

Supplementary Materials

# Supramolecular Functionalizable Linear-Dendritic Block Copolymers for the Preparation of Nanocarriers by Microfluidics

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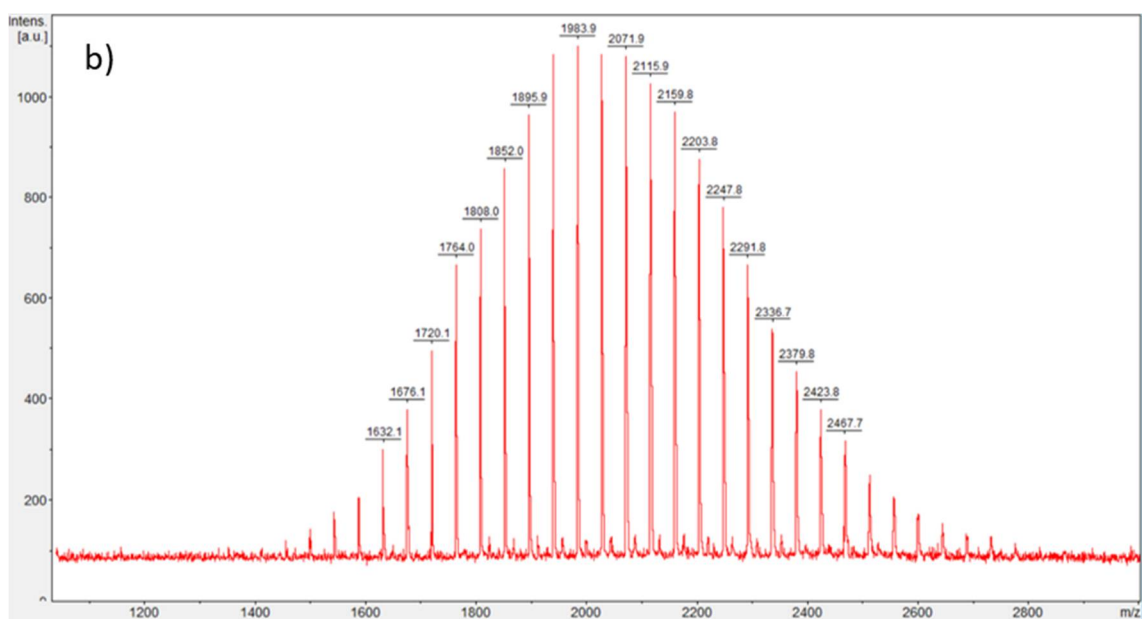
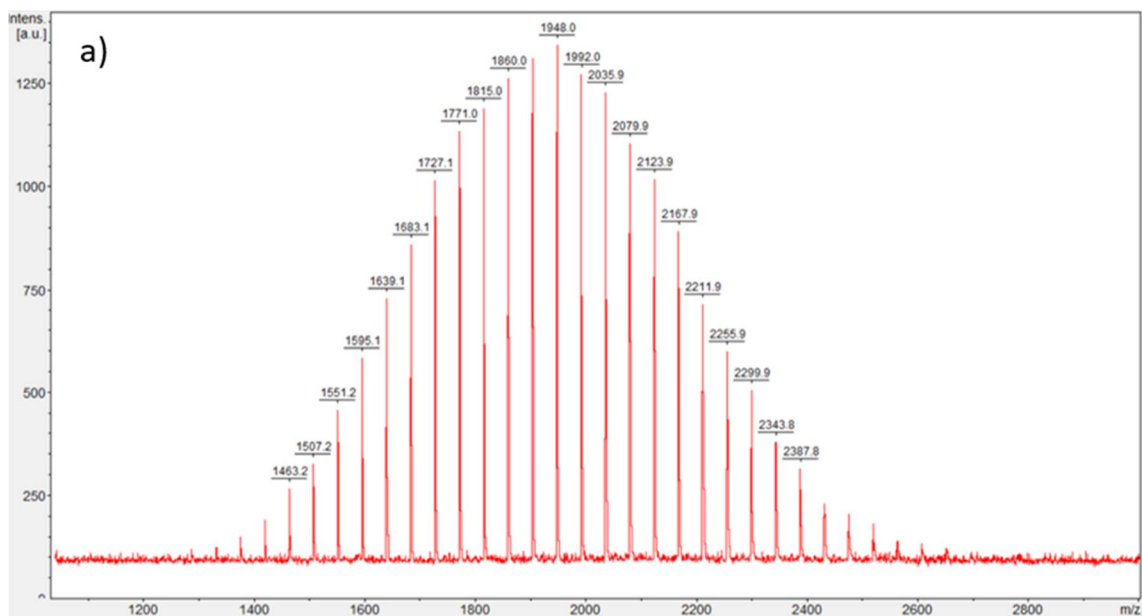
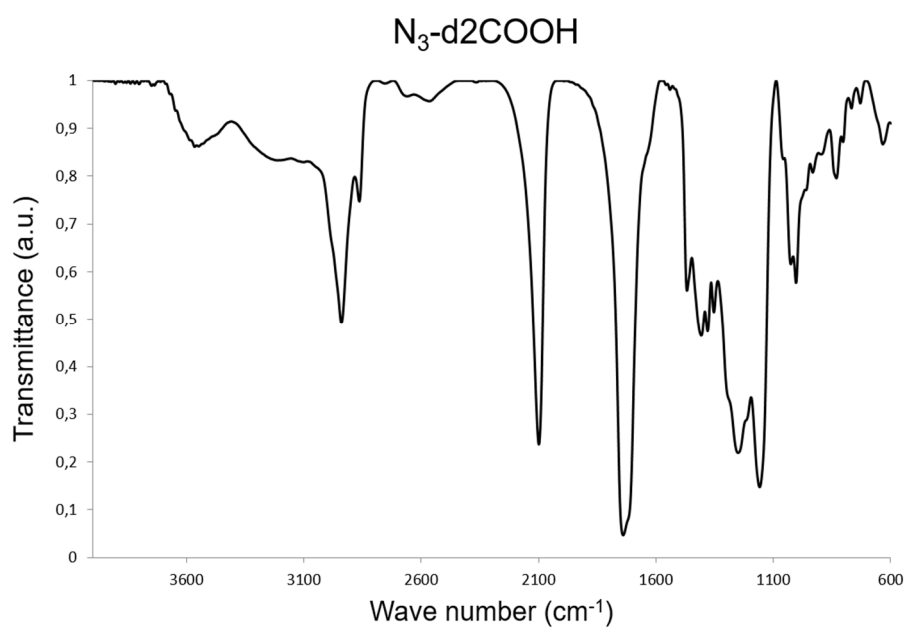
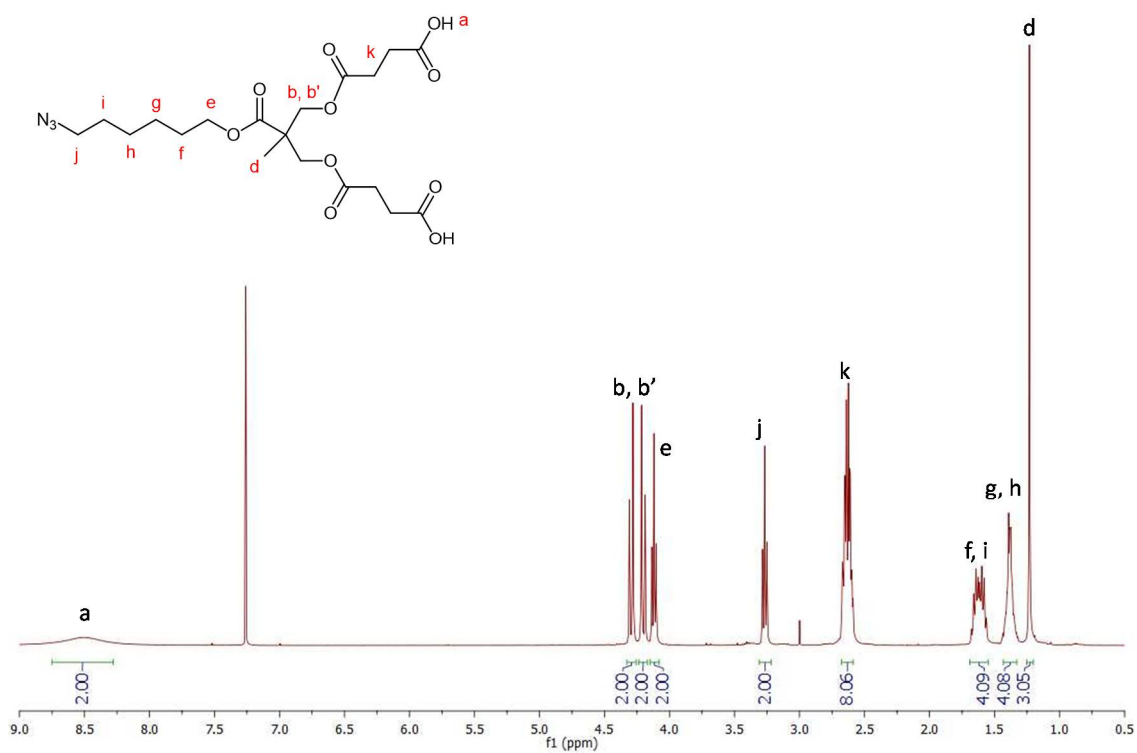


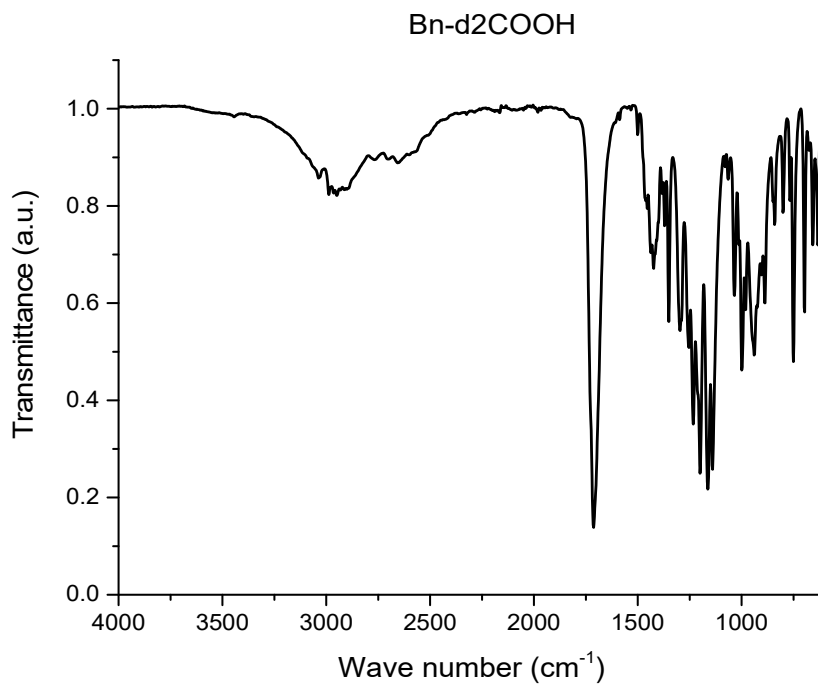
Figure S1. MALDI-TOF spectra of a) PEG<sub>2k</sub>-OH and b) PEG<sub>2k</sub>-Alky.



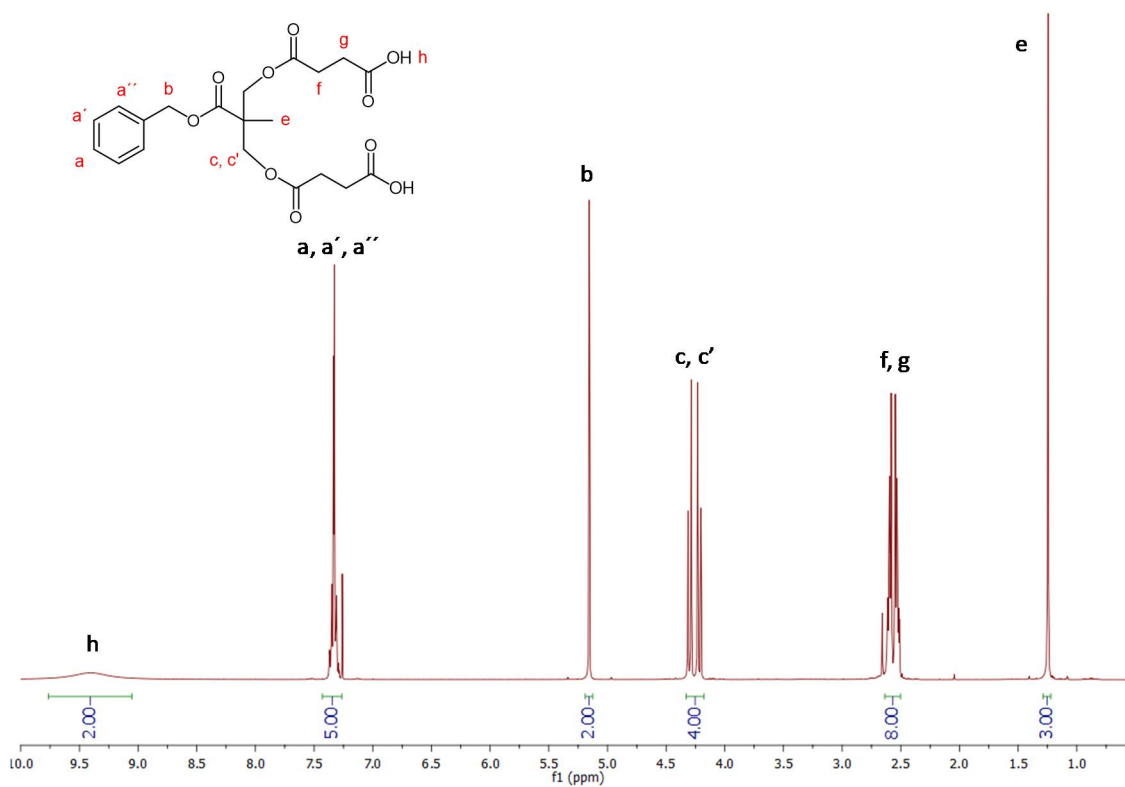
**Figure S2** FTIR spectrum of N<sub>3</sub>-d<sub>2</sub>COOH.



**Figure S3.** <sup>1</sup>H-NMR spectrum of N<sub>3</sub>-d<sub>2</sub>COOH (CDCl<sub>3</sub>, 400MHz) δ (ppm).



**Figure S4.** FTIR spectrum of **Bn-d2COOH**.



**Figure S5.** <sup>1</sup>H-NMR spectrum of **Bn-d2COOH** (CDCl<sub>3</sub>, 400MHz) δ (ppm).

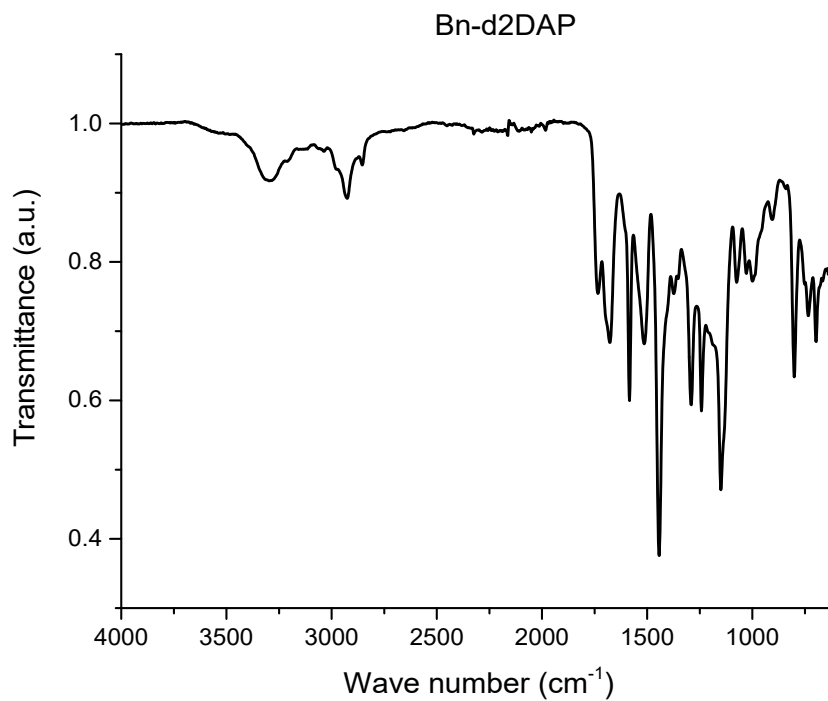


Figure S6. FTIR spectrum of **Bn-d2DAP**.

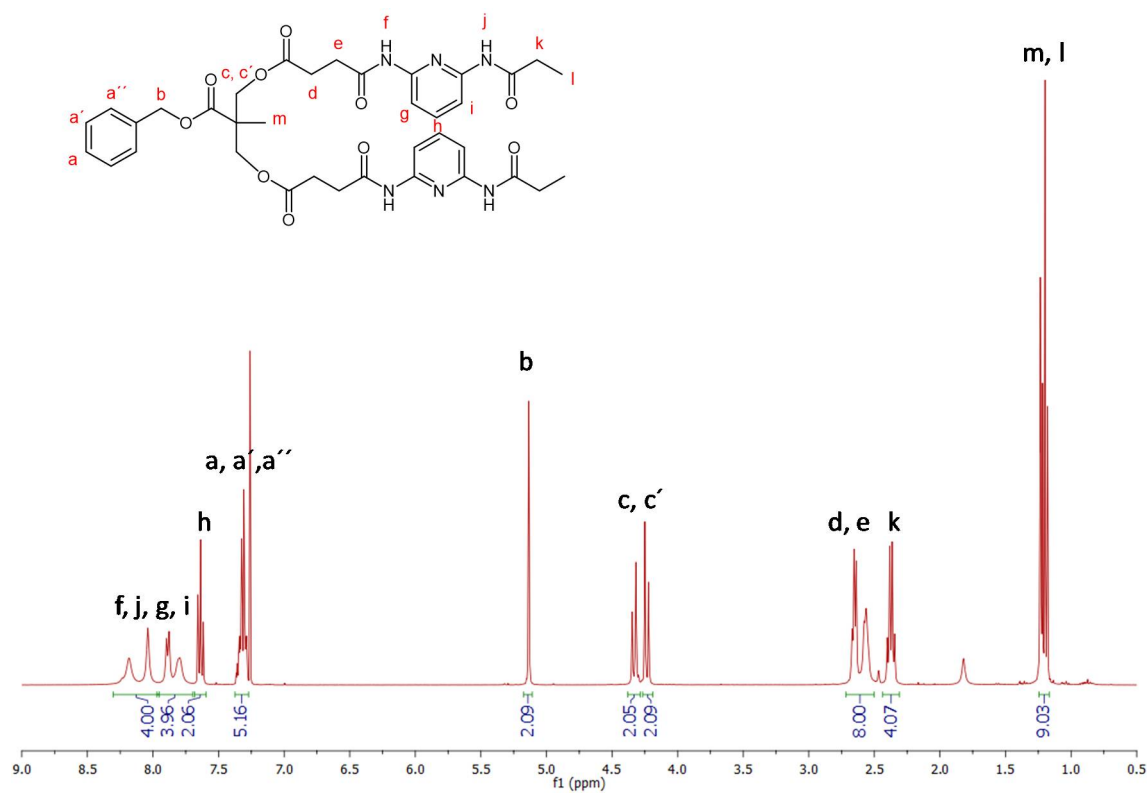
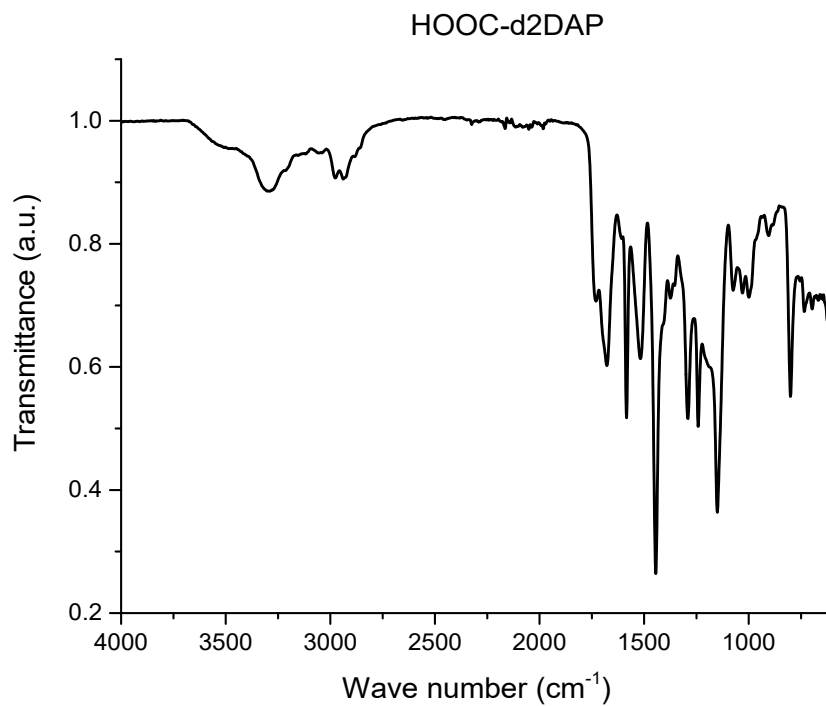
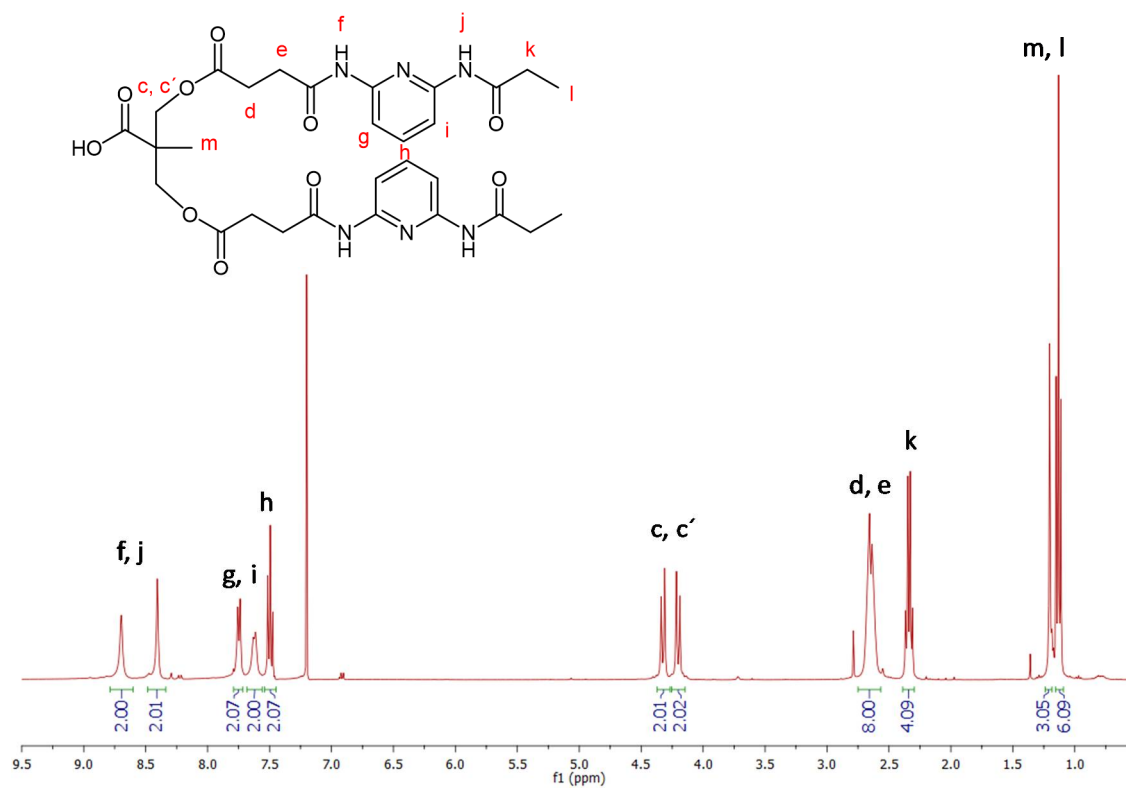


Figure S7. <sup>1</sup>H-NMR spectrum of **Bn-d2DAP** (CDCl<sub>3</sub>, 400MHz) δ (ppm).



**Figure S8.** FTIR spectrum of **HOOC-d2DAP**.



**Figure S9.** <sup>1</sup>H-NMR spectrum of **HOOC-d2DAP** (CDCl<sub>3</sub>, 400MHz) δ (ppm).

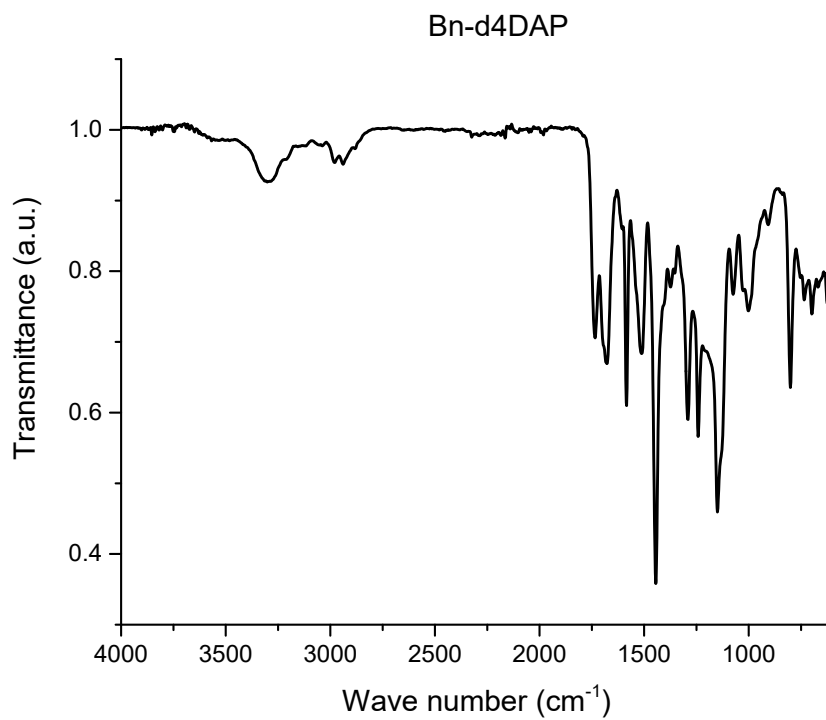


Figure S10. FTIR spectrum of **Bn-d4DAP**.

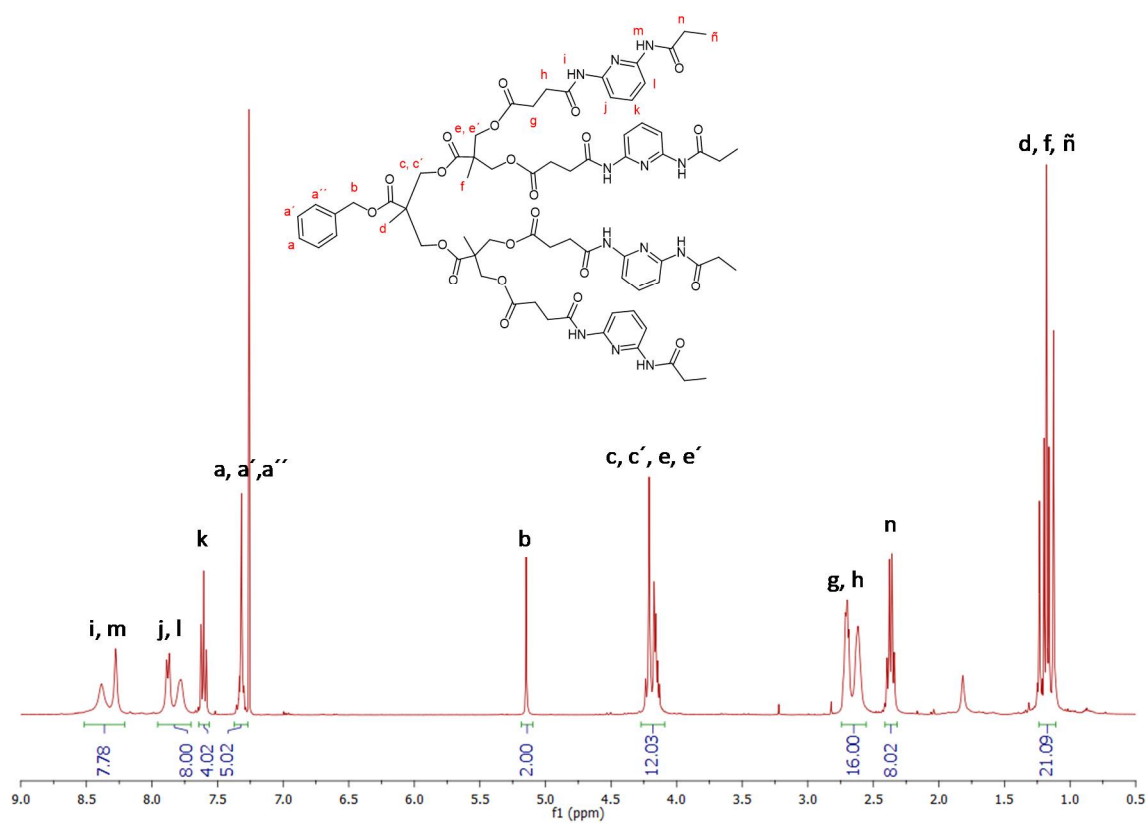
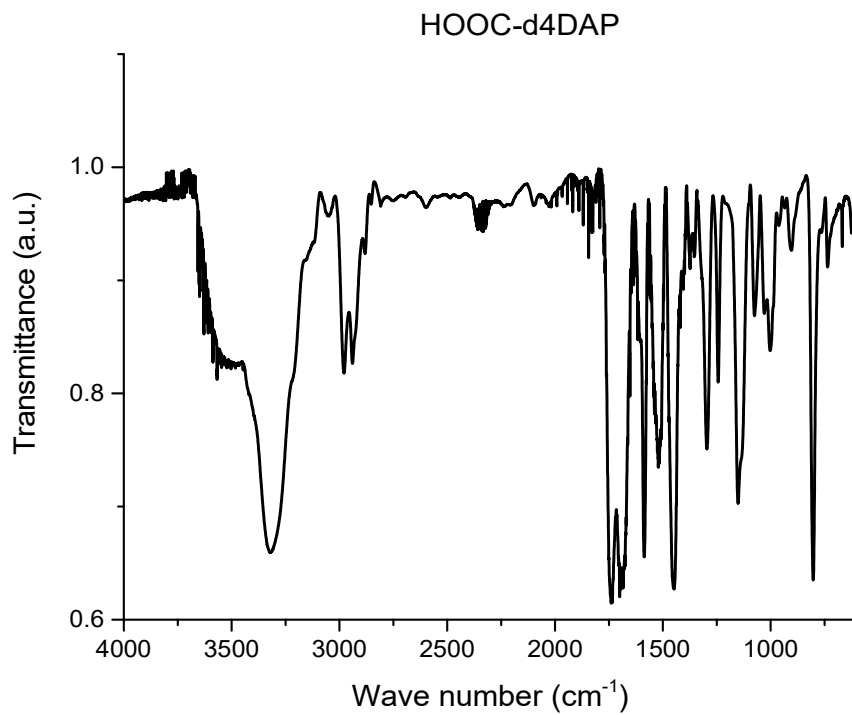
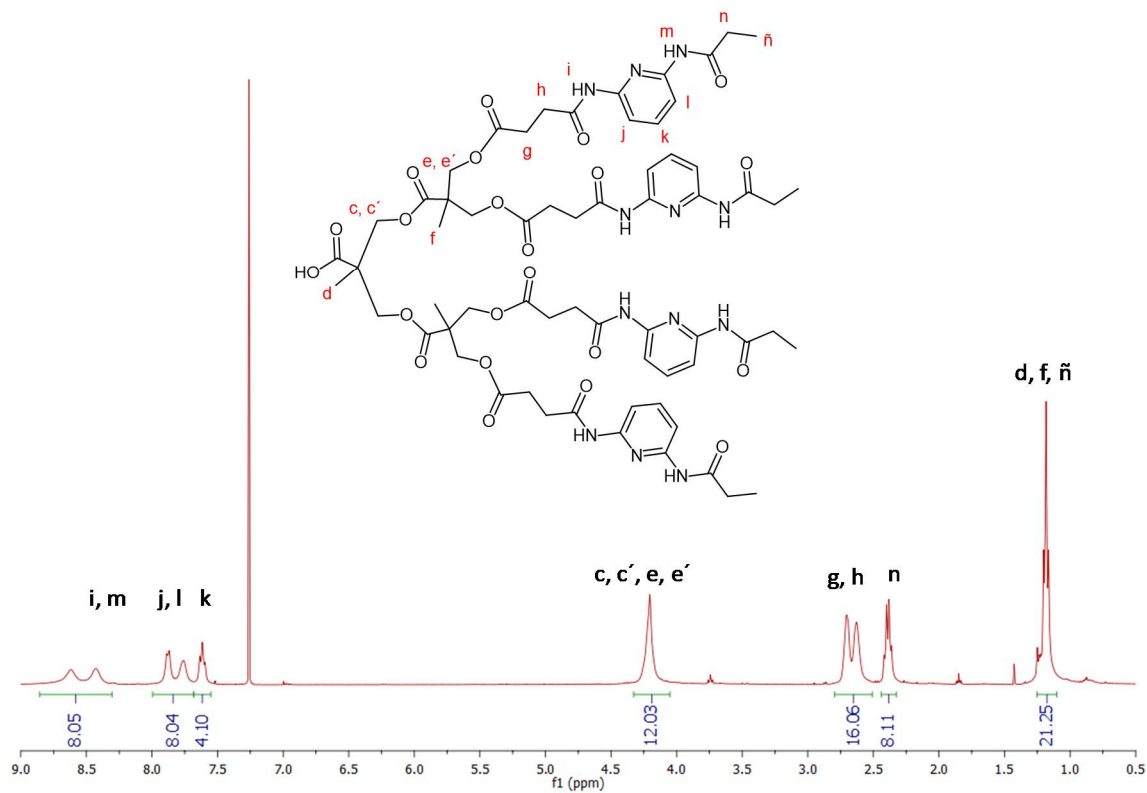


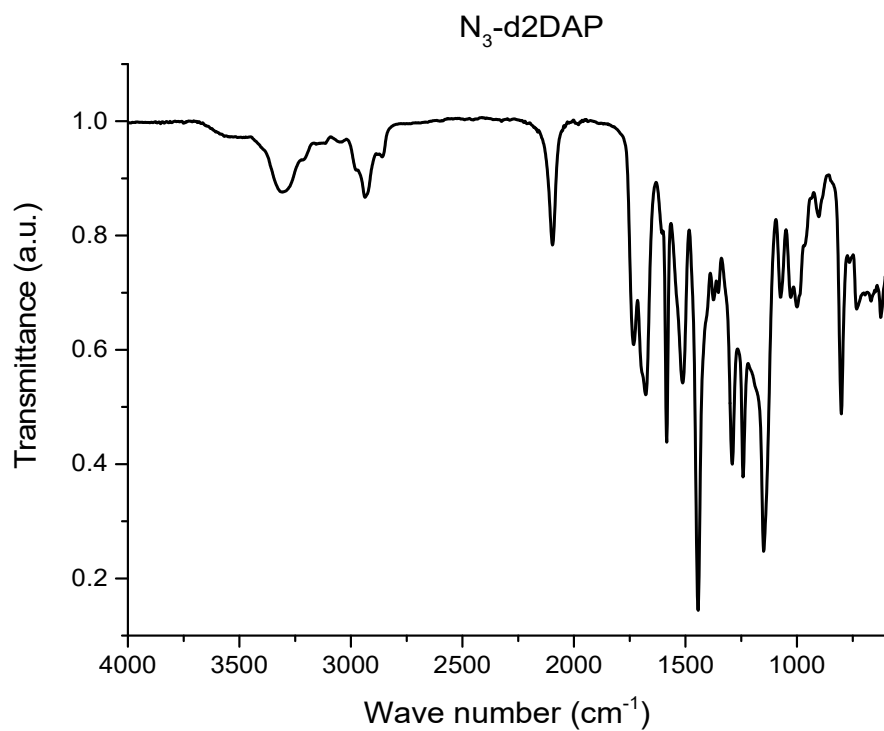
Figure S11. <sup>1</sup>H-NMR spectrum of **Bn-d4DAP** (CDCl<sub>3</sub>, 400MHz) δ (ppm).



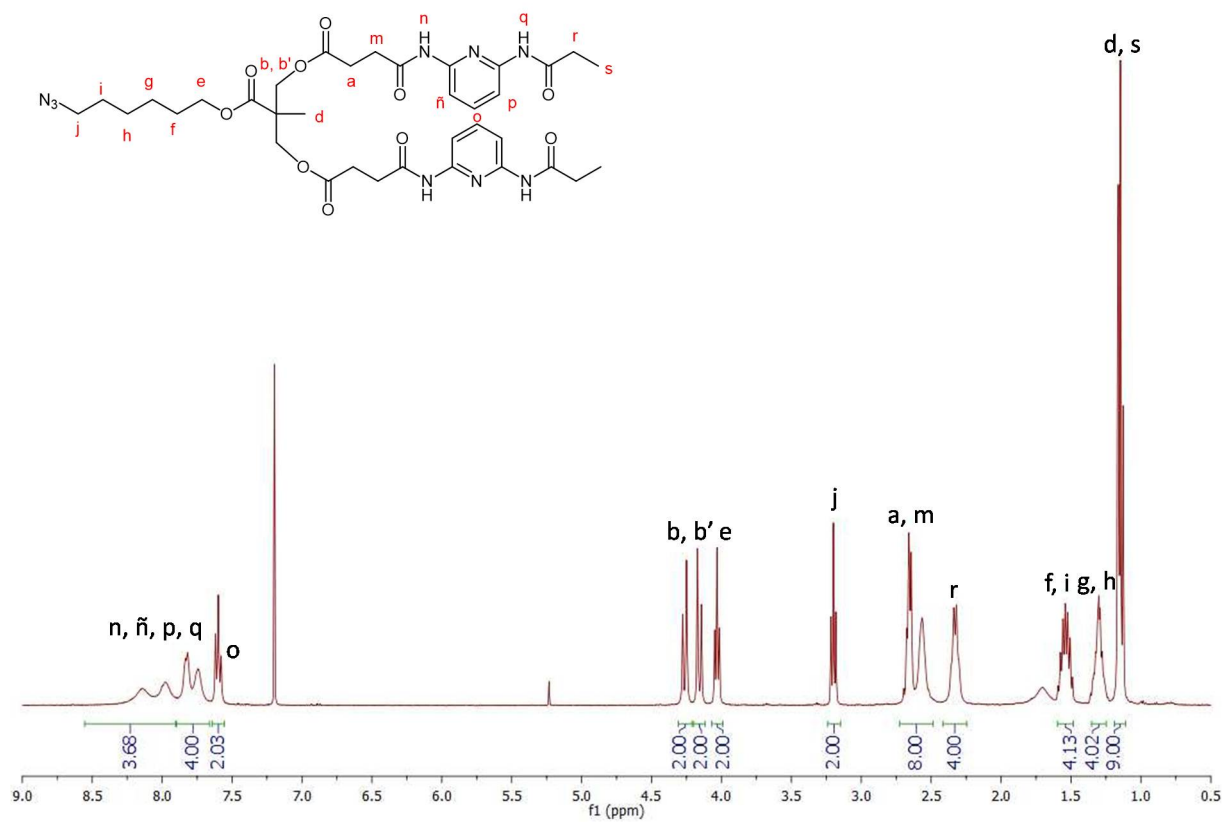
**Figure S12.** FTIR spectrum of HOOC-d4DAP.



**Figure S13.**  $^1\text{H}$ -NMR spectrum of HOOC-d4DAP ( $\text{CDCl}_3$ , 400MHz)  $\delta$  (ppm).

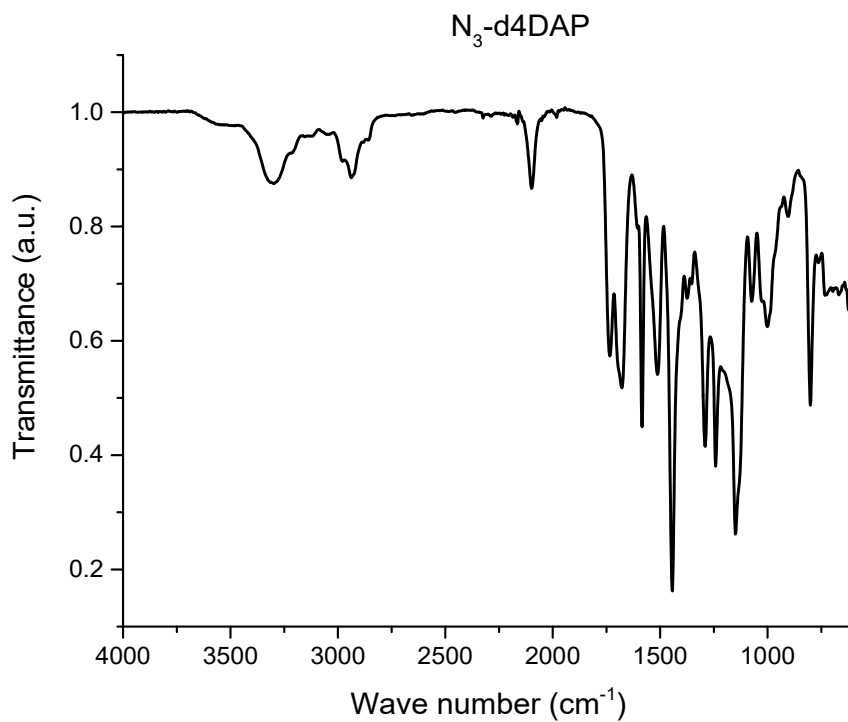


**Figure S14.** FTIR spectrum of N<sub>3</sub>-d2DAP.

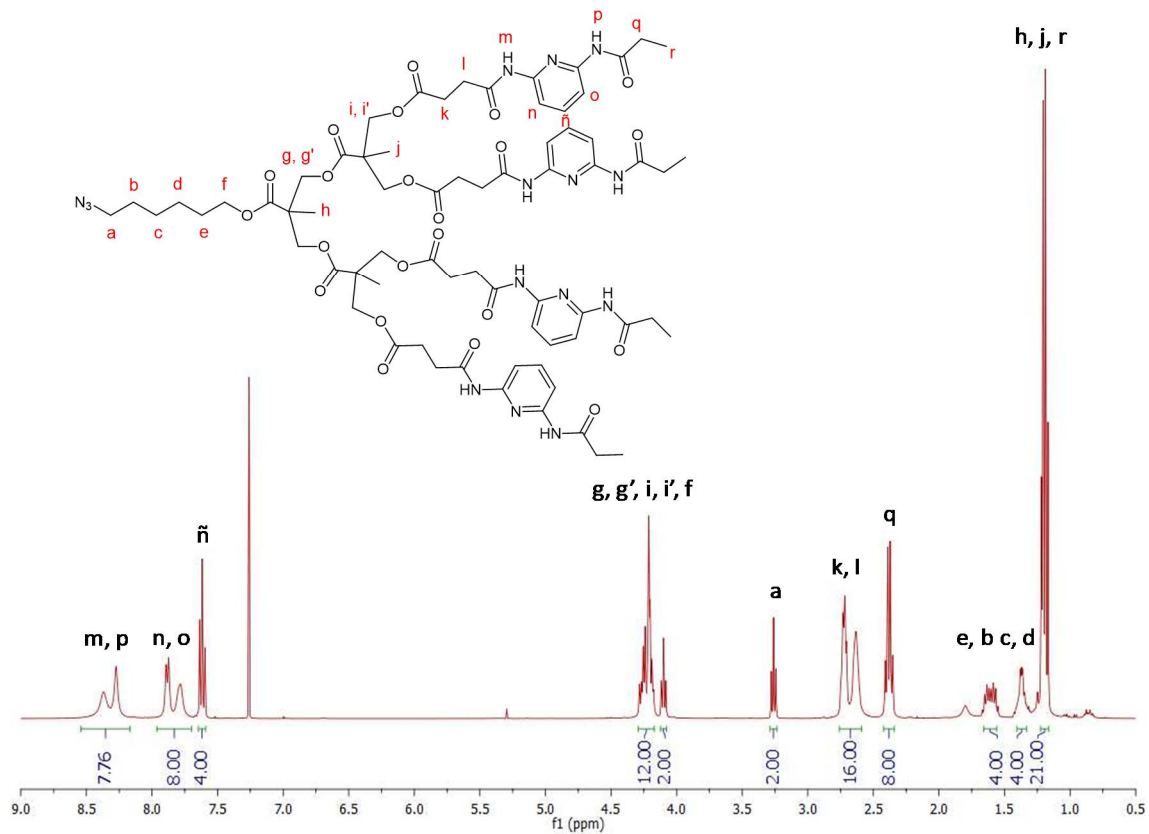


**Figure S15.** <sup>1</sup>H-NMR spectrum of N<sub>3</sub>-d2DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).

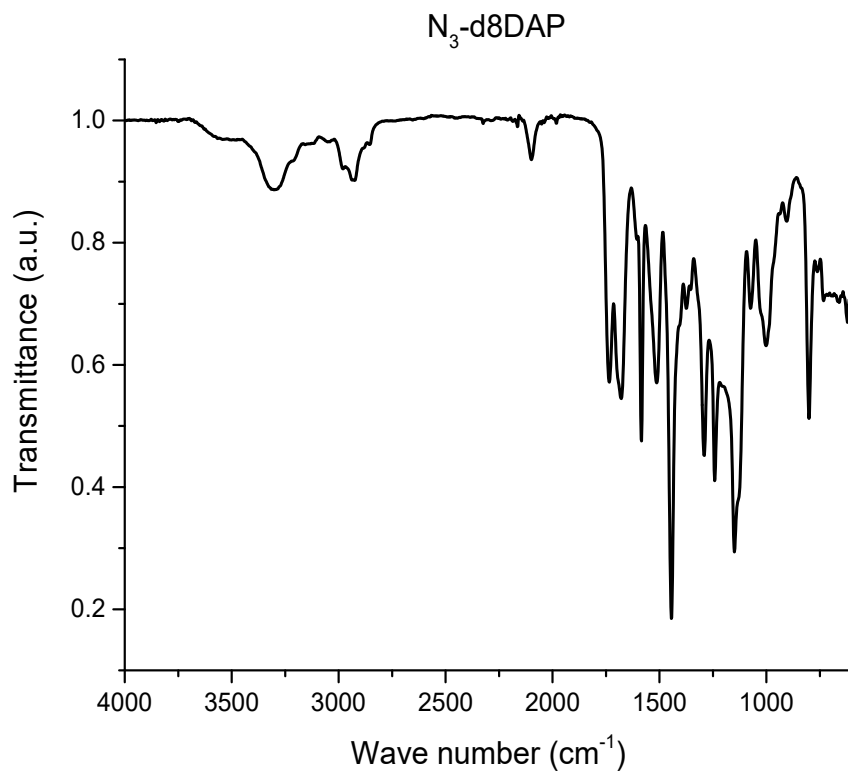




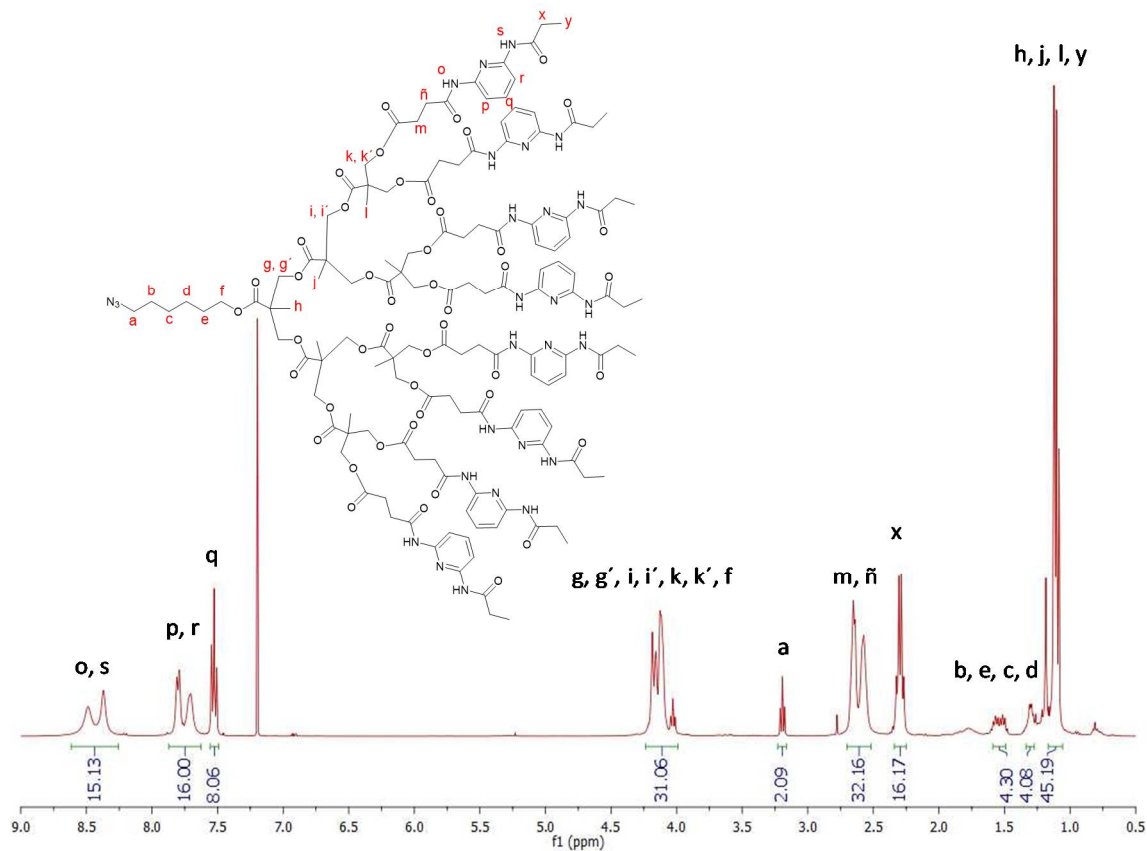
**Figure S16.** FTIR spectrum of N<sub>3</sub>-d4DAP.



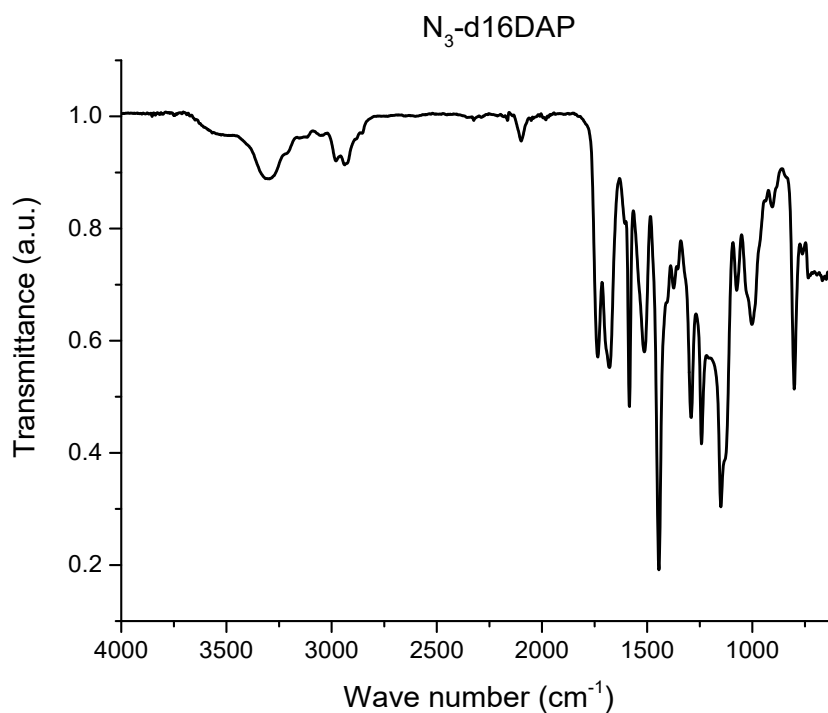
**Figure S17.** <sup>1</sup>H-NMR spectrum of N<sub>3</sub>-d4DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



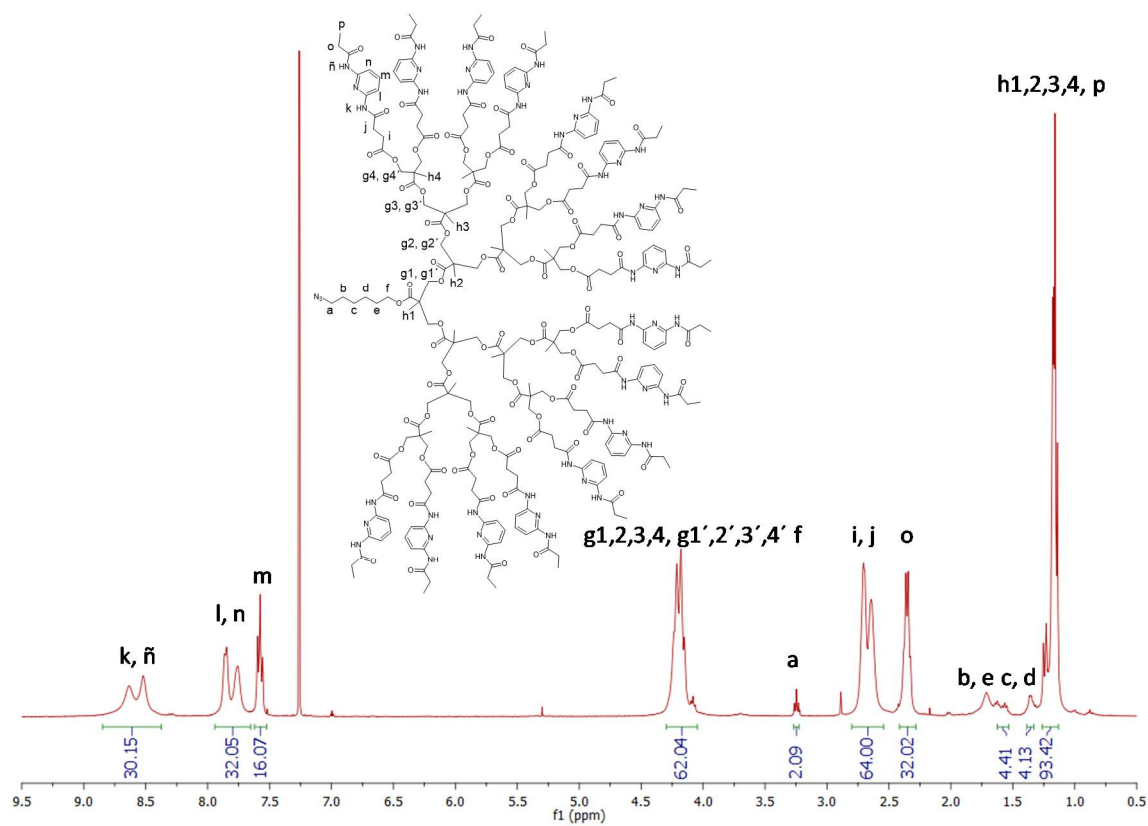
**Figure S18.** FTIR spectrum of N<sub>3</sub>-d8DAP.



**Figure S19.** <sup>1</sup>H-NMR spectrum of N<sub>3</sub>-d8DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



**Figure S20.** FTIR spectrum of N<sub>3</sub>-d16DAP.



**Figure S21.** <sup>1</sup>H-NMR spectrum of N<sub>3</sub>-d16DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).

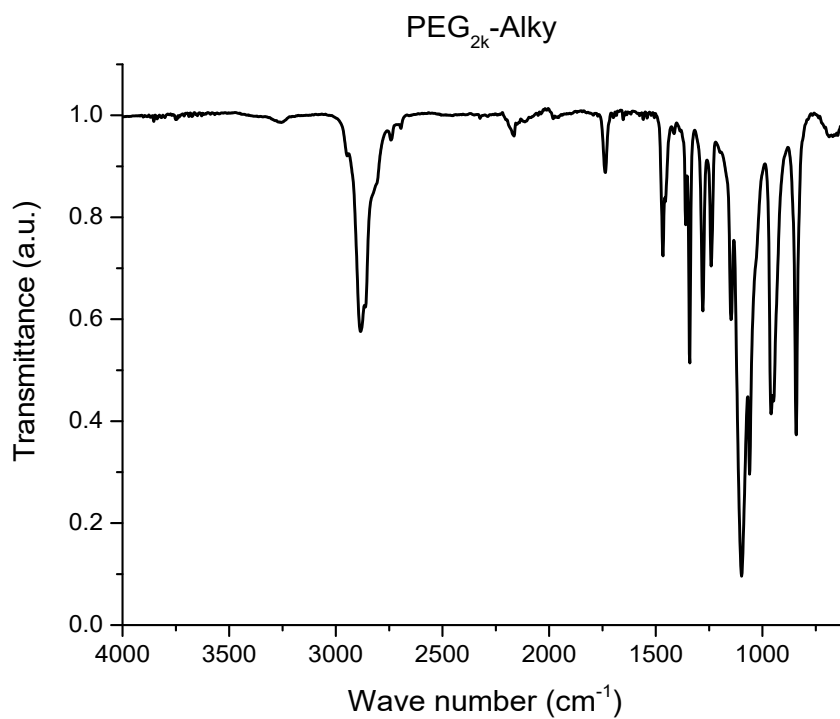


Figure S22. FTIR spectrum of PEG<sub>2k</sub>-Alky.

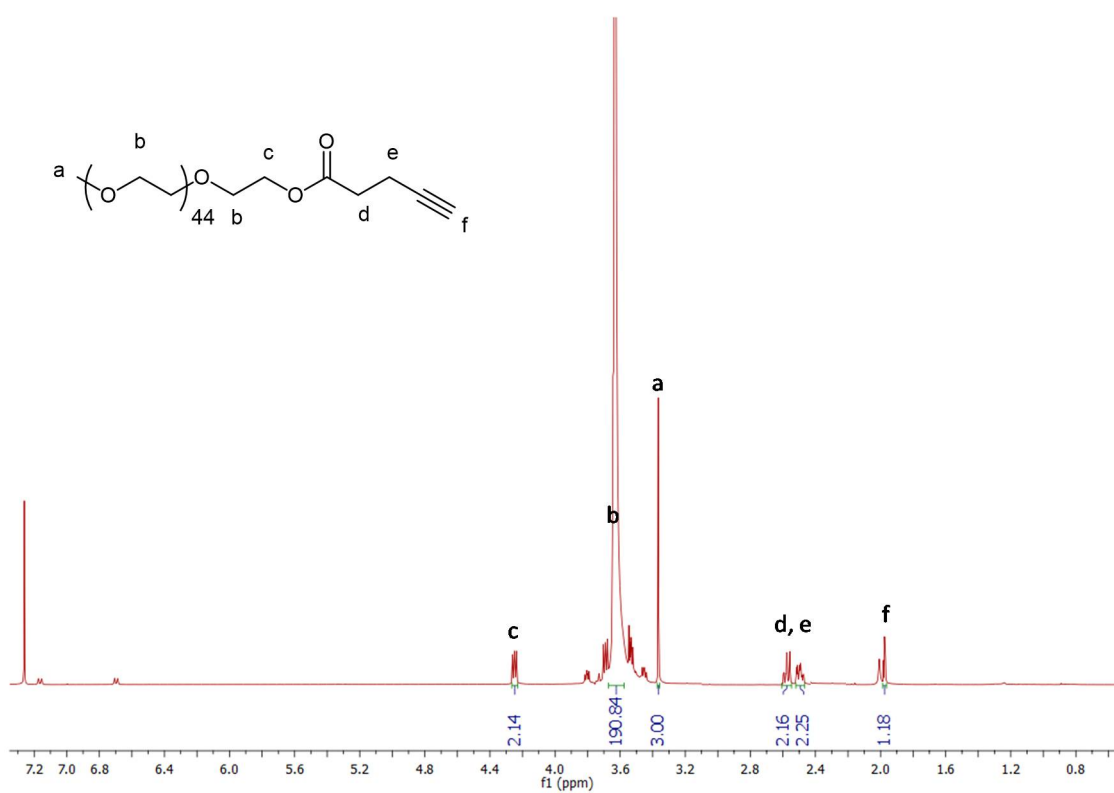
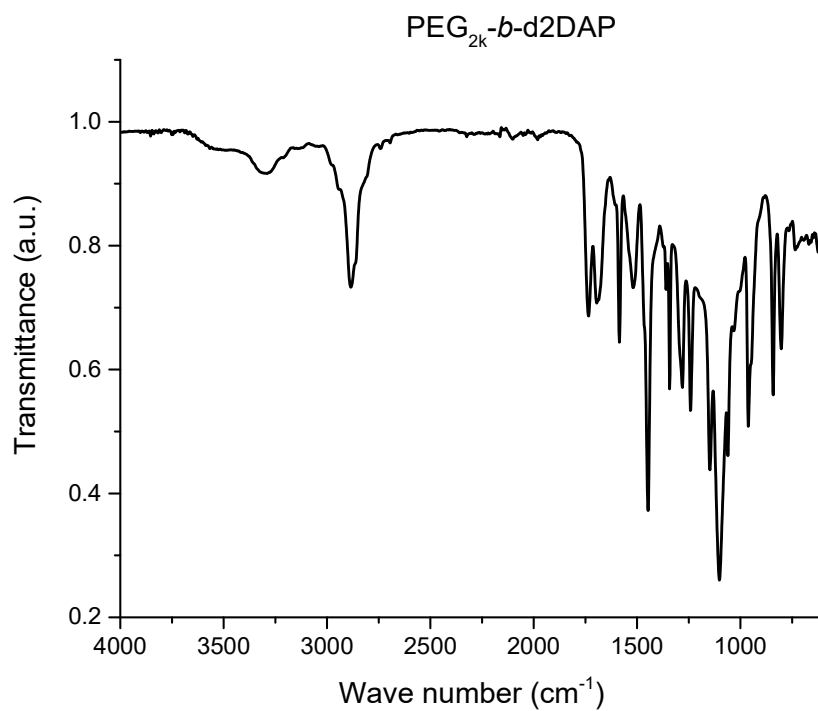
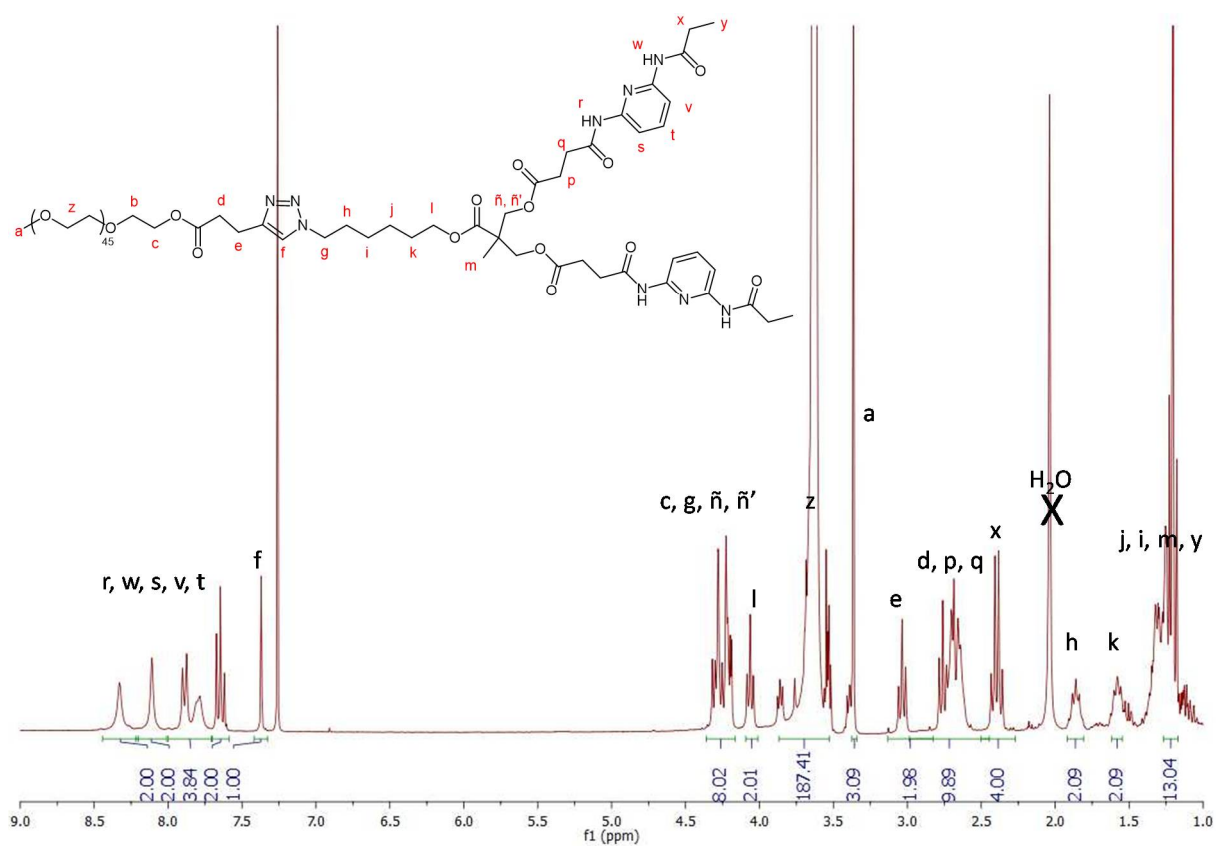


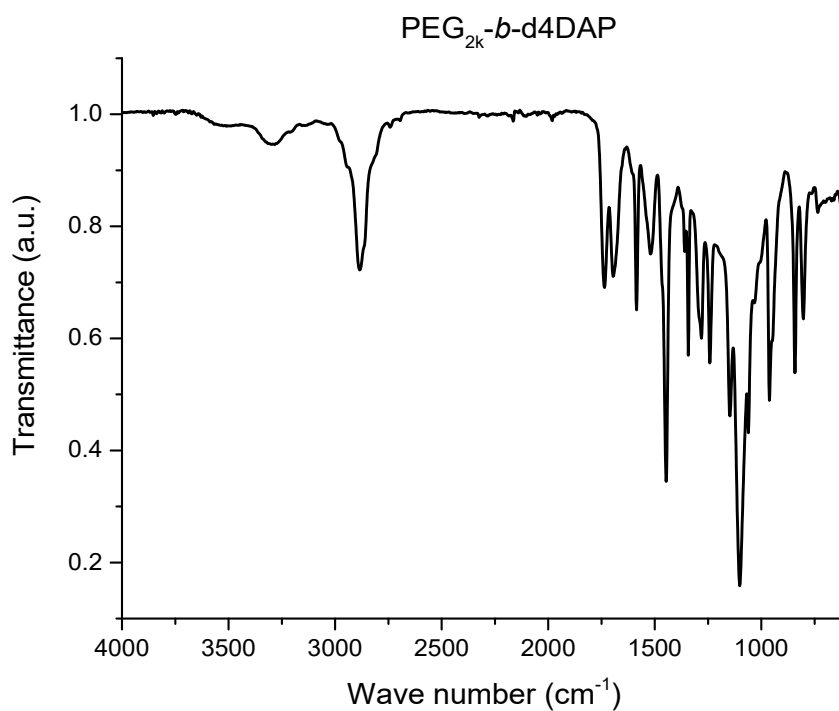
Figure S23. <sup>1</sup>H-NMR spectrum of PEG<sub>2k</sub>-Alky (CDCl<sub>3</sub>, 400MHz) δ (ppm).



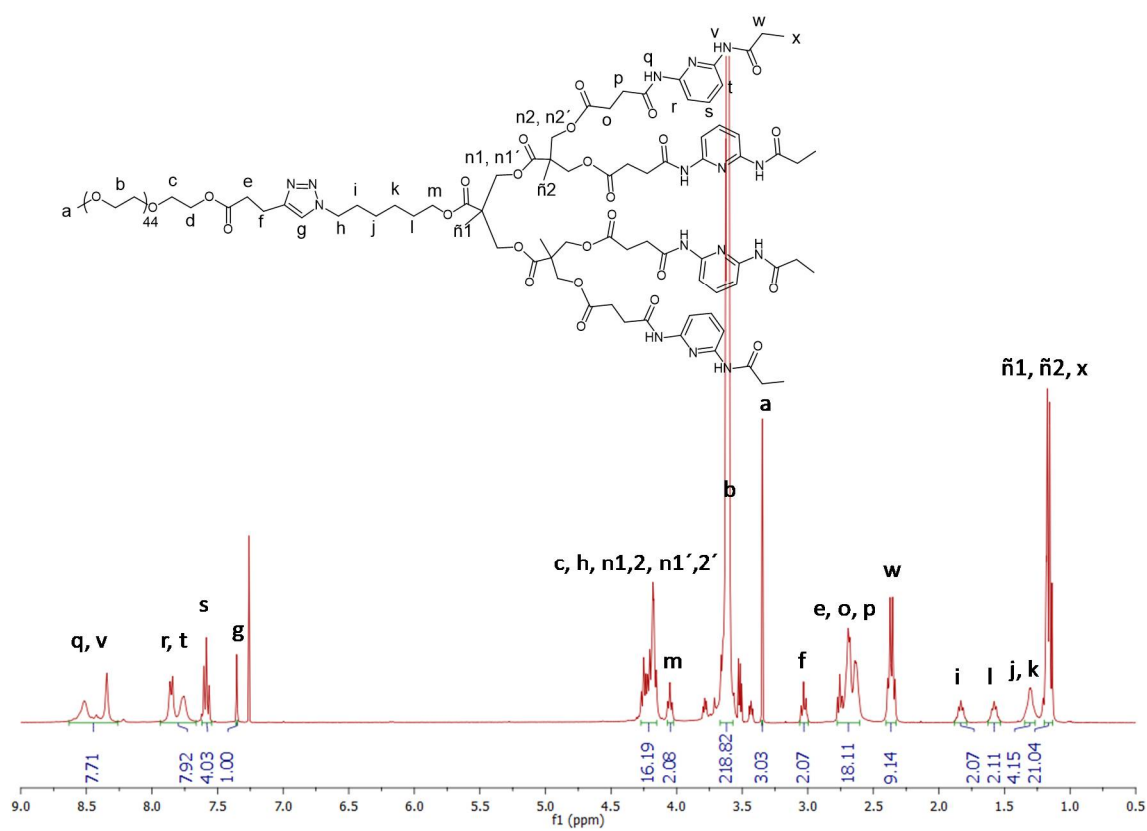
**Figure S24.** FTIR spectrum of PEG<sub>2k</sub>-*b*-d2DAP.



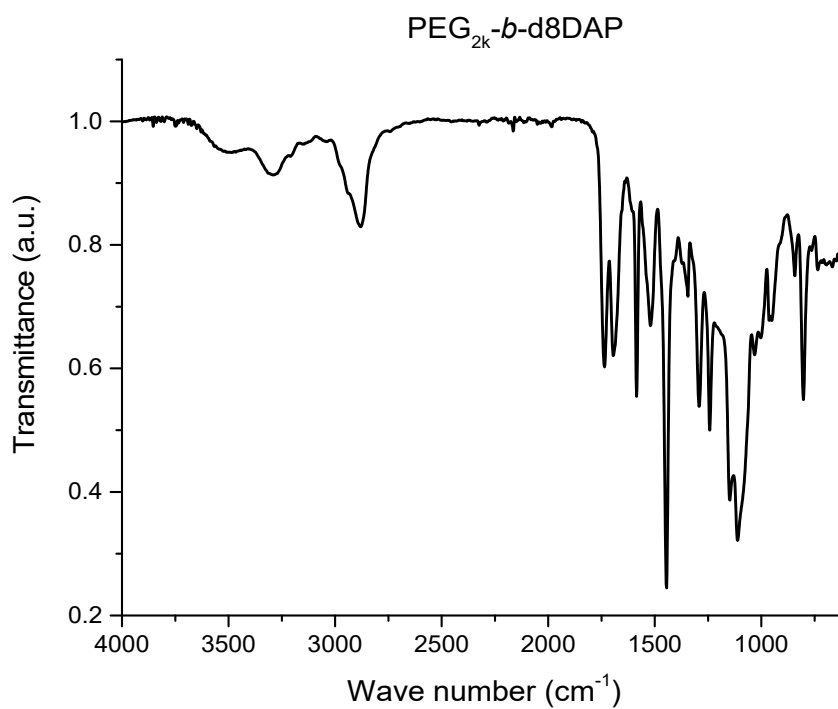
**Figure S25.** <sup>1</sup>H-NMR spectrum of PEG<sub>2k</sub>-*b*-d2DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



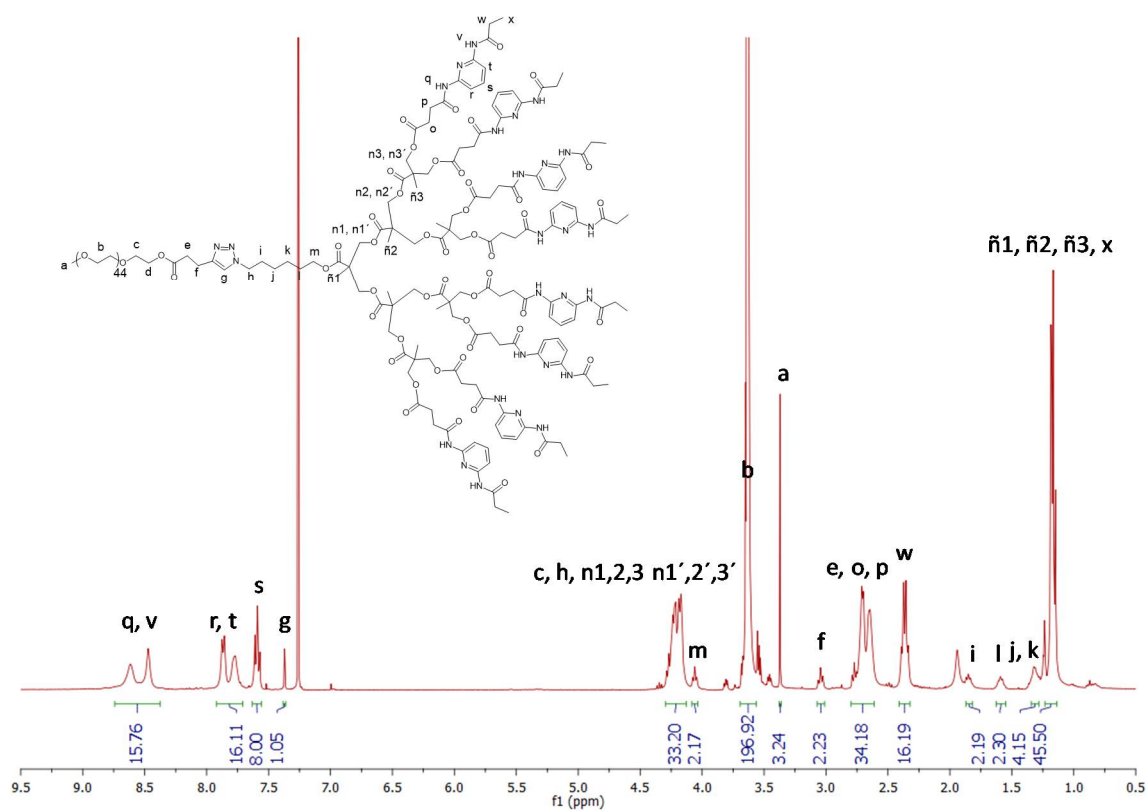
**Figure S26.** FTIR spectrum of PEG<sub>2k</sub>-*b*-d4DAP.



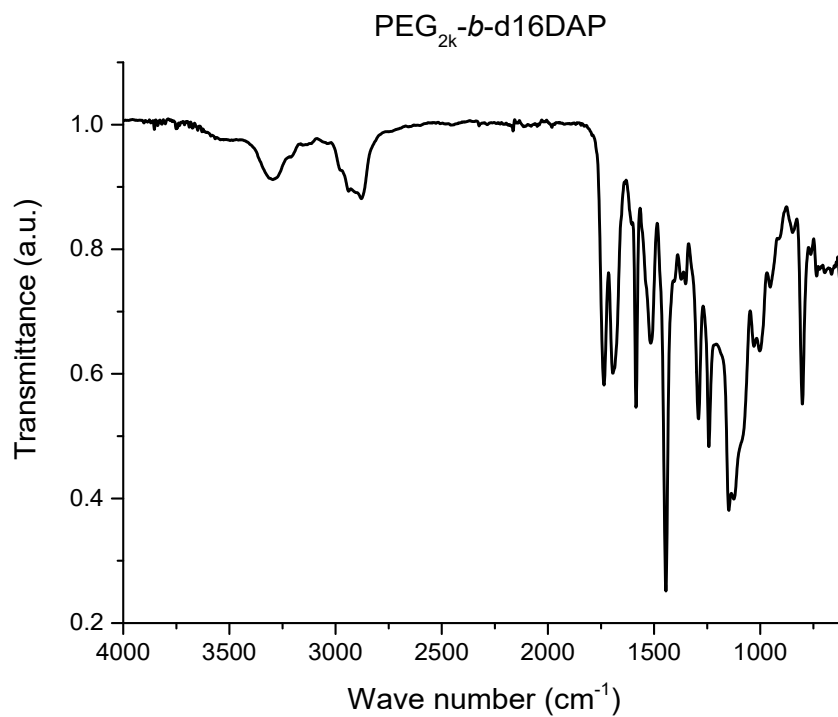
**Figure S27.** <sup>1</sup>H-NMR spectrum of PEG<sub>2k</sub>-*b*-d4DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



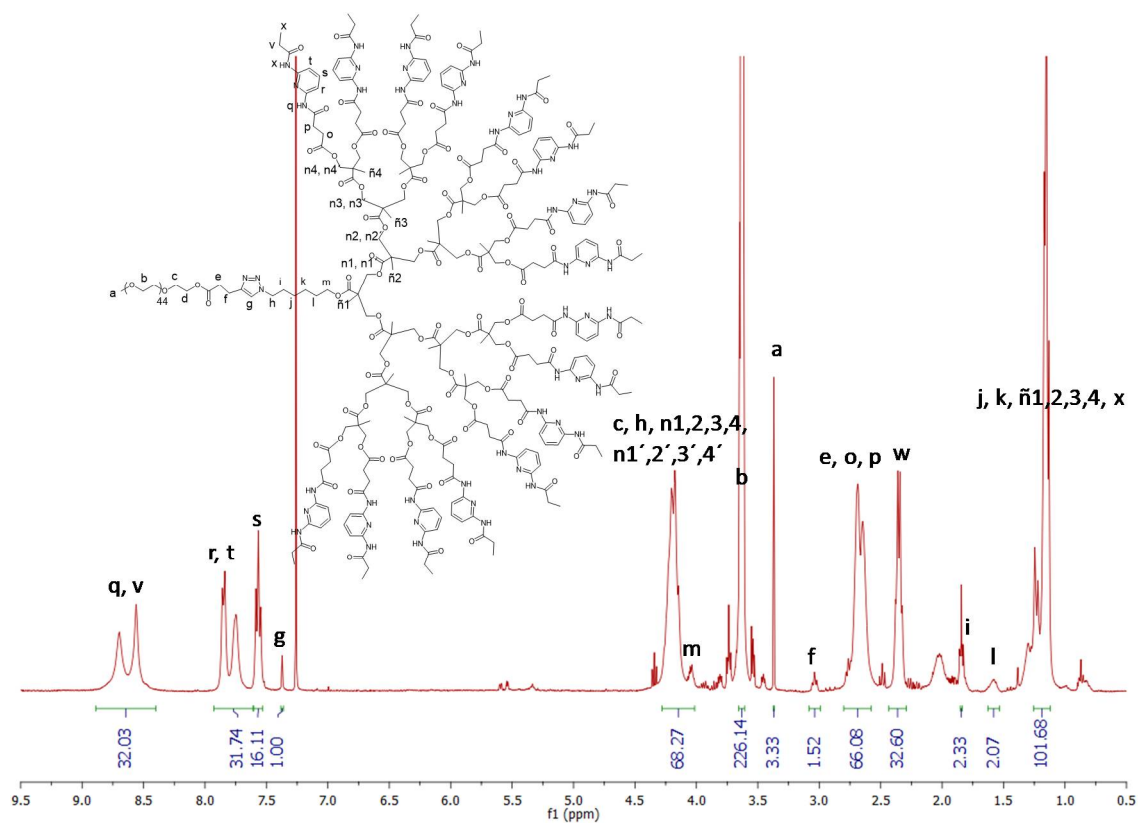
**Figure S28.** FTIR spectrum of PEG<sub>2k</sub>-*b*-d8DAP.



**Figure S29.** <sup>1</sup>H-NMR spectrum of PEG<sub>2k</sub>-*b*-d8DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



**Figure S30.** FTIR spectrum of PEG<sub>2k</sub>-*b*-d16DAP.



**Figure S31.** <sup>1</sup>H-NMR spectrum of PEG<sub>2k</sub>-*b*-d16DAP (CDCl<sub>3</sub>, 400MHz) δ (ppm).



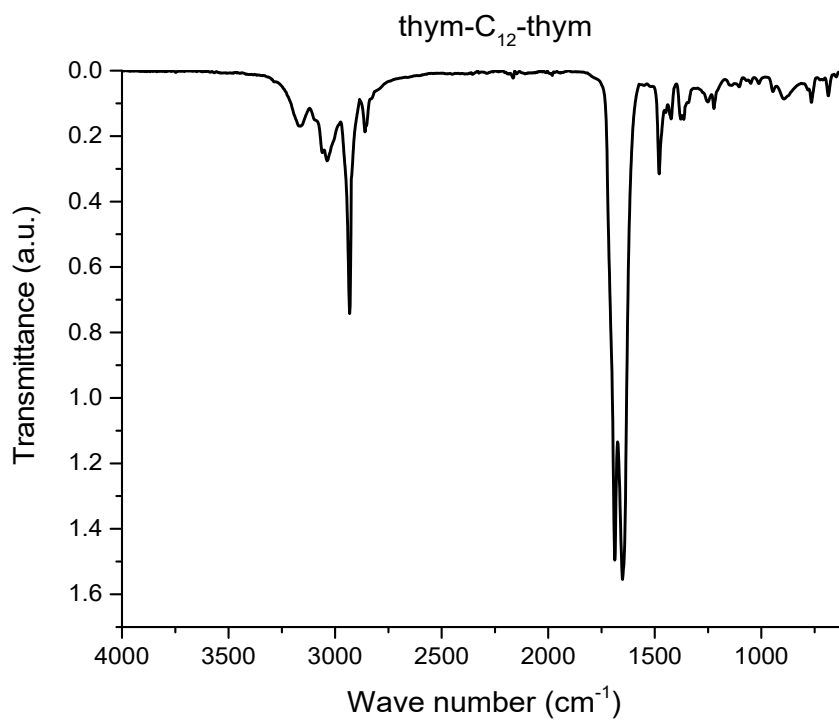


Figure S32. FTIR spectrum of **thym-C<sub>12</sub>-thym**.

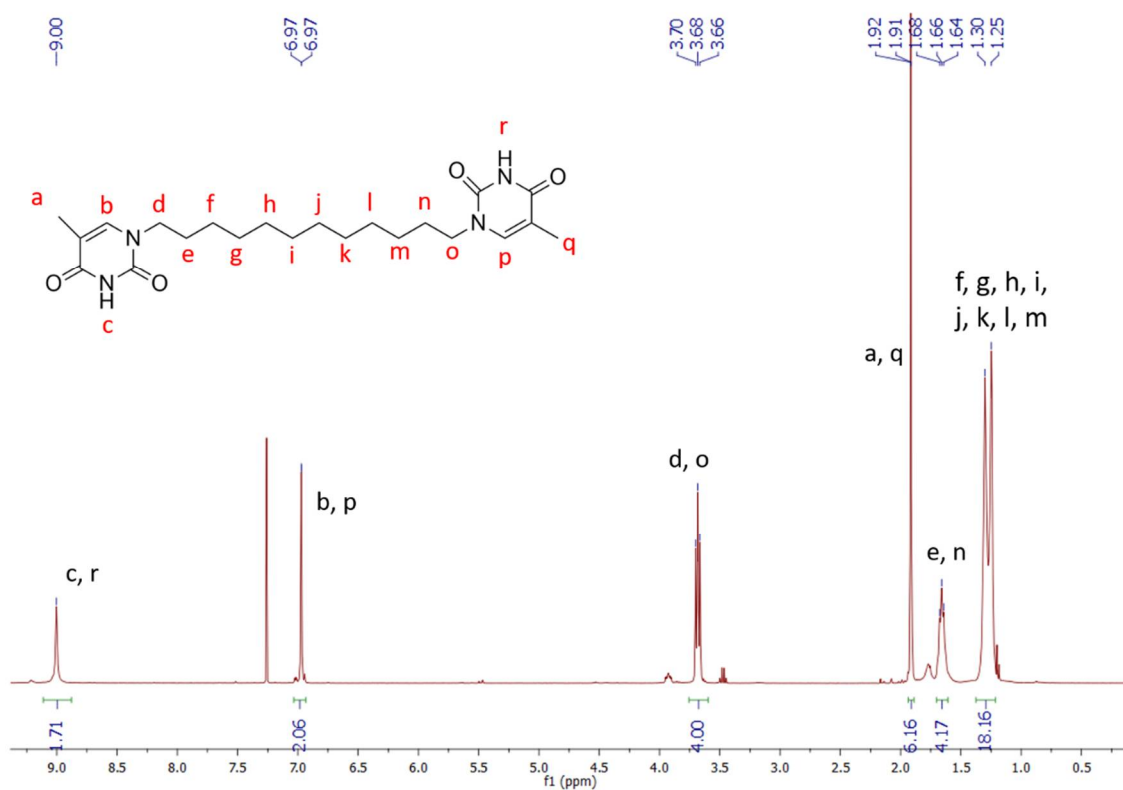


Figure S33. <sup>1</sup>H-NMR spectrum of **thym-C<sub>12</sub>-thym** (CDCl<sub>3</sub>, 400MHz) δ (ppm).

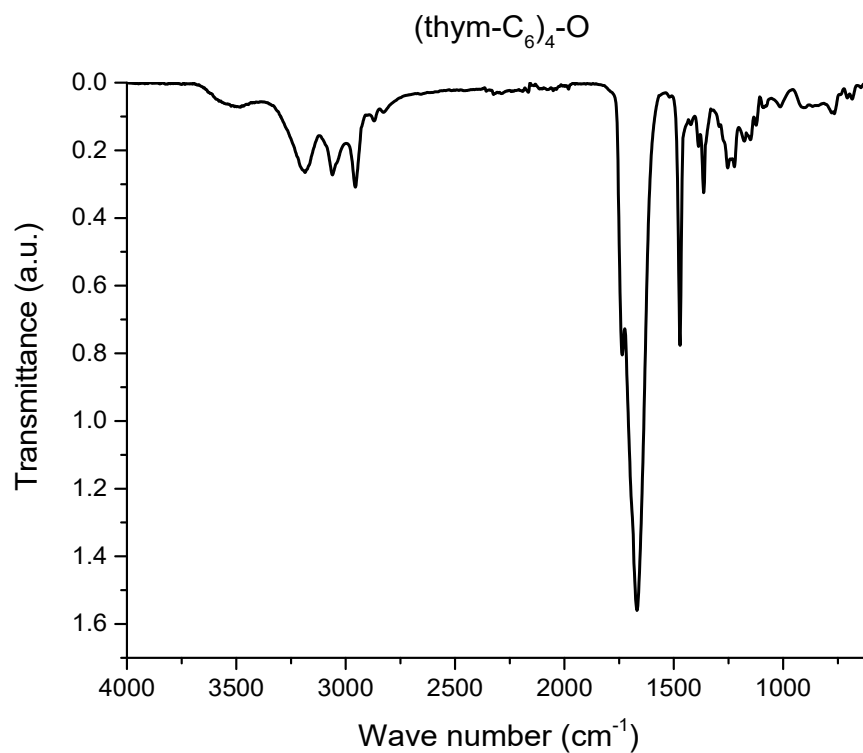


Figure S34. FTIR spectrum of (thym-C<sub>6</sub>)<sub>4</sub>-O.

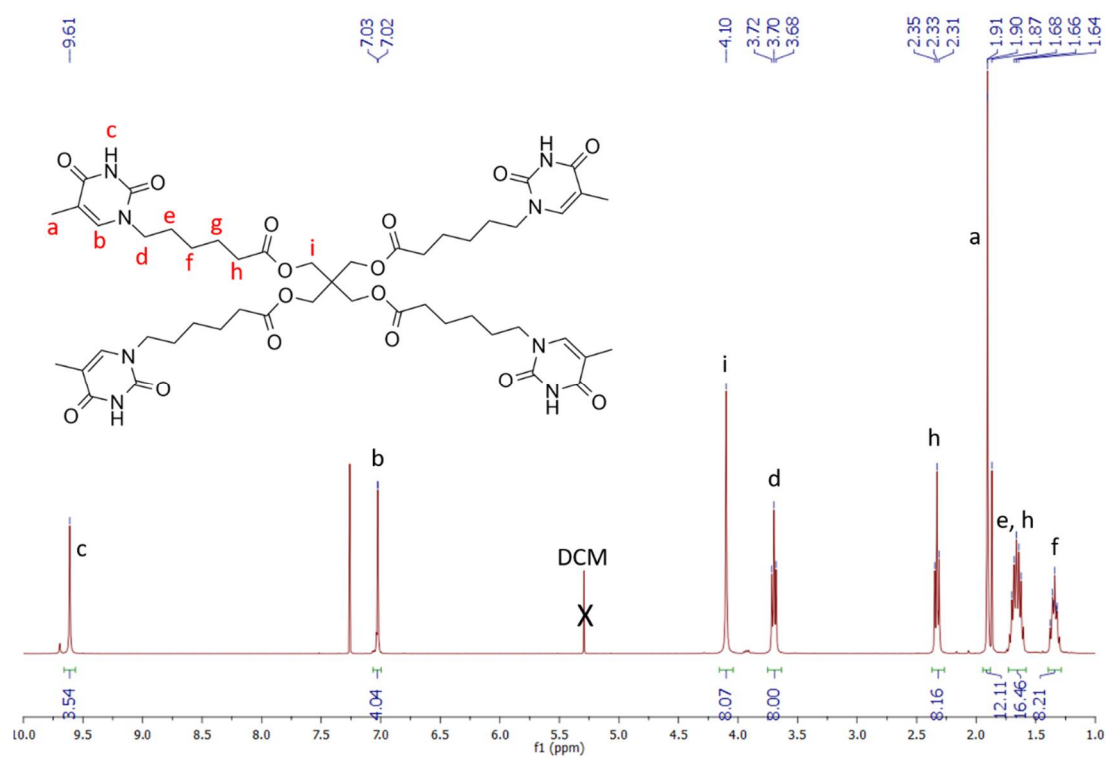


Figure S35. <sup>1</sup>H-NMR spectrum of (thym-C<sub>6</sub>)<sub>4</sub>-O (CDCl<sub>3</sub>, 400MHz) δ (ppm).

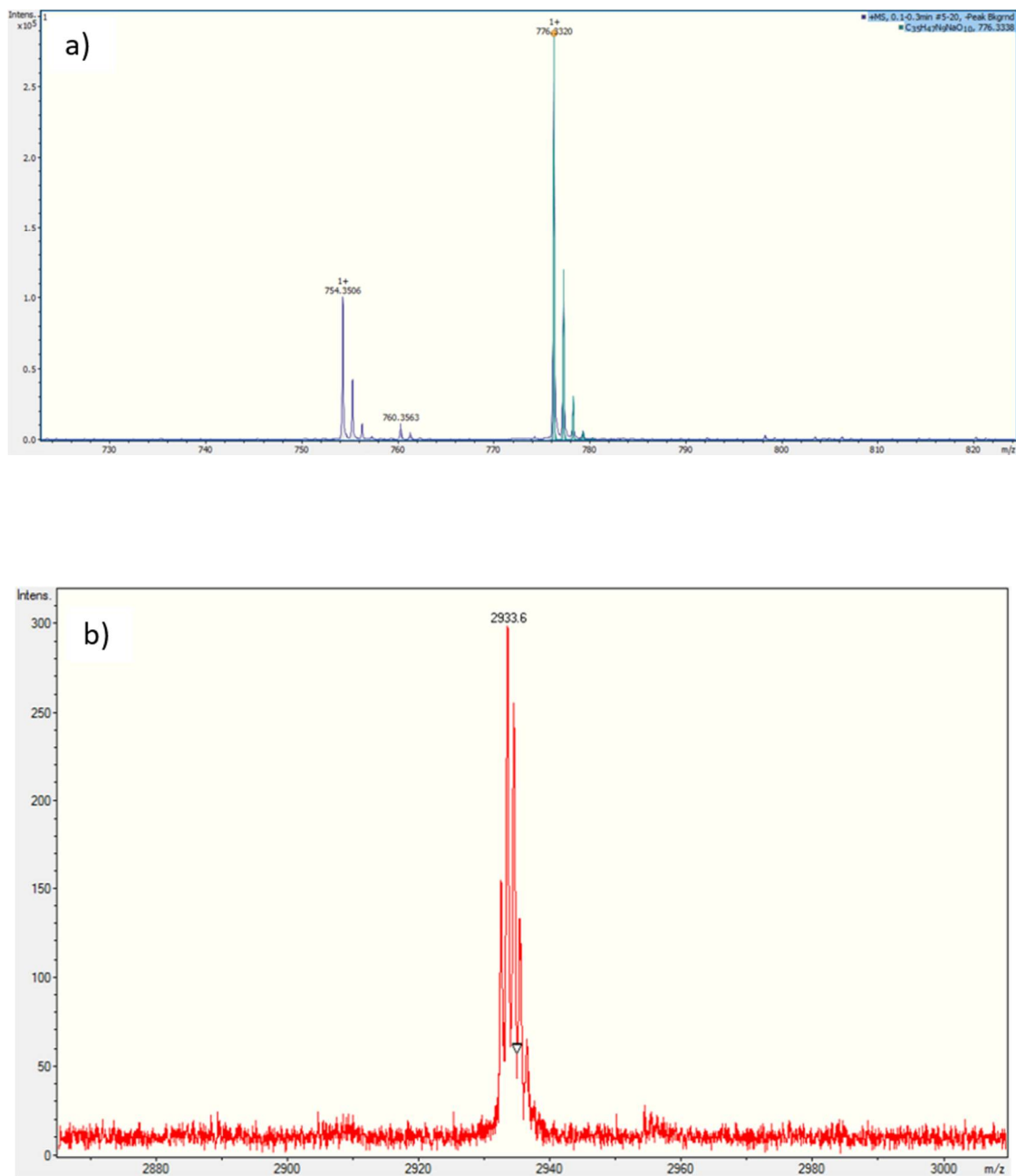


Figure S36. a) HR-ESI spectrum of  $N_3$ -d2DAP. b) MALDI-TOF spectra of  $N_3$ -d4DAP.

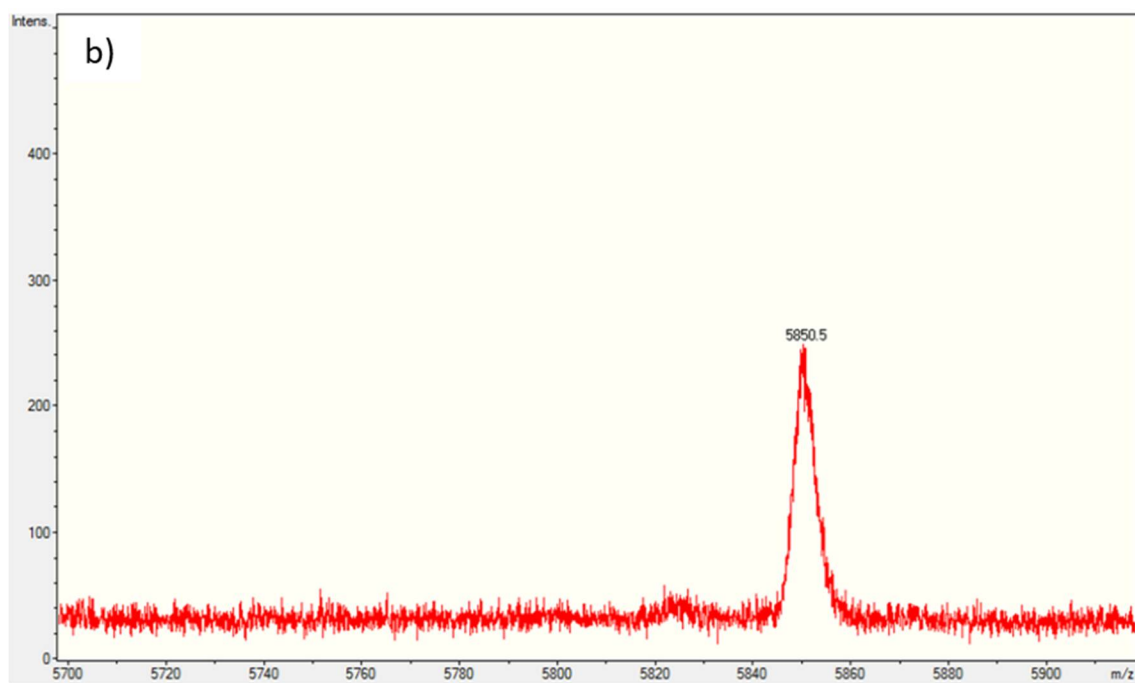
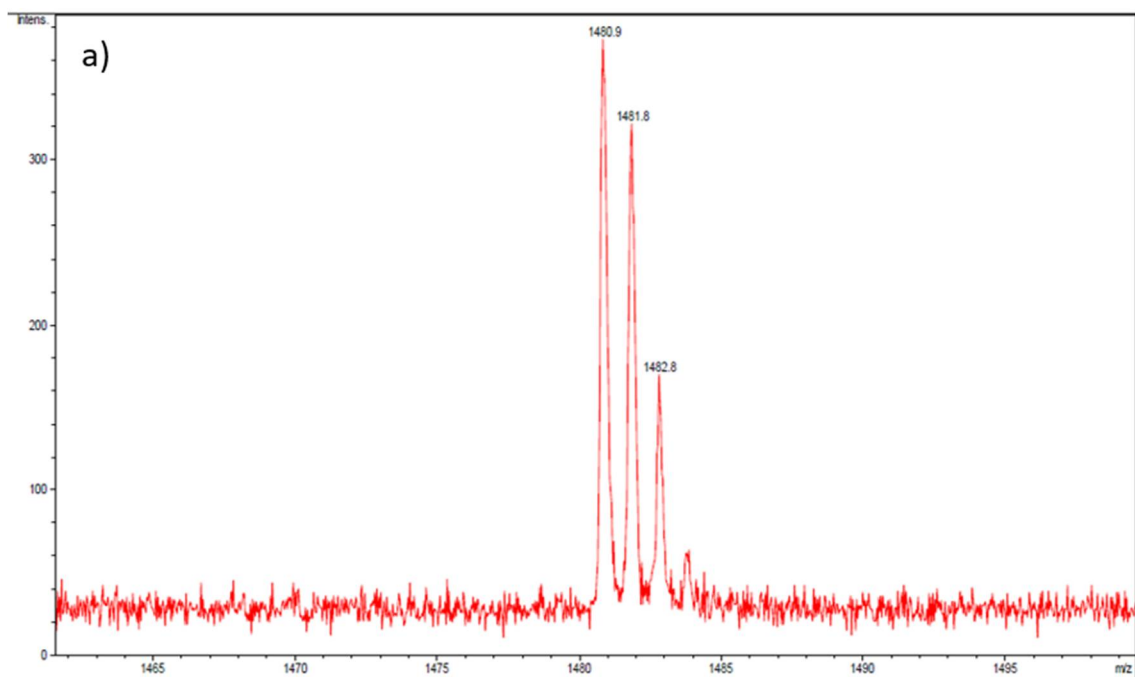


Figure S37. MALDI-TOF spectra of a) N<sub>3</sub>-d<sub>8</sub>DAP and b) N<sub>3</sub>-d<sub>16</sub>DAP.

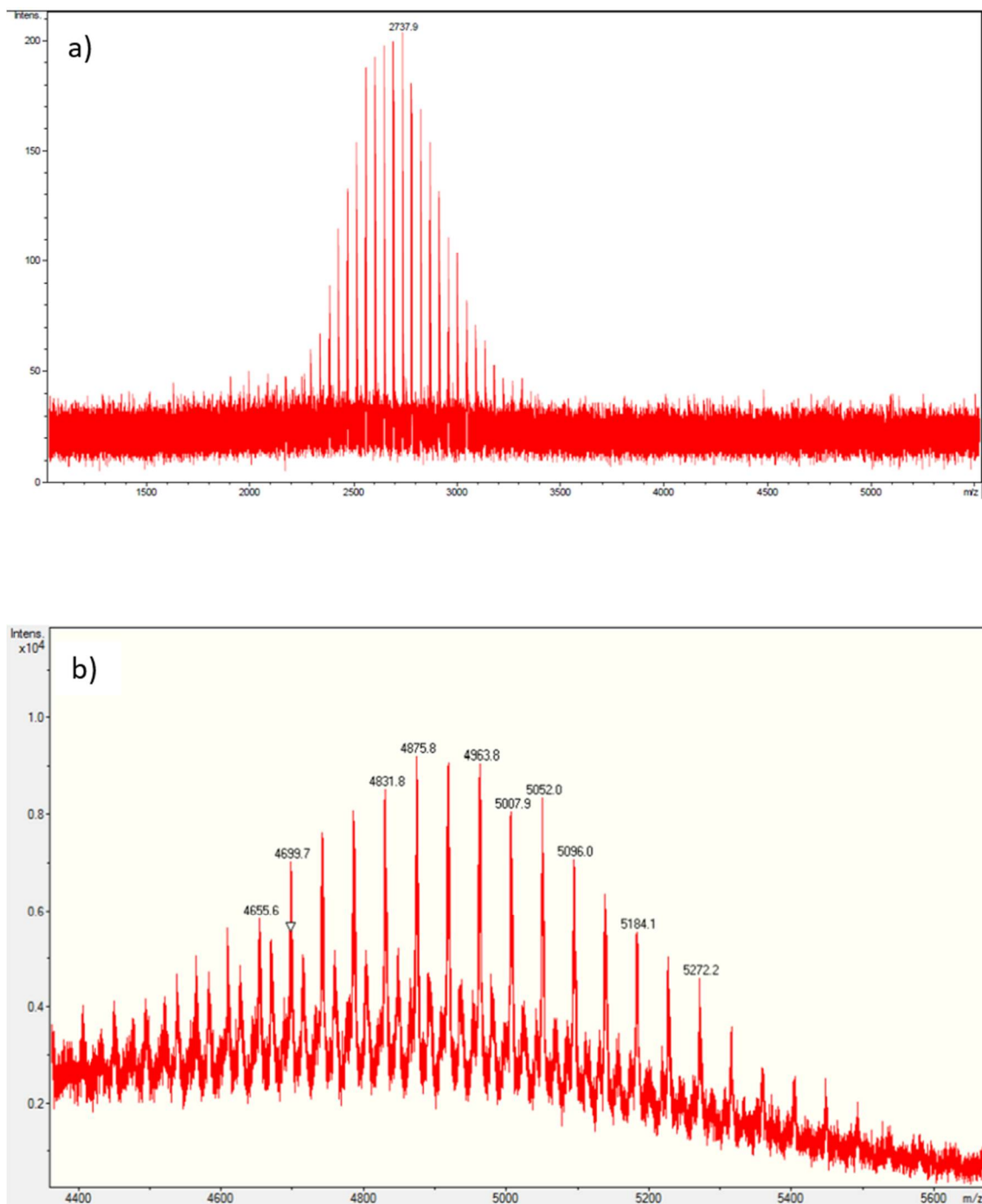


Figure S38. MALDI-TOF spectra of a) PEG<sub>2k</sub>-*b*-d<sub>2</sub>DAP and b) PEG<sub>2k</sub>-*b*-d<sub>4</sub>DAP.

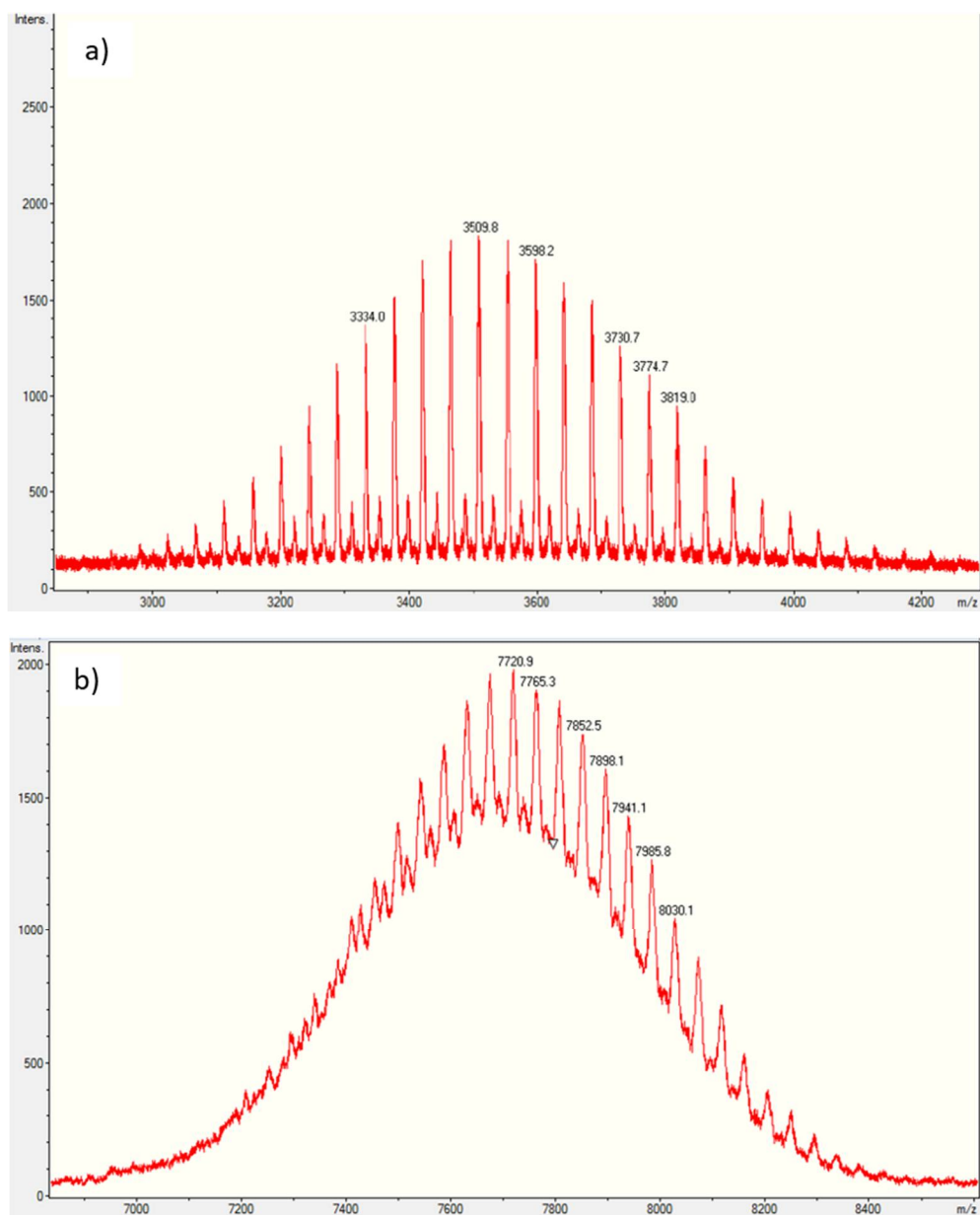


Figure S39. MALDI-TOF spectra of a) PEG<sub>2k</sub>-b-d8DAP and b) PEG<sub>2k</sub>-b-d16DAP.

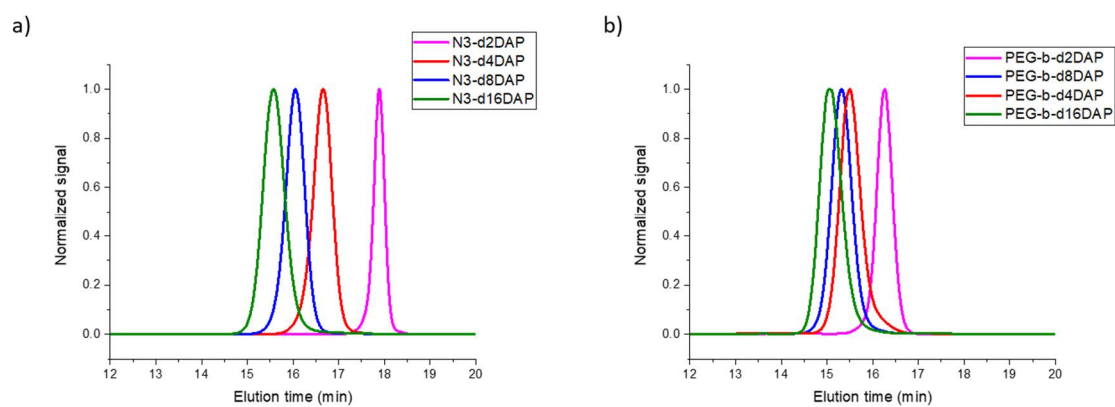
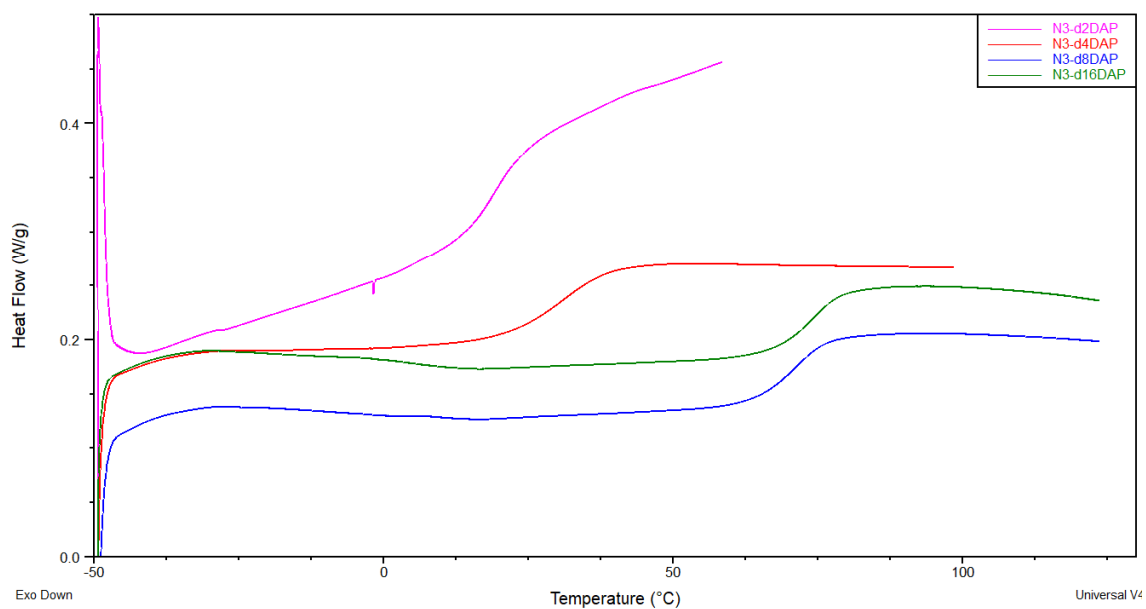
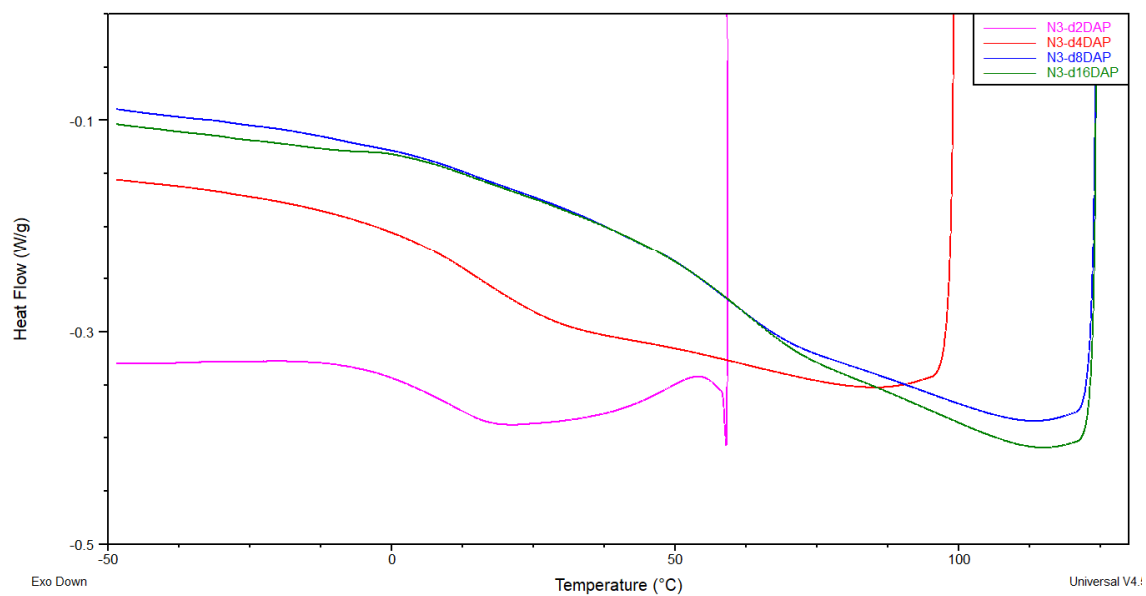
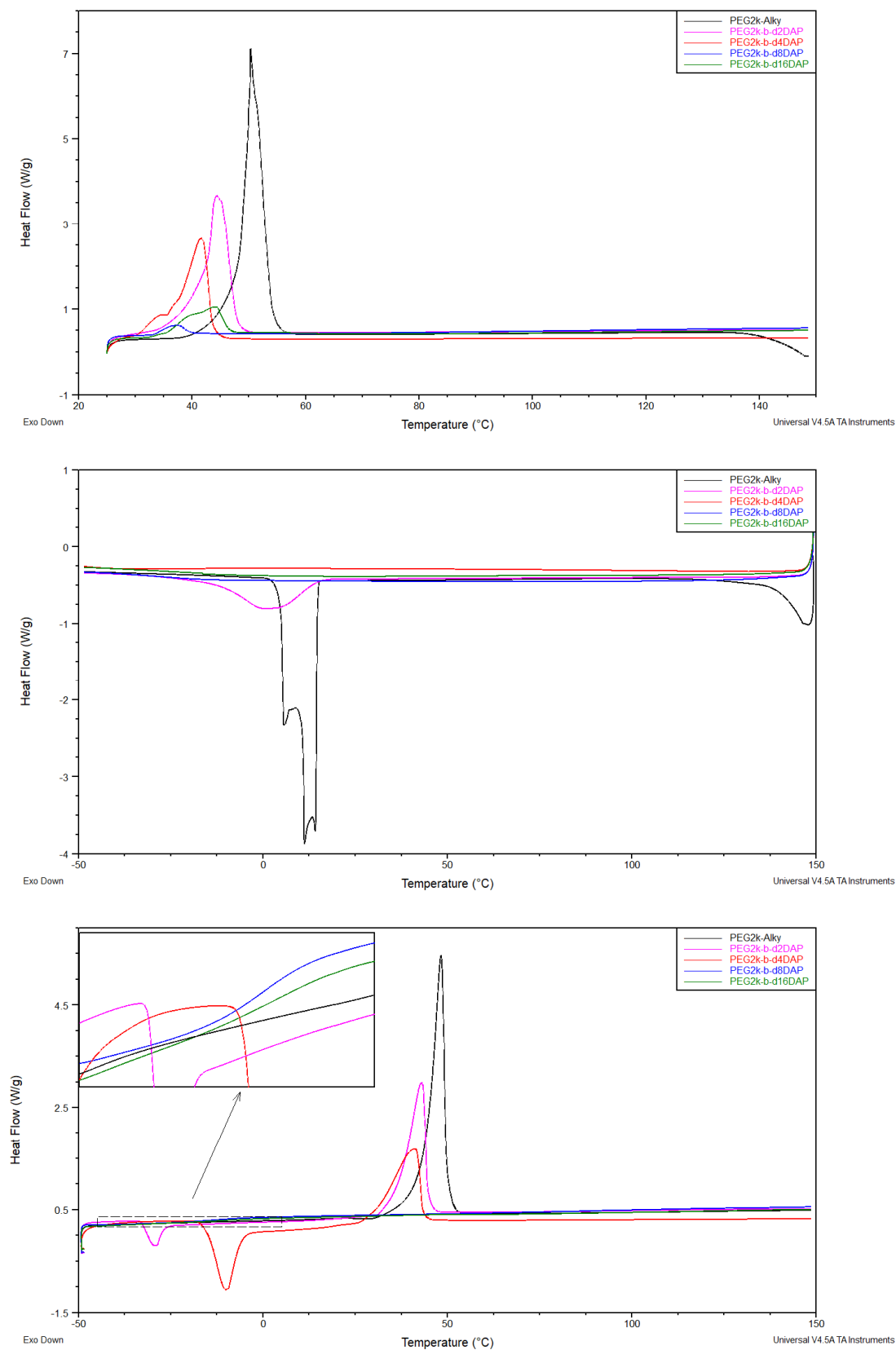


Figure S40. GPC chromatograms for a) dendrons N<sub>3</sub>-d<sub>x</sub>DAP and b) LDBC PEG<sub>2k</sub>-b-d<sub>x</sub>DAP.

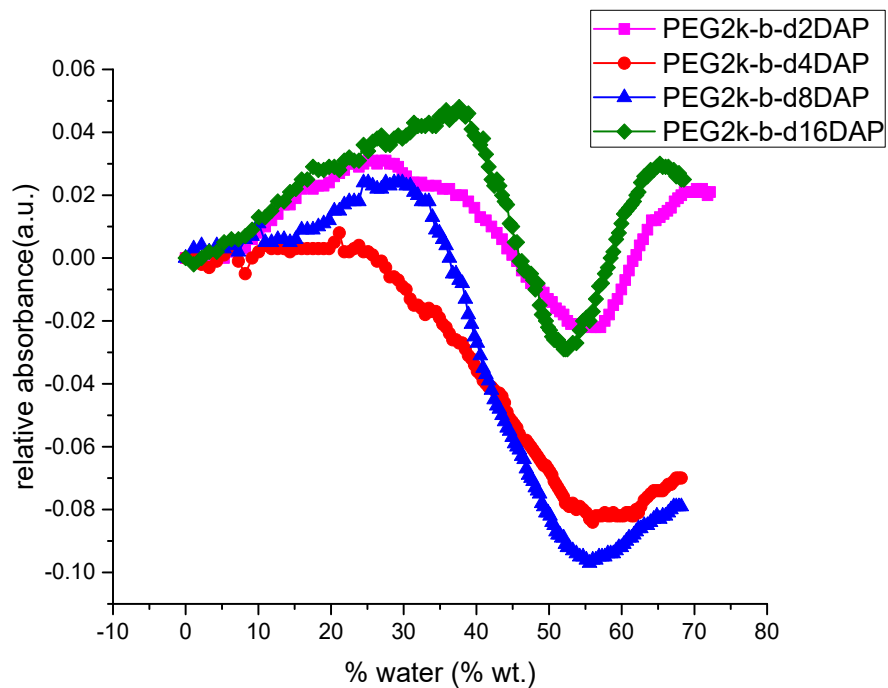


**Figure S41.** DSC curves registered on first cooling (above) and second heating (below) at  $10\text{ }^{\circ}\text{C min}^{-1}$  scanning rate of  $\text{N}_3\text{-dxDAP}$ .

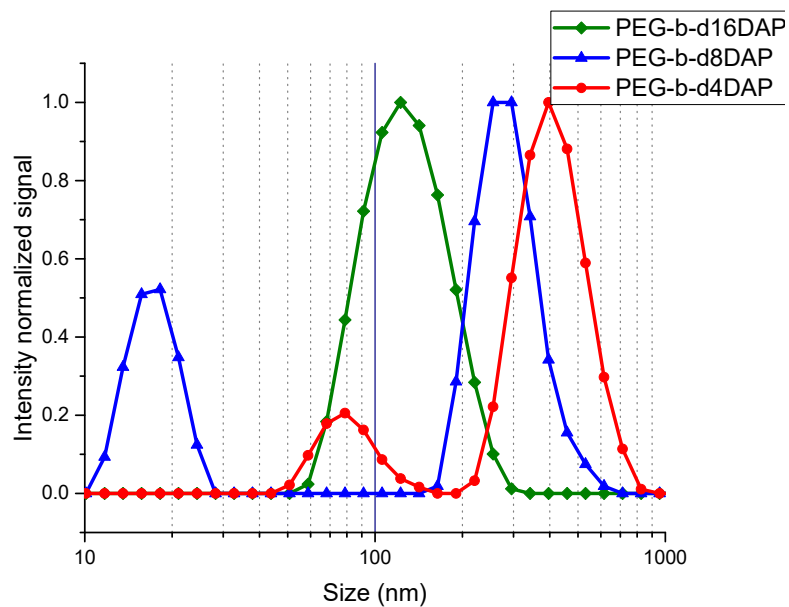


**Figure S42.** DSC curves registered on first heating (above), first cooling (middle) and second heating (below) at  $10\text{ °C min}^{-1}$  scanning rate of **PEG<sub>2k</sub>-b-dxDAP**.

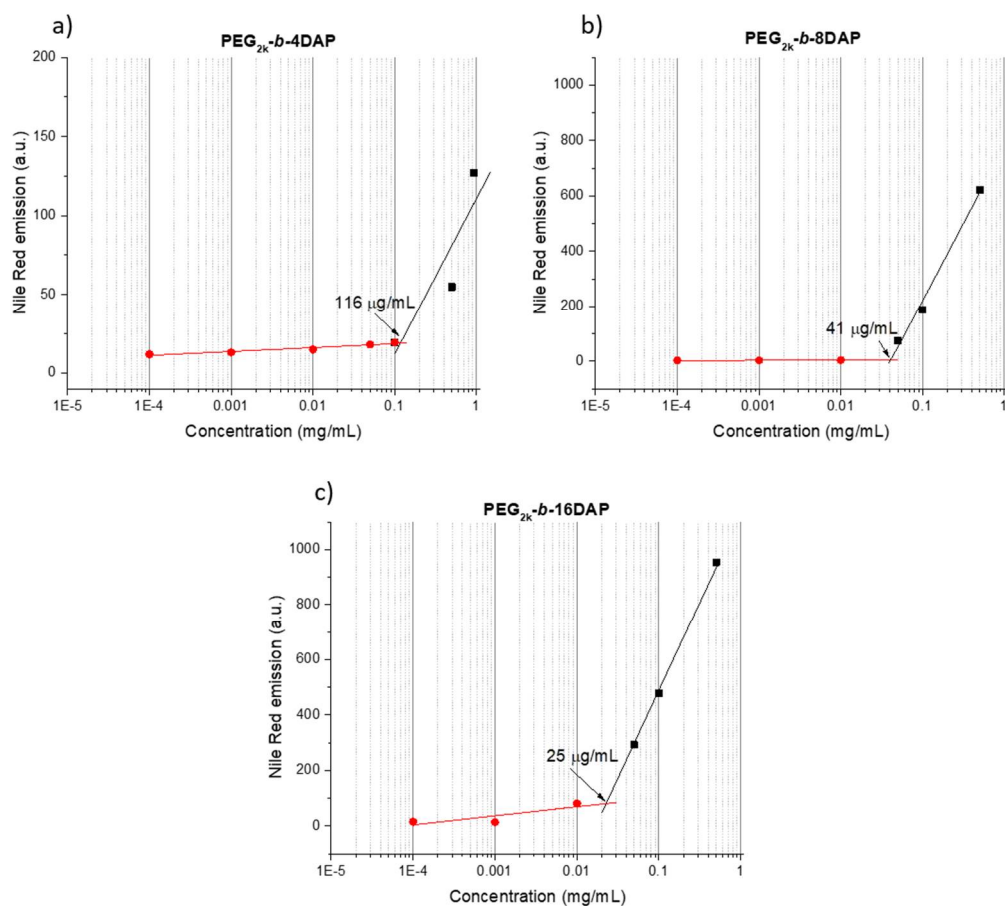




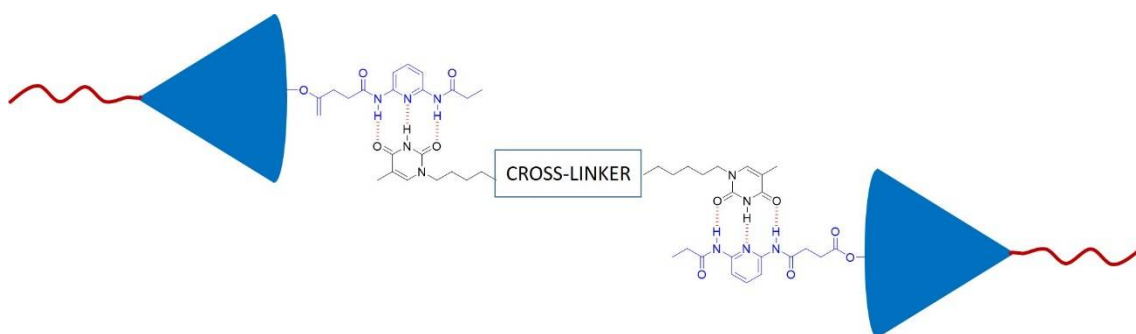
**Figure S43.** Turbidity curves of LDBC self-assemblies PEG<sub>2k</sub>-*b*-*dx*DAP.



**Figure S44.** Intensity size distributions by DLS of LDBC self-assemblies prepared by nanoprecipitation.



**Figure S45.** Fluorescence emission of Nile Red at 620 nm ( $\lambda_{\text{exc}} = 550$  nm) versus a) PEG<sub>2k</sub>-b-d4DAP, b) PEG<sub>2k</sub>-b-d8DAP and c) PEG<sub>2k</sub>-b-d16DAP concentration. CAC was determined from the intersection of the two extrapolated lines.



**Scheme S1.** Supramolecular recognition through a triple H-bond between DAP units (blue) linked at the periphery of dendron block of PEG<sub>2k</sub>-b-dxDAP and thymine moieties (black) of the crosslinkers.

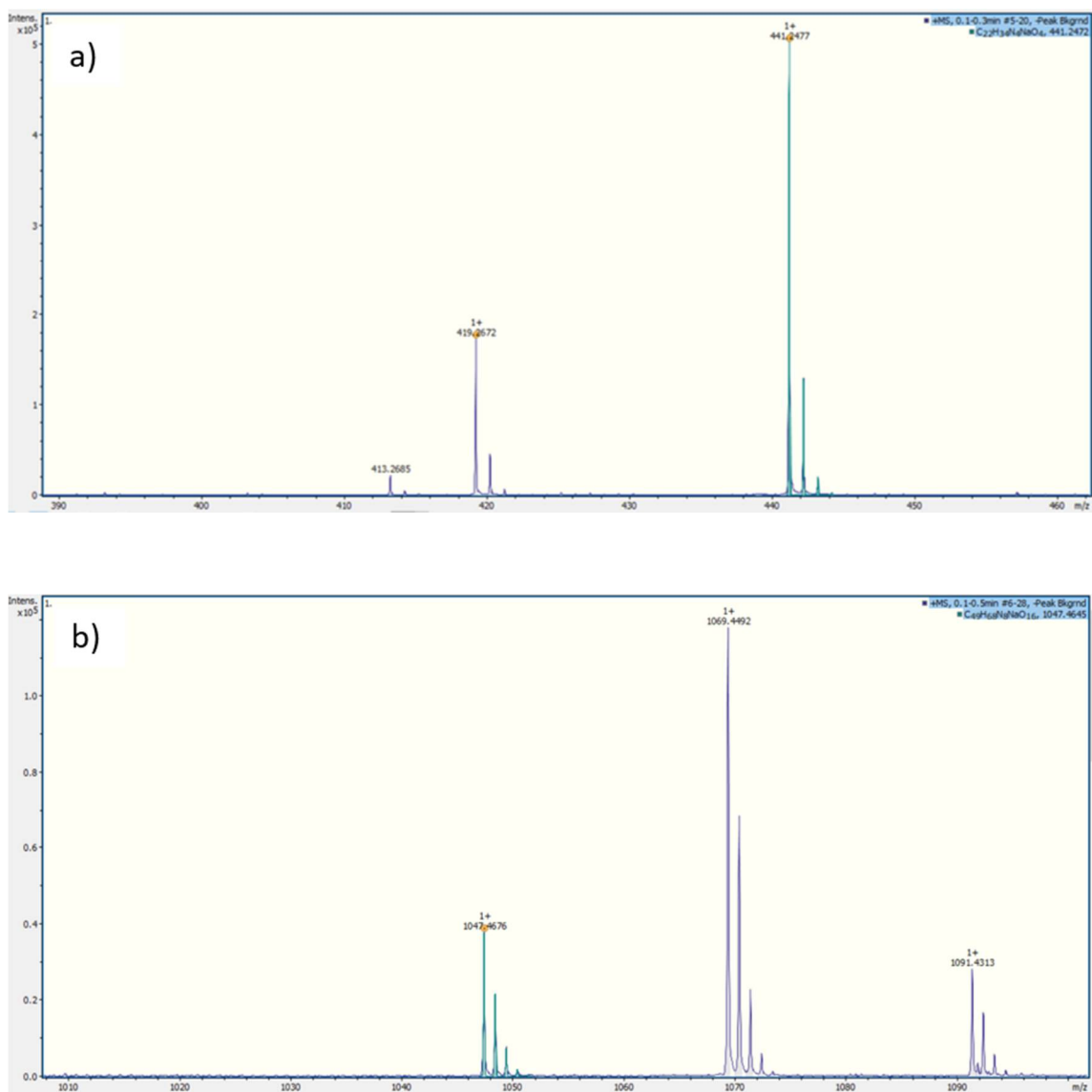


Figure S46. HR-ESI spectra of a) **thym-C<sub>12</sub>-thym** and b) **(thym-C<sub>6</sub>)<sub>4</sub>-O**.

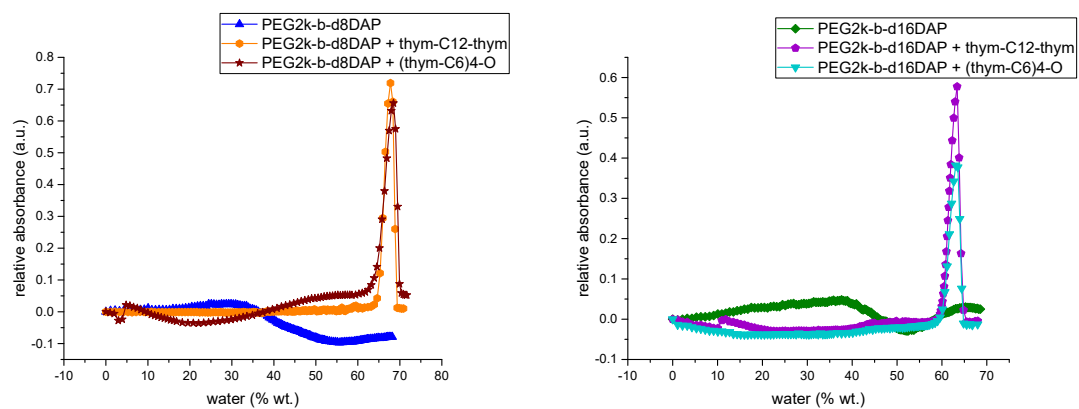
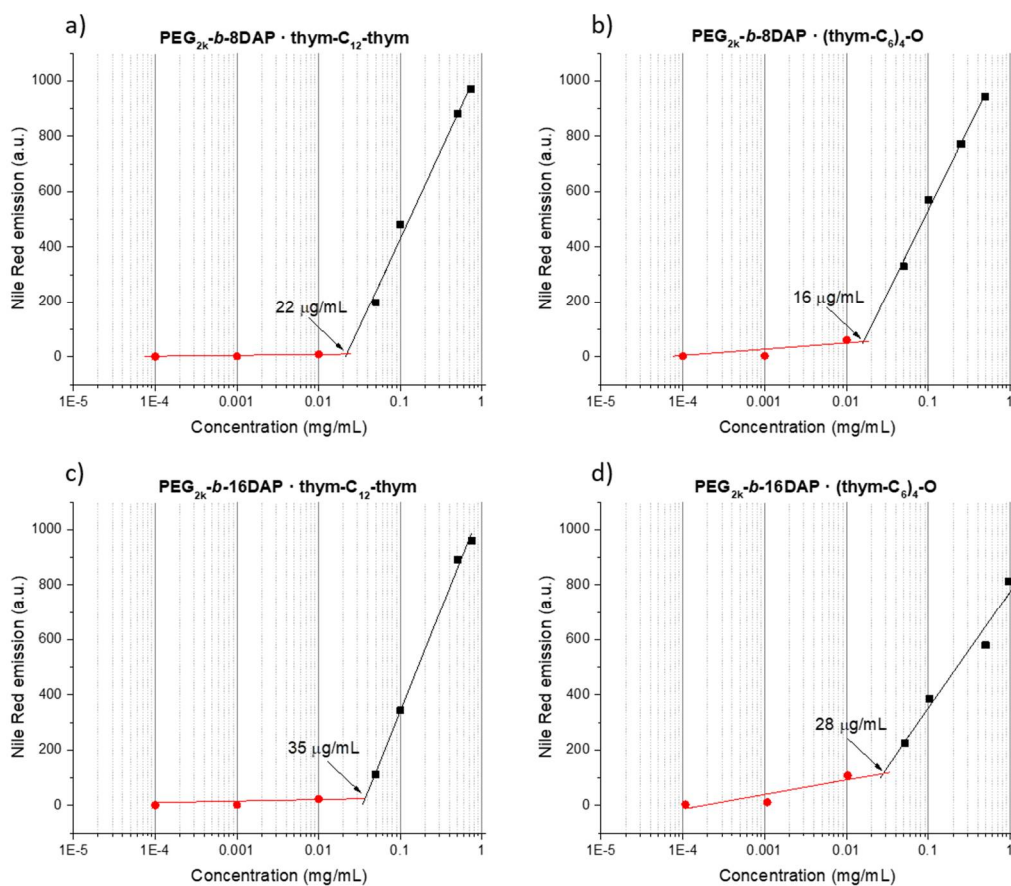


Figure S47. Turbidity curves of supramolecular cross-linked LDBC of **PEG<sub>2k</sub>-b-d8DAP** (left) and **PEG<sub>2k</sub>-b-d16DAP** (right).



**Figure S48.** Fluorescence emission of Nile Red at 620 nm ( $\lambda_{\text{exc}} = 550$  nm) versus a)  $\text{PEG}_{2k}\text{-}b\text{-}d8\text{DAP}\cdot\text{thym-C}_{12}\text{-thym}$ , b)  $\text{PEG}_{2k}\text{-}b\text{-}d8\text{DAP}\cdot(\text{thym-C}_6)_4\text{-O}$ , c)  $\text{PEG}_{2k}\text{-}b\text{-}d16\text{DAP}\cdot\text{thym-C}_{12}\text{-thym}$  and  $\text{PEG}_{2k}\text{-}b\text{-}d16\text{DAP}\cdot(\text{thym-C}_6)_4\text{-O}$  concentration. CAC was determined from the intersection of the two extrapolated lines.