

Supporting Information

Molecular Design of a Discrete Chain-folding Polyimide for Controlled Inkjet Deposition of Supramolecular Polymers

Lewis R. Hart,^a Josephine L. Harries,^b Barnaby W. Greenland,^c Howard M. Colquhoun^{*a} and Wayne Hayes^{*a}

^aDepartment of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, U.K. e-mail: w.c.hayes@reading.ac.uk, h.m.colquhoun@reading.ac.uk, Tel: +44 118 378 6491, Fax: +44 118 378 6331

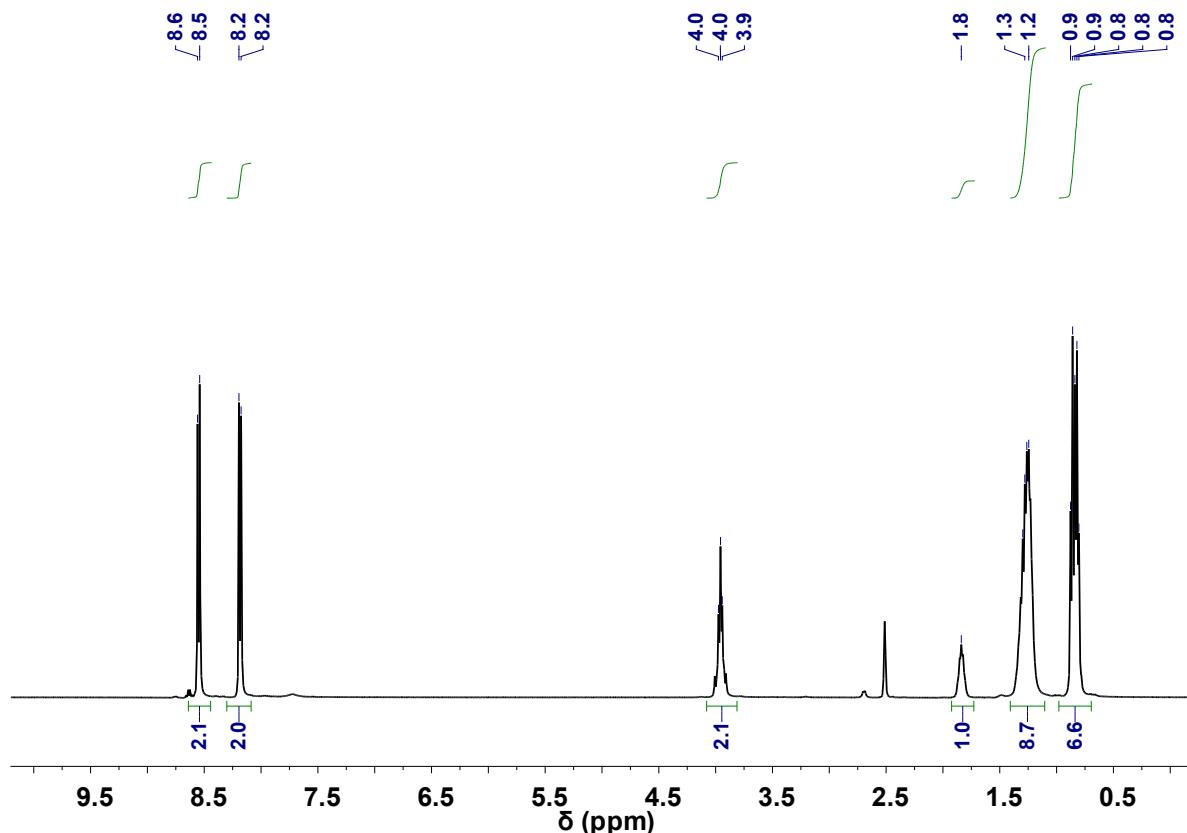
^bDomino UK Ltd, Trafalgar Way, Bar Hill, Cambridge, CB23 8TU, U.K.

^cThe Reading School of Pharmacy, University of Reading, Whiteknights, Reading, RG6 6AD, U.K.

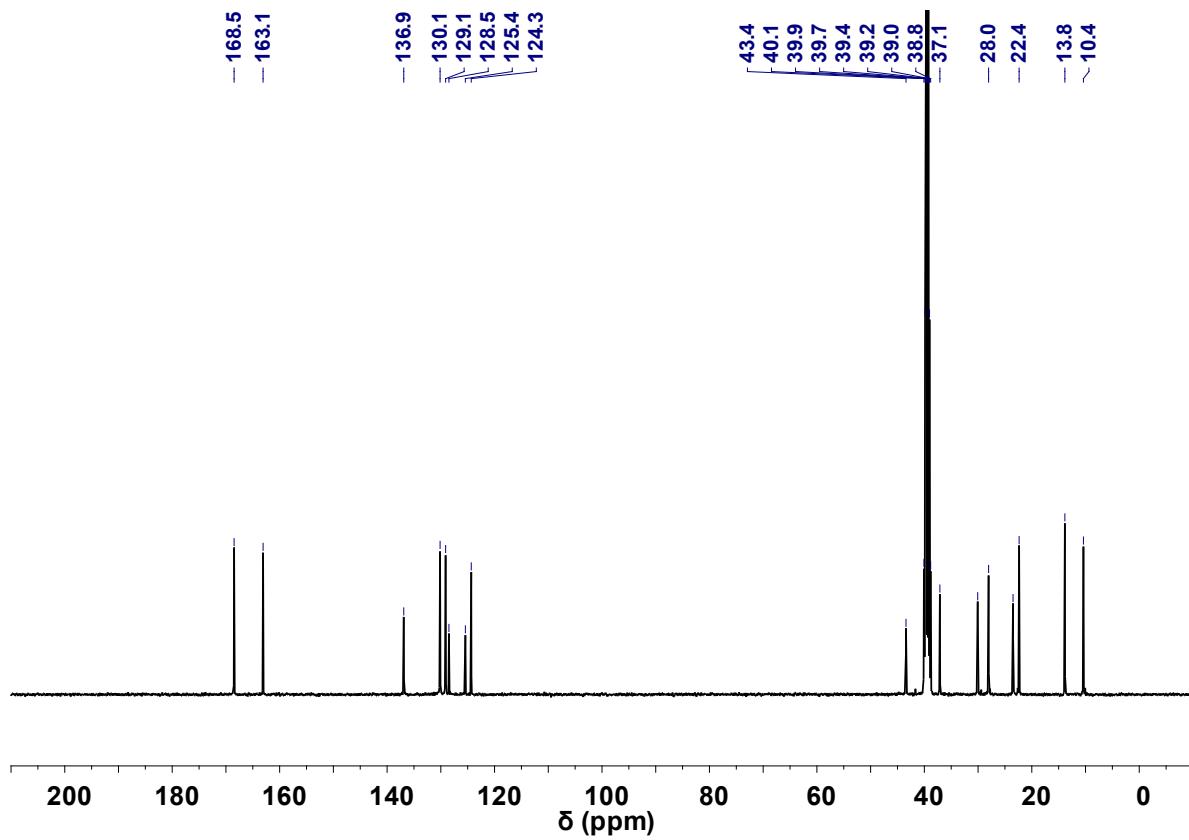
Contents

S1: ¹ H NMR spectra of ethylhexyl imide-anhydride 4	S2
S2: ¹³ C NMR spectra of ethylhexyl imide-anhydride 4	S3
S3: Mass spectra of ethylhexyl imide-anhydride 4	S3
S4: ¹ H NMR spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) 6	S4
S5: ¹³ C NMR spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) 6	S4
S6: Mass spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) 6	S5
S7: ¹ H NMR spectra of Boc-protected diimide 7	S5
S8: ¹³ C NMR spectra of Boc-protected diimide 7	S6
S9: Mass spectra of Boc-protected diimide 7	S6
S10: ¹ H NMR spectra of amino-terminated diimide 1	S7
S11: ¹³ C NMR spectra of amino-terminated diimide 1	S7
S12: Mass spectra of amino-terminated diimide 1	S8
S13: ¹ H NMR spectra of azide-terminated imide-acid 9	S8
S14: ¹³ C NMR spectra of azide-terminated imide-acid 9	S9
S15: Mass spectra of azide-terminated imide-acid 9	S9
S16: ¹ H NMR spectra of azide-terminated chain-folding diimide 10	S10

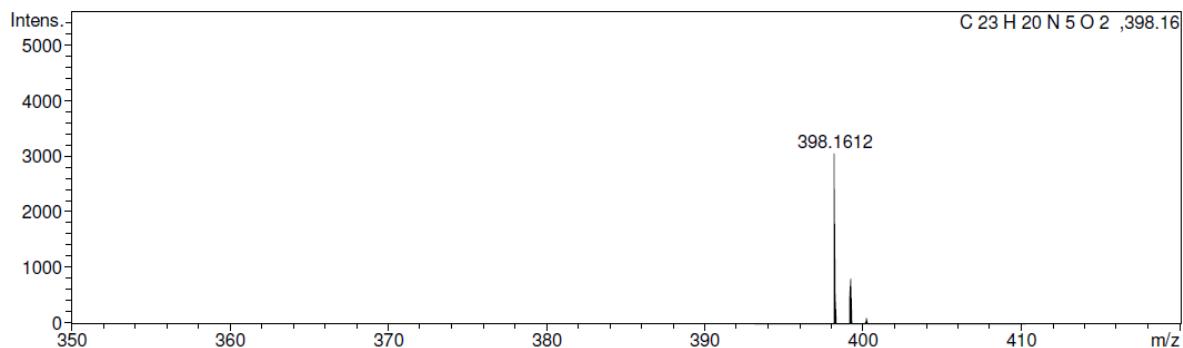
S17: ^{13}C NMR spectra of azide-terminated chain-folding diimide 10	S10
S18: Mass spectra of azide-terminated chain-folding diimide 10	S11
S19: ^1H NMR spectra of bis-alkyne-terminated poly(ethylene glycol) 13	S11
S20: ^{13}C NMR spectra of bis-alkyne-terminated poly(ethylene glycol) 13	S12
S21: Mass spectra of bis-alkyne-terminated poly(ethylene glycol) 13	S12
S22: ^1H NMR spectra of the ‘clicked’ polyimide 14	S13
S23: ^{13}C NMR spectra of the ‘clicked’ polyimide 14	S13
S24: MALDI-TOF MS spectra of the ‘clicked’ polyimide 14	S14
S25: Stacked ^1H NMR spectra of precursors 10 , 13 and ‘clicked’ polydiimide 14	S14
S26: VT UV-Vis spectra of polymers 14 , 15 and the subsequent blend (14 + 15)	S15
S27: VT ^1H NMR spectra of polymers 14 , 15 and the subsequent blend (14 + 15)	S15
S28: Fluorescence spectra of polymers 14 , 15 and the subsequent blend (14 + 15)	S16
S29: Images of the Fujifilm Dimatix TM materials Printer and Dimatix TM materials cartridge	S16



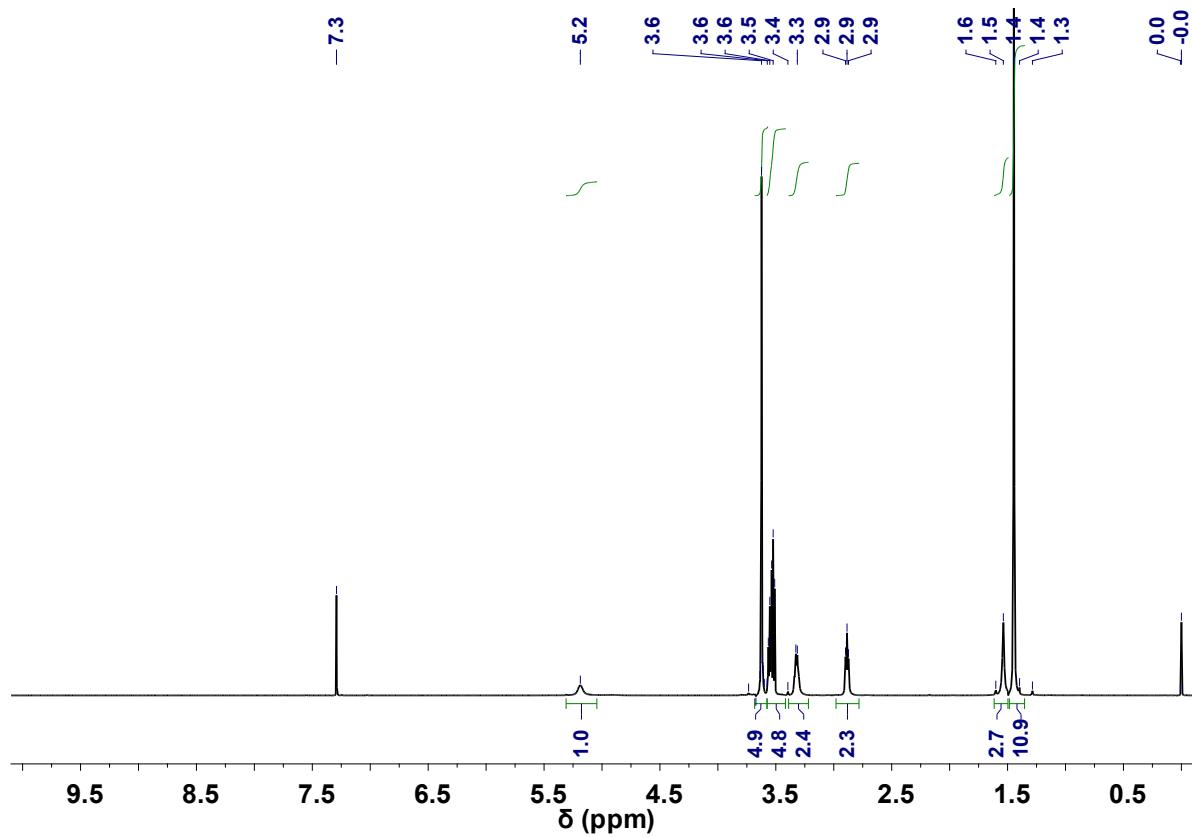
S1: ^1H NMR spectra of the ethylhexyl imide-anhydride **4**.



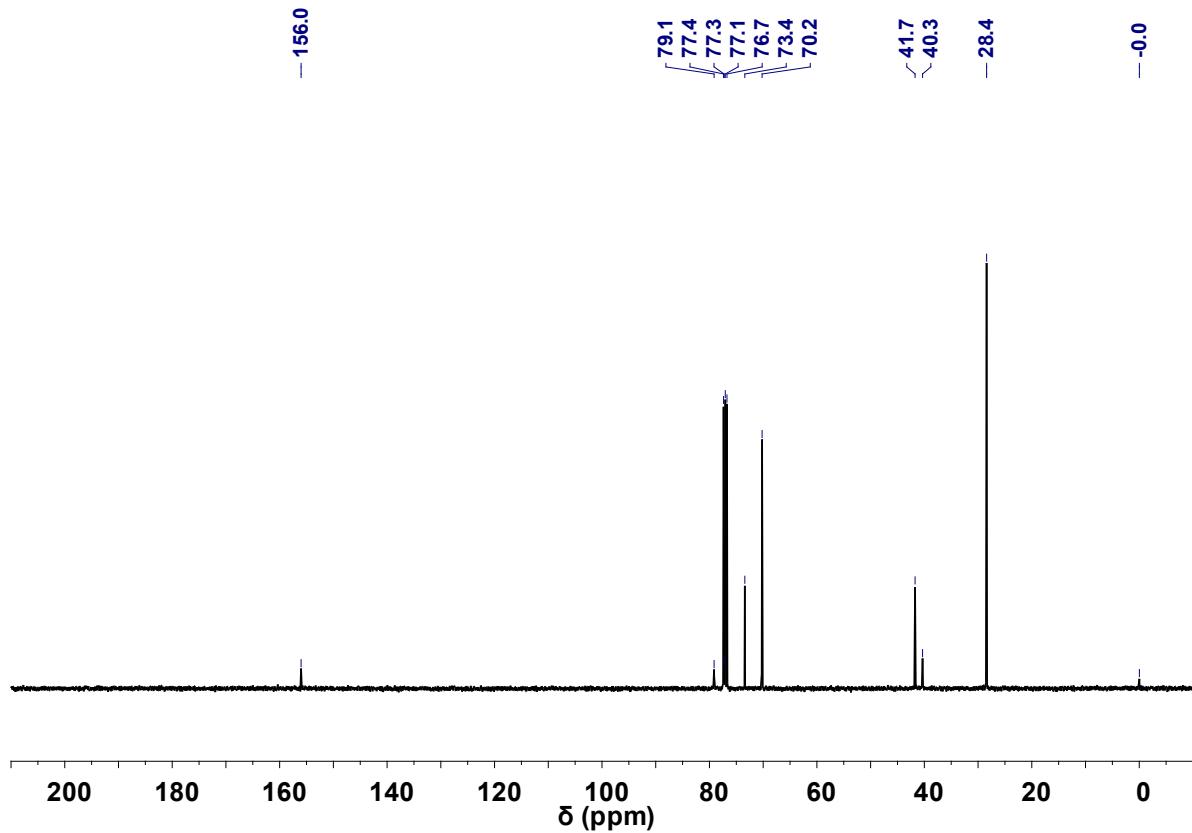
S2: ^{13}C NMR spectra of the ethylhexyl imide-anhydride **4**.



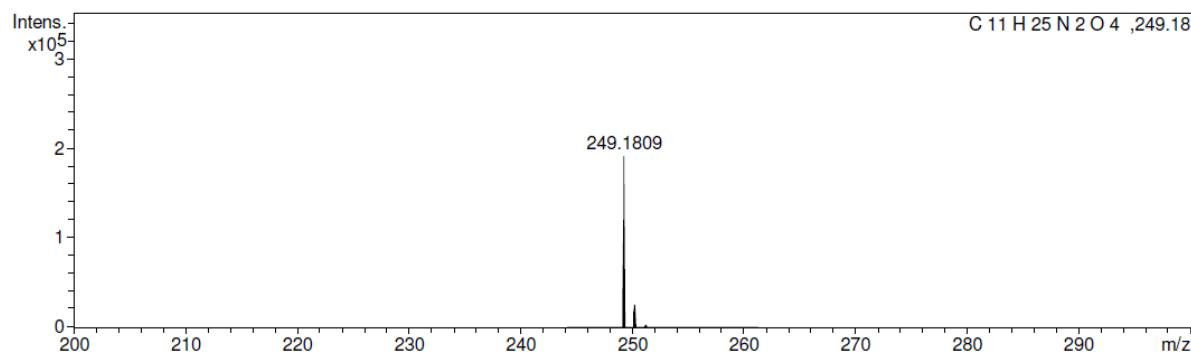
S3: Mass spectra of the ethylhexyl imide-anhydride **4**.



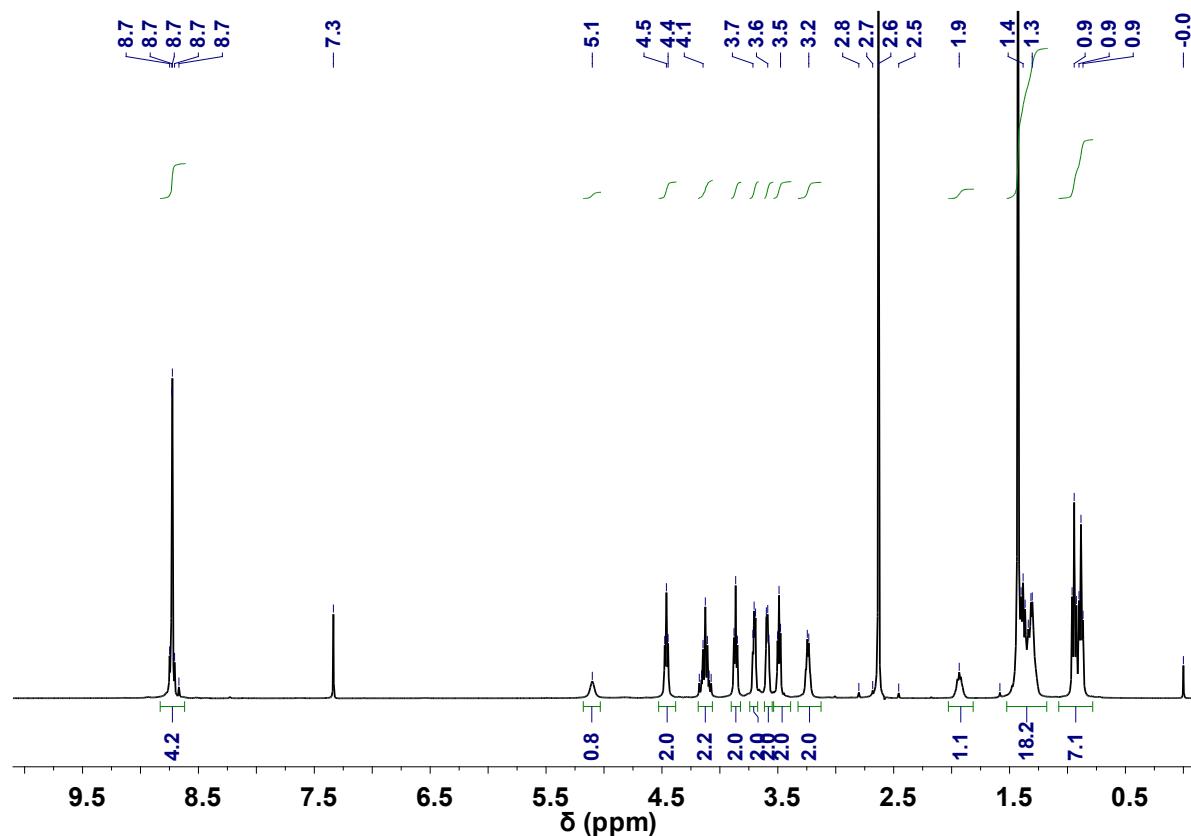
S4: ^1H NMR spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) **6**.



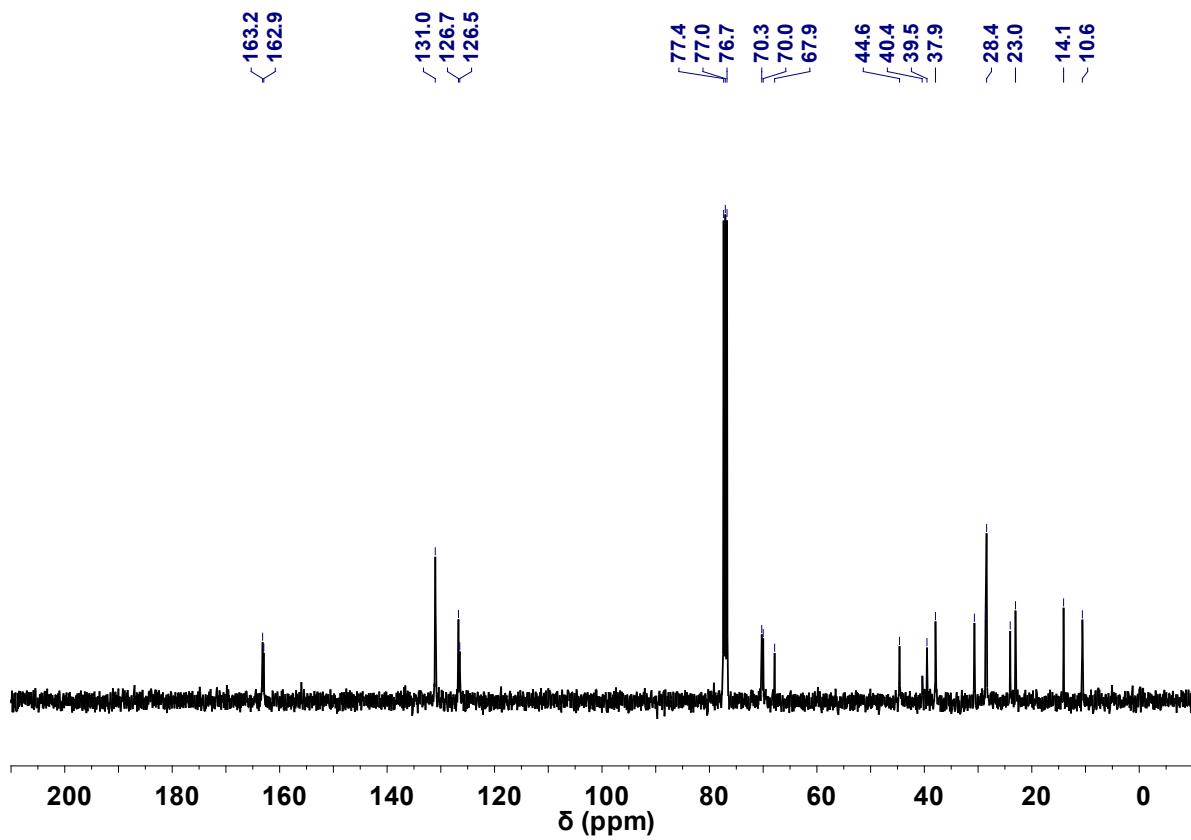
S5: ^{13}C NMR spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) **6**.



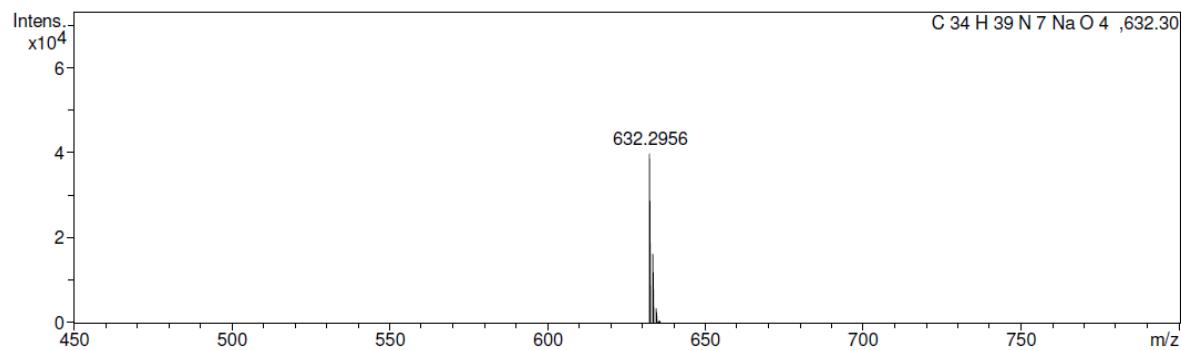
S6: Mass spectra of mono-Boc-protected 2,2'-(ethylenedioxy)bis(ethylamine) **6**.



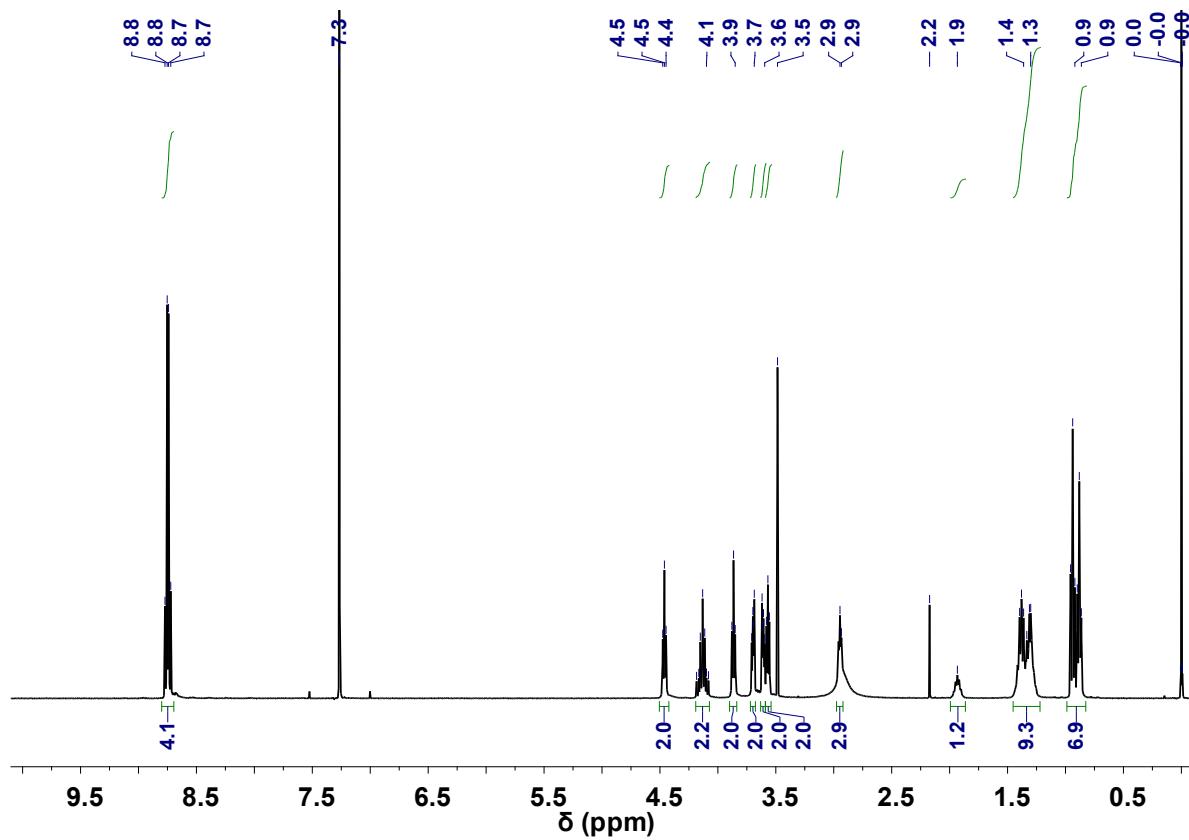
S7: ^1H NMR spectra of Boc-protected diimide **7**.



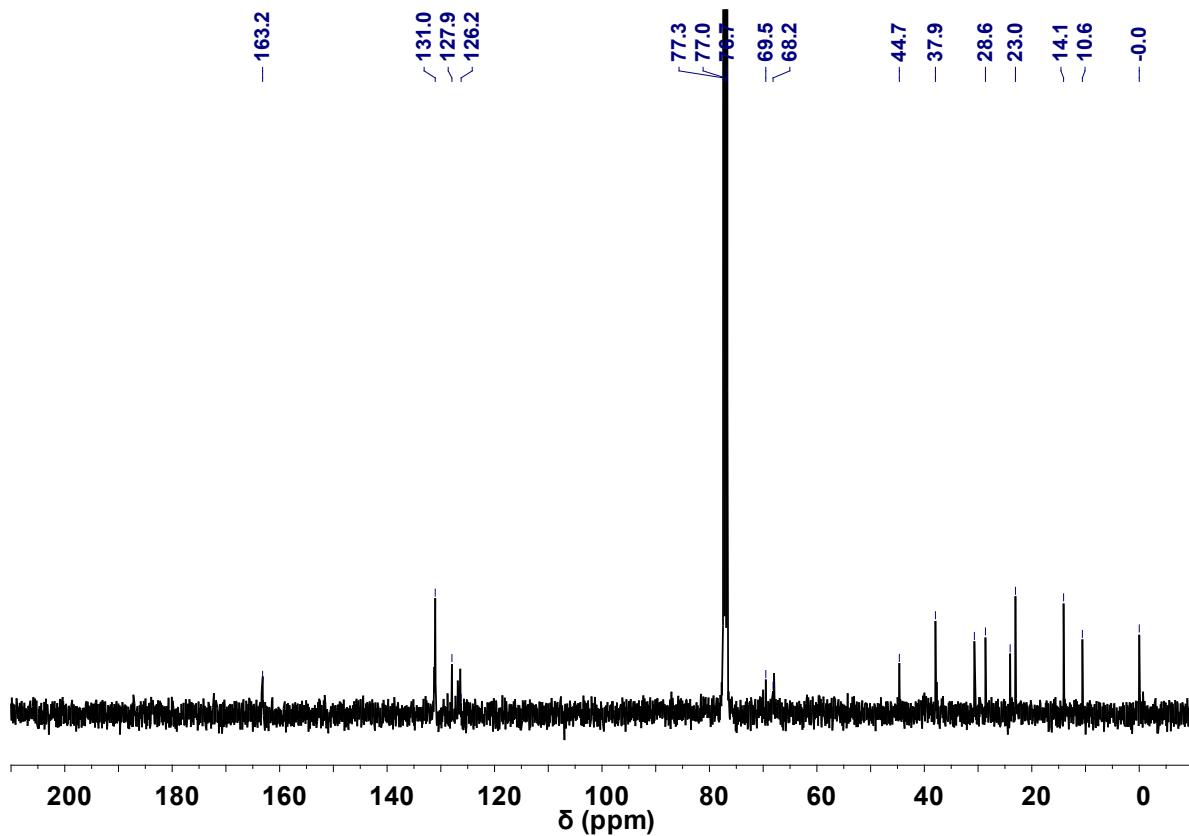
S8: ^{13}C NMR spectra of Boc-protected diimide 7.



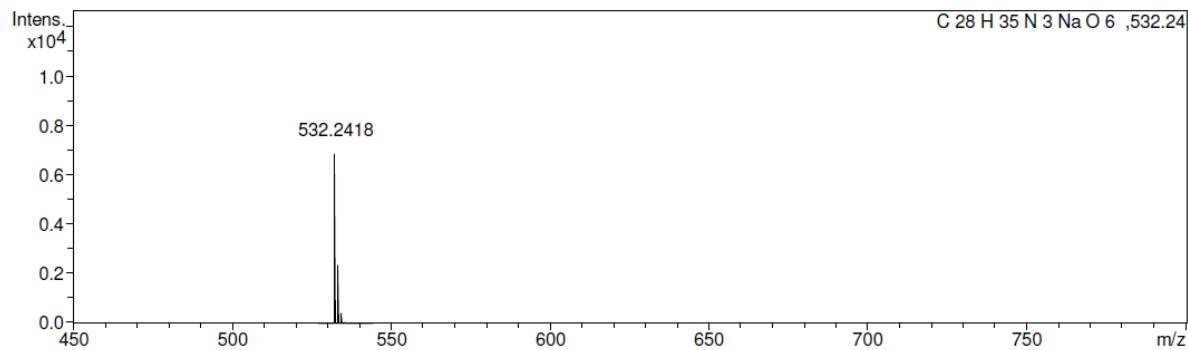
S9: Mass spectra of Boc-protected diimide 7.



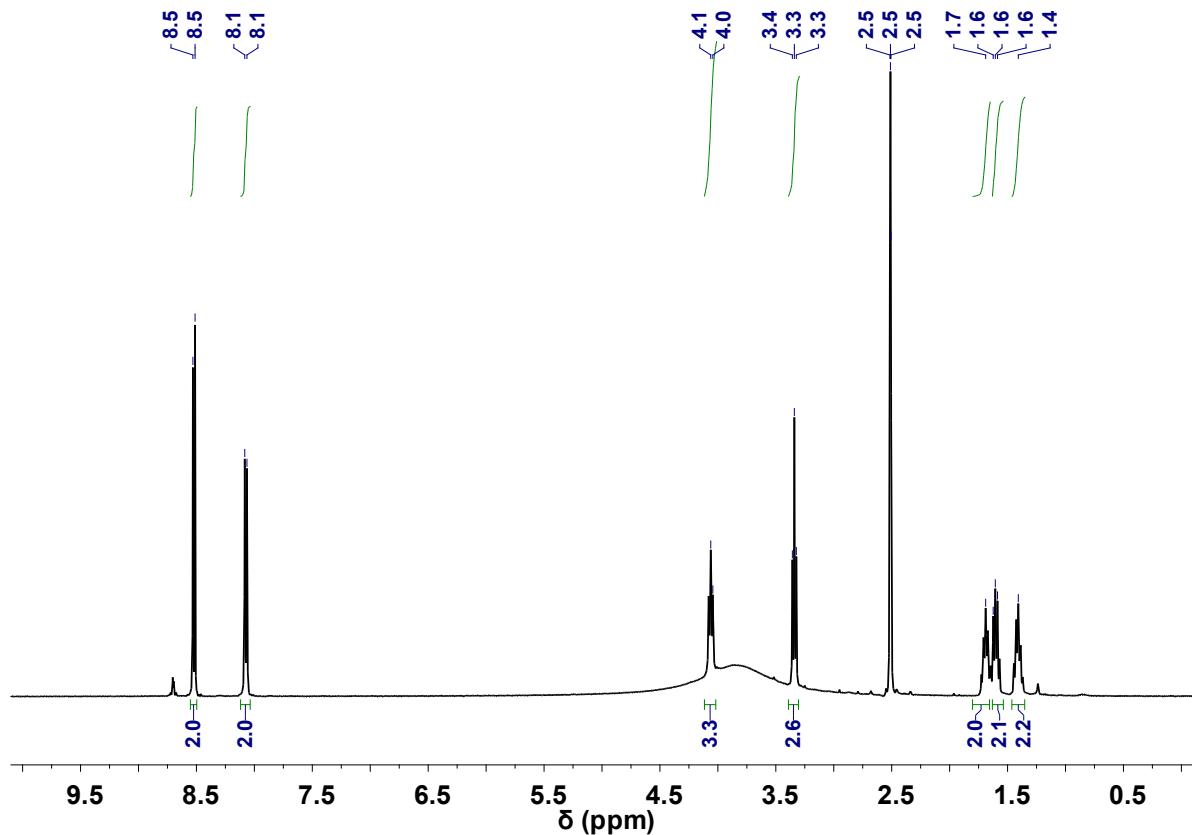
S10: ^1H NMR spectra of the amino-terminated diimide **1**.



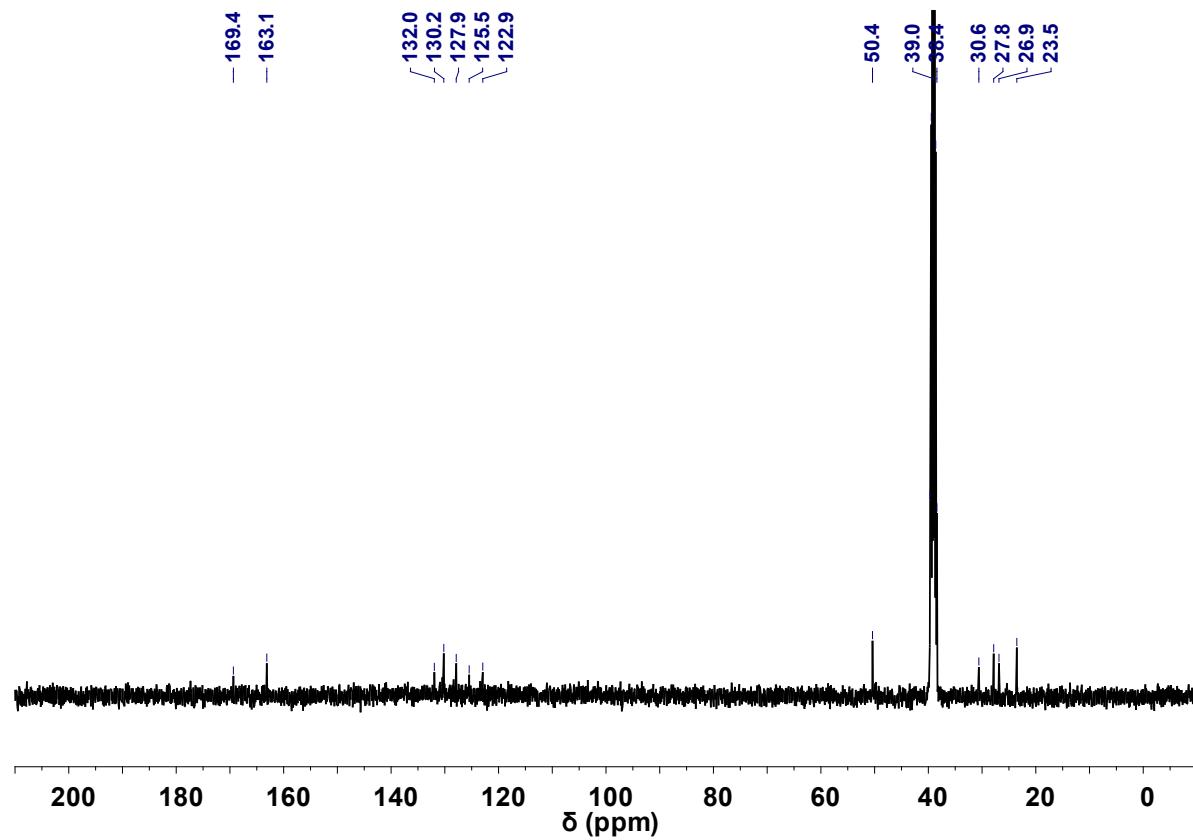
S11: ^{13}C NMR spectra of the amino-terminated diimide **1**.



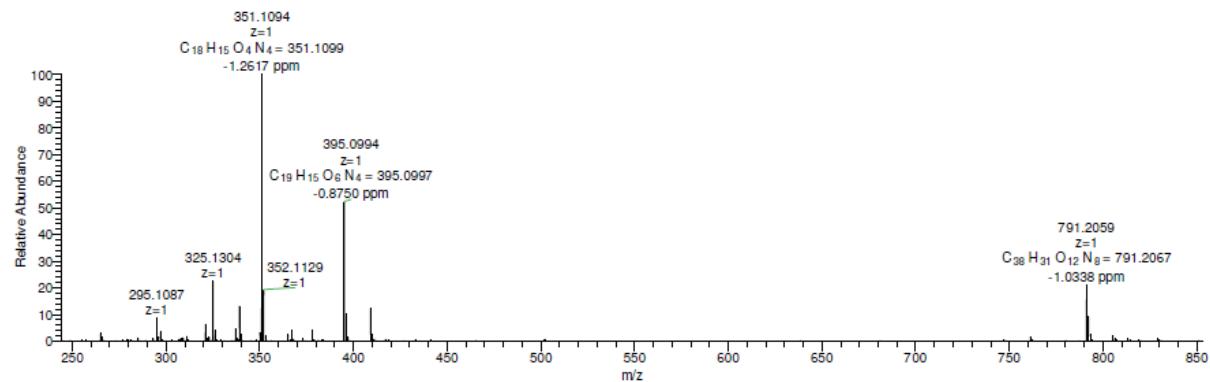
S12: Mass spectra of the amino-terminated diimide **1**.



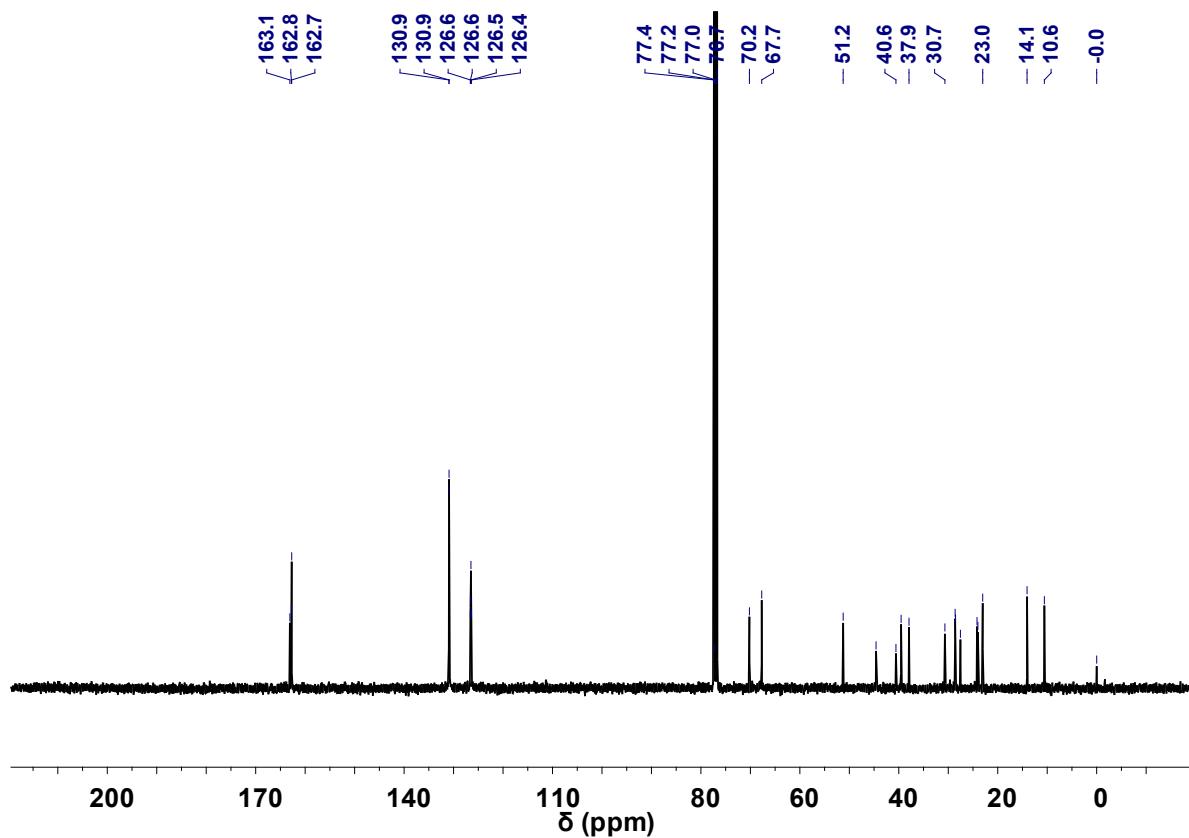
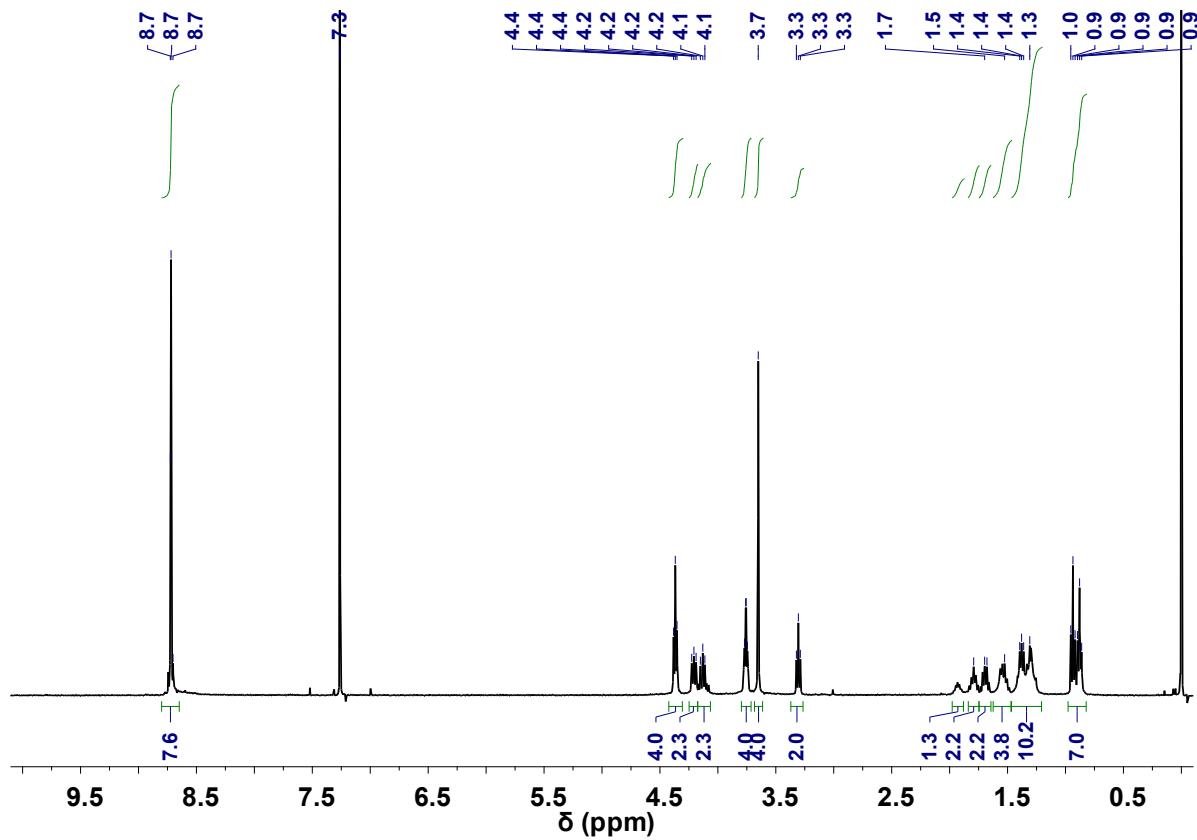
S13: ^1H NMR spectra of azide-terminated imide-diacid **9**.

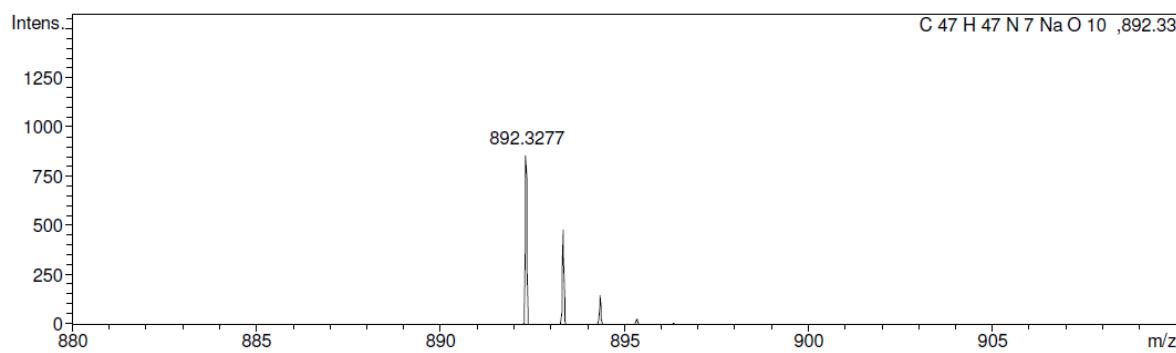


S14: ^{13}C NMR spectra of azide-terminated imide-diacid **9**.

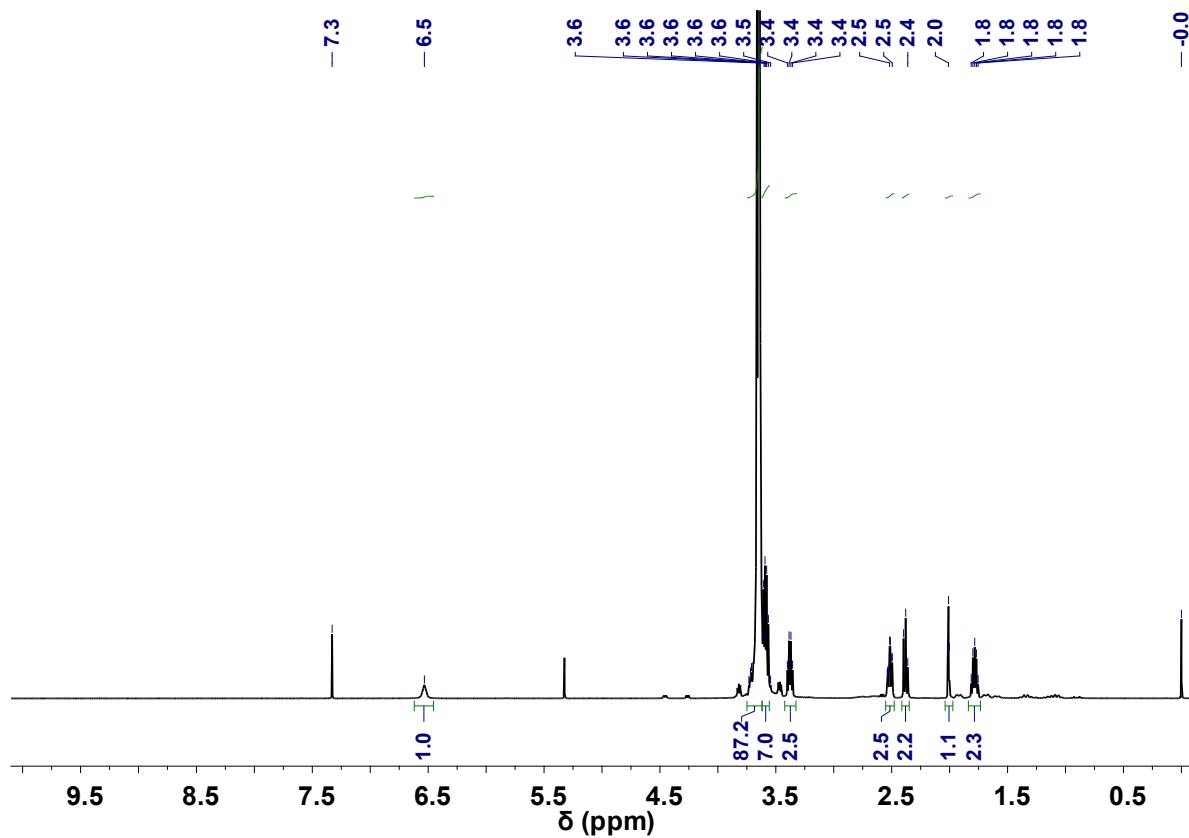


S15: Mass spectra of azide-terminated imide-diacid **9** in negative mode, showing the desired species and the associated dimer.

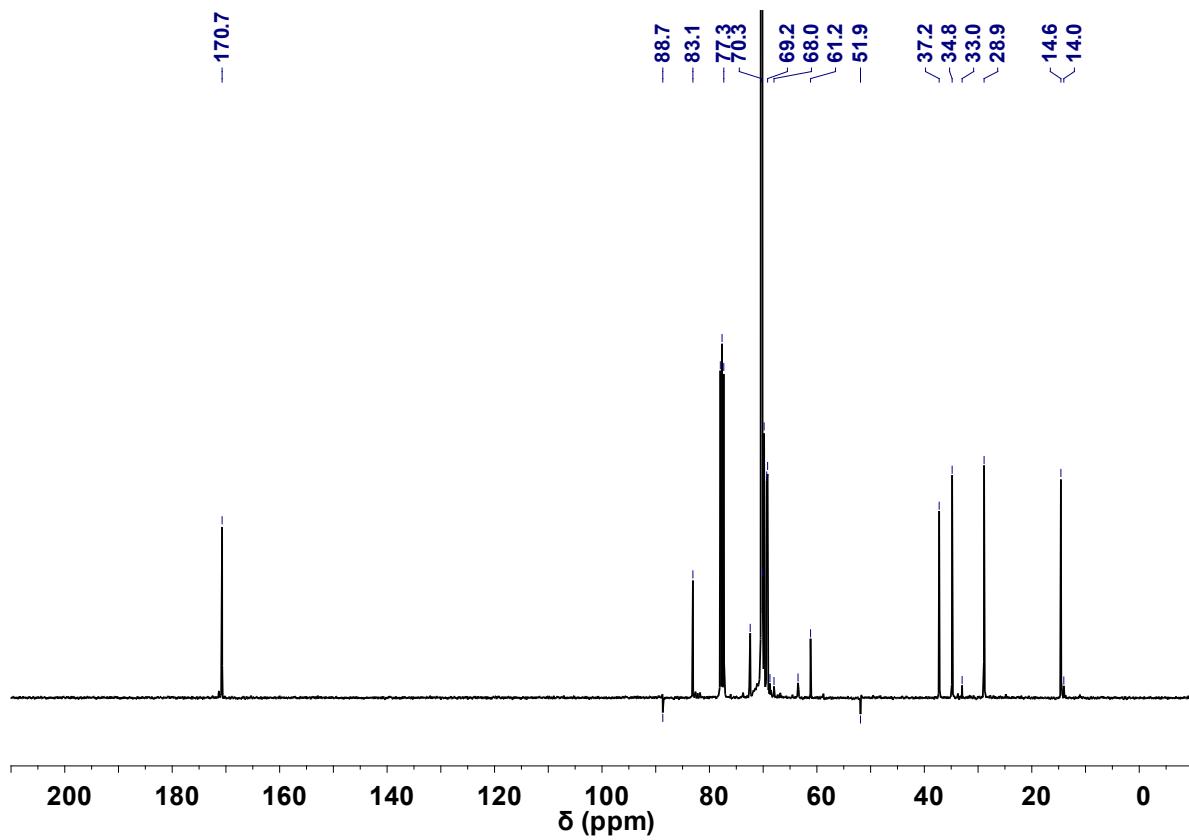




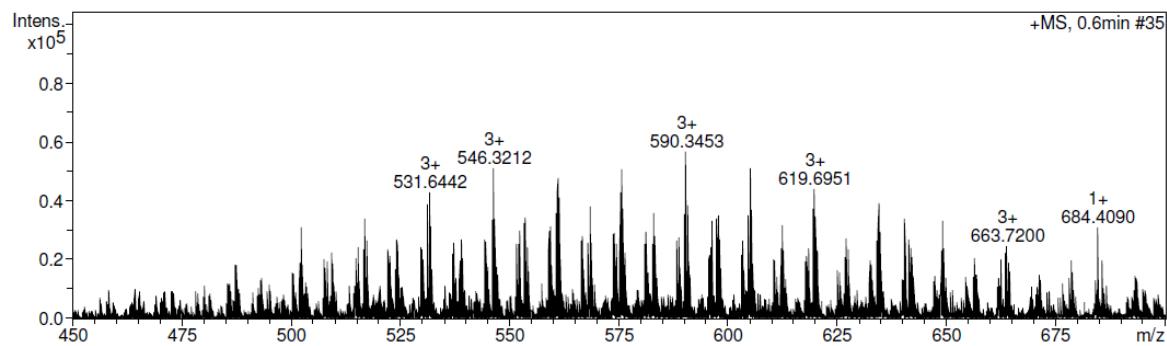
S18: Mass spectra of the azide-terminated chain-folding diimide **10**.



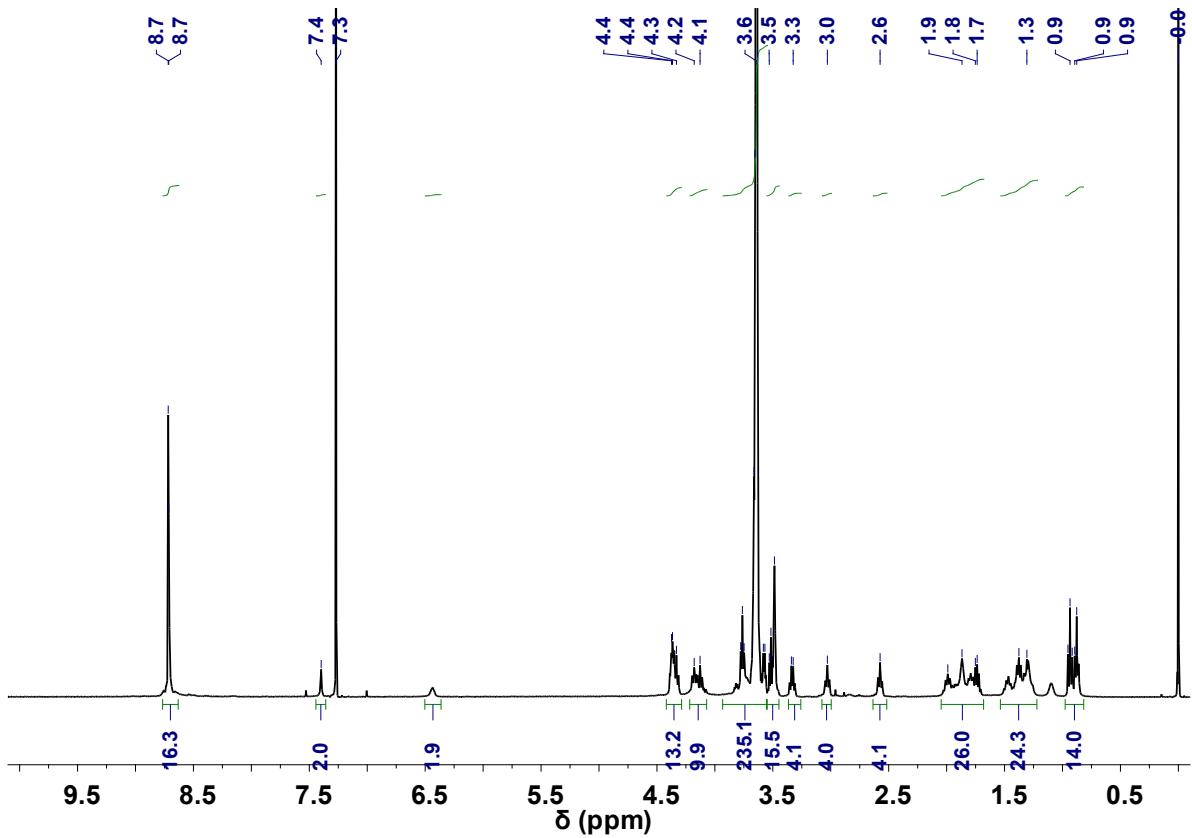
S19: ^1H NMR spectra of bis-alkyne-terminated poly(ethylene glycol) **13**.



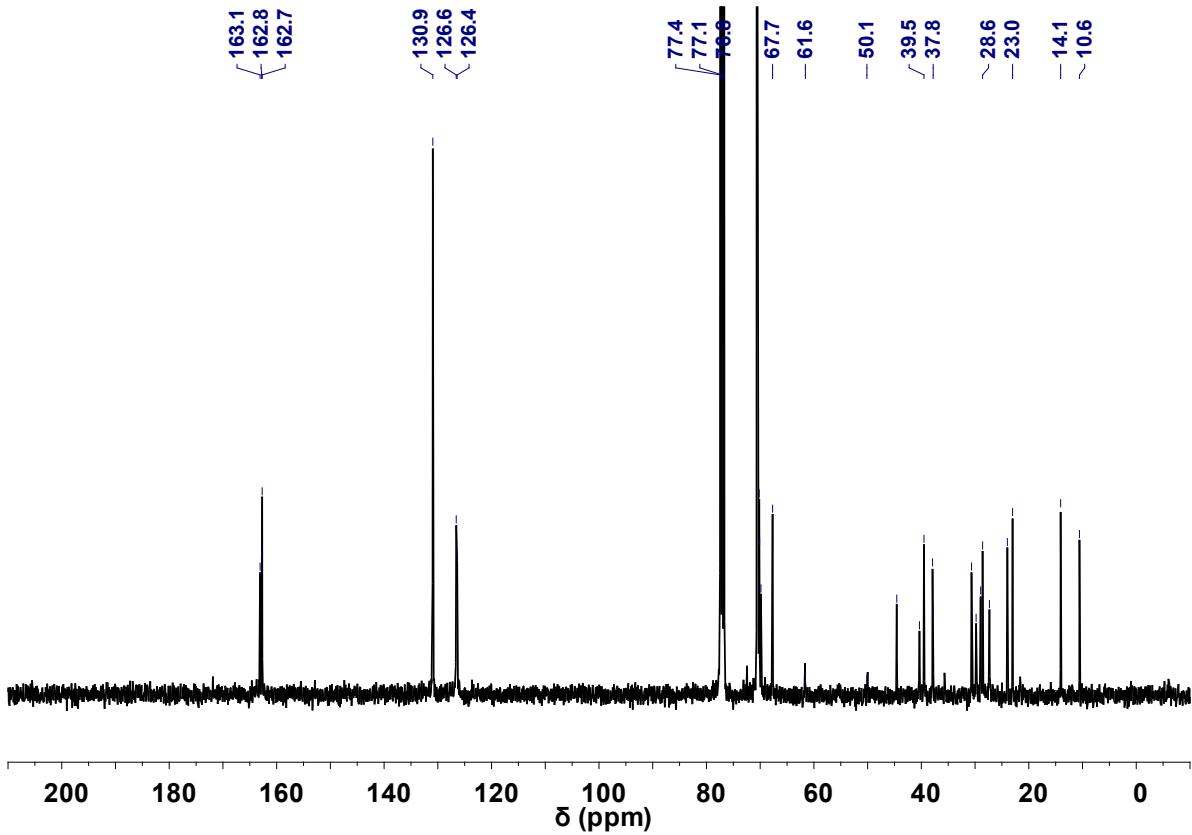
S20: ^{13}C NMR spectra of bis-alkyne-terminated poly(ethylene glycol) **13**.



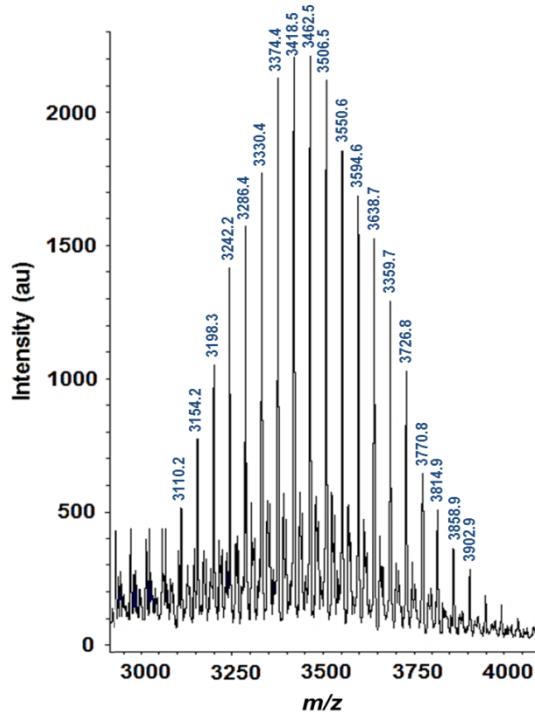
S21: Mass spectra of bis-alkyne-terminated poly(ethylene glycol) **13**.



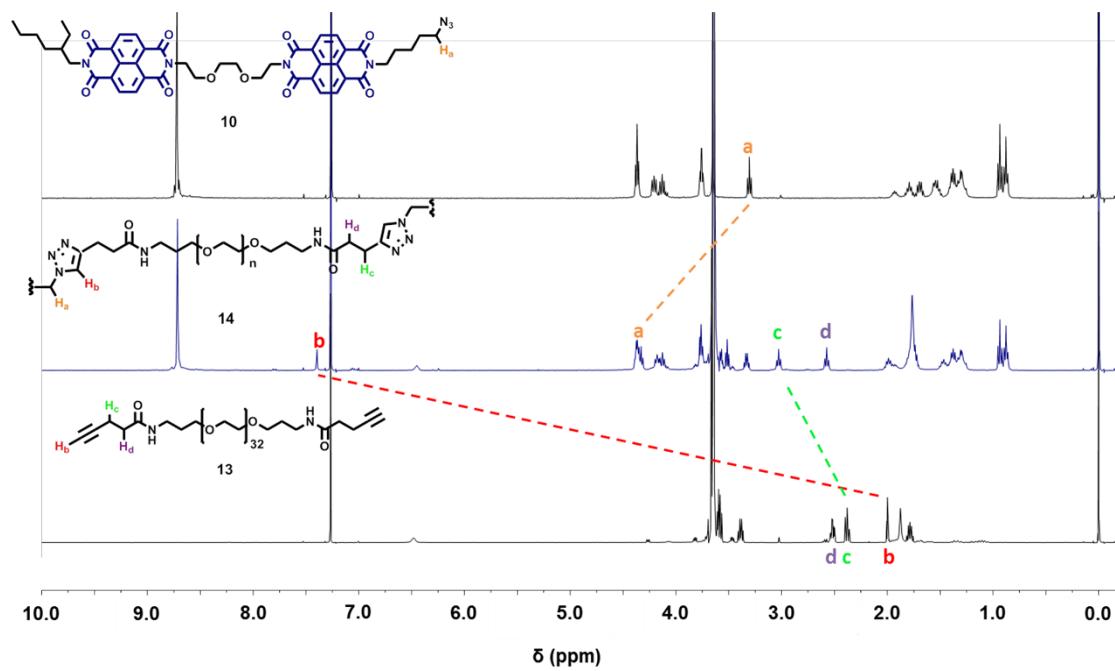
S22: ^1H NMR spectra of the ‘clicked’ chain-folding polydiimide **14**.



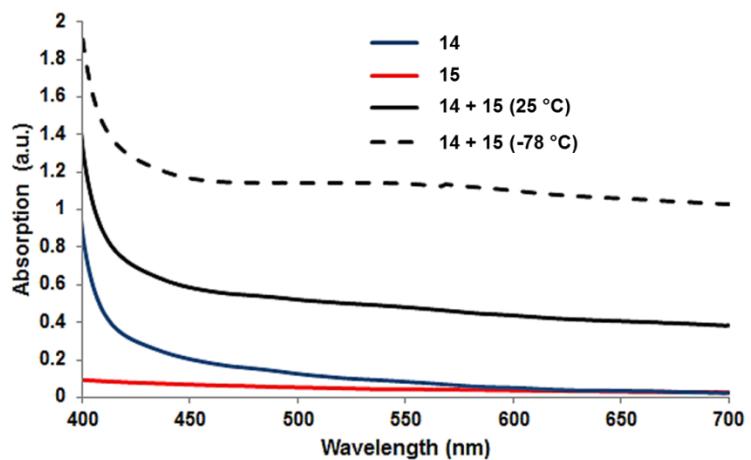
S23: ^{13}C NMR spectra of the ‘clicked’ chain-folding polydiimide **14**.



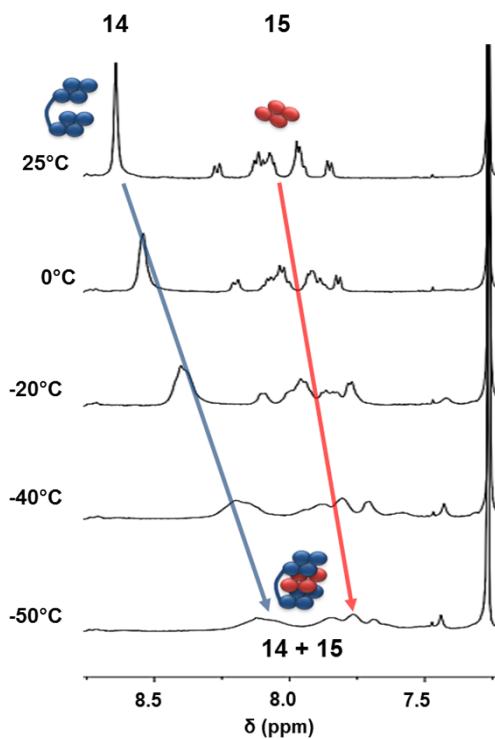
S24: MALDI-TOF mass spectrometric analysis of the ‘clicked’ chain-folding polydiimide **14**. The spacing between signals (44 Da) corresponds to a single repeat unit of poly(ethylene glycol).



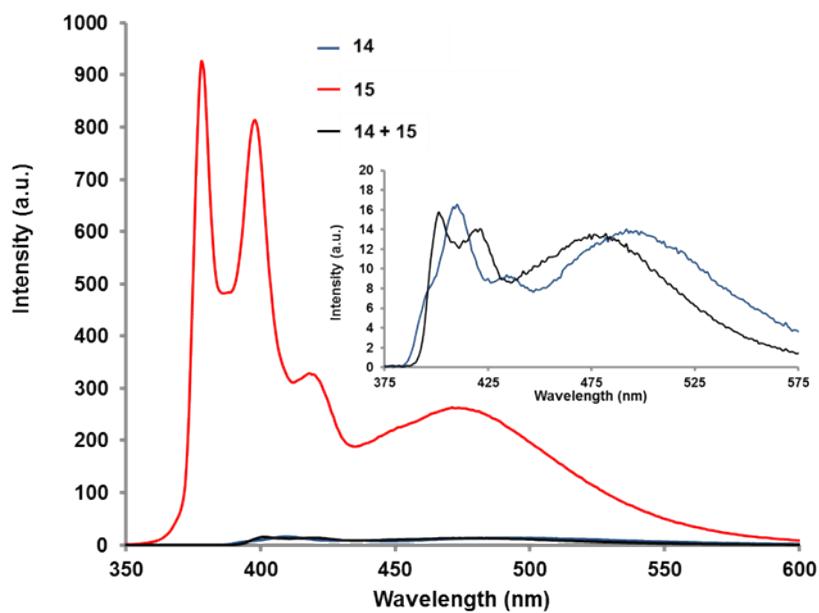
S25: ¹H NMR spectra of precursors **10** and **13** showing triazole formation through the appearance of the singlet at 7.45 ppm in the polyimide **14**.



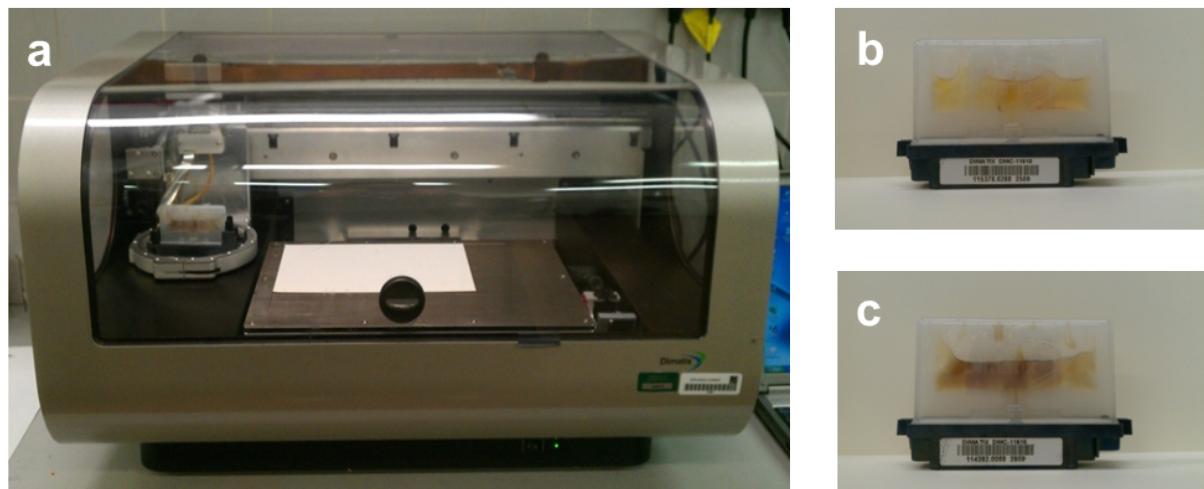
S26: UV-Vis spectra of the chain-folding polyimide **14** and pyrenyl terminated polymer **15** and on blending (**14 + 15**) at room temperature and -78 °C at a concentration of 3×10^{-3} M with respect to binding motifs in CHCl_3/TFA (9:1 v/v).



S27: Partial ^1H NMR spectra of the blend between the discrete chain-folding polymer **14** and the divalent pyrenyl polymer **15** showing significant complexation only at low temperature.



S28: Fluorescence spectra of emission inactive polyimide **14** and pyrenyl terminated poly(ethylene glycol) **15** and the equimolar (with respect to the binding motifs) blend (**14+15**). Insert shows expanded region between 375 nm and 575 nm, revealing the quenching of pyrenyl emissions in the blend (**14+15**) at room temperature.



S29: **a.** Fujifilm Dimatix™ Materials Printer (DMP-2800), **b.** Dimatix™ materials cartridge containing π -electron-rich polymer and **c.** π -electron deficient polydiimide containing cartridge