

**Supporting information for**  
**Construction of Well-Defined Difluoromethylthio-Containing**  
**Amphiphilic Homopolymers by RAFT Polymerization**

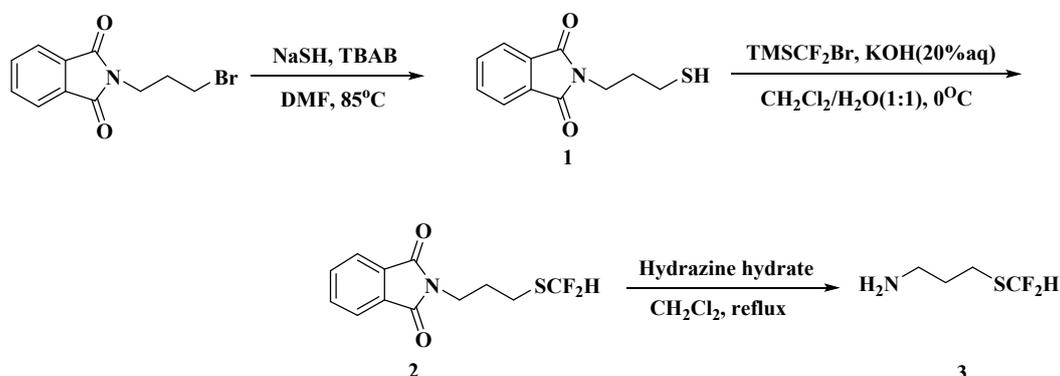
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## Synthesis of 3-difluoromethylthio-1-propylamine

The key intermediate, 3-difluoromethylthio-1-propylamine, was prepared from *N*-(3-bromopropyl)phthalimide via three steps (**Scheme S1**) as below.



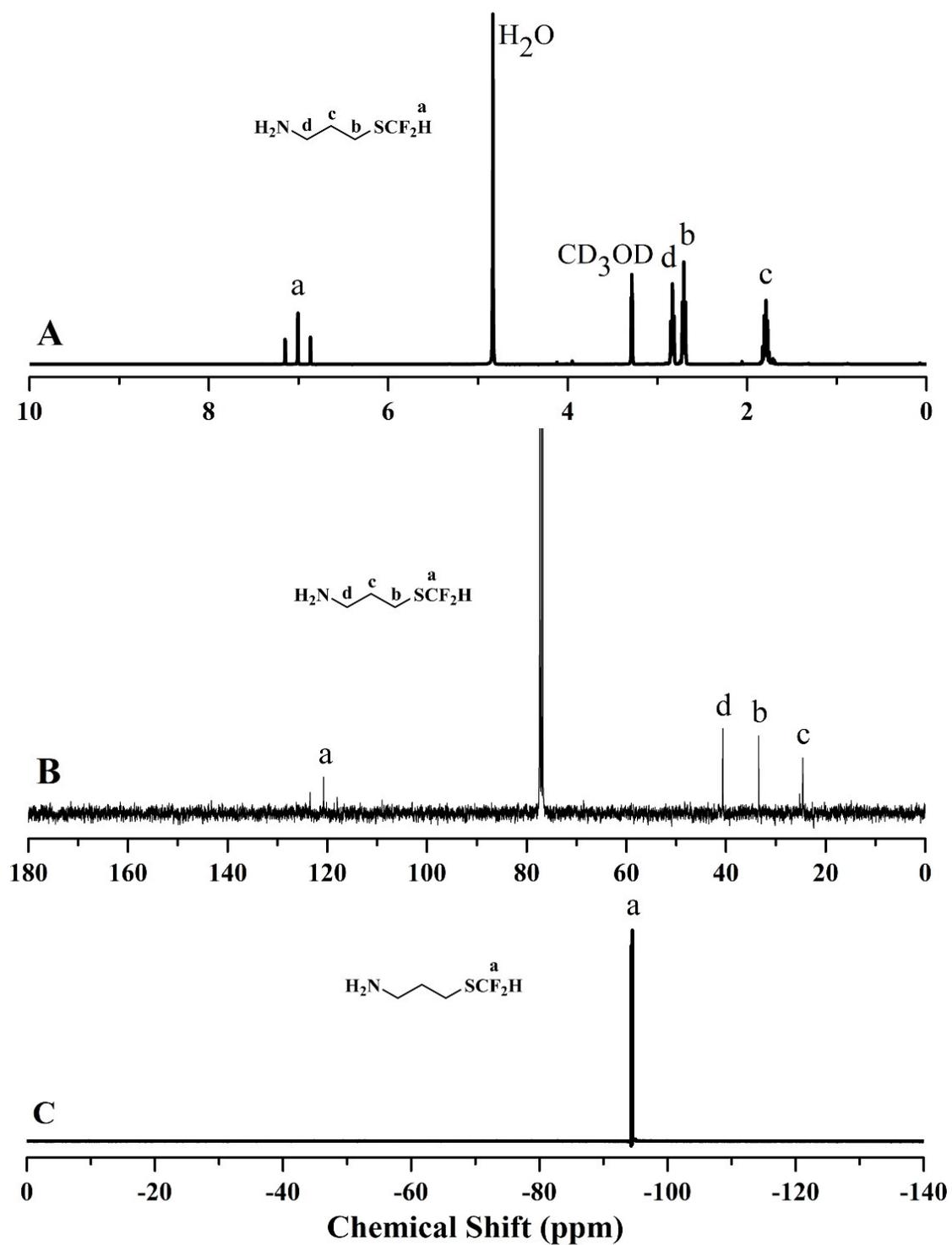
**Scheme S1.** Synthetic route of 3-difluoromethylthio-1-propylamine.

*N*-(3-bromopropyl)phthalimide (100.0 g, 373.1 mmol), NaHS (41.8 g, 74.6 mmol) and 3-difluoromethylthio-1-propylamine (62.7 g, 298.6 mmol) were stirred in *N,N*-dimethylformamide (DMF, 500 mL) at room temperature for 12 h followed by adding water (150 mL) to quench the reaction. The mixture was extracted with dichloromethane (DCM, 100 mL×3), and the organic phase was then collected and washed with water (200 mL×3). After rotary evaporation, the crude product was purified by flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane, v:v = 1:5), affording 45.6 g (55.1%) of *N*-(3-mercaptopropyl)phthalimide **1** as a white crystal. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm): 7.84, 7.71 (4H, phenyl), 3.80 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 2.53 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 1.98 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 1.58 (1H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm): 168.3, 133.9, 132.0, 123.2, 36.3, 32.6, 21.8. FT-IR: ν (cm<sup>-1</sup>): 3451, 2940, 2554, 2081, 1761, 1693, 1467, 1435. ESI-MS *m/z*: 222.06 [M+H]<sup>+</sup>. HR-MS (ESI) *m/z*: [M+H]<sup>+</sup>, calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>NS<sup>+</sup> 222.0583, Found 222.0582.

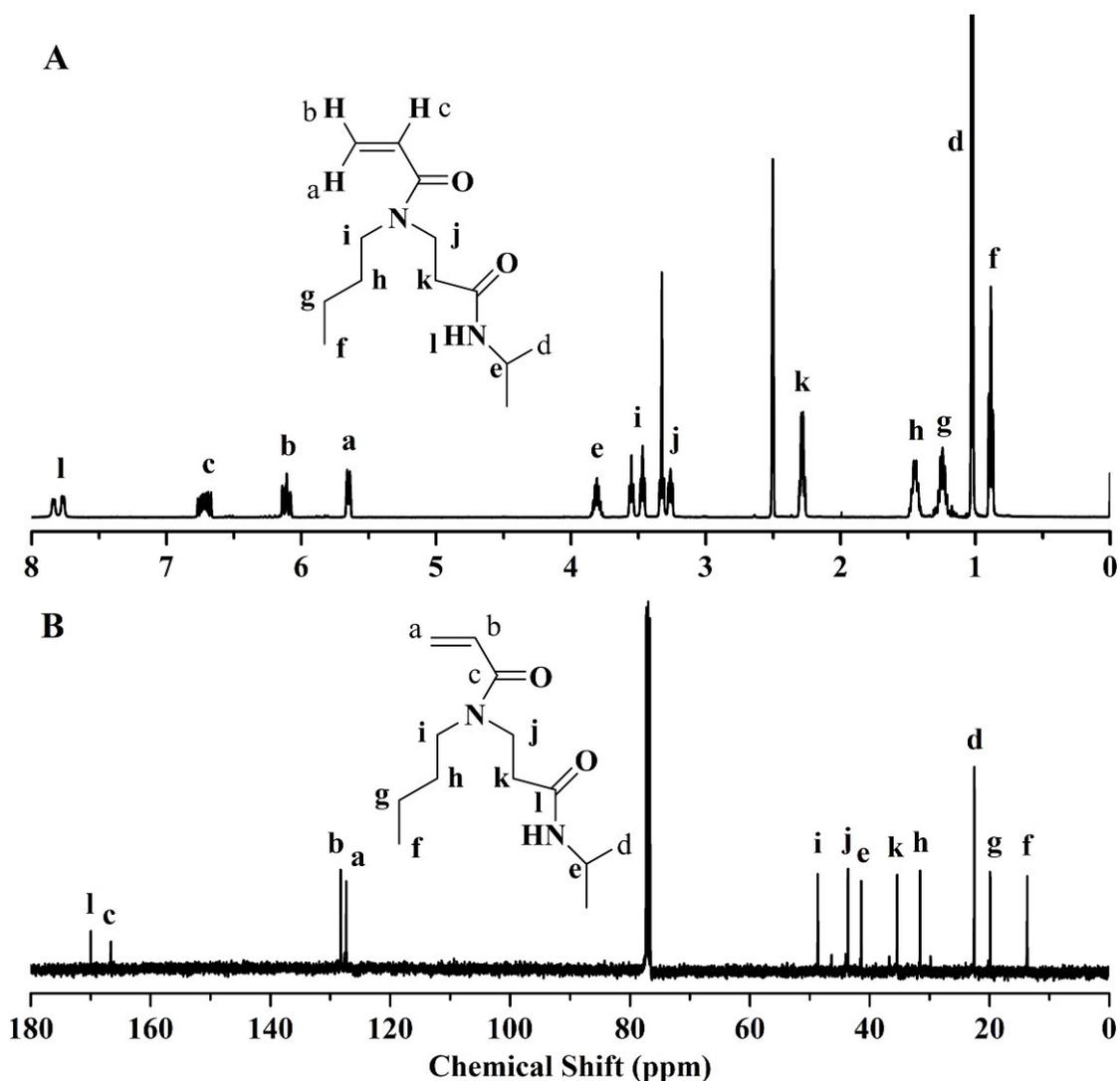
*N*-(3-Mercaptopropyl)phthalimide **1** (16.0 g, 72.1 mmol) and KOH (24.2 g, 96.9 mL, 20% aq) were first added to 200 mL of DCM and the solution was cooled to 0°C. TMSCF<sub>2</sub>Br (22.4 mL, 144.2 mmol) in 50 mL of DCM was then added dropwise within 30 min under stirring. The reaction lasted 1 h and was quenched by water. The organic phase was collected and washed with water (200 mL×3). After rotary evaporation, the crude product was purified by column chromatography on silica gel (eluent: *n*-hexane), affording 10.2 g (54.3%) of *N*-(3-difluoromethylthiopropyl)-phthalimide **2** as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm): 7.84, 7.72 (4H, phenyl), 6.80 (1H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H), 3.80 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H), 2.82 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H), 2.06 (2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm): 168.2, 134.1, 131.9, 123.3, 120.5 (SCF<sub>2</sub>H), 36.6, 29.3, 24.5. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ (ppm): -92.74 (2F, SCF<sub>2</sub>H). FT-IR: ν (cm<sup>-1</sup>): 3459, 2942, 1769, 1701, 1612, 1464, 1437. ESI-MS *m/z*: 294.04 [M+Na]<sup>+1</sup>. HR-MS (ESI) *m/z*: [M+Na]<sup>+1</sup>, calcd for C<sub>12</sub>H<sub>11</sub>O<sub>2</sub>NF<sub>2</sub>NaS<sup>+1</sup> 294.0371, Found 294.0372.

*N*-(3-difluoromethylthiopropyl)phthalimide **2** (8.60 g, 31.7 mmol) and hydrazine hydrate (50 mL, 20 eq) were refluxed in DCM (100 mL) at 75°C for 8 h. The mixture was washed by dichloromethane. The solution was cooled to room temperature and filtered. The obtained white solid was washed with DCM (50 mL×3) followed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After rotary evaporation, the residue was distilled at 50°C under reduced pressure to give 3.00 g (67.1%) of 3-difluoromethylthio-1-propylamine **3** as a colorless liquid. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ (ppm): 7.01 (1H, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H), 2.83 (2H, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCF<sub>2</sub>H), 2.70 (2H,

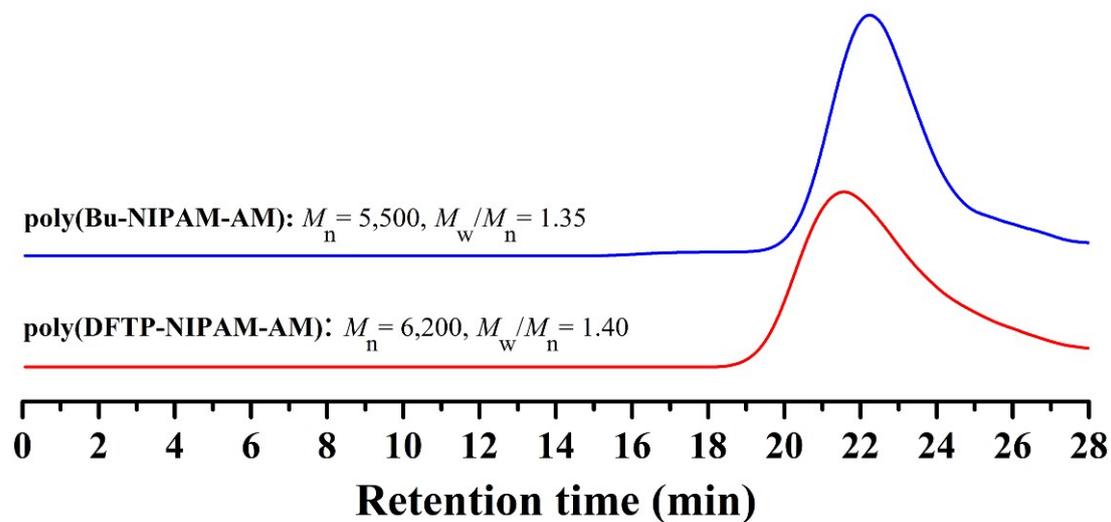
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCF}_2\text{H}$ , 1.79 (2H,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCF}_2\text{H}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm): 120.7 ( $\text{SCF}_2\text{H}$ ), 40.6, 33.4, 24.5.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm): -94.44 (2F,  $\text{SCF}_2\text{H}$ ). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ): 2936, 2863, 1653, 1591, 1442, 1325. ESI-MS  $m/z$ : 142.05  $[\text{M}+\text{H}]^+$ . HR-MS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ , calcd for  $\text{C}_4\text{H}_{10}\text{O}_2\text{NF}_2\text{S}^+$  142.0497, Found 142.0496.



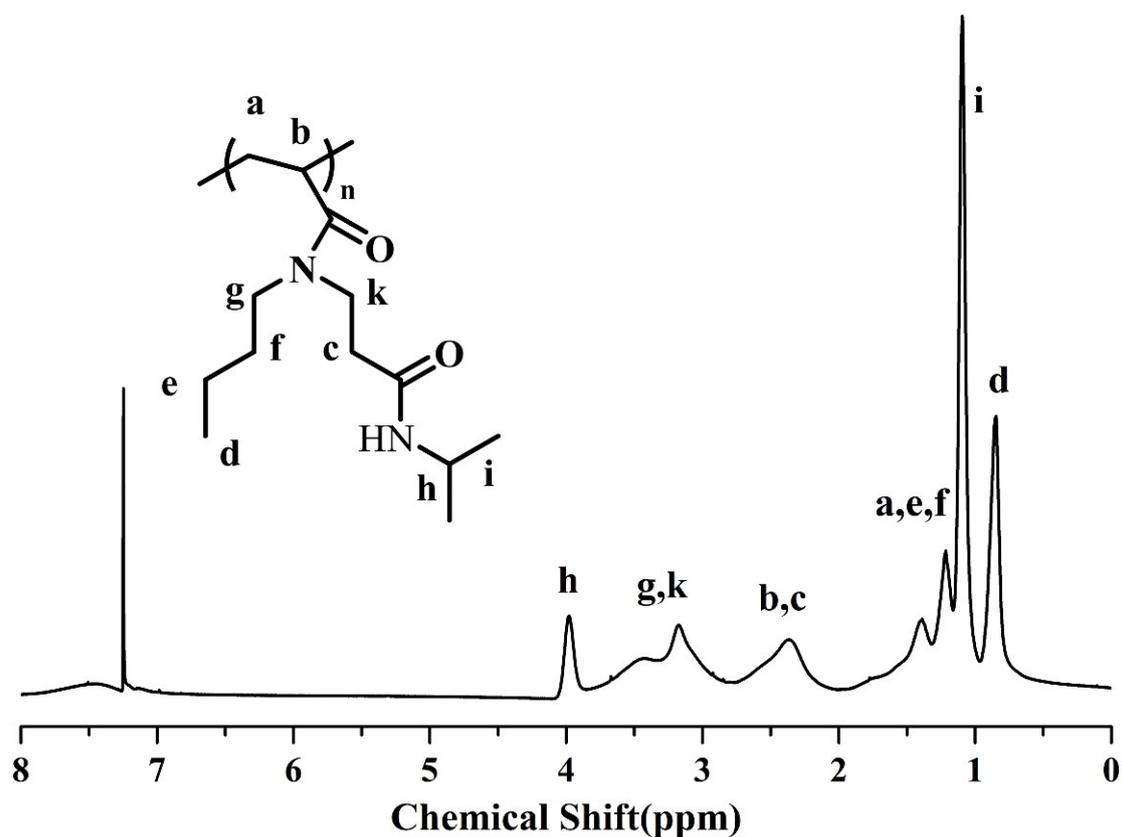
**Figure S1.** <sup>1</sup>H (A), <sup>13</sup>C (B) and <sup>19</sup>F (C) NMR spectra of 3-difluorothiomethyl-1-propylamine in CD<sub>3</sub>OD.



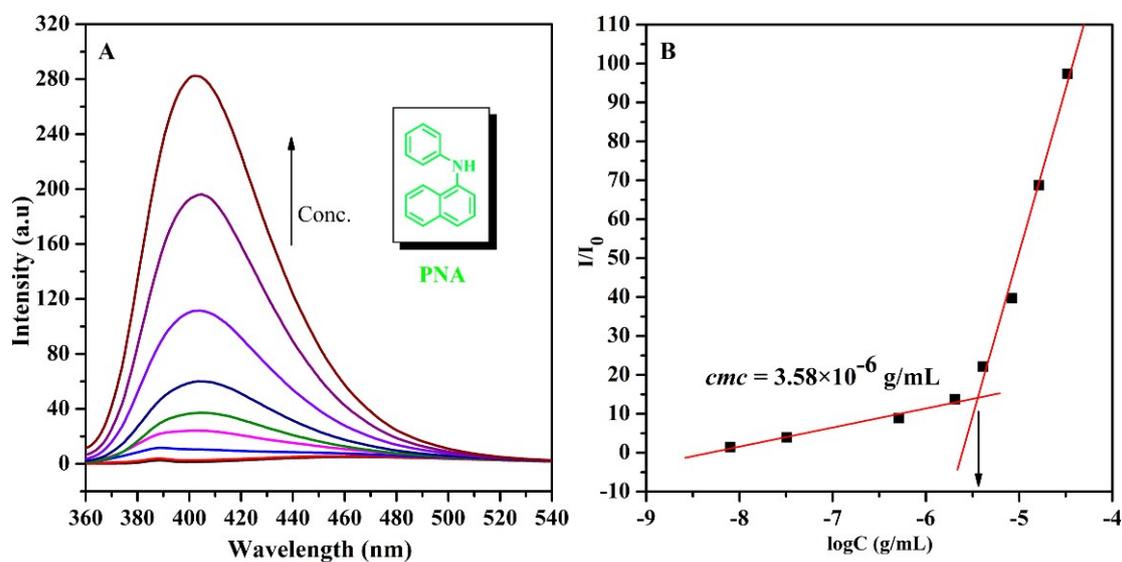
**Figure S2.** (A)  $^1\text{H}$  (in  $\text{DMSO-}d_6$ ) and (B)  $^{13}\text{C}$  (in  $\text{CDCl}_3$ ) NMR spectra of Bu-NIPAM-AM.



**Figure S3.** GPC curves of poly(DFTP-NIPAM-AM) and poly(Bu-NIPAM-AM) in THF.



**Figure S4.**  $^1\text{H}$  NMR spectrum of poly(Bu-NIPAM-AM) in  $\text{CDCl}_3$ .



**Figure S5.** (A) Fluorescence emission spectra of PNA in the aqueous solution of poly(Bu-NIPAM-AM) homopolymer ( $[\text{PNA}] = 2 \times 10^{-6} \text{ mol/L}$ ) and (B) dependence of fluorescence intensity ratio of PNA emission band at 418 nm on the concentration of poly(Bu-NIPAM-AM) homopolymer.