.; Jiang, W.; Curtin, P. N.; Ting, A. Y.; Nocera, D. G.; Fukumura, D.; Jain, R. K.; Bawendi, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 472–483.

(2) Mori, T.; Watanabe, T.; Minagawa, K.; Tanaka, M. *J. Polym. Sci. Part Polym. Chem.* **2005**, *43*, 1569–1578.

(3) Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Muellen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634–2647.

(4) Barashkov, N. N.; Guerrero, D. J.; Olivos, H. J.; Ferraris, J. P. *Indo-Fr. Work. Electron. Conduct. Polym.* **1995**, *75*, 153–160.

(5) Klingelhöfer, S.; Schellenberg, C.; Pommerehne, J.; Bässler, H.; Greiner, A.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1511–1530.

(6) Gill, R. E.; van Hutten, P. F.; Meetsma, A.; Hadziioannou, G. *Chem. Mater.* **1996**, *8*, 1341–1346.

(7) Olsen, B. D.; Alcazar, D.; Krikorian, V.; Toney, M. F.; Thomas, E. L.; Segalman, R. A. *Macromolecules* **2008**, *41*, 58–66.

(8) Wang, H.; Wang, H. H.; Urban, V. S.; Littrell, K. C.; Thiyagarajan, P.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6855–6861.