Supporting Information

Thermoinduced crystallization-driven self-assembly of bioinspired block copolymers in aqueous solution

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Results and Discussion

Table S1. Molecular parameters of all the polymers.

Samples	Feed ratio[a]	m/n[b]	Mn [c] (kDa)	Mn [d] (kDa)	Dispersity (*Đ*) [d]	X_{PNOG}[e]
$PNOG_{20}$	20	20	3.4	2.7	1.07	-
$PNAG_{95}$-*g*-EG_3	95	95	18.0	14.9	1.09	-
$PNAG_{78}$-*g*-EG_3	80	78	14.7	11.1	1.09	
$PNAG_{59}$-*g*-EG_3	60	59	11.2	8.8	1.06	-
$PNAG_{81}$-*b*-$PNOG_{52}$	95/60	81/52	16.6	12.4	1.16	0.39
$(PNAG\text{-}g\text{-}EG_3)_{81}$-*b*-$PNOG_{52}$	-	81/52	24.1	18.5	1.18	0.39
$PNAG_{102}$-*b*-$PNOG_{49}$	100/50	102/49	18.1	15.6	1.06	0.32
$(PNAG\text{-}g\text{-}EG_3)_{102}$-*b*-$PNOG_{49}$	-	102/49	27.6	19.7	1.10	0.32
$PNAG_{93}$-*b*-$PNOG_{40}$	95/30	93/40	15.8	12.3	1.12	0.30
$(PNAG\text{-}g\text{-}EG_3)_{93}$-*b*-$PNOG_{40}$		93/40	24.3	18.6	1.15	0.30
$PNAG_{59}$-*b*-$PNOG_{22}$	60/30	59/22	9.4	8.6	1.18	0.27
$(PNAG\text{-}g\text{-}EG_3)_{59}$-*b*-$PNOG_{22}$	-	59/22	14.9	11.8	1.24	0.27
$PNAG_{94}$-*b*-$PNOG_{15}$	95/20	94/15	11.6	9.7	1.11	0.14
$(PNAG\text{-}g\text{-}EG_3)_{94}$-*b*-$PNOG_{15}$	-	94/15	20.3	17.3	1.13	0.14
$PNAG_{142}$-*b*-$PNOG_{23}$	150/30	142/23	17.6	15.2	1.07	0.14
$(PNAG\text{-}g\text{-}EG_3)_{142}$-*b*-$PNOG_{23}$	-	142/23	30.7	21.2	1.09	0.14

[a] Feed molar ratio of PEG / Oct-NCA; [b] Calculated from ^{1}HNMR spectra; [c] Calculated from ^{1}HNMR spectra;[d] Determined from GPC, [e] Mole fraction of PNOG.

Table S2. DSC data for all the polymers.

Samples	ΔH_1 (J/g)	ΔH_2 (J/g)	T_1 (°C)	T_2(°C)	T_g (°C)
$PNAG_{95}$-*g*-EG_3	-	-	-	-	53.0
$PNOG_{20}$	12.3	25.2	50.8	163.5	-
$(PNAG\text{-}g\text{-}EG_3)_{81}$-*b*-$PNOG_{52}$	7.4	9.2	46.7	150.8	-
$(PNAG\text{-}g\text{-}EG_3)_{102}$-*b*-$PNOG_{49}$	3.0	2.7	46.8	147.6	-
$(PNAG\text{-}g\text{-}EG_3)_{93}$-*b*-$PNOG_{40}$	2.6	1.7	56.0	104.3	-
$(PNAG\text{-}g\text{-}EG_3)_{59}$-*b*-$PNOG_{22}$	5.5	-	60.5	-	-
$(PNAG\text{-}g\text{-}EG_3)_{142}$-*b*-$PNOG_{23}$	4.2	-	60.9	-	-
$(PNAG\text{-}g\text{-}EG_3)_{94}$-*b*-$PNOG_{15}$	2.3	-	53.3	-	-

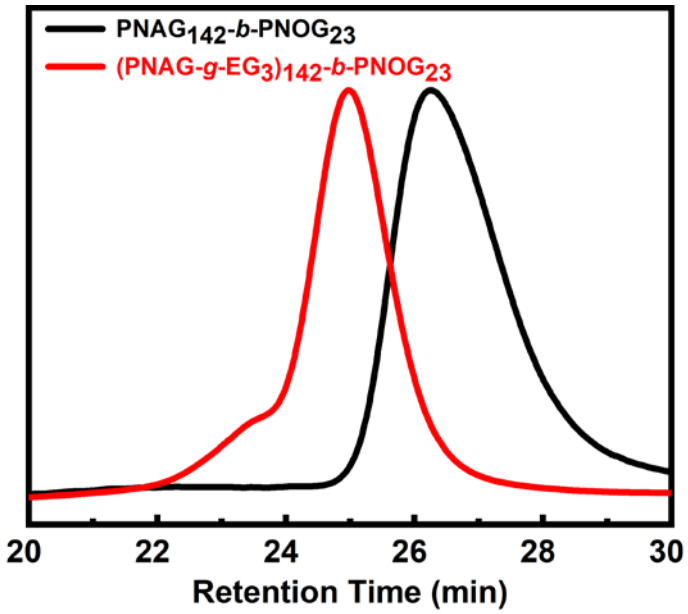

Figure S1. GPC chromatograms of the polymers. The molecular characteristics are shown in Table S1.

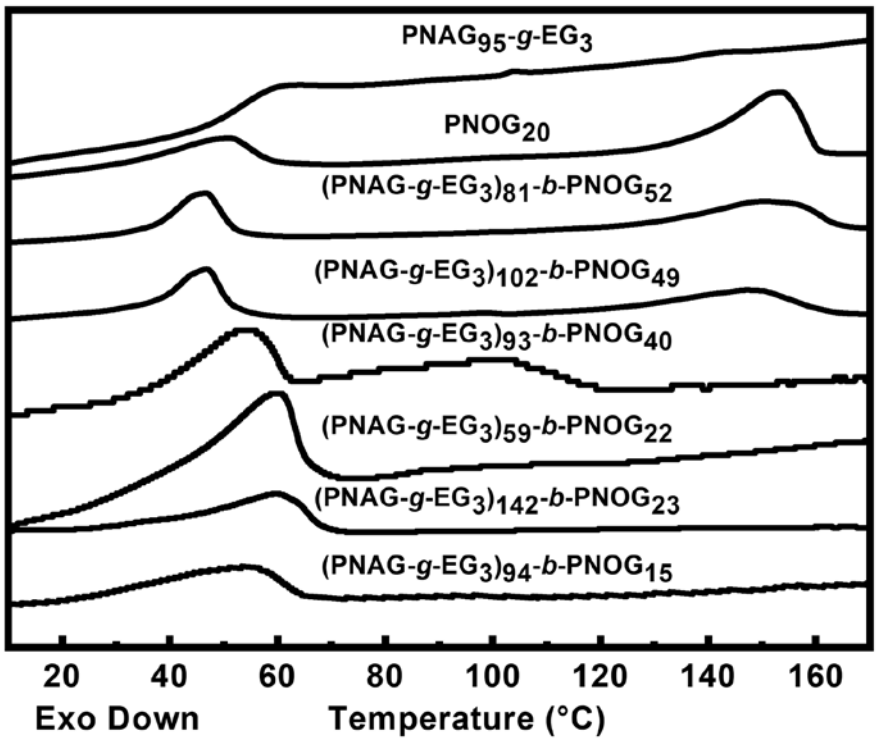

Figure S2. The DSC thermograms of all the polymers. The detailed information is summarized in Supplementary Table 2.

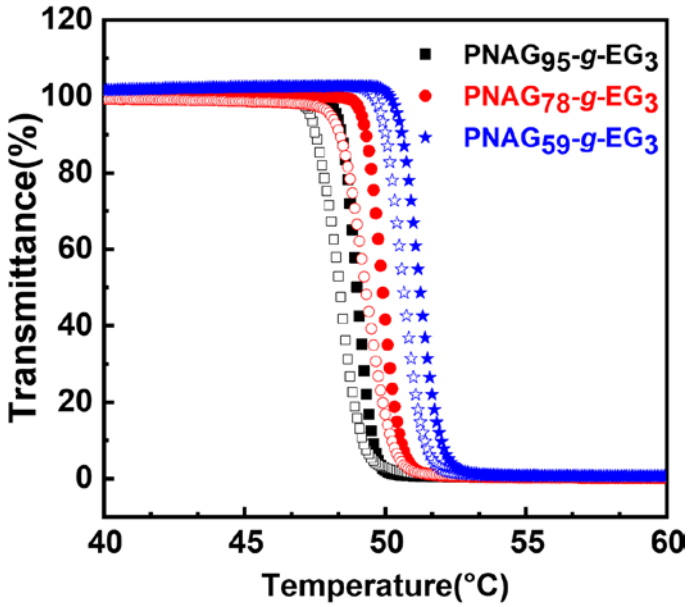

Figure S3. Plots of the transmittance versus temperature for aqueous solutions of PNAG-*g*-EG_3 at a concentration of 5 mg/mL. Filled symbol: heating ramp, open symbol: cooling ramp.

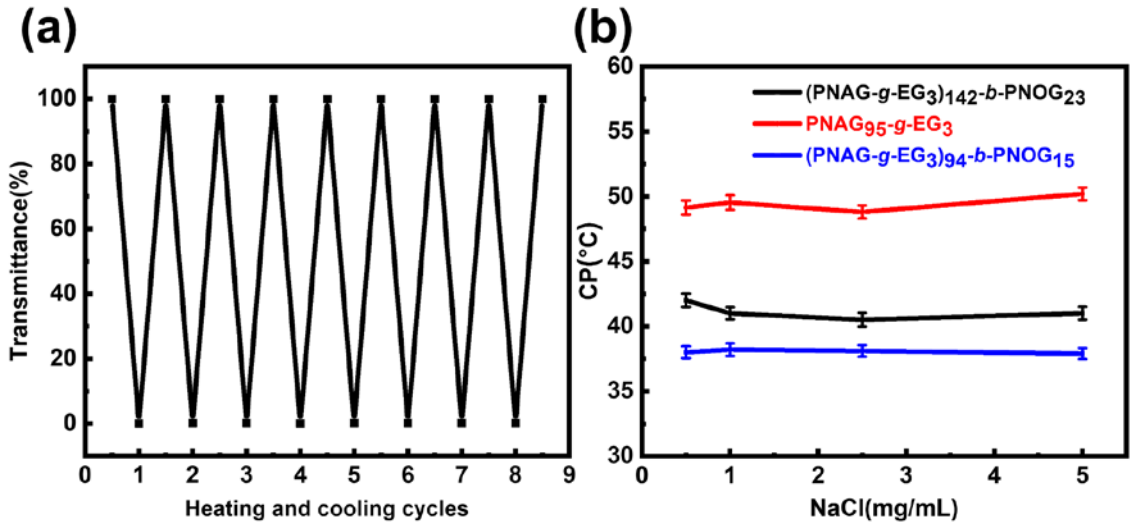

Figure S4. (a) Transmittance of (PNAG-*g*-EG$_3$)$_{142}$-*b*-PNOG$_{23}$, PNAG$_{95}$-*g*-EG$_3$ and (PNAG-*g*-EG$_3$)$_{94}$-*b*-PNOG$_{15}$ aqueous solution at a concentration of 5 mg/mL versus 8 heating and cooling cycles between 30 and 60 °C. (b) Plots of CP as a function of NaCl concentration for (PNAG-*g*-EG$_3$)$_{142}$-*b*-PNOG$_{23}$, PNAG$_{95}$-*g*-EG$_3$ and (PNAG-*g*-EG$_3$)$_{94}$-*b*-PNOG$_{15}$ solution at a concentration of 5 mg/mL.

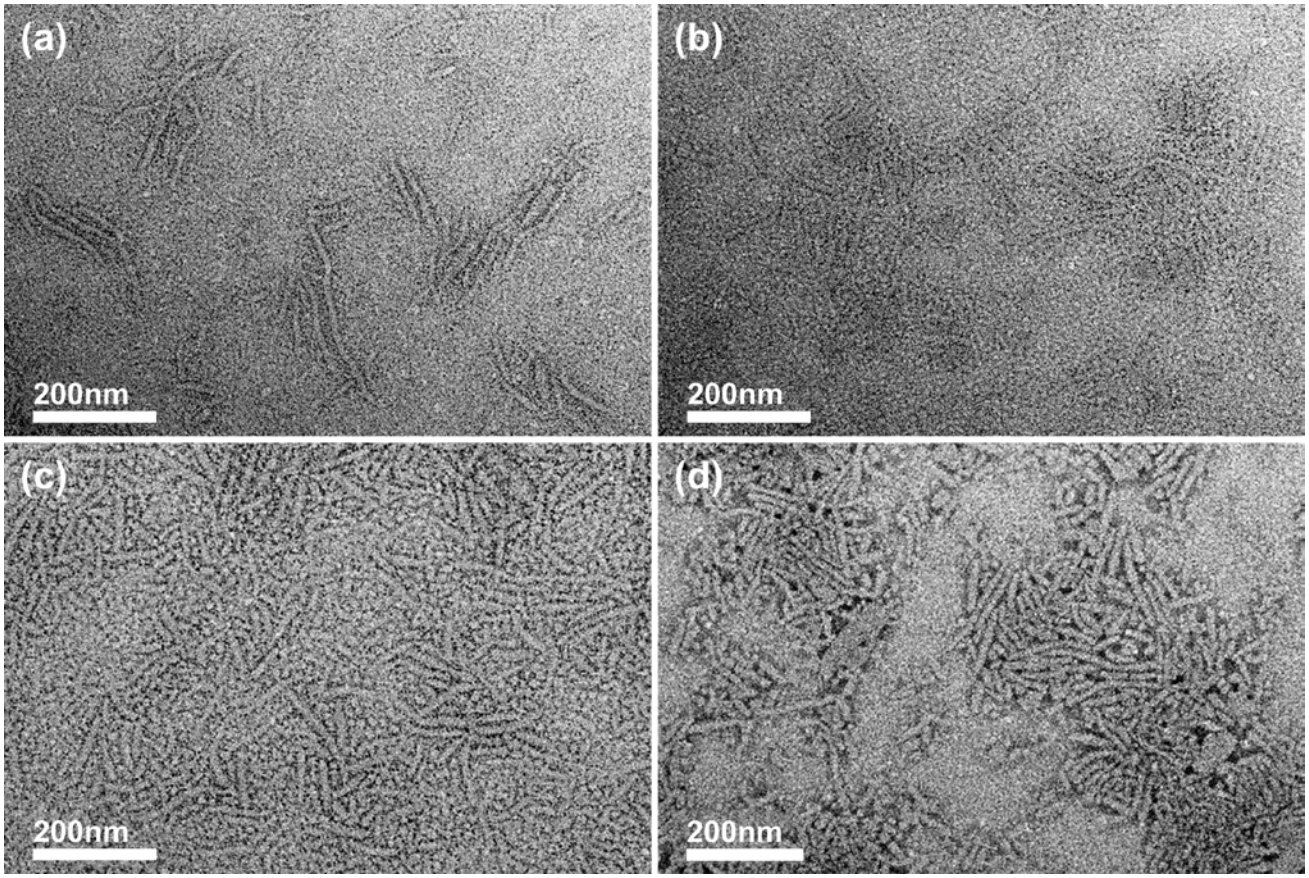

Figure S5. TEM images of (PNAG-*g*-EG$_3$)$_{59}$-*b*-PNOG$_{22}$ (a), (PNAG-*g*-EG$_3$)$_{93}$-*b*-PNOG$_{40}$ (b), (PNAG-*g*-EG$_3$)$_{102}$-*b*-PNOG$_{49}$ (c) and (PNAG-*g*-EG$_3$)$_{81}$-*b*-PNOG$_{52}$ (d) stirred for 24 h at room temperature in aqueous solution at a concentration of 1 mg/mL.

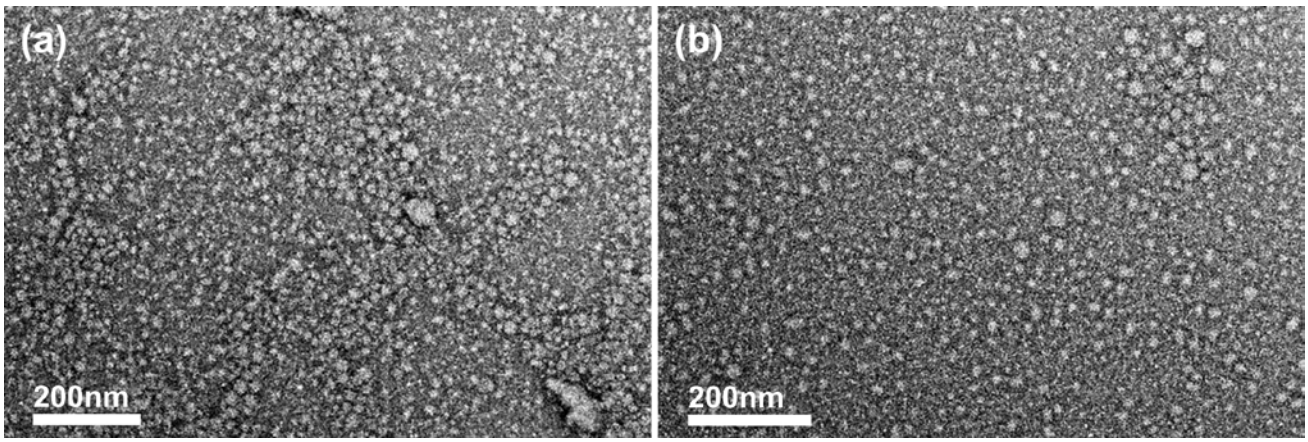

Figure S6. TEM images of (PNAG-*g*-EG$_3$)$_{142}$-*b*-PNOG$_{23}$ stirred for 5 days at room temperature in aqueous solution at a concentration of 1 mg/mL (a) and 5 mg/mL (b).

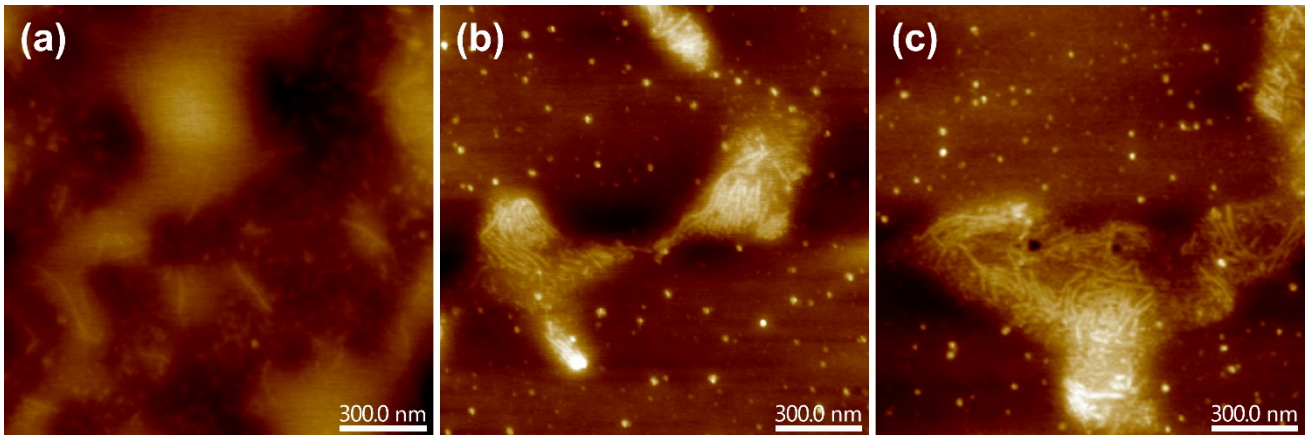

Figure S7. AFM images of (PNAG-*g*-EG$_3$)$_{142}$-*b*-PNOG$_{23}$ incubated at 60 °C for 1 h (a), 2 h (b) and 3 h (c) after stirring for 24 h at room temperature in aqueous solution at a concentration of 1 mg/mL.

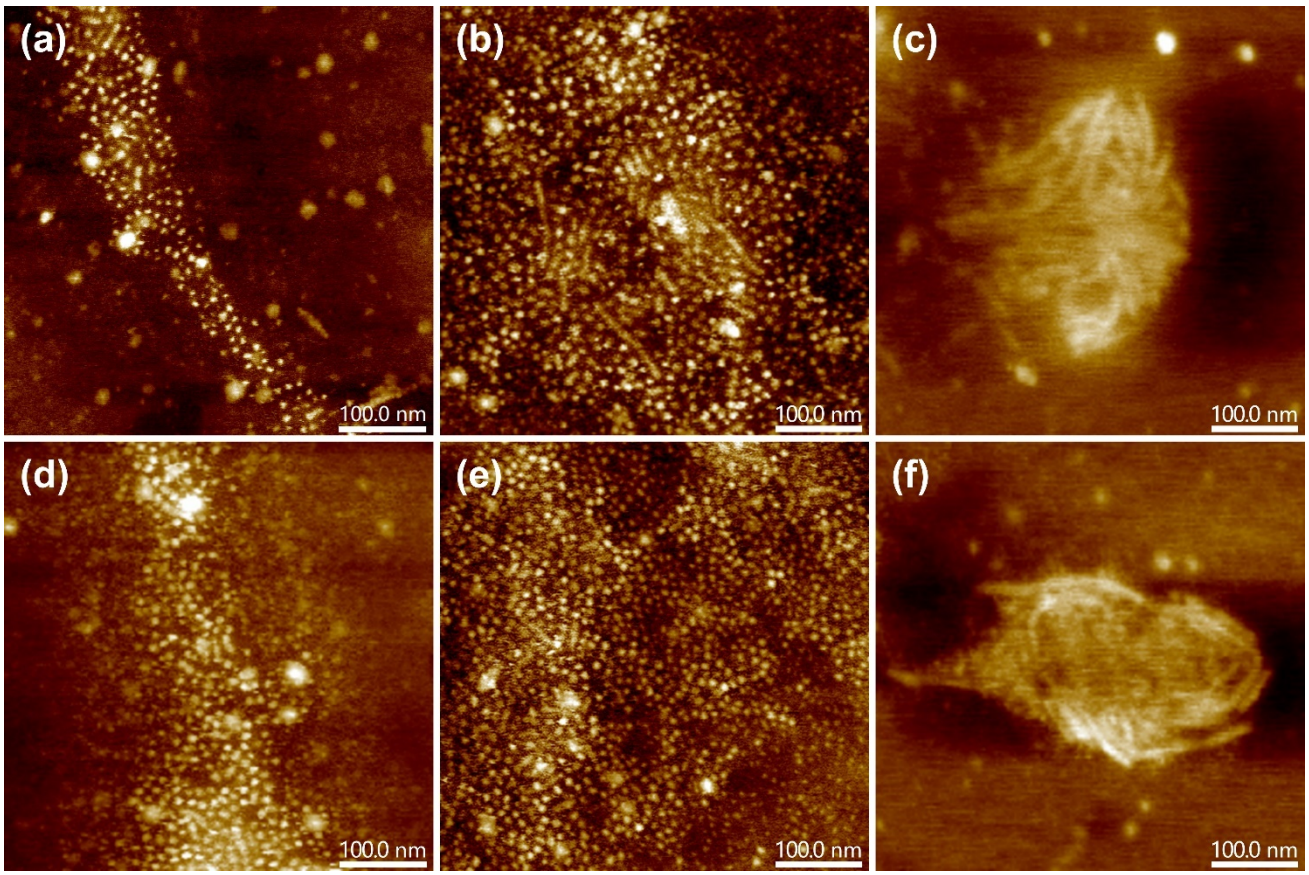

Figure S8. AFM images of (PNAG-*g*-EG_3)$_{142}$-*b*-$PNOG_{23}$ incubated at 40 °C (a), 50 °C (b) and 80 °C (c) for 2 h after stirring for 24 h at room temperature in aqueous solution at a concentration of 1 mg/mL. AFM images of assemblies (d), (e) and (f) after cooling solution of (a), (b) and (c) to the room temperature, respectively.

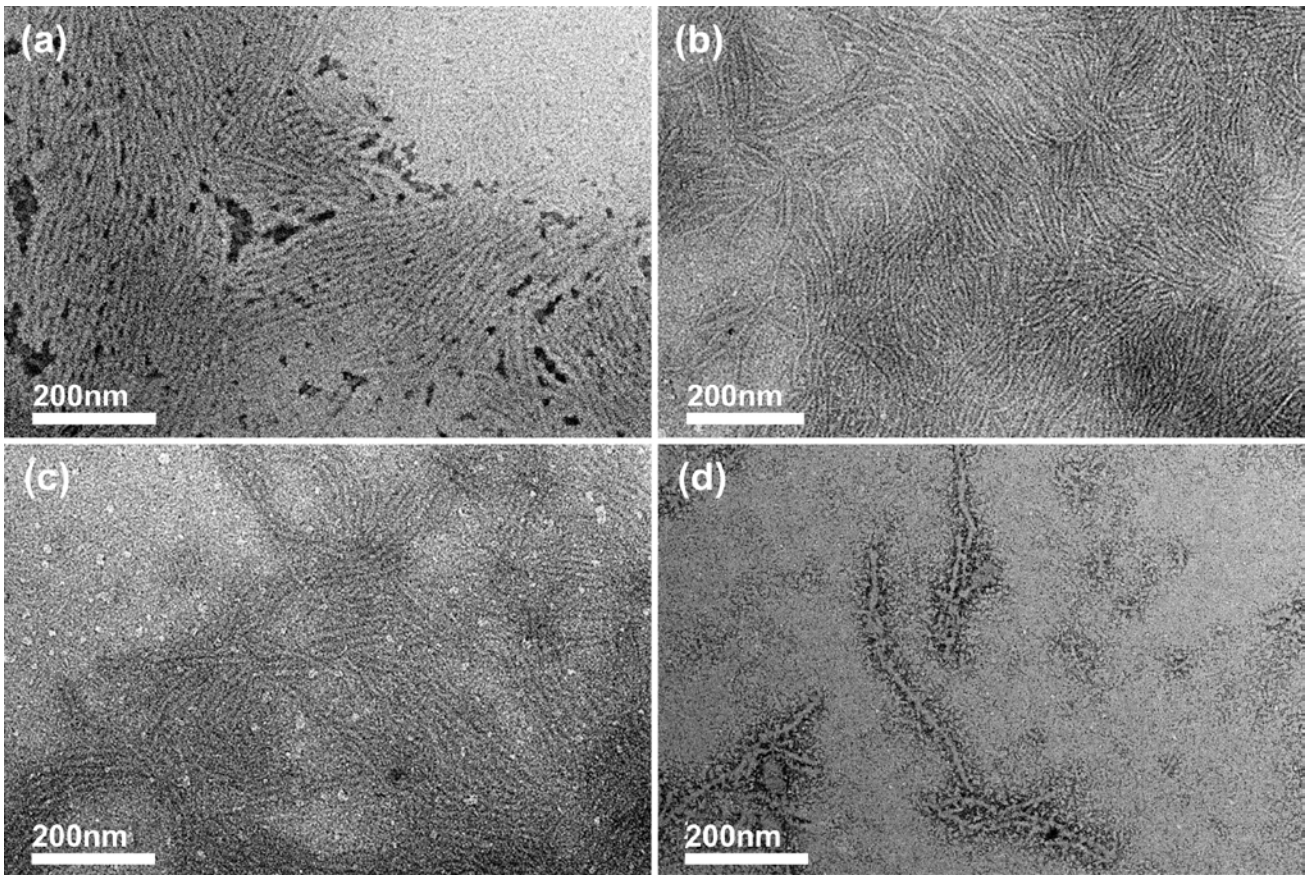

Figure S9. TEM images of (PNAG-*g*-EG$_3$)$_{59}$-*b*-PNOG$_{22}$ (a), (PNAG-*g*-EG$_3$)$_{93}$-*b*-PNOG$_{40}$ (c), incubated at 60 °C for 2 h after stirring for 24 h at room temperature in aqueous solution at a concentration of 1 mg/mL. TEM images of (PNAG-*g*-EG$_3$)$_{59}$-*b*-PNOG$_{22}$ (b), (PNAG-*g*-EG$_3$)$_{93}$-*b*-PNOG$_{40}$ (d) after cooling the solutions in (a) and (c) to the room temperature, respectively.

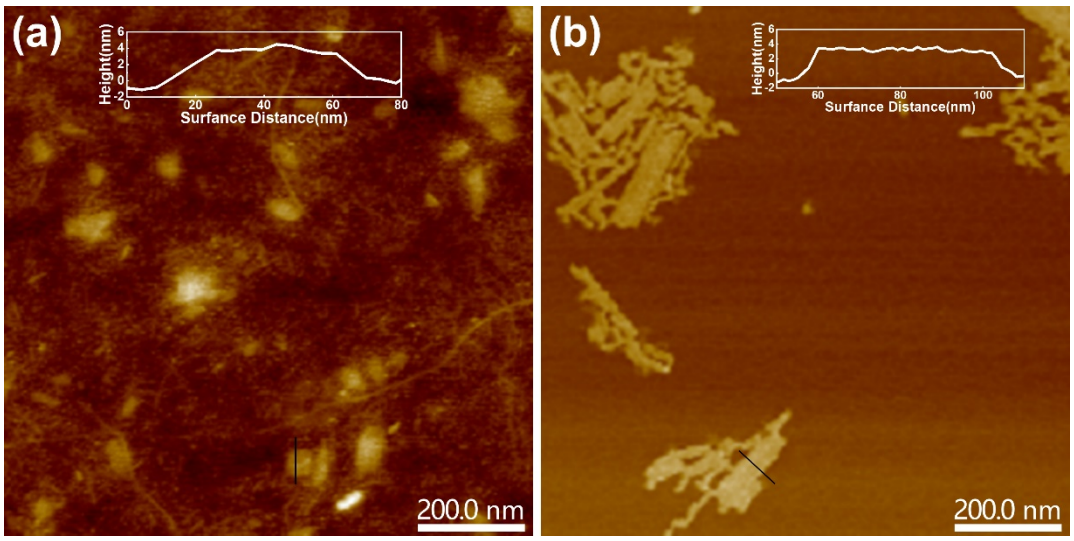

Figure S10.AFM images of (PNAG-*g*-EG$_3$)$_{81}$-*b*-PNOG$_{52}$ (a) and (PNAG-*g*-EG$_3$)$_{102}$-*b*-PNOG$_{49}$ (b) incubated at 60 °C for 2 h after stirring for 24 h at room temperature in aqueous solution at a concentration of 1 mg/mL.

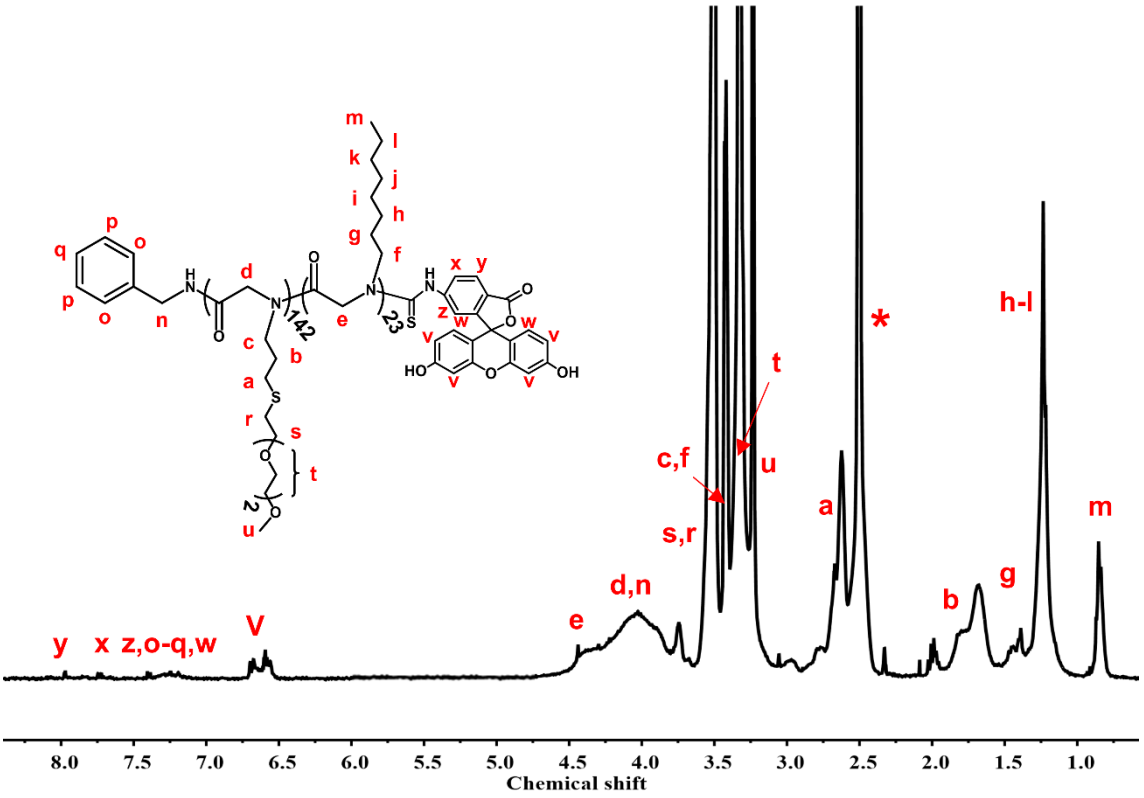

Figure S11. ^{1}H NMR spectra of $(PNAG\text{-}g\text{-}EG3)_{142}\text{-}b\text{-}PNOG_{23}$ labeled with fluorescein isothiocyanate (FITC) quantitatively in DMSO-d_6 (* indicates DMSO-d_6).

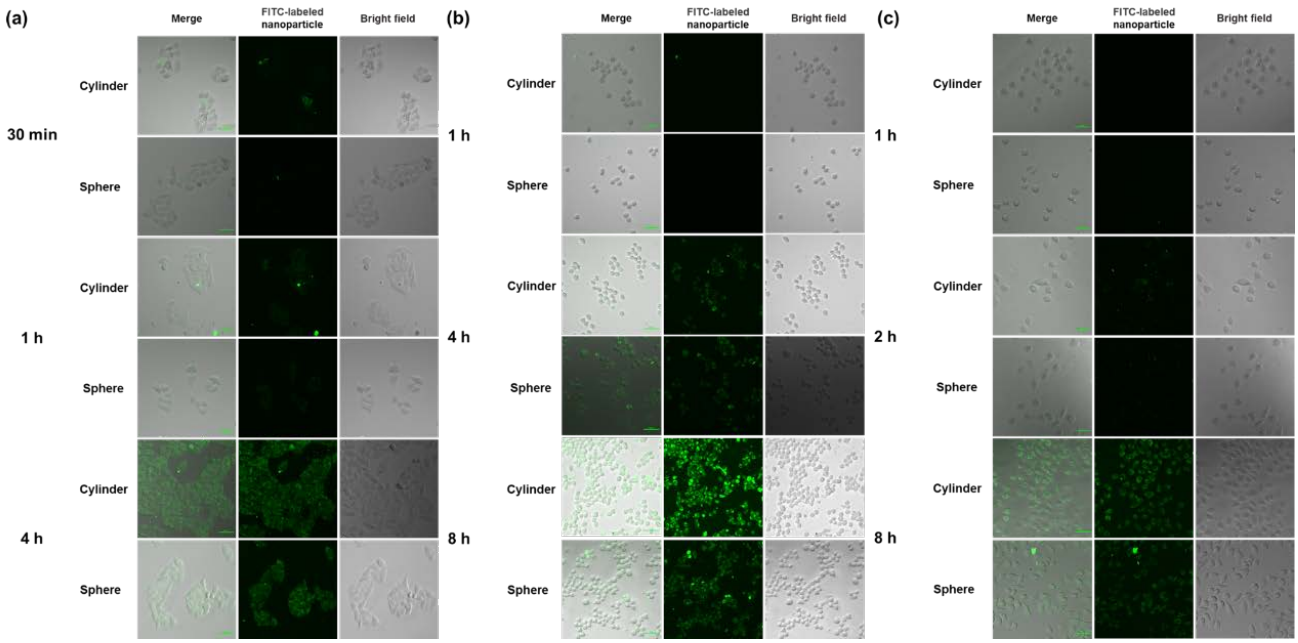

Figure S12. Confocal laser scanning microscope images of Hela cells (a), RAW264.7 (b) and L929 (c) cells incubated with FITC-labeled assemblies at a concentration of 0.5 mg/ml for different incubation time at 37 °C. Scale bars = 50 μm.