Supporting information

Uniform soluble supports for the large-scale synthesis of sequence-defined macromolecules

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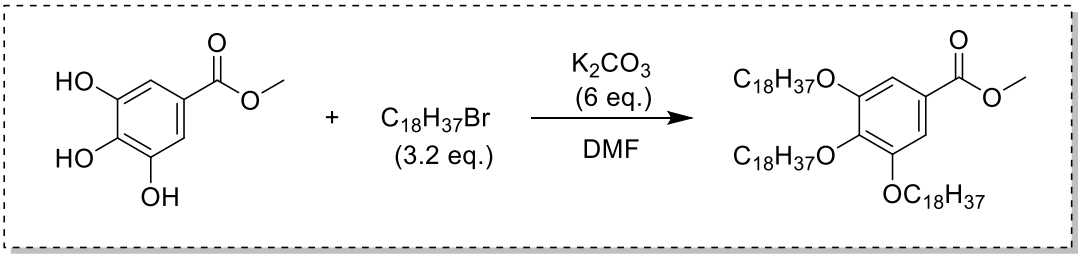
Summary

Synthetic procedures

A. Synthesis of non-cleavable Soluble Support

Methyl 3,4,5-tris(octadecyloxy)benzoate



Scheme S1: Synthesis of methyl 3,4,5-tris(octadecyloxy)benzoate.

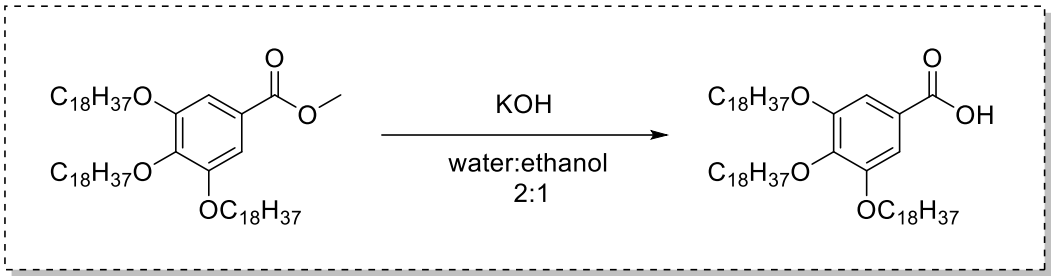
The synthesis was adapted from a literature procedure.[1] Methyl gallate (50 g, 271.5 mmol, 1 eq.), 1-bromooctadecane (290 g, 869 mmol, 3.2 eq.) and potassium carbonate (225 g, 1.63 mol, 6 eq.) were solubilised in dimethylformamide (1 L). The reaction mixture was stirred overnight at 100 °C. Afterwards, the reaction mixture was precipitated in water (10 L). The precipitate was isolated by filtration and dried in a vacuum oven. Finally, the crude product was recrystallised in hexane to obtain the pure product.

Yield: 255 g white powder (quant.). MW: 941.61 g/mol.

MALDI: 963.97 $[M+Na]^+$.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.25 (s, 2 H, Ar-H), 4.02 (m, 6 H, O-CH_2), 3.89 (s, 3 H, CH_3), 1.79 (m, 6 H, O-CH_2-CH_2), 1.47 (m, 6 H, O-CH_2-CH_2-CH_2), 1.29 (m, 84 H, CH_2), 0.89 (t, 9 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.96 (Cq), 152.83 (Cq), 142.38 (Cq), 124.60 (Cq), 107.99 (CH), 73.50 (CH_2), 69.18 (CH_2), 52.11 (CH_2), 31.94 (CH_2), 30.35 (CH_2), 29.73 (CH_2), 29.68 (CH_2), 29.66 (CH_2), 29.59 (CH_2), 29.41 (CH_2), 29.38 (CH_2), 29.33 (CH_2), 26.10 (CH_2), 26.07 (CH_2), 22.71 (CH_2), 14.13 (CH_3).

3,4,5-Tris(octadecyloxy)benzoic acid



Scheme S2: Synthesis of 3,4,5-tris(octadecyloxy)benzoic acid.

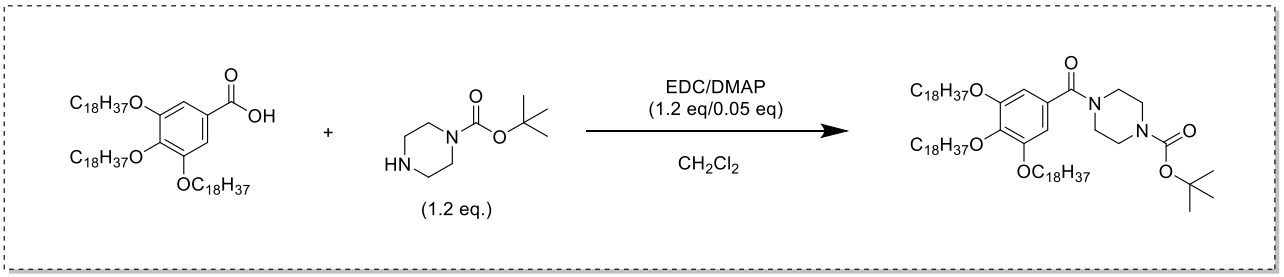
The synthesis was adapted from a literature procedure.[1] Methyl 3,4,5-tris(octadecyloxy) benzoate (61.5 g, 65.31 mmol, 1 eq.) and potassium hydroxide (36.64 g, 653.14 mmol, 10 eq.) were suspended in a mixture of water (0.65 L) and ethanol (0.32 L). The reaction mixture was refluxed overnight. Afterwards, the reaction mixture was cooled down in an ice bath, acidified using 1 M HCl solution, and filtered. The residue was washed with additional water and hexane. Finally, the residue was dried in a vacuum oven, yielding the pure product as a white powder.

Yield: 52.46 g white powder (86.6 %).

MW: 927.58 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (s, 2 H, Ar-H), 4.02 (m, 6 H, O-CH_2), 1.80 (m, 6 H, O-CH_2-CH_2), 1.84 (m, 6 H, O-CH_2-CH_2-CH_2), 1.27 (m, 84 H, CH_2), 0.89 (t, 9 H, CH_3).

Tert-butyl 4-(3,4,5-tris(octadecyloxy)benzoyl)piperazine-1-carboxylate



Scheme S3: Synthesis of tert-butyl 4-(3,4,5-tris(octadecyloxy)benzoyl)piperazine-1-carboxylate.

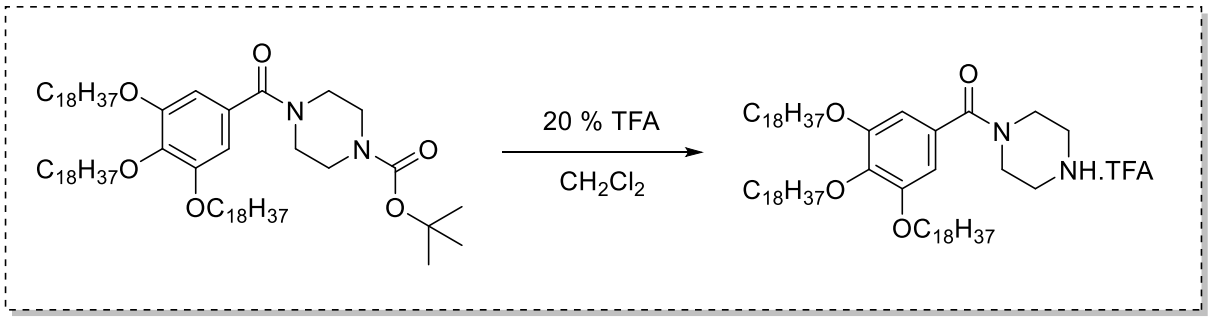
3,4,5-Tris(octadecyloxy)benzoic acid (10 g, 10.78 mmol, 1 eq.) and tert-butyl piperazine1-carboxylate (2.41 g, 12.94 mmol, 1,2 eq.) were suspended in 350 mL dichloromethane. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (2.48 g, 12.94 mmol, 1.2 eq.) was solubilised in 40 mL dichloromethane and added slowly to the reaction mixture under continuous stirring. The reaction mixture was stirred overnight under inert atmosphere. Approximately 200 mL dichloromethane was removed in vacuo, before the mixture was precipitated in cold methanol (1 L). After filtration, the residue was washed with additional cold methanol and subsequently dried in a vacuum oven, yielding the product as a white powder.

Yield: 10.2 g white powder (86.3 %).

MW: 1095.82 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.58 (s, 2 H, Ar-H), 3.96 (m, 6 H, O-CH_2), 3.79–3.26 (m, 8 H, N-CH_2-CH_2-N), 1.78 (m, 6 H, O-CH_2-CH_2), 1.48 (m, 6 H, O-CH_2-CH_2-CH_2, O-$(CH_3)_3$), 1.27 (m, 84 H, CH_2), 0.89 (t, 9 H, CH_3)

Piperazin-1-yl(3,4,5-tris(octadecyloxy)phenyl)methanone TFA salt



Scheme S4: Synthesis of piperazin-1-yl(3,4,5-tris(octadecyloxy)phenyl)methanone TFA salt.

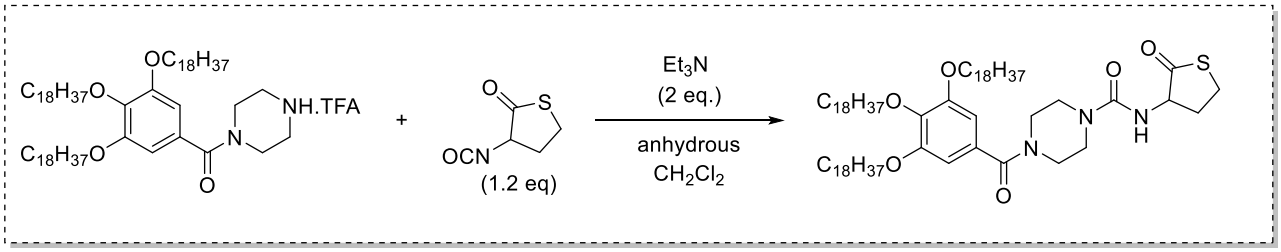
Tert-butyl 4-(3,4,5-tris(octadecyloxy)benzoyl)piperazine-1-carboxylate (44 g, 40.15 mmol, 1 eq.) was solubilised in 800 mL dichloromethane. Subsequently, trifluoroacetic acid (200 mL) was added and the reaction was stirred overnight. The solvent was removed in vacuo, yielding the product as a white solid.

Yield: 40.9 g white solid (quant.).

MW: 1092.72 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.73 (br s, 2 H, NH + 2), 6.59 (s, 2 H, Ar-H), 3.98 (m, 10 H, O-CH_2 , CH_2-NH + 2 CH_2), 3.21 (m, 4 H, CH_2-N-CH_2), 1.79 (m, 6 H, O-CH_2-CH_2), 1.48 (m, 6 H, O-CH_2-CH_2-CH_2), 1.27 (, 84 H, CH_2), 0.89 (t, 9 H, CH_3).

TLa-functionalised Soluble Support



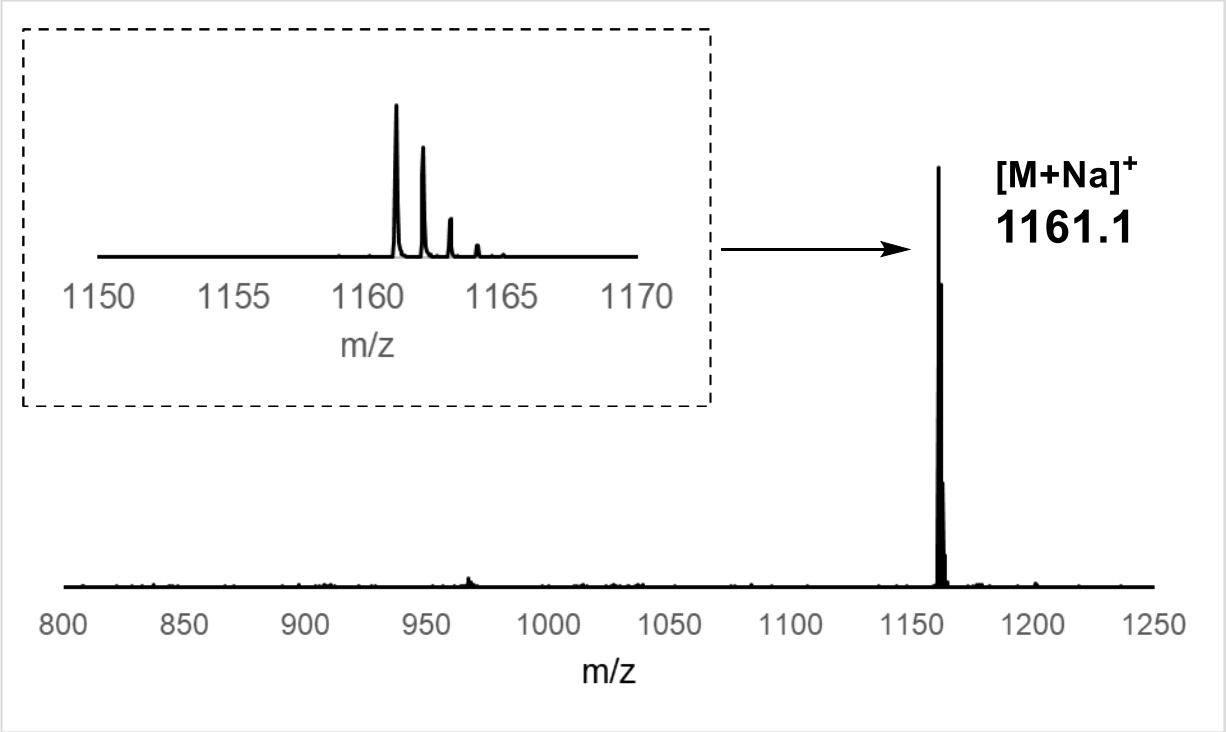
Scheme S5: Synthesis of TLa-functionalised support.

In a 250 mL two-neck flask, piperazin-1-yl(3,4,5-tris(octadecyloxy)phenyl)methanone TFA salt (8 g, 7.75 mmol, 1 eq.) was added and placed under an inert atmosphere. Subsequently, anhydrous dichloromethane (100 mL) and anhydrous triethylamine (2.16 mL, 15.5 mmol, 2 eq.) were added and the mixture was stirred until the compound was fully dissolved. Next, α-isocyanato-γ-thiolactone (0.98 mL, 9.30 mmol, 1.2 eq.) was added. After stirring for 3 h under inert atmosphere, the conversion was checked via MALDI-ToF, before the product was precipitated in cold methanol (1 L). The residue was isolated by filtration and washed with additional methanol, before it was dried in a vacuum oven, yielding the pure product as a white powder.

Yield: 8.71 g white powder (98.7 %).

MW: 1138.86 g/mol.

MALDI-ToF: 1161.09 $[M+Na]^+$



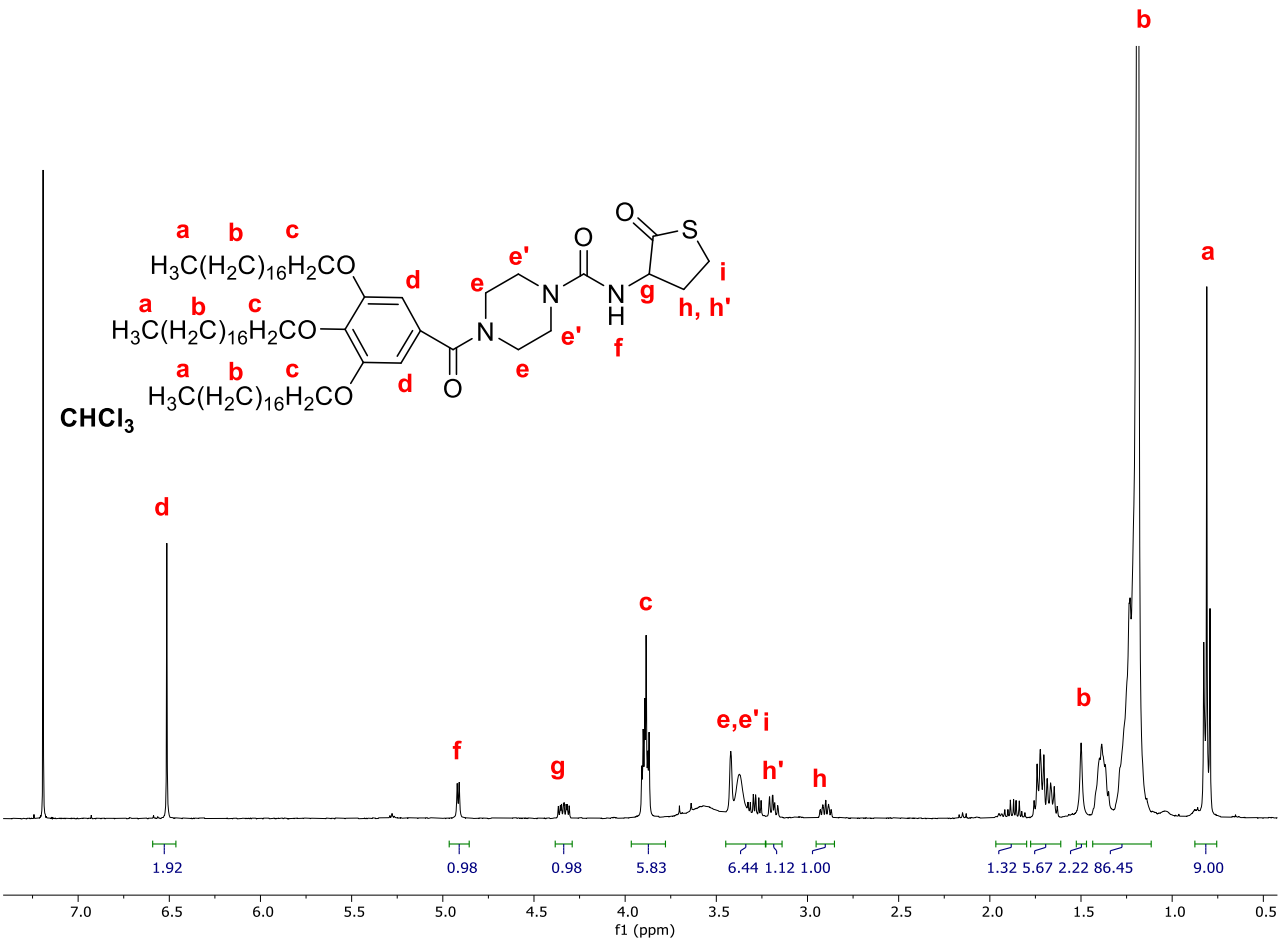
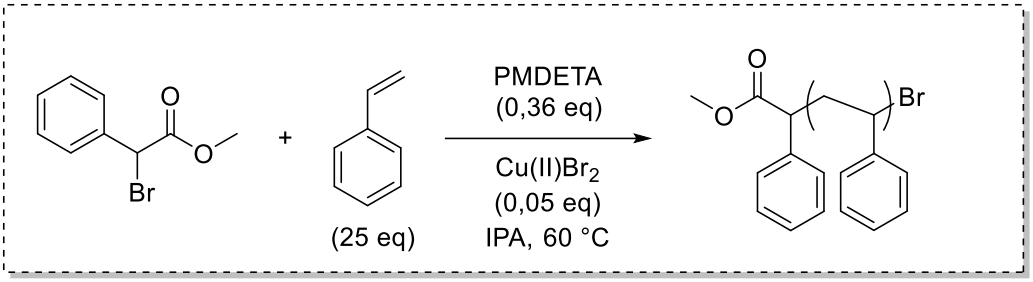


Figure S1: MALDI-ToF and ^{1}H-NMR of Tla-functionalised support.

B. Synthesis of Polystyrene Soluble Support (PS_{25})

Cu(0)-mediated RDRP of styrene (S) with targeted DP_n=25



Scheme S6: Synthesis of polystyrene with targeted DPn = 25.

The synthesis was adapted from a literature procedure.[2] Styrene (8 mL, 25 eq.), methyl α-bromophenylacetate (MBPA) (0.444 mL, 1 eq.), $CuBr_2$ (31.2 mg, 0.05 eq.), propan-2-ol (8 mL), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (0.208 mL, 0.36 eq.) and preactivated copper wire (5 cm) wrapped around a stirring bar were added to a septum sealed vial. The polymerisation was done at 60 ° C for 36 h. After 36 h, a sample was taken and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR in $CDCl_3$, and SEC in THF. The synthesised polymer is redissolved in acetone and precipitated in cold methanol twice obtaining a white powder further dried in a vacuum oven.

Yield: 4.80 g white powder (86.5 %).

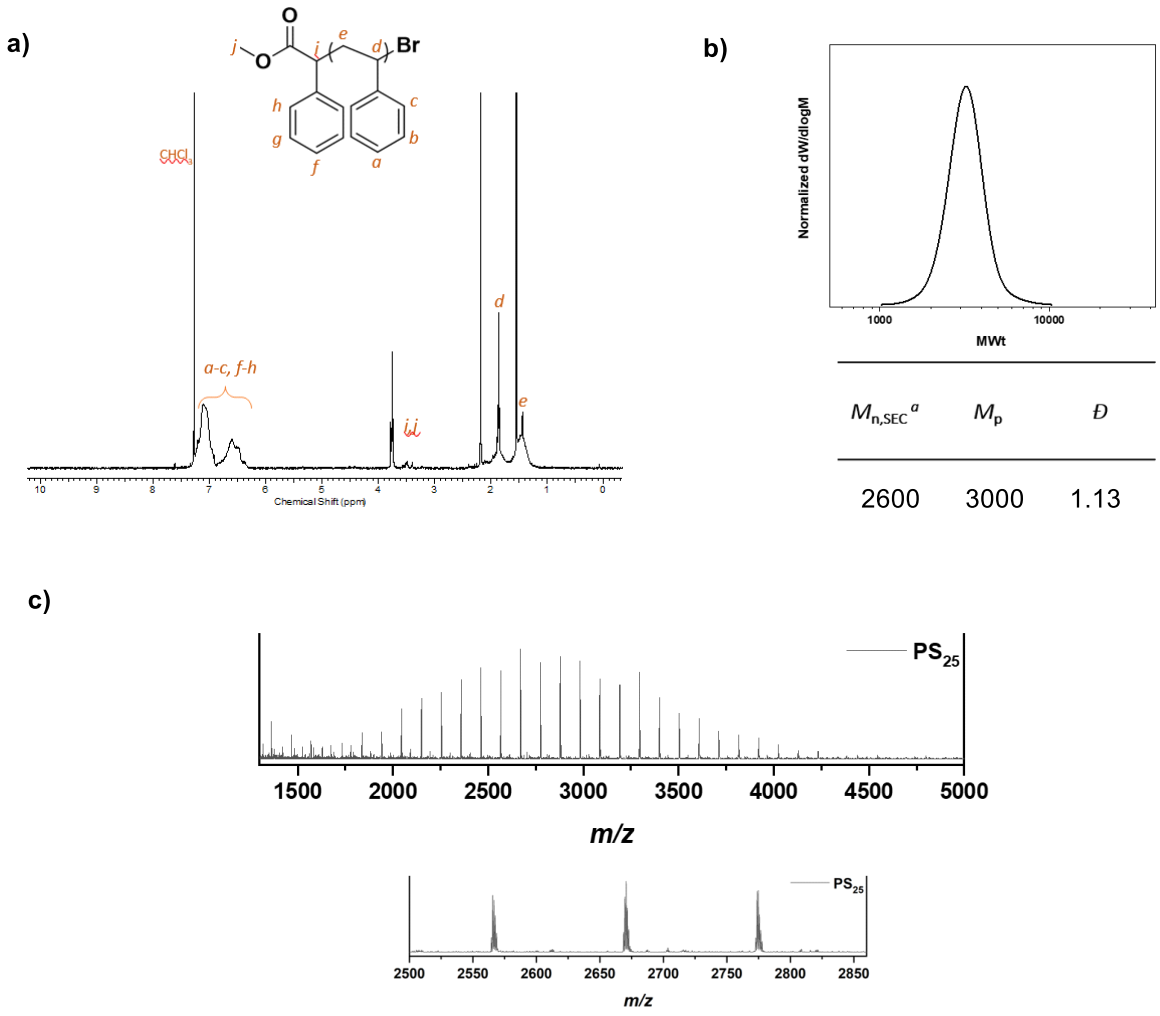
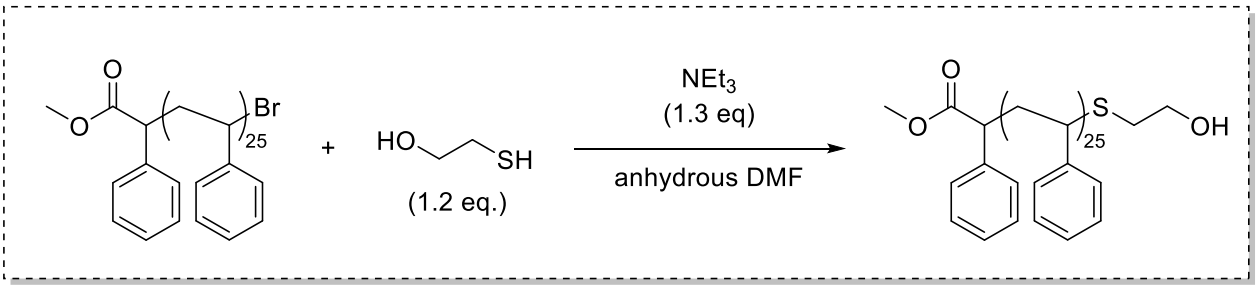


Figure S2: [1]H-NMR, SEC and MALDI-ToF of PS_{25}.

Polystyrene-OH terminated with mercaptoethanol



Scheme S7: Post modification of Br-ending PS_{25} with mercaptoethanol.

The synthesis was adapted from a literature procedure.[3] Bromine-terminated PS_{25} (2.60 g, 1 eq.), 2 mercaptoethanol (144 mg, 2 eq.), triethylamine (121 mg, 1.3 eq.) and dry DMF (2 mL) were all added in a sealed vial and the reaction was left to proceed overnight for approximately 12 hours. The dimethylformamide and triethylamine were removed by an aqueous workup. In the first extraction the entire reaction solution was added dropwise to 20 mL of aqueous NaOH (1M) and 20 mL of ethyl acetate were subsequently added in the vial. After shaking the organic layer was isolated and

injected into a second aliquot of 20 mL of aqueous NaOH (1 M). In an identical manner two more extractions were conducted, first one with aqueous HCl (1 M) and the second one with brine. The organic layer was collected, dried over anhydrous $MgSO_4$ and the volatiles were removed via rotary evaporation. The final product is a white powder.

Yield: 2.30 g white powder (88.5 %).

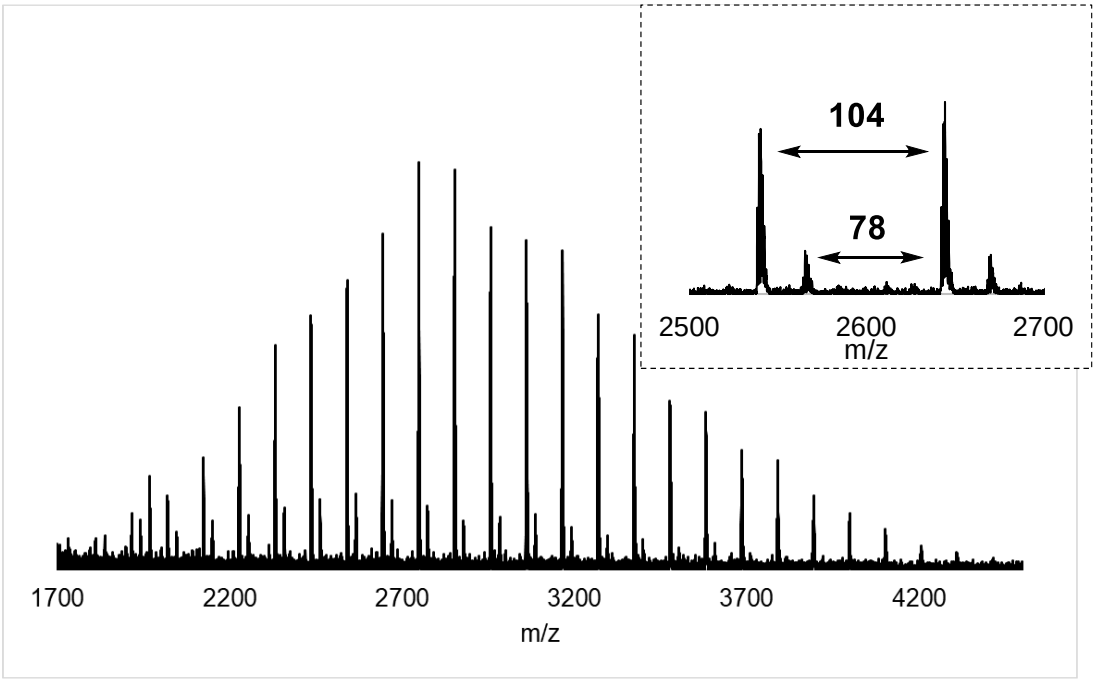
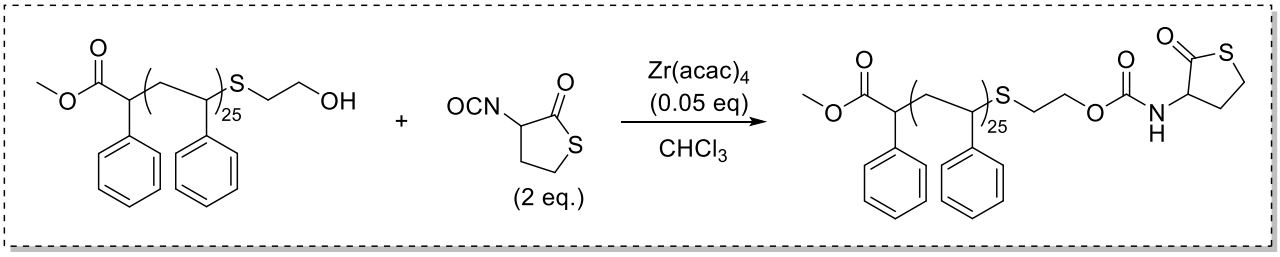


Figure S3: MALDI-ToF of OH-terminated PS_{25} with mercaptoethanol.

104 Da is the difference between two styrene units and 78 Da is the difference between starting bromine terminated PS_{25} and hydroxy-terminated PS_{25}.

Tla-functionalised Polystyrene Soluble Support



Scheme S8: Synthesis of Tla-functionalised PS_{25}.

Hydroxy-terminated PS_{25} (2.20 g, 0.780 mmol, 1 eq.), $Zr(acac)_4$ (0.05 eq.) and $CHCl_3$ were added in a two necks 50 mL round bottom flask under controlled argon atmosphere. Then Tla-NCO (222 mg, 2 eq.) was added under stirring in the solution. The product is purified with a precipitation in cold methanol twice and recollected in the form of a white powder, which then was dried in a vacuum oven.

Yield: 2.1 g white powder (90.1 %):

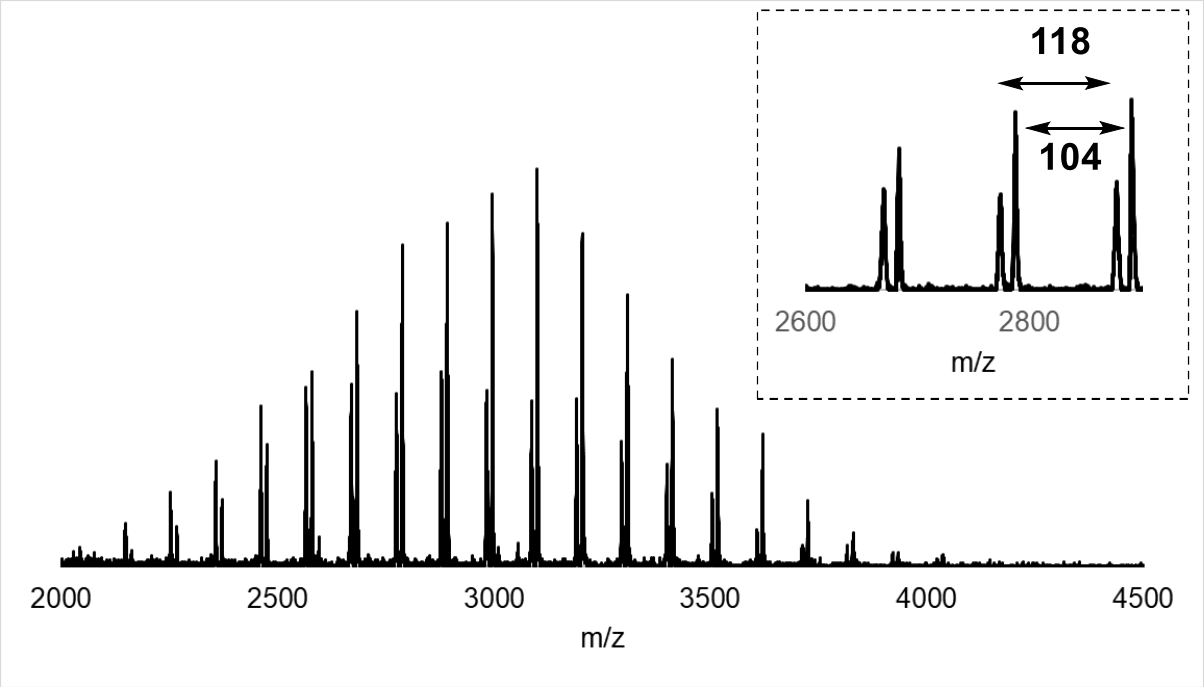
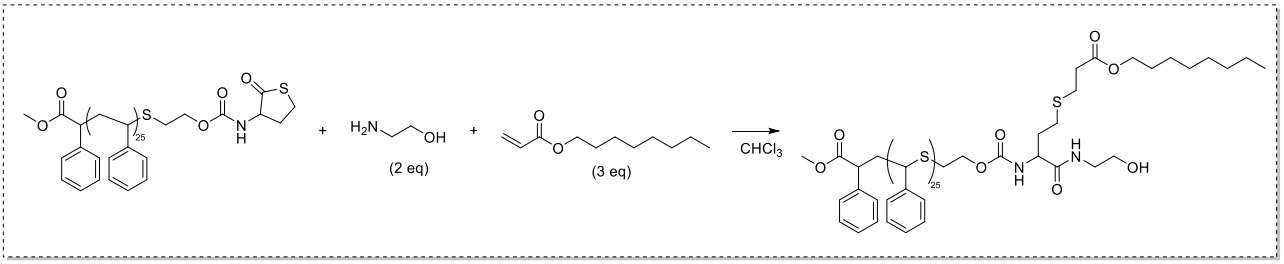


Figure S4: MALDI-ToF of Tla-functionalised PS_{25}.

104 Da is the difference between two styrene units and 118 Da is the difference between starting hydroxy-terminated PS_{25} and Tla-terminated PS_{25}.

1-mer on Tla-Polystyrene Soluble Support



Scheme S9: Coupling of first monomer (octyl acrylate) on PS_{25}.

Tla-terminated PS_{25} (2 g, 0.672 mmol, 1 eq.) was placed in a vial under constant stirring in inert argon atmosphere and dissolved in 3.8 mL of $CHCl_3$ (0.175 M, see Tla protocol with soluble support). Then octyl acrylate (371 mg, 2.02 mmol, 3 eq.) is added followed by ethanolamine (82.18 mg, 1.35 mmol, 2 eq.). The reaction is left under constant stirring for 2 hours and the conversion is checked via MALDI. The product is precipitated in cold methanol, washed through the filter with additional methanol and the white powder obtained is left to dry in a vacuum oven at 40 ° C.

Yield: 2.1 white solid (97 %)

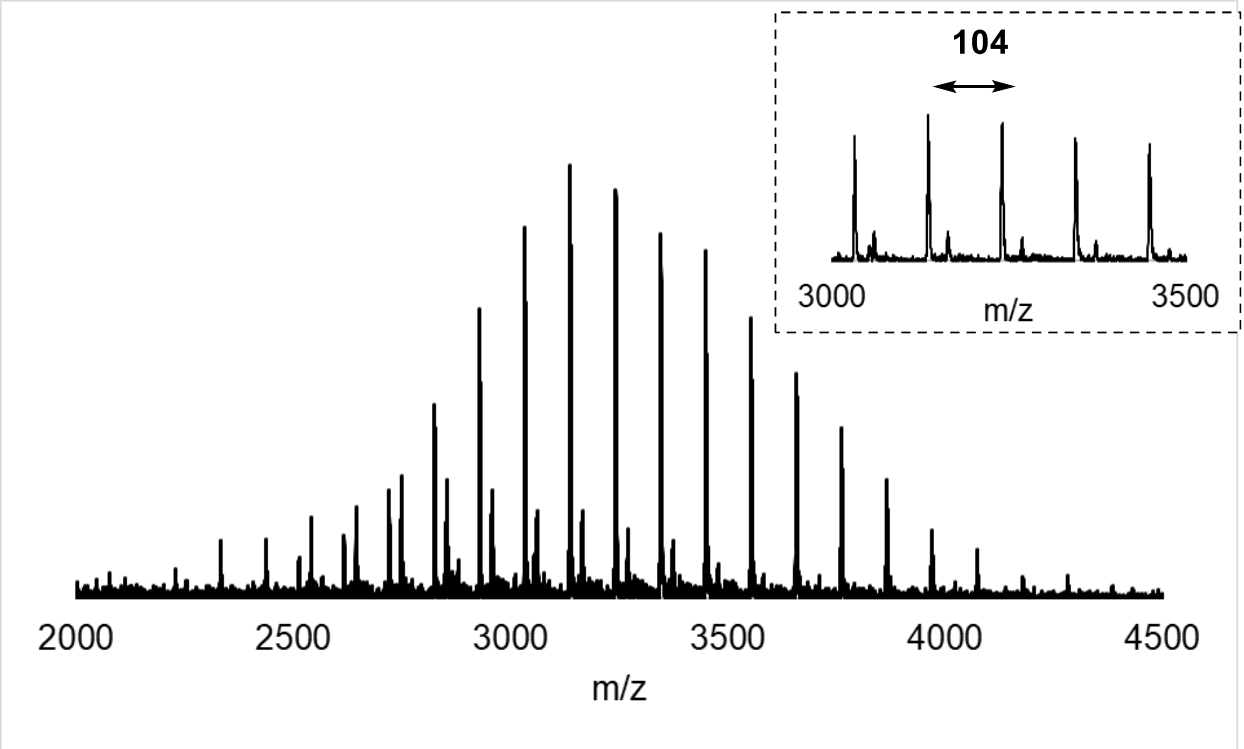


Figure S5: MALDI-TOF of the 1-mer grown on the PS_{25}.

C. Synthesis of an 8-mer using a non-cleavable Soluble Support

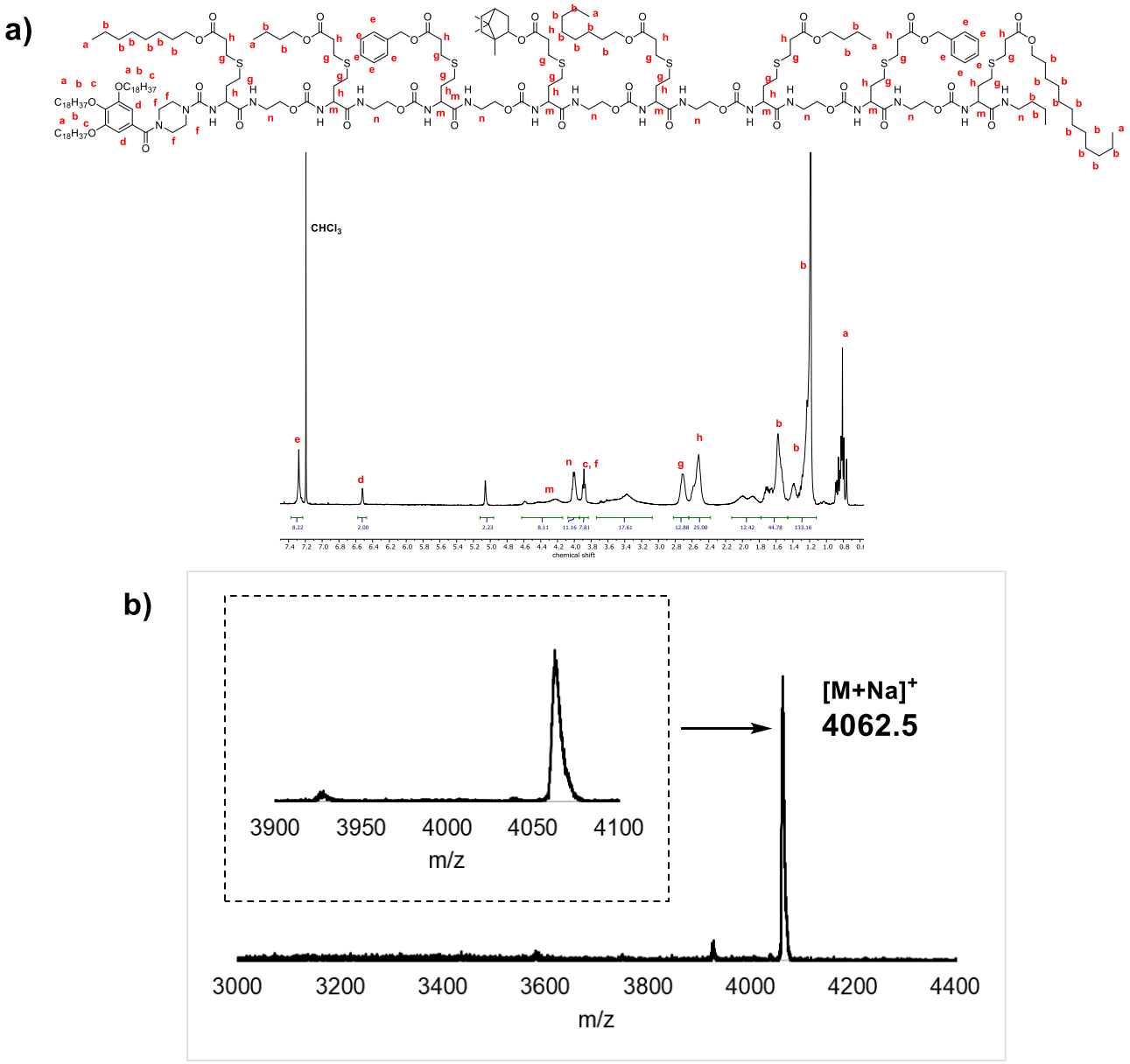
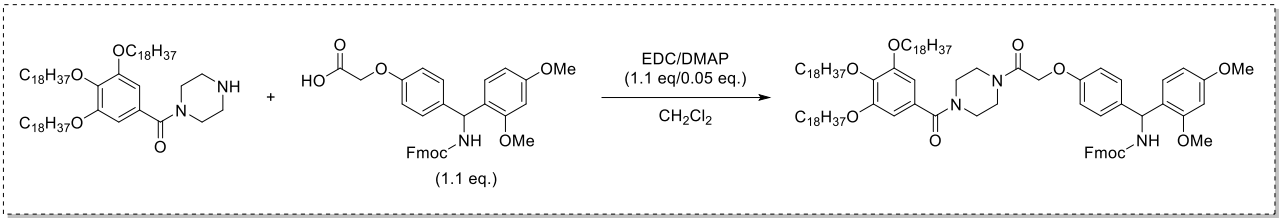


Figure S6: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of sequence-defined octamer synthesised with thiolactone protocol using: 1mer octyl acrylate, 2mer butyl acrylate, 3mer benzyl acrylate, 4mer isobornyl acrylate, 5mer octyl acrylate, 6mer butyl acrylate, 7mer benzyl acrylate, 8mer dodecyl acrylate.

D. Synthesis of Rink Amide Soluble Support

Fmoc-(4-(amino(2,4-dimethoxyphenyl)methyl)phenoxy)-1-(4-(3,4,5-tris(octadecyloxy)benzoyl)piperazin-1-yl)ethan-1-one



Scheme S10: Synthesis of Rink amide Fmoc protected soluble support.

In a 250 mL two-neck flask, (10 g, 10.4 mmol, 1 eq.), Fmoc-protected Rink amide linker (5.96 g, 11.05 mmol, 1.1 eq.) and DMAP (0.05 eq.) were added and placed under an inert atmosphere. Subsequently, anhydrous dichloromethane (100 mL) was added to the flask and the mixture was stirred until the compounds were fully dissolved. The reaction is cooled down to 0°C and next, EDC (2.21 g, 11.05 mmol, 1.1 eq.) is dissolved in 5 mL of dichloromethane and transferred into the reaction mixture dropwise. The reaction is allowed to reach room temperature. After stirring for 2 hours under inert atmosphere, the conversion was checked via MALDI before the product was precipitated in cold methanol. The residue was isolated by filtration and washed with additional methanol, before it was dried in a vacuum oven, yielding the pure product as a white powder.

Yield: 8.71 g white powder (98.7 %).

MW: 1517.27 g/mol

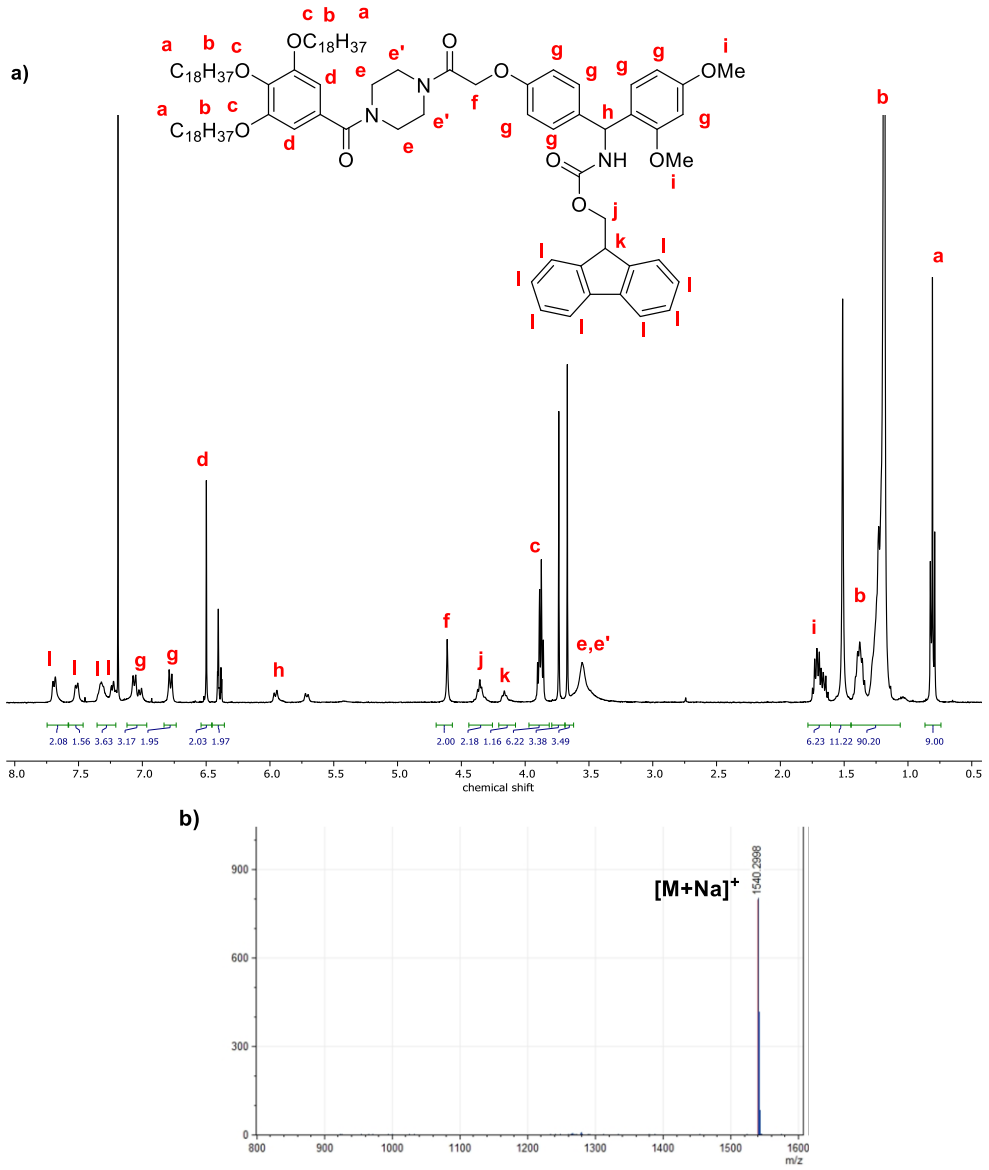
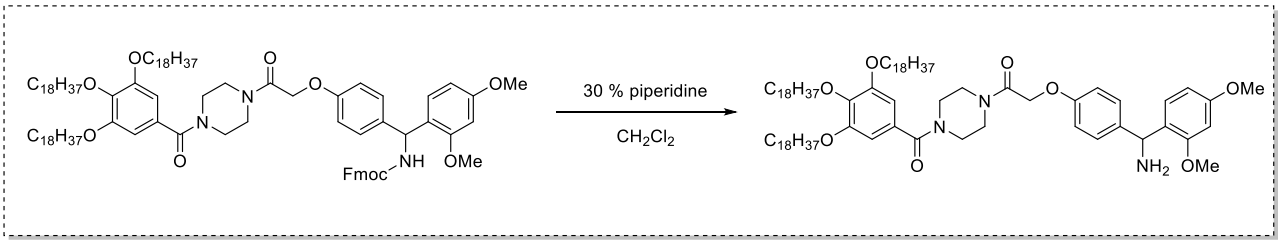


Figure S7: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of Rink amide Fmoc protected soluble support.

2-(4-(amino(2,4-dimethoxyphenyl)methyl)phenoxy)-1-(4-(3,4,5-tris(octadecyloxy)benzoyl)piperazin-1-yl)ethan-1-one



Scheme S11: Synthesis of Rink amide soluble support.

Fmoc-(4-(amino(2,4-dimethoxyphenyl)methyl)phenoxy)-1-(4-(3,4,5-tris(octadecyloxy)benzoyl)piperazin-1-yl)ethan-1-one (12.20 g, 8.05 mmol, 1 eq.) is dissolved in a solution of 70 mL of dichloromethane. After complete dissolution, 30 mL of piperidine is added under continuous stirring. The reaction mixture was stirred for 1 hour. Approximately 50 mL of the solution is removed in the rotavap, before the mixture was precipitated in cold methanol. After filtration, the residue was washed with additional cold methanol and subsequently dried in a vacuum oven, yielding the product as a white powder.

Yield: 9.96 g of white solid (95.5 %); MW: 1295.03 g/mol

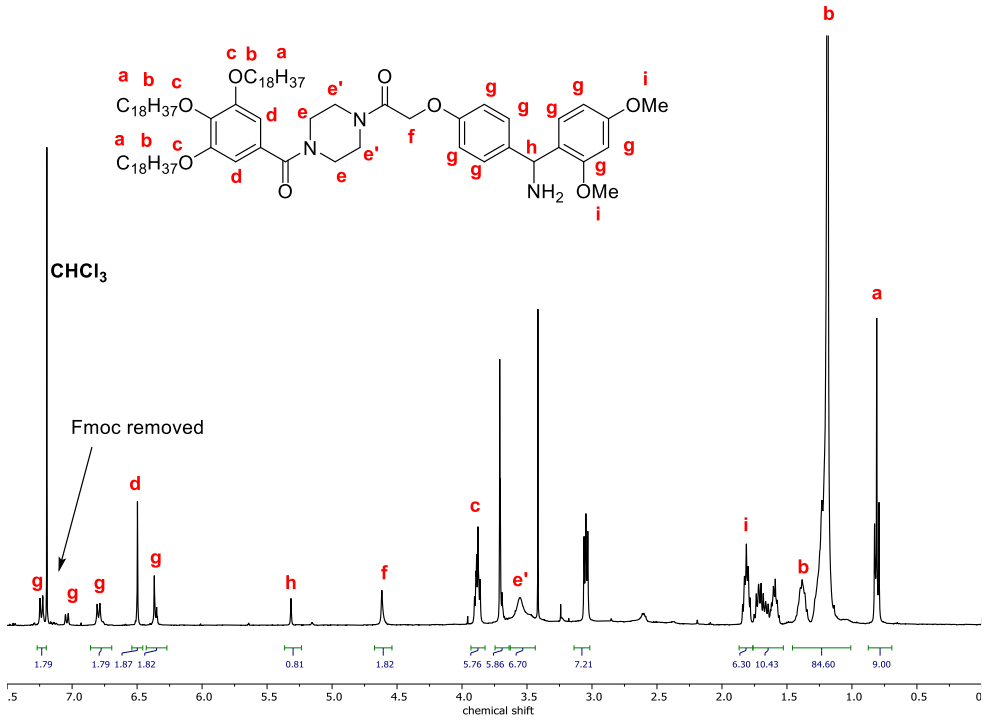
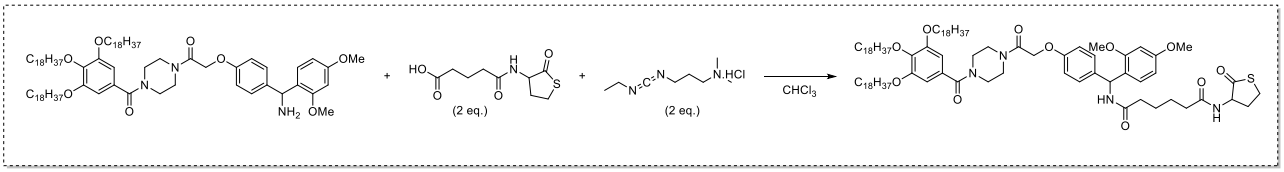


Figure S8: ^{1}H-NMR of Rink amide soluble support.

Tla-Rink amide Soluble Support



Scheme S12: Synthesis of Tla-functionalised Rink amide soluble support.

Rink amide soluble support deprotected in the previous step (9 g, 6.95 mmol, 1 eq.) and COOH-Tla (3.21 g, 13.9 mmol, 2 eq.) were dissolved in 100 mL of chloroform under inert atmosphere (argon). After complete dissolution, EDC (2.66 g, 13.9 mmol, 2 eq.) was dissolved in 5 mL of $CHCl_3$. The reaction mixture is cooled down to 0°C and EDC solution is added dropwise to the reaction under constant stirring. The reaction proceeded for 2 hours at room temperature and conversion was checked via MALDI. Approximately 50 mL of the solvent is removed in vacuo, before the mixture was precipitated in cold methanol. After filtration, the residue was washed with additional cold methanol and subsequently dried in a vacuum oven, yielding the product as a white powder.

Yield: 10.1 g white solid (96.6 %);

MW: 1508.28 g/mol

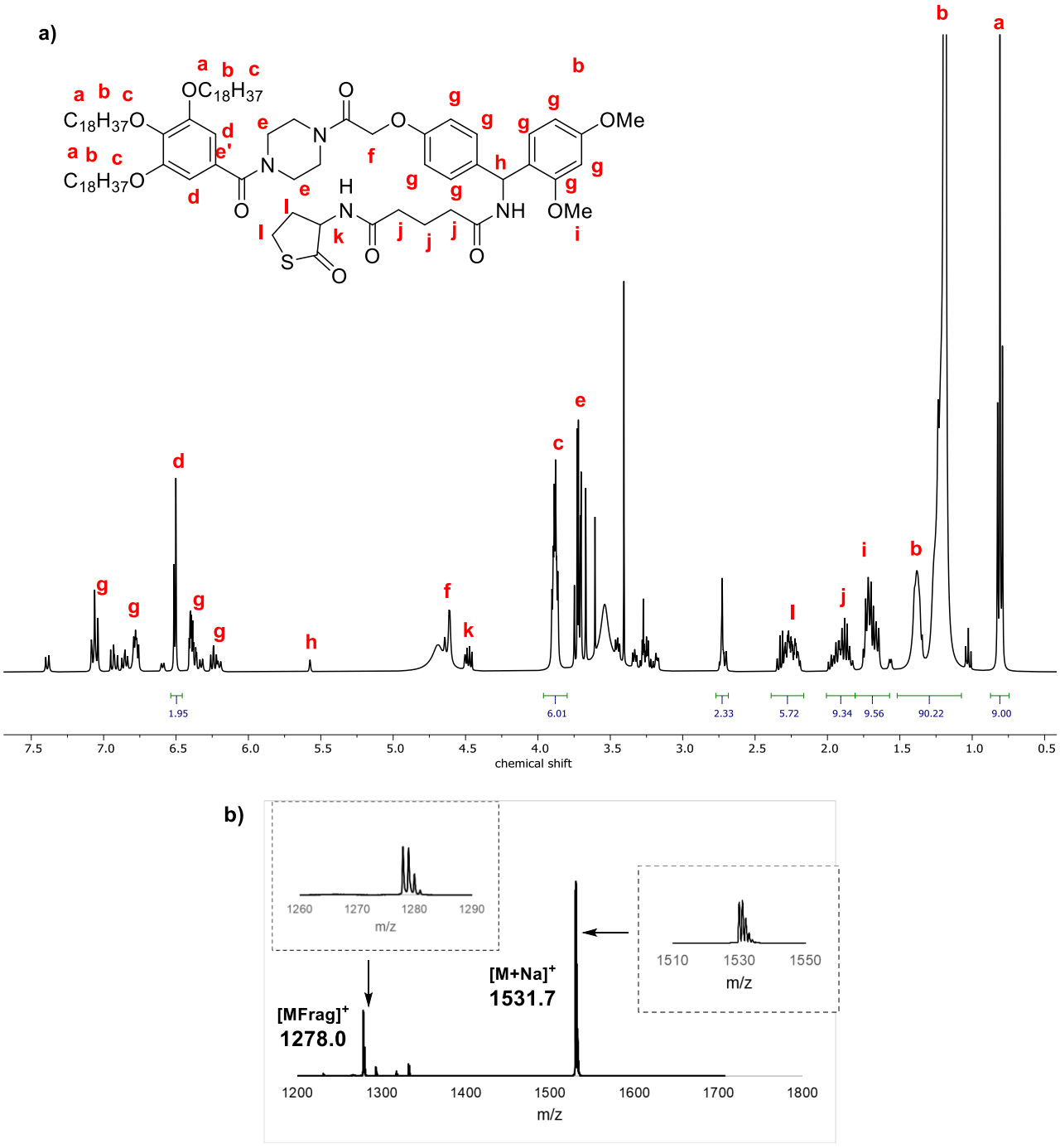
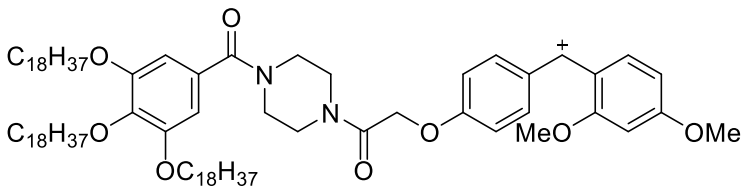


Figure S9: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of Tla-functionalised Rink Amide Soluble Support.

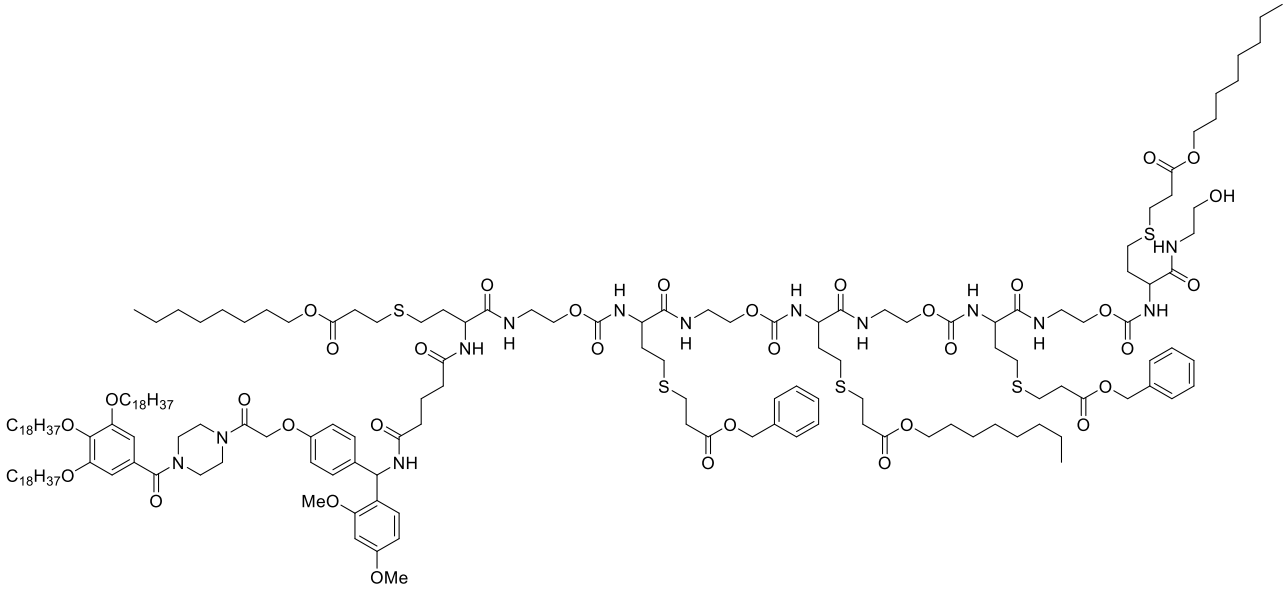
Product of ionisation with MALDI laser.



Exact Mass: 1278.04

E. Synthesis of a 5-mer on Rink Amide Soluble Support

Pentamer alternated octyl-benzyl on Rink Amide Soluble Support



Exact Mass: 3260.96

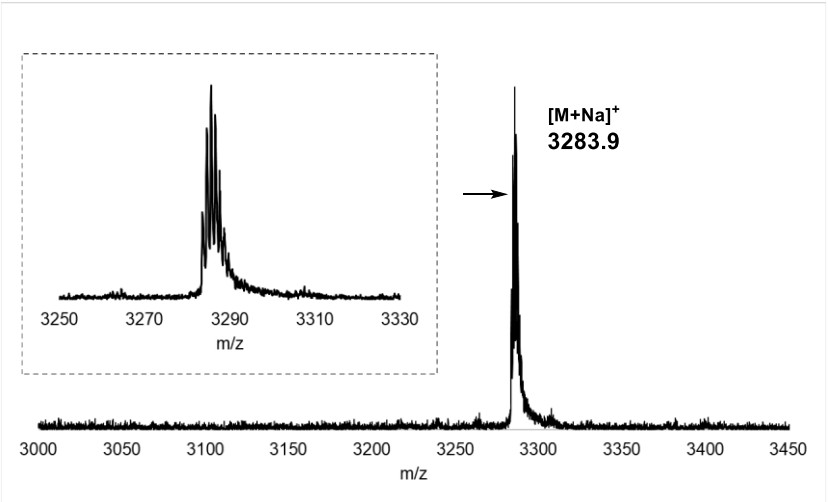
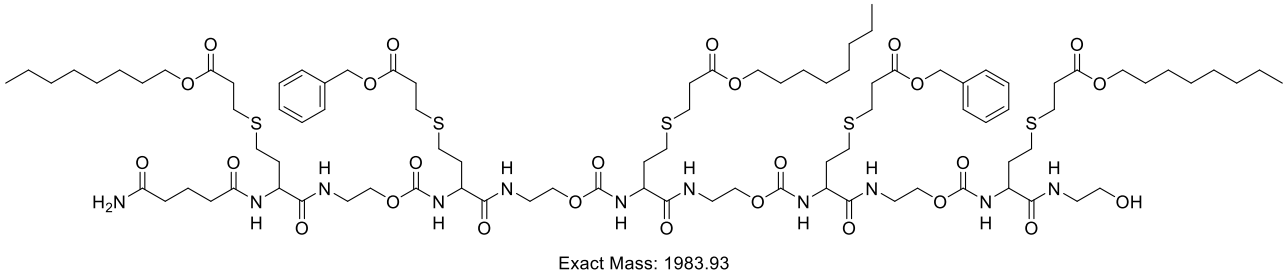


Figure S10: Structure and MALDI-ToF of sequence-defined pentamer with octyl and benzyl acrylate alternated on Rink Amide Soluble Support.

Cleavage pentamer

The pentamer is cleaved from the Rink Amide support with a solution of 10 % TFA in CH_2Cl_2 for 1 h. The volume is reduced to half with rotavap and precipitated in ethanol. The solid is filtrated and the solution containing the sequence-defined pentamer is collected after which the solvent is evaporated.

Structure:



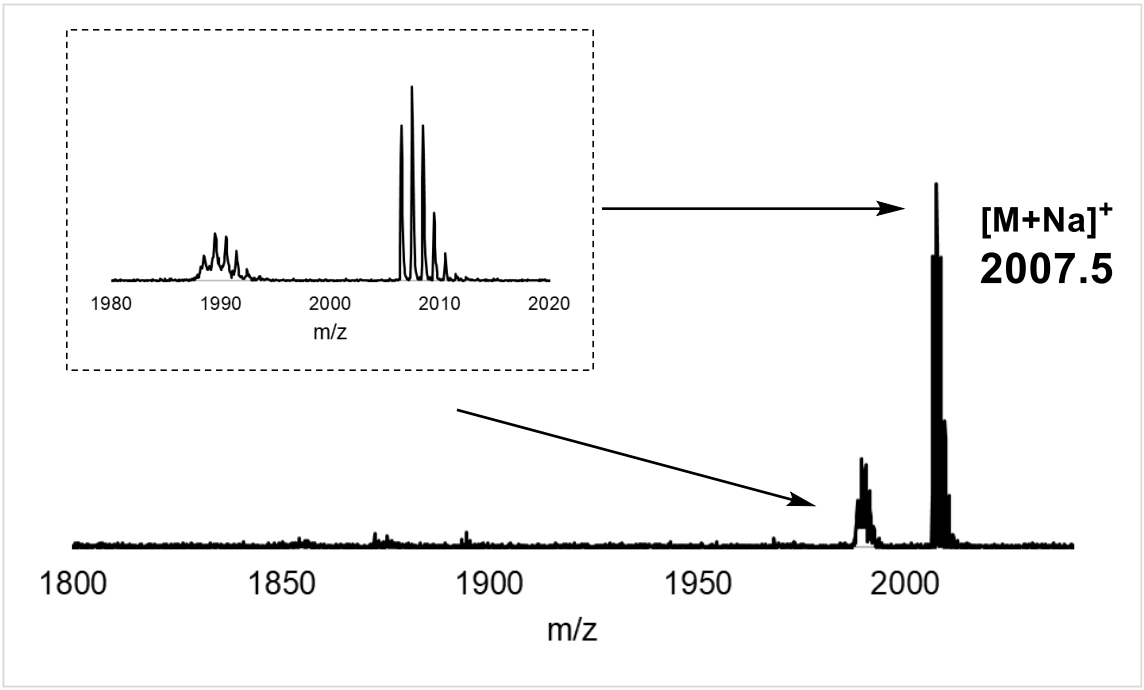
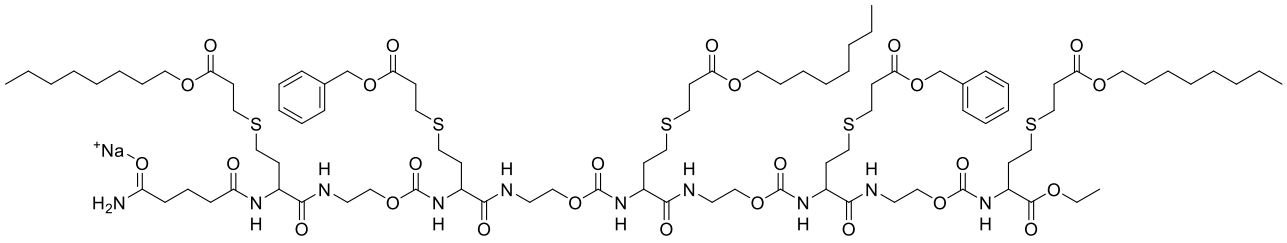


Figure S11: MALDI-ToF of sequence-defined pentamer after cleavage from Rink Amide Soluble Support with 10 % TFA in CH_2Cl_2 for 1 h.

Byproduct from MALDI:

Ring opening of thiolactone with ethanol (used for precipitation)

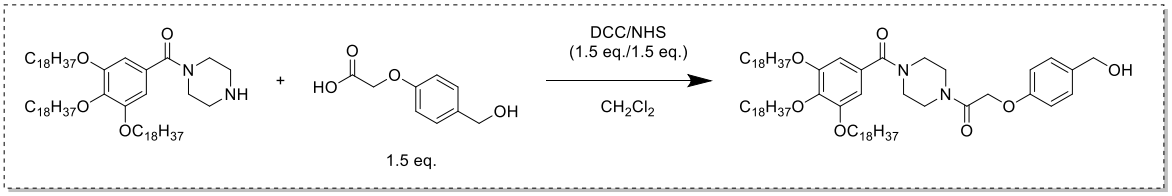


Exact Mass: 1991.91

The formation of this byproduct occurred when there was still methanol present (from the precipitation) during the next ring-opening step of the thiolactone. Under these basic conditions, methanol effectively competed with ethanolamine for the ring opening of the thiolactone. It should be noted that this side-reaction was only observed during basic conditions, and never during the precipitation step itself. Therefore, this unwanted reaction could be avoided by thoroughly drying the support-attached product after precipitation.

F. Synthesis of HMPA Soluble Support

2-(4-(hydroxymethyl)phenoxy)-1-(4-(3,4,5-tris(octadecyloxy)benzoyl)piperazin-1-yl)ethan-1-one



Scheme S13: Synthesis of HMPA Soluble Support.

In a 250 mL two-neck flask (10 g, 10.4 mmol, 1 eq), HMPA (2.74 g, 15.06 mmol, 1.5 eq.) and NHS (1.73 g, 15.06 mmol, 1,5 eq.) were added and placed under an inert atmosphere. Subsequently, anhydrous dichloromethane (100 mL) was added to the flask and the mixture was stirred until the compounds were fully dissolved. The reaction is cooled down to 0°C and next, DCC (3.11 g, 15.06 mmol, 1.5 eq.) is dissolved in 5 ml of dichloromethane and transferred into the reaction mixture dropwise. The reaction is allowed to reach room. After stirring for 2 hours under inert atmosphere, the conversion was checked via MALDI before the product was precipitated in cold methanol. The residue was isolated by filtration and washed with additional methanol, before it was dried in a vacuum oven, yielding the pure product as a white powder.

Yield: 11.2 g of white powder (96.2 %)

Mw: 1159.86 g/mol

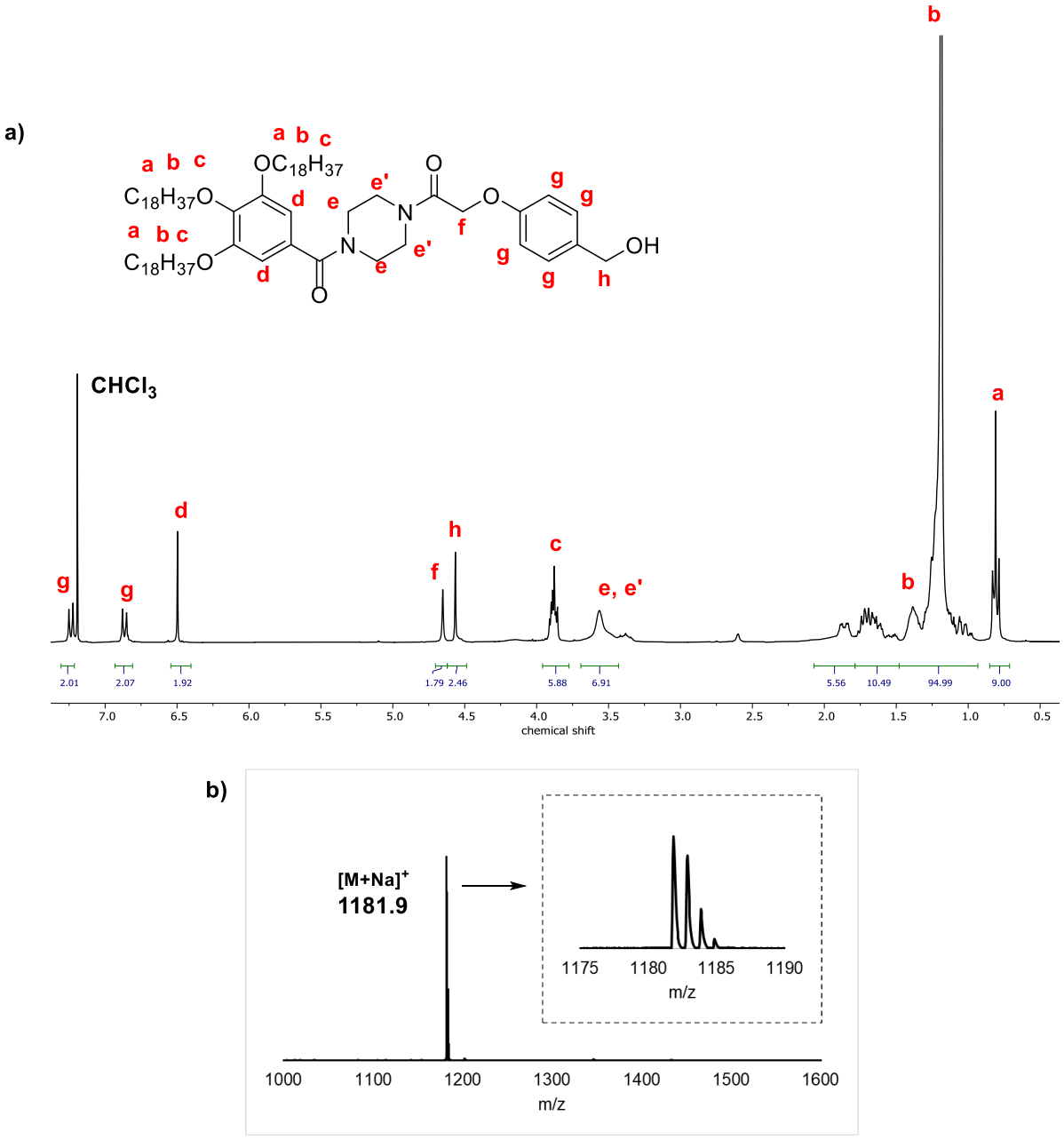
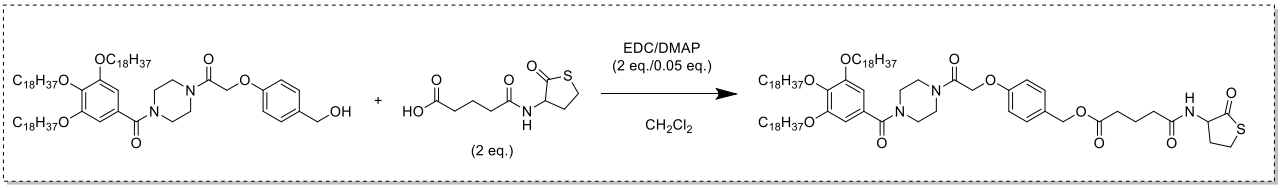


Figure S12: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of HMPA Soluble Support.

Tla-HMPA Soluble Support



Scheme S14: Synthesis of Tla-functionalised HMPA Soluble Support.

HMPA Soluble Support synthesised in the previous step (11 g, 9.48 mmol, 1 eq), COOH-Tla (4.39 g, 18.97 mmol, 2 eq) and DMPA (57.93 mg, 0,47 mmol, 0.05 eq), were dissolved in 100 mL of chloroform under inert atmosphere (argon). After complete dissolution, EDC (2.94 g, 18.97 mmol, 2 eq) was dissolved in 5 mL of $CHCl_3$. The reaction mixture is cooled down to 0°C and EDC solution is added dropwise to the reaction under constant stirring. The reaction proceeded for 2 hours at room temperature and conversion was checked via MALDI. Approximately 50 mL of the solvent is removed in vacuo, before the mixture was precipitated in cold methanol. After filtration, the residue was washed with additional cold methanol and subsequently dried in a vacuum oven yielding the product as a white powder.

Yield: 12.00 g of white solid (92 %)

Mw: 1373.11 g/mol

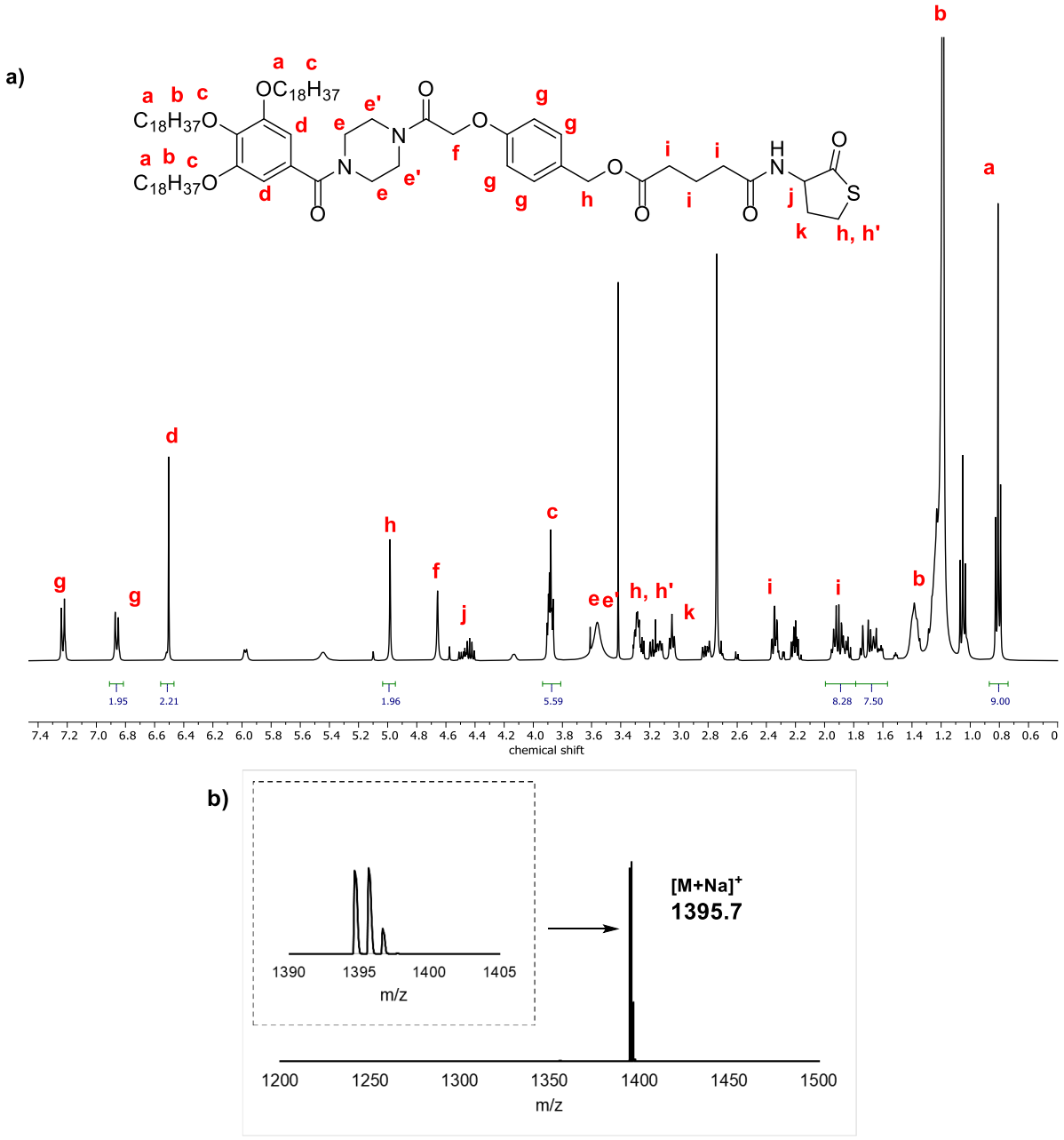


Figure S13: Structure, ^{1}H-NMR (a) and MALDI-TOF (b) of Tla-functionalised Soluble Support.

G. Synthesis of a 6-mer on HMPA Soluble Support'

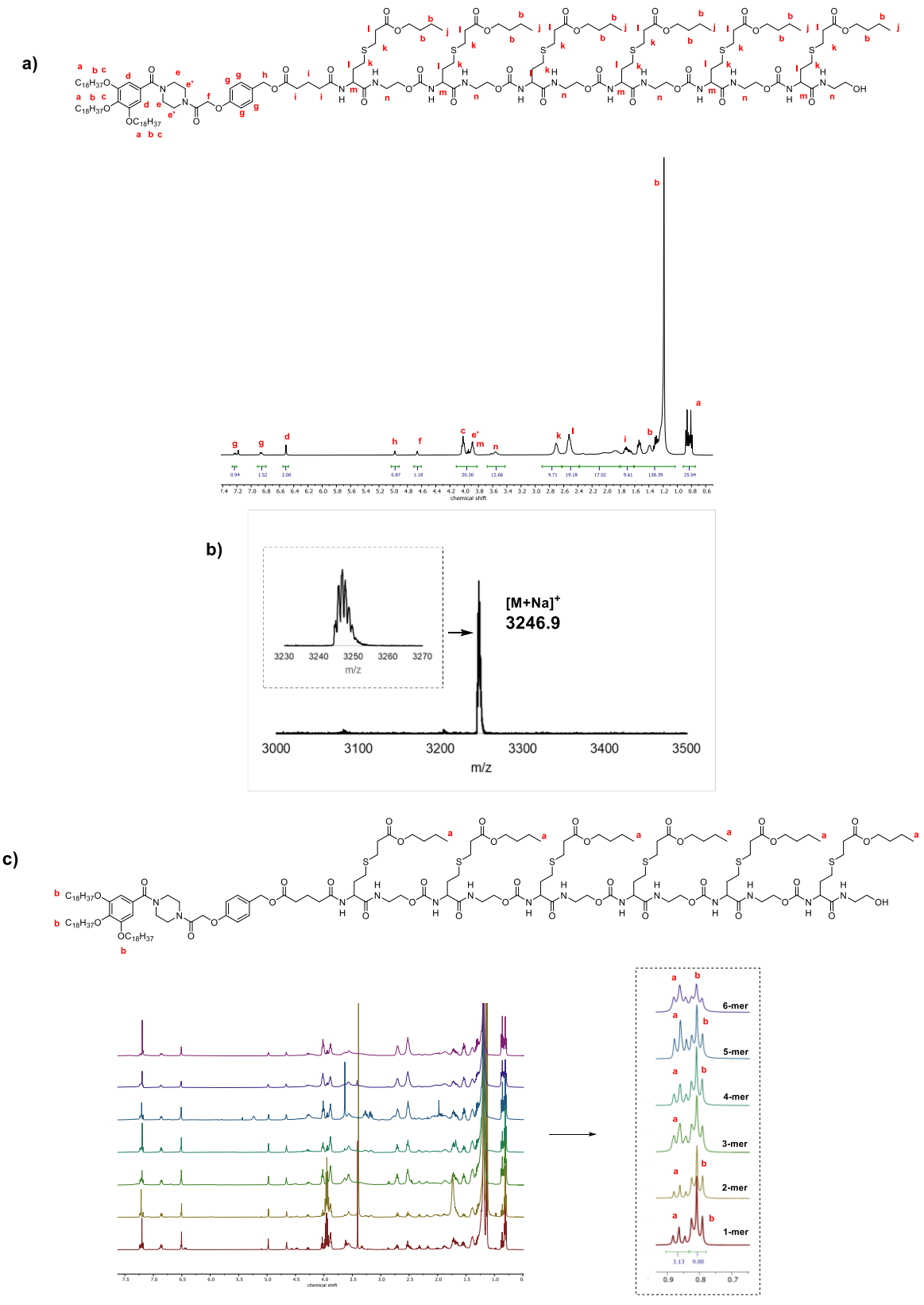


Figure S14: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of Sequence-defined hexamer on HMPA Soluble Support. Evolution after each monomer addition is followed via ^{1}H-NMR (c).

Cleavage of hexamer from HMPA Soluble Support

1st non-ideal cleavage:

40 % TFA in CH_2Cl_2, 1 h precipitated in methanol. Solution phase is collected and evaporated, dried under vacuum.

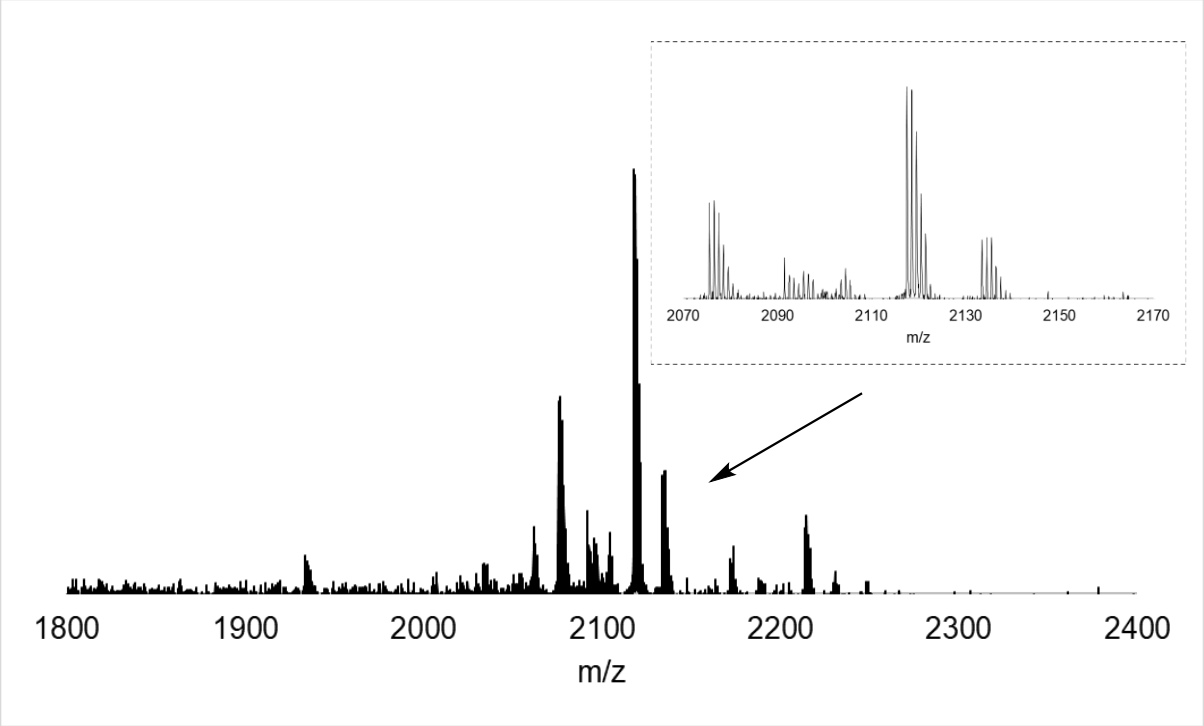
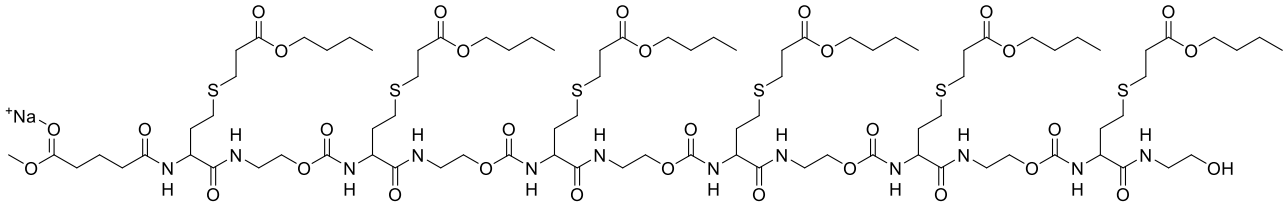


Figure S15: MALDI-ToF of sequence-defined hexamer cleaved from HMPA Soluble Support.

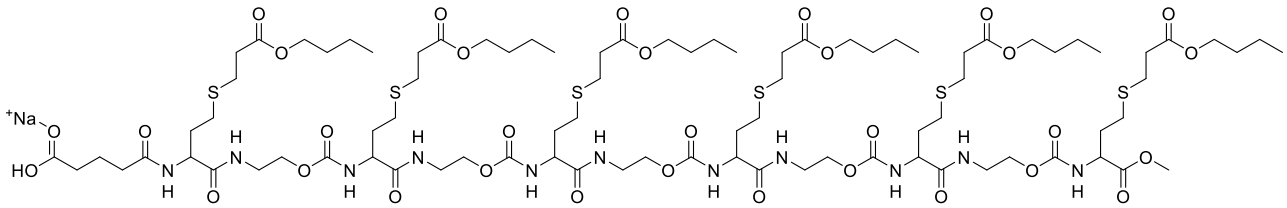
Byproducts shown by MALDI after cleavage.

Methyl ester after cleavage.



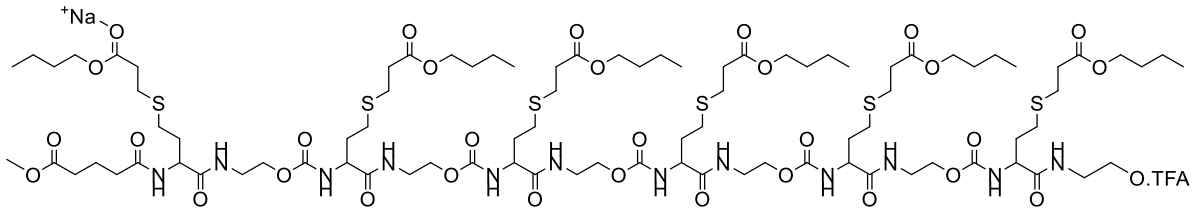
Exact Mass: 2117.90

Methanolysis last thiolactone.



Exact Mass: 2074.86

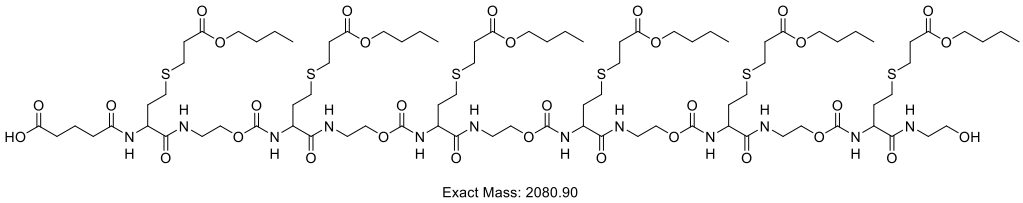
TFA salt final OH and methyl ester.



Exact Mass: 2213.88

2nd optimized cleavage:

40 % TFA in CH_2Cl_2, 1 h. Diluted with water, extracted and collected organic phase. Dried and precipitated in cold IPA to avoid esterification with methanol. Solution phase is collected and the solvent evaporated.



Exact Mass: 2080.90

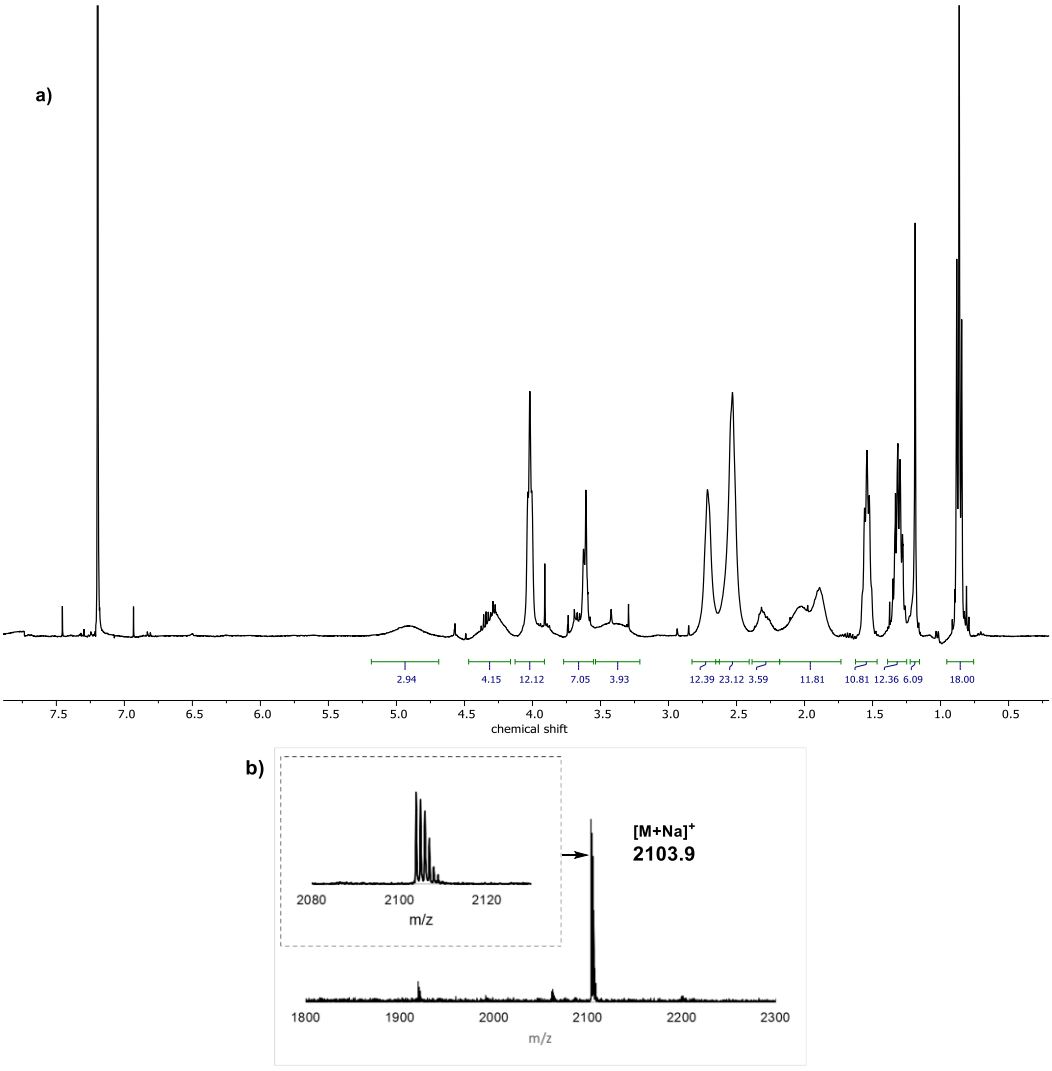
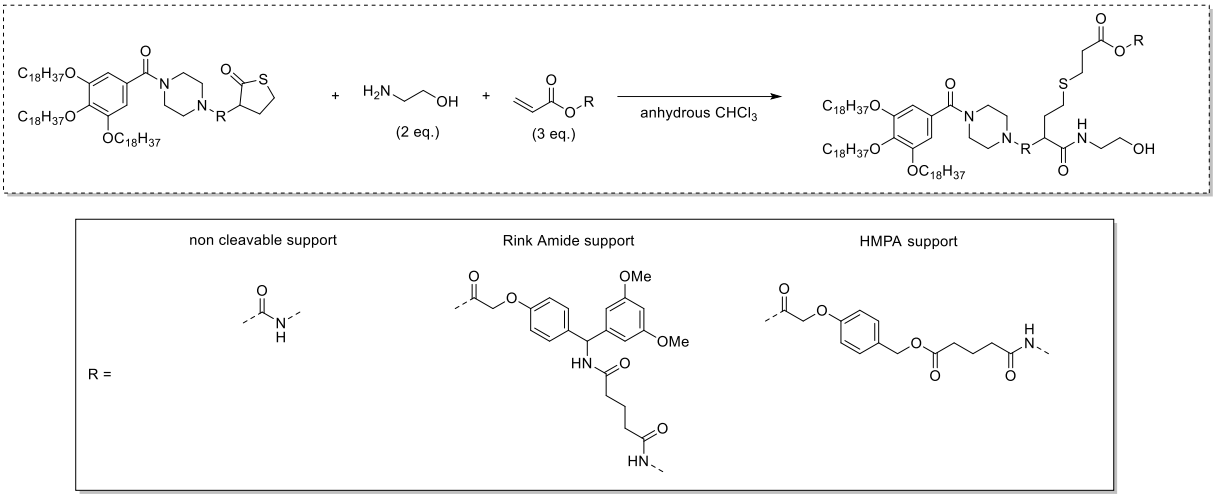


Figure S16: Structure, ^{1}H-NMR (a) and MALDI-ToF (b) of sequence-defined hexamer cleaved from HMPA Soluble Support.

H. Additional: general procedure for synthesis of Tla-based sequence-defined oligomers on Soluble Support

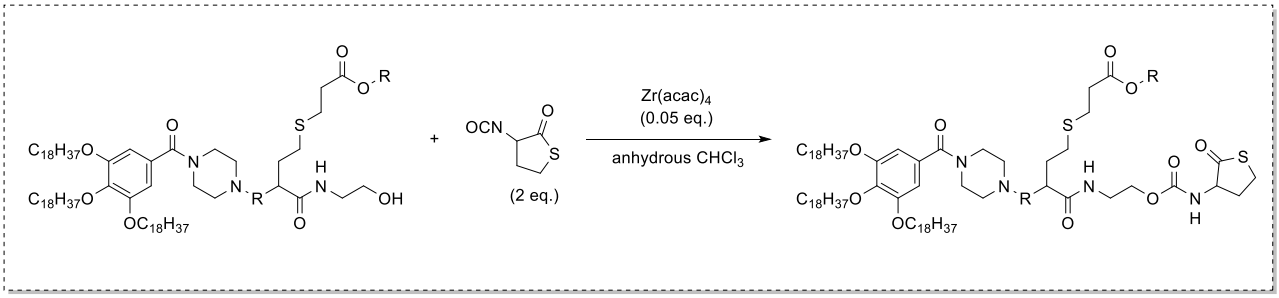
Aminolysis-thiol-ene coupling



Scheme S15: Reaction scheme for aminolysis-thiol-ene coupling in thiolactone protocol with three different supports.

The soluble support (non-cleavable, Rink Amide or HMPA 1 eq.) is placed in a 250 mL round bottom flask with two necks, dissolved in anhydrous $CHCl_3$ with an average concentration of 0.175 M and left stirring under Argon atmosphere. Then acrylate (2 eq.) was added in the stirring solution followed by ethanolamine (3 eq.). The reaction is left stirring for 2 hours for non-cleavable support and for HMPA support, 4 hours for Rink Amide support, and the conversion is checked via MALDI When the reaction is finished, almost half of the solvent is evaporated in the rotavap and the reaction mixture is precipitated in cold IPA, allowing the recovery of the product attached to the soluble support in the form of a white powder. The product is washed through the filter with additional IPA and is dried in a vacuum oven at 40 °C.

Chain extension with Tla-NCO



Scheme S16: Reaction scheme for chain extension with Tla-NCO with thiolactone protocol.

The soluble support (non-cleavable, Rink Amide or HMPA 1 eq.) and $Zr(acac)_4$ (0.05 eq.) were placed in a 250 mL round bottom flask with two necks, dissolved in anhydrous $CHCl_3$ with an average

concentration of 0.175 M and left stirring under Argon atmosphere. Then Tla-NCO (1.2 eq.) was added in the stirring solution. The reaction is left stirring for 2 hours non-cleavable and HMPA support, for 4 hours for Rink Amide support, and the conversion is checked via MALDI. When the reaction is finished, almost half of the solvent is evaporated in the rotavap and the reaction mixture is precipitated in cold IPA, allowing the recovery of the product attached to the soluble support in the form of a white powder. The product is washed through the filter with additional IPA and is dried in a vacuum oven at 40 °C.

References

1. Kim, S.; Matsumoto, M.; Chiba, K., Liquid-Phase RNA Synthesis by Using Alkyl-Chain-Soluble Support. *Chemistry a European Journal* **2013,** *19* (26), 8615-8620.
2. Liarou, E.; Whitfield, R.; Anastasaki, A.; Engelis, N. G.; Jones, G. R.; Velonia, K.; Haddleton, D. M., Copper-Mediated Polymerization without External Deoxygenation or Oxygen Scavengers. *Angewandte Chemie International Edition* **2018,** *57* (29), 8998-9002.
3. Anastasaki, A.; Willenbacher, J.; Fleischmann, C.; Gutekunst, W. R.; Hawker, C. J., End group modification of poly(acrylates) obtained via ATRP: a user guide. *Polymer Chemistry* **2017,** *8* (4), 689-697.