

Fluorescent Thermometer Operating in Aggregation-Induced Emission Mechanism: Probing Thermal Transitions of PNIPAM in Water

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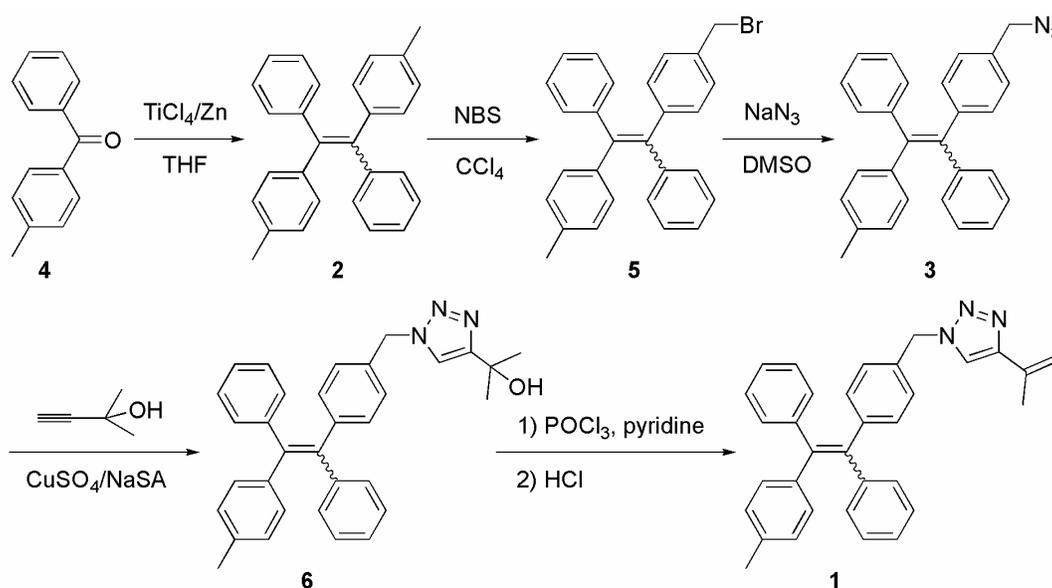
Experimental Section

General Information. Sodium azide (NaN_3) was purchased from Alfa Aesar and used as received without further purification. *N*-Isopropylacrylamide (NIPAM), azodiisobutyronitrile (AIBN) and *N*-bromosuccinimide (NBS) were purchased from Acros and recrystallized from hexane, ethanol and acetate, respectively. 4-Methylbenzophenone (**4**), 2-methyl-3-butyn-2-ol and sodium ascorbate (SA) were purchased from Aldrich. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use. Dimethyl sulfoxide (DMSO) was distilled under normal pressure over calcium hydride under nitrogen. Other reagents such as titanium tetrachloride, benzoyl peroxide (BPO), zinc powder, K_2CO_3 , CuSO_4 , and POCl_3 were purchased from East China Medical and Reagent Co. Ltd. Other solvents such tetrachloromethane, dichloromethane (DCM), chloroform, petroleum ether, *N,N*-dimethylformamide (DMF), hexane, ethyl acetate, ethyl ether, and methanol were purchased in analytic pure grade.

^1H and ^{13}C NMR spectra were measured on a Mercury plus 300 MHz NMR spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Mass spectra were obtained on a GCT Premier CAB 048 mass spectrometer and elemental analysis was performed on a ThermoFinnigan Flash EA1112. Average molecular weights (M_w and M_n) and polydispersity indexes (PDIs) of the polymers were estimated by a Waters Associates GPC system in THF. A set of monodisperse polystyrene standards covering molecular weight range of 10^3 – 10^7 was used for molecular weight calibration. UV absorption spectra were taken on a Varian CARY 100 Bio spectrophotometer with a temperature controller. Photoluminescence (PL) spectra were taken on a Hitachi 4500 spectrofluorometer with a temperature controller. Dynamic light scattering experiments were performed on a Brookhaven 90 plus spectrometer with a temperature controller. An argon ion laser operating at 658 nm was used as light source. The temperature-variable experiment was carried out in a quartz cell with 1 cm path length after the solution was left at the preset temperature for 30 min and the temperature was change with a step width of 1 °C.

Monomer Synthesis. The synthetic route to monomer **1** is given in Scheme 1 and the experimental procedures are described below.

Scheme S1. Synthesis of TPE-Containing Vinyl Monomer 1



Preparation of 1,2-Diphenyl-1,2-di(p-tolyl)ethene (2). To a two-necked reaction flask were added 4-methylbenzophenone (**4**; 1.96 g, 10 mmol) and zinc powder (1.93 g, 30 mmol). The flask was then evacuated under vacuum and flushed with dry nitrogen three times. Into the flask dry THF (50 mL) was injected and TiCl₄ (1.7 mL, 15 mmol) was added dropwise by a syringe at 0 °C. The mixture was refluxed overnight and quenched with 10% K₂CO₃. After the solvent was removed under reduced pressure, the crude product was purified with a silica gel column using a mixture of petroleum ether and ethyl acetate (20:1 v/v) as eluent. A white solid was obtained in 64.6% yield. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.10 (m, 12H), 7.04 (m, 4H), 6.91 (d, 4H), 2.26 (d, 6H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 144.1, 140.9, 140.4, 135.9, 131.3, 131.2, 128.3, 127.5, 126.2, 21.1. MS (ESI): Anal. Calcd: 360.2. Found: 359.9 (M⁺).

Preparation of 1-[4-(Bromomethyl)phenyl]-2-(p-tolyl)-1,2-diphenylethene (5). Compound **2** (0.90 g, 2.5 mmol), NBS (0.45 g, 2.5 mmol) in CCl₄ (50 mL) and a catalytic amount of BPO were added into a two-necked flask under stirring. The resultant mixture was refluxed overnight. After cooled to room temperature, the precipitate was filtered and washed with DCM. The filtrate was concentrated and

purified by a silica gel column using a mixture of petroleum ether and ethyl acetate (5:1 v/v) as eluent. A white solid was obtained in 73.5% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.12 (m, 8H), 7.04 (m, 6H), 6.90 (d, 4H), 4.43 (d, 2H), 2.27 (d, 3H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 144.2, 143.7, 143.6, 141.5, 140.5, 139.7, 136.2, 135.5, 131.6, 131.3, 131.2, 128.5, 127.7, 126.5, 33.6, 21.2. MS (ESI): Anal. Calcd: 438.1. Found: 358.9 ($\text{M}-\text{Br}$) $^+$.

Preparation of 1-[4-(Azidomethyl)phenyl]-2-(p-tolyl)-1,2-diphenylethene (3). To a round-bottom flask was added **5** (0.33 g, 0.75 mmol), sodium azide (60 mg, 0.9 mmol) and DMSO (10 mL). The mixture was refluxed overnight. The crude product was purified by a silica gel column using a mixing of chloroform and hexane (1:2 v/v) as eluent. The greenish oil was obtained in 98% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.10 (m, 8H), 7.04 (m, 6H), 6.89 (d, 4H), 4.25 (d, 2H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 144.1, 143.8, 143.7, 141.5, 140.6, 139.8, 136.2, 133.2, 131.8, 131.3, 131.2, 128.5, 127.8, 126.5, 54.5, 21.2. MS (ESI): Anal. Calcd: 401.2. Found: 358.9 ($\text{M}-\text{N}_3$) $^+$.

Preparation of 2-(1-{4-[1,2-Diphenyl-2-(p-tolyl)vinyl]benzyl}-1H-1,2,3-triazol-4-yl)propan-2-ol (6). This compound was prepared according to the procedures described elsewhere.¹ Compound **3** (0.30 g, 0.74 mmol), 2-methyl-3-butyn-2-ol (0.1 mL, 1 mmol) in DMF (5 mL), SA (0.013 g, 0.074 mmol), and CuSO_4 (0.01 g, 0.037 mmol) were added to a flask equipped with a condenser. The mixture was heated at 70 °C with stirring overnight. After cooling to room temperature, water was added into the mixture and the solution was extracted with DCM three times. The organic layer was washed once with distilled water, dried over MgSO_4 and concentrated by a rotary evaporator. The crude product was purified by a silica gel column using a mixing of chloroform and hexane (1:4 v/v) as eluent. A pink solid was obtained in 55.7% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.29 (s, 1H), 7.11 (m, 8H), 7.04 (m, 6H), 6.90 (d, 4H), 5.42 (d, 2H), 2.26 (d, 3H), 1.63 (d, 6H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 144.5, 143.6, 143.4, 141.6, 140.4, 139.5, 136.3, 132.2, 131.9, 131.2, 131.1, 128.4, 127.7, 127.4, 126.4, 118.9, 68.4, 53.8, 30.4, 21.1. Elementary analysis: Calcd for $\text{C}_{33}\text{H}_{31}\text{N}_3\text{O}$: C, 81.62; H,

6.43; N, 8.65; O, 3.29. Found: C, 79.79; H, 6.45; N, 8.89. MS (ESI): Anal. Calcd: 485.3. Found: 485.9 (M^+).

Synthesis of 1-{4-[1,2-Diphenyl-2-(p-tolyl)vinyl]benzyl}-4-(prop-1-en-2-yl)-1H-1,2,3-triazole (1).

To a round-bottom flask was added **6** (0.148 g, 0.3 mmol) and pyridine (1.5 mL). After stirring for 5 min, $POCl_3$ (0.092g, 0.6 mmol) was added dropwise. The reaction mixture was then stirred for 2 h at 120 °C. After cooling to room temperature, the mixture was poured into ice-water under stirring and extracted with DCM three times. The organic layer was washed with saturated aqueous $CuSO_4$ and then dilute hydrochloric acid, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by a silica gel column using a mixture of petroleum ether and ethyl acetate (1:4 v/v) as eluent. A pink powder was obtained in 71.4% yield. 1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.32 (s, 1H), 7.10 (m, 8H), 7.03 (m, 6H), 6.89 (d, 4H), 5.72 (s, 1H), 5.43 (d, 2H), 5.12 (s, 1H), 2.12 (d, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 148.9, 144.5, 143.60, 143.4, 141.6, 140.4, 139.5, 136.3, 133.5, 132.4, 131.9, 131.2, 128.4, 127.7, 127.3, 126.5, 119.4, 112.4, 53.7, 21.1, 20.5. Elementary analysis: Calcd for $C_{33}H_{29}N_3$: C, 84.76; H, 6.25; N, 8.99. Found: C, 84.39; H, 6.28; N, 9.16. MS (ESI): Calcd: 467.2. Found: 467.2 (M^+).

Copolymerization of Monomer 1 with NIPAM. The polymerization reactions were carried out under nitrogen using Schlenk techniques in a vacuum-line system except for the purification of the resulting polymers, which was done in an open atmosphere. The synthetic route to the polymers are shown in Scheme 2 and the experiment procedures are according to published literature.²

Into a 10 mL Schlenk tube with a stopcock in the sidearm was added NIPAM (0.25 g, 2.2 mmol), **1** (in different feed, see Table 1) and AIBN (3 mg). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled THF (2 mL) was injected into the tube to dissolve the monomer. The reaction mixture was stirred at 70 °C under nitrogen for 15 h. The mixture was dropped into a large amount of diethyl ether. The precipitate was collected and dissolved in THF and the solution was dropped into diethyl ether again. The precipitate was filtered

and dried in an oven under vacuum. A white solid was obtained in 87.3% yield. $^1\text{H NMR}$ (300 MHz, D_2O), δ (TMS, ppm): 3.97 (s, 1H), 1.4–2.2 (m, 3H), 1.18 (s, 6H).

Scheme S2. Copolymerization of 1 with NIPAM

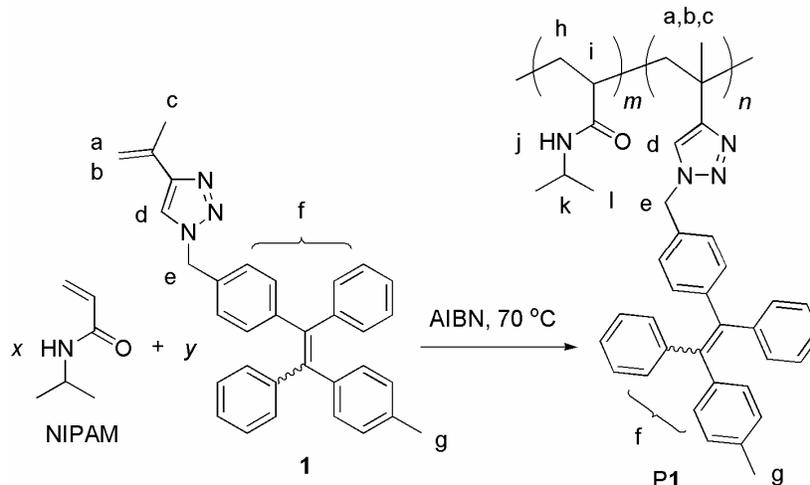


Table S1. Copolymerization Results^a

| Polymer | $x:y^b$ | $m:n^{c,d}$ | M_w^e | PDI ^e |
|---------|---------|-------------|---------|------------------|
| P1a | 300:1 | 372:1 | 12, 400 | 1.66 |
| P1b | 150:1 | 171:1 | 11, 100 | 1.31 |
| P1c | 100:1 | 89:1 | 12, 400 | 1.98 |
| PNIPAM | | | 12, 500 | 1.31 |

^a Polymerization reaction carried out at 70 °C under nitrogen for 15 h using AIBN as initiator.

^b Monomer feed ratio.

^c Copolymer composition calculated using the calibration curve given in Figure S5.

^e Determined by GPC in THF on the basis of a polystyrene calibration.

References

- (1) R. J. Thibault, K. Takizawa, P. Lowenheilm, B. Helms, J. L. Mynar, J. M. J. Frechet, C. J. Hawker, *J. Am. Chem. Soc.*, 2006, **128**, 12084–12085.
- (2) Y. Shiraishi, R. Miyamoto, X. Zhang, T. Hirai, *Org. Lett.*, 2007, **9**, 3921–3924

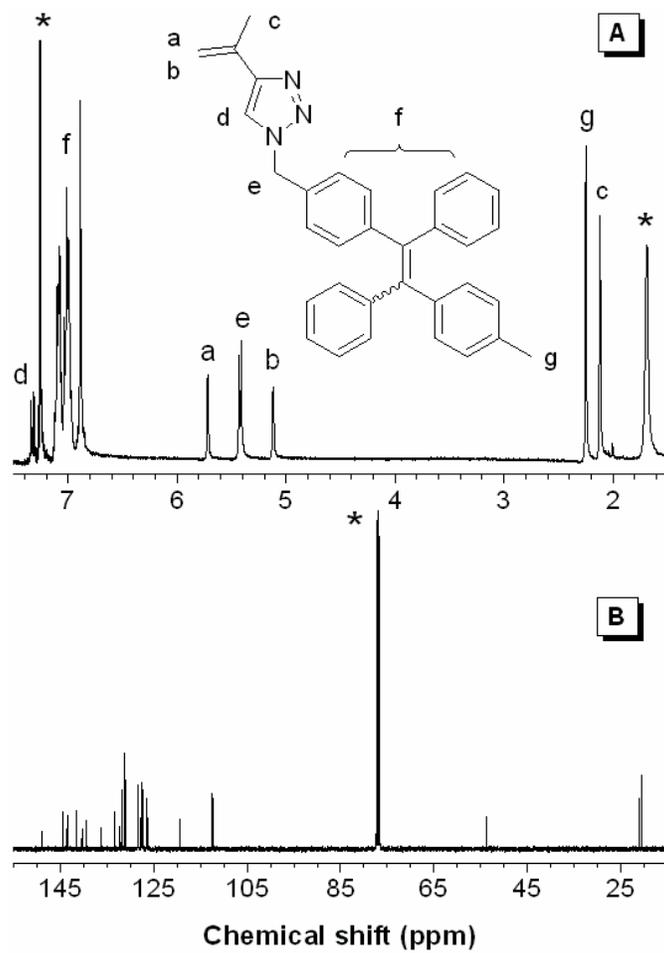


Figure S1. (A) ^1H and (B) ^{13}C NMR spectra of **1** in chloroform-*d*. The solvent and water peaks are marked with asterisks.

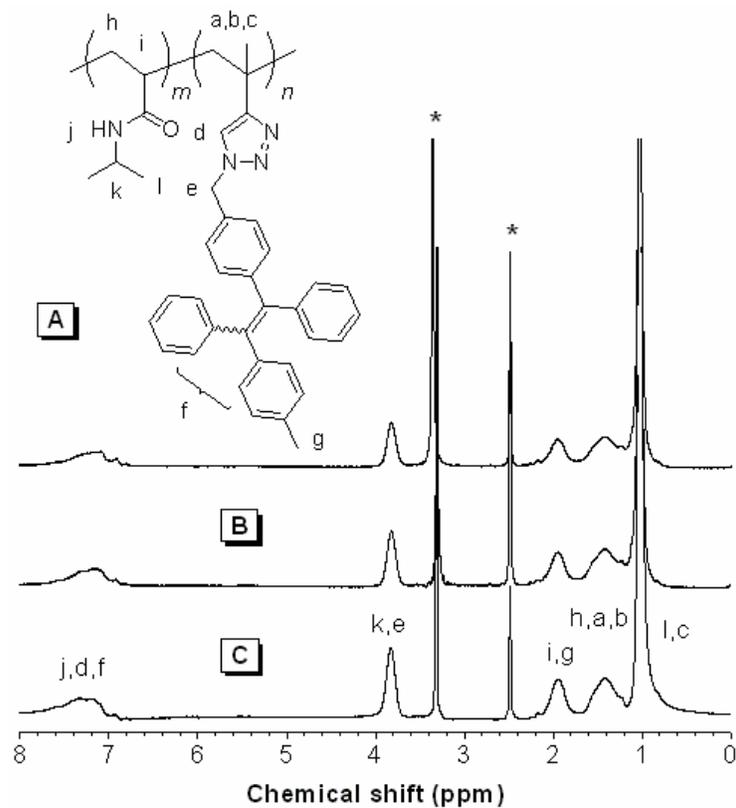


Figure S2. ^1H NMR spectra of (A) P1a, (B) P1b, (C) P1c measured in $\text{DMSO-}d_6$ at room temperature. The solvent peaks are marked with asterisks.

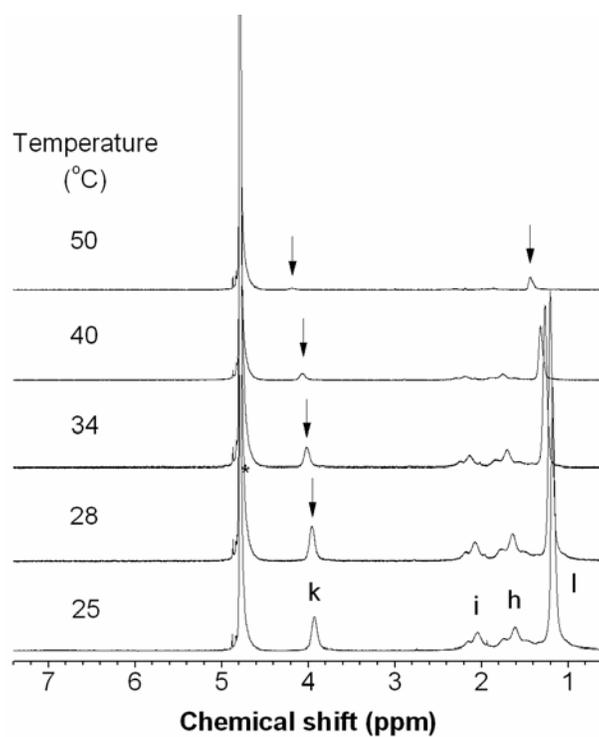


Figure S3. Temperature-dependent ^1H NMR spectra of P1c in D_2O .

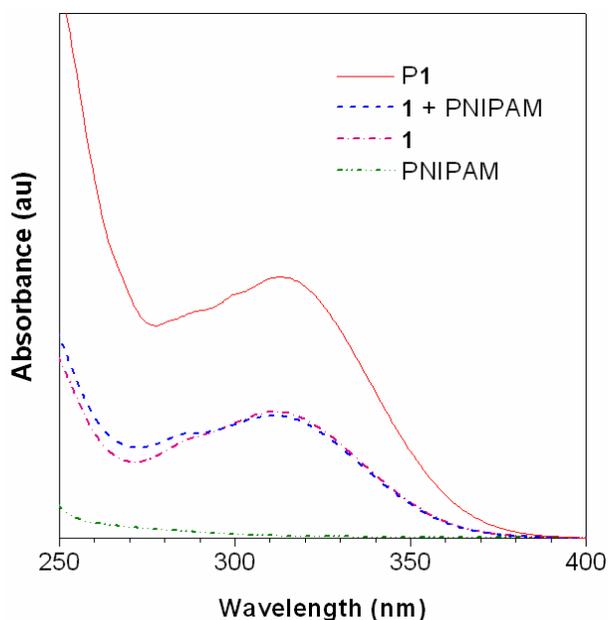


Figure S4. Absorption spectra of THF solutions of **1** (5×10^{-5} M), PNIPAM (1 mg/mL), **1** (5×10^{-5} M) in PNIPAM (1 mg/mL), and P1a measured at 21 °C.

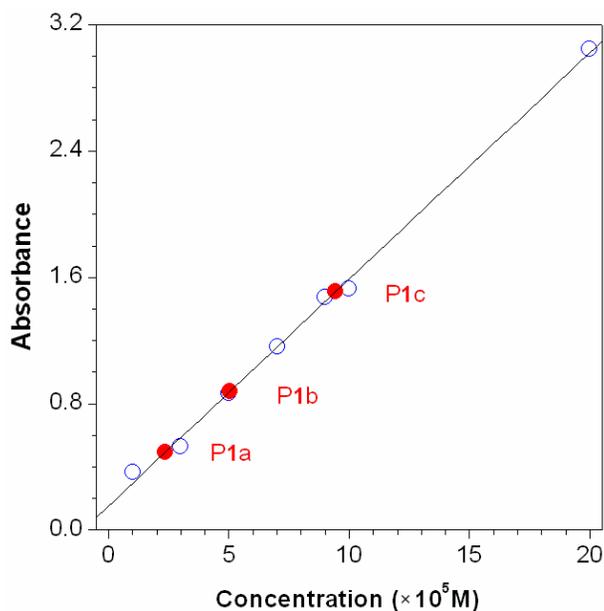


Figure S5. Calibration curve for determination of copolymer composition, using 1-(*p*-Methylphenyl)-1,2,2-triphenylethane (**7**) as standard. The absorbance of **7** at 322 nm was recorded in the presence of PNIPAM in THF. Concentrations of **7** and PNIPAM were 10^{-5} – 2×10^{-4} M and 1 mg/mL, respectively. Open and solid circles are the data points for the standard and the copolymers, respectively.

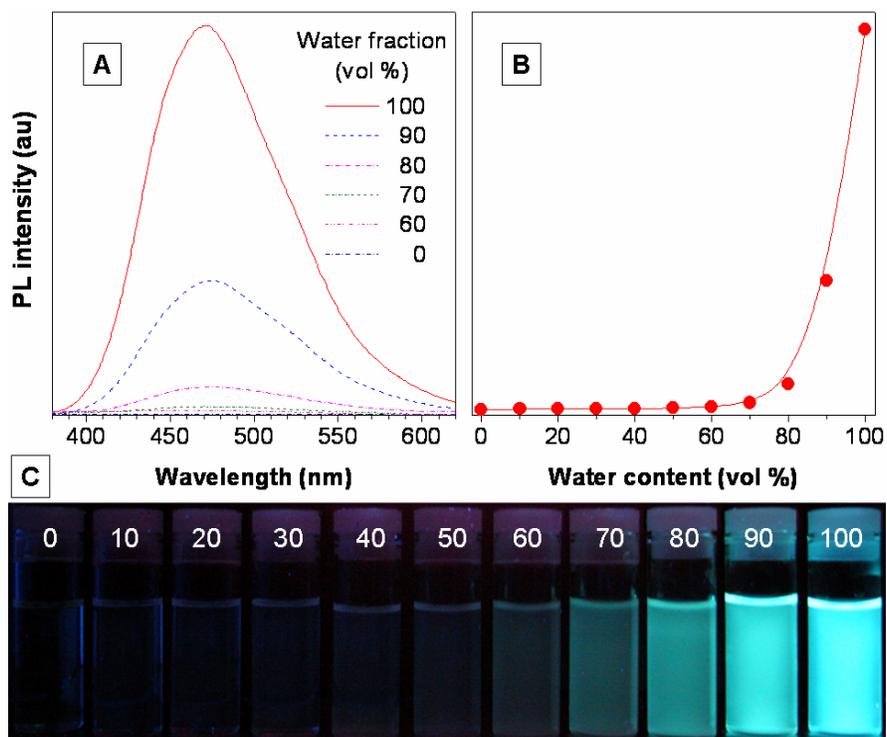


Figure S6. (A) Photoluminescence spectra of P1c (1 mg/mL) in water/THF mixtures with different water contents (measured at ~ 17 °C and $\lambda_{\text{ex}} = 322$ nm). (B) Change of PL maximum of P1c with water content of the aqueous mixture. (C) Photos of P1c in the aqueous mixtures (taken under illumination of a handheld UV lamp).

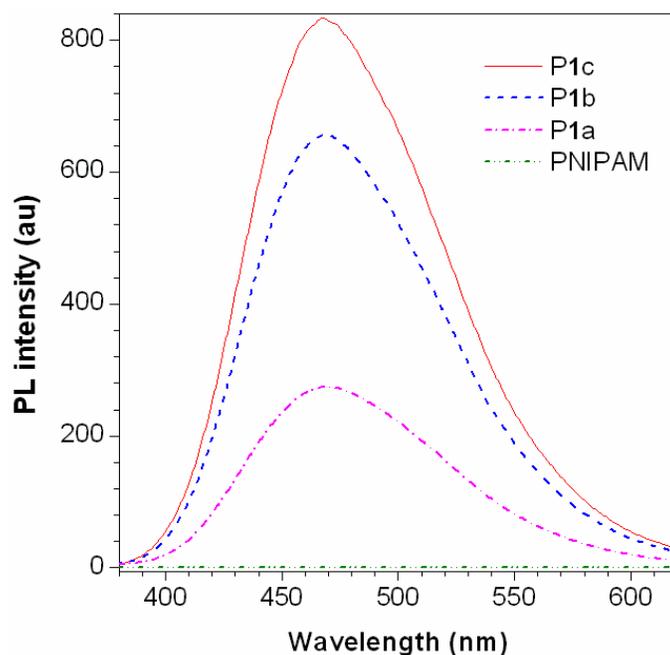


Figure S7. Photoluminescence spectra of aqueous solutions of copolymers P1a–P1c. Concentration of

P1: 1 mg/mL; temperature: 21 °C; excitation wavelength: 322 nm.

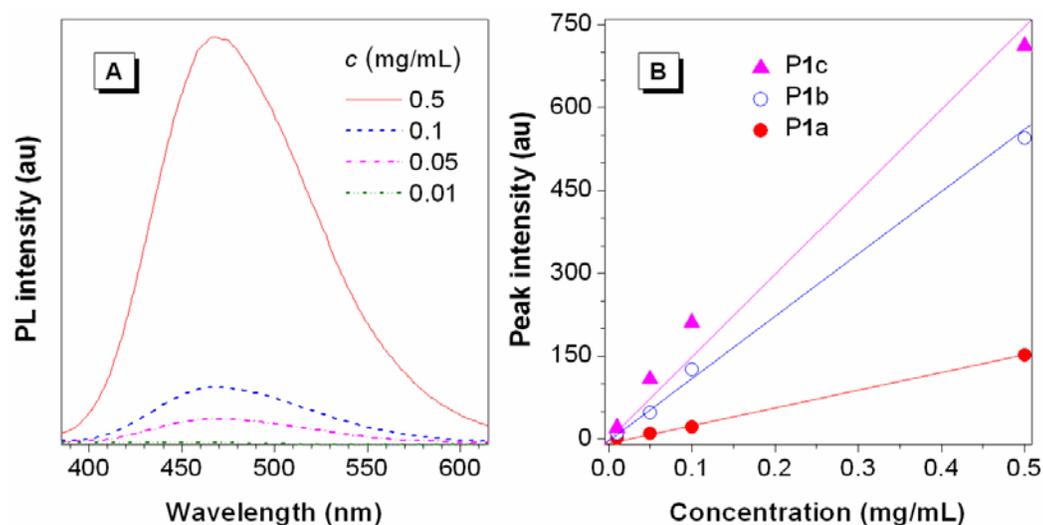


Figure S8. (A) Variation of emission spectrum of aqueous solution of P1a with its concentration (c). (B) Plots of photoluminescence intensities of P1a–P1c at 468 nm vs. solution concentration. Temperature: 21 °C; excitation wavelength: 322 nm.

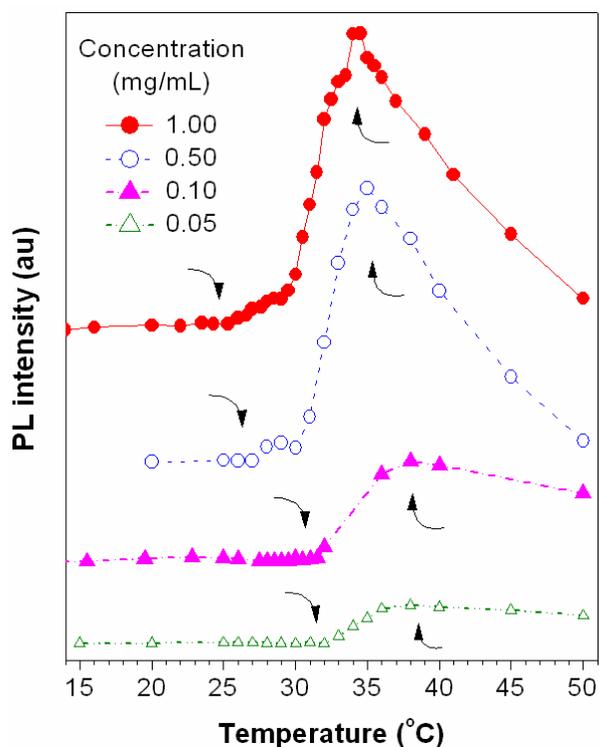


Figure S9. Concentration- and temperature-dependent PL intensity of P1a at 468 nm in water ($\lambda_{\text{ex}} = 322$ nm).