Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Trigger-Responsive Chain-Shattering Polymers

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Experimental section

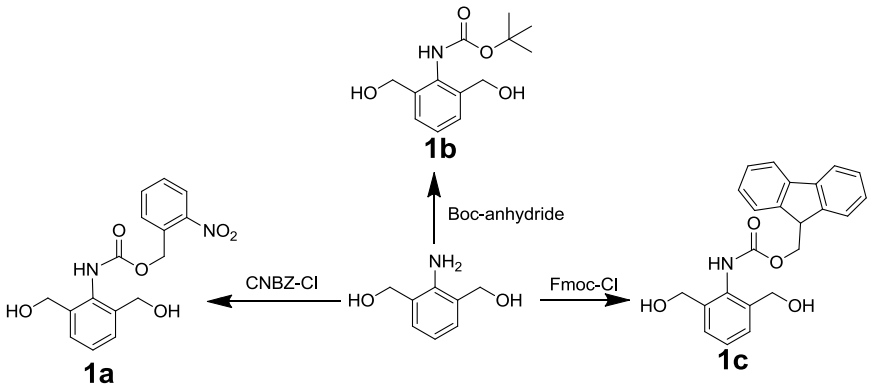
Materials. All chemicals, reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received, unless otherwise specified. Anhydrous dimethylformamide (DMF) was dried with a column packed with 4Å molecular sieves. Tetrahydrofuran (THF) and hexane were dried with a column packed with alumina. 2-Nitro-1,3-phenylenedimethanol was prepared according to the previously reported procedure.[1]

Instrumentation. NMR spectra were recorded on a Varian U400 (400 MHz), a UI500NB (500 MHz), or a VXR-500 (500 MHz) spectrometer. Tandem gel permeation chromatography (GPC) was performed on a system equipped with an isocratic pump (Model 1100, Agilent Technologies, Santa Clara, CA, USA), a DAWN HELEOS 18-angle laser light scattering detector (also known as multi-angle laser light scattering detector (MALLS), Wyatt Technology, Santa Barbara, CA, USA), and an Optilab rEX refractive index detector (Wyatt Technology). The detection wavelength of the HELEOS was set at 658 nm. Separations were performed on serially connected size exclusion columns (100 Å, 500 Å, 10^3 Å, and 10^4Å Phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex, Torrance, CA, USA) at 60°C with DMF containing 0.1 M LiBr as the mobile phase. The HELEOS detector was calibrated with pure toluene without the need of external polymer standards and was used for the determination of the absolute molecular weights. The molecular weight of each polymer was determined from the dn/dc value calculated offline by means of the internal calibration system processed by the ASTRA V software (Version 5.1.7.3, Wyatt Technology). Particle size and dispersity were measured with a ZetaPlus dynamic light scattering detector (15 mW laser, incident beam at 676 nm, Brookhaven Instruments, Holtsville, NY, USA). HPLC was performed on a System Gold system (Beckman Coulter,

Fullerton, CA, USA) equipped with a 126P solvent module, a System Gold 128 UV detector, and an analytical C18 column (Luna C18, 250 mm × 4.6 mm, 5 µm, Phenomenex, Torrance, CA, USA). The UV wavelength for detecting pyrene-based compounds was 340 nm. The UV wavelength for detecting CPT was 370 nm.

Synthesis of 2,6-bis(hydroxymethyl)aniline (BHA). A mixture of 2-nitro-1,3-benzenedimethanol (1.46 g, 8 mmol) and Pd/C (0.12 g, 10 wt%) in MeOH (30 mL) was refluxed under N_2 for 30 min. Hydrazine hydrate (1.25 mL, 25.8 mmol) was then added slowly. The resulting mixture was refluxed for another 8 h. The catalyst was removed by filtration. After the solvent was removed under reduced pressure, the crude residue was re-dissolved in EtOAc (150 mL), washed with brine (3 × 10 mL) and dried with anhydrous $MgSO_4$. The organic solvent was removed under reduced pressure to afford 2,6-bis(hydroxymethyl)aniline (**BHA**) as a white solid (0.90 g, yield 63%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 6.98 (d, J = 7.4 Hz, 2H, Ar*H*), 6.50 (s, 1H, Ar*H*), 5.02 (s, 2H, Ar–NH_2), 4.79 (s, 2H, O*H*), 4.40 (d, J = 5.4 Hz, 4H, ArCH_2–OH). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 143.1, 125.3, 118.6, 60.2. ESI-MS (low resolution, positive mode): calculated for $C_8H_{12}NO_2$, m/z, 154.1 $[M + H]^+$; found 154.1 $[M + H]^+$.

Scheme S1. Synthesis of **1a**, **1b**, and **1c** from 2,6-Bis(hydroxymethyl)aniline (**BHA**).



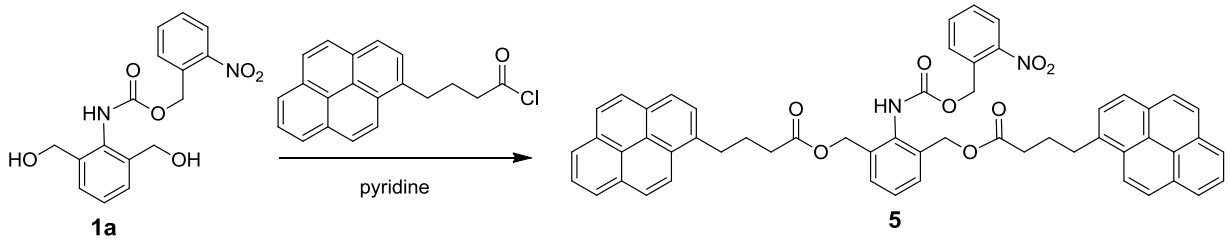
Synthesis of 2-nitrobenzyl(2,6-bis(hydroxymethyl)phenyl)carbamate (1a). 1-(Chlorocarbonyl-oxy-methyl)-2-nitrobenzene was first prepared. A phosgene solution in toluene (15 mL, 20% w/w, 28.8 mmol) was added to a stirred solution of 2-nitrobenzyl alcohol (1.84 g, 12 mmol) in dry THF (20 mL). The mixture was stirred for 16 h at room temperature. The excess phosgene and solvents were removed under reduced pressure, and the phosgene in the vacuum traps was deactivated by aqueous NaOH. The resulting yellowish, oily residue (1-(chlorocarbonyl-oxy-methyl)-2-nitrobenzene) was used in the subsequent reaction without further purification.

BHA (1.50 g, 10 mmol) was dissolved in a mixed solvent (30 mL, THF: saturated $NaHCO_3$: water = 2:2:1, v/v/v). 1-(Chlorocarbonyl-oxy-methyl)-2-nitrobenzene (2.60 g, 12 mmol) in dry THF (6 mL) was added dropwise and stirred for 1 h. The mixture was extracted with EtOAc (3 × 50 mL). The organic phase was washed with brine (3 × 50 mL) and dried with Na_2SO_4. The solvent was evaporated under vacuum. Recrystallization from EtOAc gave **1a** as a white crystalline solid (1.50 g, yield 45%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.88 (s, 1H, –CO–N*H*–Ar–), 8.13 (d, *J* = 8.1 Hz, 1H, NO_2–Ar–*H*), 7.83 (t, *J* = 7.5 Hz, 1H, NO_2–Ar–*H*), 7.76 (d, *J* = 7.7 Hz, 1H, NO_2–Ar–*H*), 7.63 (t, *J* = 7.9 Hz, 1H, NO_2–Ar–*H*), 7.36 (d, *J* = 7.6 Hz, 2H, –CH_2–Ar*H*), 7.28 (t, *J* = 7.6 Hz, 1H, –CH_2–Ar*H*), 5.44 (s, 2H, NO_2–Ar–C*H*$_2$–), 5.10 (t, *J* = 5.7 Hz, 2H, –CH_2O*H*), 4.45 (d, *J* = 5.7 Hz, 4H, –C*H*$_2$OH). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 155.6, 149.3, 134.6, 130.7, 129.6 128.5, 125.3, 124.3, 61.8, 60.0. ESI-MS (low resolution, positive mode): calculated for $C_{16}H_{17}N_2O_6$, *m*/*z*, 333.1 $[M + H]^+$; found 333.4 $[M + H]^+$.

Synthesis of *tert*-butyl(2,6-bis(hydroxymethyl)phenyl)carbamate (1b). BHA (0.65 g, 4.2 mmol) and di-*tert*-butyl dicarbonate (1.83 g, 8.4 mmol) were added to EtOH (20 mL) under nitrogen. After the solution was refluxed for 24 h, the solvent was removed under reduced pressure. The resulting solid residue was dissolved in EtOAc (200 mL) and then washed with saturated $NaHCO_3$ solution (3 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography (1:1 EtOAc/hexane) and then crystallized with EtOAc and hexane to afford **1b** as a white crystalline solid (0.51 g, yield 48%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.24 (s, 1 H, –CO–N*H*–Ar–), 7.33–7.23 (m, 3H, –Ar*H*), 5.05 (s, 2H, –CH_2O*H*), 4.4 (d, 4 H, –C*H*$_2$OH), 1.43 (s, 9 H, –C–(C*H*$_3$)$_3$). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 154.4, 139.9, 131.7, 126.7, 125.4, 79.2, 59.9, 28.8. ESI-MS (low resolution, positive mode): calculated for $C_{13}H_{19}NO_4Na$, *m*/*z*, 276.1 $[M + Na]^+$; found 276.1 $[M + Na]^+$.

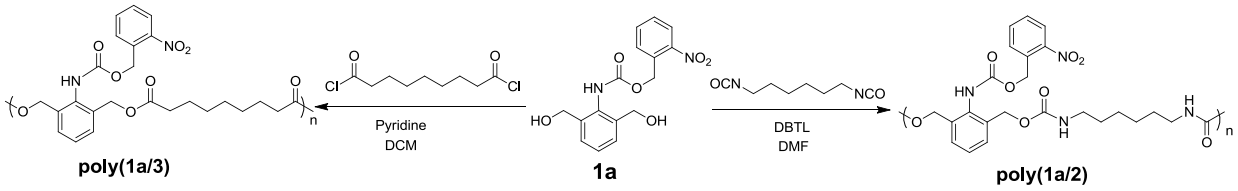
Synthesis of (9H-fluoren-9-yl)methyl(2,6-bis(hydroxymethyl)phenyl)carbamate (1c). Fluorenylmethyloxycarbonyl chloride (0.60 g, 2.4 mmol) in 1,4-dioxane (20 mL) was added to a solution of **BHA** (0.35 g, 2 mmol) in 10% aqueous AcOH (20 mL). The mixture was stirred overnight. The white precipitate in the reaction solution was collected by filtration, washed with water (3 × 100 mL), and recrystallized from EtOH to give a white solid (0.33 g, yield 44%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.75 (s, 1H, –CO–N*H*–Ar–), 7.60-7.93 (m, 11H, Ar*H*), 5.08 (s, 2H, –CH_2O*H*), 4.30-4.43 (m, 7H, –C*H*–C*H*$_2$–, –C*H*$_2$OH). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 196.8, 154.9, 144.4, 141.4, 140.1, 131.2, 128.3, 127.8, 127.0, 125.8, 125.4, 121.6, 120.8, 96.1, 66.2, 59.7, 47.5, 40.7, 40.5, 40.3, 40.2, 40.2, 40.1, 40.0, 39.8, 39.7. ESI-MS (low resolution, positive mode): calculated for $C_{23}H_{21}NO_4Na$, *m*/*z*, 398.1 $[M + Na]^+$; found 398.1 $[M + Na]^+$.

Scheme S2. Synthesis of **5** from **1a**.



Synthesis of 5. 1-Pyrenebutyric acid (288 mg, 1 mmol) was dissolved in dry dichloromethane (DCM, 5 mL) to which $SOCl_2$ (1.5 mL, 20 mmol) was added. The solution was refluxed for 3 h. After the solvent was removed under vacuum, the resulting 1-pyrenebutyric chloride was dissolved in DCM (5 mL) and a solution of **1a** (100 mg, 0.3 mmol) in DCM/THF (16 mL, 1:3, v/v) was added, followed by pyridine (80 µL, 1 mmol). The reaction mixture was stirred at room temperature for 16 h and then was filtered. The filtrate was washed with water (2 × 100 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent and purification by silica gel chromatography (2:1 EtOAc/hexane) afforded the crude product as a yellow solid (yield 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 – 7.29 (m, 25H, Ar–*H*), 5.55 (s, 2H, , –CH_2O*H*), 5.17 (d, *J* = 4.9 Hz, 4H, –C*H*$_2$OH), 3.45 – 3.19 (m, 4H, –OCO–C*H*$_2$–CH_2–CH_2–Ar), 2.43 (t, *J* = 7.2 Hz, 4H, –OCO–CH_2–CH_2–C*H*$_2$–Ar), 2.14 (p, *J* = 7.4 Hz, 4H, –OCO–CH_2–C*H*$_2$–CH_2–Ar). ^{13}C NMR (500 MHz, $CDCl_3$): δ 170.5, 168.2, 165.9, 154.3, 149.8, 135.6, 133.9, 131.0, 130.5, 129.4, 128.8, 127.5, 126.9, 126.0, 125.1, 124.9, 123.4, 33.9, 32.8, 26.8. MALDI-MS (low resolution, positive mode): calculated for $C_{56}H_{44}N_2O_8Na$, *m*/*z*, 895.3 $[M + Na]^+$; found 895.3 $[M + Na]^+$.

Scheme S3. Synthesis of UV-Responsive Polyurethane (poly(**1a**/**2**)) and Polyester (poly(**1a**/**3**)) from **1a**.

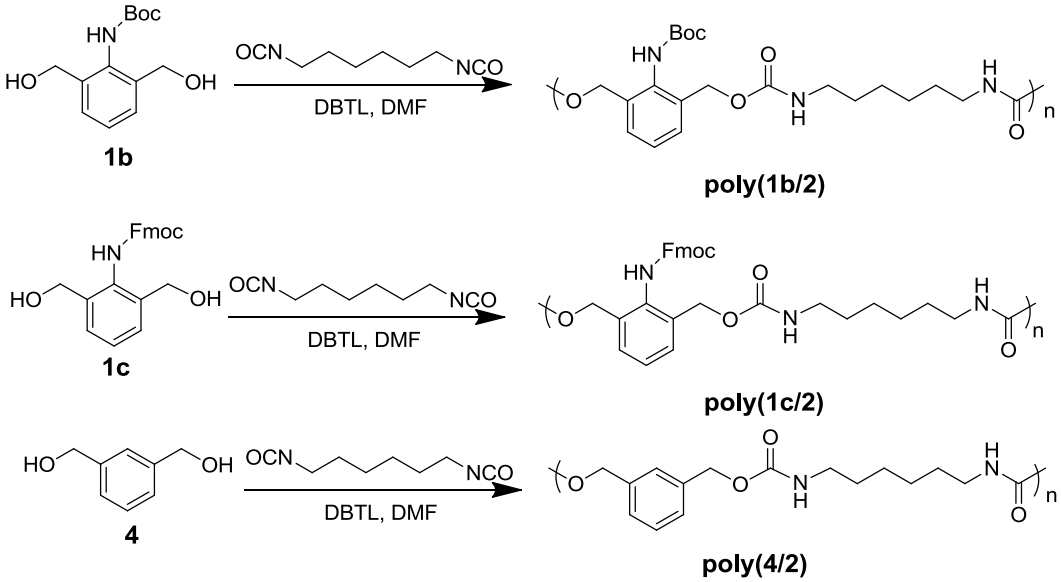


General procedure for the synthesis of poly(1a/2). A dry schlenk storage tube was charged with **1a** (99.3 mg, 0.3 mmol), hexamethylene diisocyanate (**2**) (50.3 mg, 0.3 mmol), dibutyltin dilaurate (DBTL) (5 µL) and dry DMF (3 mL) under nitrogen. The solution was degassed under reduced pressure for 1 min to remove oxygen and then sealed. The reaction was allowed to proceed at 80°C for 16 h. An aliquot of the polymerization solution was diluted to 10 mg/mL for the GPC analysis. Precipitation of the polymerization solution with ether followed by centrifugation afforded poly(**1a/2**) as a white solid (yield 58%). M_w = 6.9 kDa; M_w/M_n = 1.48. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.13 (d, 1H, Ar*H*), 7.81–7.61 (m, 2H, Ar*H*) 7.25–7.00 (m, 4H, Ar*H*), 5.70 (s, 1H, –CON*H*–Ar), 5.47 (s, 2H, –PhC*H*$_2$O–CO–), 4.99 (s, 4H, –PhC*H*$_2$O–CO–), 2.94 (m, 4H, –NH–C*H*$_2$–CH$_2$–), 1.44–1.06 (br m, 8H, –NH–CH$_2$–C*H*$_2$–C*H*$_2$–).

General procedure for the synthesis of poly(1a/3). Azelaic acid dichloride (99 µL, 0.5 mmol) and **1a** (166 mg, 0.5 mmol) were dissolved in dry DCM (2 mL) under nitrogen, to which pyridine (200 µL, 2.5 mmol) was added dropwise over the course of 3 min. The polymerization was allowed to proceed for 16 h at room temperature. The reaction mixture was concentrated to 0.5 mL. Subsequent addition of cold EtOH (20 mL) yielded a yellow polymer. Precipitation of

the polymerization solution with cold ethanol followed by centrifugation for 3 times afforded poly(**1a/3**) as a white solid (yield 68%). M_w = 13.8 kDa; M_w/M_n = 1.46. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.30 (s, 1H, –CON*H*–Ar), 8.11 (d, 1H, Ar*H*), 7.81–7.59 (m, 3H, Ar*H*) 7.35–7.20 (m, 3H, Ar*H*), 5.45 (s, 2H, –PhC*H*$_2$O–CO–), 5.05 (s, 4H, –PhC*H*$_2$O–CO–), 2.26 (m, 4H, –OCO–C*H*$_2$–CH$_2$–), 1.45 (m, 4H, –OCO–CH$_2$–C*H*$_2$–), 1.17 (br m, 8H, –OCO–CH$_2$–C*H*$_2$–C*H*$_2$–).

Scheme S4. Synthesis of Polyurethane-Based Polymers.



General Procedure for the Synthesis of Poly(4/2) . A dry schlenk storage tube was charged with 1,3-benzenedimethanol (**4)** (276 mg, 2 mmol), **2** (0.32 mL, 2 mmol), DBTL (20 µL), and dry DMF (8 mL) under nitrogen. The solution was degassed under reduced pressure for 1 min and then sealed. The reaction was allowed to proceed at 80°C for 20 h. The polymerization solution was diluted to 10 mg/mL for the GPC analysis. Precipitation of the polymerization solution with ether followed by centrifugation afforded poly(**4/2**) as a white solid (0.23 g, yield 38%). M_n = 4.0 kDa; M_w/M_n = 1.30. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.4–7.1 (br m, 6H, Ar*H*,

–CO–N*H*–CH_2–), 4.98 (d, 2H, –C*H*$_2$O–CO–), 2.95 (m, 4H, –NH–C*H*$_2$–), 1.36 (m, 4H, –NH–CH_2–C*H*$_2$–CH_2–), 1.22 (m, 4H, –NH–CH_2–CH_2–C*H*$_2$–).

General Procedure for the Synthesis of Poly(1b/2). A dry schlenk storage tube was charged with **1b** (253 mg, 1 mmol), **2** (168 mg, 1 mmol), DBTL (20 µL) and dry DMF (8 mL) under nitrogen. The solution was degassed under reduced pressure for 1 min and sealed. The reaction was allowed to proceed at 80°C for 20 h. Precipitation of the polymerization solution with ether followed by centrifugation afforded poly(**1b/2**) as a white solid (0.21 g, yield 50%). M_n = 10.9 kDa; M_w/M_n = 1.3. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.64 (s, $(CH_3)_3$C–O–CO–N*H*–Ar), 7.29 (m, 5H, Ar*H*, –CO–N*H*–CH_2–), 4.97 (d, 2H, –C*H*$_2$O–CO–), 2.96 (m, 4H, –NH–C*H*$_2$–), 1.44–1.23 (br m, 17H, –NH–CH_2–C*H*$_2$–C*H*$_2$– and (C*H*$_3$)$_3$C–).

General Procedure for the Synthesis of Poly(1c/2). A dry schlenk storage tube was charged with trigger **1c** (187 mg, 0.5 mmol), **2** (84 mg, 0.5 mmol), DBTL (5 µL), and dry DMF (4 mL) under nitrogen. The solution was degassed under vacuum for 1 min and then sealed. The reaction was allowed to proceed at 80°C for 20 h. Precipitation of the polymerization with ether followed by centrifugation afforded poly(**1c/2**) as a white solid (0.13 g, yield 70%). M_n = 60.4 kDa; M_w/M_n = 2.25. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.1 (s, 1H, –CO–N*H*–Ar–), 7.93–7.0 (m, 11H, Ar*H* and –Ar–CH_2–OCO–N*H*–), 4.9 (d, 2H, –Ar–C*H*$_2$O–*)*, 4.43–4.3 (m, 3H, -C*H*–C*H*$_2$–), 2.95 (m, 4H, –NH–C*H*$_2$–), 1.38–1.21 (br m, 8H, –NH–CH_2–C*H*$_2$–C*H*$_2$–).

General Procedure for the Photolysis of Polymers and Analysis of the MWs by GPC. A polymer solution (10 mg/mL) in DMF/water (95:5 v/v) in a quartz cuvette was placed inside a

photoreactor (365 nm, 40 mW/cm^2) and irradiated for a specified period of time. The resulting solution was directly used for the MW analysis by GPC.

General Procedure for the Acid-Induced Degradation of Polymers and the MW Analysis by GPC. Polymer was dissolved in TFA/CH_2Cl_2 (1:1, v/v) at a concentration of 10 mg/mL. The degradation of polymer was allowed to proceed for a specified period of time. The solvent was removed under vacuum. The residue was dissolved in DMF (10 mg/mL) and used for the MW analysis by GPC.

General procedure for the base-induced degradation of polymers and Analysis of the MWs by GPC. Polymer was dissolved in piperidine/DMF (9:95, 10:90, or 20:80, v/v) at a concentration of 10 mg/mL. The degradation of polymer was allowed to proceed for a specified period of time. The solution was used for the polymer MW analysis by GPC directly.

General Procedure for the Preparation of Nile Red–Containing Nanoparticles and UV-Triggered Release of Nile Red from the Nanoparticles. Poly(**1a**/**3**) (7.5 mg) and Nile Red (0.5 mg) were dissolved in DCM (1 mL). The solution was added to PBS containing 1% poly(vinyl alcohol) (15 mL). The mixture was emulsified by stirring at 1000 rpm for 10 min. The nanoparticle emulsion was stirred at 1000 rpm using a magnetic stirrer to evaporate DCM. Un-encapsulated Nile Red was removed by filtration of the suspension through a 1-μm glass fiber prefilter (Millipore, Billerica, MA, USA). The suspension was lyophilized and stored as a solid. The encapsulation efficiency was determined to be 9%. An aqueous solution of Nile Red–encapsulated nanoparticles of poly(**1a**/**3**) in a quartz cuvette was placed inside a photoreactor and

irradiated for a specified period of time. The resulting solution was used for fluorescence analyses (λ_{ex} = 556 nm; λ_{em} = 634 nm).

General Procedure for the Preparation of Camptothecin (CPT)-Encapsulated Nanoparticles and Analysis of UV-Triggered Release of the CPT from Nanoparticles. A DMSO solution (1mL) of poly(**1a**/**3**) or poly(**4**/**3**) (10 mg), PEG-*b*-PLLA (10 mg) and CPT (1 mg) was added to a rapidly stirred PBS solution (pH 7.4, 9 mL, 1300 rpm). The mixture was stirred for another 15 min at room temperature. Free CPT was removed by centrifugation (1,000 rpm for 10 min). The loading of CPT in poly(**1a**/**3**)/PEG-*b*-PLLA and poly(**4**/**3**)/PEG-*b*-PLLA nanoparticles were 3.2% and 2.8%, respectively, based on HPLC analysis. The loading efficiency of CPT in poly(**1a**/**3**)/PEG-*b*-PLLA and poly(**4**/**3**)/PEG-*b*-PLLA nanoparticles were determined to be 64% and 56%, respectively. The CPT-encapsulated nanoparticles in water was placed in a quartz cuvette at a concentration of 0.2 mg/mL and then treated with UV for a specified period of time. After UV treatment, the nanoparticle solution was stirred for pre-defined periods of time at room temperature. The solution was centrifuged for 15 min at 15,000 rpm and the upper layer was used for HPLC analysis to determining the released CPT.

Table S1. Synthesis of polyurethanes and polyesters.

Polymer	Monomers	Catalyst[a]	Solvent	Temp.(°C)	Time (h)	M_n (kDa)[b]	MWD
poly(**1a**/**2**)	**1a**/**2**	DBTL	DMF	80	16	6.9	1.48
poly(**1a**/**3**)	**1a**/**3**	Pyridine	DCM	25	16	13.8	1.46
poly(**1b**/**2**)	**1b**/**2**	DBTL	DMF	80	20	10.9	1.36
poly(**1c**/**2**)	**1c**/**2**	DBTL	DMF	80	20	15.6	1.56
poly(**4**/**2**)	**4**/**2**	DBTL	DMF	80	20	4.0	1.30
poly(**4**/**3**)	**4**/**3**	Pyridine	DCM	25	16	9.3	1.58

[a]DBTL: dibutyltin dilaurate; [b]Determined by GPC

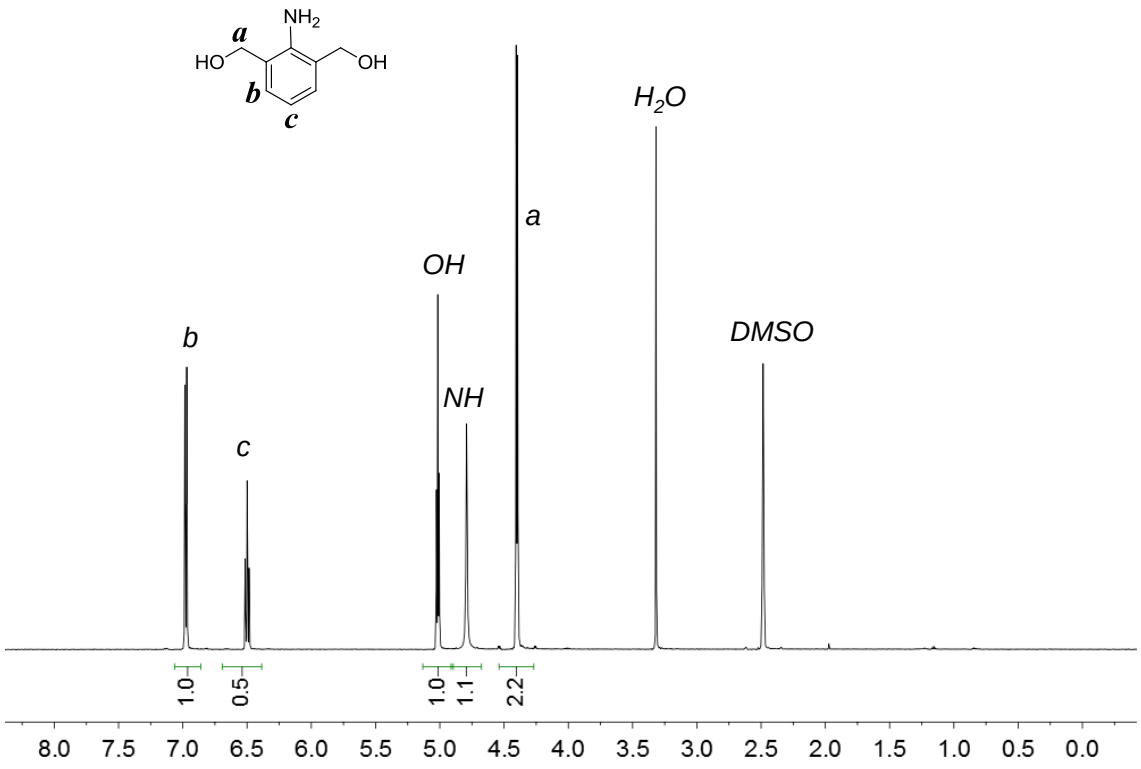


Figure S1. ^{1}H NMR spectrum of 2,6-bis(hydroxymethyl)aniline (**BHA**) in DMSO-d_6.

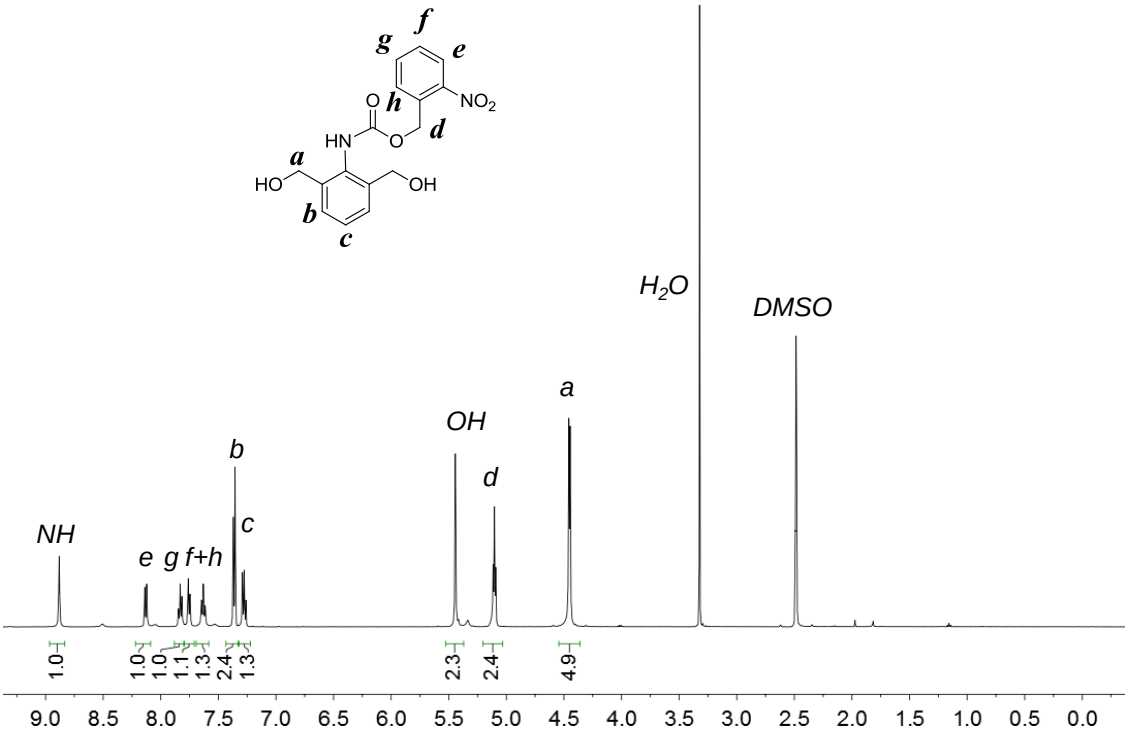


Figure S2. ^{1}H NMR spectrum of **1a** in DMSO-d_6.

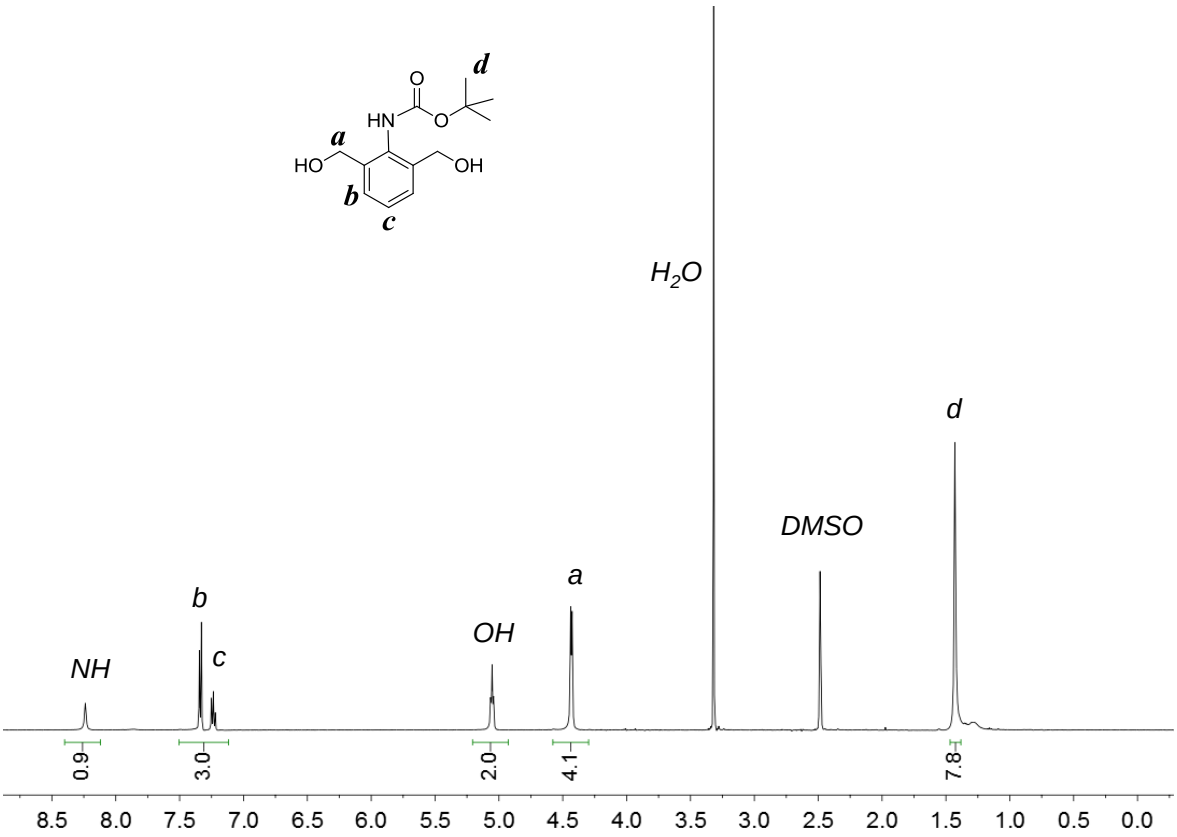


Figure S3. ^{1}H NMR spectrum of **1b** in DMSO-d_6.

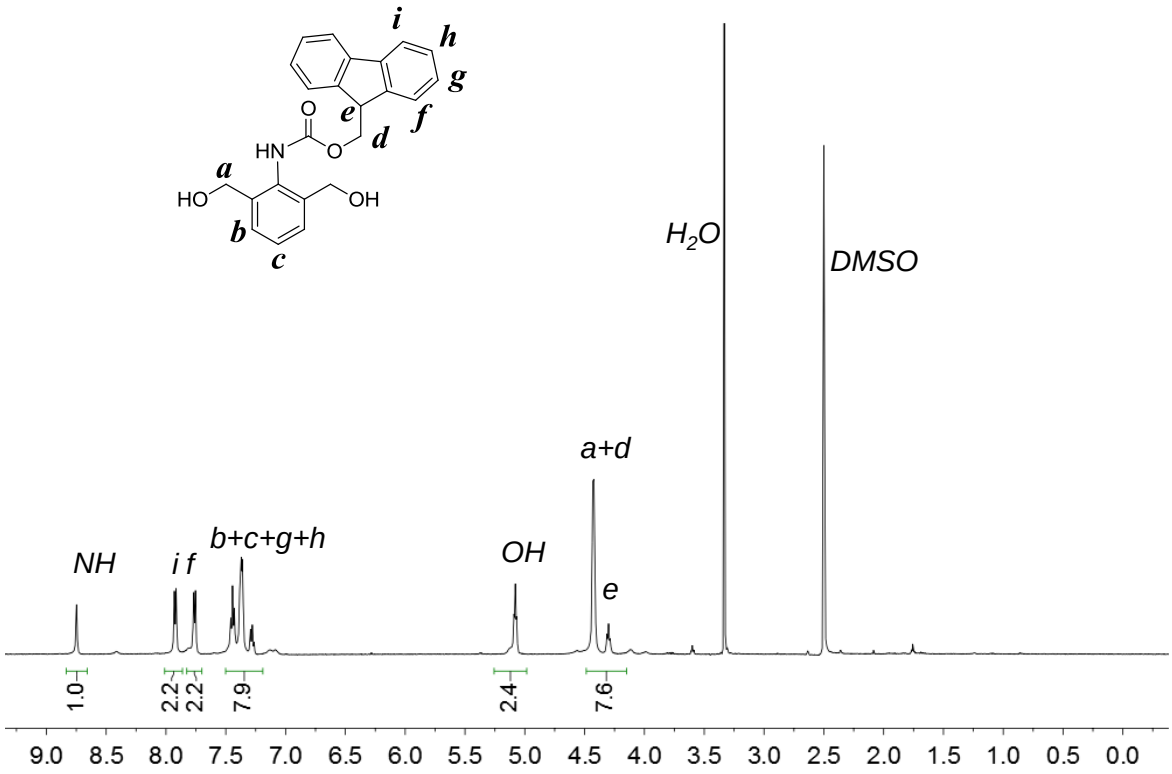


Figure S4. ^{1}H NMR spectrum of **1c** in DMSO-d_6.

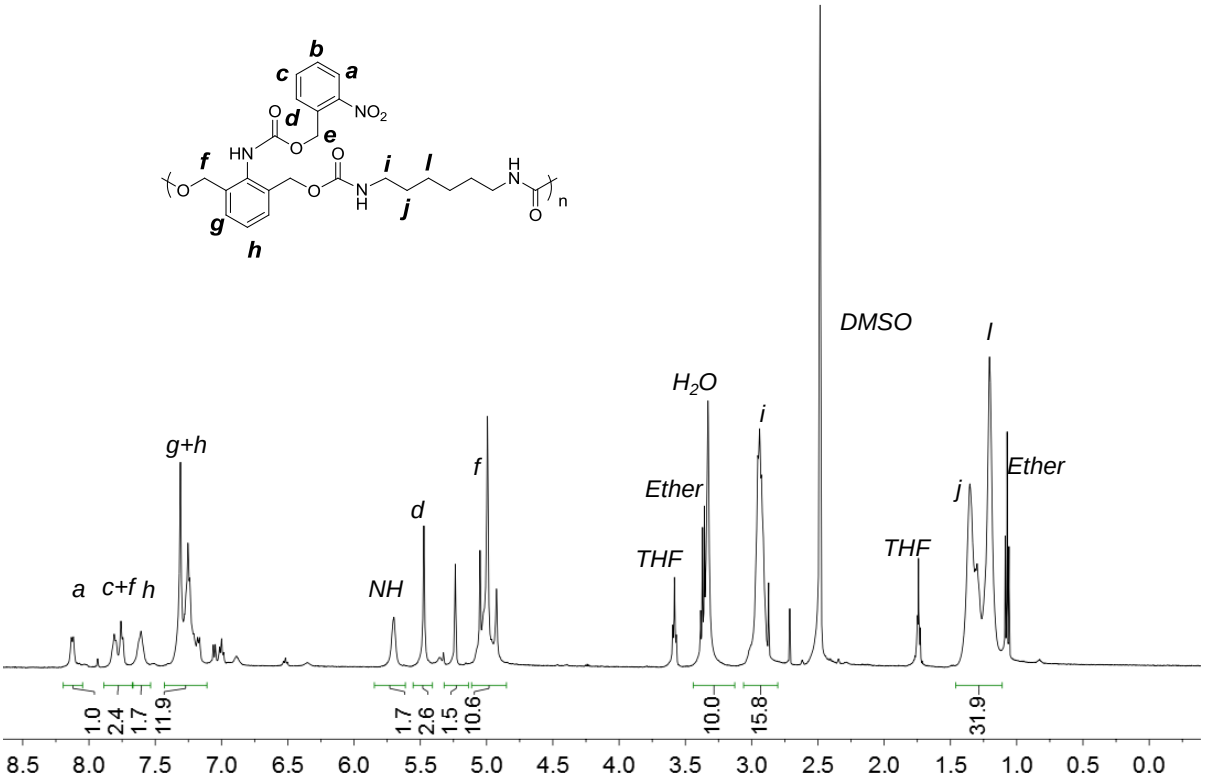


Figure S5. ^{1}H NMR spectrum of poly(**1a**/**2**) in DMSO-d_6.

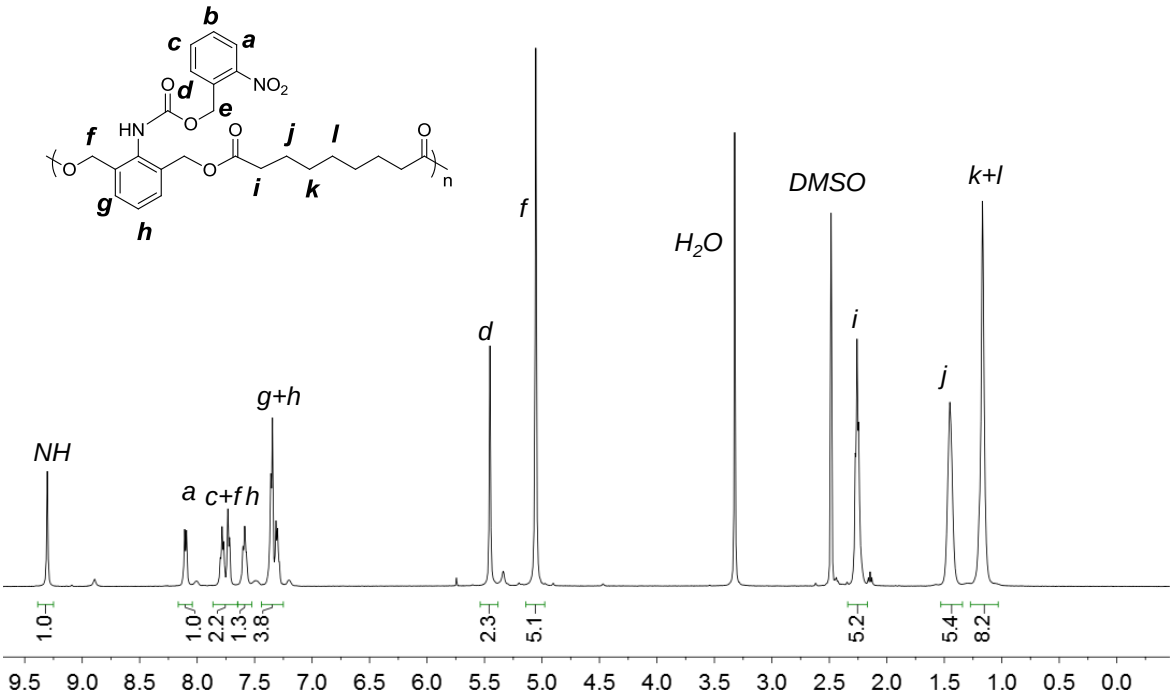


Figure S6. ^{1}H NMR spectrum of poly(**1a**/**3**) in DMSO-d_6.

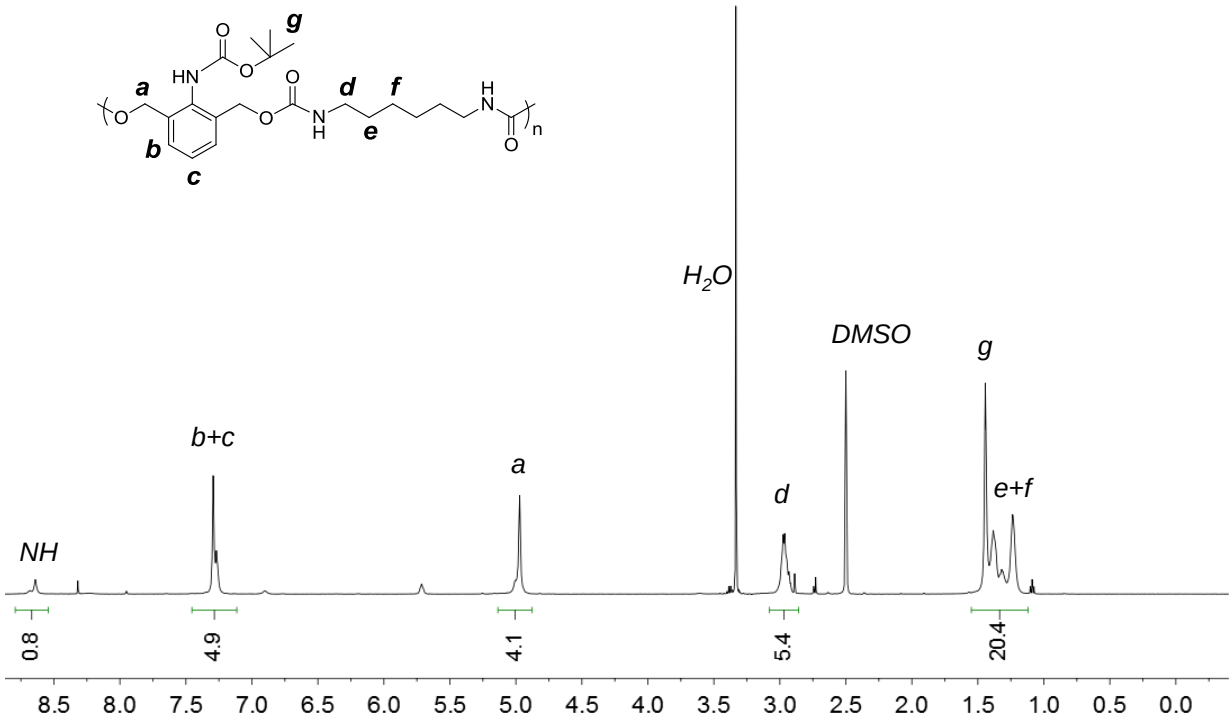


Figure S7. ^{1}H NMR spectrum of poly(**1b**/**2**) in DMSO-d_6.

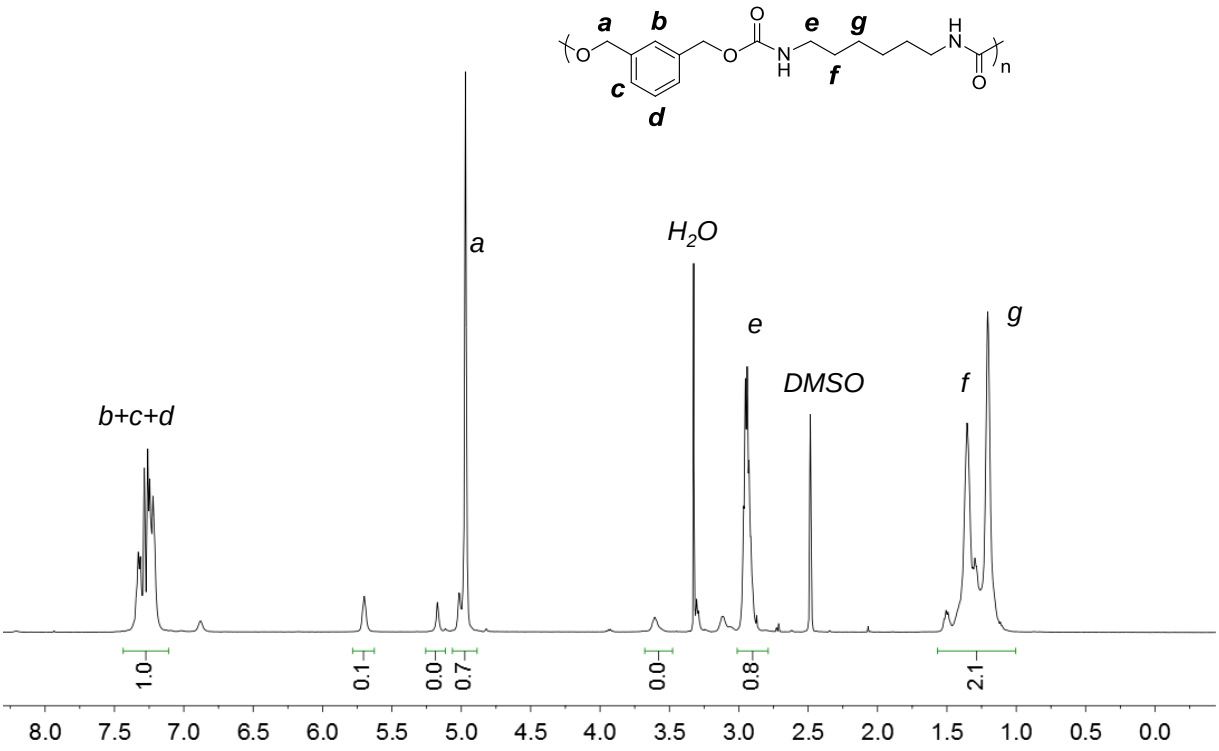


Figure S8. ^{1}H NMR spectrum of poly(**4**/**2**) in DMSO-d_6.

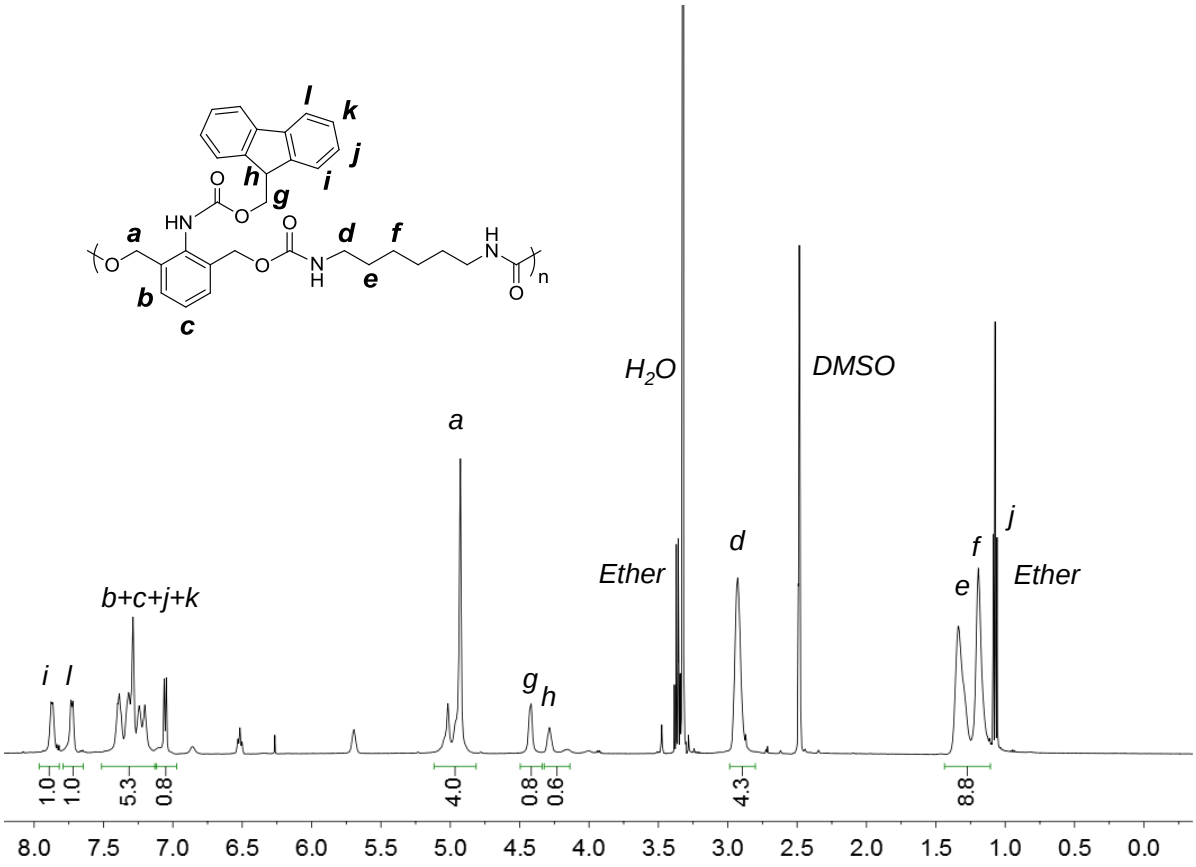


Figure S9. ^{1}H NMR spectrum of poly(**1c**/**2**) in DMSO-d_6.

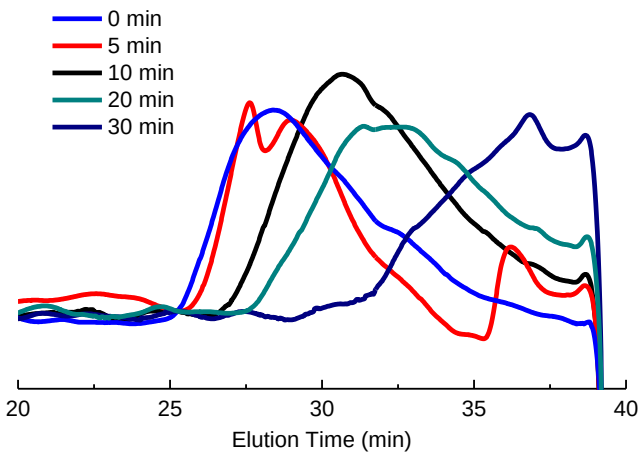


Figure S10. Overlay of GPC curves of poly(**1a**/**3**) in DMF/water (9:1, v/v) before and after UV treatment for specified periods of time (365 nm UV, 40 mW/cm^2).

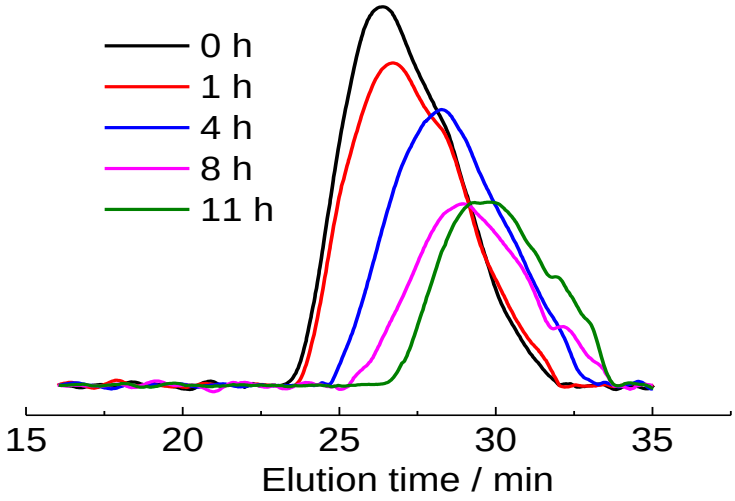


Figure S11. Overlay of GPC curves of poly(**1b**/**2**) before and after treatment with TFA/CH_2Cl_2 (1:1, v/v).

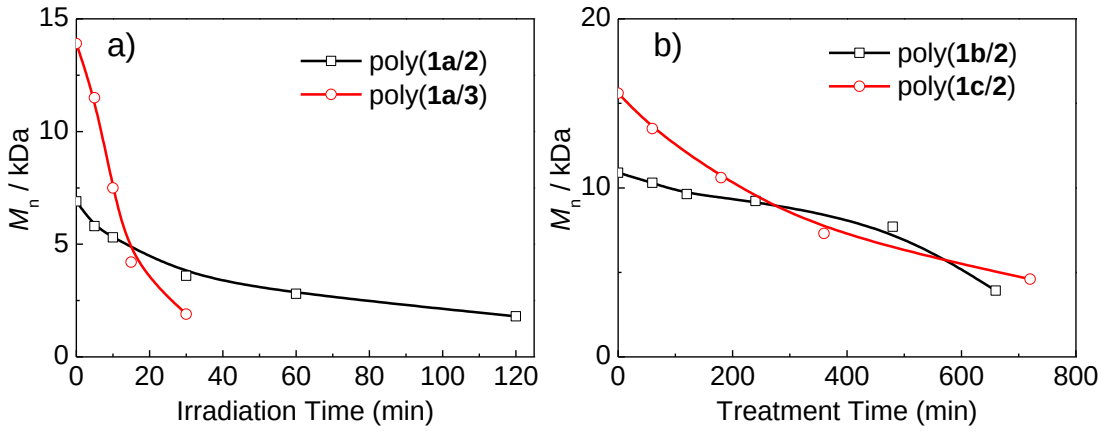


Figure S12. (a) UV-induced degradation of poly(**1a**/**2**) and poly(**1a**/**3**); (b) Acid-induced (TFA/DCM, 2:1 v/v) degradation of poly(**1b**/**2**) (black trace) and base-induced (20% piperidine in DMF) degradation of poly(**1c**/**2**) (red trace) .

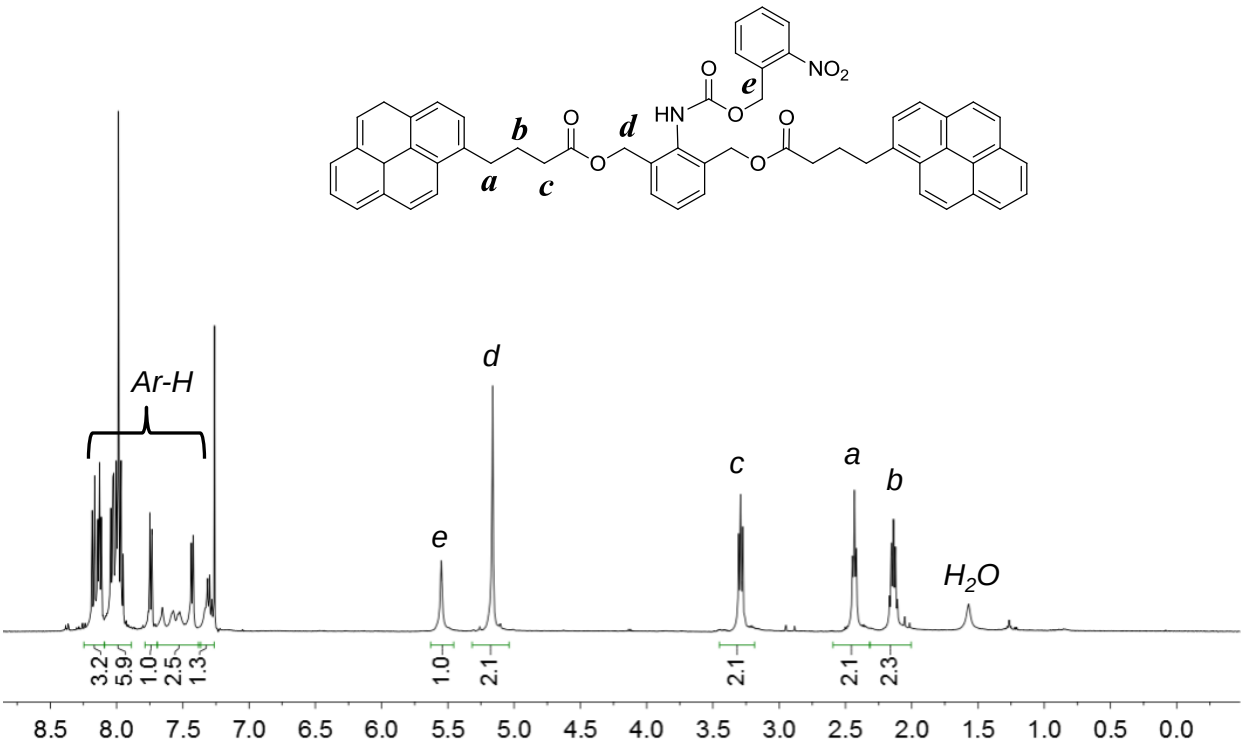


Figure S13. ^{1}H NMR spectrum of **5** in $CDCl_3$.

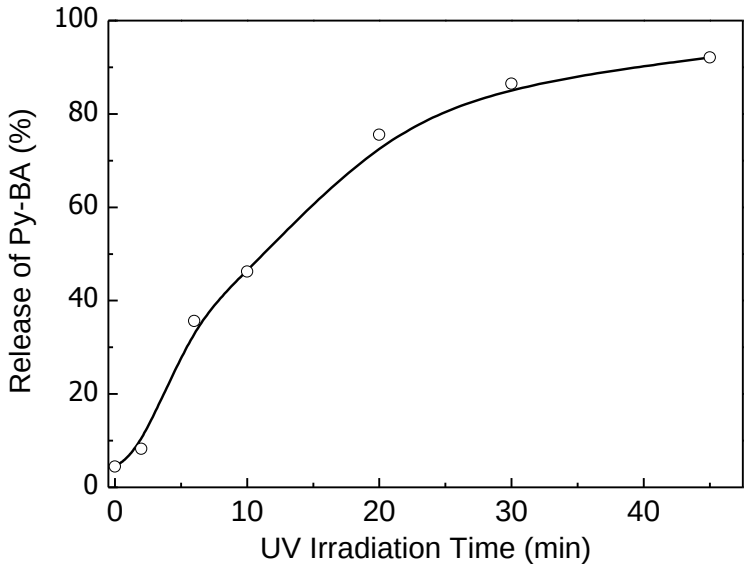


Figure S14. Release of **PBA** from **5** in CH_3CN/water (0.1 mg/mL, 9:1, v/v) upon UV treatment (365 nm, 40 mW/cm^2).

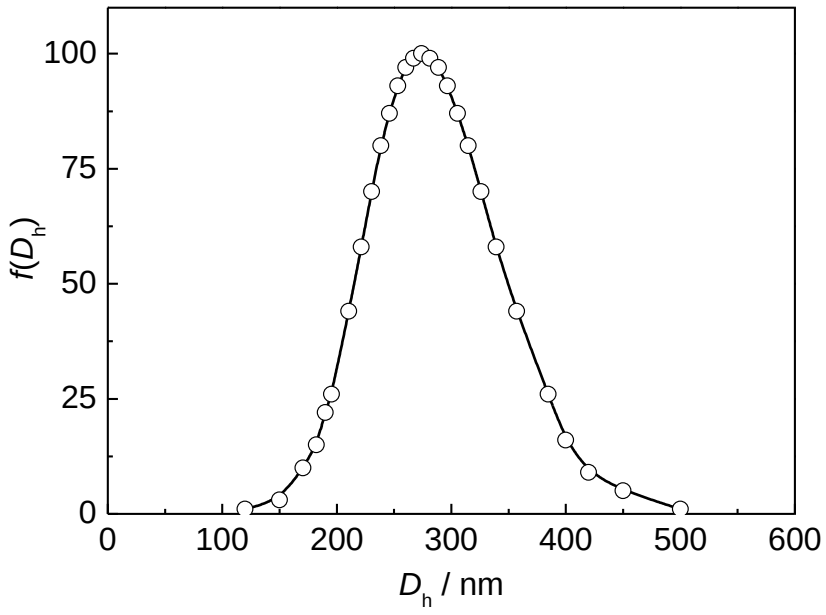


Figure S15. Distribution of hydrodynamic diameters of Nile-Red encapsulated poly(**1a**/**3**) nanoparticles in PBS at pH 7.4.

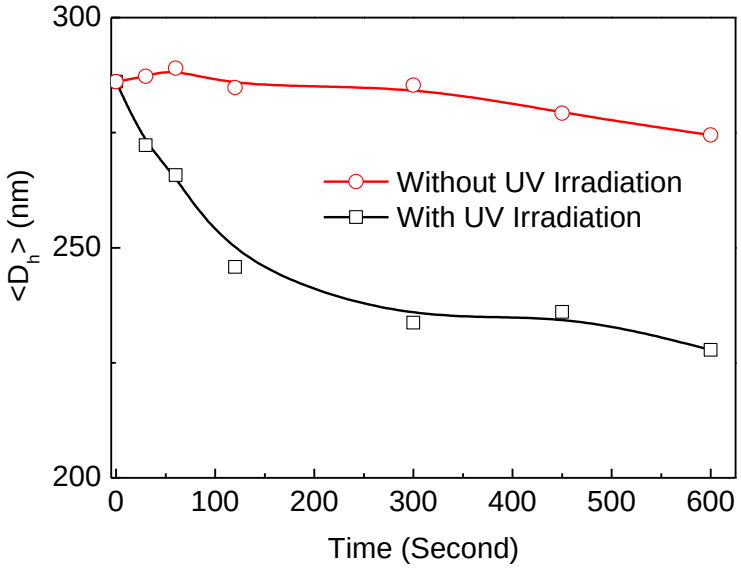


Figure S16. Change of the hydrodynamic diameter of Nile Red encapsulated poly(**1a**/**3**) nanoparticles upon UV treatment (365 nm, 40 mW/cm^2) in PBS at pH 7.4.

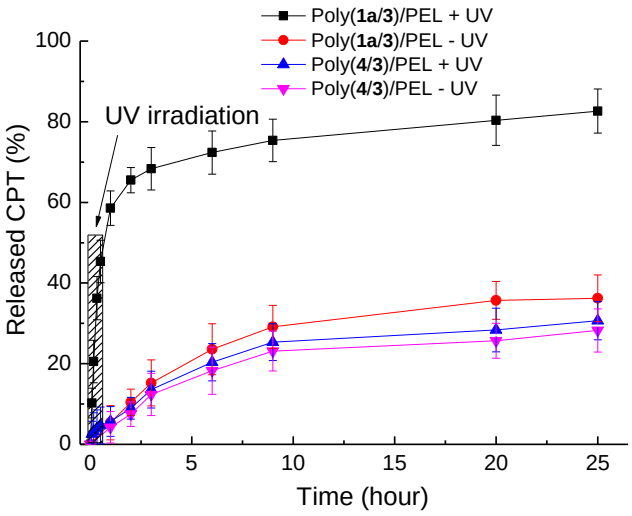


Figure S17. Release of CPT from poly(**1a**/**3**)/PEG-*b*-PLLA and poly(**4**/**3**)/PEG-*b*-PLLA NPs with or without UV treatment (365 nm, 20 mW/cm^2).

Reference

(1) Han, D. H.; Tong, X.; Zhao, Y. *Macromolecules* **2011**, *44*, 437-439.