

## Supplementary Information

# Multicolor circularly polarized luminescence: pendant primary amine/diphenylalanine chiral copolymers with clustering-triggered emission

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## Materials

2,2'-Azobis(isobutyronitrile) (AIBN, 97%) and *N,N*-dimethylformamide (DMF, 99.5%) were purchased from Kanto Chemical. Hydrazine monohydrate (80 %) and trimethylsilyldiazomethane (10% solution in hexane) were purchased from Tokyo Chemical Industry. AIBN was recrystallized from methanol. *N*-acryloyl-*L,L*-diphenylalanine (APhePheOH),<sup>1, 2</sup> *N*-vinylphthalimide (NVPI),<sup>3-7</sup> and benzyl 1-pyrrolocarbodithioate<sup>8, 9</sup> were synthesized as reported previously. All the other reagents were used as received.

## Synthesis of ampholytic block copolymer

Adapting a reported procedure,<sup>5-7</sup> the dithiocarbamate-terminated PNVPI ( $M_{n,NMR} = 10500$ ,  $M_{n,SEC} = 3300$ ,  $M_w/M_n = 1.36$ ) was prepared, which was used for the synthesis of ampholytic block copolymer. The dithiocarbamate-terminated PNVPI (0.29 g, 0.027 mmol), APhePheOH (1.5 g, 4.1 mmol), AIBN (2.2 mg, 0.014 mmol), and DMF (8.9 mL) were placed in a polymerization ampule. After degassing the mixture, followed by sealing, the mixture was stirred at 60 °C for 24 h. Thereafter, the reaction mixture was poured into a large excess of diethyl ether twice. The product was finally dried in vacuo at 40 °C to yield PNVPI-*b*-PAPhePheOH (1.34 g, yield = 74 %). <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ 8.70-8.15 (broad, 2H: -NH in APhePheOH), 7.84-6.68 (broad, 4H: -phenyl in NVPI and 10H: -phenyl in APhePheOH), 5.00-4.22 (broad, 2H: -NHCHCH<sub>2</sub>-phenyl and -NHCHCOOH), 3.18-2.46

(broad, 4H:  $-CH_2$ -phenyl), 2.27-0.70 (broad, 3H:  $CH$  and  $CH_2$  in the polymer main chain) ppm.

SEC measurement was performed for the methylated sample, which was prepared by treating PNVPI-*b*-PAPhePheOH with trimethylsilyldiazomethane, as reported previously.<sup>1</sup> The comonomer composition (NVPI/APhePheOH = 63/37) was determined by comparison of the <sup>1</sup>H NMR peaks (See Eqn. S1).

$$\frac{10-6x}{2(1-x)} = \frac{\text{Integral at 7.84-6.68 ppm}}{\text{Integral at 5.00-4.22 ppm}} \quad (\text{S1})$$

where  $x$  is the fraction of NVPI and  $1-x$  is the fraction of APhePheOH in the copolymer.

Deprotection of PNVPI-*b*-PAPhePheOH to PVAm-*b*-PAPhePheOH was carried out using a similar procedure reported previously<sup>5-7</sup> with slight modifications. PNVPI-*b*-PAPhePheOH (1.0 g,  $M_{n,NMR} = 23,500$ ,  $M_w/M_n = 1.31$ , NVPI/APhePheOH composition = 63/37) and methanol (10.0 mL) were placed in a flask. After introducing hydrazine monohydrate (2.5 mL, 0.051 mol, ~20 equiv. with respect to the phthalimide unit), the mixture was refluxed at 70 °C under a nitrogen atmosphere for an overnight. The reaction product was purified by dialysis using a dialysis bag (MWCO 1000 Da) against 0.05 M NaOH aqueous solution for 1 day and then distilled water for 1 day. The product was finally dried in vacuo at room temperature to afford PVAm-*b*-PAPhePheOH (0.55 g, yield = 83%).

**Table S1.** Synthesis of PNVPI-*b*-PAPhePheOH by reversible addition–fragmentation chain transfer (RAFT) polymerization using macro-CTA in DMF at 60 °C for 24 h <sup>a)</sup>

Run	[I]/[macro-CTA]/[M]	Conv. <sup>b)</sup> (%)	Yield <sup>c)</sup> (%)	$M_n$ <sup>d)</sup> (theory)	$M_n$ <sup>b)</sup> <sup>(<sup>1</sup>H NMR)</sup>	$M_n$ <sup>e)</sup> (SEC)	$M_w/M_n$ <sup>e)</sup> (SEC)	NVPI:APhePheOH <sup>b)</sup>
1	1/2/50	73	70	17300	14300	4300	1.27	85:15
2	1/2/100	60	56	21600	16500	4900	1.30	78:22
3	1/2/300	74	74	51100	23500	5900	1.31	63:37

<sup>a)</sup> Macro-CTA= PNVPI ( $M_n$  NMR = 10700,  $M_n$  SEC = 3300,  $M_w/M_n$  = 1.36), monomer concentration = 0.20 g/mL, where AIBN = 2,2'-azobis(isobutyronitrile). <sup>b)</sup> Calculated using <sup>1</sup>H NMR spectroscopy in DMSO-*d*<sub>6</sub>. <sup>c)</sup> Diethyl ether-insoluble fraction <sup>d)</sup> Theoretical molecular weight ( $M_n$ , theory) = (MW of APhePheOH) × [APhePheOH]/[macro-CTA] × conv. + (MW of macro-CTA). <sup>e)</sup> Methylated samples were measured by SEC using PSt standards in DMF (0.01 M LiBr).

### Synthesis of ampholytic random copolymer

NVPI (0.19 g, 1.1 mmol), APhePheOH (1.2 g, 3.3 mmol), benzyl 1-pyrrolicarbodithioate (10.2 mg, 0.043 mmol), AIBN (3.6 mg, 0.022 mmol), and DMF (6.9 mL) were added in a dry polymerization ampule equipped with a magnetic stir bar. After degassing the mixture by three freeze-evacuate-thaw cycles, the glass ampule was flame-sealed under vacuum. The mixture was stirred at 60 °C for 24 h. Thereafter, the reaction mixture was poured into a large excess of diethyl ether and collected by filtration. The product was finally dried in vacuo at 40 °C to yield P(NVPI-*co*-APhePheOH) as a yellow powder (1.10 g, yield = 80 %). <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ 8.70-8.15 (broad, 2H: -NH in APhePheOH), 7.84-6.68 (broad, 4H: -phenyl in NVPI and 10H: -phenyl in APhePheOH), 5.00-4.22 (broad, 2H: -NHCHCH<sub>2</sub>-phenyl and -NHCHCOOH), 3.18-2.46 (broad, 4H: -CH<sub>2</sub>-phenyl), 2.27-0.70 (broad, 3H: CH and CH<sub>2</sub> in the

polymer main chain) ppm. The comonomer composition (NVPI/APhePheOH = 60/40), the molecular weight ( $M_{n,SEC} = 5600$ ) and polydispersity ( $M_w/M_n = 1.37$ ) were evaluated by  $^1\text{H}$  NMR and SEC measurements using the similar procedures described for block copolymer. The deprotection of P(NVPI-*co*-APhePheOH) was carried out using the same procedures described for block copolymer to yield P(VAm-*co*-APhePheOH) (0.24 g, yield = 34%).

**Table S2.** Synthesis of P(NVPI-*co*-APhePheOH) by RAFT copolymerization in DMF at 60 °C for 24 h <sup>a)</sup>

Run	[I]/[CTA]/[NVPI]/[APhePheOH]	Yield <sup>b)</sup> (%)	$M_n^c)$ (theory)	$M_n^d)$ (SEC)	$M_w/M_n^d)$ (SEC)	NVPI: APhePheOH <sup>e)</sup>
1	1/2/100/100	80	21800	6200	1.41	78:22
2	1/2/50/150	80	25600	5600	1.37	60:40

<sup>a)</sup> Monomer concentration = 0.20 g/mL,  $[M] = [NVPI] + [APhePheOH]$ ; AIBN = 2,2'-azobis(isobutyronitrile). <sup>b)</sup> Diethyl ether-insoluble fraction. <sup>c)</sup> Theoretical molecular weight ( $M_n$ , theory) =  $(M_{\text{monomer}}) \times [M]_0/[CTA]_0 \times \text{yield} + (\text{MW of CTA})$ ,  $M_{\text{monomer}} = A_1F_1 + A_2F_2$  (A = molecular weight, F = molar fraction). <sup>d)</sup> Methylated samples were analyzed by SEC using PSt standards in DMF (0.01 M of LiBr). <sup>e)</sup> Calculated using  $^1\text{H}$  NMR spectroscopy in DMSO- $d_6$ .

## Instrumentation

The proton nuclear magnetic resonance ( $^1\text{H}$  NMR, 400 MHz) was recorded on a JEOL JNM-ECX400. The molecular weight and polydispersity were estimated by size exclusion chromatography (SEC) using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors, four consecutive gel columns [TSK-GEL  $\alpha$ -M,  $\alpha$ -4000,  $\alpha$ -3000, and

$\alpha$ -2500], and a guard column [TSK-guardcolumn  $\alpha$ ], in DMF containing 10 mM LiBr (flow rate: 1.0 mL/min) at 40 °C. Polystyrene standards were employed to prepare calibration plot. The ultraviolet–visible (UV–vis) spectra were recorded on JASCO V-630BIO UV–vis spectrophotometer, and fluorescence spectra were recorded on JASCO FP-6100 spectrofluorophotometer. Fluorescence quantum yields (QYs) of polymer solutions were evaluated by comparing 9,10-diphenylanthracene in cyclohexane. The FRET efficiency of energy transfer was determined from the quenching of the donor fluorescence in the presence of acceptor.<sup>10</sup>

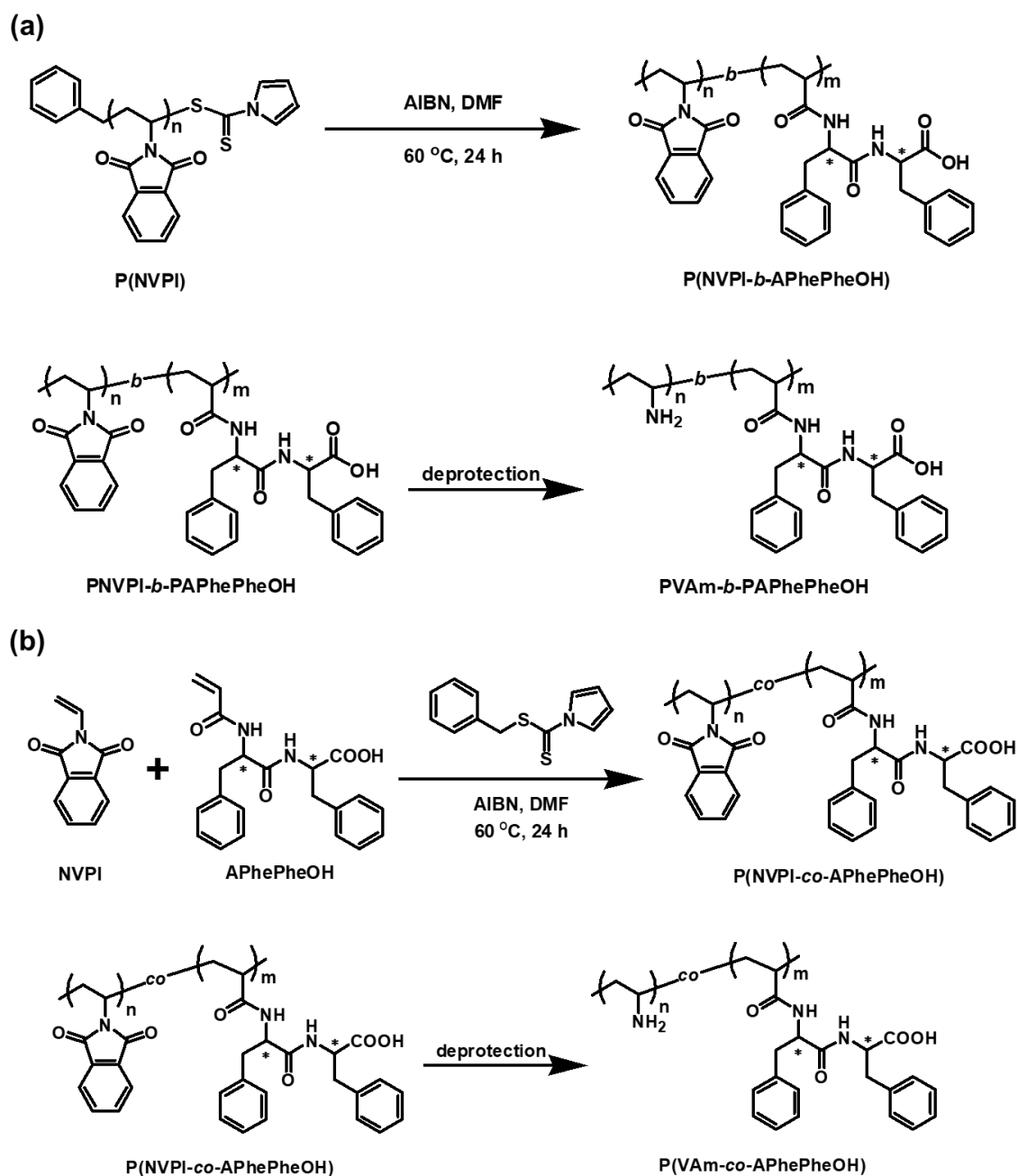
$$E = 1 - \frac{I_{DA}}{I_D} \quad (\text{S2})$$

where  $I_D$  and  $I_{DA}$  are the copolymer donor fluorescence intensities in the absence and presence of dye as the acceptor molecule, respectively.

Dynamic light scattering (DLS) analyses were conducted using a Zetasizer Nano (Sysmex) with a He-Ne laser (detection angle = 173°), as reported previously.<sup>7, 11</sup> Zeta potential data were collected on a Zetasizer Nano-ZS instrument. For the measurements, the polymer sample was dissolved in an aqueous solution at a predetermined concentration, and then the mixture was allowed to leave for at least 24 h to achieve an equilibrated state, followed by filtration using a Millipore Teflon Filter with a pore size of 0.2  $\mu\text{m}$ . Atomic force microscopy (AFM) measurements were conducted using an Agilent AFM 5500, using microfabricated cantilevers with a force constant of approximately 34 N/m, and the images were acquired under ambient

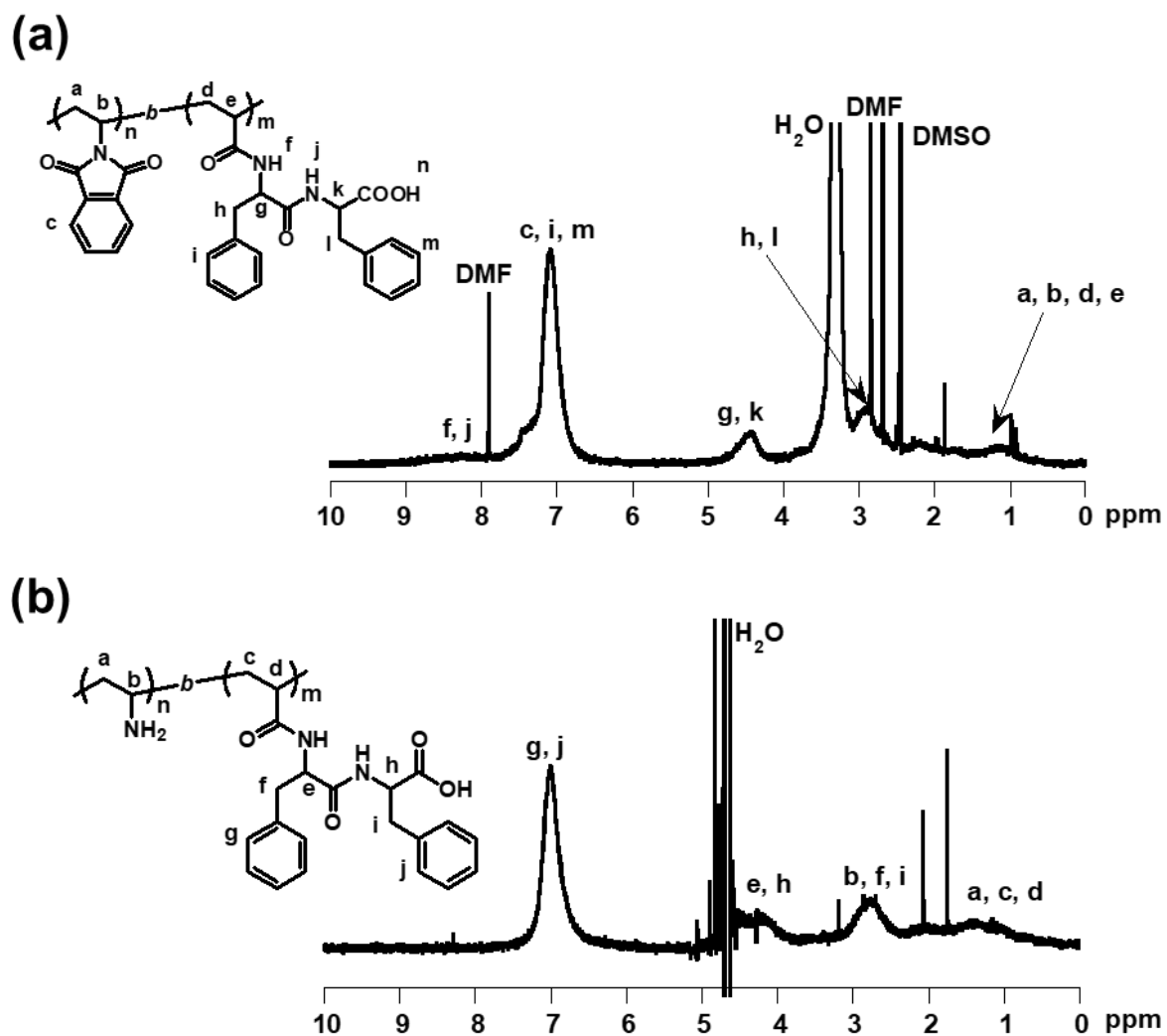
conditions and room temperature. The sample was prepared as follows: a droplet of an aqueous solution of the copolymer was cast onto the mica substrate and dried at room temperature. Field-emission scanning electron microscope (FE-SEM) measurements were performed on a Hitachi SU8000 microscope at an accelerating voltage of 1.0 kV. The sample prepared by mounting a drop of the polymer solution on carbon-coated Cu grid was employed without coating for SEM observation.

Circular dichroism (CD) measurements were performed with JASCO J-720 spectropolarimeter. The absorbance dissymmetry factor ( $g_{\text{abs}}$ ) was calculated according to  $g_{\text{abs}} = \Delta\text{Abs}/\text{Abs}$ . CPL spectra were measured with an assembled apparatus based on a photo elastic modulator and a photomultiplier designed according to the literature<sup>12, 13</sup> with modifications. The band width in excitation and emission in CPL/PL measurements was 25 nm. The emission anisotropy factor ( $g_{\text{lum}}$ ) was calculated according to  $g_{\text{lum}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$  where  $I_{\text{L}}$  and  $I_{\text{R}}$  are the emission intensities of L- and R-CPL, respectively.



**Scheme S1.** Synthesis of (a) PVAm-*b*-PAPhePheOH and (b) P(VAm-*co*-APhePheOH) by RAFT polymerization, followed by the deprotection.

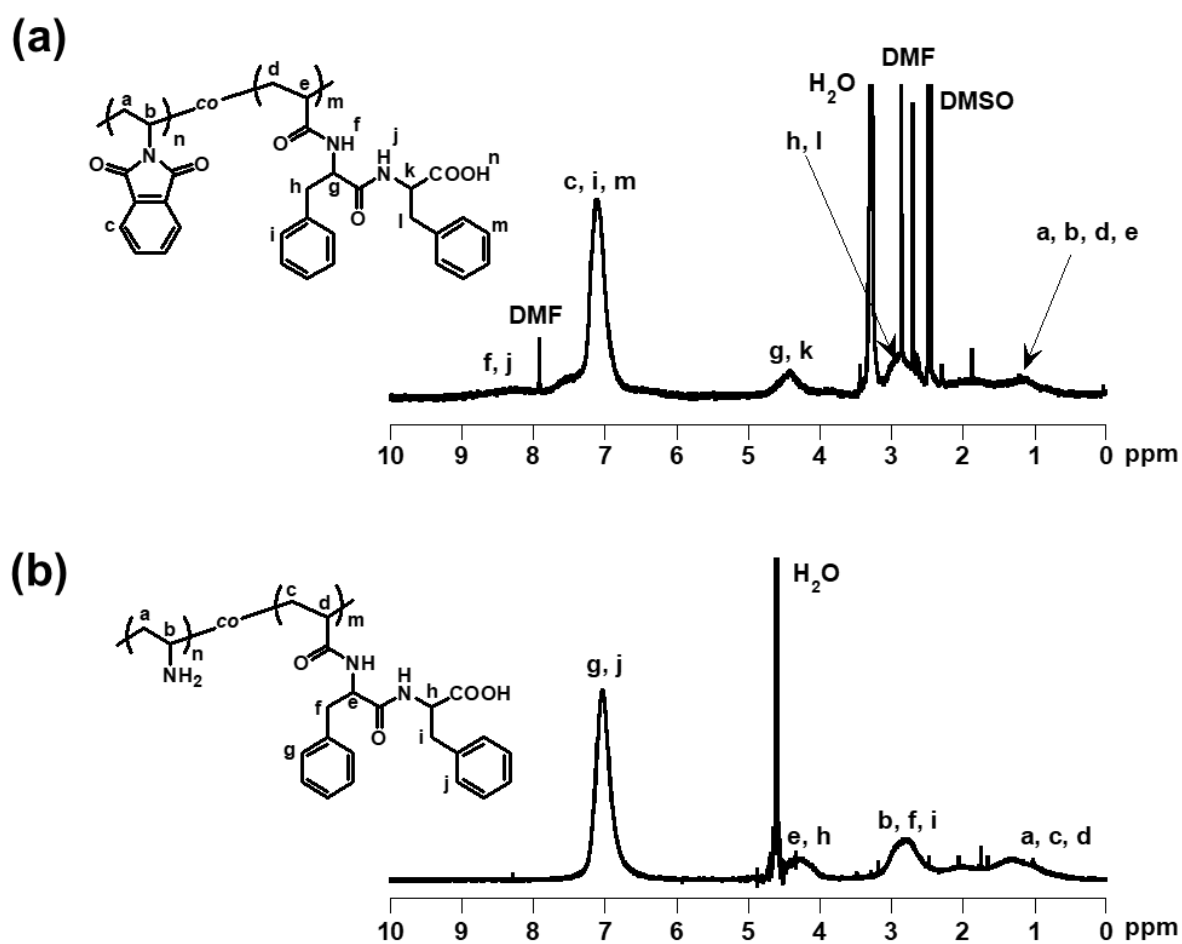




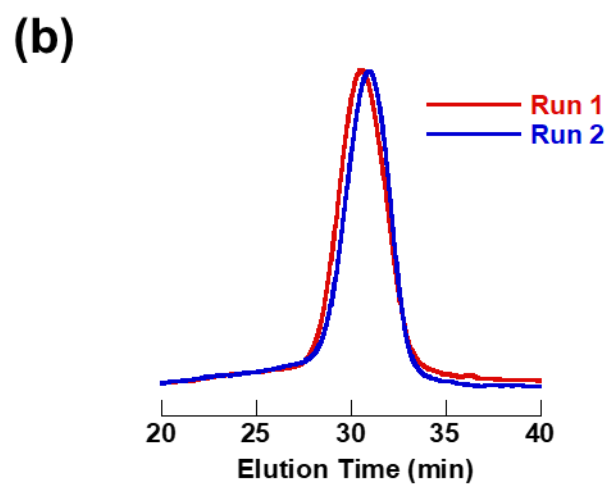
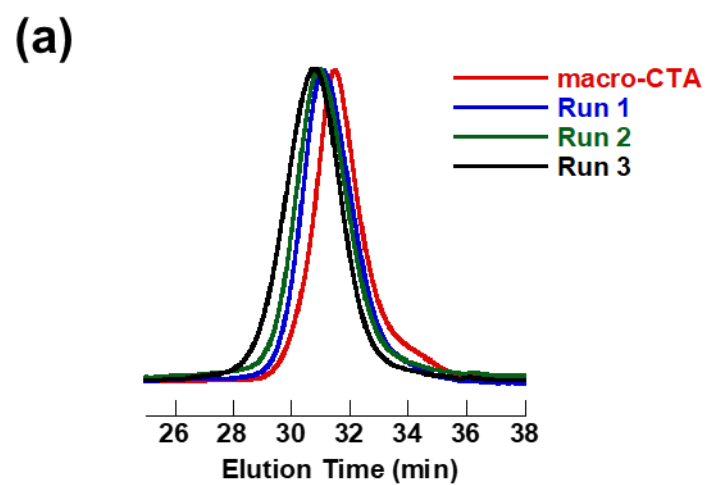
**Figure S1.**  $^1\text{H}$  NMR spectra of (a) PNVPI-*b*-PAPhePheOH in  $\text{DMSO-}d_6$ , and (b) PVAm-*b*-PAPhePheOH in  $\text{D}_2\text{O}$ .

**Table S3.** Comparison of proton peaks of diphenylalanine-based polymers

Samples	-CH (4 ~ 5 ppm)	-phenyl (7 ~ 8 ppm)
Theory (APhePheOH part)	2	10
APhePheOH	2	10.70
PAPhePheOH	2	11.52
PNVPI- <i>b</i> -PAPhePheOH	2	15.93
PVAm- <i>b</i> -PAPhePheOH	2	11.82



**Figure S2.**  $^1\text{H}$  NMR spectra of (a) P(NVPI-*co*-APhePheOH) in  $\text{DMSO-}d_6$ , and (b) P(VAm-*co*-APhePheOH) in  $\text{D}_2\text{O}$ .

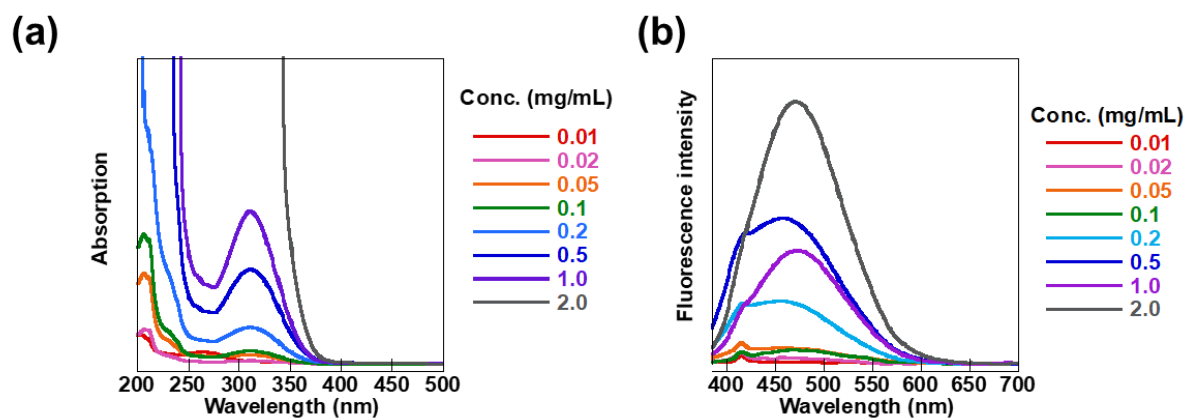


**Figure S3.** SEC curves of methylated (a) PNVPI-*b*-PAPhePheOHs and (b) P(NVPI-*co*-APhePheOH)s (see Table S1 and S2).

**Table S4.** Solubility of PNVPI, PVAm, PAPhePheOH, PNVPI-*b*-PAPhePheOH, PVAm-*b*-PAPhePheOH), and their random copolymers

	PNVPI	PVAm	PAPhePheOH	PNVPI- <i>b</i> - PAPhePheOH 63:37	PVAm- <i>b</i> - PAPhePheOH 63:37	P(NVPI-co- APhePheOH) 60:40	P(VAm-co- APhePheOH) 60:40
MeOH	-	-	+	-	-	-	-
EtOH	-	-	+	-	-	-	-
HFIP	-	-	+	-	-	-	-
DMSO	+	-	+	+	-	+	-
DMF	+	-	+	+	-	+	-
Acetone	-	-	+	-	-	-	-
THF	-	-	+	-	-	-	-
AcOEt	-	-	-	-	-	-	-
CHCl <sub>3</sub>	+	-	-	-	-	-	-
DCM	+	-	-	-	-	-	-
Dioxane	-	-	-	-	-	-	-
H <sub>2</sub> O (pH = 3)	-	+	-	-	-	-	-
H <sub>2</sub> O (pH = 4)	-	+	-	-	+	-	+
H <sub>2</sub> O (pH = 7)	-	+	-	-	+	-	+
H <sub>2</sub> O (pH = 12)	-	+	+	-	+	-	+

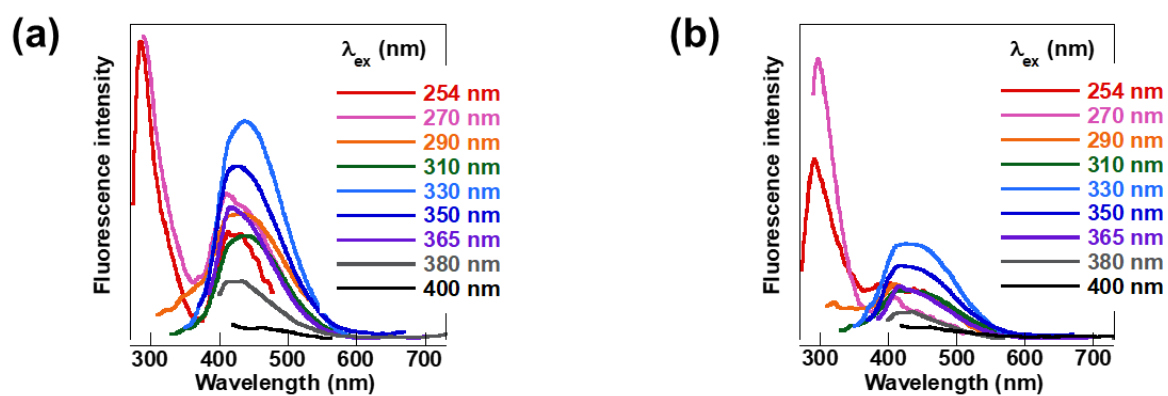
<sup>a)</sup> + : soluble at room temperature, - : insoluble at room temperature, conc. = 2.0 mg/mL. PNVPI-*b*-PAPhePheOH:  $M_{n,NMR} = 23500$ ,  $M_w/M_n = 1.31$ , NVPI/APhePheOH composition = 63/37, P(NVPI-co-APhePheOH):  $M_{n, sec} = 5600$ ,  $M_w/M_n = 1.37$ , NVPI/APhePheOH composition = 60/40, and their deprotected products.



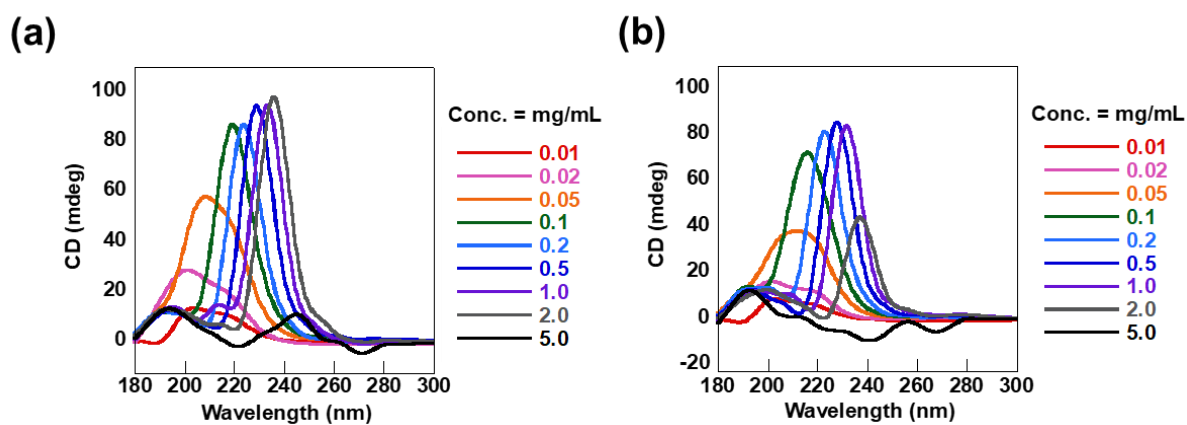
**Figure S4.** (a) UV-vis and (b) fluorescence spectra of PVAm homopolymer at different concentrations ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\text{pH} = 7$ ).

**Table S5.** Fluorescence quantum yield of VAm/APhePheOH copolymers

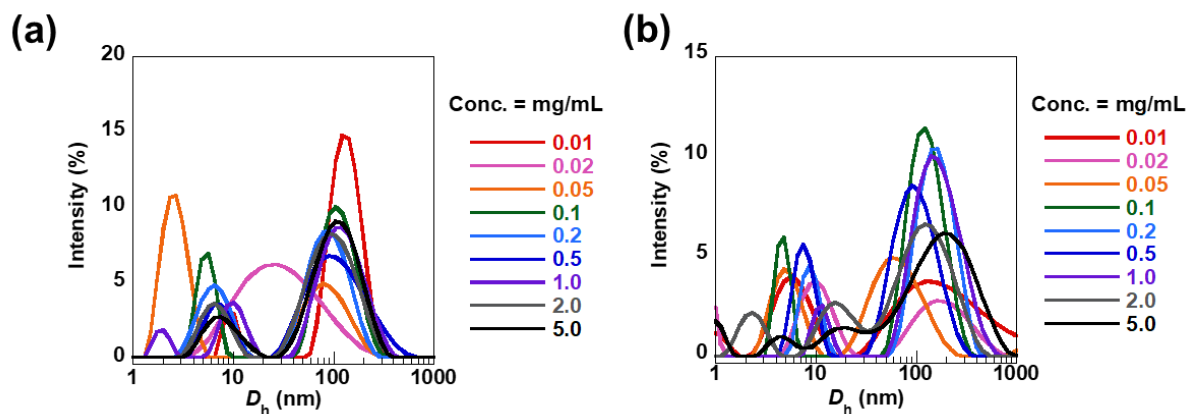
Sample	pH value	QY (%)
PVAm	7	1.4
PVAm- <i>b</i> -PAPhePheOH	7	6.3
P(VAm- <i>co</i> -APhePheOH)	7	4.8
PAPhePheOH	12	1.2
PVAm- <i>b</i> -PAPhePheOH	12	1.6
P(VAm- <i>co</i> -APhePheOH)	12	1.9



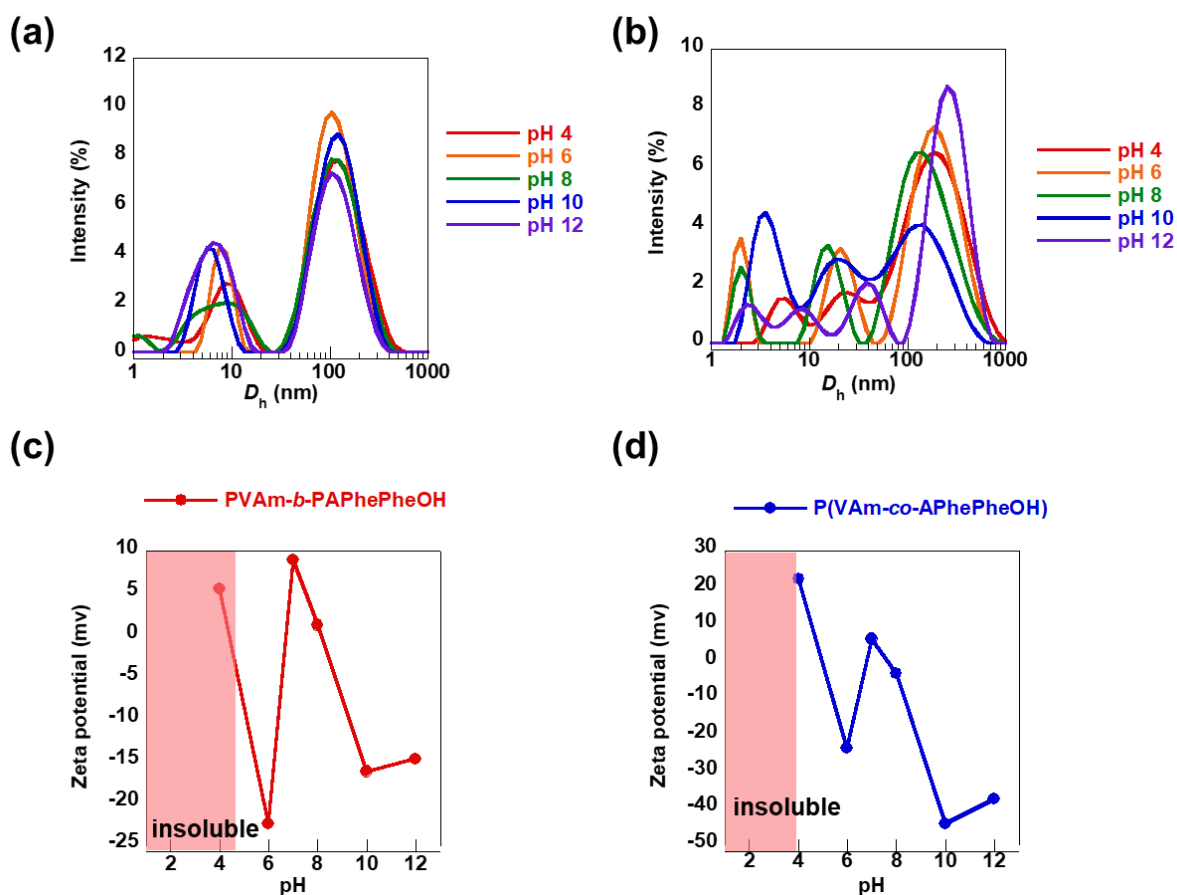
**Figure S5.** Excitation wavelength-dependent emission of (a) PVAm-*b*-PAPhePheOH and (b) P(VAm-*co*-APhePheOH) (conc. = 2.0 mg/mL, pH = 7).



**Figure S6.** CD spectra of (a) PVAm-*b*-PAPhePheOH and (b) P(VAm-*co*-APhePheOH) at different polymer concentrations in water (pH = 7).



**Figure S7.** DLS traces of (a) PVAm-*b*-PAPhePheOH and (b) P(VAm-*co*-APhePheOH) at different polymer concentrations in water (pH = 7).

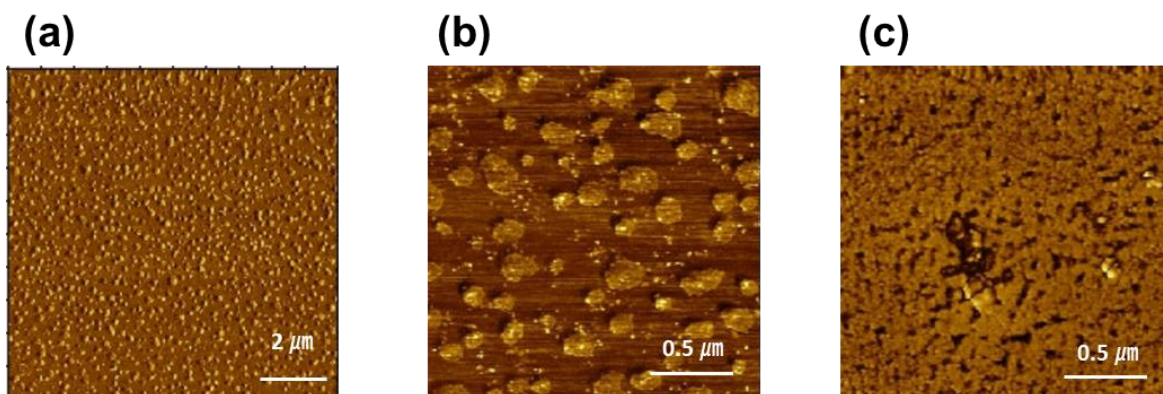


**Figure S8.** pH-Dependent (a, b) DLS traces and (c, d) zeta potentials of (a, c) PVAm-*b*-PAPhePheOH and (b, d) P(VAm-*co*-APhePheOH) in aqueous solution at different pHs (conc. = 2.0 mg/mL).

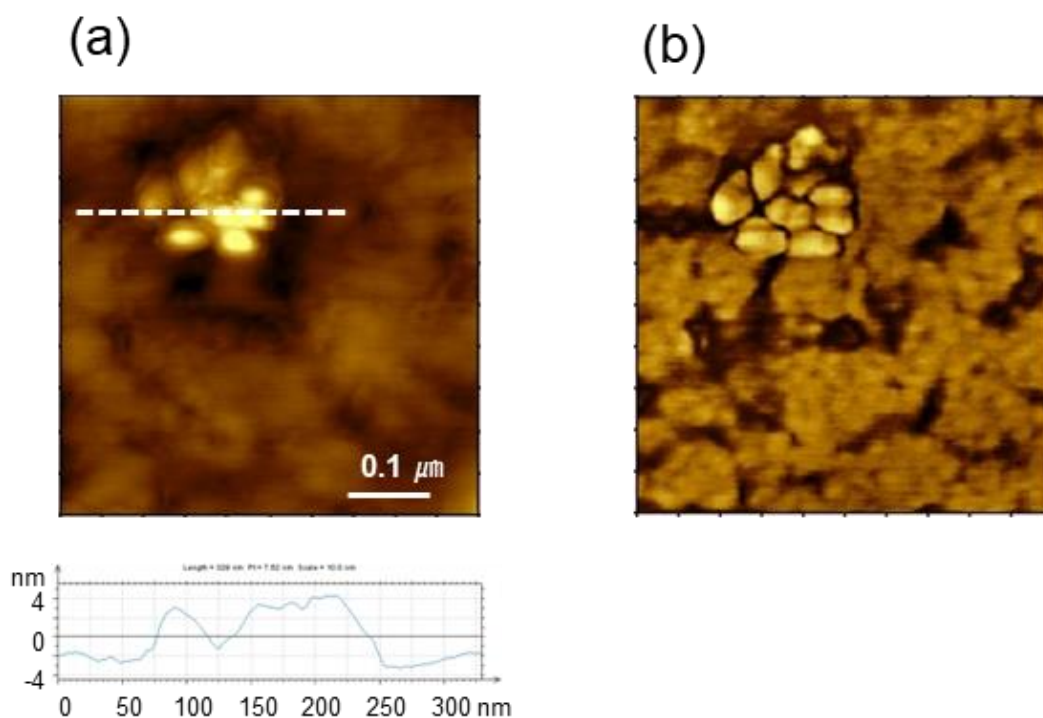
**Table S6.** DLS and zeta potential results of PVAm-*b*-PAPhePheOH and P(VAm-*co*-APhePheOH) in aqueous solutions at different pHs

pH	PVAm- <i>b</i> -PAPhePheOH		P(VAm- <i>co</i> -APhePheOH)	
	$D_h$ (nm)	Zeta potential (mv)	$D_h$ (nm)	Zeta potential (mv)
4	1.7, 9.2, 141.2	5.48	6.0, 23.2, 221.8	39.9
6	8.1, 122.0	-22.4	2.0, 21.8, 221.7	-23.7
7	6.8, 109.7	8.96	1.5, 14.8, 136.0	6.01
8	2.6, 9.8, 128.0	1.18	2.1, 16.0, 182.0	-3.43
10	6.2, 131.5	-15.2	4.2, 22.9, 154.1	-44.2
12	6.7, 124.1	-14.7	5.3, 24.3, 141.6	-35.7

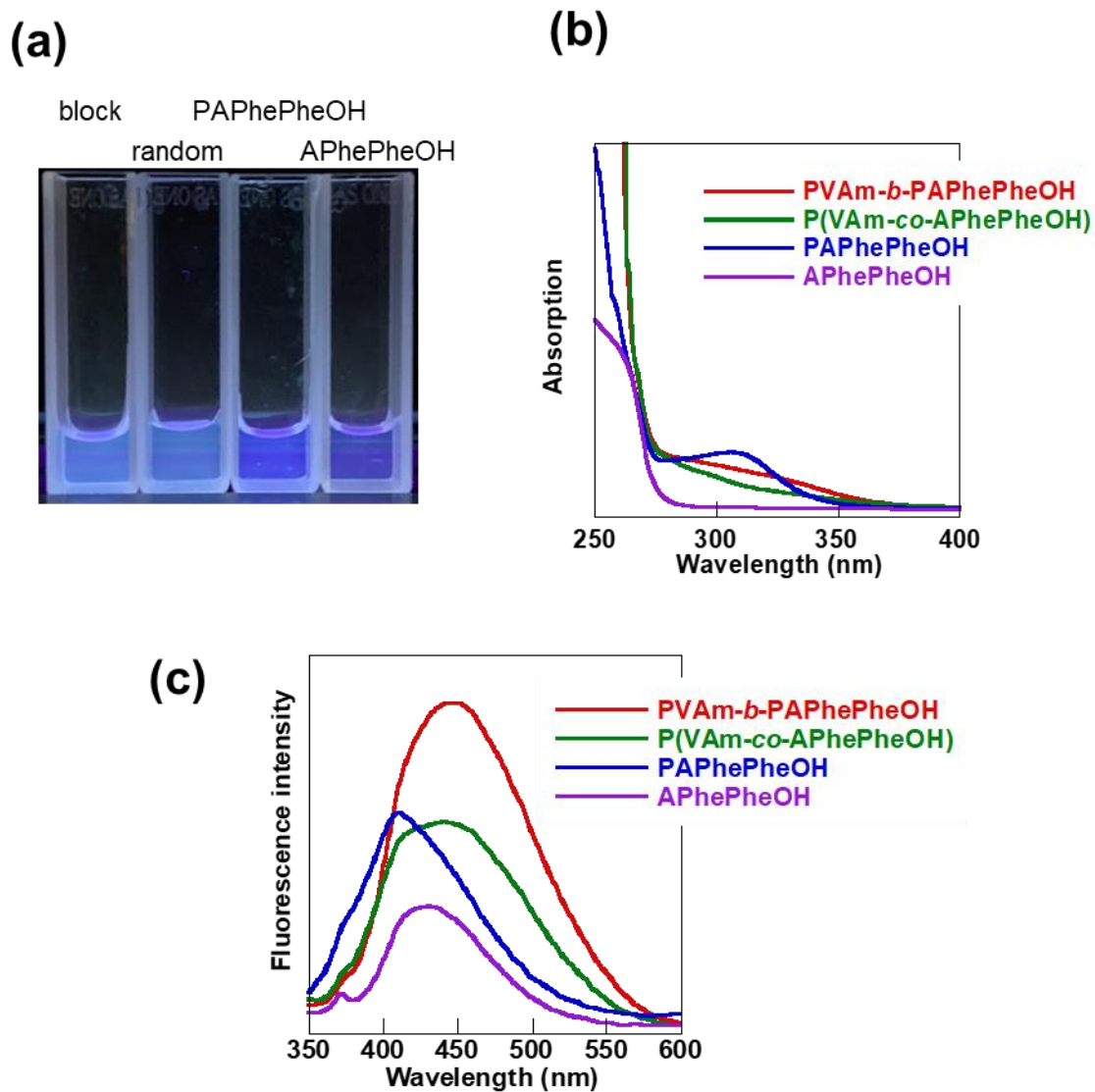




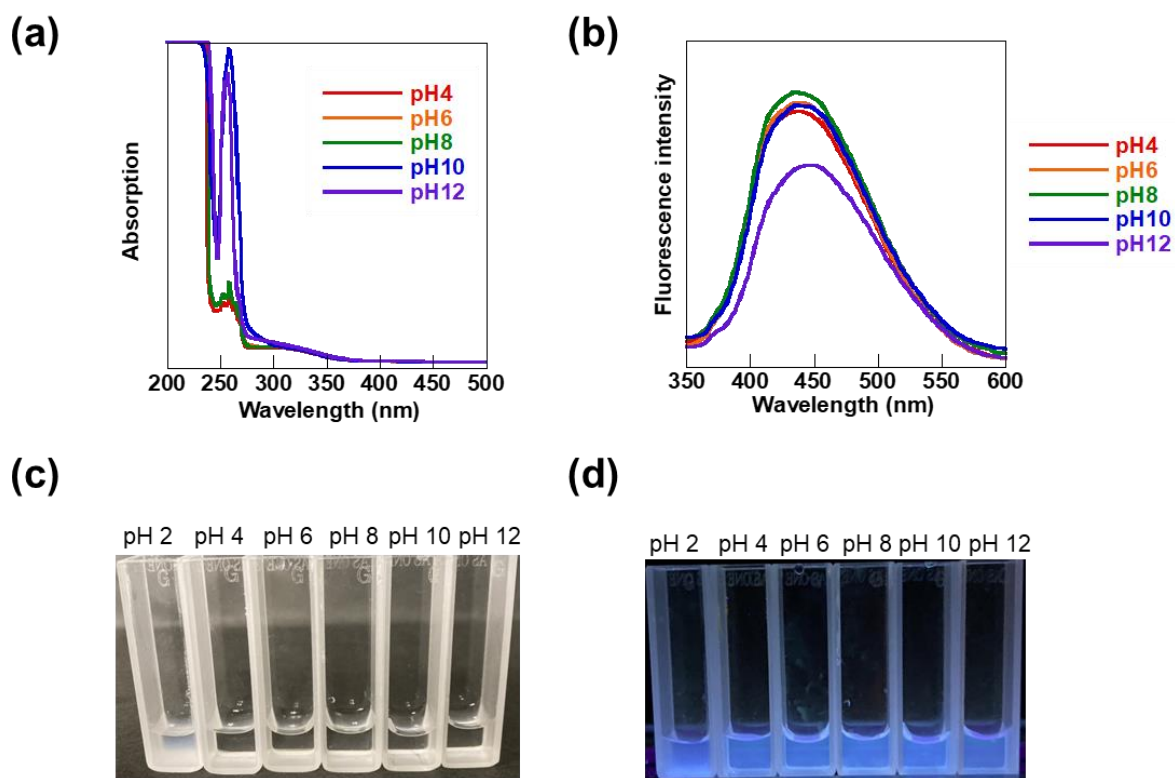
**Figure S9.** Atomic force microscopy (AFM) phase images of (a,b) PVAm-*b*-PAPhePheOH and (c) P(VAm-*co*-APhePheOH), corresponding to the height images shown in Figures 4e-g. Z-range = (a) 25.0 deg, (b) 22.5 deg, and (c) 47.5 deg. The samples were prepared from aqueous solution (pH = 7, conc. = 2.0 mg/mL).



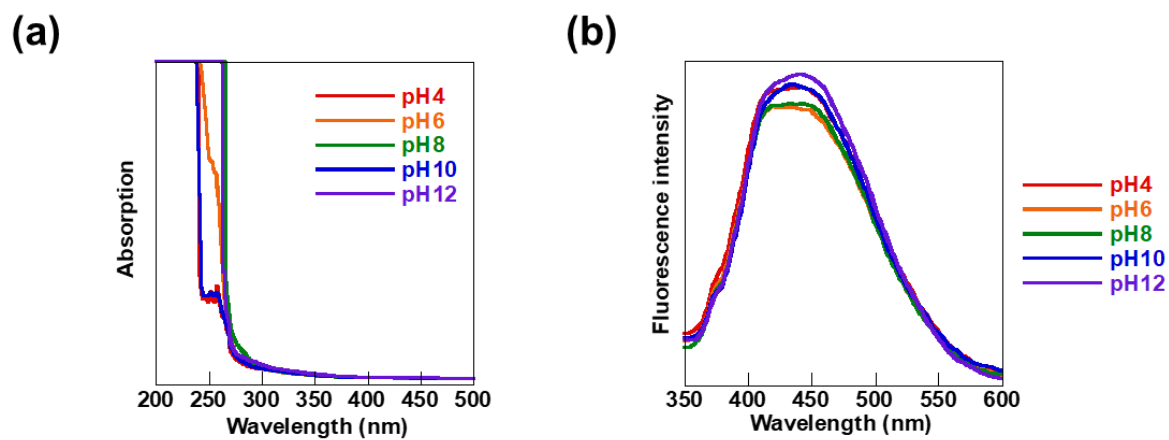
**Figure S10.** Atomic force microscopy (AFM) (a) height and (b) phase images of P(VAm-*co*-APhePheOH). The sample was prepared from aqueous solution (pH = 7, conc. = 2.0 mg/mL). (a) Cross section through the line indicated by the dotted line in the AFM height image.



**Figure S11.** (a) Photograph, and (b) absorption and (c) fluorescence spectra of PVAm-*b*-PAPhePheOH, P(VAm-*co*-APhePheOH), PAPhePheOH, and APhePheOH in a basic water (pH = 12, conc. = 2.0 mg/mL,  $\lambda_{\text{ex}} = 330$  nm).



**Figure S12.** pH-Dependent emission behavior of PVAm-*b*-PAPhePheOH, (a) UV-vis spectra, (b) fluorescence spectra ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ), (c, d) photographs of aqueous solutions under (c) daylight and (d) UV light at 330 nm (conc. = 2.0 mg/mL).

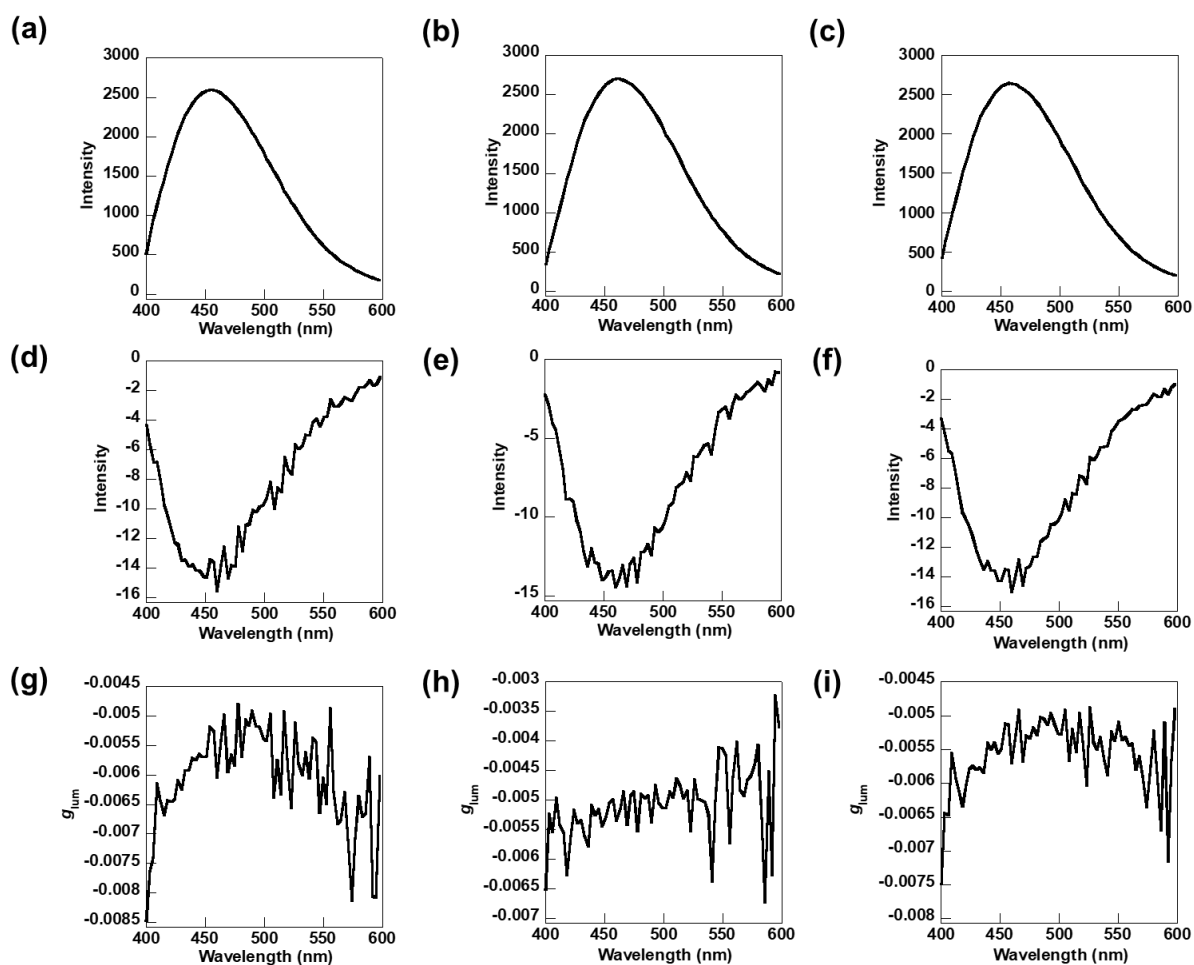


**Figure S13.** pH-Dependent emission behavior of P(VAm-co-APhePheOH), (a) UV-vis spectra, (b) fluorescence spectra ( $\lambda_{\text{ex}} = 330$  nm, conc. = 2.0 mg/mL).

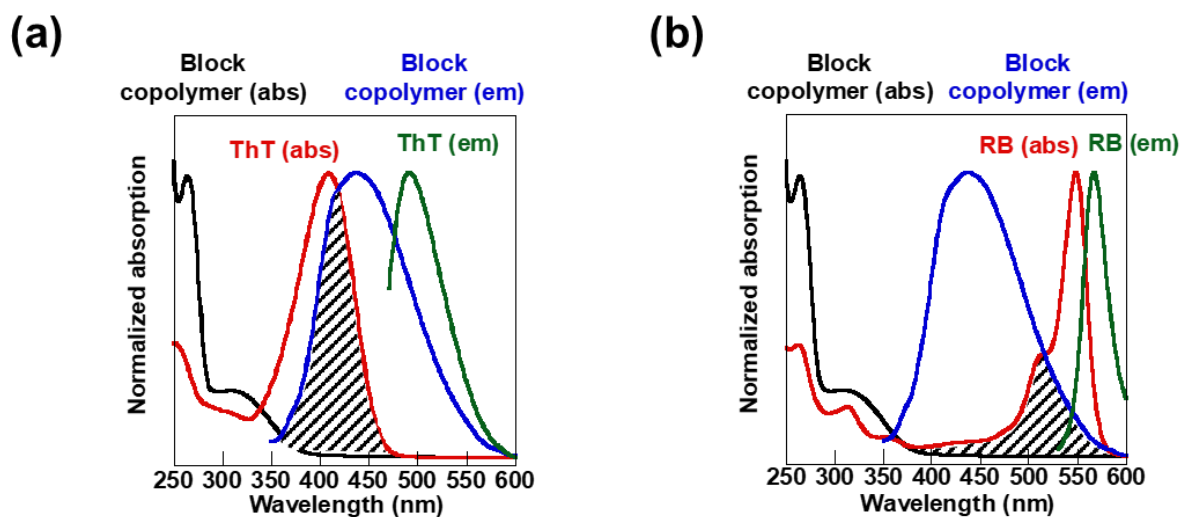
**Table S7.** The emission dissymmetry factor ( $g_{lum}$ ) of PVAm-*b*-PAPhePheOH at different states<sup>a)</sup>

States	Maximal emission wavelength (nm)	$g_{lum}$
Solution	422	+0.000200
Suspension	451	-0.000241
Thin film	457	-0.00513

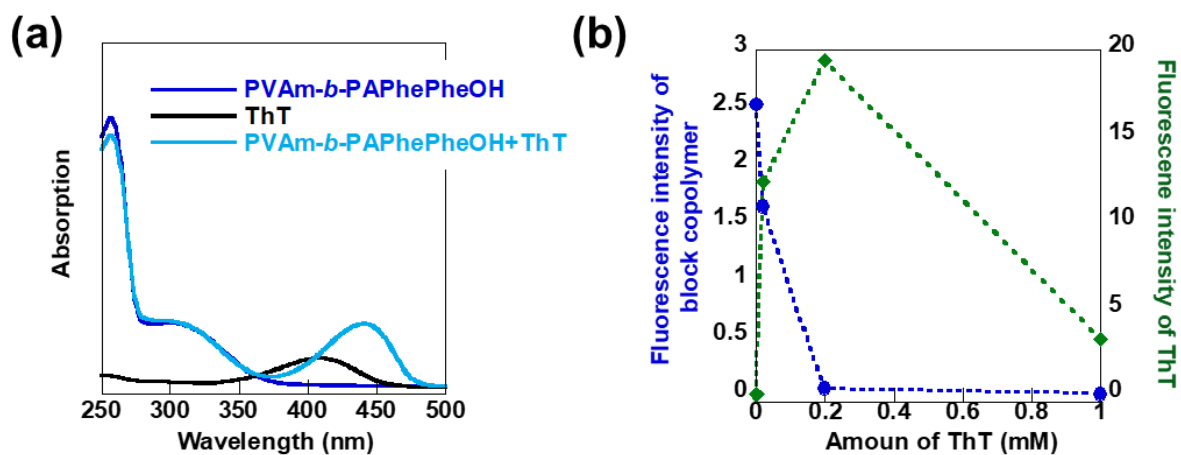
<sup>a)</sup> Solution: water (conc. = 2.0 mg/mL, pH = 7), suspension: water/THF = 4/96 (conc. = 2.0 mg/mL), and thin film prepared at concentrated aqueous solution (conc. = 20.0 mg/mL).



**Figure S14.** (a–c) Fluorescence, (d–f) CPL, and (g–i)  $g_{lum}$  spectra of PVAm-*b*-PAPhePheOH thin film measured at (a, d, g) “vertical” and (b, e, h) “horizontal” orientations of the films with the backside of film face positioned orthogonally to the excitation light beam and those obtained by averaging the horizontal and vertical data (c, f, i) [ $\lambda_{ex} = 350$  nm].



**Figure S15.** Normalized absorbance and fluorescence spectra of (a) PVAm-*b*-PAPhePheOH and Thioflavin T (ThT) and (b) PVAm-*b*-PAPhePheOH and Rose Bengal (RB) in water.



**Figure S16.** (a) UV-vis spectra and (b) plots of fluorescence intensity of PVAm-*b*-PAPhePheOH and Thioflavin T (ThT) in water (polymer conc. = 2.0 mg/mL).

**Table S8.** Fluorescence quantum yield and FRET efficacy of PVAm-*b*-PAPhePheOH + ThT

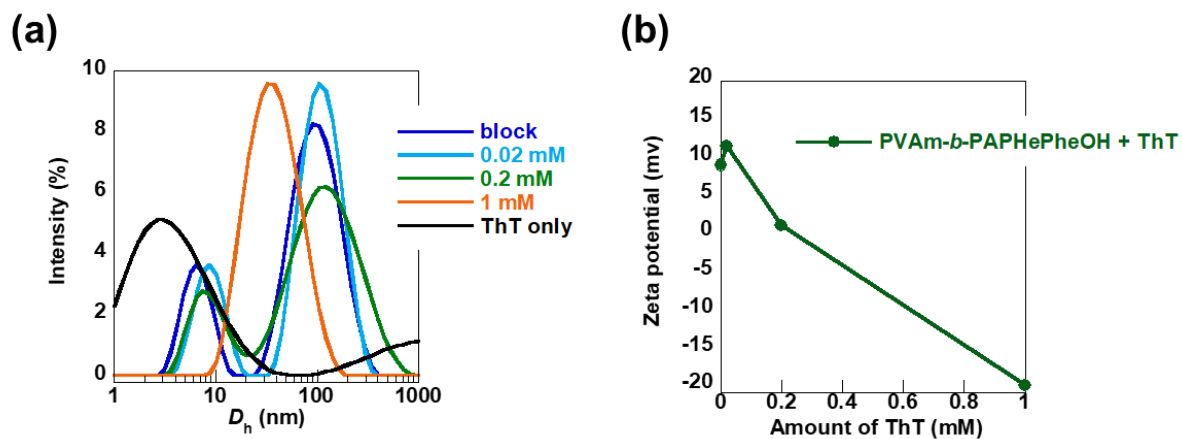
Sample	QY (%)	FRET Efficacy
PVAm- <i>b</i> -PAPhePheOH	6.3	-
PVAm- <i>b</i> -PAPhePheOH + ThT (0.02 mM)	18.5	0.352
PVAm- <i>b</i> -PAPhePheOH + ThT (0.2 mM)	25.6	0.979
PVAm- <i>b</i> -PAPhePheOH + ThT (1 mM)	5.8	0.998

**Table S9.** The absorbance dissymmetry factor ( $g_{\text{abs}}$ ) of PVAm-*b*-PAPhePheOH + ThT solutions <sup>a)</sup>

Sample (solution)	Wavelength (nm)	$ g_{\text{abs}} $
PVAm- <i>b</i> -PAPhePheOH + ThT (0.02 mM)	456	$6.98 \times 10^{-5}$
PVAm- <i>b</i> -PAPhePheOH + ThT (0.2 mM)	422	$1.66 \times 10^{-4}$
PVAm- <i>b</i> -PAPhePheOH + ThT (1 mM)	475	$4.08 \times 10^{-4}$

<sup>a)</sup> Polymer conc. = 2.0 mg/mL.



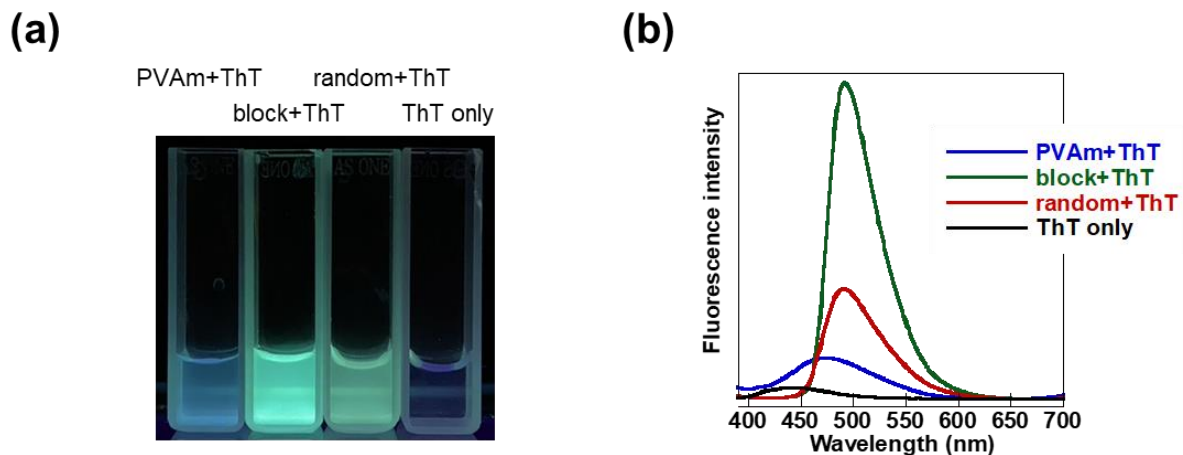


**Figure S17.** (a) DLS traces and (b) zeta potential of PVAm-*b*-PAPhePheOH and Thioflavin T (ThT) at different ThT concentrations (polymer conc. = 2.0 mg/mL).

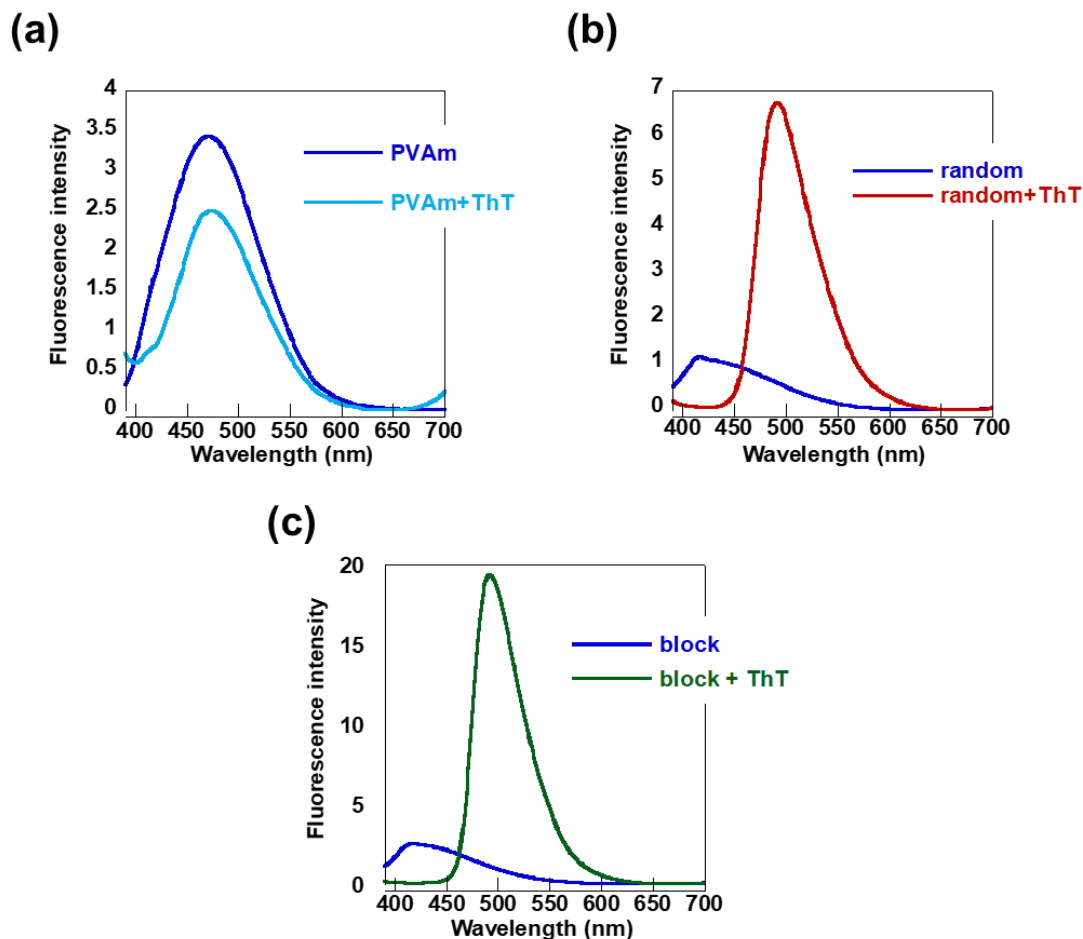
**Table S10.** DLS and zeta potential of PVAm-*b*-PAPhePheOH + ThT solutions <sup>a)</sup>

ThT content (mM)	$D_h$ (nm)	Zeta potential (mv)
0	6.8, 109.7	8.96
0.02	9.0, 120.0	11.5
0.2	9.5, 143.3	1.05
1	42.9	-19.9

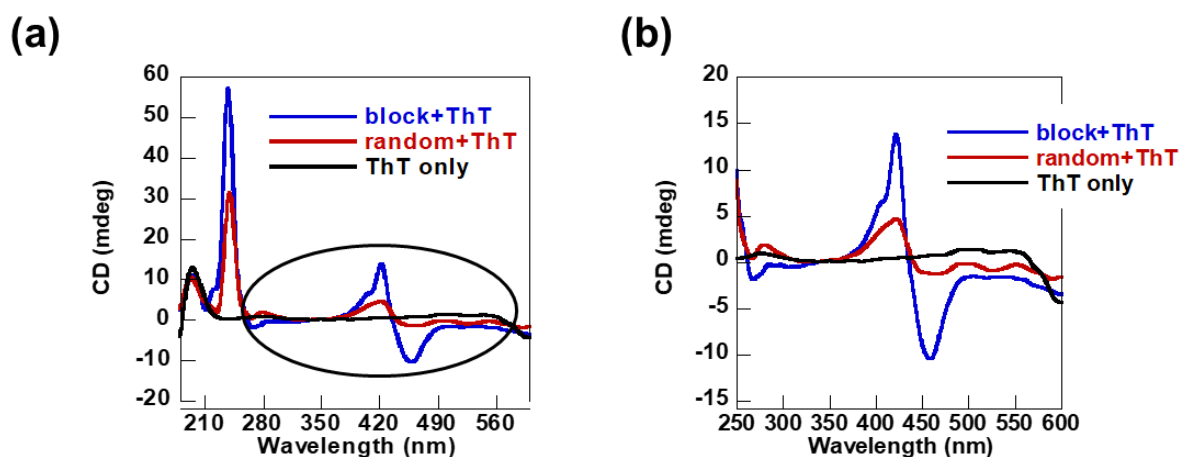
<sup>a)</sup> Polymer conc. = 2.0 mg/mL.



**Figure S18.** (a) Photograph and (b) fluorescence spectra of PVAm, block (PVAm-*b*-PAPhePheOH) and random (P(VAm-*co*-APhePheOH)) copolymers with ThT solutions (polymer conc. = 2.0 mg/mL, ThT conc. = 0.2 mM,  $\lambda_{\text{ex}}$  = 365 nm).



**Figure S19.** Fluorescence spectra of (a) PVAm with ThT, (b) P(VAm-*co*-APhePheOH) with ThT, and (c) PVAm-*b*-PAPhePheOH with ThT in aqueous solution (polymer conc. = 2.0 mg/mL,  $\lambda_{\text{ex}}$  = 365 nm).

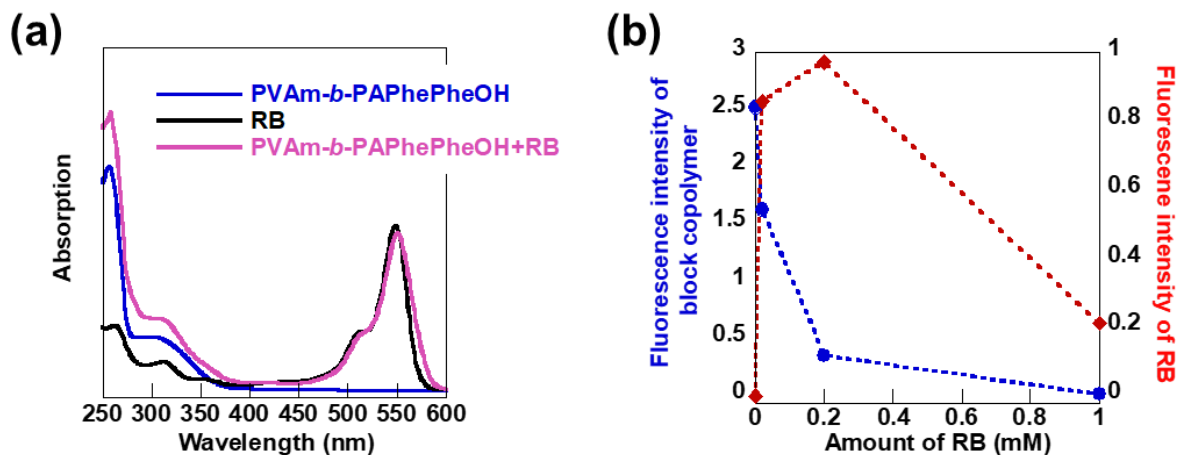


**Figure S20.** CD spectra of block (PVAm-*b*-PAPhePheOH) and random (P(VAm-*co*-APhePheOH)) copolymers with ThT solutions (polymer conc. = 2.0 mg/mL, ThT conc. = 0.2 mM). (b) Magnified CD spectra of the region inside the black circle.

**Table S11.** The absorbance dissymmetry factor ( $g_{\text{abs}}$ ) of VAm/APhePheOH copolymers + ThT solutions <sup>a)</sup>

Sample (solution)	Wavelength (nm)	$ g_{\text{abs}} $
PVAm- <i>b</i> -PAPhePheOH + ThT (0.2 mM)	422	$1.66 \times 10^{-4}$
P(VAm- <i>co</i> -APhePheOH) + ThT (0.2 mM)	422	$5.04 \times 10^{-5}$
ThT only	-	-

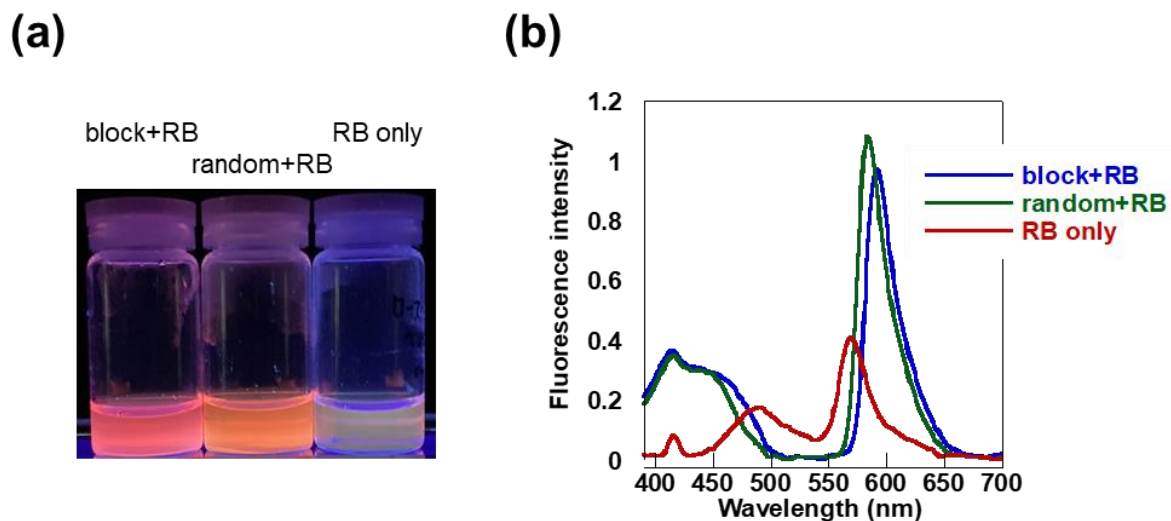
<sup>a)</sup> Polymer conc. = 2.0 mg/mL.



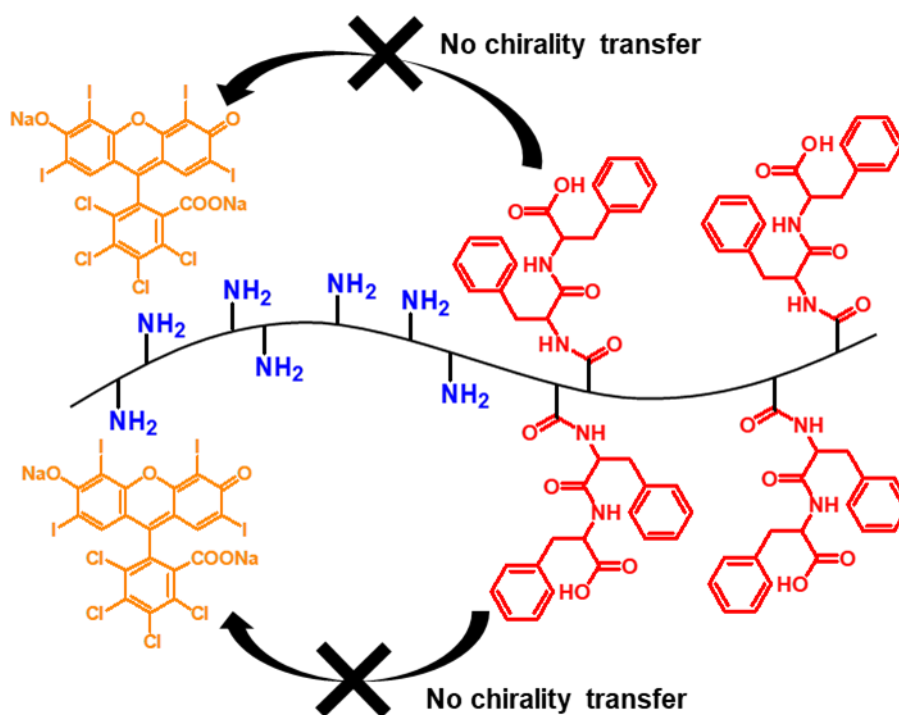
**Figure S21.** (a) UV-vis spectra and (b) plots of fluorescence intensity of PVAm-*b*-PAPhePheOH and Rose Bengal (RB) in water (polymer conc. = 2.0 mg/mL).

**Table S12.** Fluorescence quantum yield and FRET efficacy of PVAm-*b*-PAPhePheOH + RB

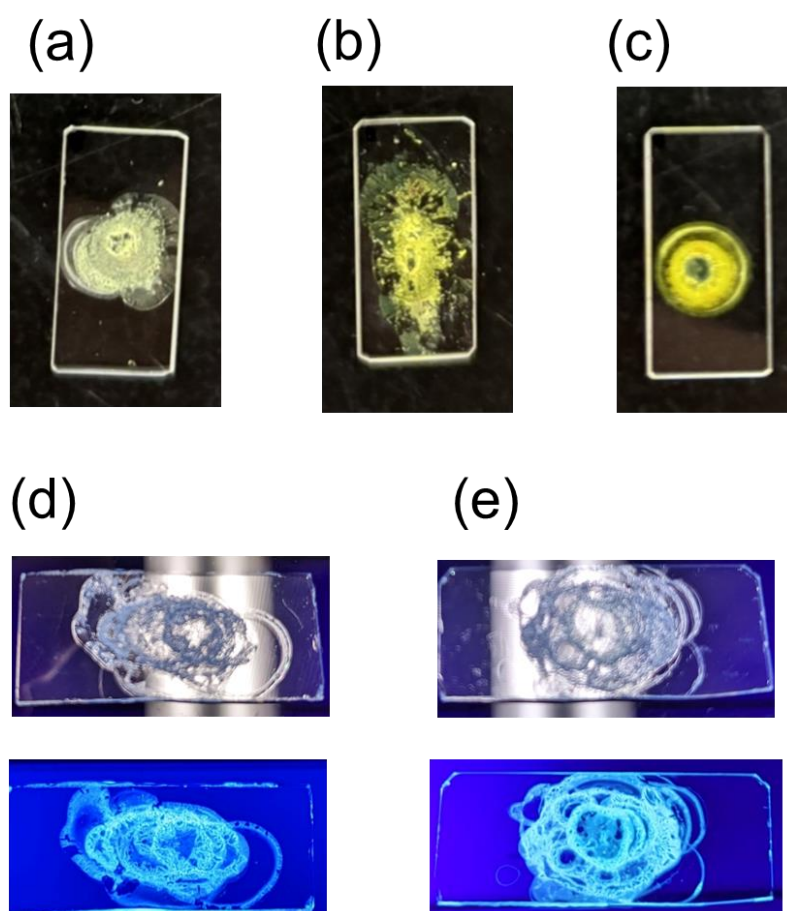
Sample	QY (%)		FRET Efficacy
	PVAm- <i>b</i> -PAPhePheOH	RB	
PVAm- <i>b</i> -PAPhePheOH	6.3	-	-
PVAm- <i>b</i> -PAPhePheOH + RB (0.02 mM)	2.7	0.3	0.353
PVAm- <i>b</i> -PAPhePheOH + RB (0.2 mM)	2.2	1.0	0.859
PVAm- <i>b</i> -PAPhePheOH + RB (1 mM)	0.7	1.0	0.994



**Figure S22.** (a) Photograph and (b) fluorescence spectra of block (PVAm-*b*-PAPhePheOH) and random (P(VAm-*co*-APhePheOH)) copolymers with RB solutions (polymer conc. = 2.0 mg/mL, RB conc. = 0.2 mM,  $\lambda_{\text{ex}}$  = 365 nm).



**Figure S23.** Schematic illustration of no chirality transfer from PVAm-*b*-PAPhePheOH to RB.



**Figure S24.** Photographs of (a-c) PVAm-*b*-PAPhePheOH/ThT films used for CPL measurements. The samples were prepared by drop-casting from the aqueous solution (10.0 mg/mL) with ThT (conc. = (a) 0.02 mM, (b) 0.2 mM, and 1.0 mM), followed by annealing at 100°C. Photographs of (d) PVAm-*b*-PAPhePheOH and (e) PVAm-*b*-PAPhePheOH/ThT films taken under room light and 365 nm UV light. The samples were prepared by drop-casting from (d) the aqueous solution (5.0 mg/mL) and (e) the aqueous solution (2.0 mg/mL) with ThT (0.02 mM).

**Table S13.** The emission dissymmetry factor ( $g_{lum}$ ) of PVAm-*b*-PAPhePheOH + ThT (0.2 mM) at different states <sup>a)</sup>

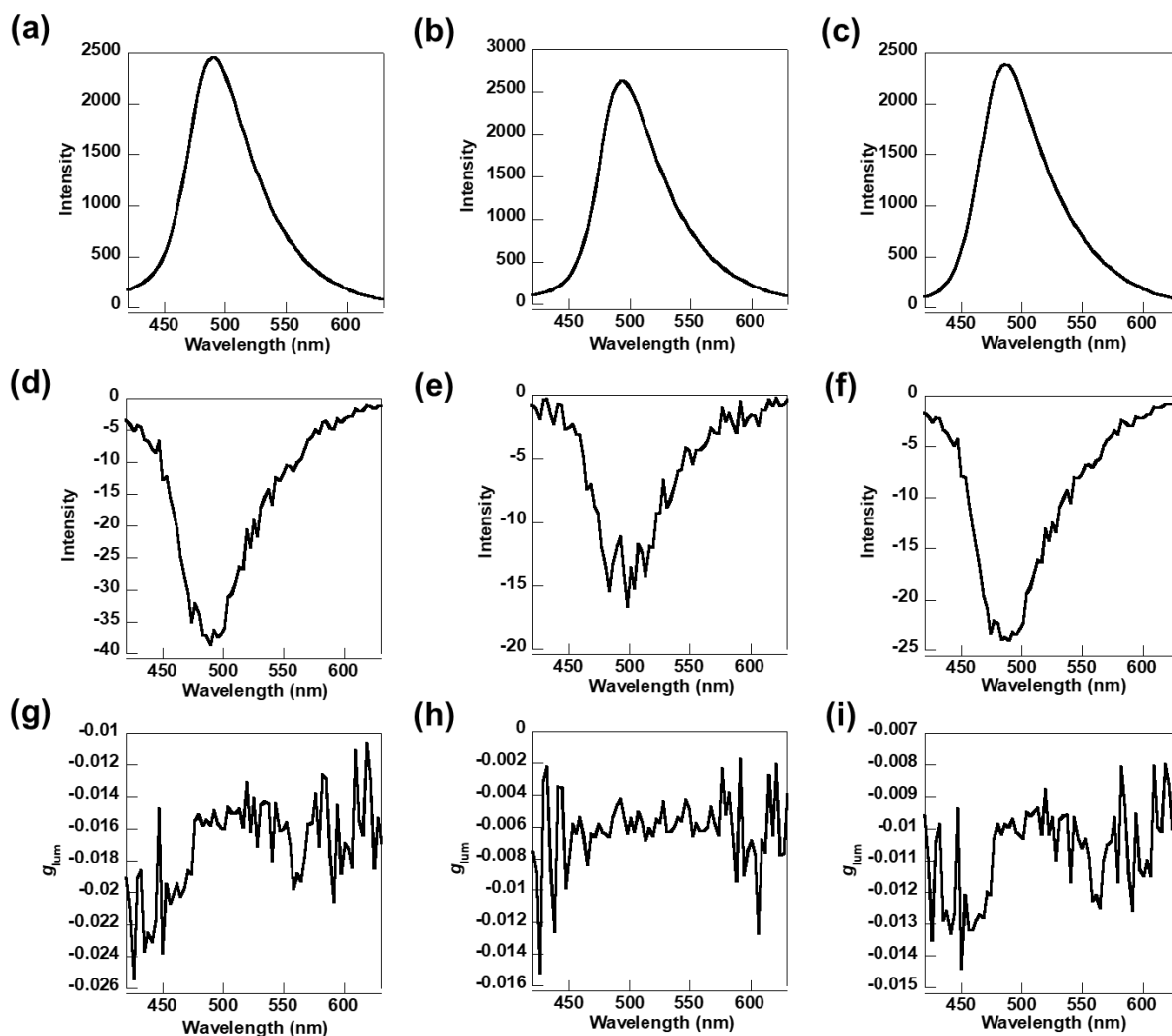
States	Maximal emission wavelength (nm)	$g_{lum}$
Solution	480	-0.000971
Thin film	500	-0.00577

<sup>a)</sup> Polymer conc. = 10.0 mg/mL.

**Table S14.** The emission dissymmetry factor ( $g_{lum}$ ) of PVAm-*b*-PAPhePheOH + ThT at different ThT ratios <sup>a)</sup>

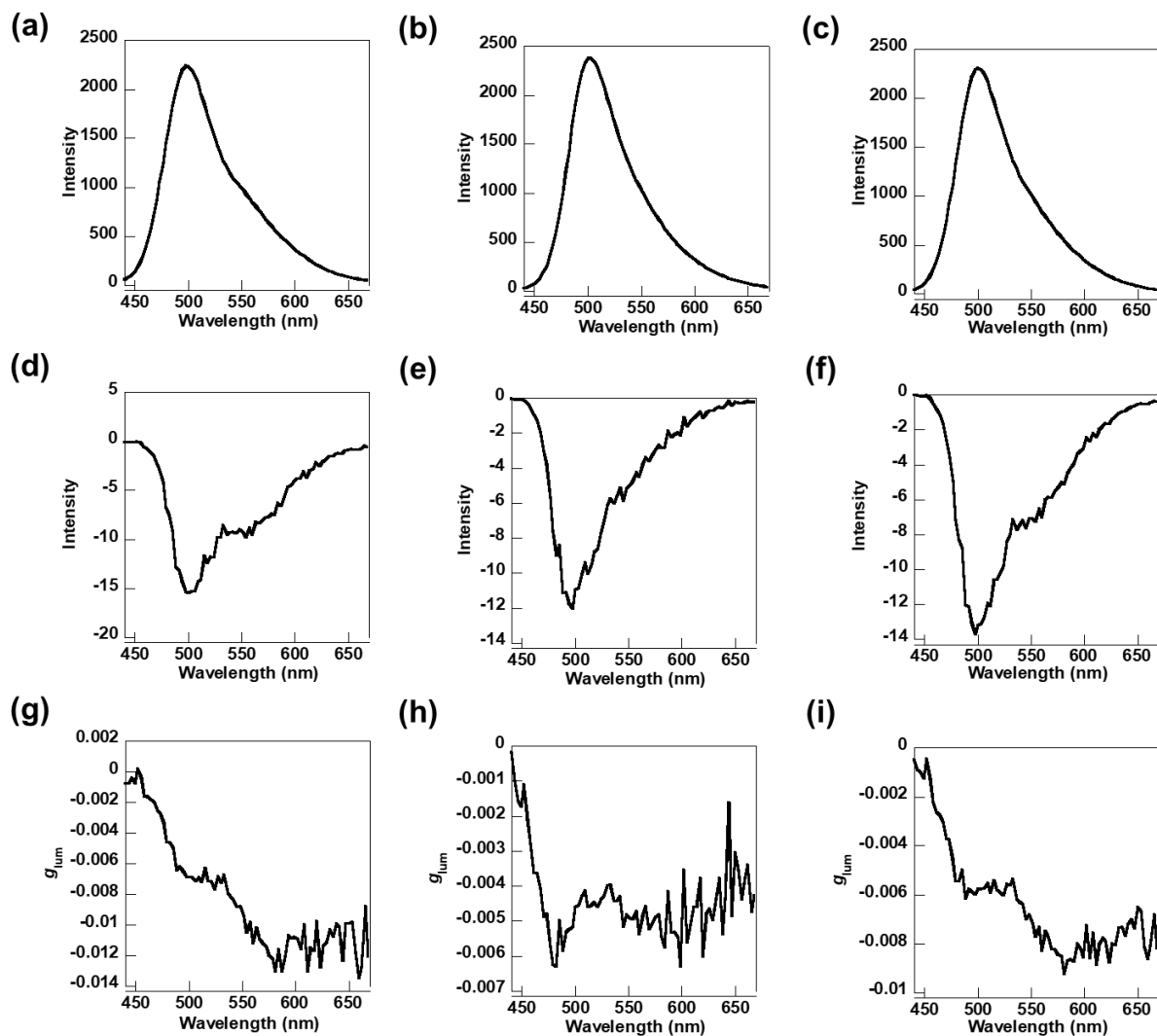
Sample (thin film)	Maximal emission wavelength (nm)	$g_{lum}$
PVAm- <i>b</i> -PAPhePheOH	457	-0.00513
PVAm- <i>b</i> -PAPhePheOH + ThT (0.02 mM)	486	-0.00985
PVAm- <i>b</i> -PAPhePheOH + ThT (0.2 mM)	500	-0.00577
PVAm- <i>b</i> -PAPhePheOH + ThT (1 mM)	511	-0.00451

<sup>a)</sup> Polymer conc. = 10.0 mg/mL.

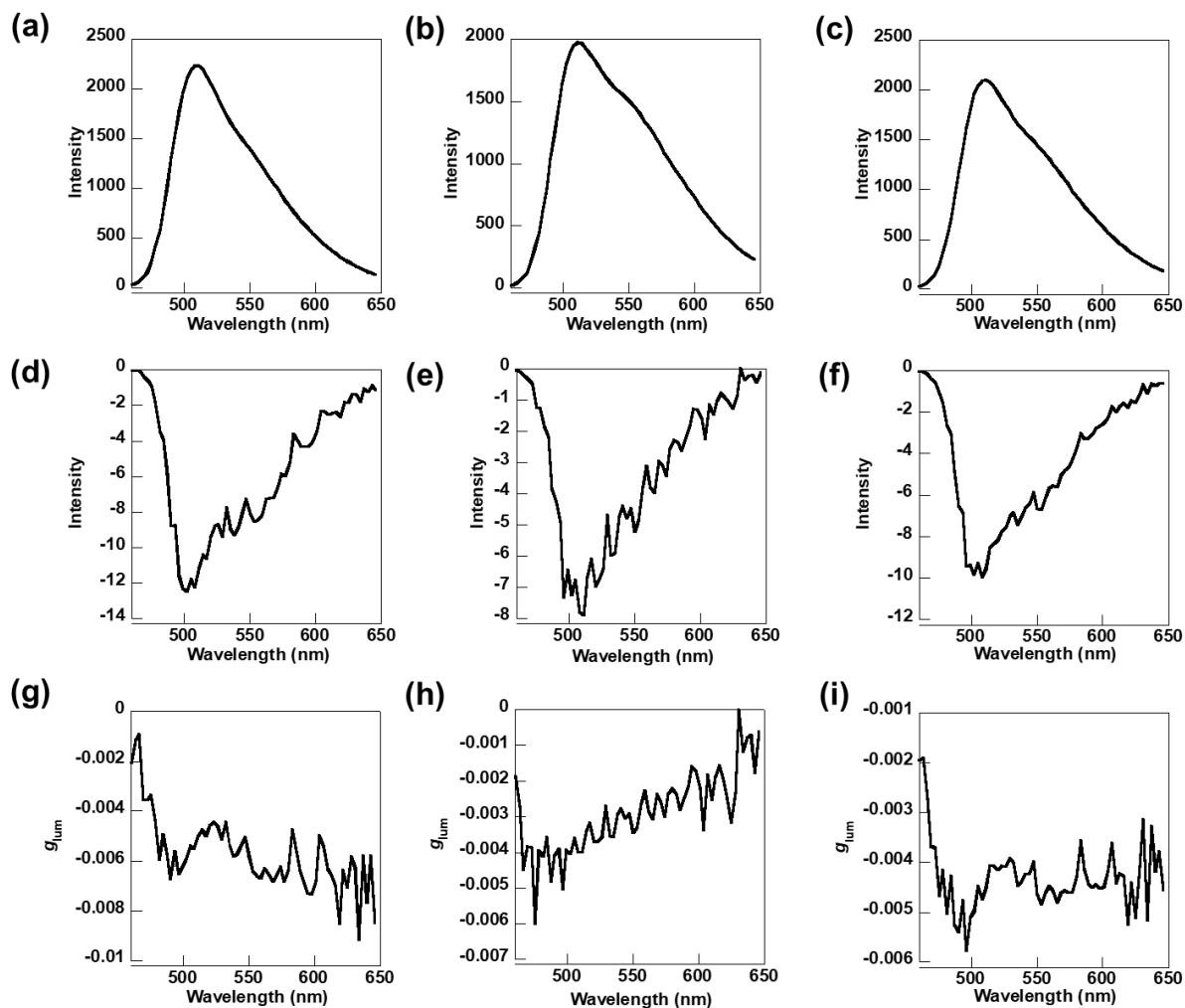


**Figure S25.** (a–c) Fluorescence, (d–f) CPL, and (g–i)  $g_{lum}$  spectra of PVAm-*b*-PAPhePheOH + ThT thin film measured at (a, d, g) “vertical” and (b, e, h) “horizontal” orientations of the films with the backside of film face positioned orthogonally to the excitation light beam and those obtained by averaging the horizontal and vertical data (c, f, i) [ $\lambda_{ex} = 350$  nm, ThT conc. = 0.02 mM].

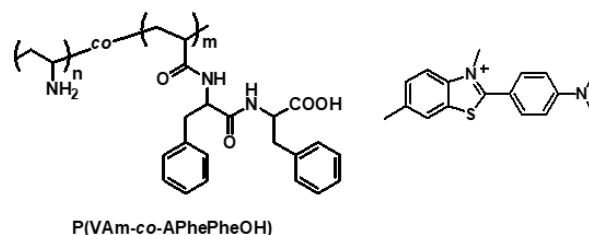




**Figure S26.** (a–c) Fluorescence, (d–f) CPL, and (g–i)  $g_{lum}$  spectra of PVAm-*b*-PAPhePheOH + ThT thin film measured at (a, d, g) “vertical” and (b, e, h) “horizontal” orientations of the films with the backside of film face positioned orthogonally to the excitation light beam and those obtained by averaging the horizontal and vertical data (c, f, i) [ $\lambda_{ex} = 350$  nm, ThT conc. = 0.2 mM].



**Figure S27.** (a–c) Fluorescence, (d–f) CPL, and (g–i)  $g_{\text{lum}}$  spectra of PVAm-*b*-PAPhePheOH + ThT thin film measured at (a, d, g) “vertical” and (b, e, h) “horizontal” orientations of the films with the backside of film face positioned orthogonally to the excitation light beam and those obtained by averaging the horizontal and vertical data (c, f, i) [ $\lambda_{\text{ex}} = 350$  nm, ThT conc. = 1 mM].

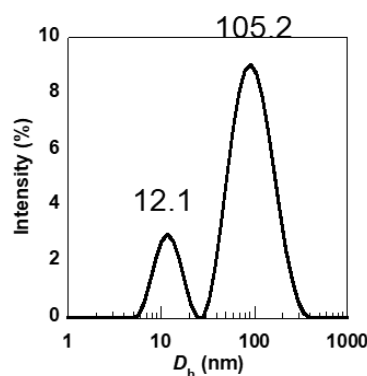
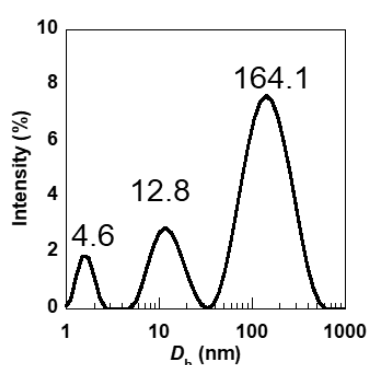


**(a) Method 1**

- ① P(VAm-co-APhePheOH)  
+ ② ThT (0.2 mM)

**(b) Method 2**

- ① ThT (0.2 mM)  
+ ② P(VAm-co-APhePheOH)



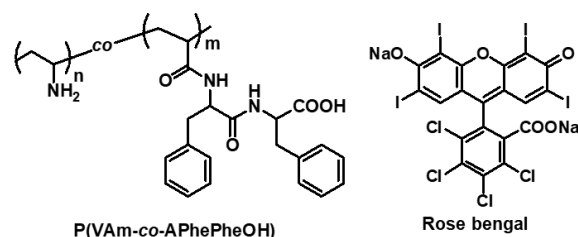
**Figure S28.** DLS traces of P(VAm-co-PAPhePheOH) with ThT in water (pH = 7) prepared by different methods.

**Table S15.** DLS and zeta potential of P(VAm-co-PAPhePheOH) with ThT solutions

Method 1 <sup>a)</sup>		Method 2 <sup>b)</sup>	
$D_h$ (nm)	Zeta Potential (mV)	$D_h$ (nm)	Zeta Potential (mV)
4.6		12.1	
12.8	- 25.85	105.2	-36.6
164.1			

<sup>a)</sup> P(VAm-co-PAPhePheOH) was dissolved in an aqueous solution at pH = 7 (conc. = 2.0 mg/mL) and then ThT aqueous solution (pH = 7, 0.2 mM) was added to the polymer solution.

<sup>b)</sup> ThT aqueous solution (pH = 7, 0.2 mM) was prepared initially, and then P(VAm-co-PAPhePheOH) aqueous solution (pH = 7, conc. = 2.0 mg/mL) was added to the ThT solution.

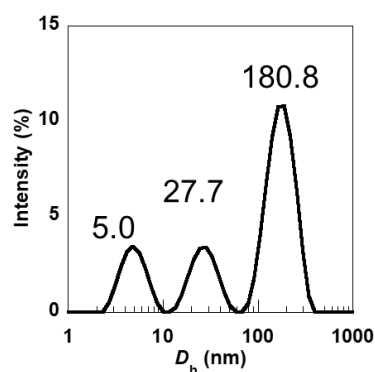
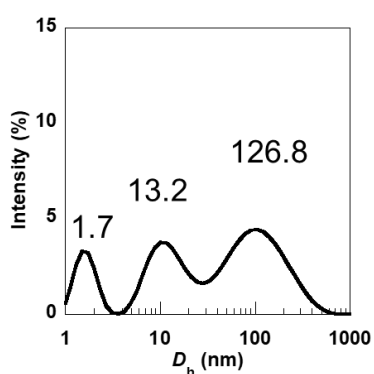


**(a) Method 1**

- ① P(VAm-co-PAPhePheOH)  
+ ② BR (0.2 mM)

**(b) Method 2**

- ① BR (0.2 mM)  
+ ② P(VAm-co-PAPhePheOH)



**Figure S29.** DLS traces of P(VAm-co-PAPhePheOH) with RB in water (pH = 7) prepared by different methods.

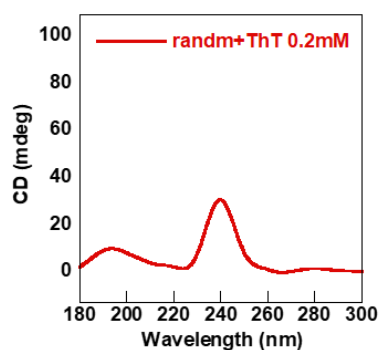
**Table S16.** DLS and zeta potential of P(VAm-co-PAPhePheOH) with RB solutions

Method 1 <sup>a)</sup>		Method 2 <sup>b)</sup>	
$D_h$ (nm)	Zeta Potential (mV)	$D_h$ (nm)	Zeta Potential (mV)
1.6		5.0	
13.2	-14.7	27.7	-34.8
126.8		180.8	

<sup>a)</sup> P(VAm-co-PAPhePheOH) was dissolved in an aqueous solution at pH = 7 (conc. = 2.0 mg/mL) and then RB aqueous solution (pH = 7, 0.2 mM) was added to the polymer solution. <sup>b)</sup> RB aqueous solution (pH = 7, 0.2 mM) was prepared initially, and then P(VAm-co-PAPhePheOH) aqueous solution (pH = 7, conc. = 2.0 mg/mL) was added to the RB solution.

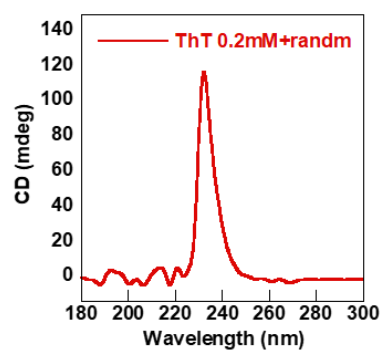
**(a) Method 1**

① P(VAm-co-PAPhePheOH) + ② ThT



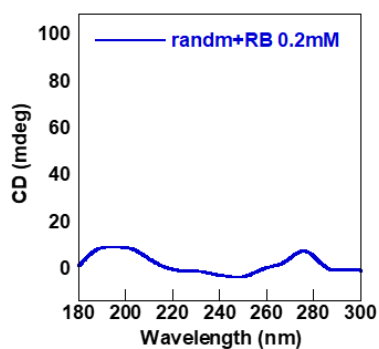
**(b) Method 2**

① ThT + ② P(VAm-co-PAPhePheOH)



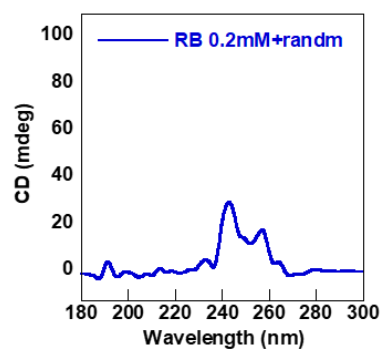
**(c) Method 1**

① P(VAm-co-PAPhePheOH) + ② RB



**(d) Method 2**

① RB + ② P(VAm-co-PAPhePheOH)



**Figure S30.** CD spectra P(VAm-co-APhePheOH) with (a,b) ThT solutions (polymer conc. = 2.0 mg/mL, ThT conc. = 0.2 mM), and (c,d) RB (polymer conc. = 2.0 mg/mL, RB conc. = 0.2 mM) prepared by different methods.

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