

## Supporting Information

### UV-Responsive Degradable Polymers Derived from 1-(4-Aminophenyl)ethane-1, 2-diol

Liang Ma<sup>1</sup>, Ryan Baumgartner<sup>2</sup>, Yanfeng Zhang<sup>1</sup>, Ziyuan Song<sup>1</sup>, Kaimin Cai<sup>1</sup> and Jianjun Cheng<sup>1,2</sup>

<sup>1</sup>Department of Materials Science and Engineering, University of Illinois at Urbana–Champaign, Urbana, Illinois, 61801, USA

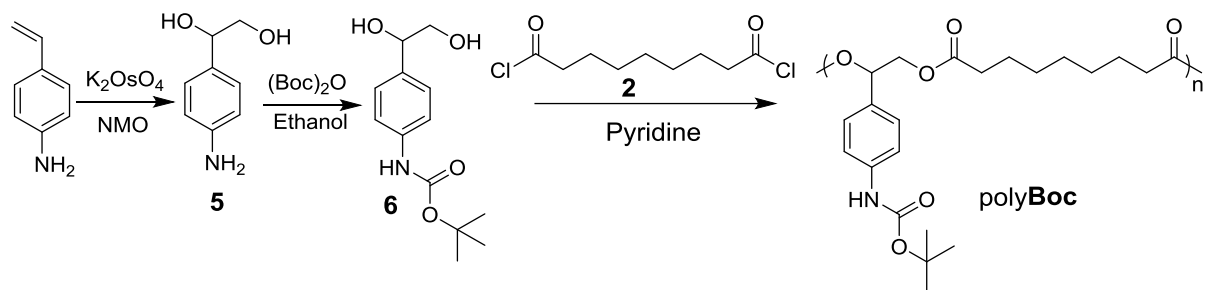
<sup>2</sup>Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois, 61801, USA

Correspondence to: Jianjun Cheng (E-mail: [jianjunc@illinois.edu](mailto:jianjunc@illinois.edu))

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### Scheme S1. Synthesis of polyBoc



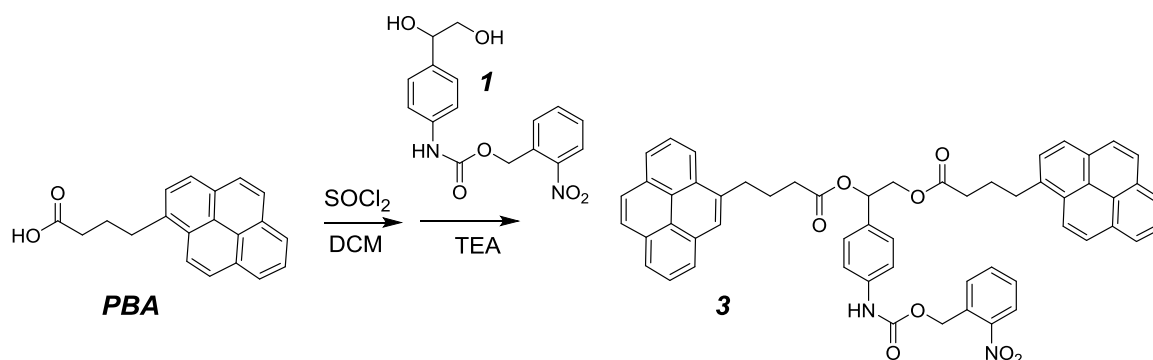
**Synthesis of 1-(4-aminophenyl)ethane-1,2-diol (5).** 4-Vinylaniline (1g, 8.4 mmol) and  $K_2OsO_4$  (9126 mg, 0.083 mmol) was dissolved in 120 mL of Acetone/ $H_2O$  (v/v = 3: 1), then 2.08 mL of NMO solution (10 mmol) was added. The reaction was allowed for overnight and ten 50 mL of saturated aqueous solution of  $Na_2S_2O_3$  was added. After stirred for overnight, the resulting solution was extracted by EtOAc. The product was purified by silica gel column after the removal of solvent to give white solid **5**. (Hexane: Ethyl Acetate = 0: 1). (0.51 g, Yield: 40 %).  $^1H$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  6.93 (d, 2H, ArH), 6.48 (d, 2H, ArH), 4.88 (s, 2H, -Ph- $NH_2$ ), 4.47 (s, 1H, -Ph-CH-OH), 4.45 (m, 1H, -Ph-CH- $CH_2$ ), 4.32 (m, 1H, -Ph-CH- $CH_2$ -OH), 3.30 (m, 2H, Ph-CH- $CH_2$ -OH).  $^{13}C$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  148.19, 131.13, 127.61, 114.06, 74.48, 68.33. ESI-MS (low resolution, positive mode): calculated for  $C_8H_{11}NO_2$ ,  $m/z$ , 154.08  $[M + H]^+$ ; found 154.08  $[M + H]^+$ .

**Synthesis of tert-butyl (4-(1,2-dihydroxyethyl)phenyl)carbamate (6).** Under  $N_2$ , compound **5** (0.3g, 2 mmol) and  $Boc_2O$  (0.915 g, 4.2 mmol) was added into the 10 mL EtOH, and the reaction was allowed to react under refluxing for 36 hours. The solvent was removed by vacuum and solid was purified by silica gel chromatography to give white solid **6** (ethyl acetate: hexane = 1: 2 to 1: 1). (0.35 g, Yield: 80%).  $^1H$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  9.25 (s, 1H, -Ph-NH), 7.36 (d, 2H, ArH), 7.16 (d, 2H, ArH), 5.10 (s, 1H, -Ph-CH-OH), 4.65 (m, 1H, -Ph-CH- $CH_2$ ), 4.41 (m, 1H, -Ph-CH- $CH_2$ -OH), 3.31 (m, 2H, Ph-CH- $CH_2$ -OH).  $^{13}C$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  153.47,

138.86, 137.71, 127.15, 118.36, 79.51, 74.16, 68.18, 28.82. ESI-MS (low resolution, positive mode): calculated for  $C_8H_{11}NO_2$ ,  $m/z$ , 276.12  $[M + Na]^+$ ; found 276.12  $[M + Na]^+$ .

**Synthesis of polyBoc.** To the solution of compound **6** (150 mg, 0.59 mmol) and azelaic acid dichloride (133.4 mg, 0.59 mmol) in DCM (5 mL), anhydrous pyridine (190  $\mu$ L, 6 mmol) was added dropwise over 10 min under nitrogen. The solution was stirred for 22 h at room temperature. The reaction mixture was concentrated to 0.5 mL under vacuum, and precipitated into cold methanol (10 mL). The precipitate was collected by centrifugation at 4000 r.p.m. and dried under vacuum. PolyBoc was obtained as a white solid (100 mg, yield 40%)  $M_n = 8.0$  kDa;  $M_w/M_n = 1.31$ .  $\delta$  7.38–7.25 (m, 4H, ArH), 6.76 (s, 1H, Ar-NH-CO-O-), 5.95 (s, 1H, Ph-CH-O-CO), 4.28 (s, 2H, -CH-CH<sub>2</sub>O-CO-), 2.37–2.23 (m, 4H, -CO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.59–1.19 (m, 10H, -OCO-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub>-CH<sub>2</sub>-), 124 (-Ph-NH-CO-O-C(CH<sub>3</sub>)<sub>3</sub>).

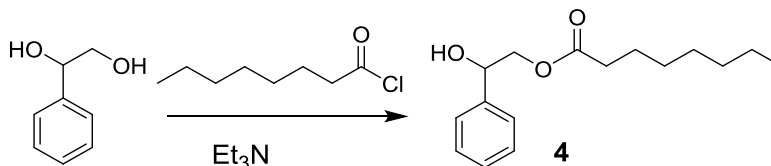
## Scheme S2. Synthesis of compound 3



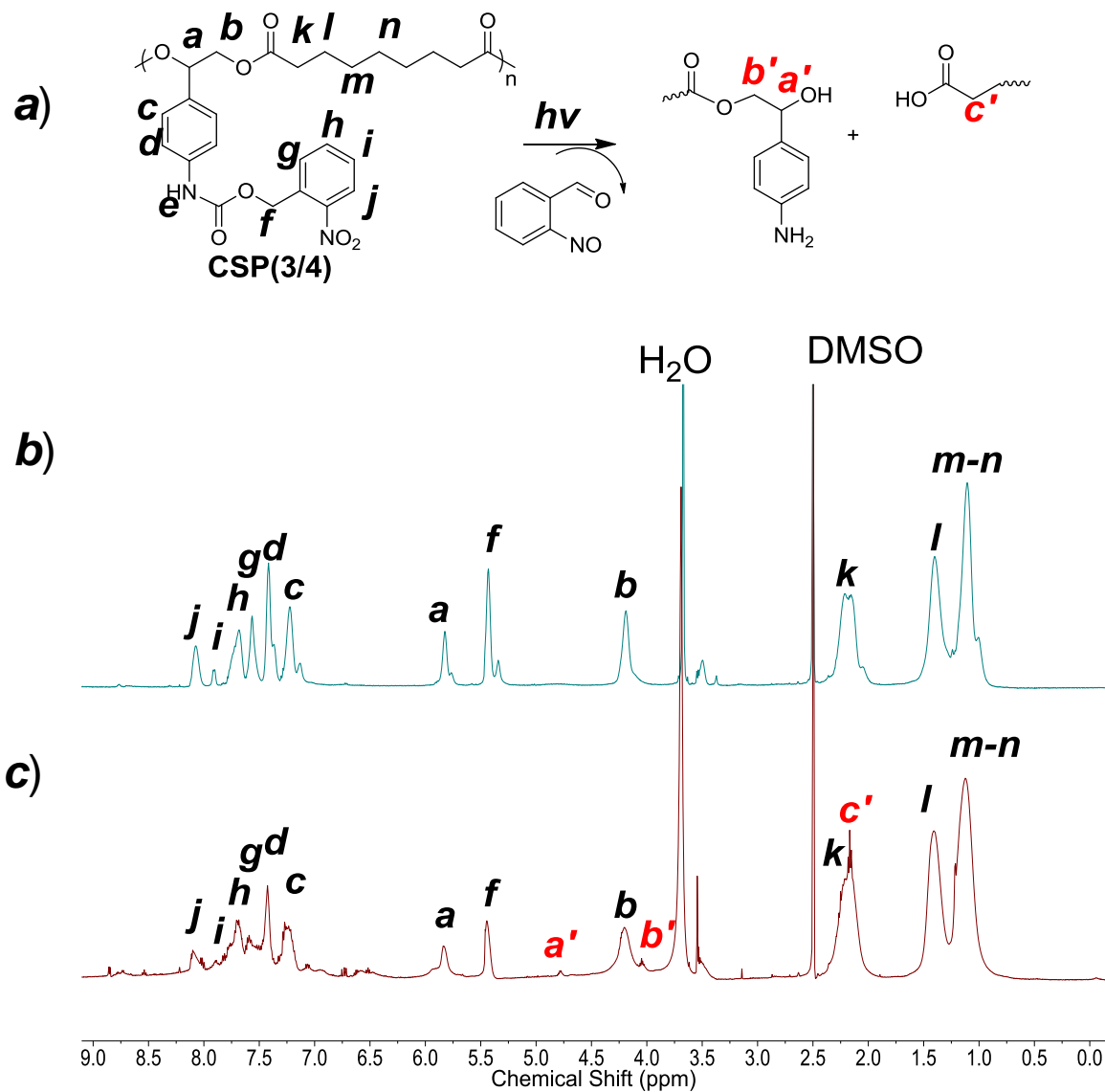
**Synthesis of 1-(4-(((2-nitrobenzyl)oxy)carbonyl)amino)phenyl)-2-((4-(pyren-1-yl)butanoyl)oxy) ethyl 4-(pyren-4-yl) butanoate (3).** To the solution of 1-pyrenebutyric acid (PBA) (228 mg, 0.792 mmol) in anhydrous DCM (7 mL), SOCl<sub>2</sub> (1.5 mL, 20 mmol) was added. The resulting solution was heated to reflux for 3 h and the solvent was removed under vacuum. The resulting liquid residue was used directly without purification. The above residue was dissolved in anhydrous DCM (5 mL) followed by addition of the solution of compound 1 (100 mg, 0.3 mmol) in DCM/THF (1: 3, v/v, 16 mL) at 0 °C. Triethylamine (210 μL, 1.5 mmol) was then added. The reaction solution was allowed to gradually warm up to room temperature and stirred overnight. The resulting solution was filtered and the filtrate was washed with brine (3 × 50 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and crude product was obtained after removal of solvent. The final product was obtained by silica gel column chromatography using a gradient elution (ethyl acetate: hexane = 1:4 to 1:2, v/v). The product was then further purified using silica gel column to give compound 3 as a white solid (60 mg, yield 23%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.21–7.89 (m, 16H, PyH), 7.76–7.68 (m, 2H, ArH), 7.58–7.48 (m, 2H, ArH), 7.45–7.19 (m, 4H, ArH), 6.78 (s, 1H, -O-CO-NH-Ph), 6.07 (d, 1H, Ph-CH-), 5.54 (d, 2H, O<sub>2</sub>N-Ph-CH<sub>2</sub>-), 4.42–4.28 (m, 2H, -CH-CH<sub>2</sub>-O-CO-), 3.25 (m, 4H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-),

2.53–2.37 (d, 4H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.17–2.02 (m, 4H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 173.2, 172.7, 152.7, 138.0, 135.6, 133.9, 132.5, 131.9, 131.5, 131.0, 130.1, 129.1, 128.9, 127.9, 127.7, 127.1, 126.0, 126.3, 125.2, 124.9, 123.8, 118.7, 77.2, 73.0, 66.0, 63.8, 34.1, 33.9, 32.7, 26.8. ESI-MS (low resolution, positive mode): calculated for C<sub>56</sub>H<sub>44</sub>N<sub>2</sub>O<sub>8</sub>Na, *m/z*, 895.3 [M + Na]<sup>+</sup>; found 895.29 [M + Na]<sup>+</sup>.

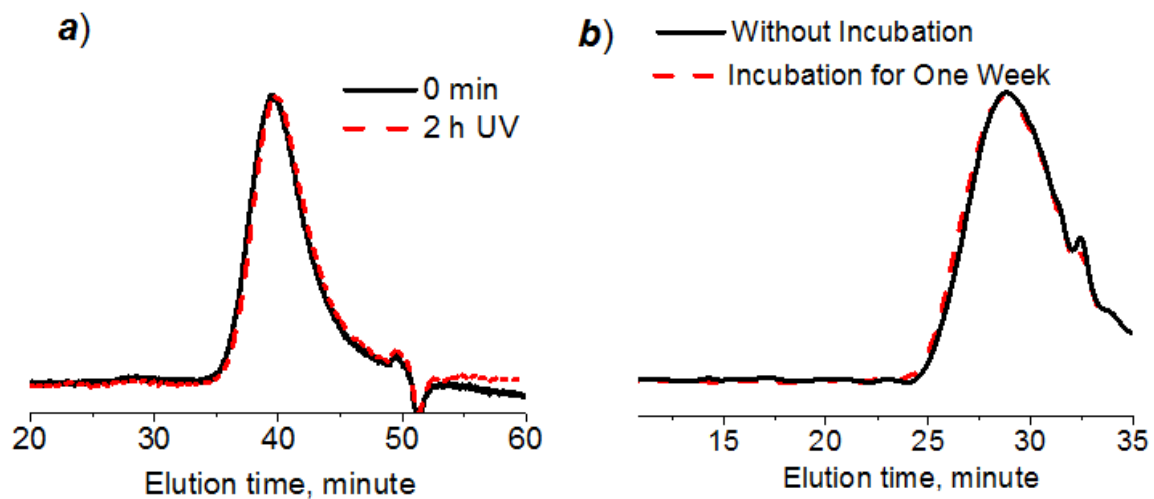
**Scheme S3.** Synthesis of 2-hydroxy-2-phenylethyl octanoate (**4**)



**Synthesis of 2-hydroxy-2-phenylethyl octanoate (4).** Triethylamine (0.242 g, 2.4 mmol) was added dropwise into the solution of 1-Phenyl-1,2-ethanediol (0.256 g, 2 mmol) and octanoyl chloride (0.325 g, 2 mmol) in DCM (20 mL) under nitrogen at 0 °C. The reaction solution was allowed to gradually warm up to room temperature and stirred overnight and filtered. The filtrate was dried and crude solid was obtained. The product was purified by silica gel column chromatography (hexane: ethyl acetate = 15: 1, v/v) to give compound **4** as a colorless oil (158 mg, yield 30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.46–7.27 (m, 5H, ArH), 4.96 (d, 1H, -CH-CH<sub>2</sub>-O), 4.37–4.26 (m, 1H, -CH-CH<sub>2</sub>-O), 4.22–4.12 (m, 1H, -CH-CH<sub>2</sub>-O), 2.55 (s, 1H, Ph-CH-OH), 2.40–2.30 (m, 2H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.71–1.57 (m, 2H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.37–1.22 (m, 8H, -O-CO-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>), 0.93–0.84 (m, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 173.4, 142.7, 128.7, 127.9, 126.9, 70.9, 69.0, 34.1, 31.7, 29.0, 25.0, 25.1, 22.7, 14.6. ESI-MS (low resolution, positive mode): calculated for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>Na, *m/z*, 287.2 [M + Na]<sup>+</sup>; found 287.17 [M + Na]<sup>+</sup>.

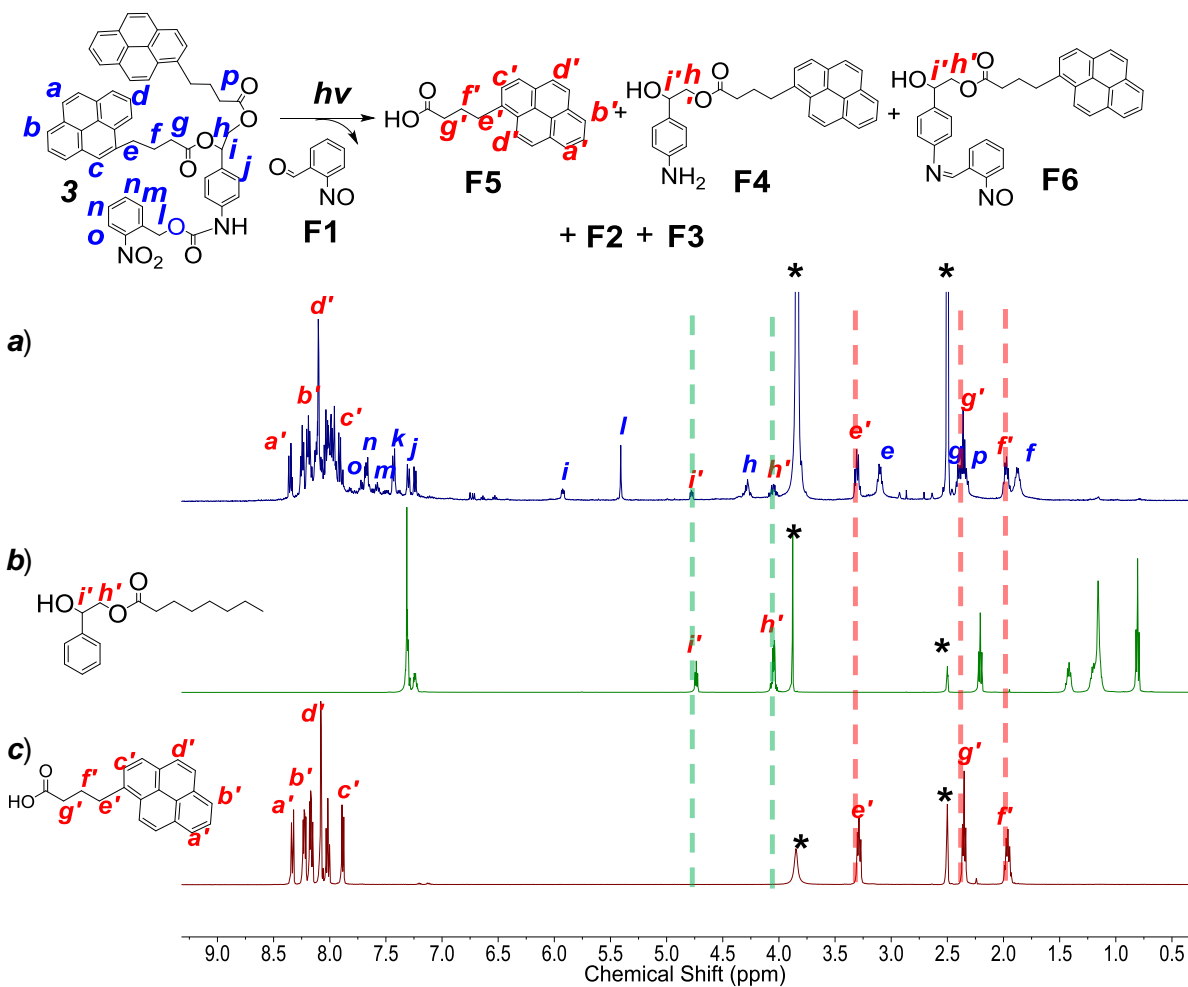


**Figure S1.** (a) Proposed mechanism of degradation of poly (**1/2**) after the removal of protecting group;  $^1\text{H}$  NMR spectra of poly (**1/2**) in  $\text{DMSO-}d_6$ :  $\text{D}_2\text{O}$  (10: 1, v/v) before (b) and after (c) UV irradiation ( $365\text{ nm}$ ,  $50\text{ mW/cm}^2$ ,  $40\text{ min}$ ) with incubation for  $72\text{ h}$  at  $37\text{ }^\circ\text{C}$ .

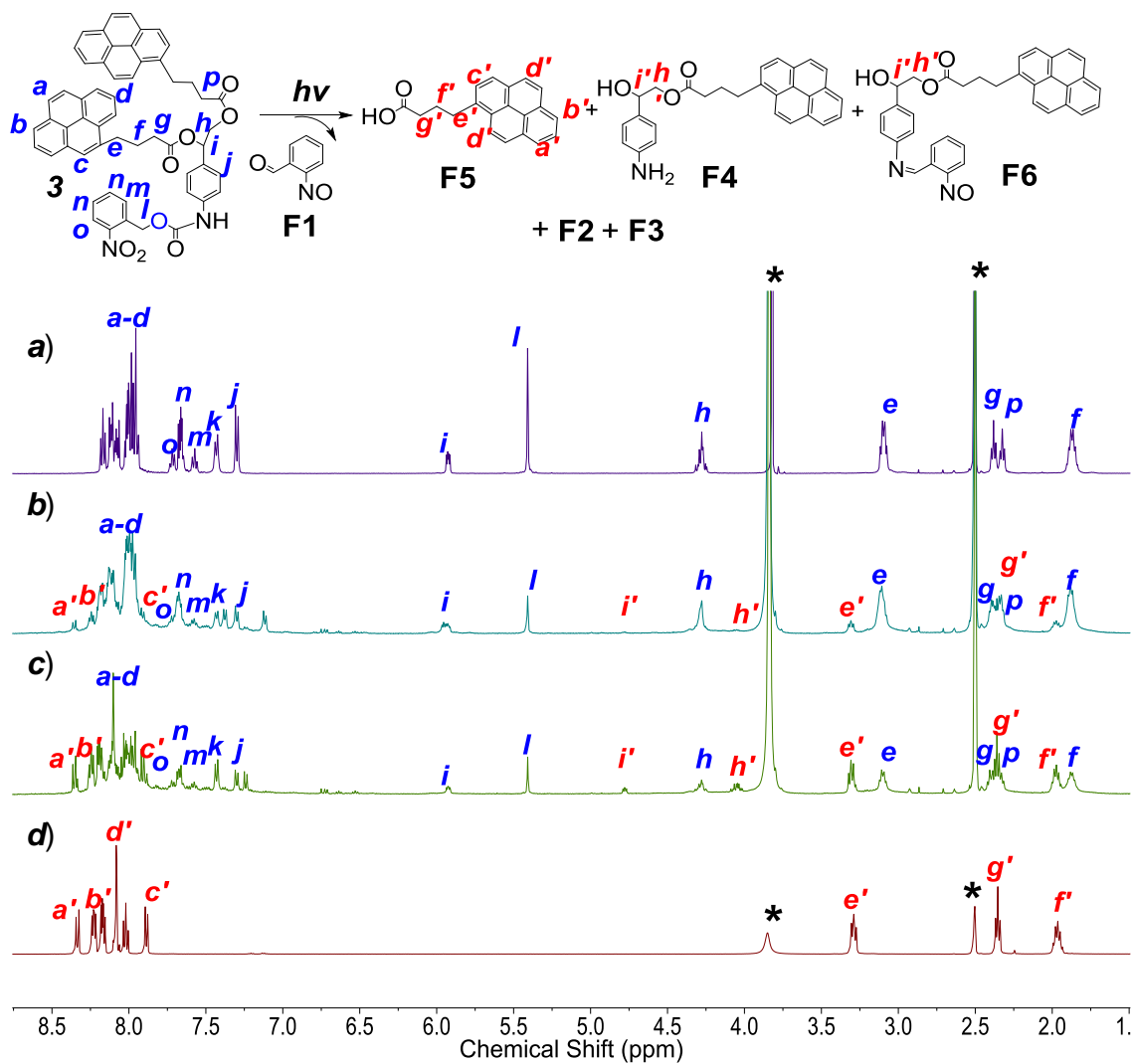


**Figure S2.** (a) GPC curves of polyBoc before UV irradiation and after UV light irradiation for 2 h in DMF/H<sub>2</sub>O (v/v, 95: 5) followed by 96 h incubation at 37 °C; (b) GPC curves of poly (1/2) before and after incubation under dark at 37 °C for 7 days in DMF/H<sub>2</sub>O (95: 5, v/v). Note: Different size exclusion column was used to characterize polyBoc and poly (1/2).





**Figure S3.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$ :  $\text{D}_2\text{O}$  (5: 1, v/v) of (a) **3** after UV irradiation (365 nm,  $50 \text{ mW cm}^{-2}$ ) for 80 min and incubation under dark for 80 h; (b) 2-hydroxy-2-phenylethyl octanoate (**4**); (c) **F5**. Asterisks represent peaks due to solvents.



**Figure S4.**  $^1\text{H}$  NMR spectra of **3** in DMSO- $d_6$ : D $_2$ O (5: 1, v/v) (a) before UV irradiation; (b) and after UV irradiation (365 nm, 50 mW/cm $^2$ ) for 80 min without incubation; and (c) incubation under dark at 37 °C for 80 h; (d)  $^1\text{H}$  NMR spectrum of **F5** in DMSO- $d_6$ : D $_2$ O (5: 1, v/v).

Asterisks represent peaks due to solvents.

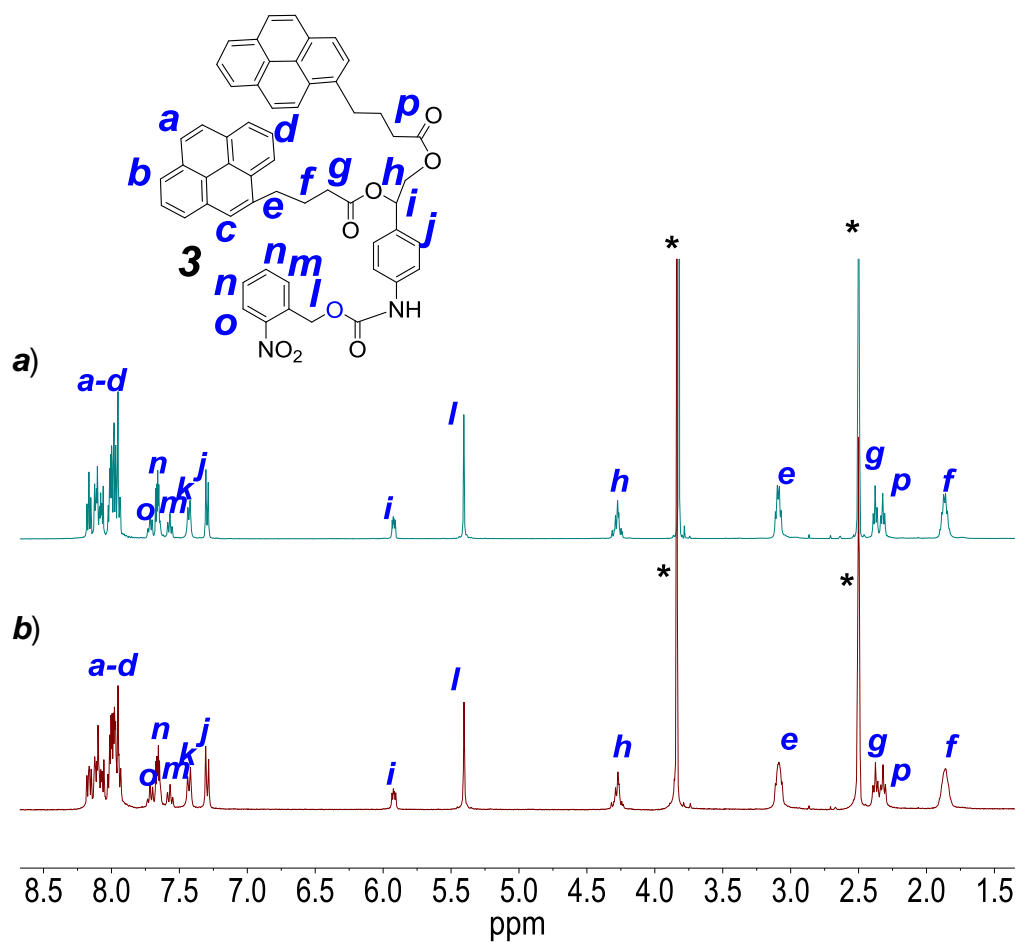
**Calculation of percentage of cleaved nitrobenzyl group and percentage of released F5.**

Percentage of cleaved nitrobenzyl group (%)

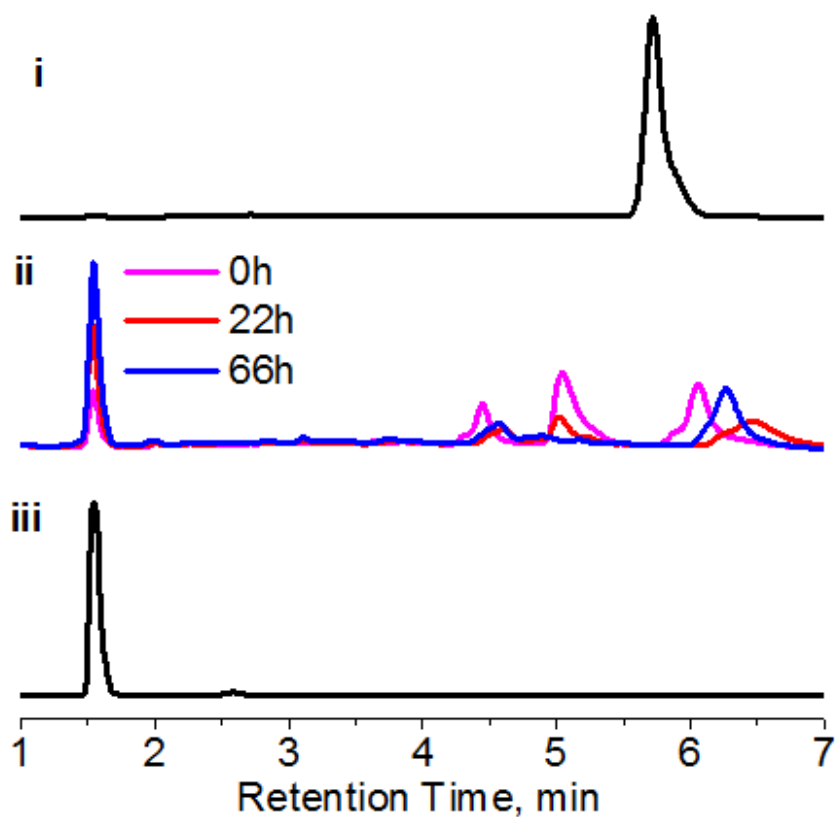
$$= \frac{\text{Integration of peak d (before UV irradiation)} - \text{Integration of peak d (after UV irradiation)}}{\text{Integration of peak f}' + \text{Integration of peak f}} \times 100\%$$

$$\text{Percentage of released F5 (\%)} = \frac{\text{Integration of peak e}'}{(\text{Integration of peak f}' + \text{Integration of peak f})/2} \times 100\%$$

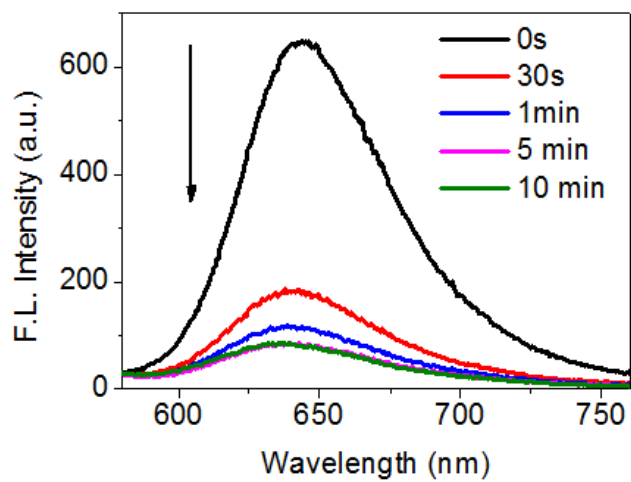
*Note:* During calculation, we set total integration of peak f' and integration of peak f as 1 and other peak's integration refer to them.



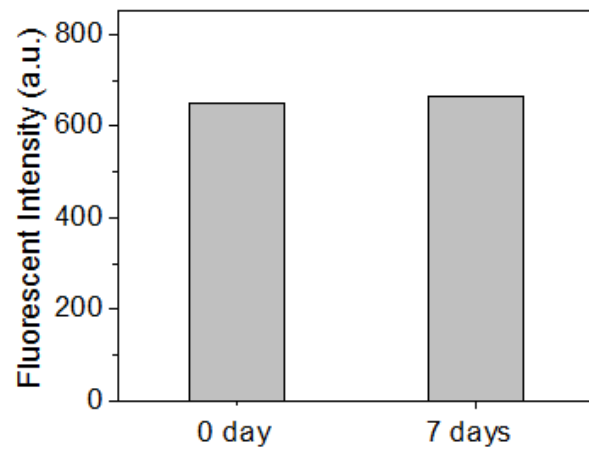
**Figure S5.**  $^1\text{H}$  NMR spectra of **3** in  $\text{DMSO-}d_6$ :  $\text{D}_2\text{O}$  (5: 1, v/v) before (a) and after (b) incubation at 37 °C for one month. Asterisks represent peaks due to solvents.



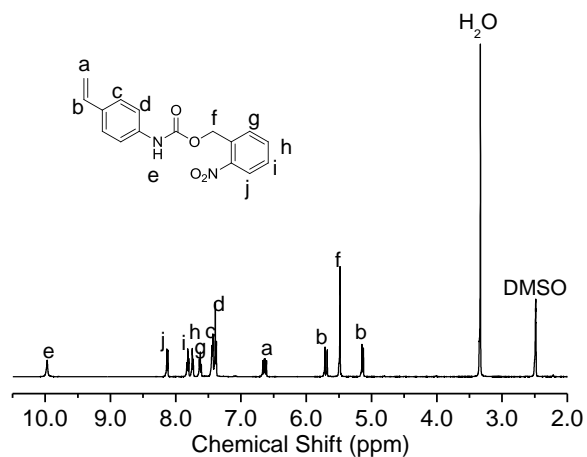
**Figure S6.** HPLC trace monitoring degradation of **3** after UV irradiation in CH<sub>3</sub>CN/H<sub>2</sub>O (9: 1, v/v). (i) **3** before UV irradiation. (ii) **3** with elongation of incubation time after UV irradiation (365 nm, 50 mW cm<sup>-2</sup>) for 1 h in CH<sub>3</sub>CN/H<sub>2</sub>O (9: 1, v/v). (iii) authentic F5 whose retention time is about 1.54 min. F2 eluted out at 5.04 min which was confirmed by HR-ESI.



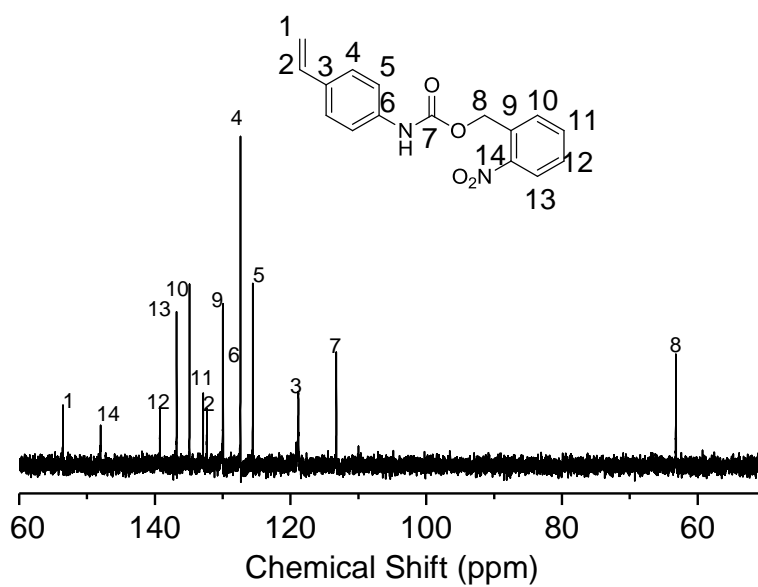
**Figure S7.** Fluorescence spectra change of Nile Red loaded Poly(1/2) nanoparticles water suspension with increase of UV light irradiation time (365 nm, 50 mW cm<sup>-2</sup>). ( $\lambda_{\text{Ex}} = 556$  nm).



**Figure S8.** Fluorescent intensity of Nile Red loaded poly (1/2) nanoparticles incubated in DI-water for seven days.

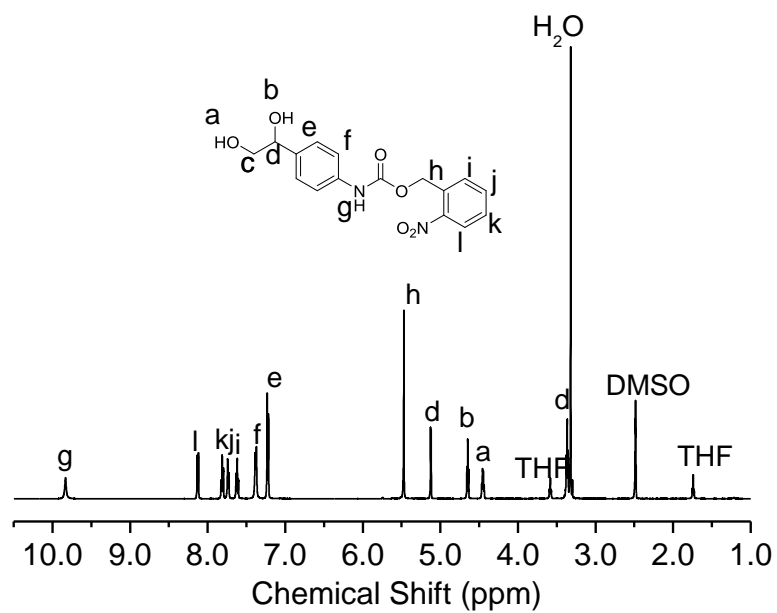


**Figure S9.**  $^1\text{H}$  NMR spectrum of **2-nitrobenzyl (4-vinylphenyl)carbamate** in  $\text{DMSO-}d_6$

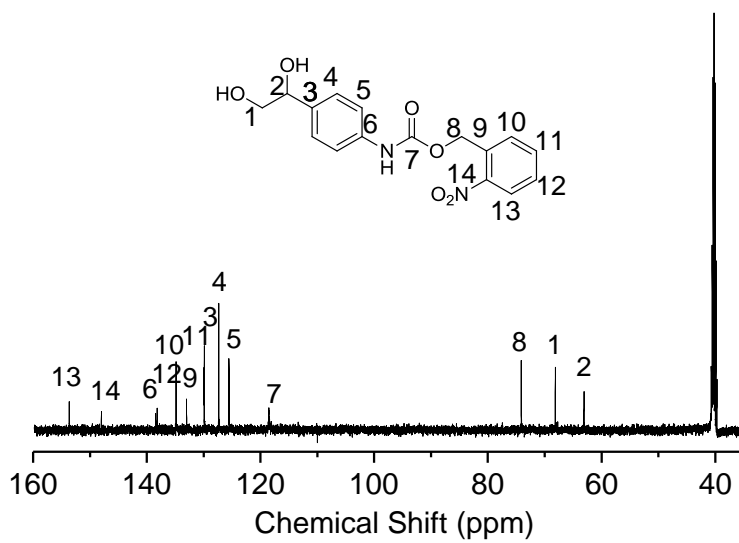


**Figure S10.**  $^{13}\text{C}$  NMR spectrum of **2-nitrobenzyl (4-vinylphenyl)carbamate** in  $\text{DMSO-}d_6$

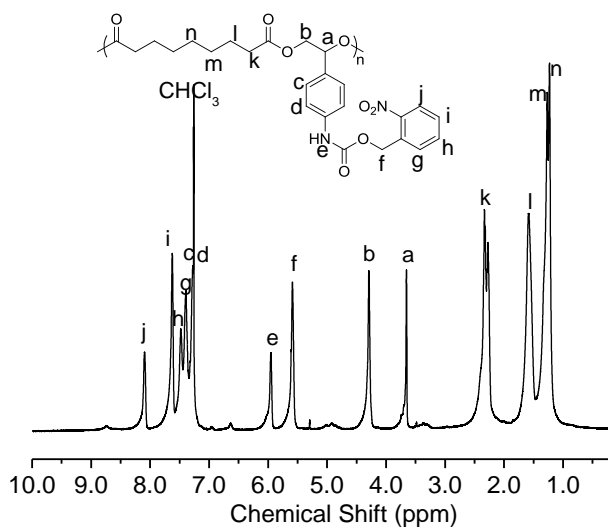




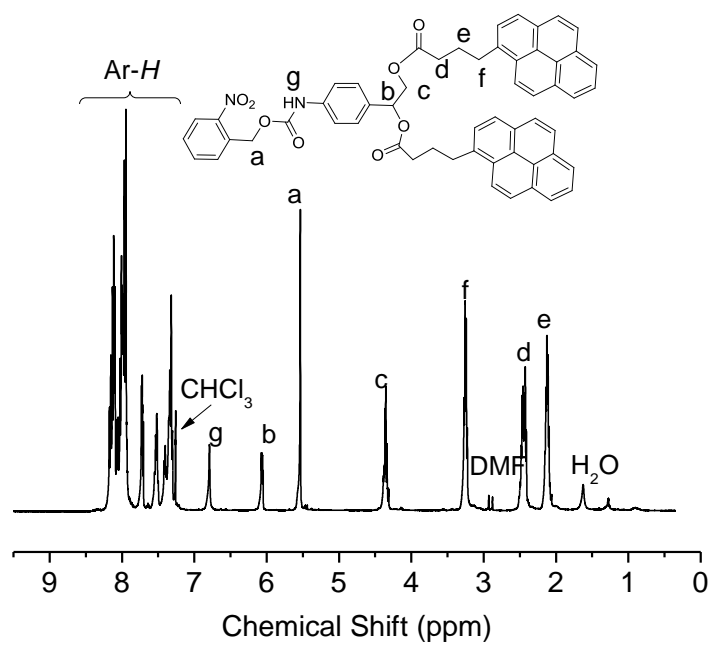
**Figure S11.** <sup>1</sup>H NMR spectrum of **1** in DMSO-*d*<sub>6</sub>.



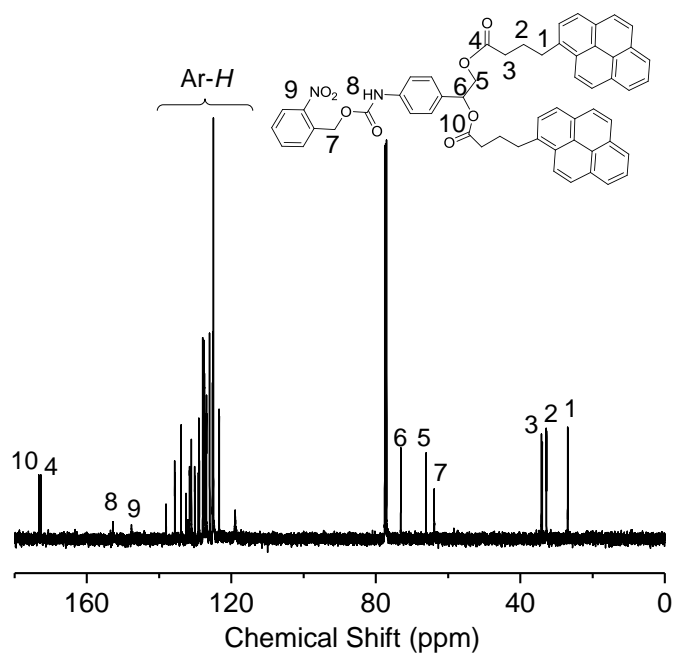
**Figure S12.** <sup>13</sup>C NMR spectrum of **1** in DMSO-*d*<sub>6</sub>.



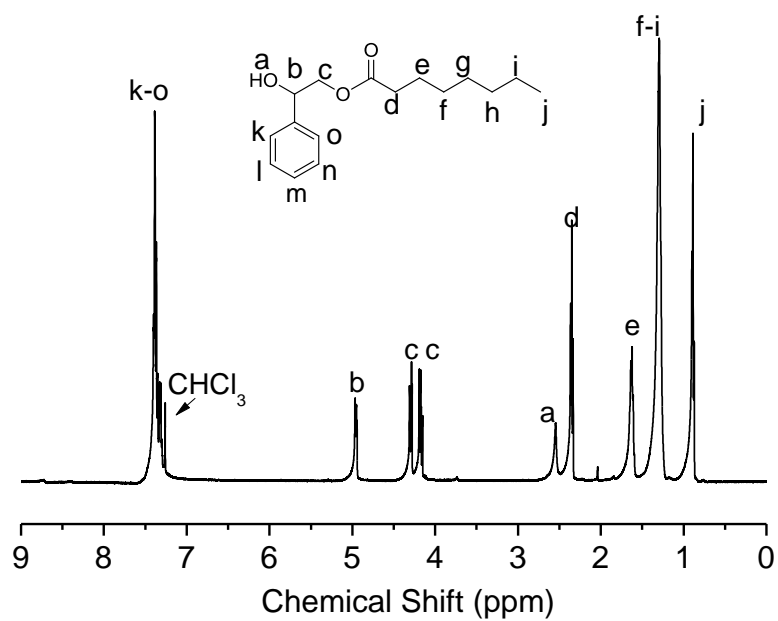
**Figure S13.**  $^1\text{H}$  NMR spectrum of poly (1/2) in  $\text{CDCl}_3$ .



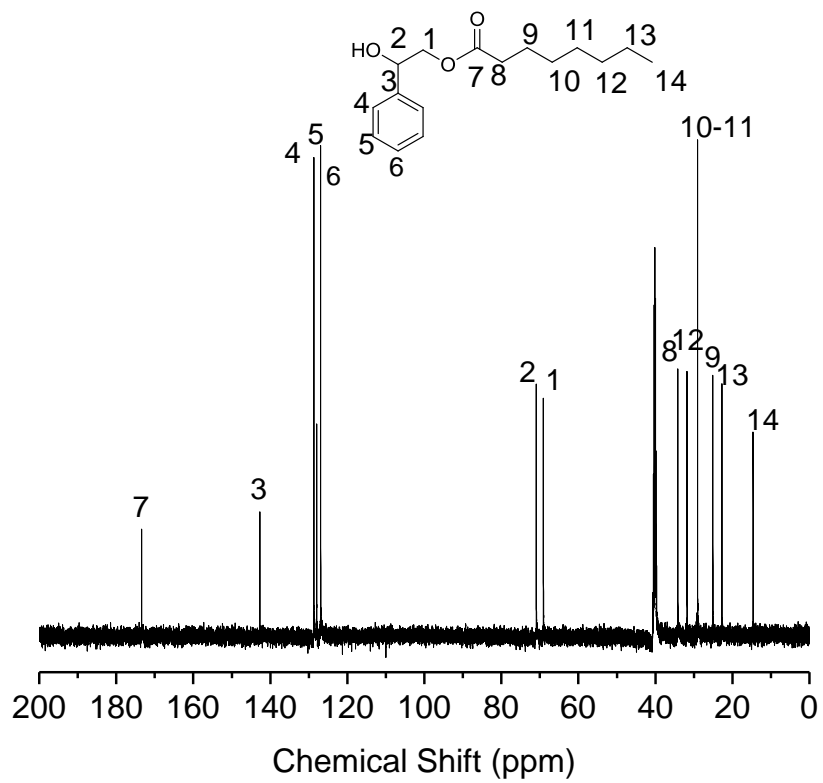
**Figure S14.**  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$



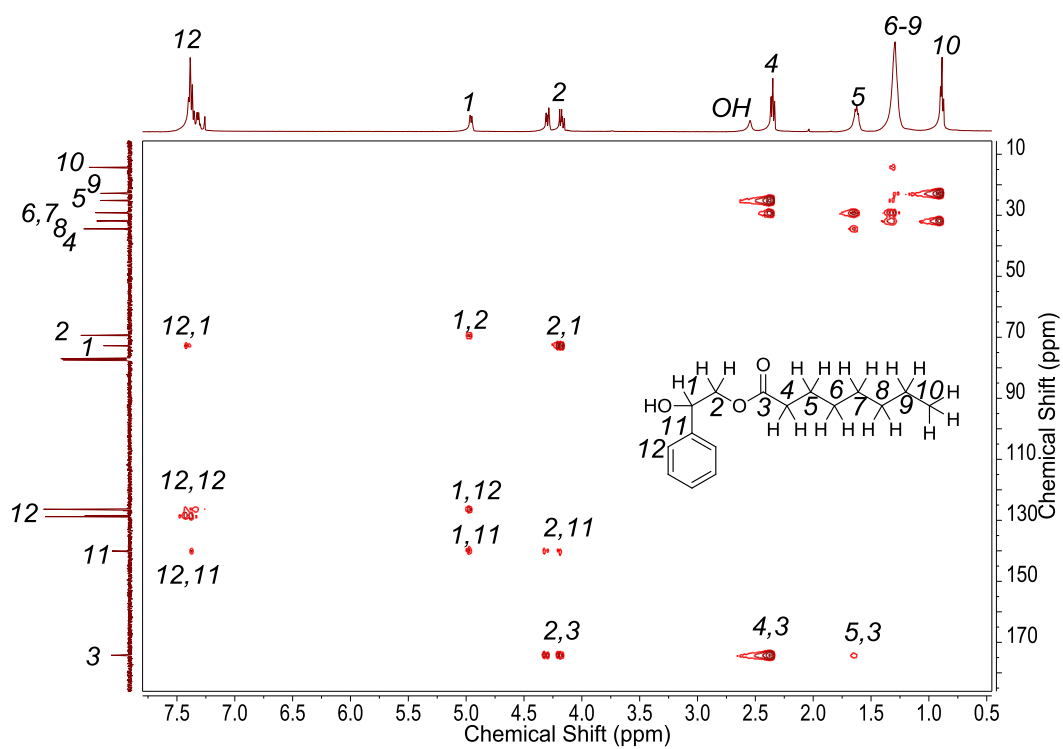
**Figure S15.**  $^{13}\text{C}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$



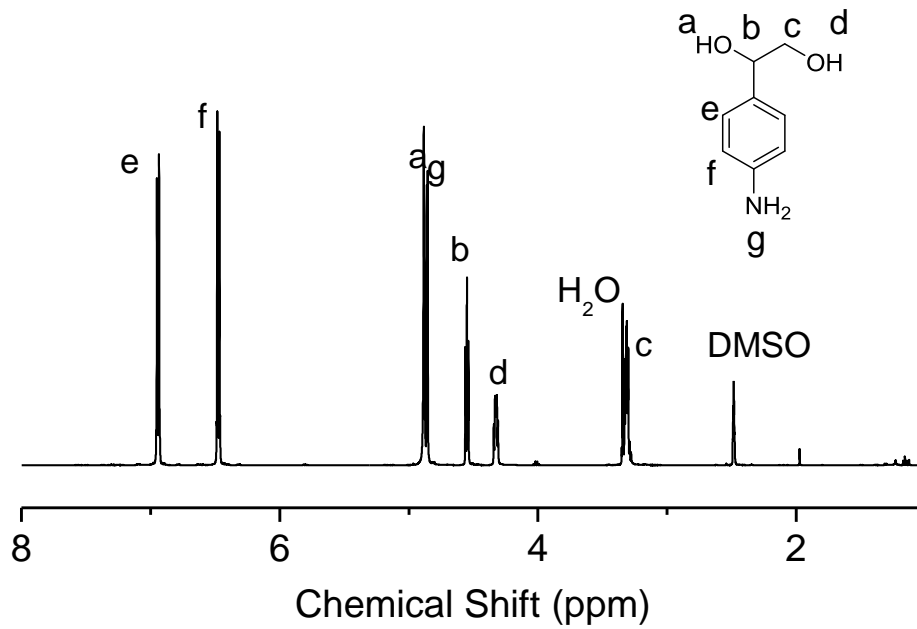
**Figure S16.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{DMSO-}d_6$ .



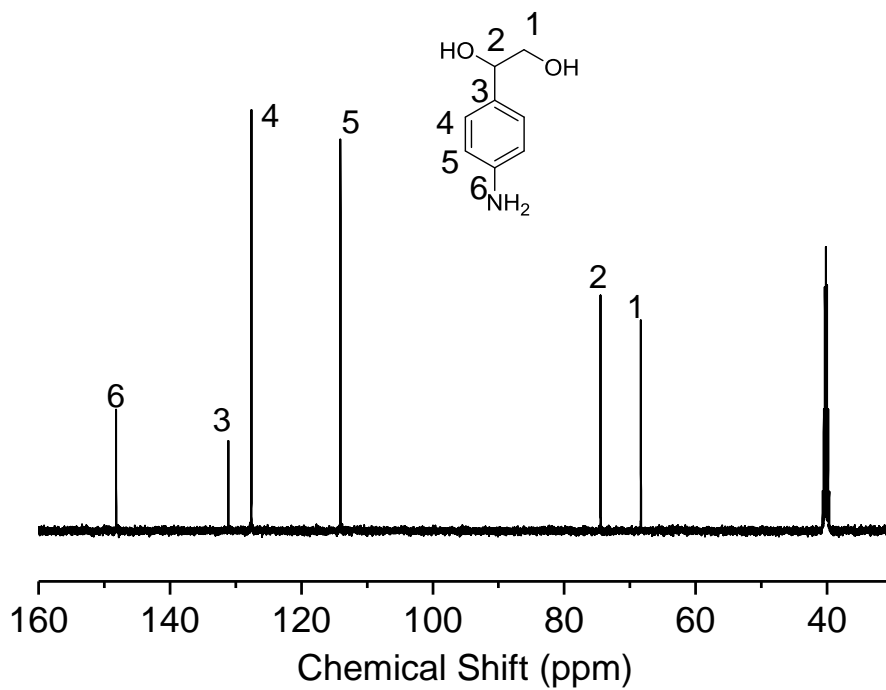
**Figure S17.**  $^{13}\text{C}$  NMR spectrum of **4** in  $\text{DMSO-}d_6$ .



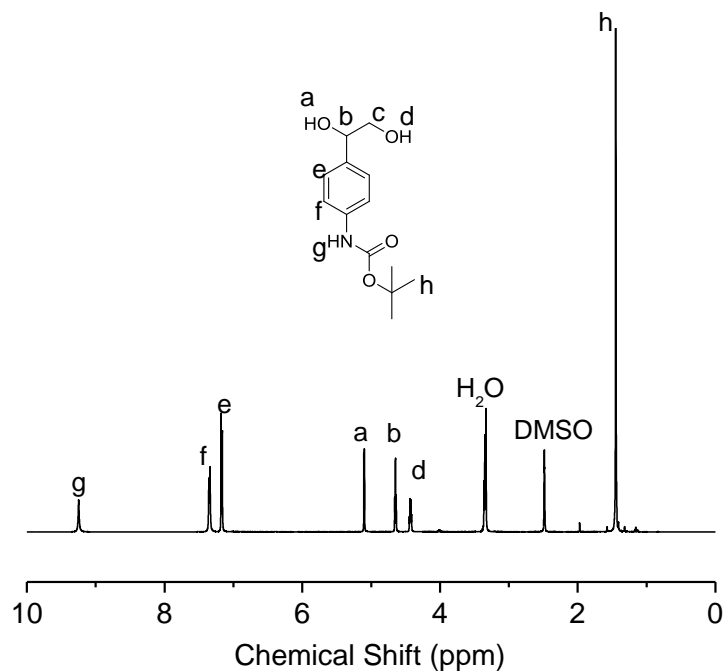
**Figure S18.** gHMBC spectrum of **4** in CDCl<sub>3</sub>.



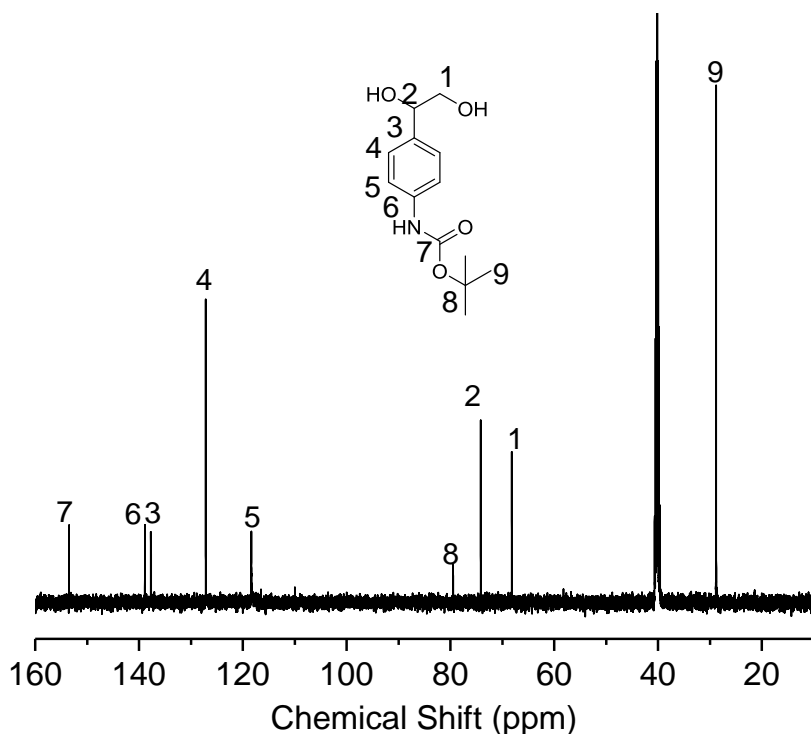
**Figure S19.** <sup>1</sup>H NMR spectrum of **5** in DMSO-*d*<sub>6</sub>.



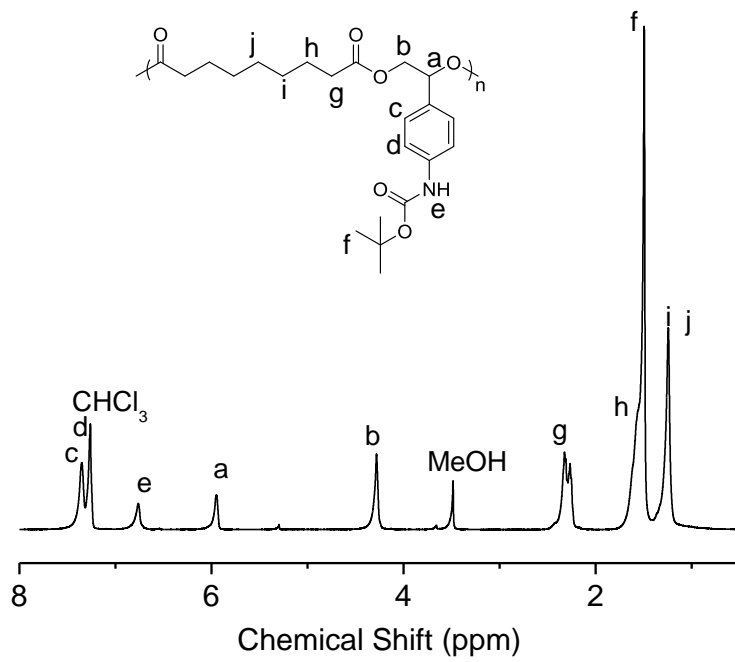
**Figure S20.** <sup>13</sup>C NMR spectrum of **5** in DMSO-*d*<sub>6</sub>.



**Figure S21.**  $^1\text{H}$  NMR spectrum of **6** in  $\text{DMSO}-d_6$ .



**Figure S22.**  $^{13}\text{C}$  NMR spectrum of **6** in  $\text{DMSO}-d_6$ .



**Figure S23.** <sup>1</sup>H NMR spectrum of polyBoc in CDCl<sub>3</sub>.