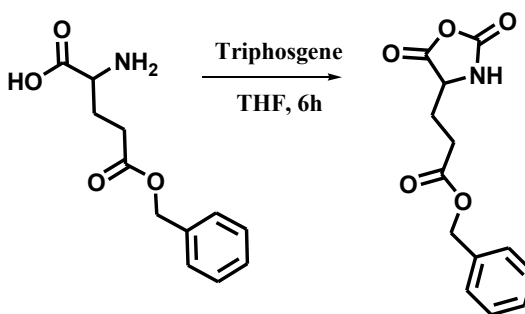


**Supporting Information for:**  
**Protein-Induced Supramolecular Disassembly of**  
**Amphiphilic Polypeptide Nanoassemblies**

Mijanur Rahaman Molla, Priyaa Prasad *and* S. Thayumanavan \*

**Materials and Methods:** All the reagents were purchased from commercial source and used as such without further purification. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-400 MHz NMR spectrometer and all the spectra were calibrated against TMS. Dynamic Light Scattering (DLS) measurements were carried out on a Malvern Nanozetasizer. TEM images were recorded on a JEOL-2000FX machine operating at an accelerating voltage of 100 KV. Fluorescence emission spectra were recorded on a JASCO (FP-6500) fluorimeter. UV-Vis spectra were recorded in a Carry 100 Scan spectrometer. Optical fluorescence microscopic images were taken on Olympus Fluorescence Microscope (BX51). Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer (Micro mass). FTIR spectra were recorded on Spectrum 100 FTIR spectrometer.

**Synthesis of monomer (M1):** Synthetic protocol of **M1** is outlined below<sup>1</sup>:



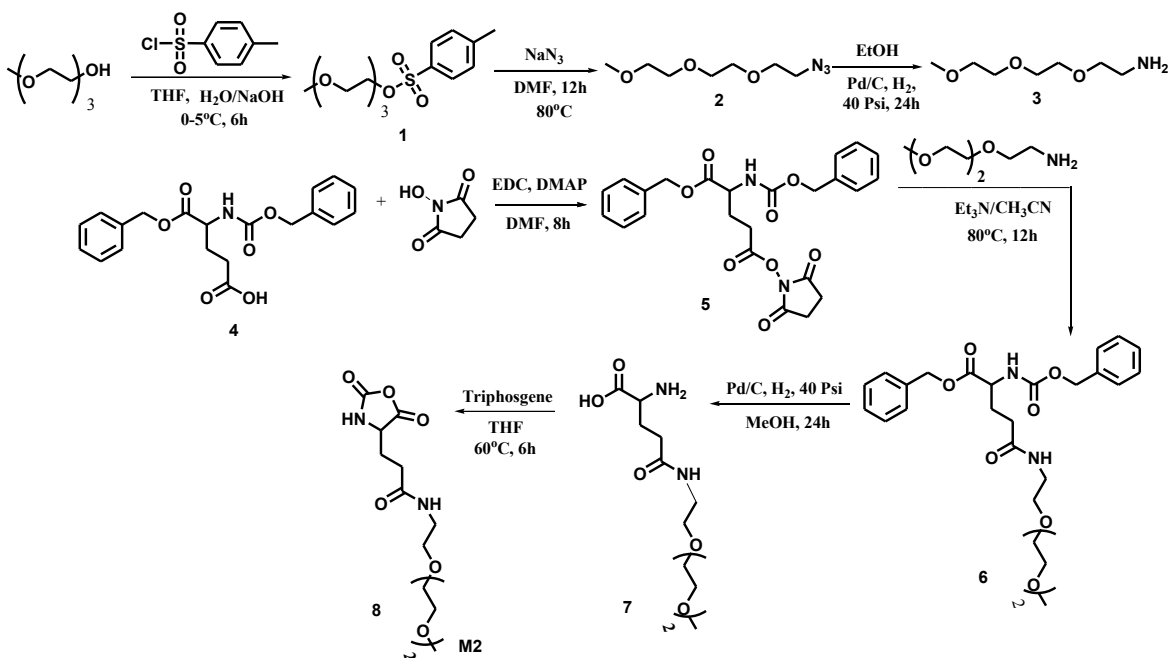
**Scheme 1:** Synthesis of **M1**

0.30 g (1.26 mmol) of L-glutamic acid  $\gamma$ -benzyl ester was dissolved in dry THF (10 mL) in a 50 mL round bottomed flask and placed in a preheated oil bath at 60°C under argon atmosphere. Triphosgene (0.208 g, 0.70 mmol) was dissolved in dry THF (5 mL) in a glass vial and added to the L-glutamic acid  $\gamma$ -benzyl ester solution. The reaction mixture

was stirred at 60°C for 6h. The reaction was stopped and allowed to cool to room temperature. It was precipitated in cold hexane to get a white color solid product in 90% yield.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 9.07 (1H, bs), 7.34 (5H, s), 5.07 (2H, s), 4.44 (1H, t), 2.47 (2H, t), 2.04-1.87 (2H, m). HRMS (ESI): m/z calcd for C<sub>13</sub>H<sub>13</sub>NO<sub>5</sub>Na [M+Na]<sup>+</sup>: 286.0692; found: 286.0695.

**Synthesis of monomer (M2):** Synthetic protocol of **M2** is outlined below:



**Scheme 2:** Synthesis of monomer **M2**

**Synthesis of compound 1:** Compound **1** was synthesized following a reported procedure.<sup>2</sup>

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 7.81 (2H, d), 7.35 (2H, d), 4.17 (2H, t), 3.70 (t, 2H), 3.62-3.61 (6H, m), 3.38 (2H, t), 3.38 (3H, s), 2.46 (3H, s). HRMS (ESI): m/z calcd for C<sub>14</sub>H<sub>23</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 319.1217; found: 319.1219.

**Synthesis of compound 2:** Compound **1** (4 g, 12.56 mol) and sodium azide (2.45 g, 37.69 mol) were taken in a 100 mL round bottomed flask and dissolved in dry DMF (30 mL) under argon atmosphere. The reaction mixture was placed in a preheated oil bath at

80°C and stirred for 12h. Then the reaction was stopped and allowed to cool to room temperature. The reaction mixture was mixed with EtOAc (50 mL) and washed with H<sub>2</sub>O (3 x 50 mL) and brine (3 x 10 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get the product as a colorless oil in quantitative yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS): 3.64-3.64 (m, 8H), 3.54 (2H, t), 3.38 (2H, t), 3.37 (3H, s). HRMS (ESI): m/z calcd for C<sub>7</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub> [M]<sup>+</sup> : 189.1113; found: 189.1115.

**Synthesis of compound 3:** Compound **2** (2.5 g, 1.32 mmol) was dissolved in 50 mL of ethanol in a reaction bottle. 150 mg of Pd/C was added slowly to the ethanol solution of compound **2**. The reaction bottle was then connected to a shaker hydrogenator apparatus under the pressure of 40 psi. After 24h the shaker was stopped and reaction mixture was filtered through celite and the solvent was evaporated to get the pure product in quantitative yield.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 3.67-3.64 (m, 6H), 3.56 (2H, t), 3.51 (2H, t), 3.38 (3H, s), 2.88 (2H, t). HRMS (ESI): m/z calcd for C<sub>7</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> : 164.1288; found: 164.1279.

**Synthesis of compound 5:** Compound **4** (1.5 g, 4.02 mmol) was taken in a round bottomed flask along with N-hydroxy succinimide (0.924 g, 8.04 mmol) and catalytic amount of DMAP. All the reactants were dissolved in dry DMF (20 mL) under argon atmosphere. 1-Ethyl-3-(3- dimethylaminopropyl) carbodiimide (EDC) (1.15 g, 6.03 mmol) was added to the reaction mixture and the solution was stirred at room temperature for 8h. Then the reaction was stopped and mixed with EtOAc (50 mL) and washed with H<sub>2</sub>O (3 x 30 mL), brine (3 x 10 mL) and sodium bicarbonate solution. The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get the product as a white solid in 80% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS): 7.37 (10H, s), 5.54 (1H, d), 5.21 (2H, s), 5.13 (2H, s), 4.53 (1H, d), 2.80 (4H, s), 2.73 (2H, t), 2.34-2.37 (1H, m), 2.15-2.11 (1H, m). HRMS (ESI): m/z calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup> : 469.1613; found: 469.1610.

**Synthesis of compound 6:** Compound **5** (1.73 g, 3.82 mmol) and **3** (0.69 g, 4.20 mmol) were taken in a 100 ml round bottomed flask and dissolved in acetonitrile solvent (20 mL) along with triethyl amine (0.463 mg, 4.58 mmol). The reaction mixture was placed in a preheated oil bath at 80°C and refluxed under argon atmosphere for 12h. The reaction was stopped and acetonitrile solvent was evaporated to get a light yellow color liquid mixture. Then it was diluted by EtOAc solvent and washed with H<sub>2</sub>O (3x 30 mL) and brine (3x 10 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get crude product as colorless liquid. It was then purified by column chromatography using silica gel as the stationary phase and ethylacetate/hexane as the eluent to get the pure product as a colorless liquid in 80% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS): 7.34 (10H, s), 6.37 (1H, s), 5.54 (1H, d), 5.18 (2H, s), 5.12 (2H, s), 4.41 (1H, t), 3.65-3.63 (6H, m), 3.56-3.53 (4H, m), 3.45-3.40 (2H, m), 2.28-2.22 (3H, m), 2.73 (2H, t), 2.05 (1H, m). HRMS (ESI): m/z calcd for C<sub>27</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup> : 517.2552; found: 517.2549.

**Synthesis of compound 7:** Compound **6** (1 g, 1.93 mmol) was dissolved in 50 mL of methanol in a reaction bottle. 100 mg of Pd/C was added slowly to the methanol solution of compound **6**. The reaction vessel was then connected to a shaker hydrogenator apparatus under the pressure of 40 psi. After 24h the shaker was stopped and reaction mixture was filtered through celite and the solvent was evaporated to get the pure product as white color solid in quantitative yield.

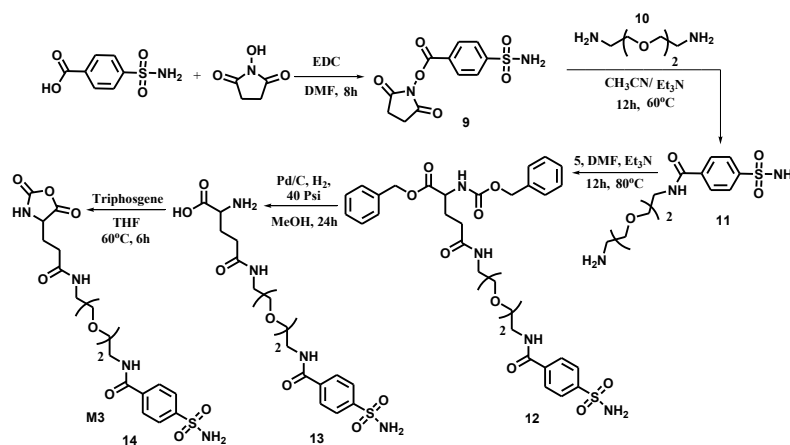
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS): 6.30 (1H, s), 3.70 (1H, t), 3.60-3.57 (8H, m), 3.34 (3H, s), 2.28 (2H, t), 1.87-1.80 (2H, m). HRMS (ESI): m/z calcd for C<sub>12</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup> : 293.1714; found: 293.1715.

**Synthesis of compound 8:** 0.30 g (1.026 mmol) of compound **7** was dissolved in dry THF (10 mL) in a 50 mL round bottomed flask and placed in a preheated oil bath at 60°C under argon atmosphere. Triphosgene (0.170 g, 0.57 mmol) was dissolved in dry THF (5 mL) in a glass vial and added to the L-glutamic acid  $\gamma$ -benzyl ester solution. The reaction

mixture was stirred at 60°C for 6h. The reaction was stopped and allowed to cool to room temperature. It was precipitated in cold hexane to get a light yellow color gummy product in 80% yield.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 9.07 (1H, bs), 7.90 (1H, bs), 4.45 (1H, t), 3.60-3.57 (8H, m), 3.34 (3H, s), 2.28 (2H, t), 2.01-1.95 (2H, m). HRMS (ESI): m/z calcd for C<sub>13</sub>H<sub>23</sub>N<sub>2</sub>O<sub>7</sub> [M+H]<sup>+</sup> : 319.1507; found: 319.1505.

**Synthesis of monomer (M3):** Synthetic protocol of **M3** is outlined in **scheme 3**:



**Scheme 3.** Synthesis of monomer **M3**

**Synthesis of compound 9:** 4-Carboxy benzenesulfonamide (1.5 g, 7.46 mmol) was taken in a round bottomed flask along with N-hydroxy succinimide (1.28 g, 11.19 mmol) and dissolved in dry DMF (20 mL) under argon atmosphere. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) (1.70 g, 8.95 mmol) was added to the reaction mixture and the solution was stirred at room temperature for 8h. Then the reaction was stopped and mixed with EtOAc (50 mL) and washed with H<sub>2</sub>O (3 x 30 mL), brine (3 x 10 mL) and sodium bicarbonate solution. The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get the product as a white solid in quantitative yield.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 8.35 (2H, d), 8.15 (2H, d), 7.72 (2H, s), 2.92 (4H, s). HRMS (ESI): m/z calcd for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup> : 299.0340; found: 299.0338.

**Synthesis of compound 11:** Compound **9** (0.79 g, 2.65 mmol) and **10** (0.43 g, 2.65 mmol) were taken in a 100 ml round bottomed flask along with triethyl amine (0.53 g, 5.24 mmol) and dissolved in acetonitrile (20 mL) solvent. The reaction mixture was placed in a preheated oil bath at 80°C and refluxed under argon atmosphere for 12h. The reaction was stopped and acetonitrile solvent was evaporated to get a light yellow color crude product. It was taken to the next step without any further purification.

**Synthesis of compound 12:** Compound **5** (1.21 g, 2.65 mmol) and 20 mL dry DMF were added to the round bottomed flask containing compound **11**. Then the reaction mixture was placed in a preheated oil bath at 80°C and refluxed under argon atmosphere for 12h. The reaction was stopped and allowed to cool at room temperature. It was diluted by EtOAc solvent and washed with H<sub>2</sub>O (3x 30 mL), brine (3x 10 mL) and saturated solution of sodium bicarbonate (1x 10 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get light brown color crude product. It was then purified by column chromatography using silica gel as the stationary phase and dichloromethane/methanol as the eluent to get the pure product as a brown color liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS): 7.87 (2H, d), 7.80 (2H, d), 7.22-7.20 (10H, m), 7.01 (1H, s), 6.13 (1H, s), 5.70 (1H, s), 5.41 (2H, s), 5.09 (2H, s), 5.01 (2H, s), 4.21 (1H, t), 3.60-3.56 (8H, m), 3.54 (2H, t), 3.19 (2H, t), 2.09-2.05 (3H, m), 1.89-1.87 (1H, m).  
HRMS (ESI): m/z calcd for C<sub>33</sub>H<sub>41</sub>N<sub>4</sub>O<sub>10</sub>SNa [M+Na]<sup>+</sup> : 707.2363; found: 707.2361.

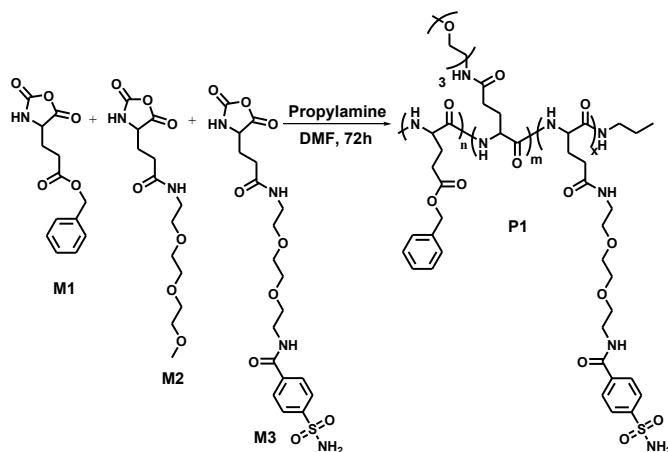
**Synthesis of compound 13:** Compound **12** (0.30 g, 0.438 mmol) was dissolved in 50 mL of methanol in a reaction bottle. 80 mg of Pd/C was added slowly to the methanol solution of compound **12**. The reaction vessel was then connected to a shaker hydrogenator apparatus under the pressure of 40 psi. After 24h the shaker was stopped and reaction mixture was filtered through celite and the solvent was evaporated to get the pure product as white color solid in quantitative yield.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS): 8.9 (1H, bs), 8.02 (2H, d), 7.89 (2H, d), 7.50 (2H, s), 3.61-3.57 (9H, m), 3.55 (2H, t), 3.19 (2H, t), 2.20-2.21 (2H, t), 1.89-1.86 (2H, m). HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{29}\text{N}_4\text{O}_8\text{S}$   $[\text{M}+\text{H}]^+$  : 461.1708; found: 461.1710.

**Synthesis of compound 14:** 0.25 g (0.542 mmol) of compound **13** was dissolved in dry THF (10 mL) in a 50 mL round bottomed flask and placed in a preheated oil bath at  $60^\circ\text{C}$  under argon atmosphere. Triphosgene (0.090 g, 0.30 mmol) was dissolved in dry THF (5 mL) in a glass vial and added to the L-glutamic acid  $\gamma$ -benzyl ester solution. The reaction mixture was stirred at  $60^\circ\text{C}$  for 6h. The reaction was stopped and allowed to cool to room temperature. It was precipitated in cold hexane to get a light yellow color gummy product in 70% yield.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS): 9.02 (1H, bs), 8.70 (1H, bs), 8.0 (2H, d), 7.88 (2H, d), 7.47 (2H, s), 4.40 (1H, t), 3.61-3.50 (8H, m), 3.19 (4H, m), 2.10-2.00 (2H, m), 1.88-1.86 (2H, m). HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{26}\text{N}_4\text{O}_9\text{SNa}$   $[\text{M}+\text{Na}]^+$  : 509.1318; found: 509.1315.

**Synthesis of polymer P1:** Synthetic procedure of **P1** is outlined in **scheme4**:



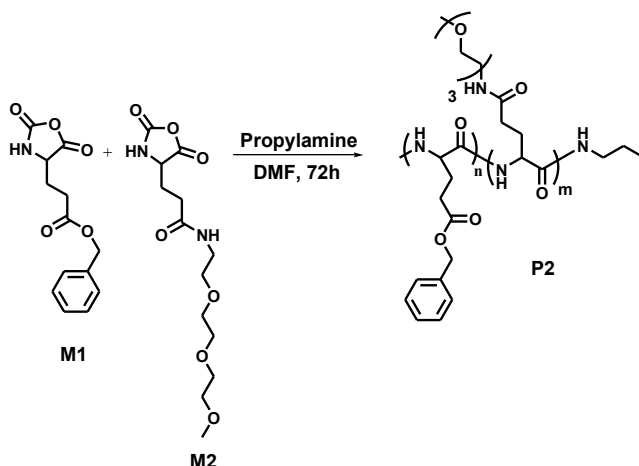
**Scheme 4:** Synthesis of polymer **P1**

Three monomers **M1** (102 mg, 0.41 mmol), **M2** (78 mg, 0.246 mmol) and **M3** (80 mg, 0.165 mmol) were taken together in a schlenk flask and dissolved in anhydrous DMF (1.3 mL) under argon atmosphere. Then propyl amine (2.5 mg, 0.041 mmol) initiator was

dissolved in anhydrous DMF (0.2 mL) and added to the schlenk flask. The reaction mixture was stirred at room temperature for 72h. The reaction was stopped and the product was precipitated from diethyl ether to get the polymer as brown color sticky product.

<sup>1</sup>H-NMR (400 MHz, acetone-d<sub>6</sub>, TMS): 8.06 (2H, broad peak), 7.97 (2H, broad peak), 7.38 (5H, broad peak), 5.12 (2H, bs), 4.4 (3H, broad peak), 3.60 (16H, broad peak), 3.34 (5H, broad peak), 3.20 (2H, broad peak), 2.85 (2H, broad peak), 2.40 (6H, broad peak), 2.10 (6H, broad peak).

**Synthesis of control polymer P2:** Synthetic protocol of control polymer **P2** was given below:



**Scheme 5:** Synthesis of control polymer **P2**

Two monomers **M1** (120 mg, 0.377 mmol) and **M2** (93 mg, 0.377 mmol) were taken together in a schlenk flask and dissolved in anhydrous DMF (0.8 mL) under argon atmosphere. Then propyl amine (3 mg, 0.05 mmol) initiator was dissolved in anhydrous DMF (0.2 mL) and added to the schlenk flask. The reaction mixture was stirred at room temperature for 72h. The reaction was stopped and the product was precipitated from diethyl ether to get the polymer as brown color sticky product.



<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, TMS): 7.35 (5H, broad peak), 5.10 (2H, bs), 4.2 (2H, broad peak), 3.80 (2H, broad peak), 3.50 (8H, broad peak), 3.3 (3H, broad peak), 2.89 (4H, broad peak), 2.2 (4H, broad peak), 1.89 (4H, broad peak).

**Dynamic Light Scattering (DLS) Study:** For the DLS measurements 0.2 mg of the polymer **P1** was dissolved in 100  $\mu$ l of DMF and 1 mL water was added drop wise to the DMF solution for 10 minutes under stirring condition. The solution was kept dialyzed against water for 24h. Final solution was filtered using hydrophilic membrane (pore size 0.450  $\mu$ m) before experiment was performed.

**Transmission Electron Microscope (TEM) Study:** The same polymer solution, prepared for DLS study was used for the TEM measurements. One drop of the sample was dropcasted on carbon coated Cu grid and air dried for 12h.

**DiI Encapsulation:** To the polymer solution, 10  $\mu$ l of DiI solution in acetone was added and stirred for 6 h at 25 °C temperature. The vial was kept open to remove the acetone from the solution. The solution was filtered through a hydrophilic membrane (pore size: 0.45  $\mu$ m) before any experiment was performed.

**Calculation of Critical Aggregation Concentration (CAC):** A stock solution (1 mM) of **P1** micelle was prepared and DiI was encapsulated to the micelle. DiI encapsulated micellar solution of **P1** was diluted into various solutions of different concentrations. The concentration range of polymer was maintained from 1 mM to 0.001 mM. Then emission spectrum was recorded for each solution and emission maxima of each spectrum were plotted as a function of concentration of polymer **P1**. The inflection point of the plot was taken as CAC of polymer **P1**.

**Fluorescence Microscopy Studies:** In a typical fluorescence microscopic experiment, 50  $\mu$ l of dye encapsulated polymer solution was placed on a cleaned cover glass, and then another cover glass was placed on it. Finally, images were taken on a fluorescence microscope (OLIMPUS BX-51) in 40 x magnification.

**UV/PL and Photoluminescence Studies:** All the experiments were carried out at 25 °C using quartz cuvette of 10 mm path length.

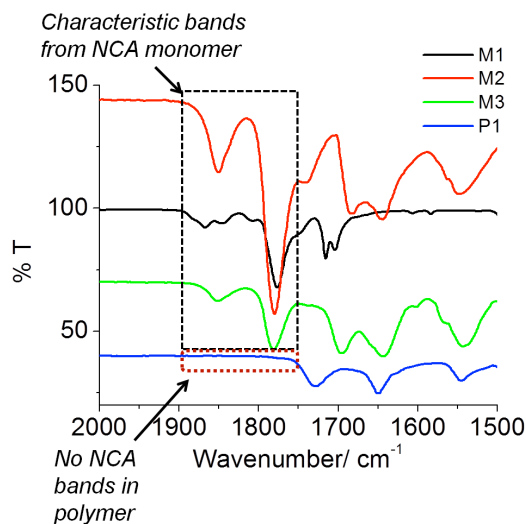
**Disassembly Study by DLS:** To the solution of **P1** (50  $\mu\text{M}$ ) in water, bCA-II enzyme solution (30  $\mu\text{M}$ ) was added and DLS was recorded overtime at room temperature.

**Guest Release Study:** To the DiI encapsulated solution of **P1** micelle (50  $\mu\text{M}$ ), bCAII enzyme solution (30  $\mu\text{M}$ ) was added and the absorption spectra of DiI were recorded overtime. The % release of the DiI was calculated by using the following equations.

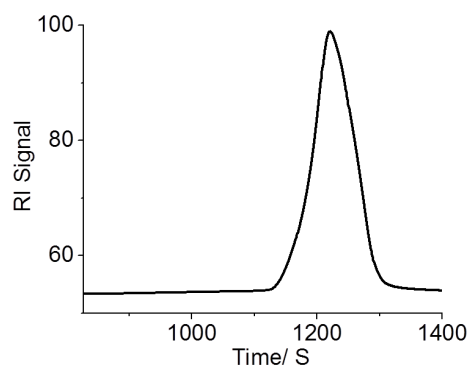
$$\% \text{ Release of DiI} = \frac{A_t - A_0}{A_0} \times 100$$

Where  $A_0$  = Initial absorbance of DiI (before addition of bCA-II)

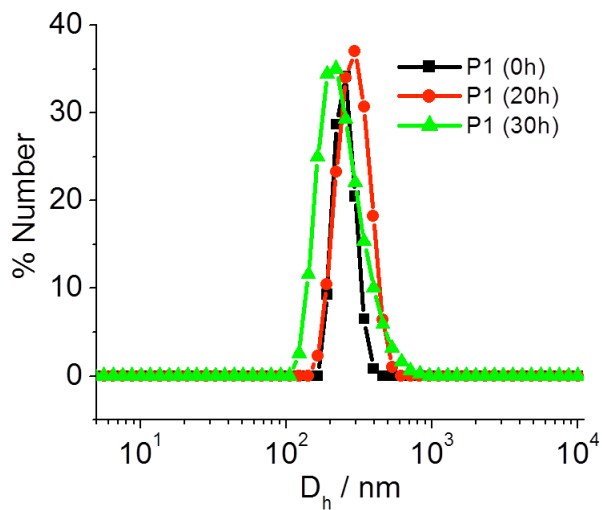
$A_t$  = Absorbance of DiI at each time point (After addition of bCA-II)



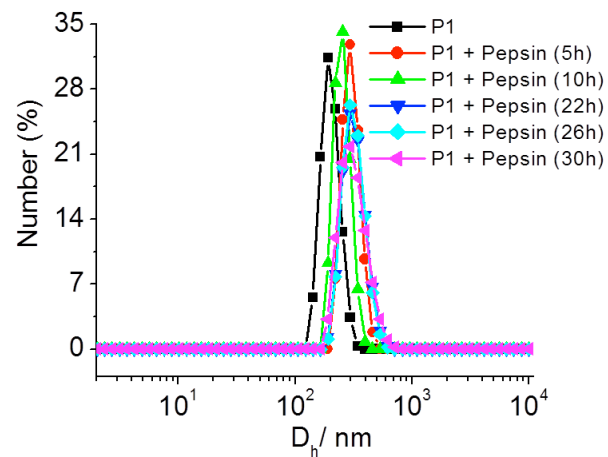
**Figure S1:** FTIR spectra of monomers and polymer **P1**. In the polymer spectrum the characteristic peaks of NCA monomer are absent and thus, suggesting formation of polymer.



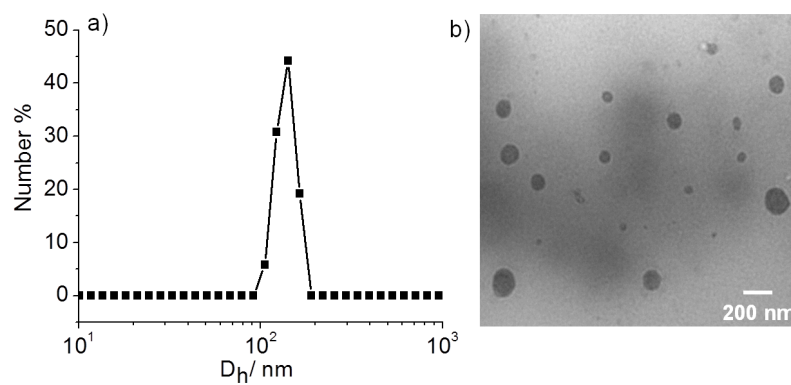
**Figure S2:** GPC chromatogram of polymer **P1**. Molecular weight and PDI were calculated with respect to PMMA standards.  $M_n = 3200$  and  $PDI = 1.2$ . Solvent = THF; Temperature =  $25^\circ\text{C}$ .



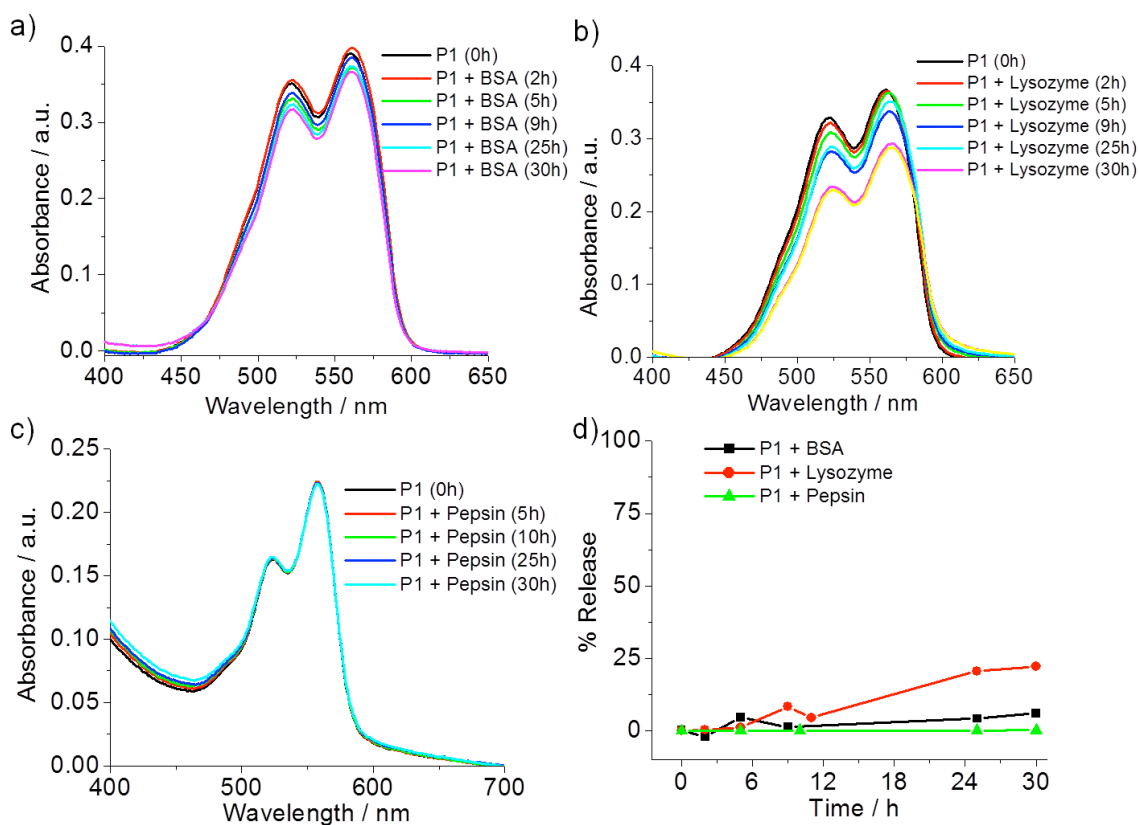
**Figure S3:** Time dependant DLS profile of **P1** micellar solution. Temperature =  $25^\circ\text{C}$ .



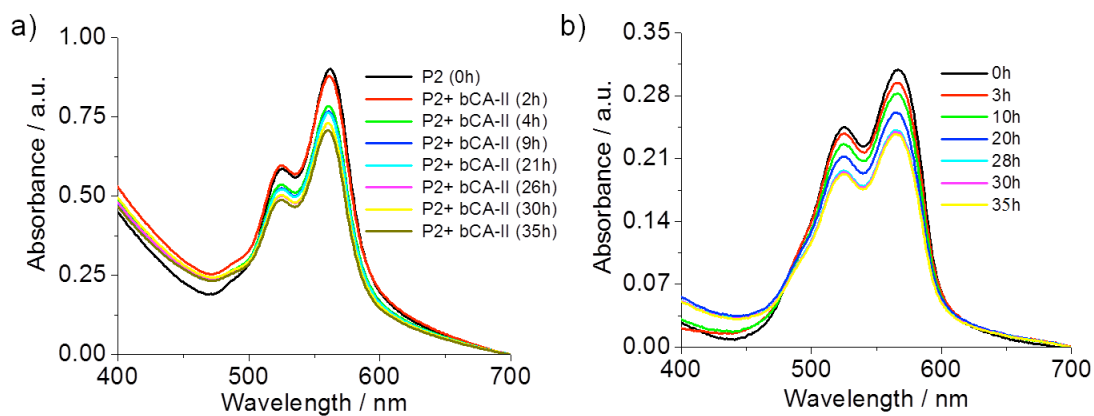
**Figure S4:** Time dependant DLS profile of **P1** micellar solution in presence of pepsin. Temperature = 25°C.



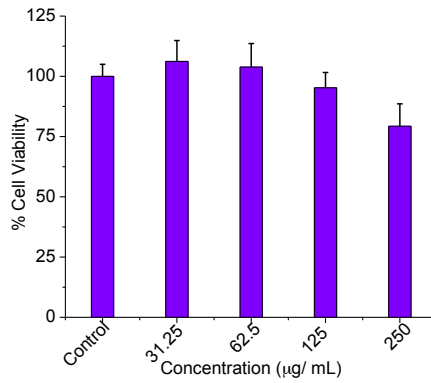
**Figure S5:** a) DLS profile and b) TEM image of polymer **P2**. Temperature = 25°C.



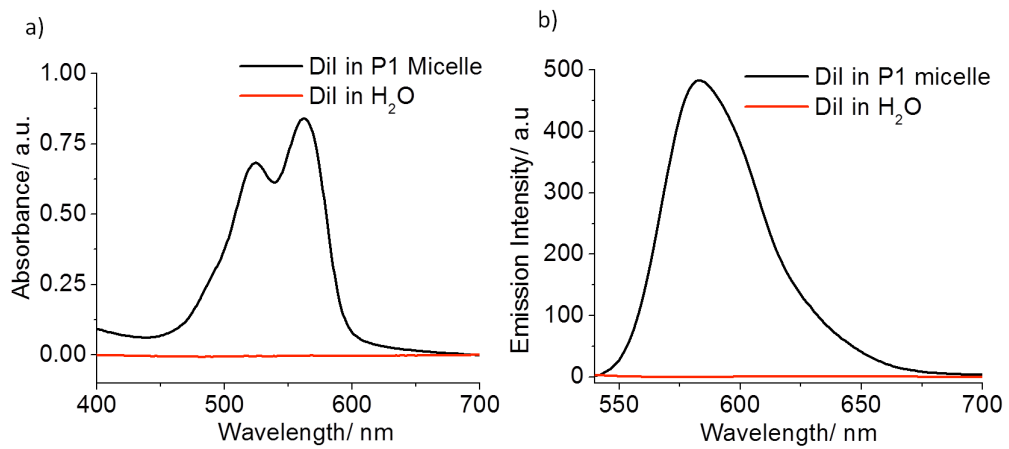
**Figure S6:** a) DiI release profile of **P1** micelle in presence of a) BSA, b) Lysozyme and c) Pepsin; d) Plot of % release of DiI as a function of time. Cuvette pathlength = 10 mm, Temperature = 25°C.



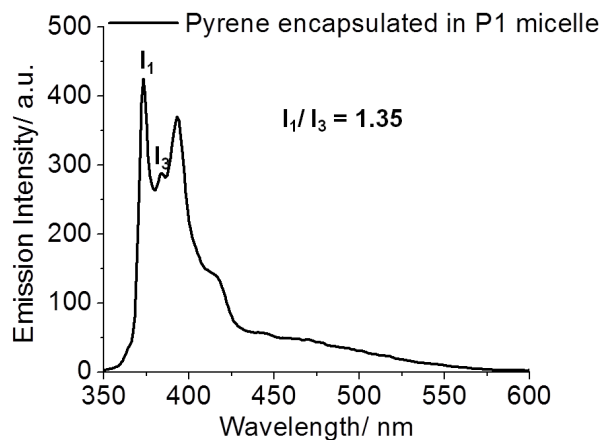
**Figure S7:** DiI release profile of control polymer **P2** a) in presence of bCA-II protein and b) in absence of bCA-II. Cuvette pathlength = 10 mm, Temperature = 25°C.



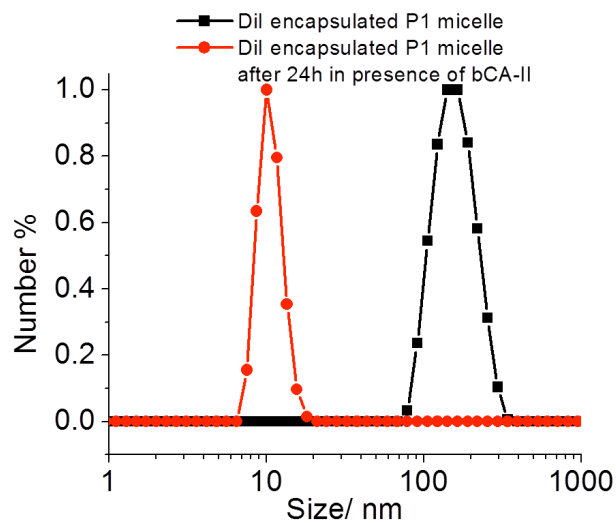
**Figure S8:** *In vitro* cytotoxicity of polymer **P1** on HeLa cell



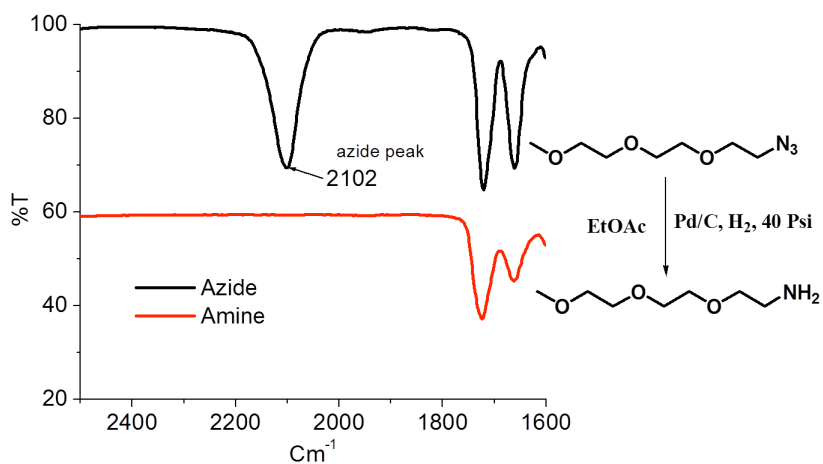
**Figure S9:** a) Absorption and b) Emission spectra of DiI in water and DiI in **P1** micelle.



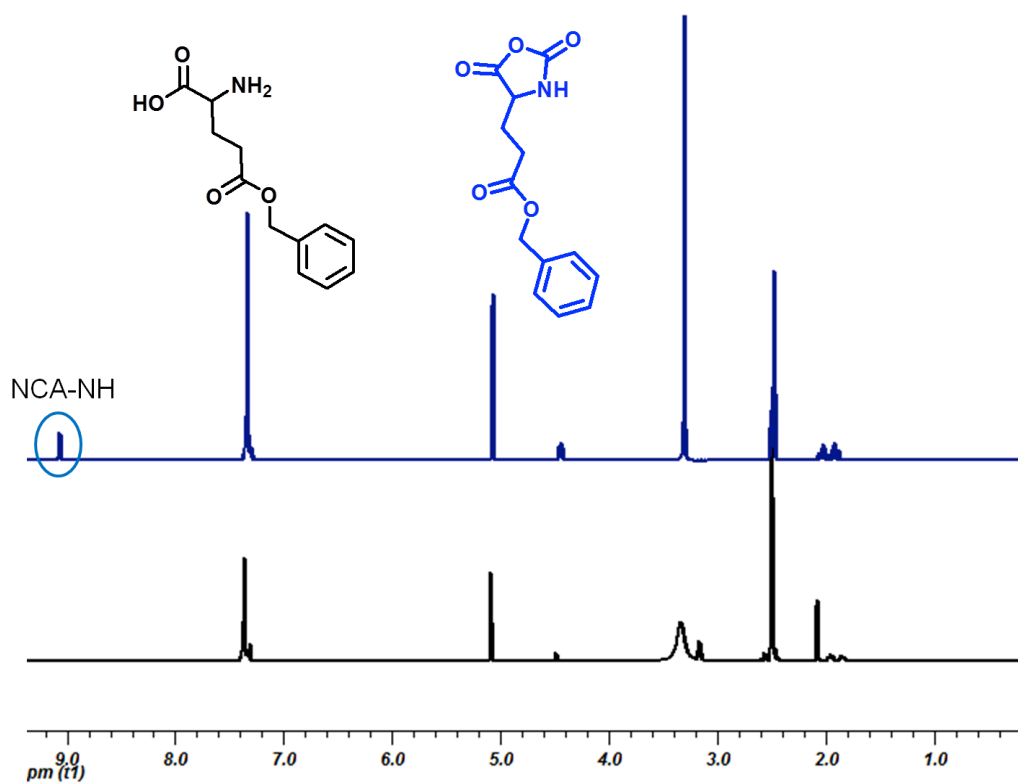
**Figure S10:** Emission spectrum of Pyrene encapsulated in **P1** micelle.  $I_1/I_3$  value indicates that pyrene is in hydrophobic environment.<sup>3</sup>



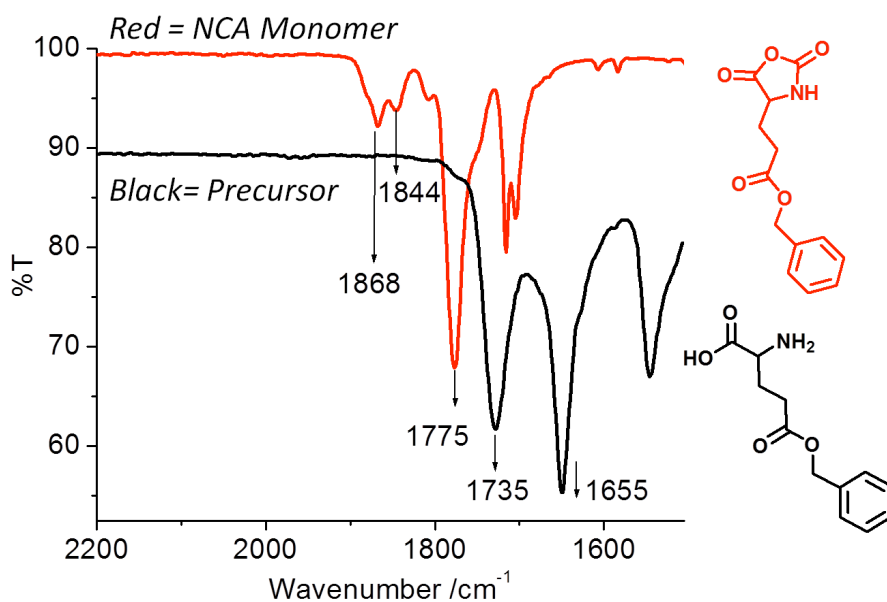
**Figure S11:** Time dependent DLS profile of DiI encapsulated **P1** micelle in presence of bCA-II protein.



**Figure S12:** Evidence of amine formation from azide

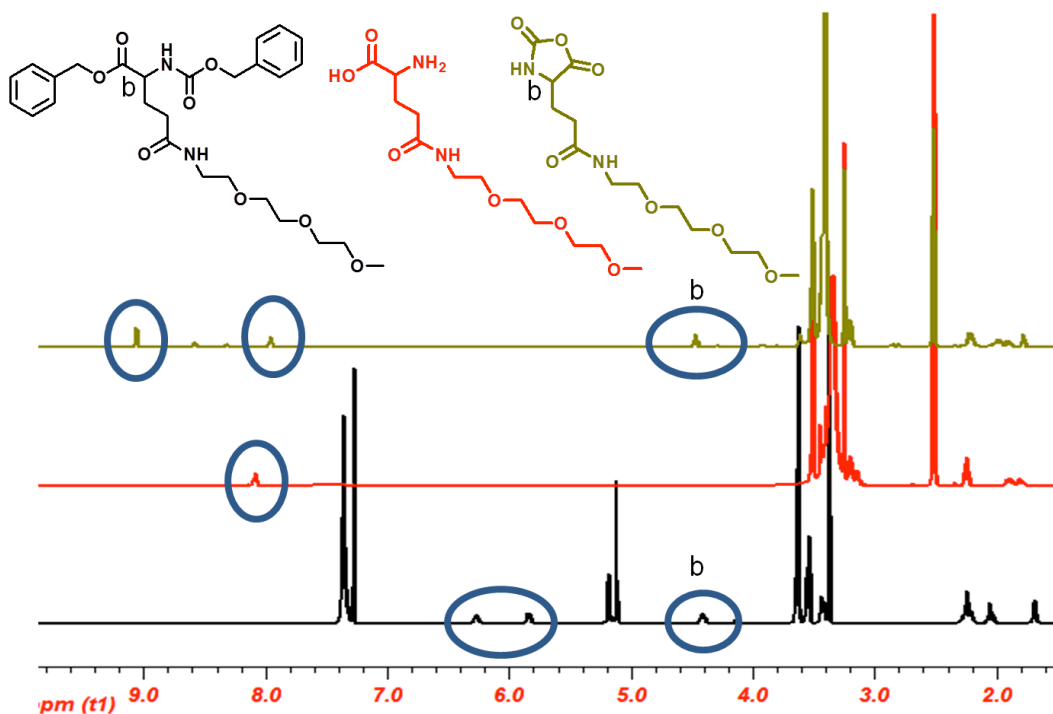


**Figure S13:** Comparison of  $^1\text{H-NMR}$  spectrum of **M1** with the corresponding precursor spectrum. Peak at 9.0 indicates formation of N-carboxy anhydride (NCA) monomer. The “\*” indicates residual solvent peak.

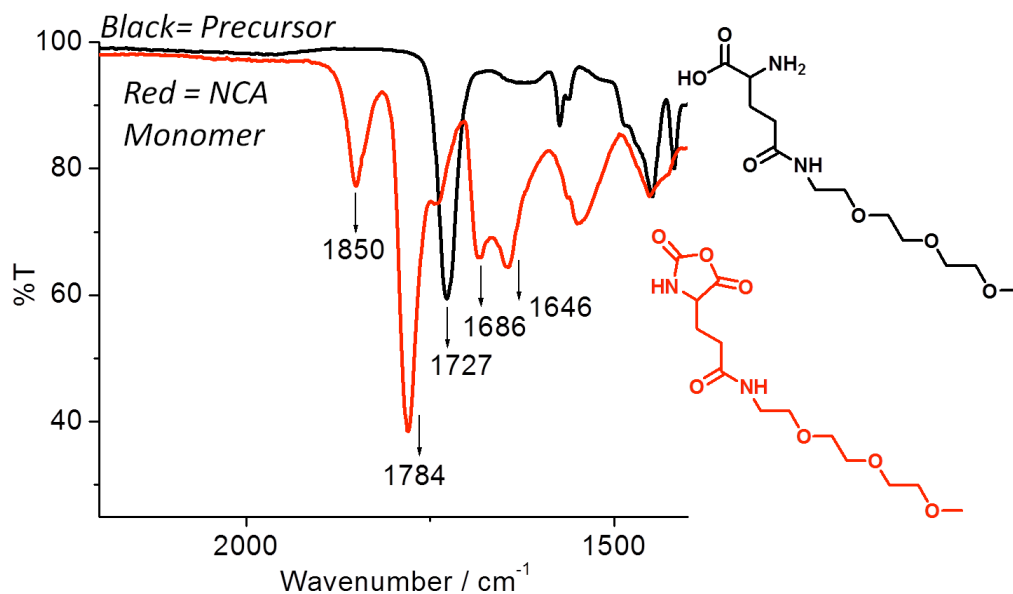


**Figure S14:** Comparison of IR spectrum of **M1** with the corresponding precursor spectrum. Appearance of characteristic bands at 1844, 1868 and 1775  $\text{cm}^{-1}$  for NCA indicates formation of NCA monomer.

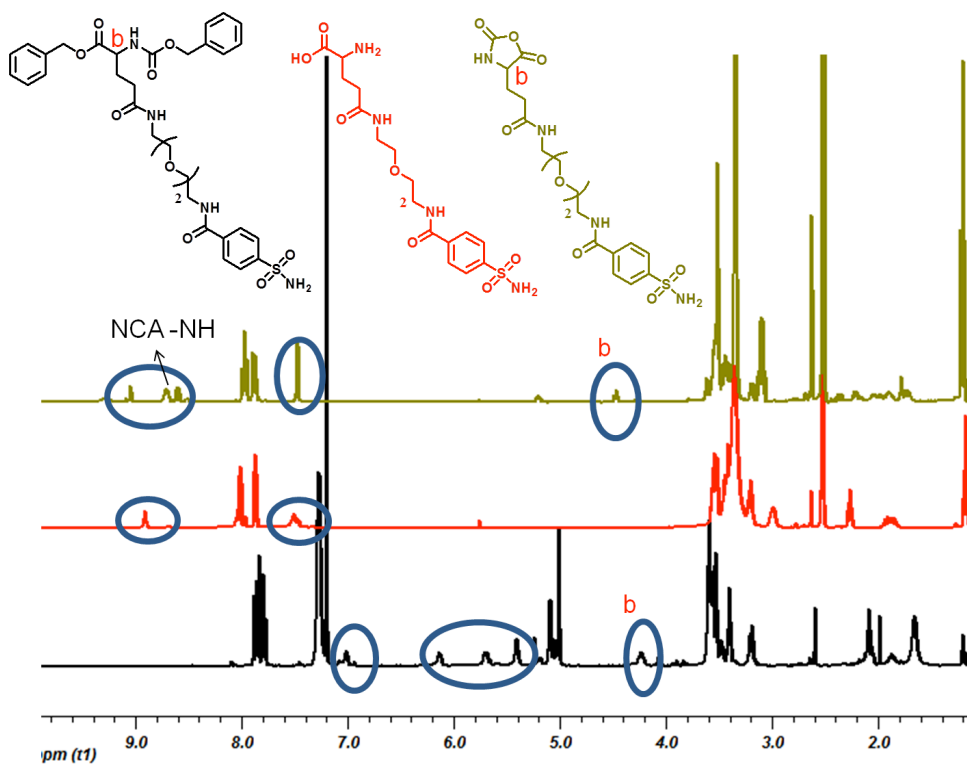




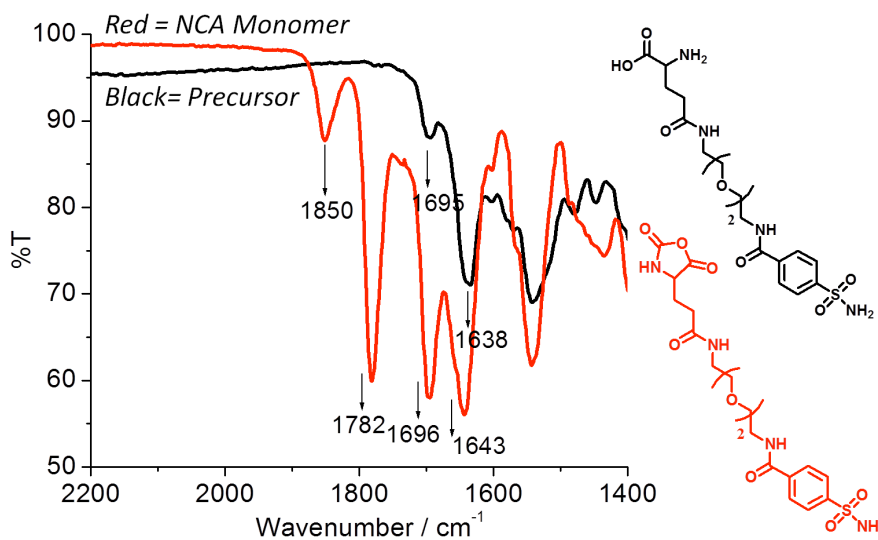
**Figure S15:** NMR stack plot which indicates formation of NCA monomer **M2**. Peak at 9.0 indicates formation of N-carboxy anhydride (NCA) monomer. The –NH and b protons are circled. The “\*” indicates residual solvent peak.



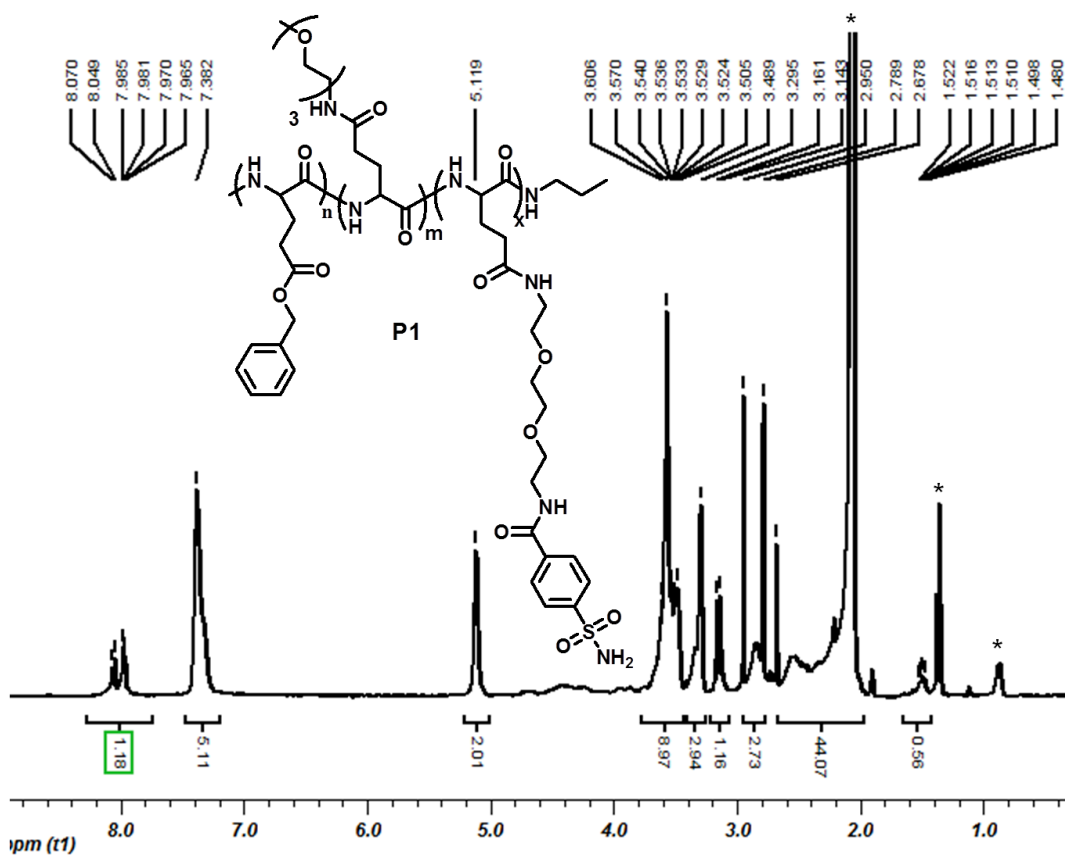
**Figure S16:** Comparison of IR spectrum of **M2** with the corresponding precursor spectrum. Appearance of characteristic bands at 1850 and 1784  $\text{cm}^{-1}$  for NCA indicates formation of NCA monomer.



**Figure S17:** NMR stack plot which indicates formation of NCA monomer **M3**. Peak at 8.90 indicates formation of N-carboxy anhydride (NCA) monomer. The –NH, –NH<sub>2</sub> and b protons are circled. The “\*” indicates residual solvent peak.



**Figure S18:** Comparison of IR spectrum of **M3** with the corresponding precursor spectrum. Appearance of characteristic bands at 1850 and 1782cm<sup>-1</sup> for NCA indicates formation of NCA monomer.



**Figure S19:** NMR spectrum of polymer **P1**. The “\*” indicates residual solvent peak.

### Calculation of % of each block present in the polymer:

Intensity of 2 benzyl protons from **M1** monomer is 2.01 (at  $\delta = 5.1$ ). So, for one proton it would be  $\sim 1.0$ .

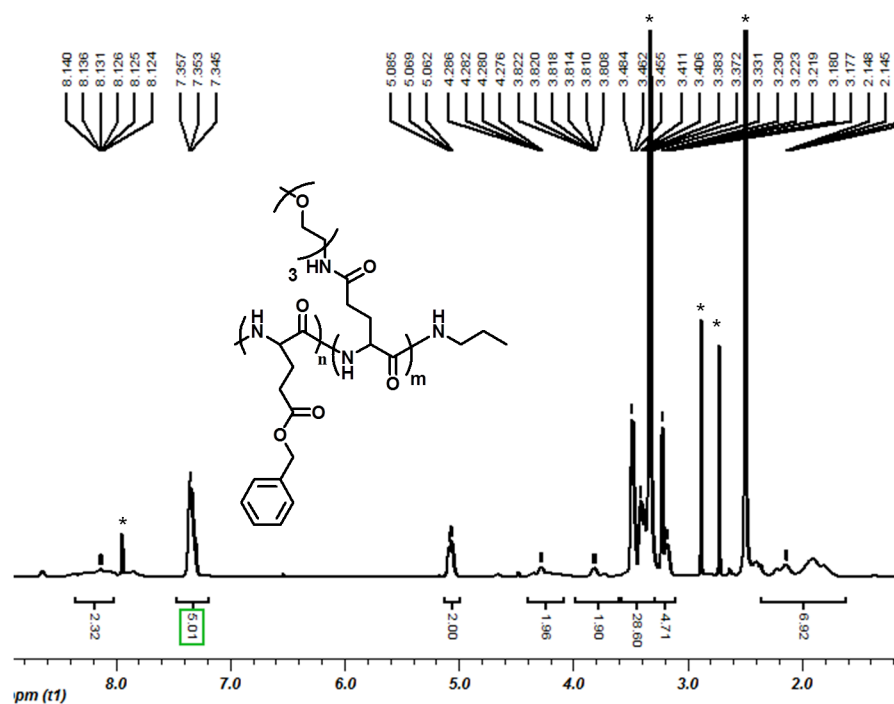
Intensity of 4 aryl protons in the **M3** monomer is 1.18 (at  $\delta = 8.0$  and 7.98). So, for one proton it would be  $\sim 0.30$ .

Intensity of 3 methyl protons in **M2** monomer and 2 methylene protons from **M3** monomer are coming together and the intensity is 2.94 (at  $\delta = 3.30$ ). So the contribution from **M2** is  $(2.94 - 0.6 = 0.78)$ . So, for one proton it would be  $\sim 0.78$ .

$$\% \text{ of M1} = (1/2.08) * 100 = 48\%$$

$$\% \text{ of M2} = (0.78/2.08) * 100 = 37\%$$

$$\% \text{ of M3} = (0.30/2.08) * 100 = 15\%$$



**Figure S20:** NMR spectrum of polymer **P2**. The “\*” indicates residual solvent peak

### Calculation of % of each block present in the polymer:

Intensity of 2 benzyl protons from **M1** monomer is 2.00 (at  $\delta = 5.08$ ). So, for one proton it would be  $\sim 1.0$ .

Intensity of 1 -CH proton in **M1** monomer and 1 -CH proton from **M2** monomer are coming together and the intensity is 1.96 (at  $\delta = 4.28$ ). So the contribution from **M2** is  $(1.96 - 1.0 = 0.96)$ . So, for one proton it would be  $\sim 0.96$ .

$$\% \text{ of } \mathbf{M1} = (1/1.96) * 100 = 51\%$$

$$\% \text{ of } \mathbf{M2} = (0.96/1.96) * 100 = 49\%$$

Additional NMR spectra:

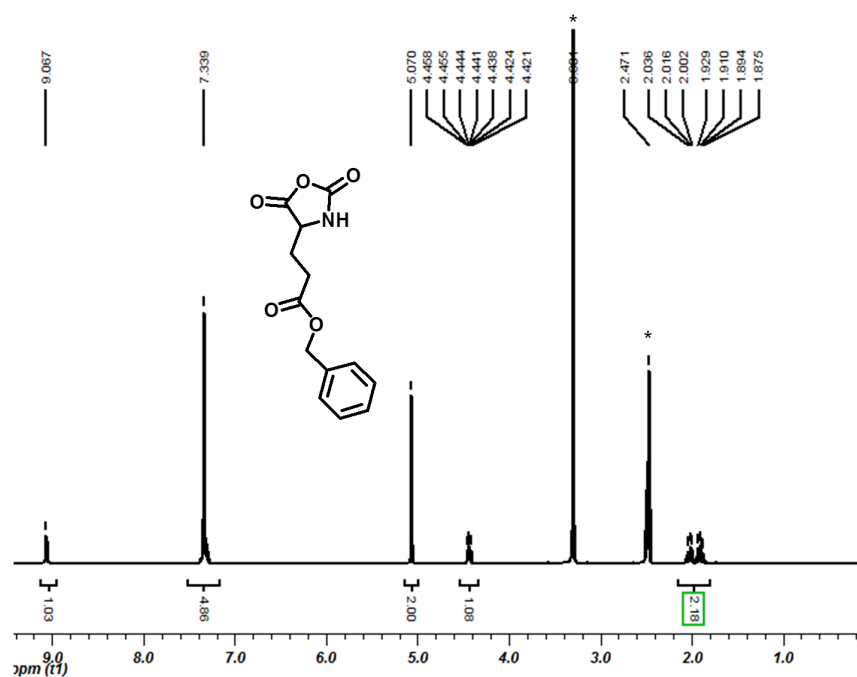


Figure S21: NMR spectrum of M1. The “\*” indicates residual solvent peak.

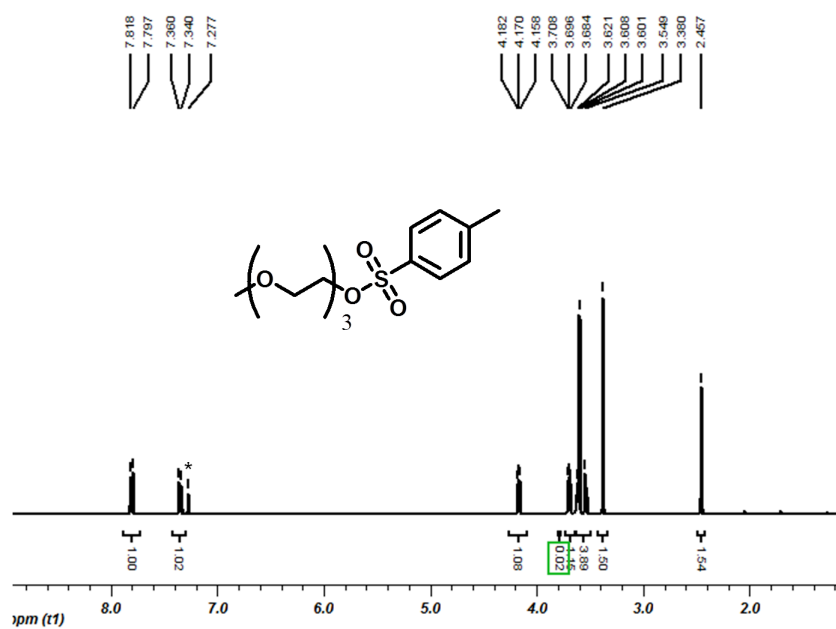
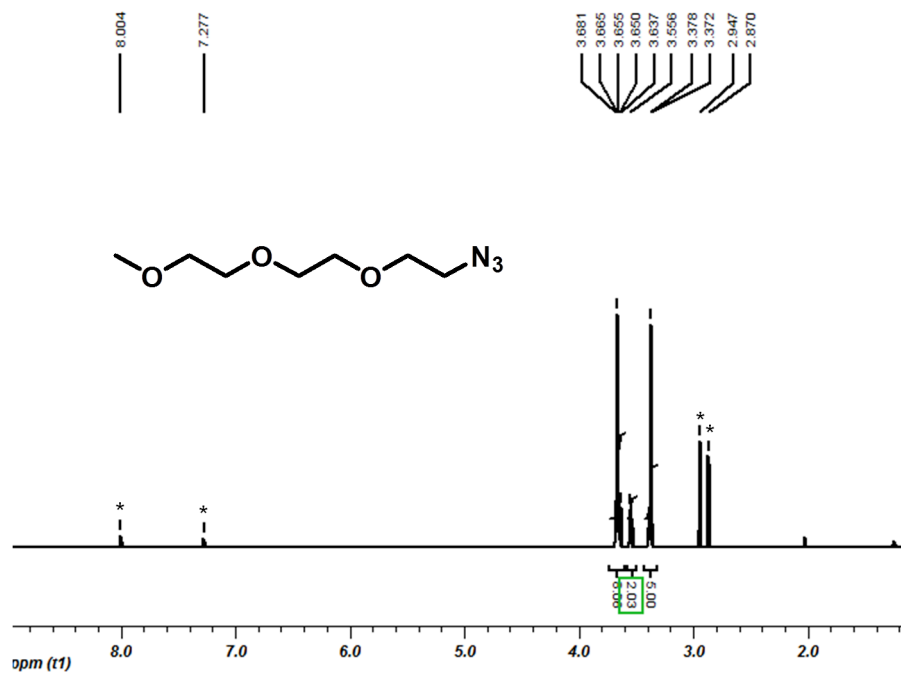
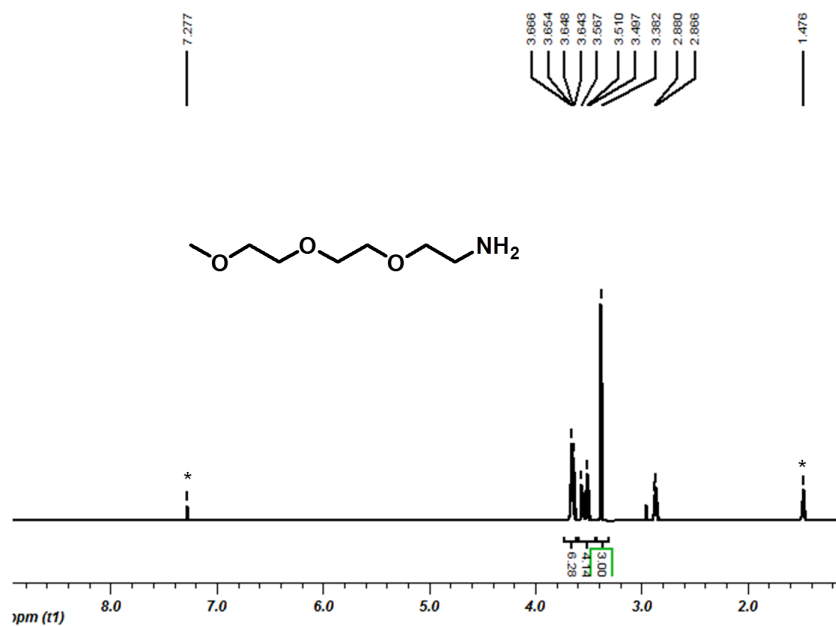


Figure S22: NMR spectrum of compound1. The “\*” indicates residual solvent peak.



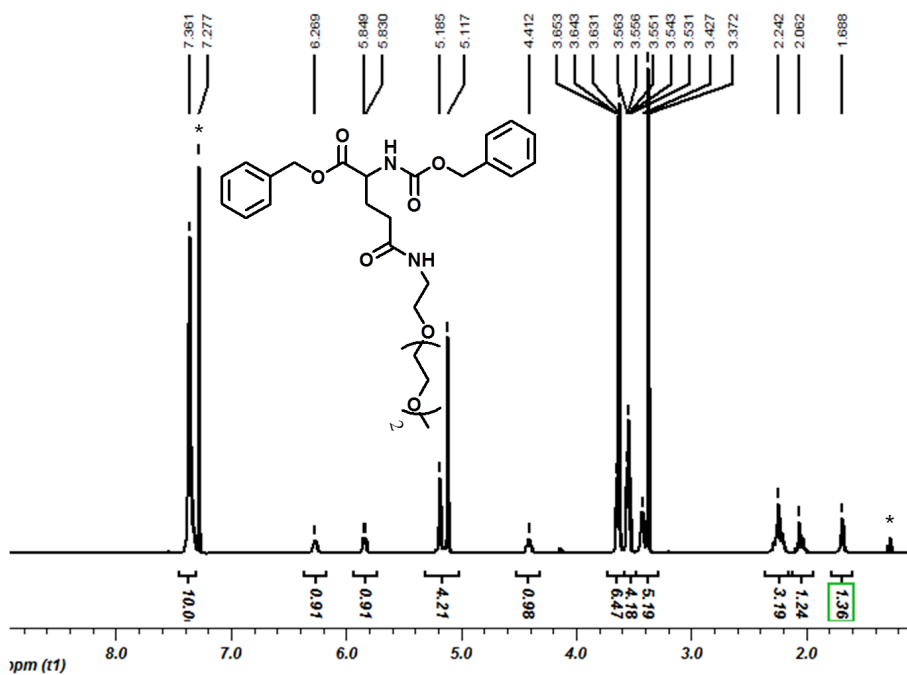
**Figure S23:** NMR spectrum of compound 2. The “\*” indicates residual solvent peak.



**Figure S24:** NMR spectrum of compound 3. The “\*” indicates residual solvent peak.



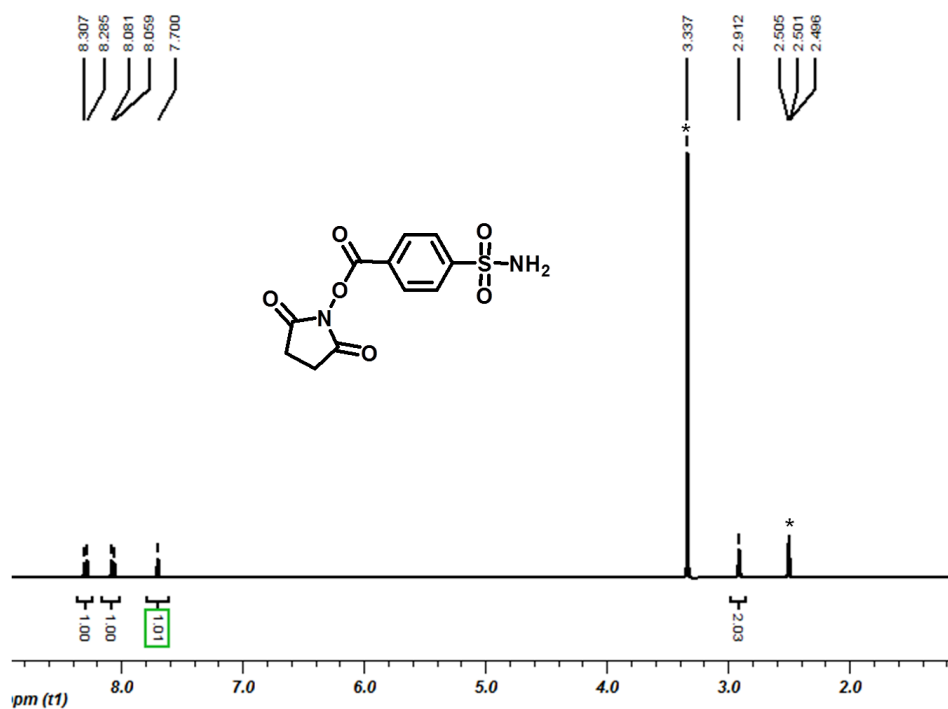
**Figure S25:** NMR spectrum of compound **5**. The “\*” indicates residual solvent peak.



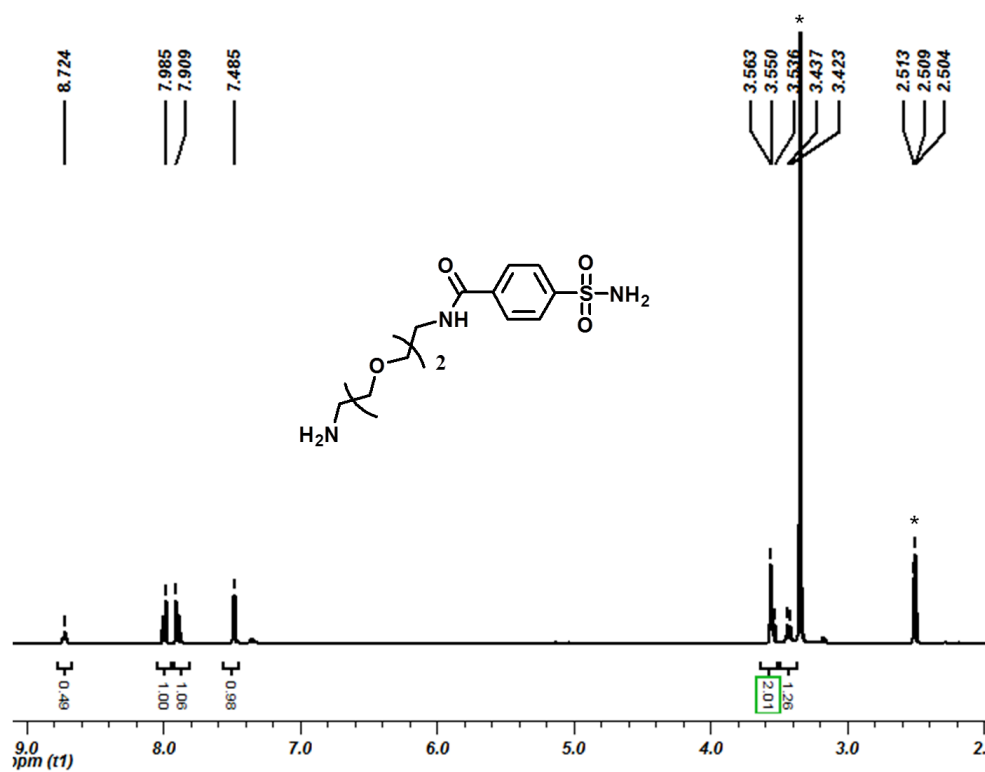
**Figure S26:** NMR spectrum of compound **6**. The “\*” indicates residual solvent peak.



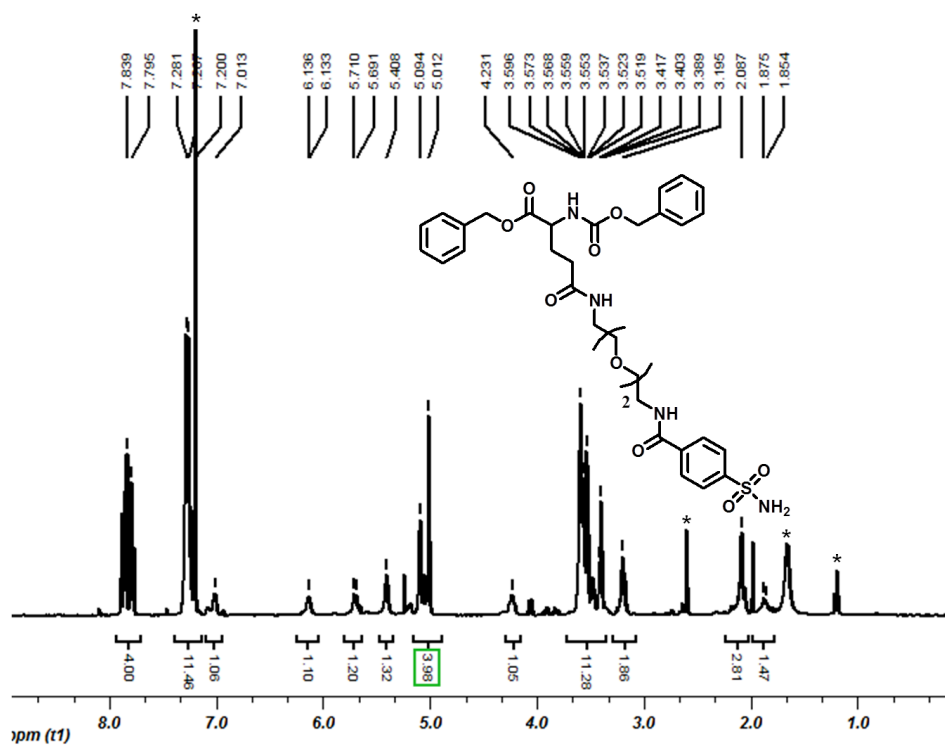




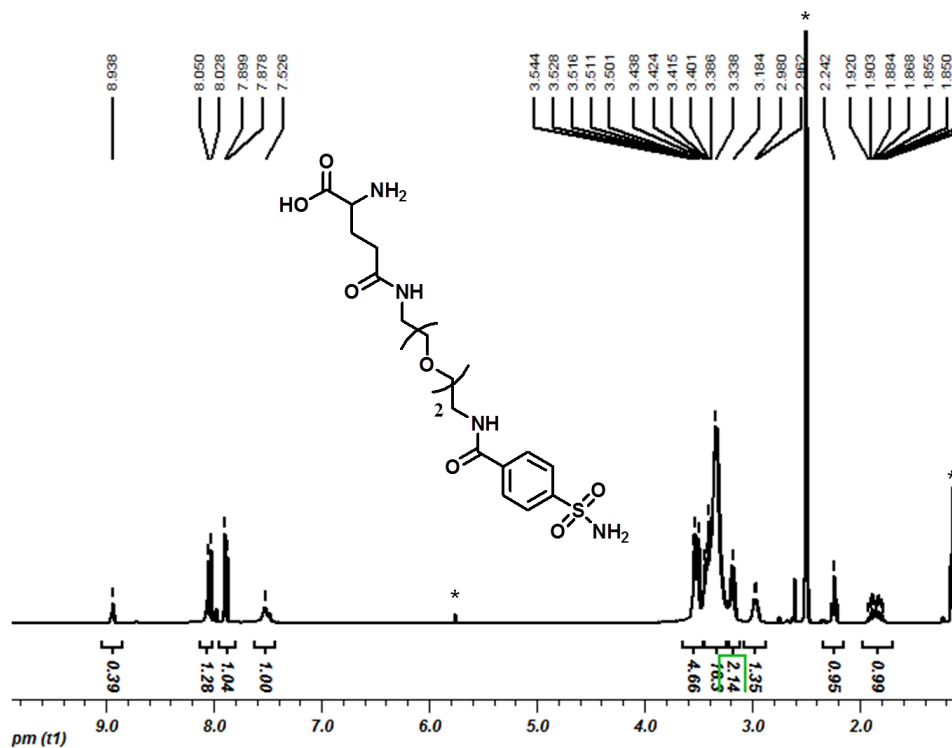
**Figure S29:** NMR spectrum of compound 9. The “\*” indicates residual solvent peak.



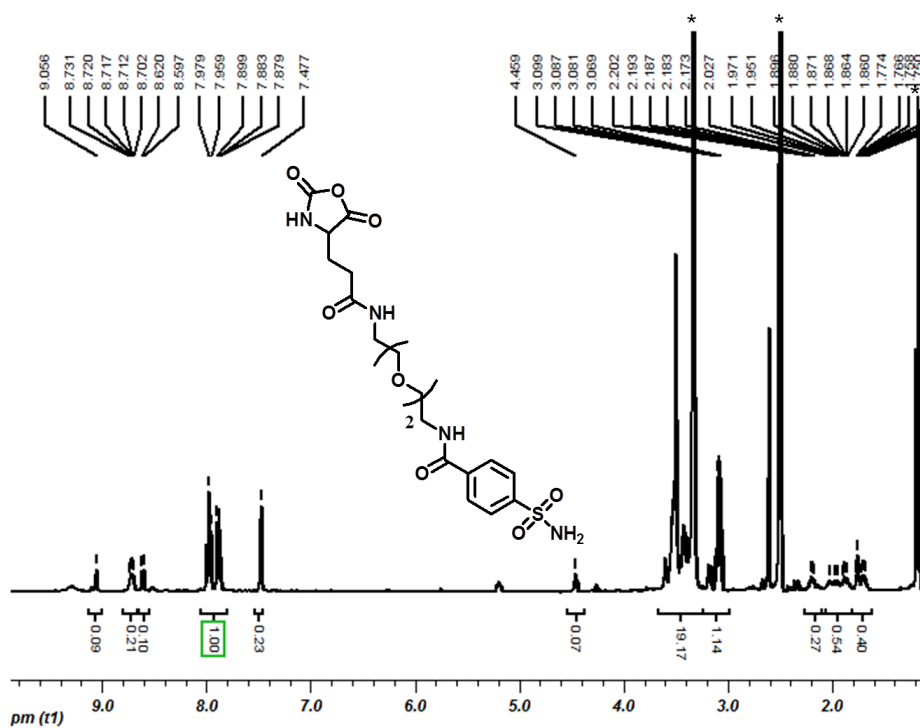
**Figure S30:** NMR spectrum of compound 11. The “\*” indicates residual solvent peak.



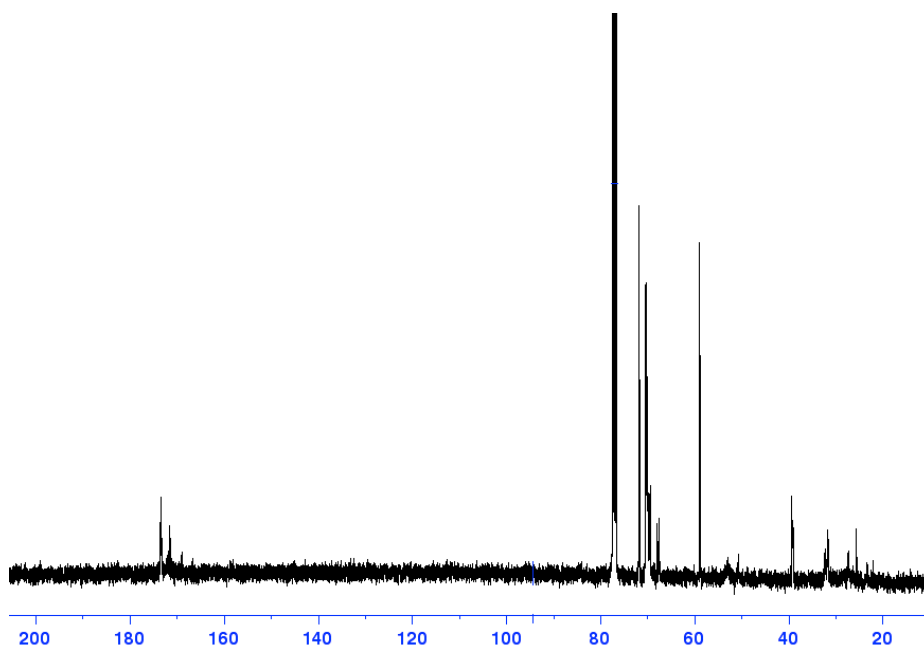
**Figure S31:** NMR spectrum of compound **12**. The “\*” indicates residual solvent peak.



**Figure S32:** NMR spectrum of compound **13**. The “\*” indicates residual solvent peak.



**Figure S33:** NMR spectrum of compound 14. The “\*” indicates residual solvent peak.



**Figure S34:** <sup>13</sup>C-NMR spectrum of M2.

**Reference:**

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2. Molla, M. R. and Ghosh, S. *Chem. Eur. J.* **2012**, *18*, 9860 – 9869.
3. Savariar, E. N., Aathimanikandan, S. V., Thayumanavan, S. *J. Am. Chem. Soc.* **2006**, *128*, 16224-16230.