Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and Self-Assembly of Diphenylalanine-Tetraphenylethylene Hybrid Monomer and RAFT Polymers with Aggregation-Induced Emission

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Experimental Section

Materials. 2,2'-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97 %) was purified by recrystallization from methanol. *N,N*-Dimethylformamide (DMF, Kanto Chemical, 99.5%), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (Aldrich, 98%), *N,N'*-dicyclohexylcarbodiimide (TCI, 98%), and 4-dimethylaminopyridine (TCI, 99%) were used as received. *N*-Acryloyl-L,L-diphenylalanine (APhePheOH)[1] and 4-hydroxytetraphenylethylene (TPEOH)[2] were synthesized as reported previously.

Synthesis of diphenylalanine-TPE hybrid monomer (APhePheTPE). To a two-neck flask, APhePheOH (0.26 g, 0.72 mmol), TPEOH (0.25 g, 0.72 mmol), and 4-dimethylaminopyridine (8.8 mg, 0.072 mmol) were dissolved into THF (30 mL). Dicyclohexylcarbodiimide (0.16 g, 0.79 mmol) was added drop wise with stirring at 0°C. The mixture was then stirred at room temperature for overnight. After completion of reaction, the reaction mixture was filtered and evaporated. The obtained crude product was purified by column chromatography (ethyl acetate:dichloromethane = 1:10). The product was finally dried under vacuum at room temperature to afford targeted APhePheTPE as a white solid (0.24 g, yield: 49%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8,75 (t, 1H: -N*H*), 8.28 (dd, 2H: -N*H*), 7.24-7.07 (m, 19H: -phenyl), 6.94 (m, 8H: -phenyl), 6.76-6.64 (dd, 2H: -phenyl), 6.22-6.14 (q, 1H: -C*H*=CH_2), 5.97-5.91 (d, 1H: -CH=C*H*), 5.55-5.49 (d, 1H: -CH=C*H*), 4.66-4.53 (m, 2H: -NHC*H*CH_2-phenyl), 3.10-2.52 (m, 4H: -CH_2-phenyl) ppm. ^{13}C NMR (100 MHz, DMSO-d_6,): δ 173.3 (>*C*=O), 171.9 (>*C*=O), 149.1, 143.6, 143.1, 141.4, 141.3, 140.2, 138.2, 137.4, 137.3, 132.2, 131.9, 131.2, 129.9, 129.8, 129.6, 128.9, 128.8, 128.5, 128.4, 128.3, 127.2, 126.8, 126.1, 121.4, 121.3 (-*C*H=*C*H_2, -phenyl), 54.7, 54.2 (-NH*C*HCH_2-phenyl), 38.4, 37.0 (-*C*H_2-phenyl) ppm. Anal. Calcd for $C_{47}H_{40}N_2O_4$: C, 80.99; H, 5.74; N, 4.02. Found: C, 80.39; H, 5.90; N, 4.04. m.p. = 158.8 °C. The ^{1}H NMR and ^{13}C NMR spectra of the APhePheTPE are shown in Figures S1-S2.

General Polymerization Procedure.

APhePheTPE (0.15 g, 0.215 mmol), CTA (3.1 mg, 0.0086 mmol), AIBN (0.71 mg, 0.0043 mmol), and DMF (0.6 mL) were placed in a dry glass ampule equipped with a magnetic stirring bar, and the solution was degassed by three freeze-evacuate-thaw cycles. After sealing the ampule by flame under vacuum, the mixture was stirred at 60 °C for 24 h. Conversion determined by the integration of the monomer C=C-*H* resonance at around 5.49-5.55 ppm compared with the sum of NH-C*H* peak intensity of the polymer and the monomer at around 4.29-4.91 ppm was 76%. The resulting polymer was purified by reprecipitation from a DMF solution into a large excess of a diethyl ether/hexane mixture (v/v = 2/1). Then the product was finally dried under vacuum at room temperature: yield 0.072 g, 48%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.80-8.00 (broad, 2H: -N*H*), 7.40-6.40 (broad, 29H: -phenyl), 4.91-4.29 (broad, 2H: -C*H*), 2.60-3.30 (broad, 4H: -CH_2-phenyl), 2.30-0.75 (broad, 3H: C*H* and CH_2 in the main chain) ppm.

Preparation of self-assembled structures

APhePheTPE was dissolved into THF as a good solvent to afford the stock solutions (0.3–100 mg/mL).

For the preparation of the sample in THF/water (10/90 vol%, conc. = 1.0 mg/mL), 0.1 mL of the stock solution (10 mg/mL) was diluted with 0.9 mL of a distilled water. A slightly turbid suspension was detected after the addition the stock solution into water, and the sample was quickly mixed and then allowed to self-assemble for 24 h. For SEM, an aliquot (conc. = 1.0 mg/mL) was dropped on carbon-coated Cu grids at room temperature and allowed to dry in the air. In the case of THF/water (50/50 vol%, conc. = 0.03 mg/mL), 1.0 mL of the stock solution (0.3 mg/mL) was introduced into THF/water (4mL/5mL) mixture, followed by mixing and then allowing to stand for 24 h. The same procedures were employed for the self-assembly of PAPhePheTPE.

Instrumentation

The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in DMSO-d_6 using a JEOL JNM-ECX400. Size exclusion chromatography (SEC) was conducted using a Tosoh HPLC HLC-8220 system equipped with four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limited molecular weight): α-M (13 μm, >1 × 10^7), α-4000 (10 μm, 4 × 10^5), α-3000 (7 μm, 9 × 10^4), α-2500 (7 μm, 5 × 10^3), 30 cm each] and a guard column [TSK-guardcolumn α, 4.0 cm] coupled with refractive index and ultraviolet detectors at 40 ^{o}C. The eluent was DMF containing 10 mM LiBr at the flow rate of 1.0 mL/min. The molecular weight mass and dispersity (M_n and $M_{\mathrm{w}}/M_{\mathrm{n}}$) were calculated using polystyrene standards. The circular dichroism (CD) was measured using a JASCO J-720 spectropolarimeter. The ultraviolet–visible (UV–vis) and fluorescence spectra were recorded on a JASCO V-630BIO UV–vis spectrophotometer and a JASCO FP-6100 spectrofluorophotometer, respectively. Fluorescence quantum yields of solutions were determined relative to 9,10-diphenylanthracene (sublimation grade) in cyclohexane.[3] Dynamic Light Scattering (DLS) was performed using a Zetasizer Nano (Sysmex) with a He-Ne laser. Tapping mode atomic force microscopy (AFM) observation was performed with an Agilent AFM 5500, using microfabricated cantilevers with a force constant of approximately 34 N/m. Scanning electron microscopy (SEM) measurements were performed on a Hitachi SU8000 microscope at accelerating voltages of 1.0 kV. FT-IR spectra were recorded on a JASCO FT/IR-210 spectrometer. The sample was prepared by pressing with KBr plates.

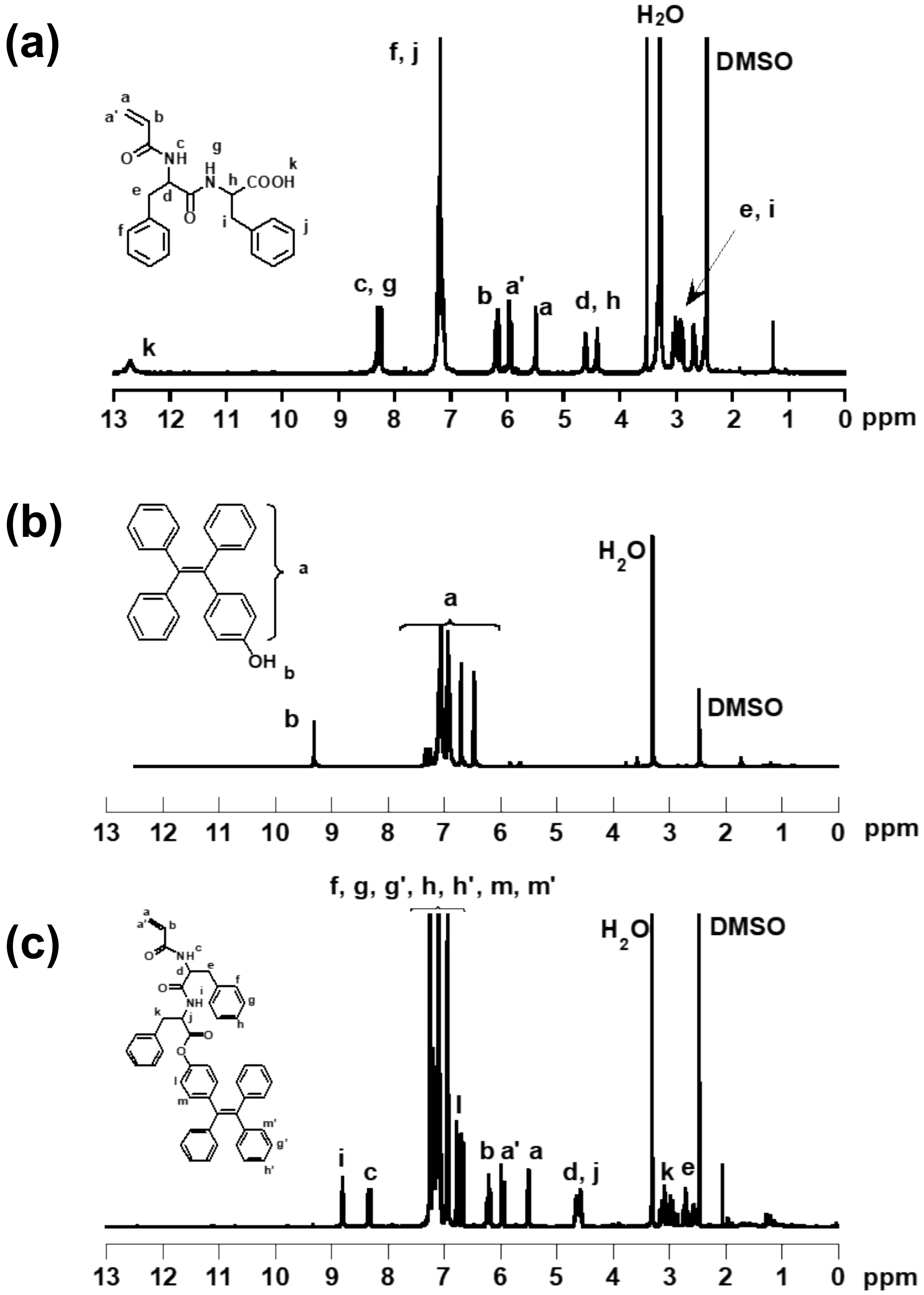


Figure S1. ^{1}H NMR spectra of (a) APhePheOH, (b) TPEOH, and (c) APhePheTPE in DMSO-d_6.

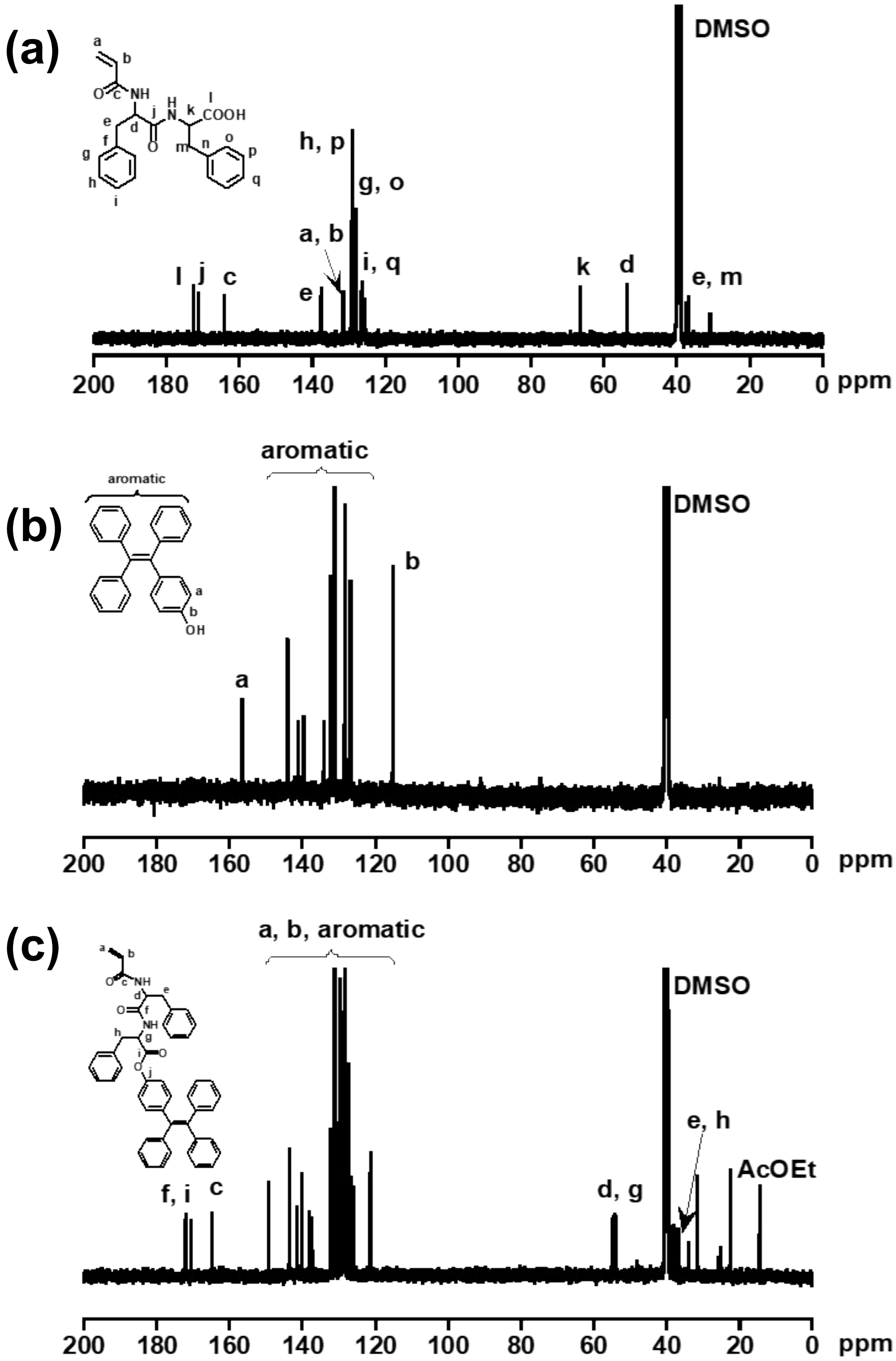


Figure S2. ^{13}C NMR spectra of (a) APhePheOH, (b) TPEOH, and (c) APhePheTPE in DMSO-d_6.

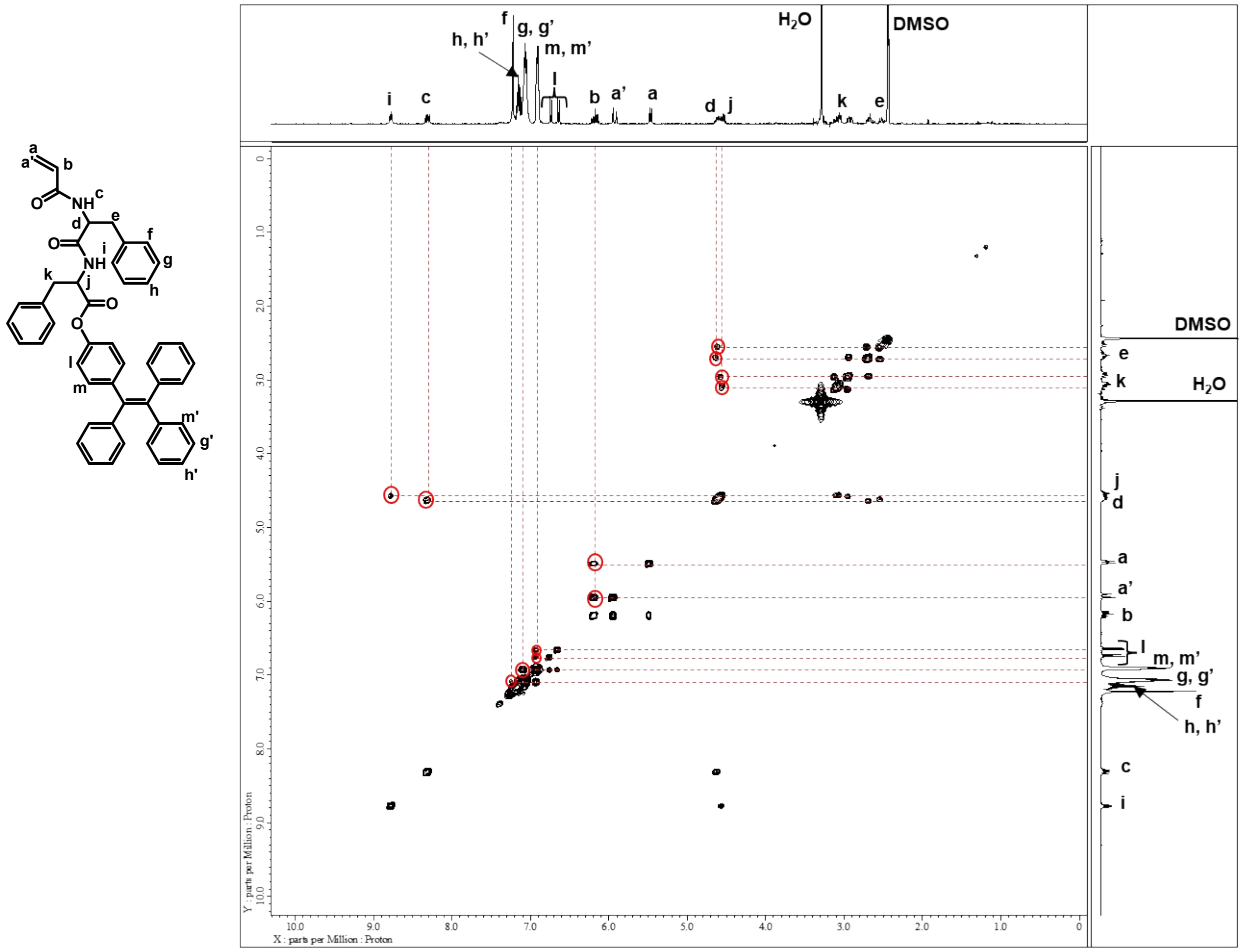


Figure S3. 2D H-H COSY NMR spectrum of APhePheTPE in DMSO-d_6 and assignment of hydrogen atoms.

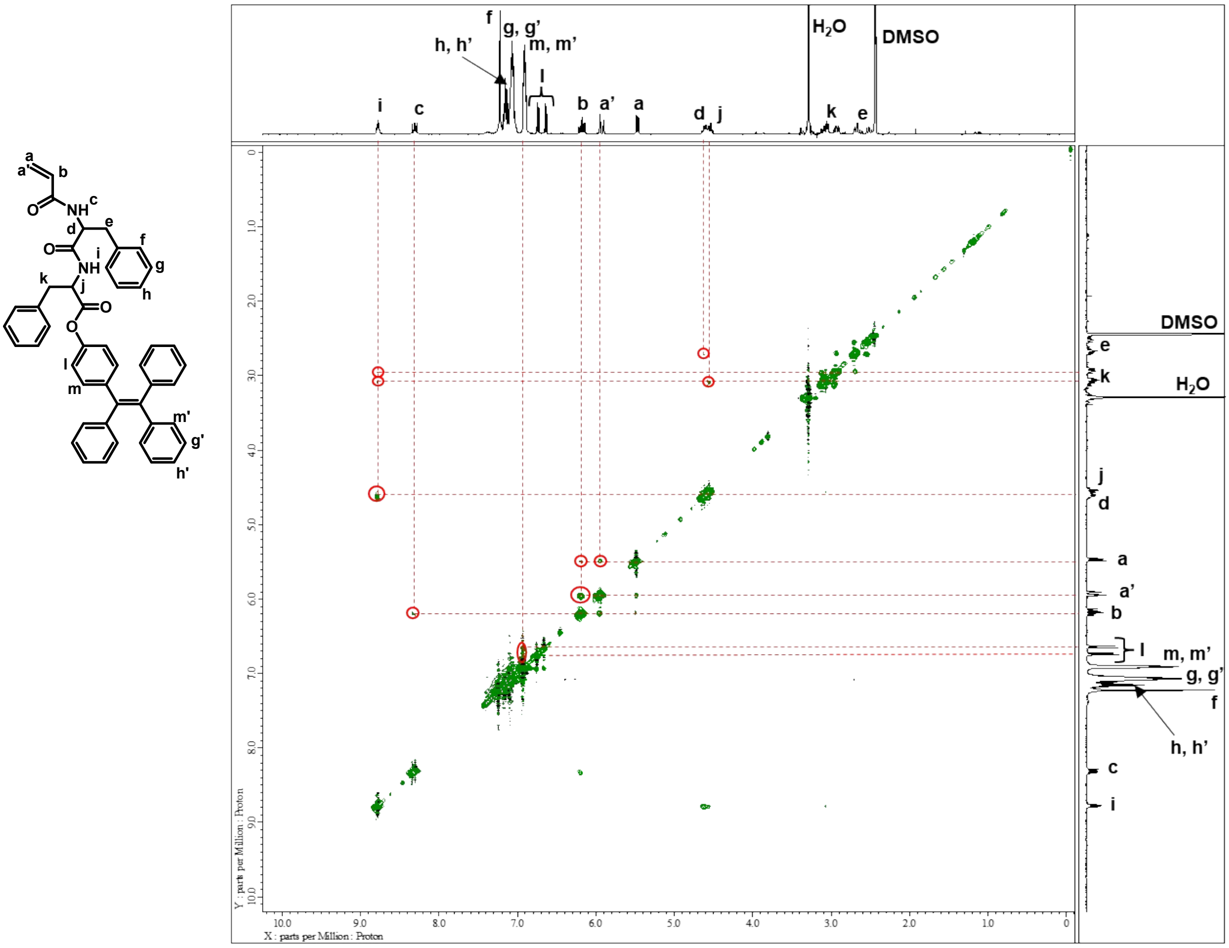
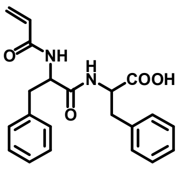


Figure S4. 2D H-H NOESY NMR spectrum of APhePheTPE in DMSO-d_6 and assignment of hydrogen atoms.

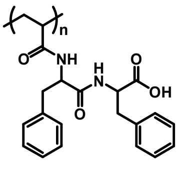
Table S1. Solubilities of diphenylalanine and TPE derivatives.

Solvent	**APhePheOH**	**PAPhePheOH**	**PATPE**	**APhePheTPE**	**PAPhePheTPE**
MeOH	+	+	-	±	-
EtOH	+	+	-	±	-
HFIP	+	+	-	-	-
DMSO	+	+	-	+	+
DMF	+	+	+	+	+
Acetone	+	+	+	+	+
THF	+	+	+	+	+
AcOEt	+	+	+	+	+
$CHCl_3$	-	-	+	+	+
DCM	-	-	+	+	+
Dioxane	-	-	+	-	-
H_2O (pH = 7)	-	-	-	-	-
H_2O (pH = 12)	+	+	-	-	-

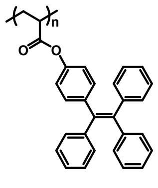
+ : soluble at room temperature (conc. = 1.0 mg/mL), - : insoluble, ± : soluble in only dilute solutions (conc. < 0.1 mg/mL).



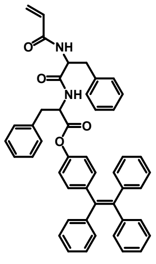
APhePheOH



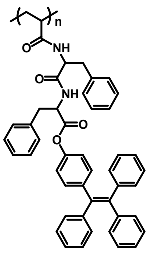
PAPhePheOH



PATPE



APhePheTPE



P(APhePheTPE)

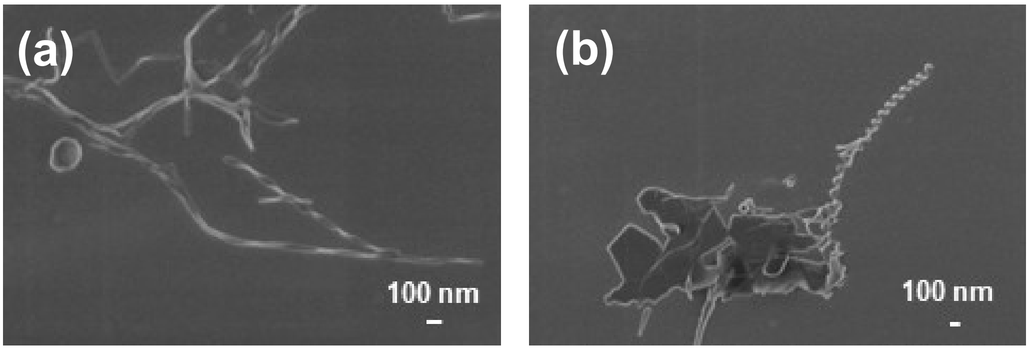


Figure S5. SEM images of (a) twisted nanofibers and (b) plate-like crystals of APhePheTPE in THF/water (10/90 vol%, conc. = 1.0 mg/mL) mixture.

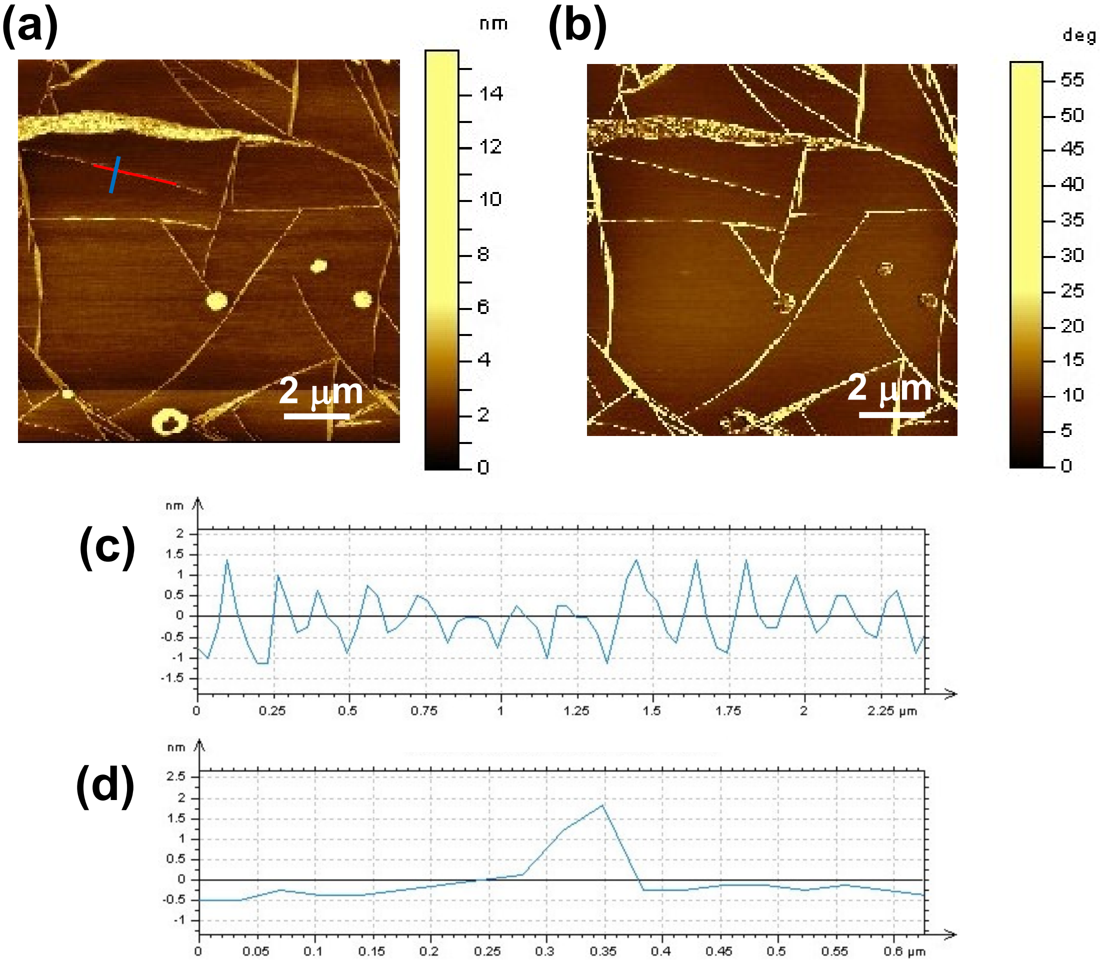


Figure S6. AFM images of APhePheTPE: (a) height image, (b) phase image, and (c,d) cross sections at the positions indicated by (c) the red line, and (d) blue line. The sample was prepared by drop-casting from THF/water (10/90 vol%) mixture (conc. = 1.0 mg/mL) onto freshly cleaved mica.

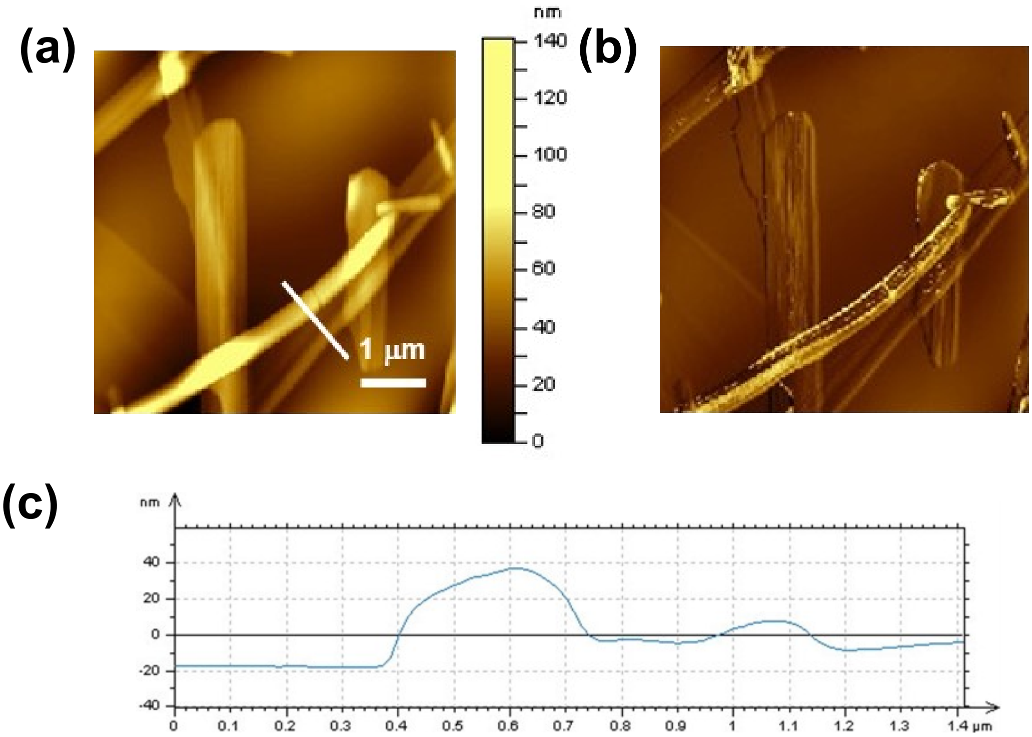


Figure S7. AFM images of APhePheTPE: (a) height image, (b) phase image, and (c) cross section at the position indicated by white line. The sample was prepared by drop-casting from THF/water (20/80 vol%) mixture (conc. = 1.0 mg/mL) onto freshly cleaved mica.

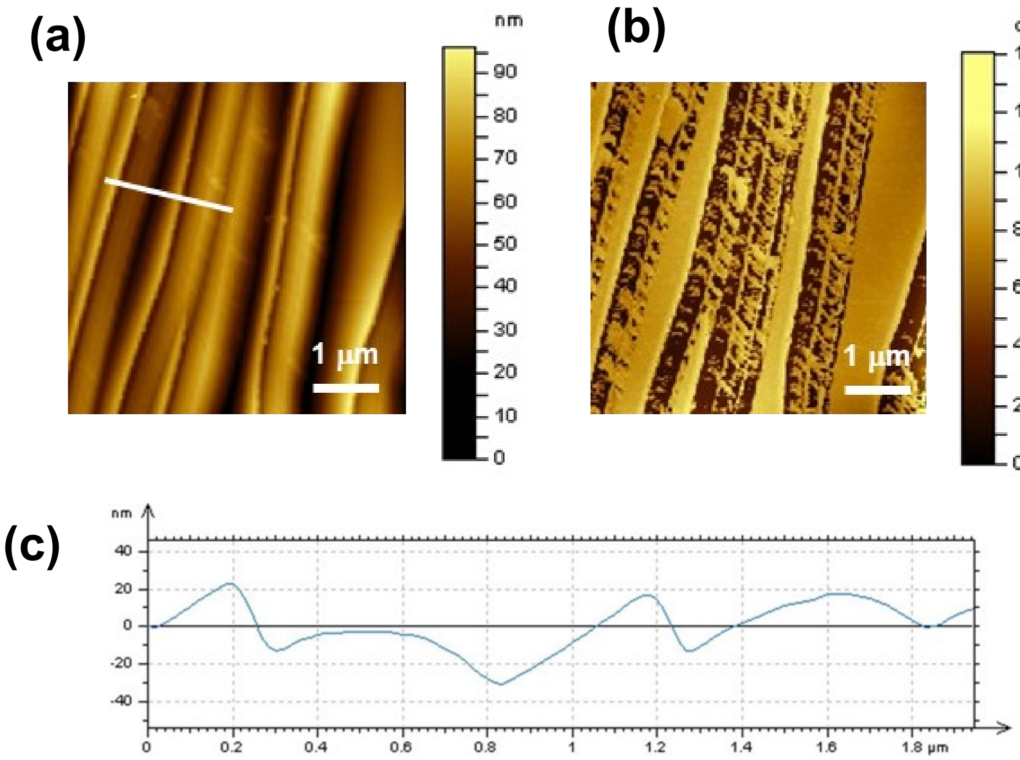


Figure S8. AFM images of APhePheTPE: (a) height image, (b) phase image, and (c) cross section at the position indicated by white line. The sample was prepared by drop-casting from THF/water (30/70 vol%) mixture (conc. = 1.0 mg/mL) onto freshly cleaved mica.

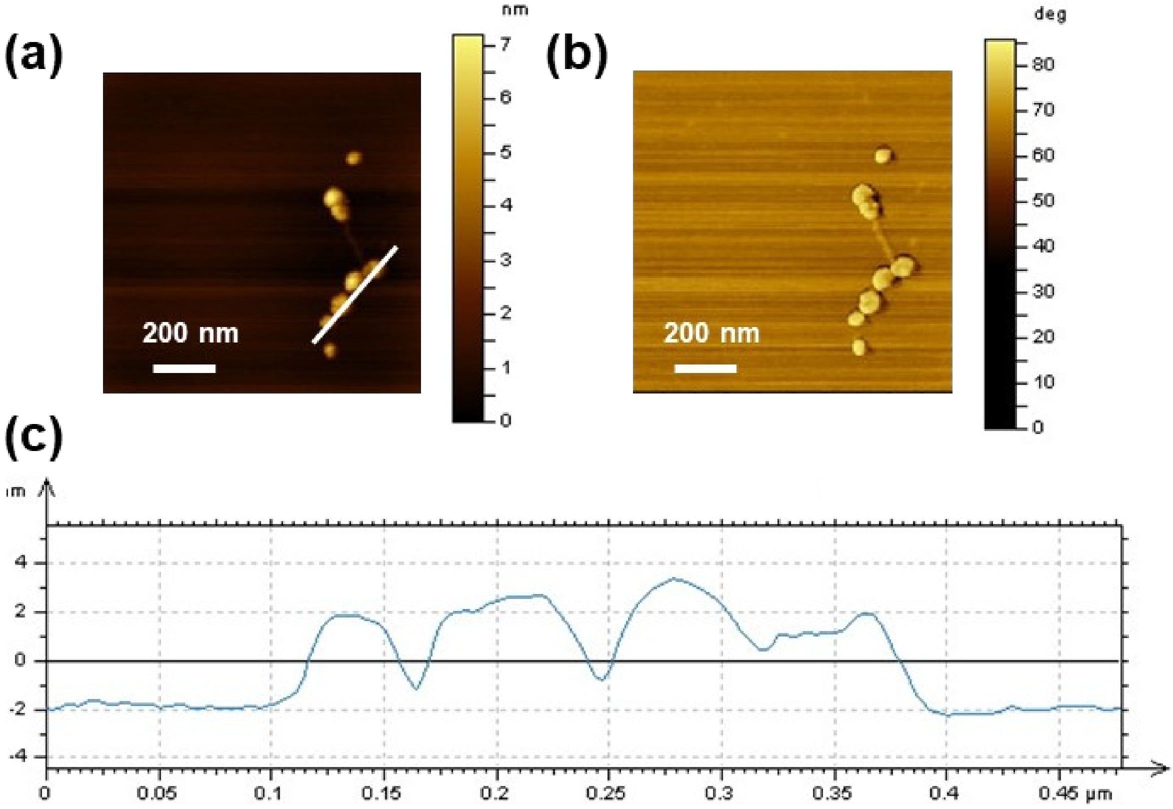


Figure S9. AFM images of APhePheTPE: (a) height image, (b) phase image, and (c) cross section at the position indicated by white line. The sample was prepared by spin-coating from THF/water (10/90 vol%) mixture (conc. = 1.0 mg/mL) onto freshly cleaved mica.

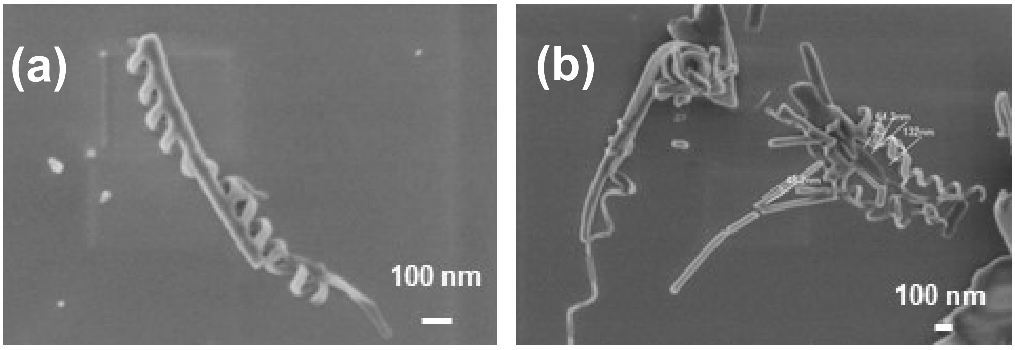


Figure S10. SEM images of helical nanoribbon structures derived from APhePheTPE at different concentrations: (a) 0.03 mg/mL and (b) 10.0 mg/mL in THF/water (10/90 vol%) mixture.

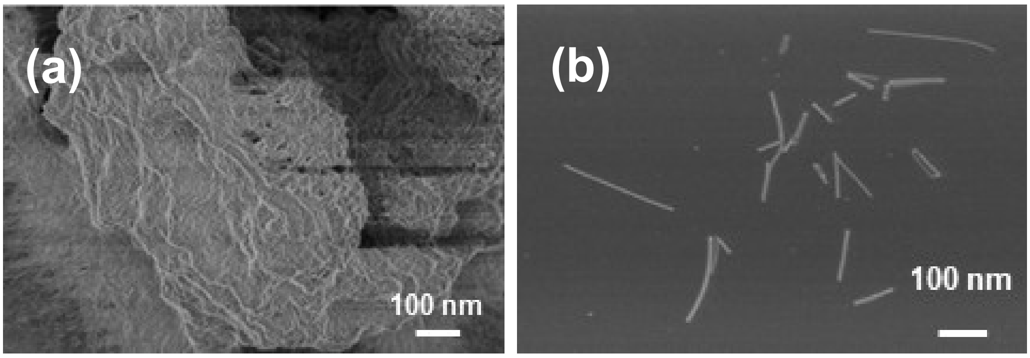


Figure S11. SEM images of self-assembled nanostructures derived from APhePheTPE in (a) DMF and (b) DMF/water (10/90 vol%, conc. = 1.0 mg/mL) mixture.

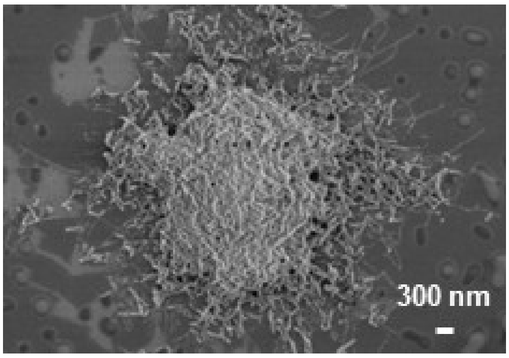
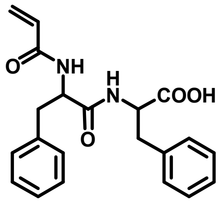


Figure S12. SEM image of self-assembled nanostructure derived from APhePheTPE in THF/MeOH (10/90 vol%, conc. = 1.0 mg/mL) mixture.



APhePheOH

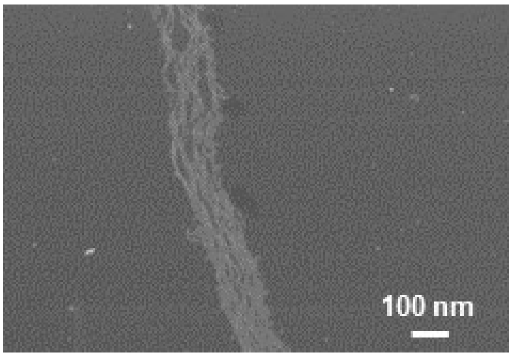


Figure S13. SEM image of self-assembled nanostructure derived from APhePheOH in THF/water (10/90 vol%, conc. = 1.0 mg/mL) mixture.

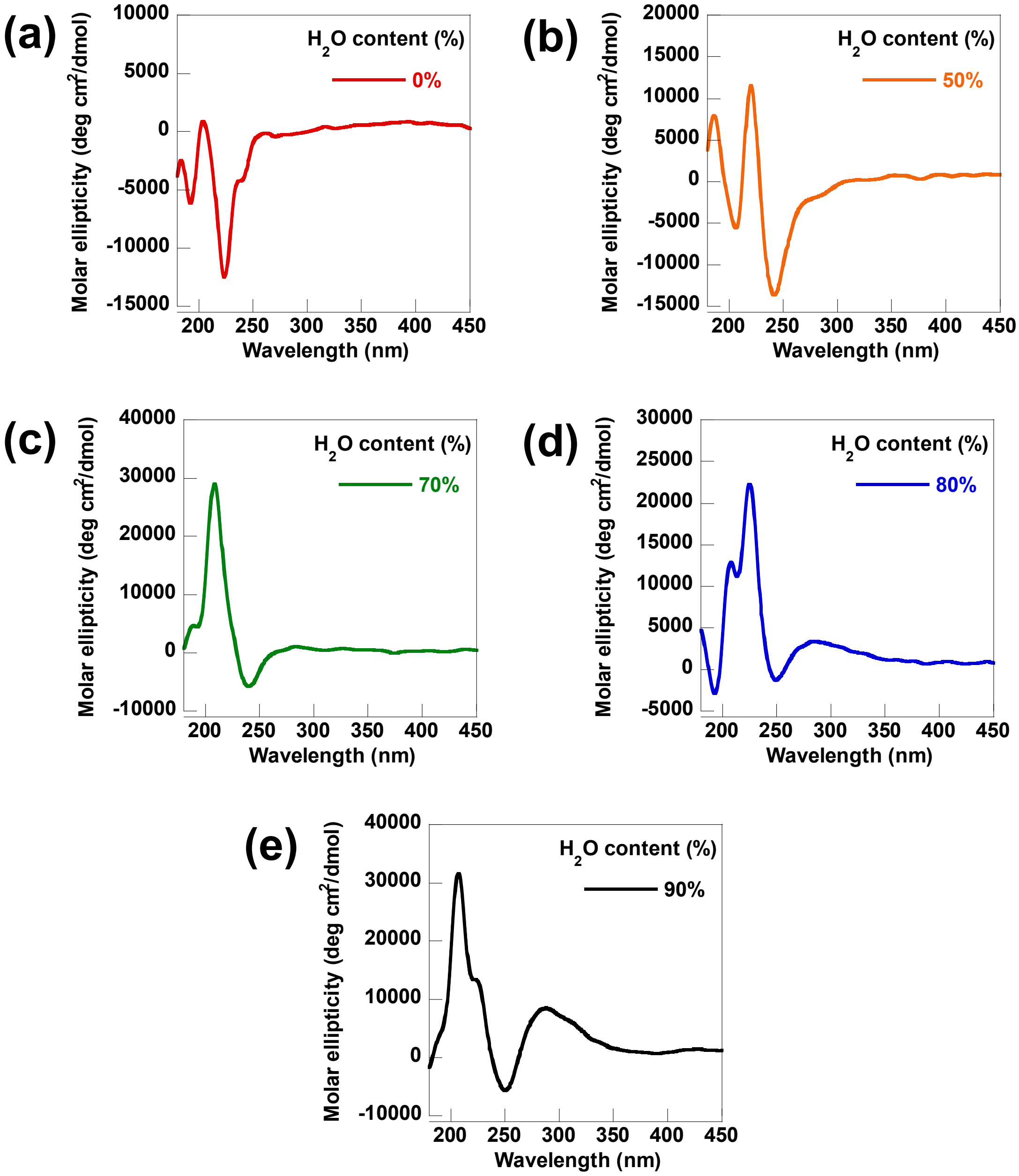


Figure S14. CD spectra of APhePheTPE in THF/water mixtures at different water contents: (a) 0%, (b) 50%, (c) 70%, (d) 80%, and (e) 90% (see Figure 2c).

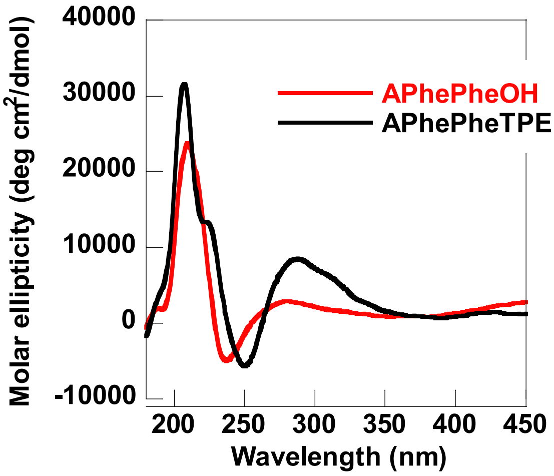


Figure S15. CD spectra of APhePheOH and APhePheTPE in THF/water (10/90 vol%, conc. = 0.03 mg/mL) mixture.

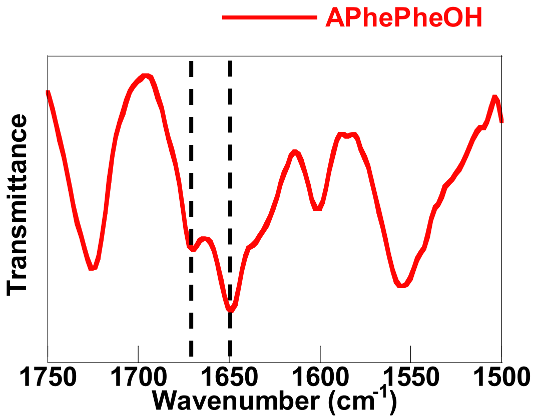


Figure S16. FT-IR spectrum of APhePheOH.

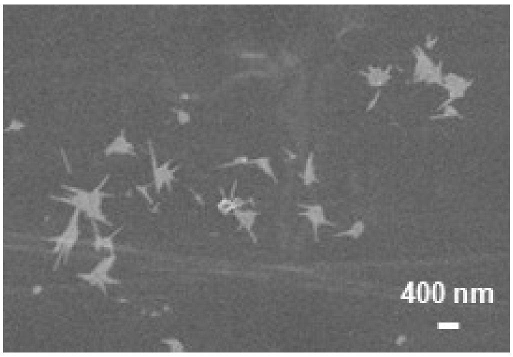


Figure S17. SEM image of self-assembled nanostructure derived from APhePheTPE in THF/water (10/90 vol%, conc. = 1.0 mg/mL) mixture. The sample was prepared by just after mixing APhePheTPE THF solution with water.

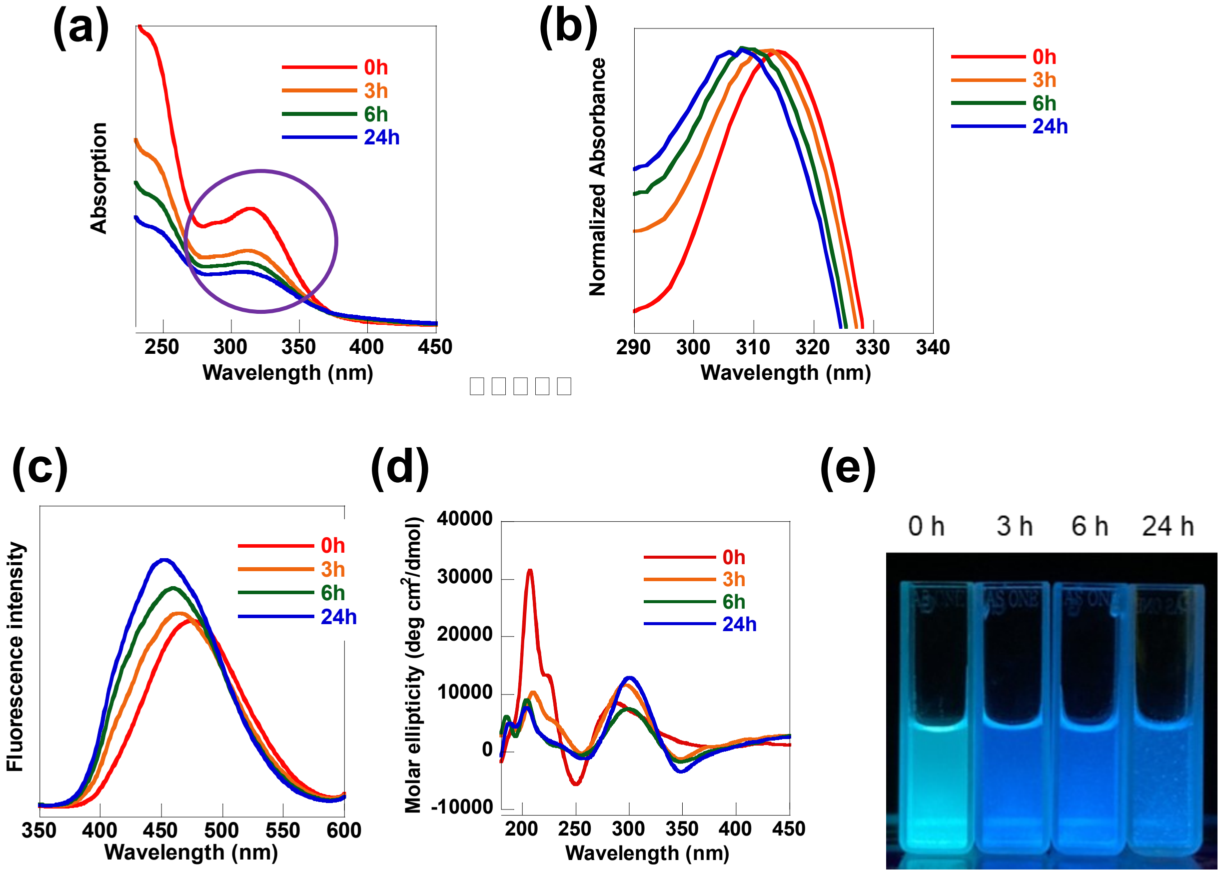


Figure S18. (a) Time-dependent UV-vis spectra, (b) normalized UV-vis spectra, (c) fluorescence spectra, (d) CD spectra, and (e) photographs of APhePheTPE in THF/water mixture (10/90 vol%).

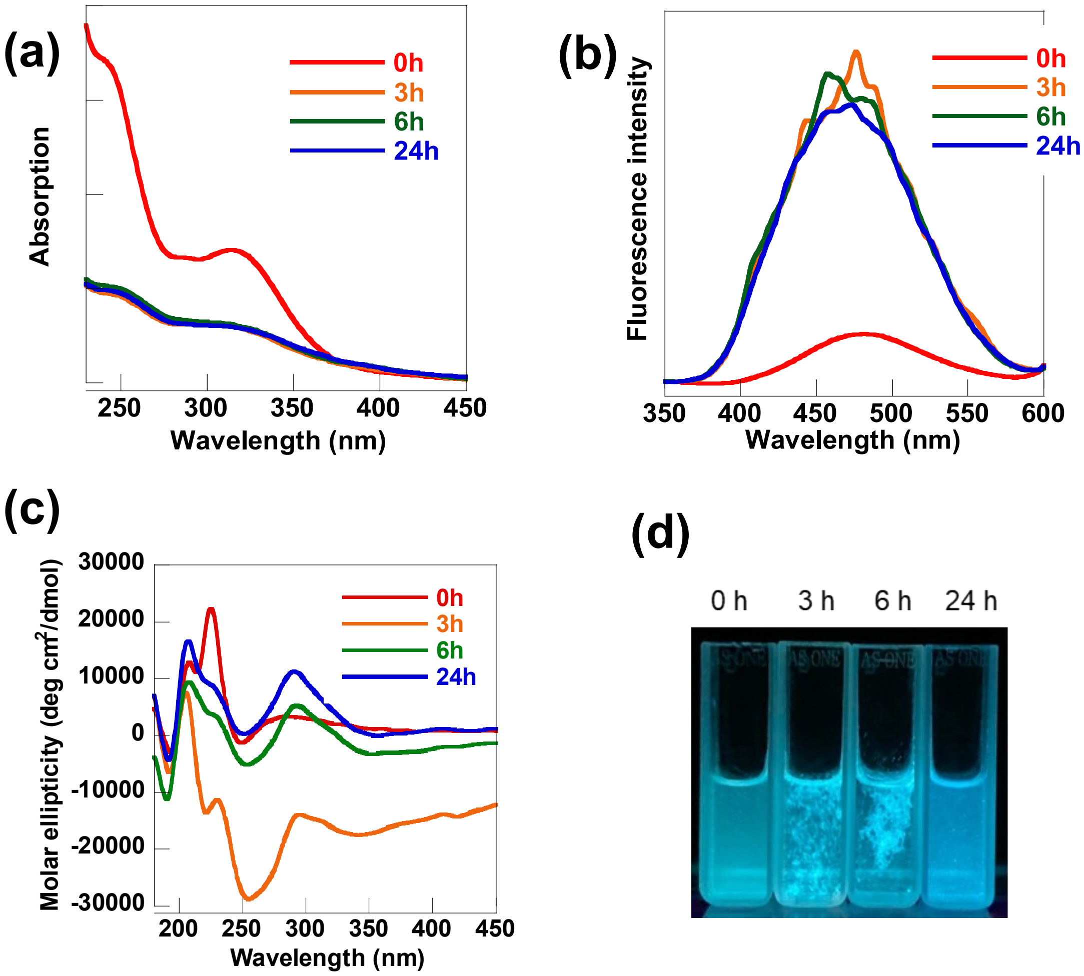


Figure S19. (a) Time-dependent UV-vis spectra, (b) fluorescence spectra, (c) CD spectra, and (d) photographs of APhePheTPE in THF/water mixture (20/80 vol%).

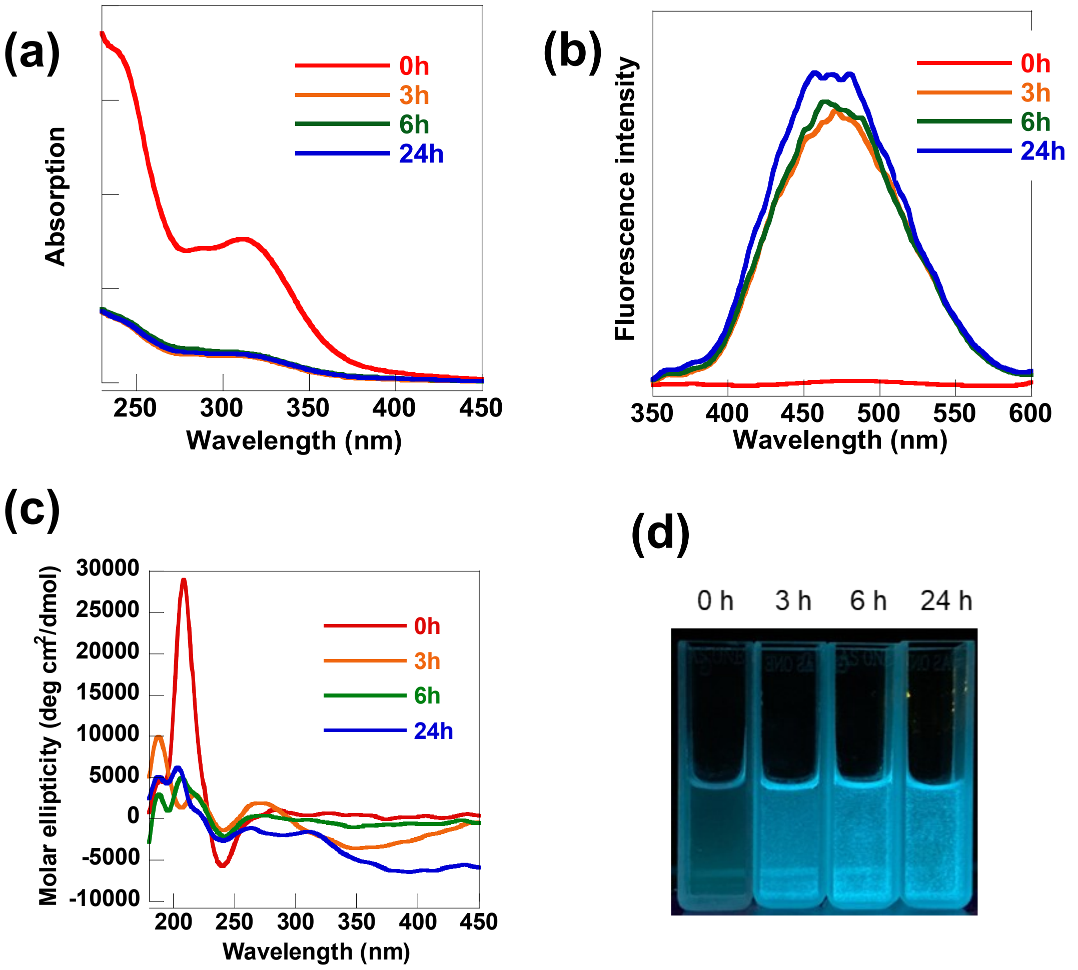


Figure S20. (a) Time-dependent UV-vis spectra, (b) fluorescence spectra, (c) CD spectra, and (d) photographs of APhePheTPE in THF/water mixture (30/70 vol%).

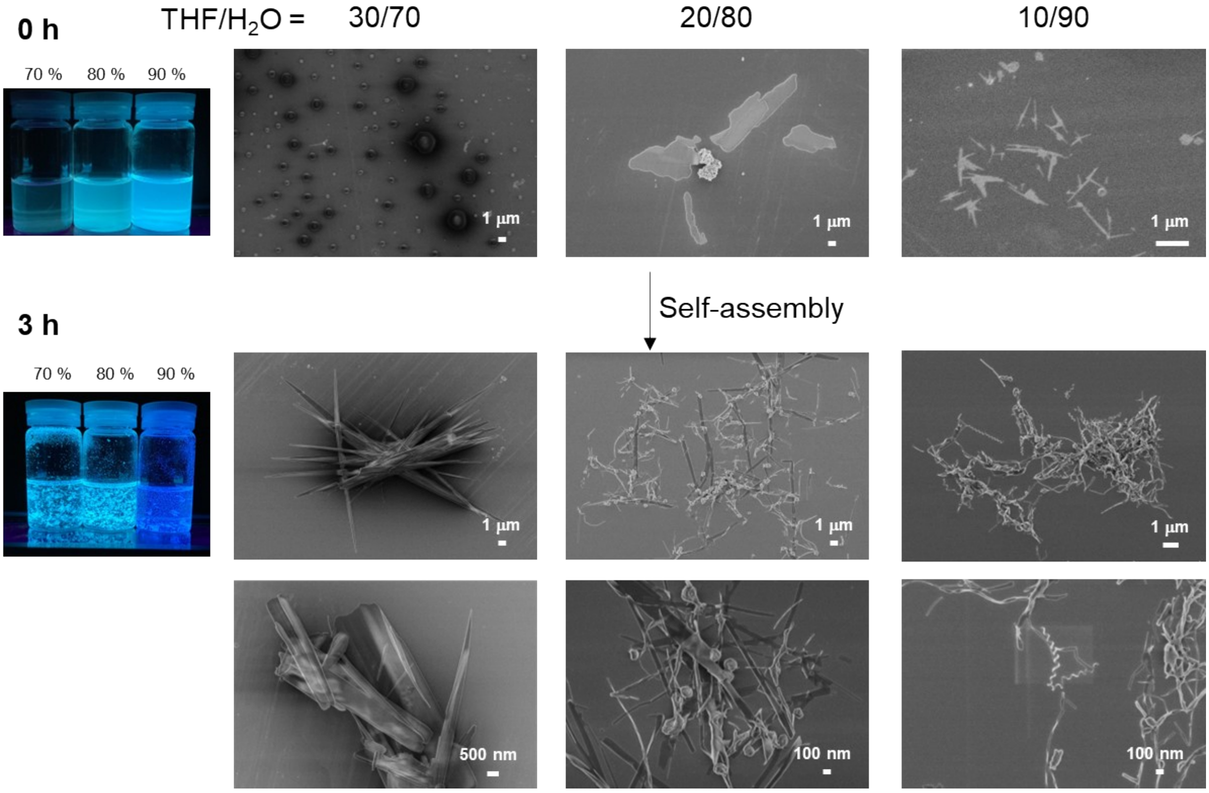


Figure S21. Time-dependent SEM images of the APhePheTPE samples prepared immediately after mixing (0 h) and after 3h in THF/water mixtures (30/70–10/90 vol%, conc. = 0.03 mg/mL) and their photographes.

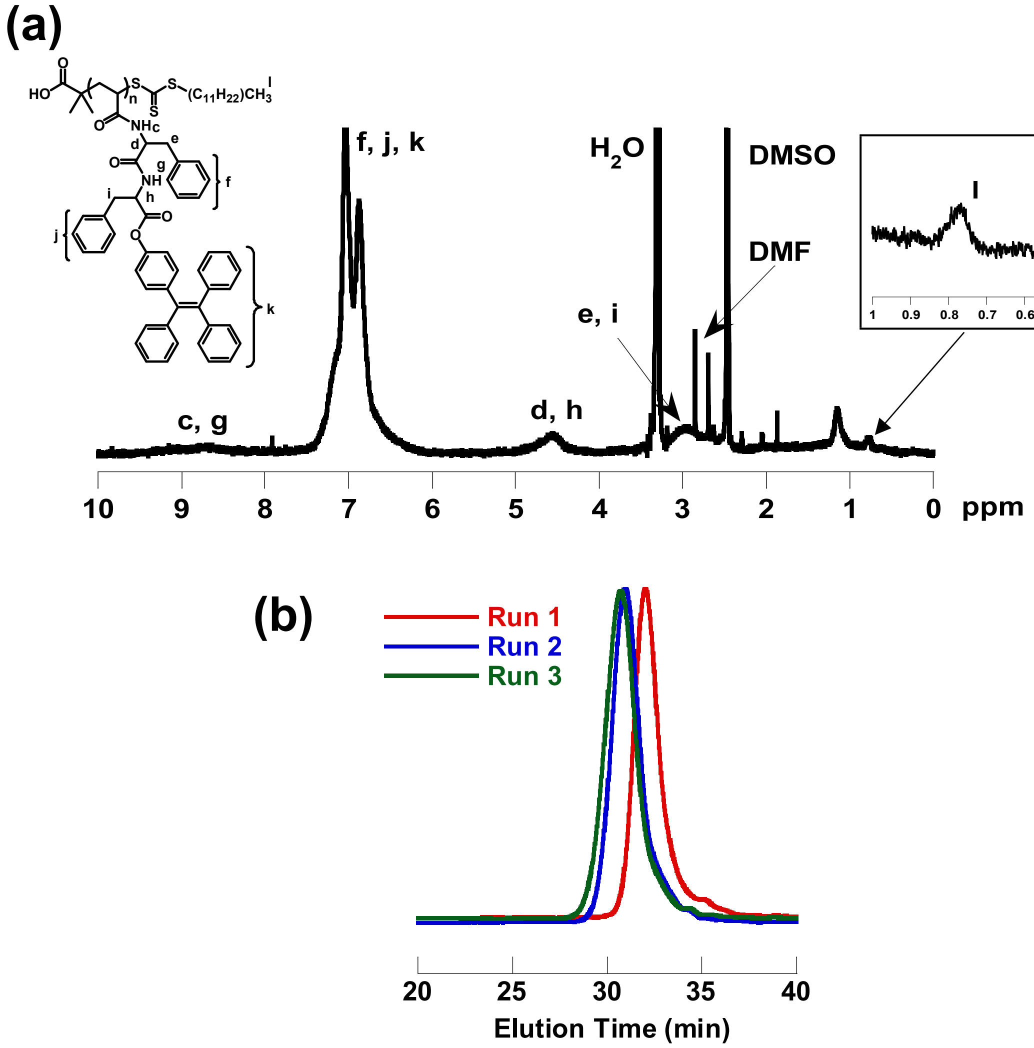


Figure S22. (a) ^{1}H NMR spectrum of PAPhePheTPE in DMSO-d_6 and (b) SEC curves of PAPhePheTPEs (see Table 1).

The molecular weight of PAPhePheTPE was calculated from the ^{1}H NMR spectrum by comparing the area of the peak at 4.29-4.91 ppm corresponding to the methine proton adjacent to the carbonyl group (broad peak "d and h" in Fig. S22a) in the APhePheTPE repeating unit to that of the peak at 0.73–0.82 ppm (Peak "l") corresponding to three protons of the end group (Z-group).

Table S2. RAFT polymerization of APhePheTPE at different [CTA]/[I] ratios.

Run	[APhePheTPE]/ [CTA]/[AIBN]	Conv.[b]/Yield[c] (%)	M_n[d] (theory)	M_n[b] (NMR)	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1	100/2/1	64/41	22600	24100	12000	1.27
2	250/5/1	20/2	7300	11300	8000	1.15
3	500/10/1	<5/-	-	-	-	-

[a] Polymerization in dimethylformamide (DMF; conc. = 0.20 g/mL) at 60 °C for 24 h. [b] Calculated using ^{1}H NMR in dimethyl sulfoxide (DMSO)-d_6. [c] Diethylether-insoluble part. [d] Theoretical molecular weight (M_n, theory) = (MW of APhePheTPE) × ([APhePheTPE]$_0$/[CTA]$_0$) × conv. + (MW of CTA). [e] Determined by size-exclusion chromatography (SEC) in DMF (0.01 M LiBr).

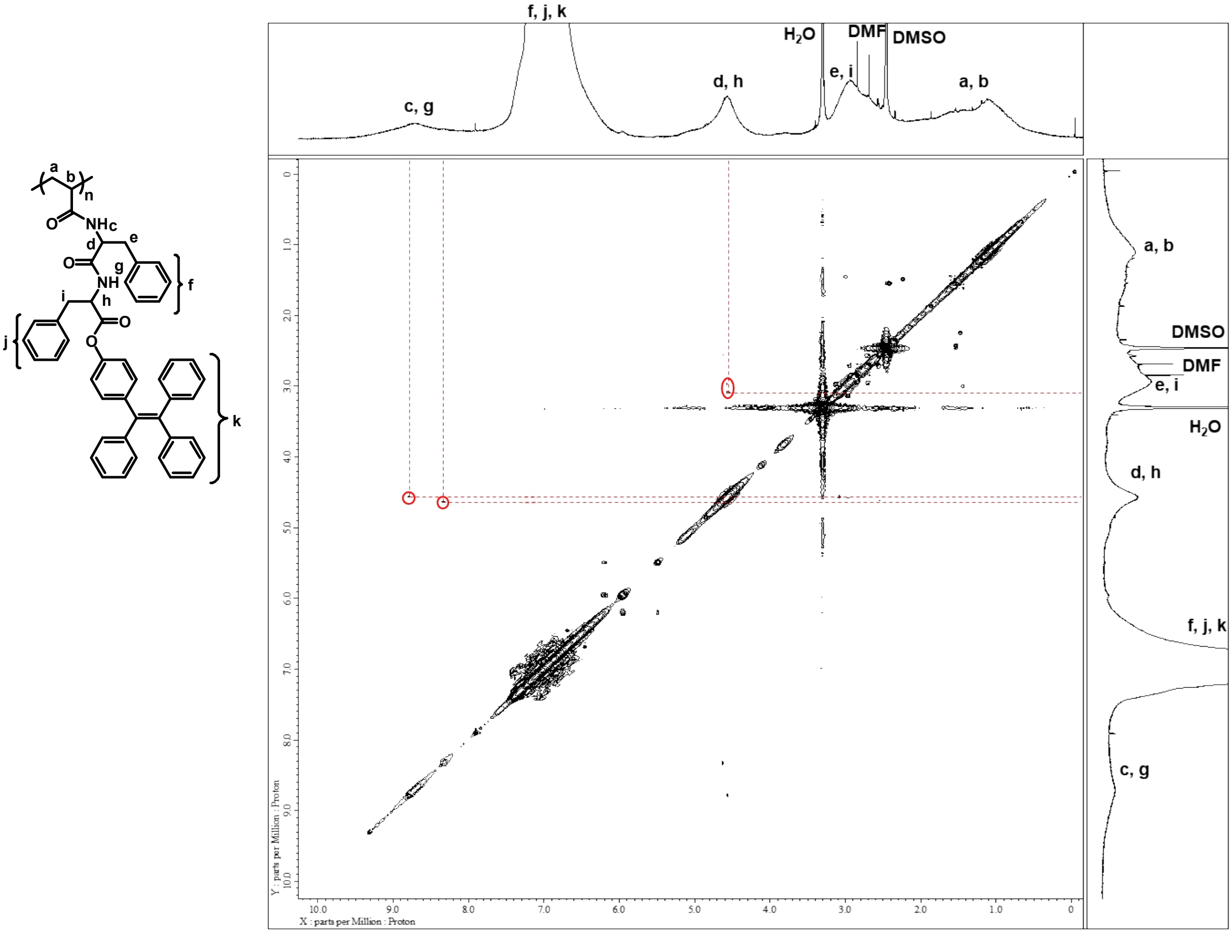


Figure S23. 2D H-H COSY NMR spectrum of PAPhePheTPE in DMSO-d_6 and assignment of hydrogen atoms.

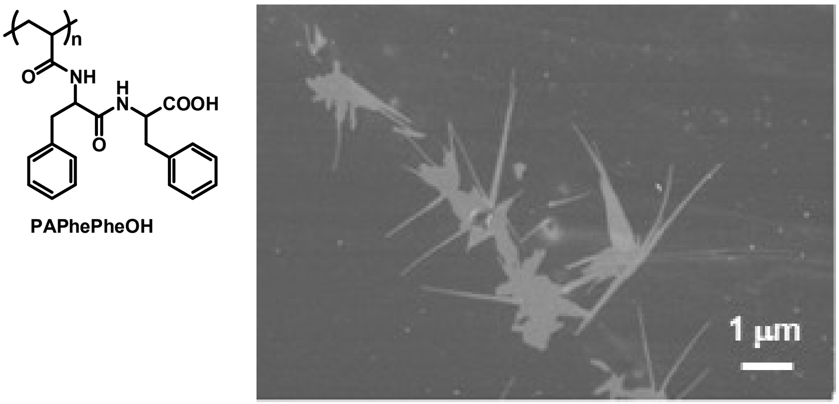


Figure S24. SEM image of self-assembled structures derived from PAPhePheOH (M_n = 10600, M_w/M_n = 1.21) in THF/water (10/90 vol%, conc. = 1.0 mg/mL) mixture.

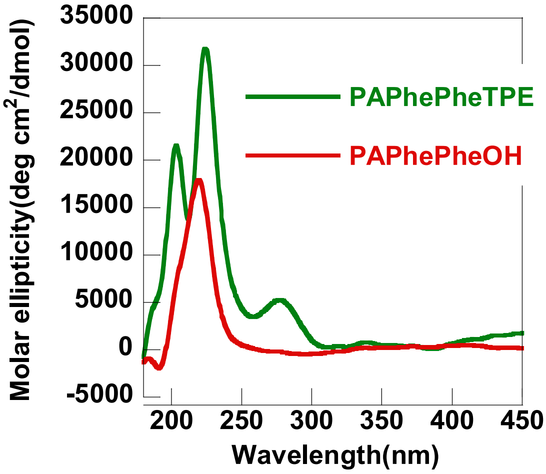


Figure S25. CD spectra of diphenylalanine-based polymers in THF/water (10/90 vol%, conc. = 0.03 mg/mL) mixture (PAPhePheTPE: M_n = 24100, PAPhePheOH: M_n = 10600).

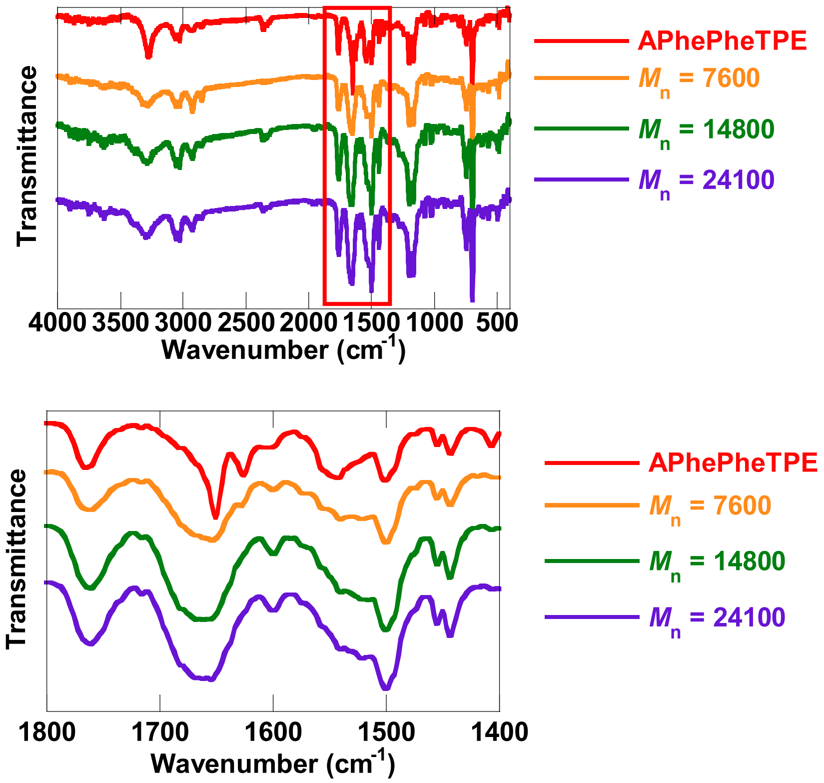


Figure S26. FT-IR spectra of APhePheTPE and PAPhePheTPEs.

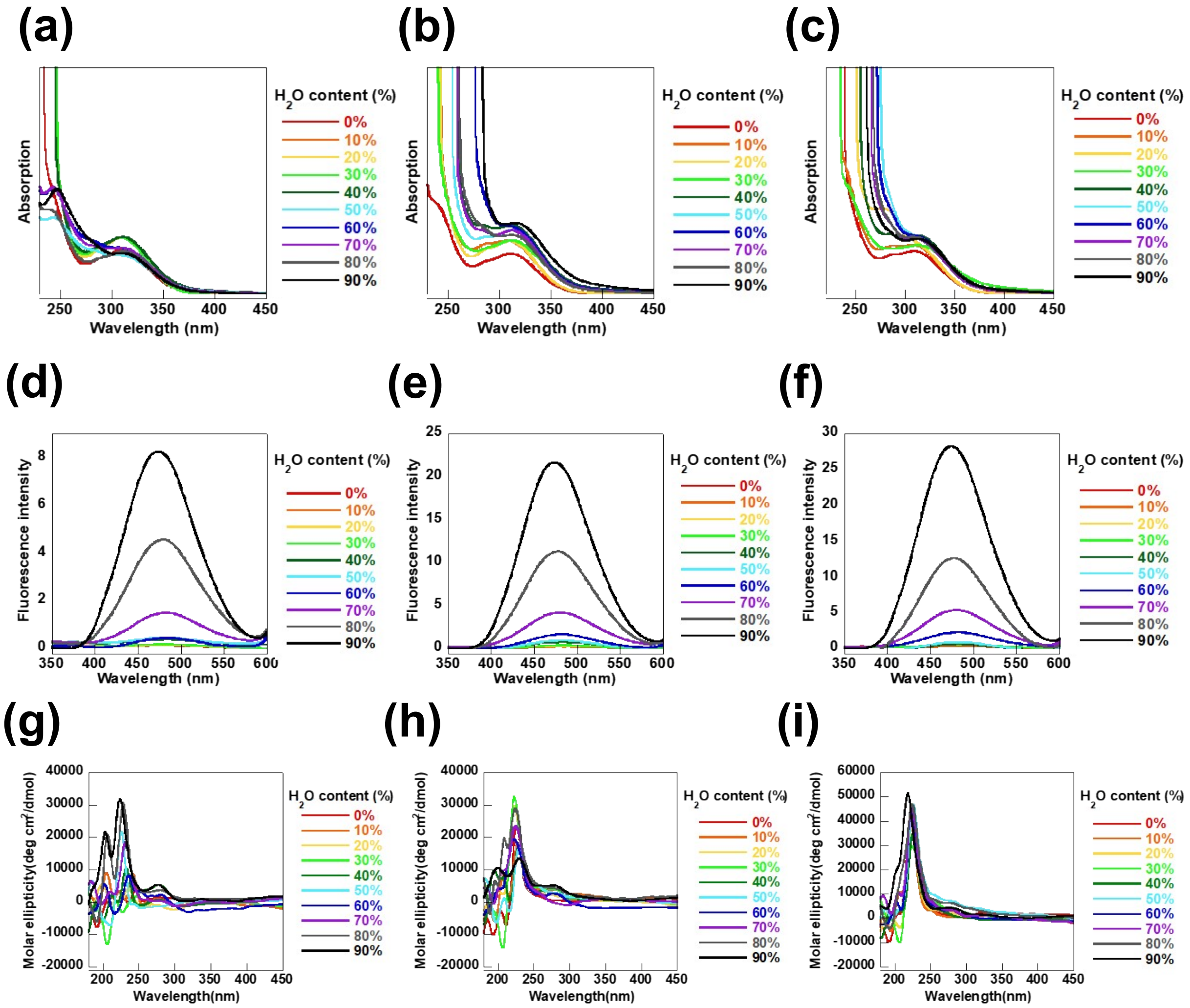


Figure S27. UV-vis, fluorescence, and CD spectra of PAPhePheTPEs having different molecular weights: M_n = (a, d, g) 7600, (b, e, h) 14800, and (c, f, i) 24100, in THF/water mixtures (conc. = 0.03 mg/mL)

Table S3. Quantum yields of APhePheTPE and PAPhePheTPE in THF/water mixture (10/90 vol%)

Sample	QY
APhePheTPE	0.074
PAPhePheTPE $M_n = 7600$	0.069
PAPhePheTPE $M_n = 14800$	0.117
PAPhePheTPE $M_n = 24100$	0.085

Fluorescence quantum yield (QY) in THF/water mixture (10/90 vol%. conc = 0.01 mM).

References

1. R. Yonenuma, A. Ishizuki, K. Nakabayashi and H. Mori, *Journal of Polymer Science Part A: Polymer Chemistry*, 2019, **57**, 2562-2574.
2. A. S. Abd-El-Aziz, C. Agatemor, N. Etkin and B. Wagner, *Macromolecular Rapid Communication*, 2016, **37**, 1235-1241.
3. M. Furukawa, K. Nakabayashi and H. Mori, *Journal of Polymer Science*, 2021, **59**, 532-546.