Supporting Information

Experimental Parts

Materials All reagents were purchased from Sigma-Aldrich unless noted. Tetrahydrofuran (THF) (Daejung Chemicals & Metals) was dried over sodium and distilled under atmospheric pressure. Dimethylaminopyridine (DMAP) (98%) was recrystallized from toluene. Toluene (99%, Daejung Chemicals & Metals), sulfadimethoxine (SD) (TCI), methacryloyl chloride (MAC) (97%), sodium hydroxide (NaOH) (Duksan Pharmaceutical), acetone (Burdick & Jackson), 1-pyrenemethylamine hydrochloride (PMA) (95%), 2-bromoisobutyryl bromide (BIB) (98%), triethylamine (TEA) (99.5%), sodium bicarbonate (DC Chemicals), magnesium sulfate anhydrous (Daejung Chemicals & Metals), ethanol (Burdick & Jackson), copper (I) bromide (99.999%), tris(2-aminoethyl)amine (TAA) (97%, Lancaster Chem.), conc. HCl (Daejung Chemicals & Metals), formalin (Yakuri Pure Chemicals), formic acid (Yakuri Pure Chemicals), potassium hydroxide (KOH) (Duksan Pharmaceutical), anhydrous *N*,*N*-dimethylformamide anhydrous (DMF) (99.8%), methanol (99%, Daejung Chemicals & Metals), ethanolamine (99+%), coumarin 343, 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (DPECH) (98+%), pH 7.2 buffer solution, and pH 10.0 buffer solution (Daejung Chemicals & Metals) were used as received.

Synthesis of Sulfadimethoxine containing Monomer (SDM) SDM was synthesized according to the previous report.[1] Briefly, SD (30 g, 9.67×10^{-2} mol) was added to a three-neck round-bottom flask and 200 mL of distilled water containing NaOH (3.87 g, 9.67×10^{-2} mol) and 200 mL of acetone were added to the flask. After cooling the flask to 0 ^{o}C, MAC (9.45 mL, 9.67×10^{-2} mol) was slowly added to the flask. The flask was then stirred at room

temperature for 12 h. The precipitated product was collected by filtration and washed with distilled water 3 times. The white product was then dried at room temperature for 24 h. Yield: 96.2%; ^{1}H NMR (300 MHz, DMSO-d_6) is shown in Figure S1.

Synthesis of Tris(2-dimethylaminoethyl)amine (Me_6TREN) Me_6TREN was prepared by the previous report.[2] TAA (36.27 mL, 0.243 mol) was added to a three-neck round-bottom flask, followed by cooling to 0 ^{o}C. Conc. HCl (59.8 mL) was slowly added to the flask and 30 mL of distilled water was then slowly added. After adding formalin (170 mL) to the solution, formic acid (200 mL) was added. The flask was then placed in a PEG bath thermostated at 120 ^{o}C for 6 h. After removing all the volatile fractions by vacuum distillation, the residue was treated with 400 mL of 10% NaOH aqueous solution. An oily layer was extracted by ether and the ethereal extract was then dried over KOH. After removal of ether, the final product was obtained as colorless oil by vacuum distillation. Yield: 30.0 %; ^{1}H NMR (300 MHz, DMSO-d_6) is shown in Figure S2.

Synthesis of Pyrene Initiator (PI) PMA (2 g, 7.47×10^{-3} mol) was placed in a three-neck round-bottom flask, and the flask was degassed and backfilled with N_2 gas repeatedly three times. THF (40 mL) was added to the flask via a syringe, followed by adding TEA (2.60 mL, 1.87×10^{-2} mol) to the flask via a syringe, followed by cooling to 0 ^{o}C. BIB (1.38 mL, 1.12×10^{-2} mol) was then slowly added using a syringe, and the temperature of the flask was slowly raised to room temperature. The reaction was allowed for 24 h under stirring. The solution was filtered and the crude product was purified by recrystallizing from CH_2Cl_2/ethanol. The product was filtered, washed with cold EtOH, and dried in vacuum. Yield: 85.9%; ^{1}H NMR (300 MHz, $CDCl_3$) is shown in Figure S3.; UV-visible spectrum (THF) is shown in Figure S4.

Atom Transfer Radical Polymerization of SDM using PI (P-PSDM) P-PSDM was synthesized via ATRP of SDM using PI as an initiator. DMF was degassed for removal of oxygen by three freeze-and-thaw cycles. Distilled water was also degassed by bubbling with N_2 gas for at least 6 h. SDM (4 g, 1.06×10^{-2} mol) was put in a three-neck round bottom flask, and the flask was degassed and backfilled with N_2 gas repeatedly three times. DMF (8 mL) was added to the flask using a syringe, followed by addition of aqueous NaOH (0.422 g, 1.06×10^{-2} mol) solution (5 mL) to the flask. Me_6TREN (0.0605 g, 2.63×10^{-4} mol) was added to the flask via a micro syringe and CuBr (0.0379 g, 2.63×10^{-4} mol) was then added to the flask. A mixture of PI (0.100 g, 2.63×10^{-4} mol) and DMF (2 ml) was added to the flask via a syringe. The flask was then placed in a PEG bath thermostated at 35 ^{o}C for 12 h to allow ATRP. For purification of P-PSDM, a solution of the crude product was precipitated in 1 N HCl solution. After filtration, the filtered product was put in a beaker with MeOH and stirred at room temperature for 24 h to remove unreacted SDM. For further purification, P-PSDM was dissolved in DMF, and the solution was dialyzed against MeOH for 96 h using cellulose dialysis membrane (molecular weight cut-off: 3500, Membrane Filtration Products, Inc.). The final product was filtered and then dried in vacuum at 30 ^{o}C. Yield: 64.8 %; molecular weight and polydispersity index is listed in Table S1.; ^{1}H NMR (500 MHz, DMSO-d_6) is shown in Figure S5.; GPC trace is shown in Figure S6.

Acid-Base Titration of P-PSDM pKa of P-PSDM was roughly determined by the method of acid-base titration, where pH was controlled by 0.01 M HCl or 0. M NaOH.[3] The P-PSDM-C solution of pH 10.0 of 0.1 mg/mL was then titrated with 0.01 M HCl. Before measuring pH, the electrode of pH meter was allowed to equilibrate with stirring. Since the second derivative of titration curve did not show a sharp end point, the pH at the end point and the pKa value

were approximately estimated to be 4.62 and 8.00, respectively. The titration curve of pH versus titrant volume, the first derivative and the second derivative of titration curve are shown in Figure S7. As a reference, the titration curve of pH 10.0 solution without P-PSDM-C is also shown in Figure S8.

Hydroxylation of P-PSDM (P-PSDM-OH) P-PSDM-OH was synthesized by reaction of P-PSDM with EA. P-PSDM (2 g) was placed in a three-neck round-bottom flask, and the flask was degassed and backfilled with N_2 gas repeatedly three times. DMF (4 mL) was added to the flask, followed by addition of TEA (0.0310 mL, 2.22×10^{-4} mol) to the flask using a micro syringe. After adding distilled water (0.1 mL) to the flask, EA (0.0134 mL, 2.22×10^{-4} mol) was then added to the flask via a micro syringe. The flask was then placed in a PEG bath thermostated at 40 ^{o}C for 24 h. The crude product was purified by precipitating in cold MeOH. The precipitate was filtered and then dried in vacuum at 30 ^{o}C. Yield: 50.0%.

Conjugation of P-PSDM-OH with Coumarin 343 (P-PSDM-C) P-PSDM-C was synthesized by esterification between hydroxyl group of P-PSDM-OH and carboxylic group of coumarin 343. P-PSDM-OH (1 g), coumarin 343 (0.0317 g, 1.11×10^{-4} mol), and DMAP (0.0136 mL, 1.11×10^{-4} mol) were put in a three-neck round-bottom flask, and the flask was degassed and backfilled with N_2 gas repeatedly three times. DMF (2 mL) was added to the flask, followed by addition of DPECH (0.0213 g, 1.11×10^{-4} mol). The reaction was continued for 24 h at room temperature under stirring. After filtration, the resulting P-PSDM-C was purified by precipitating in cold MeOH and then the precipitate was dried in vacuum at 30 ^{o}C. For further purification, P-PSDM-C was dissolved in DMF, and the solution was dialyzed against MeOH for 96 h to completely remove unreacted coumarin 343 using cellulose dialysis

membrane (molecular weight cut-off: 3500, Membrane Filtration Products, Inc.). The final solution was filtered and the filtered product was dried in vacuum 30 ^{o}C. Yield: 68.0 %; ^{1}H NMR (500 MHz, DMSO-d_6) is shown in Figure S9.

Release of Coumarin 343 from P-PSDM-C The release experiment was performed to check the possibility of hydrolysis of the ester linkage between the polymeric backbone and coumarin 343. After P-PSDM-C (0.0024 g) was dissolved in pH 10.0 buffer solution (20 mL), 1 mL of this solution was put into a regenerated cellulose dialysis bag (molecular weight cut-off: 1000, Spectrum Laboratories, Inc.) and then the dialysis bag was placed into pH 7.2 buffer solution (240 mL) at room temperature. At an appropriate time interval, 10 mL of the solution was sampled and the absorbance was measured using a UV/visible spectrometer. The degree of hydrolysis was determined by the absorbance change at the specific absorption wavelength of coumarin 343. UV-visible spectra are shown in Figure S10.

Determination of Förster Radius (R_o) for Pyrene and Coumarin 343 in Water The Forster radius R_o (Å) is defined as $R_o = 9.7\times10^3\left(\frac{\kappa^2\Phi_D J}{n^4}\right)^{\frac{1}{6}}$.[4] κ^2, the orientation factor, is assumed to be $\frac{2}{3}$ for random orientation, n, the refractive index of the medium, is usually taken as 1.4 for aqueous media in biological studies, Φ_D, the quantum yield of the donor in the absence of the acceptor, is calculated to be 0.0021 in water,[5] and J, the overlap integral, is defined as $J = \frac{\int F(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda}{\int F(\lambda)d\lambda}$, where $F(\lambda)$ is the fluorescence of the donor in arbitrary units, $\varepsilon(\lambda)$ is the extinction coefficient of the acceptor in $cm^{-1}\cdot M^{-1}$, and λ is in cm.

When the above values are used for calculation of the Forster radius, R_o is finally determined to be 13.4 Å. UV-visible spectrum of pyrene in water and fluorescence emission spectrum of coumarin 343 in water are shown in Figure S11.

Fluorescence Resonance Energy Transfer (FRET) Study It was previously reported that a dilute solution below 10^{-5} M undergoes a coil-globule transition without intermolecular aggregation.[6-11] Since the concentration of P-PSDM-C solution in this study was set to be below 0.1 mg/mL for FRET study, we believe that the intermolecular aggregation is avoided. To justify that the intramolecular chain conformational process is solely responsible for FRET and the intermolecular aggregation hardly occurs, the fluorescence excitation spectra with the emission wavelength of coumarin 343 at 491 nm were obtained at various concentrations under pH 7.0. The spectra shows that a peak at around 334 nm corresponding to the absorption peak of pyrene is observed as well as a peak of coumarin 343 at around 440 nm, indicating that the FRET occurs from pyrene to coumarin 343. Since the excitation spectra at all concentrations show a constant intensity ratio of pyrene to coumarin 343, it is reasonable to conclude that the FRET in this study is independent of the concentration under our experimental condition, indicating that the intramolecular chain conformational change is responsible for the FRET. We specified the polymer concentration for FRET in the caption of Figure 2 in the revised manuscript, and more details are described in Supporting Information (see Supporting Information page 6, lines 5-18 and Figure S12).

Characterization The composition and the number-average molecular weight of polymers were determined by ^{1}H NMR (Avance DPX-300 or Avance 500, Bruker) and gel permeation chromatography (GPC 410, Waters) equipped with three ultrahydrogel^{TM}(120, 250, 500) after

calibration with standard pullulan (Shodex standard p-82, SHOWA DENKO) samples at a flow rate of 0.6 mL/min in distilled water/DMF (v/v=9.5/0.5 containing NaOH 0.05 mol/L). Absorption spectra were taken by a UV/visible spectroscopy (HP 8452A, Hewlett Packard). Fluorescence spectra were obtained by a fluorescence spectrometer (RF 5301, Shimadzu). Before obtaining absorption and fluorescence spectra, the polymer solution was filtered using Teflon syringe filter (MFS HP050, Advantec).

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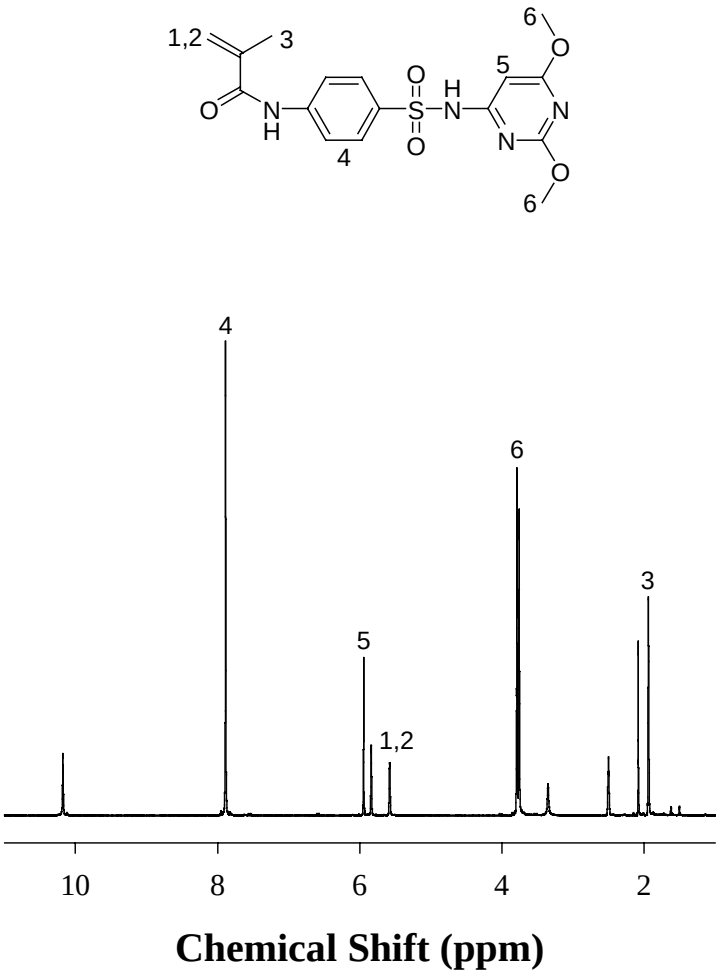

Figure S1. ^{1}H NMR spectrum of SDM in DMSO-d_6.

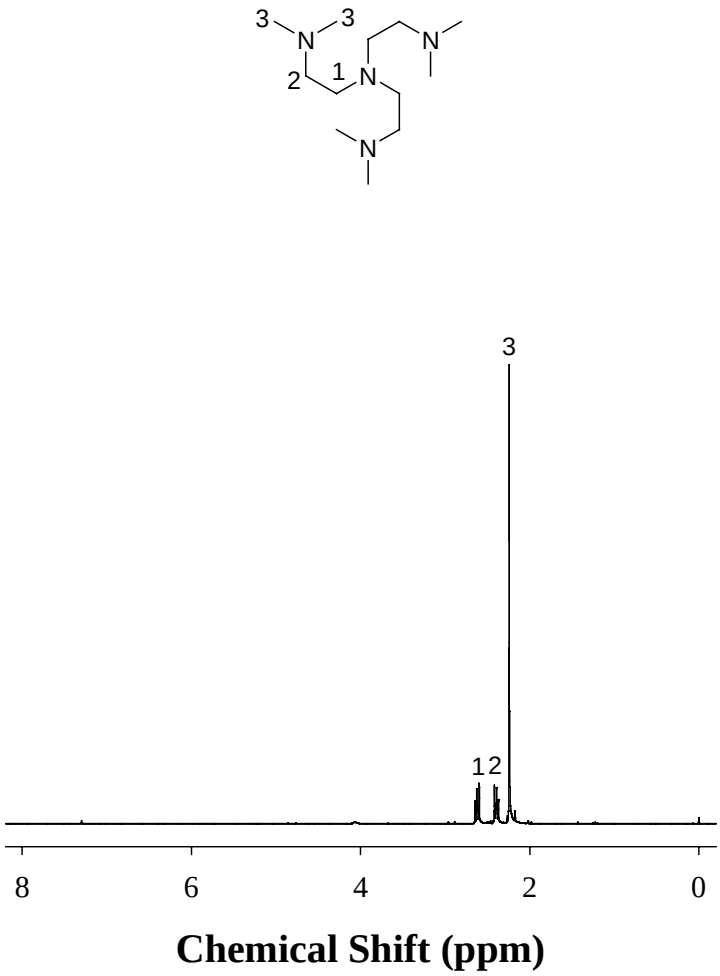

Figure S2. ^{1}H NMR spectrum of Me_6TREN in $CDCl_3$.

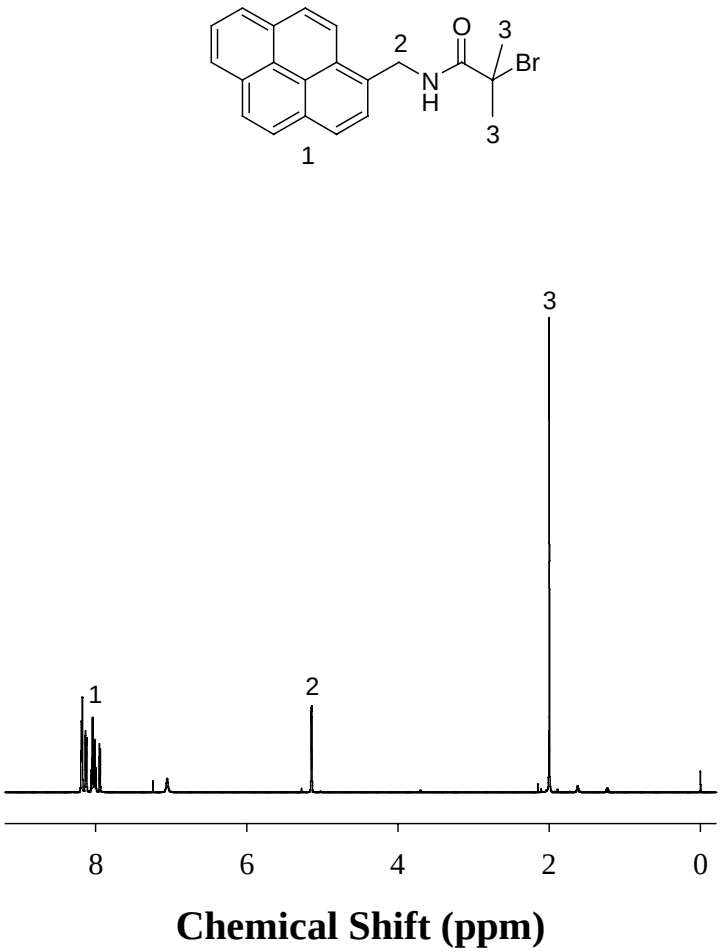

Figure S3. ^{1}H NMR spectrum of PI in $CDCl_3$.

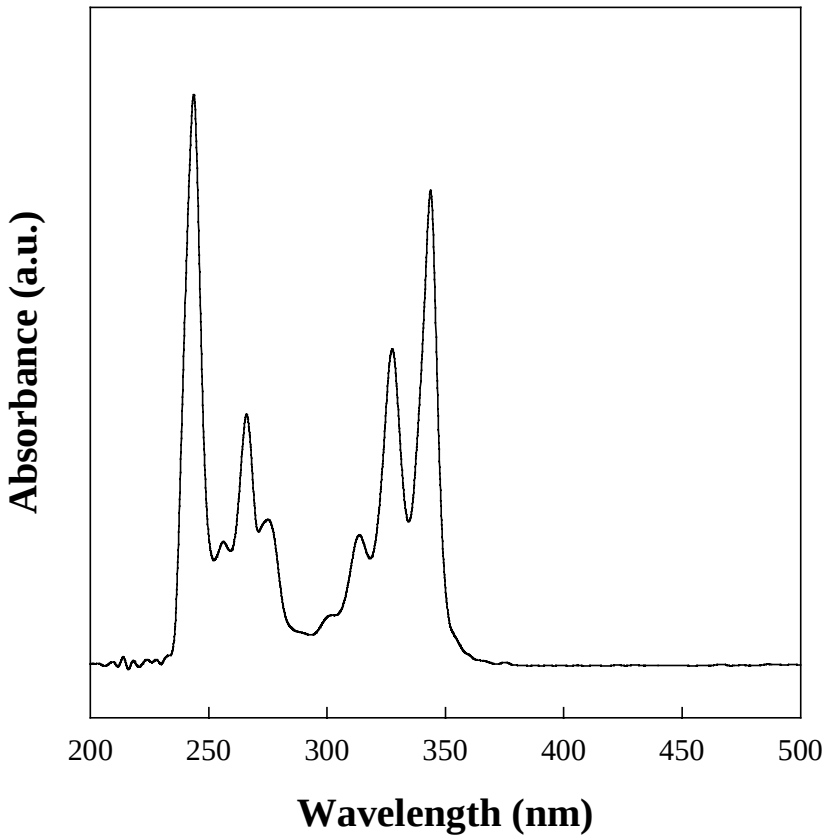

Figure S4. UV-visible spectrum of PI in THF.

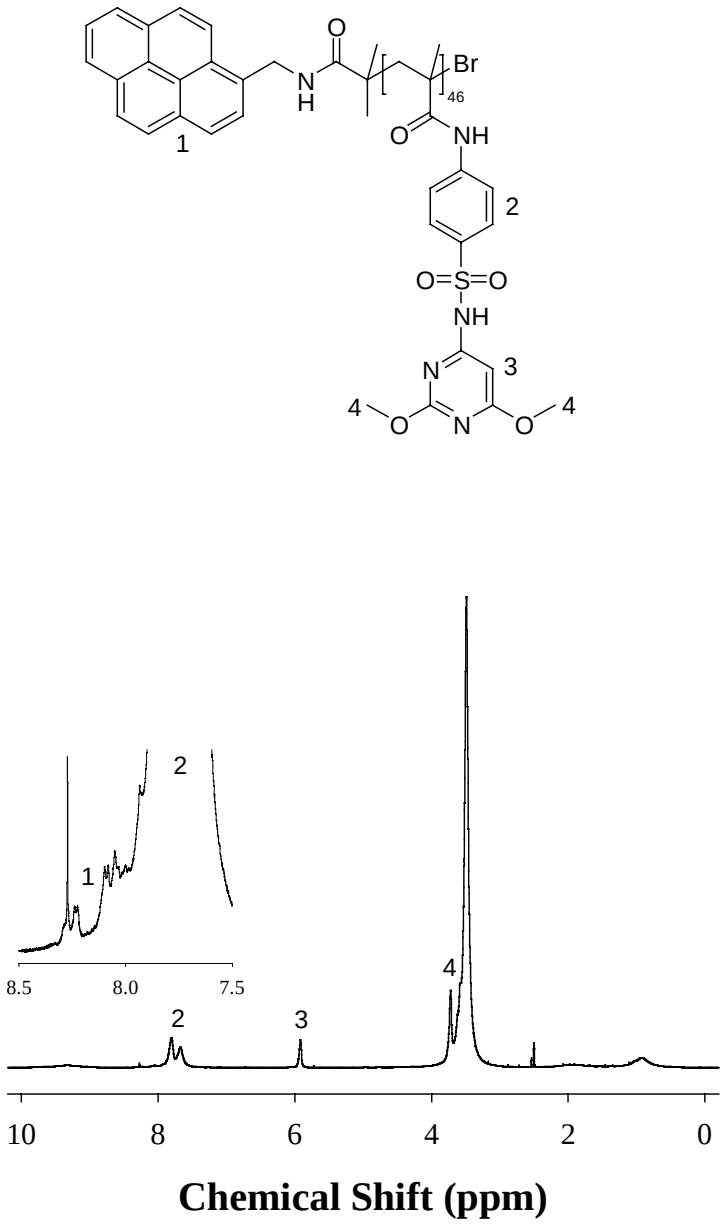

Figure S5. ^{1}H NMR spectrum of P-PSDM in DMSO-d_6.

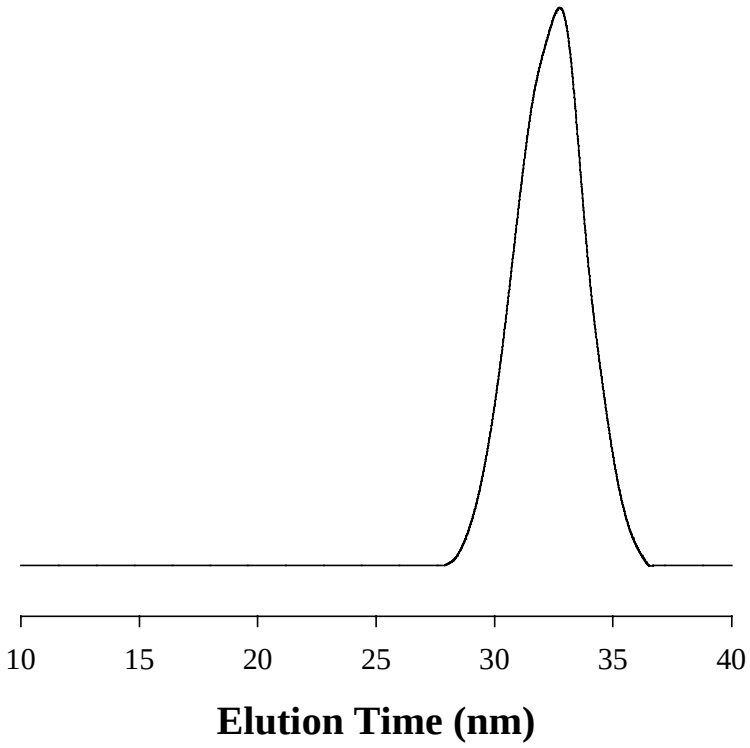

Figure S6. GPC trace of P-PSDM determined by water/DMF (v/v=9.5/0.5 containing NaOH 0.05 mol/L).

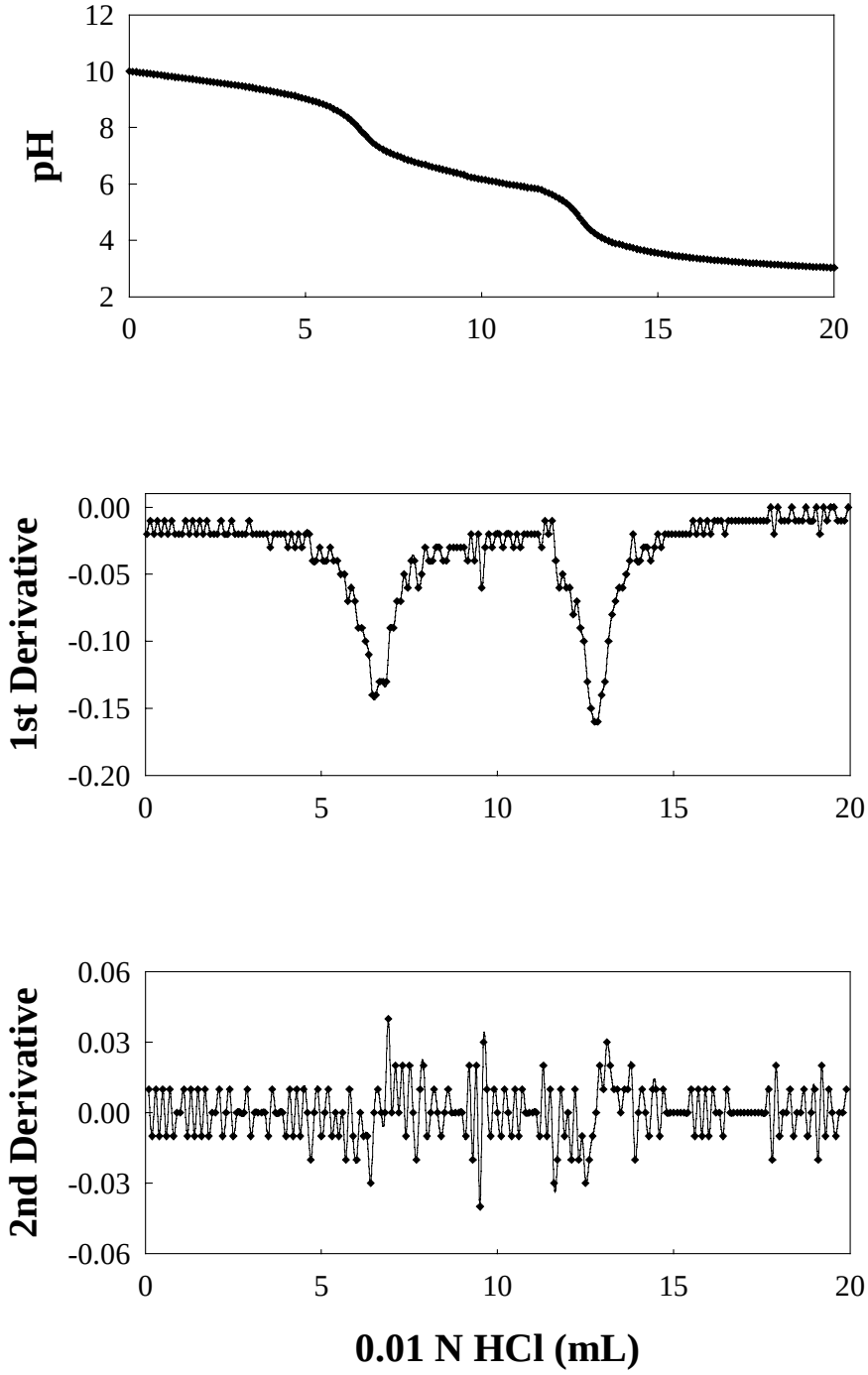

Figure S7. The titration curve of P-PSDM-C, the first derivative of the titration curve, and the second derivative of the titration curve.

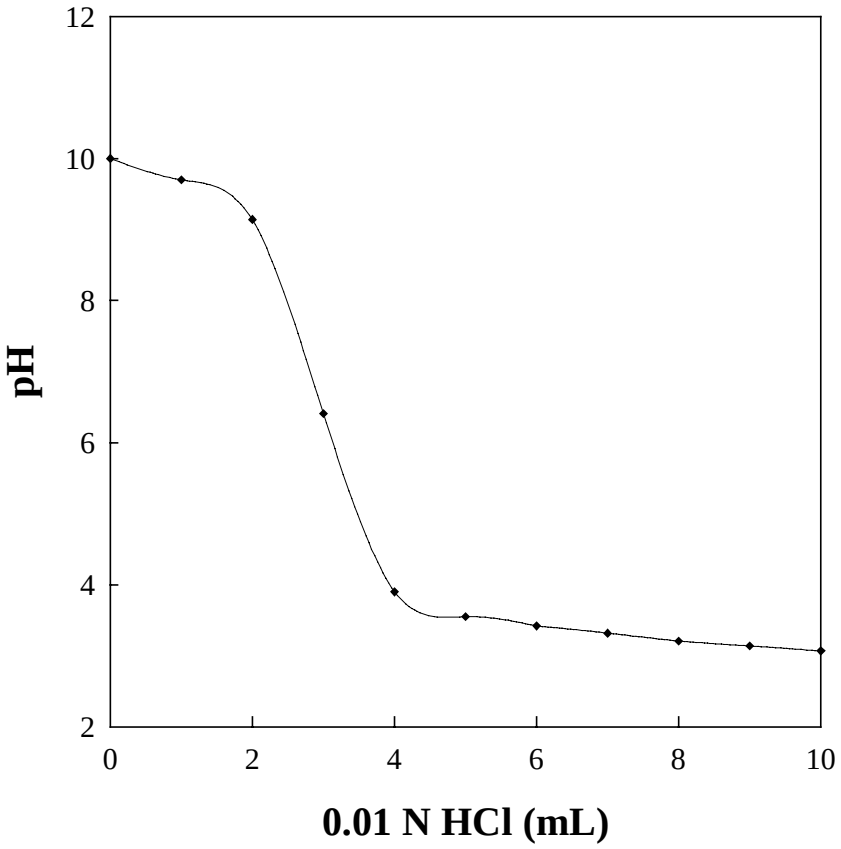

Figure S8. The titration curve of pH 10.0 solution without P-PSDM-C.

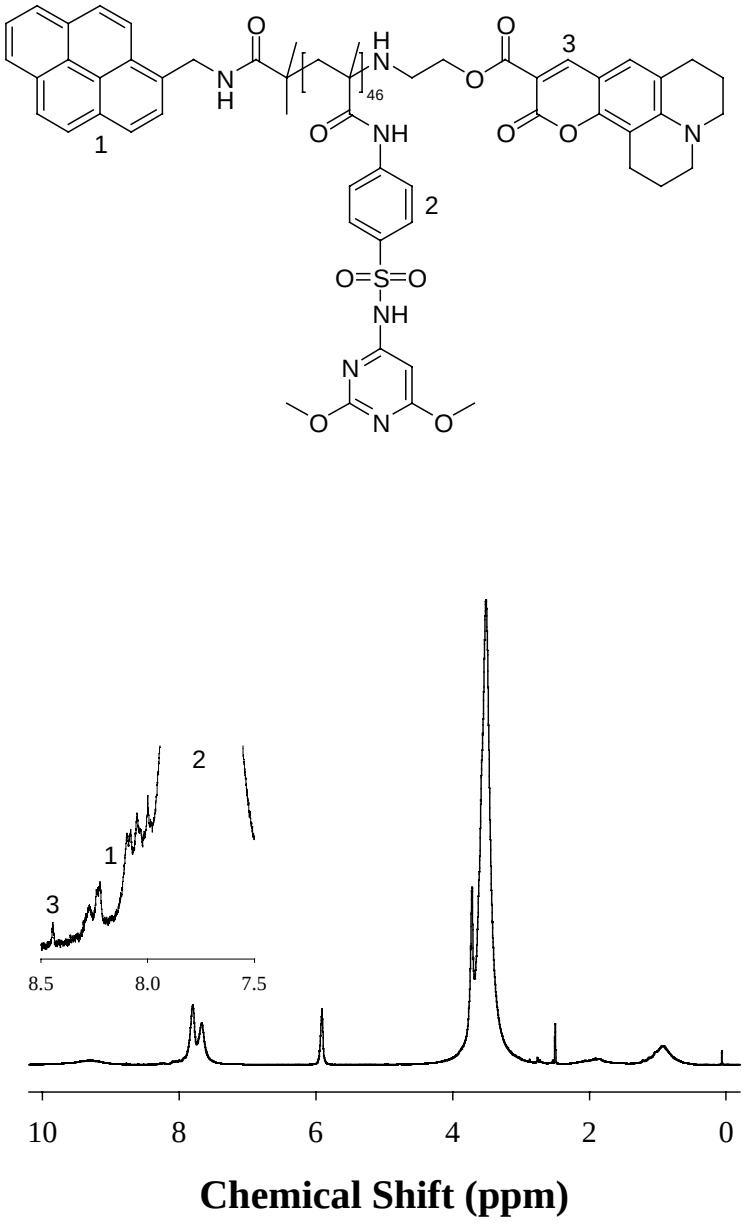

Figure S9. ^{1}H NMR spectrum of P-PSDM-C in DMSO-d_6.

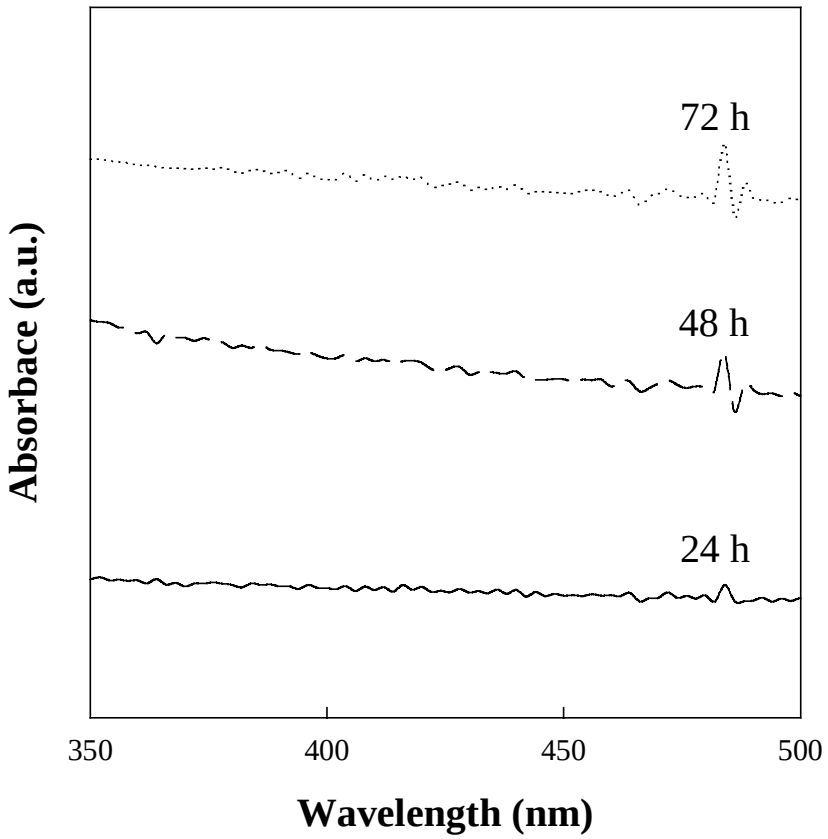

Figure S10. UV-visible spectra after 24 h (solid line), 48 h (dashed line), and 72 h (dotted line).

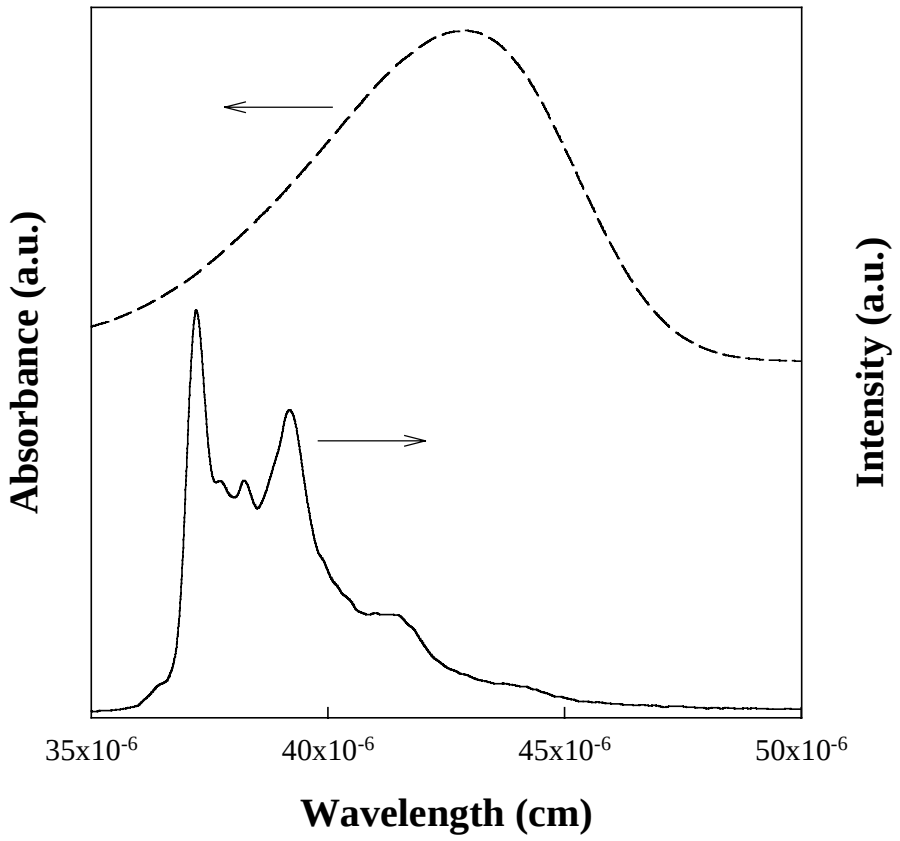

Figure S11. The UV-visible spectrum (solid line) of pyrene in water and the fluorescence emission spectrum (dashed line) of coumarin 343 in water.

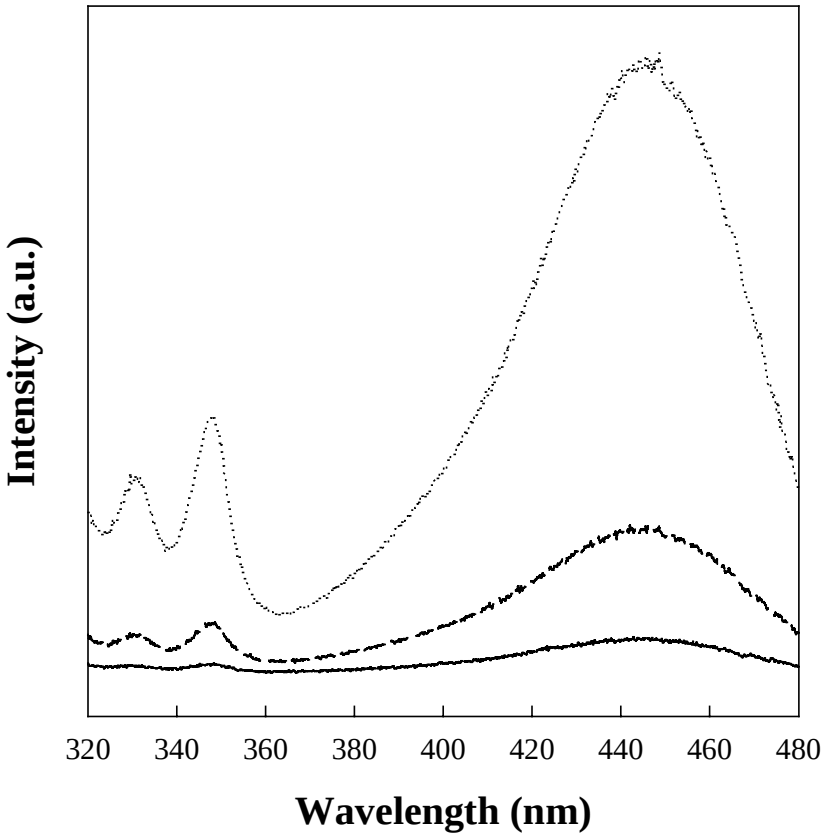

Figure S12. Fluorescence excitation spectra at concentration of 0.001 mg/mL (solid line), 0.01 mg/mL (dashed line), and 0.1 mg/mL (dotted line) maintaining pH 7.0 with the emission wavelength at 491 nm.

Table S1. Molecular weight and molecular weight distribution of P-PM*b*SDM by ^{1}H NMR and GPC

	$M_{n,calc..}$ [a]	$M_{n,\ NMR}$ [b]	$M_{n,\ GPC}$	PDI_{GPC}
P-PM*b*SDM	16000	18000	22000	1.33

[a]calculated by using the mole ratio of monomer to initiator in the feed.

[b]calculated by using the ratio of the peak area from sulfadimethoxine moiety (at 5.9 ppm) moiety to the peak area from pyrene moiety.