# Supporting Information

to

# Solid-phase synthesis of iterative RAFT single unit monomer insertion adducts

Karen Hakobyan,[a] Benjamin B. Noble,[b] Jiangtao Xu[a,*]

[a]School of Chemical Engineering, UNSW Sydney, NSW 2052, Australia; [b]School of Engineering, RMIT University, 2476, Melbourne, Australia

*Email correspondence to j.xu@unsw.edu.au

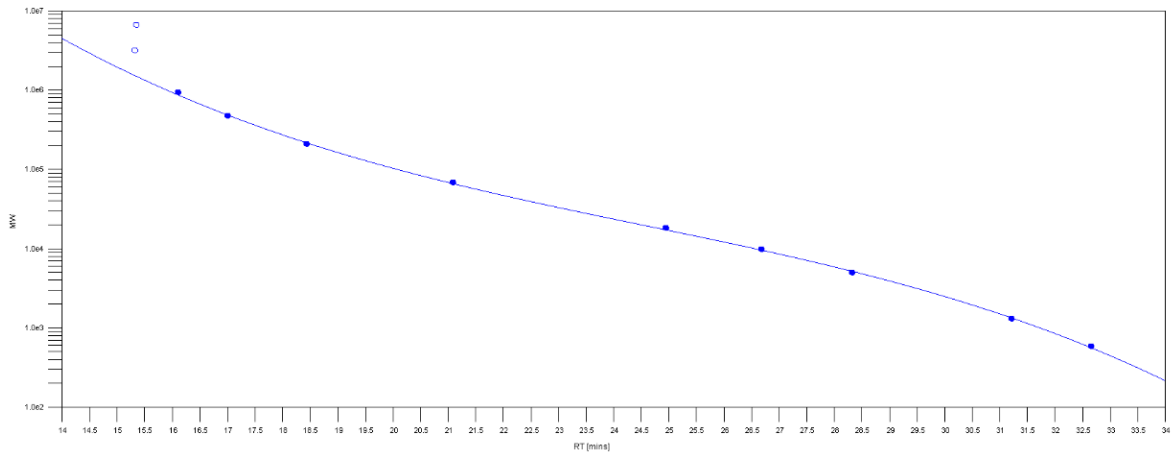
## Table of Contents

# SUPPLEMENTARY METHODS AND MATERIALS

*Solid-phase photochemistry setup*

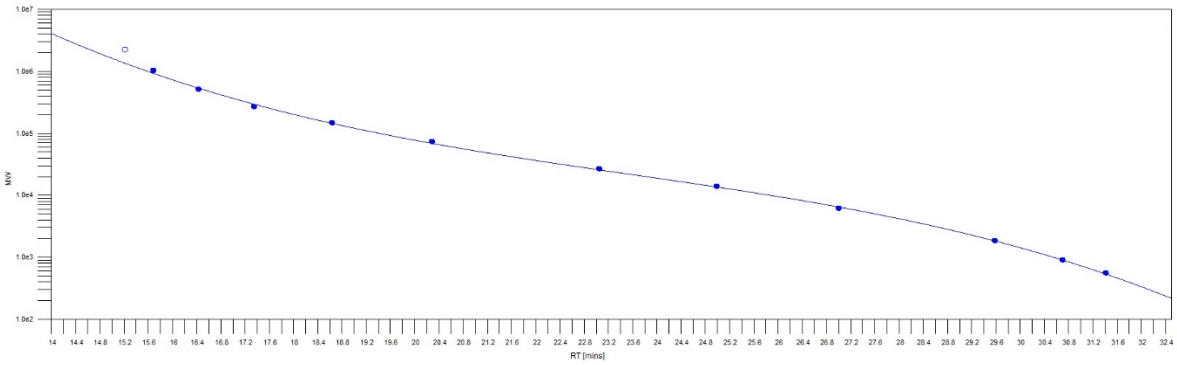

*Gel permeation chromatography (GPC) calibration*

A third order Taylor series ($ax^3+bx^2+cx+d$) was used to model the peak retention time based on the logarithm of the molecular weight calibrated against polystyrene standards. The optimised coefficients ($R^2$= 0.99) were a= - 0.0007195, b= 0.05300, c = - 1.445, d = 18.47




| Peak retention time (min) | $M_p$ (g mol$^{-1}$) | Log($M_p$) | Error (%) |
|---|---|---|---|
| 16.1 | 920000 | 5.9638 | 5.3092 |
| 17.0 | 466300 | 5.6687 | -4.1683 |
| 18.4 | 206000 | 5.3139 | -5.1403 |
| 21.1 | 67600 | 4.8299 | 2.1113 |
| 25.0 | 18000 | 4.2545 | 4.1458 |
| 26.7 | 9800 | 3.9921 | 2.5716 |
| 28.3 | 4900 | 3.6911 | -5.7412 |
| 31.2 | 1300 | 3.1139 | -2.6526 |
| 32.7 | 600 | 2.7634 | 2.8274 |

A third order Taylor series ($ax^3+bx^2+cx+d$) was used to model the peak retention time based on the logarithm of the molecular weight calibrated against poly(methyl methacrylate) standards for the GPC data in Table S5-1. The optimised coefficients ($R^2$= 0.99) were a= -0.001048, b= 0.0742, c = - 1.892, d = 21.43




| Peak retention time (min) | $M_p$ (g mol$^{-1}$) | Log($M_p$) | Error (%) |
|---|---|---|---|
| 15.2 | 2210000 | 6.3444 | 38.9078 |
| 15.7 | 1020000 | 6.0086 | 9.085 |
| 16.4 | 504500 | 5.7029 | -5.8306 |
| 17.4 | 265300 | 5.4237 | -10.8733 |
| 18.6 | 146500 | 5.1658 | 1.2340 |
| 20.3 | 72000 | 4.8573 | 4.3683 |
| 23.1 | 26550 | 4.4241 | 3.1707 |
| 25.0 | 13900 | 4.1430 | 1.9276 |
| 27.0 | 6140 | 3.7882 | -5.5616 |

# SUPPLEMENTARY DATA

## Residual CDTPA from resin loading

Since a large excess of CDTPA is used in the resin loading procedure, it is feasible to isolate the leftover material using the procedure detailed in the Experimental section (Immobilisation of CDTPA onto Rink amide resin).

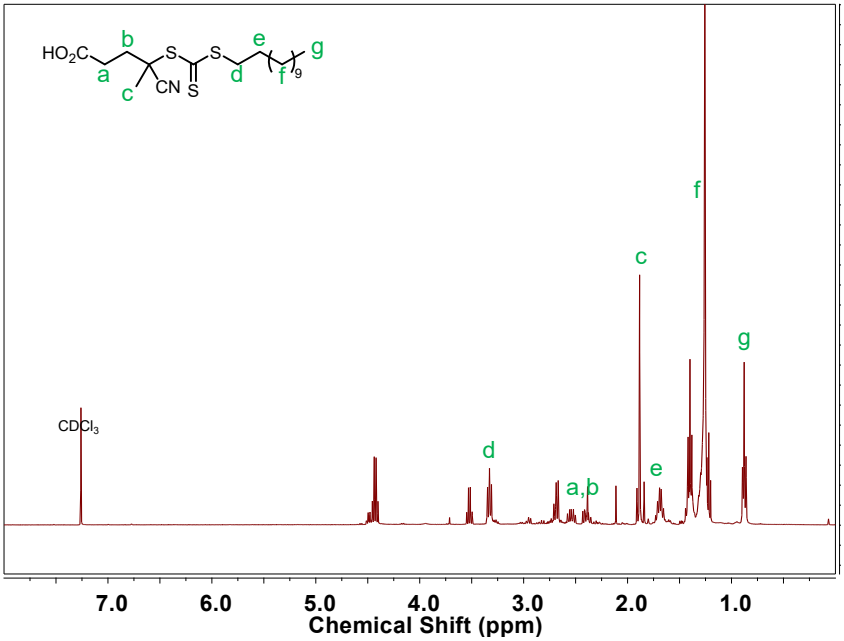



**Figure S1.** $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of CDTPA left over from Rink-amide resin immobilisation conditions.

## First SUMI addition

The NMR spectrum of the product compared well to that of the analogous material prepared under normal solution phase conditions indicating both complete single addition and a pure product (**Figure S2**).

*$^1$H NMR* (400.17 MHz, $CDCl_3$, *δ*) *assignment* 7.33-7.17 (m, 4H), 6.01 (dd, *J* = 11.7, 7.0 Hz, 1H), 3.42 (td, *J* = 13.2, 5.9 Hz, 2H), 3.35-3.30 (m, 1 H) 2.90-2.52 (m, 2 H), 2.28-1.85 (m, 4H), 1.78-1.66 (m, 2H), 1.40 (d, J = 8.3 Hz, 3H), 1.26 (br s, 18H) 0.88 (t, J = 6.8 Hz, 3H)

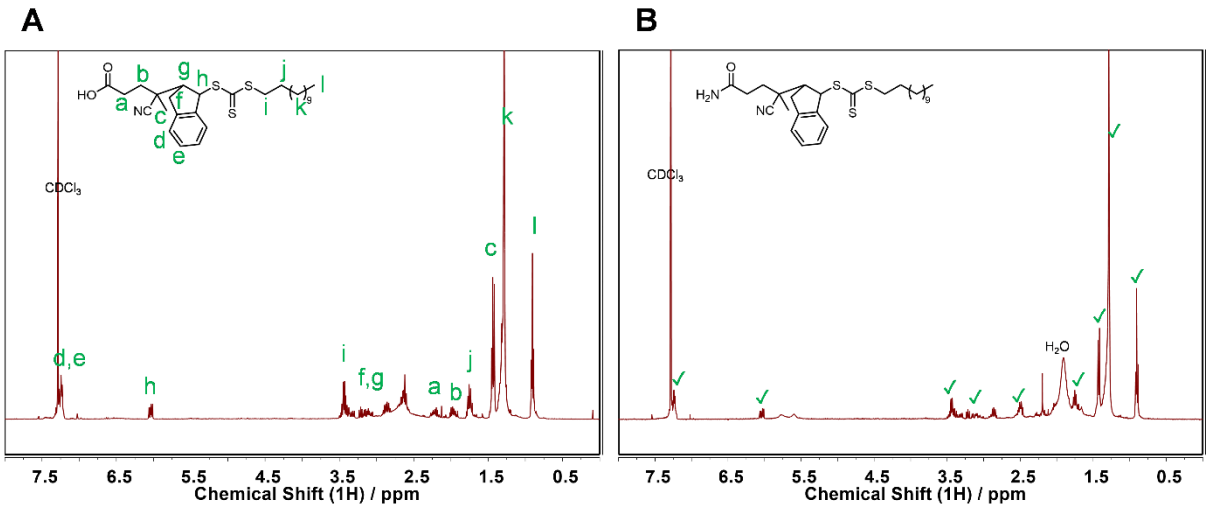
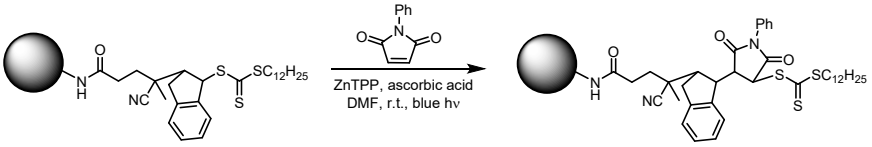



**Figure S2.** $^1$H NMR spectra (400 MHz, $CDCl_3$) of the single-adduct of CDTPA and indene synthesised by solution phase conditions (A) and solid phase conditions (B).

## Reaction conversion data of the 2nd, 3rd, 4th and 5th additions

In contrast with early additions discussed in the main text, conversion data was collected independently and thus showed a slight variation with the data in Table 1.




| Reaction time (h) | Ph-Mal conversion |
|---|---|
| 0 | 0 |
| 3 | 0.21 |
| 6 | 0.41 |
| 9 | 0.47 |
| 16 | 0.55 |

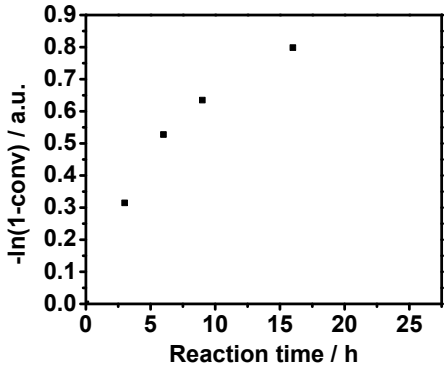
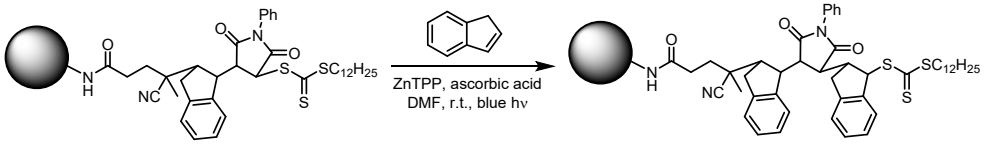



**Figure S3.** Kinetics for the second SUMI addition on-resin with the stoichiometry n(PhMal): n(CDTPA@Rink) = ~2:1.




| Reaction time (h) | Ind conversion |
|---|---|
| 0 | 0 |
| 3 | 0.09 |
| 6 | 0.12 |
| 9 | 0.21 |
| 33 | 0.50 |

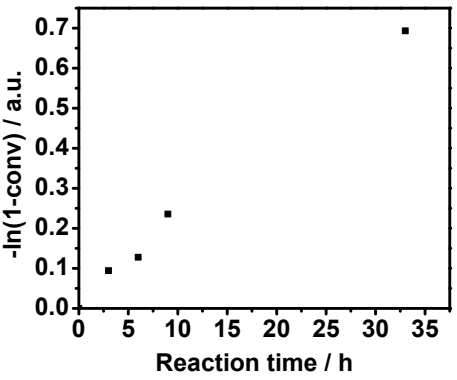
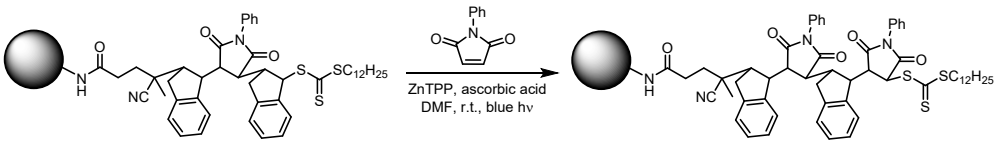



**Figure S4.** Kinetics for the third SUMI addition on-resin with the stoichiometry n(Ind): n(CDTPA@Rink) = ~2:1.




| Reaction time (h) | Ph-Mal conversion |
|---|---|
| 0 | 0 |
| 3 | 0.18 |
| 6 | 0.22 |
| 9 | 0.31 |
| 12 | 0.41 |
| 17 | 0.61 |
| 22 | 0.63 |

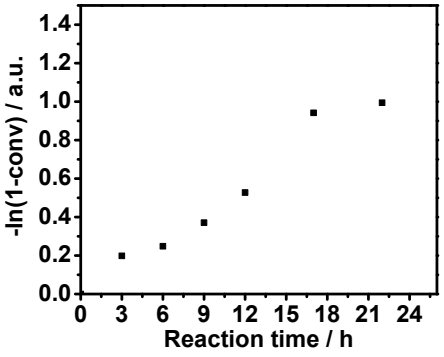
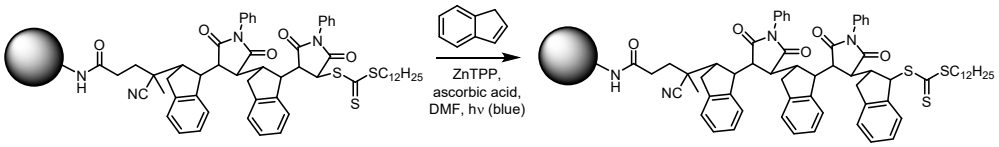



**Figure S5.** Kinetics for the fourth SUMI addition on-resin with the stoichiometry n(PhMal): n(CDTPA@Rink) = ~2:1.




| Reaction time (h) | Ind conversion |
|---|---|
| 0 | 0 |
| 5 | 0.25 |
| 9 | 0.42 |
| 24 | 0.52 |

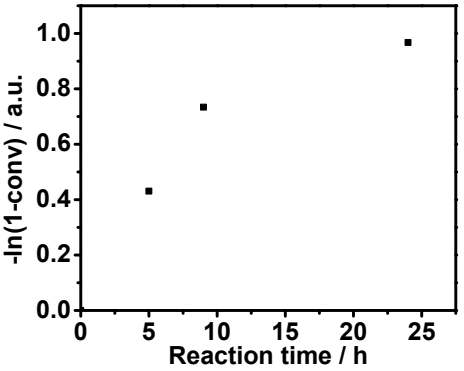



**Figure S6.** Kinetics for the fifth SUMI addition on-resin with the stoichiometry n(Ind): n(CDTPA@Rink) = ~2:1.

## End group analysis by NMR spectroscopy

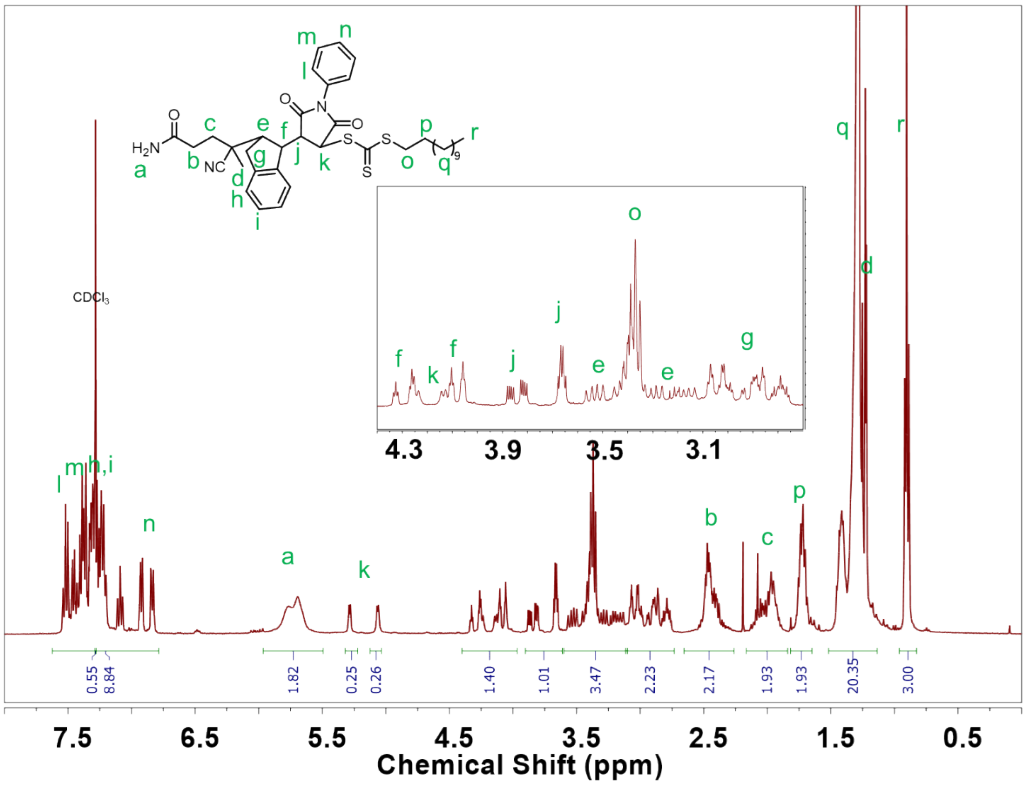



**Figure S7.** $^1$H NMR spectrum (400 MHz, $CDCl_3$) of the apparent 2-mer oligo(indene-*alt*-phenylmaleimide).

Potential evidence of phenylmaleimide multi-addition may be from the resonance at 4.19 ppm (dd, J = 43.6, 6.8 Hz)

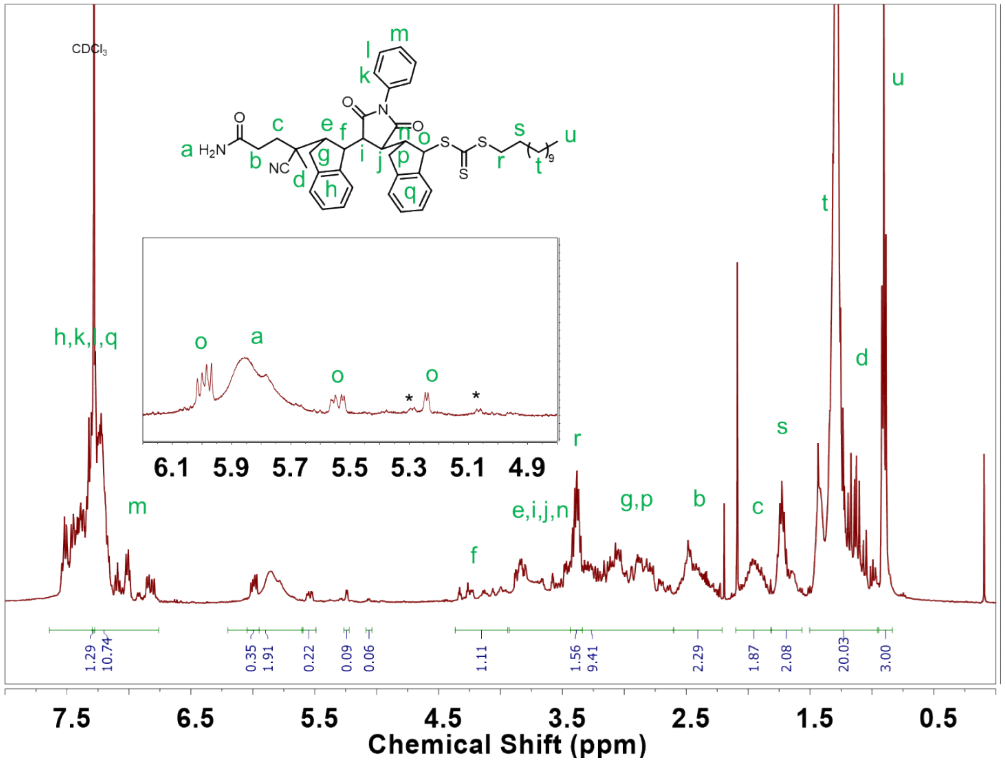



**Figure S8.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of the apparent 3-mer oligo(indene-*alt*-phenylmaleimide) with diagnostic resonances corresponding to the unreacted 2-mer marked with an asterisk.

Evidence for incomplete indene addition can be found from the residual 2-mer terminal unit alpha-proton resonance. This represented <10% remaining 2-mer.

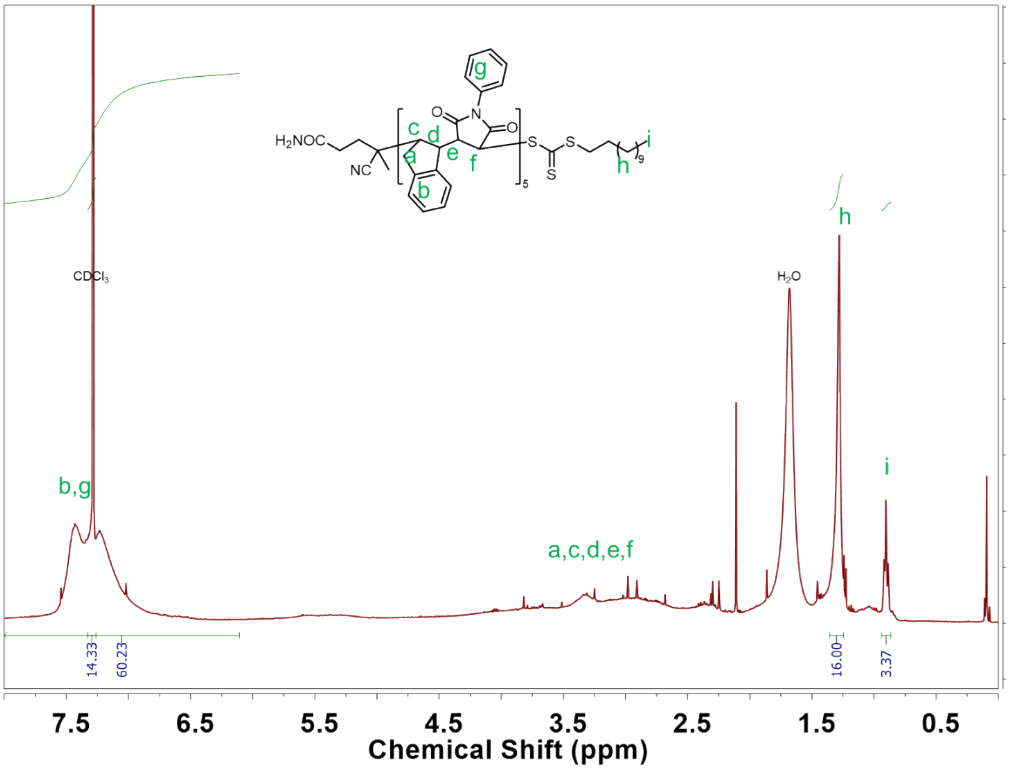



**Figure S9.** $^1$H NMR spectrum (400 MHz, $CDCl_3$) of the apparent 10-mer oligo(indene-*alt*-phenylmaleimide)

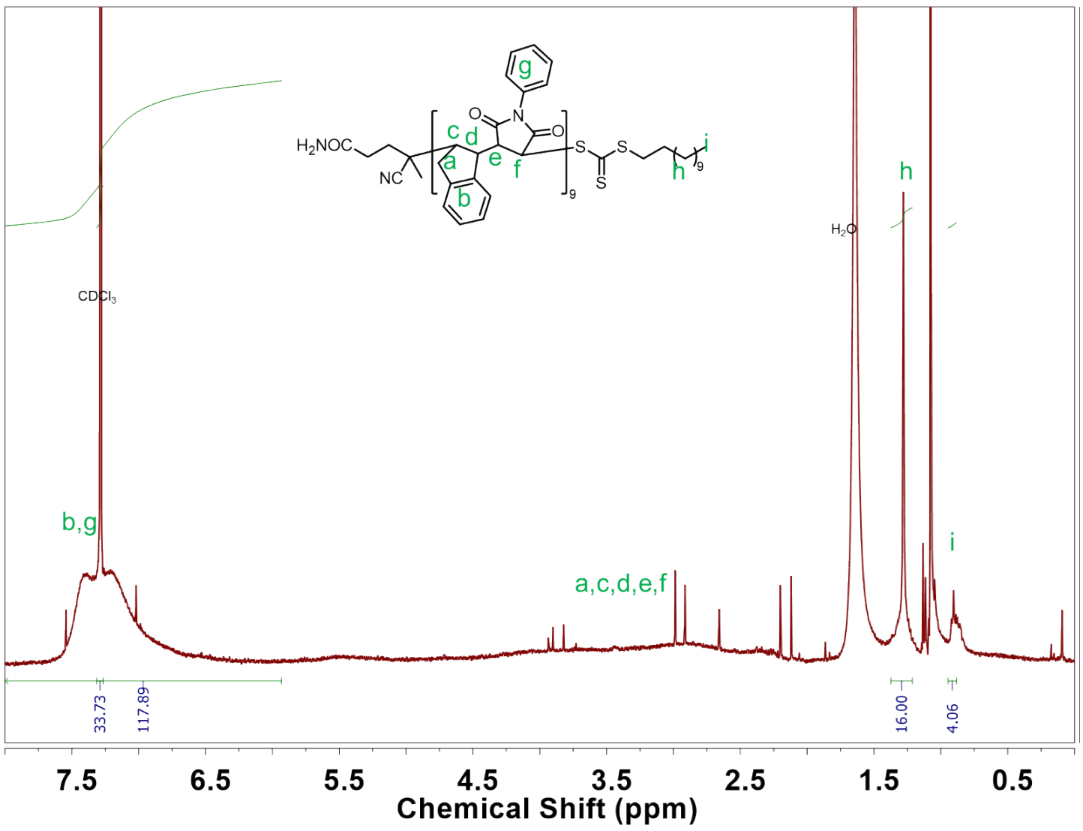
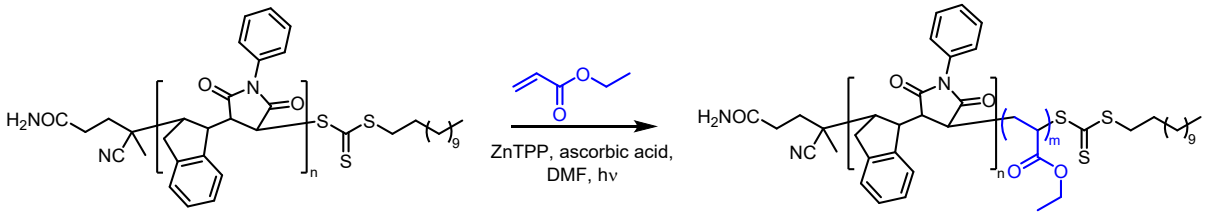



**Figure S10.** $^1$H-NMR spectrum (400 MHz, $CDCl_3$) of the apparent 18-mer oligo(indene-*alt*-phenylmaleimide)

## End group analysis by chain extension

**Table S1.** Summary data of the chain extension of the apparent 18-mer of Ind-*alt*-PhMal with ethyl acrylate.




| Entry # | [macroCTA]: [EA]: [ZnTPP] | Reaction time, conversion | $M_{n,\,conv}$ (g mol$^{-1}$) | $M_{n,\,GPC}$ (g mol$^{-1}$, *vs* PMMA) | *Đ* (*vs* PMMA) |
|---|---|---|---|---|---|
| 1 | 100: 1: 0.01 | 24 h, 62% | 9,208 | 19,000 | 1.18 |
| 2 | 100: 0: 0.01 | 24 h, 0% | 3,008 | N/A | N/A |

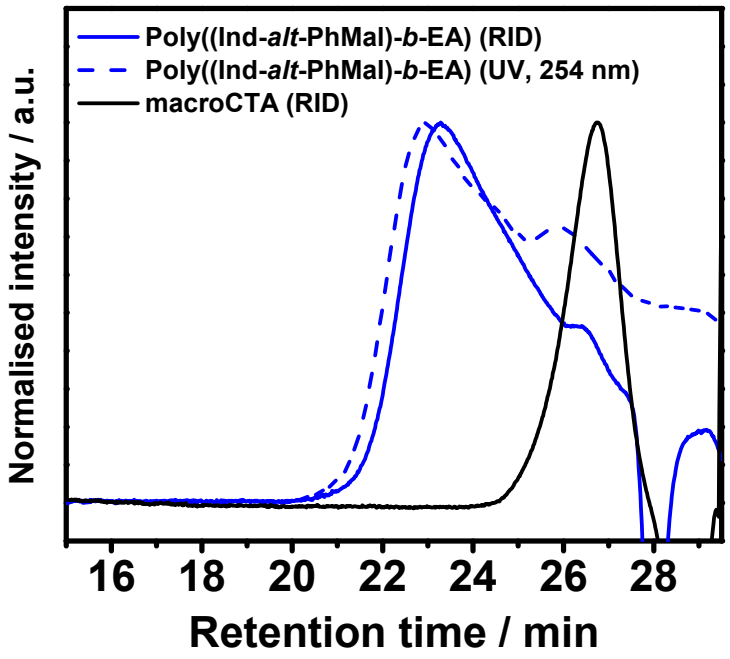



**Figure S11.** GPC elugrams (DMAc, 1 mL min$^{-1}$, 50 °C) of the chain extension products from the 18-mer macroCTA including the RI trace (blue solid) and the UV trace (254 nm, blue dashed), and the 18-mer macroCTA (black solid).

In order to calculate the proportion of macroCTA to chain extended product, the UV trace was fitted to two bigaussian functions after a linear baseline correction and their integrals were compared. Bigaussian functions were used because they are generally more suitable to model distributions with tailing, such as that of the chain extension product. A few assumptions undergird such calculations:

- UV absorbance of the polymer relates to number of macromolecules in a molecular-weight-independent fashion.
- All residual macroCTA comes only from disproportionation during previous iterative PET-RAFT SUMI reactions (*i.e.,* the chain extension or RAFT-terminal macroCTA went with complete livingness).

- There is a minimal difference between the 254 nm absorption of RAFT-terminal macroCTA and that which has undergone disproportionation (*i.e.,* the key fluorophore are the aromatic rings).
- The ethyl acrylate block doesn't alter the 254 nm absorption of the block copolymer.

With these points in mind, the integral ratio of the two deconvoluted peaks was 2.09:0.35 corresponding to a chain end fidelity of **86%** of the apparent 18mer.

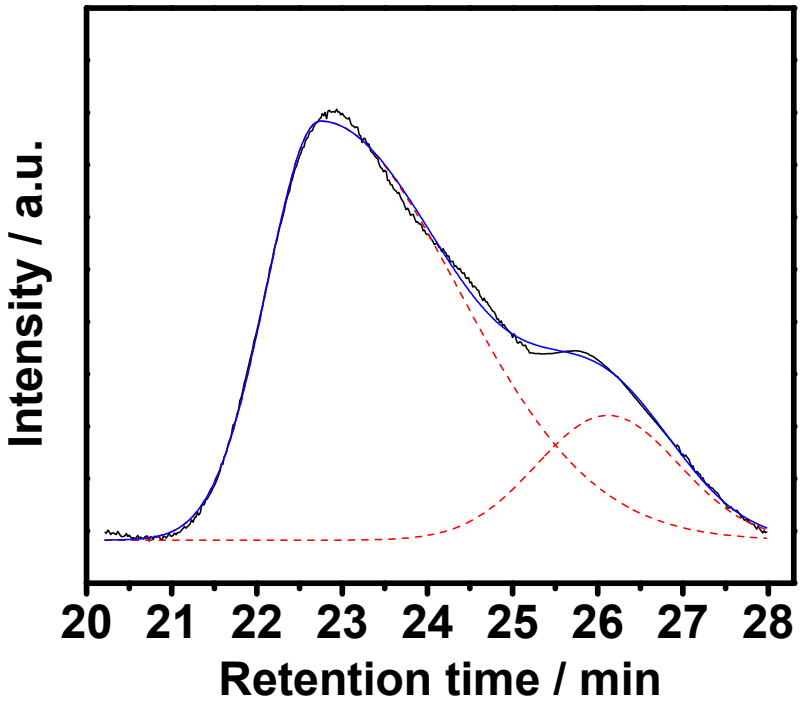



**Figure S12.** Deconvolution of the UV trace from Figure S5-1 as two bigaussian distributions including the experimental data after baseline correction (black), the individual fitting peaks (red) and the total fit (blue). $\chi^2$ (reduced) = 1.12 x$10^{-4}$

## Synthesis of conventional polymers on-resin

*Synthesis of Poly(indene-alt-phenylmaleimide)*

Poly(indene-*alt*-phenylmaleimide) was made by a single polymerisation step on-resin in comparison with iterative RAFT SUMI reactions using the method as follows:

CDTPA-functional rink amide resin (56 mg, 2.19 mmol $g^{-1}$) was swelled in DMF (3 mL) for 15 min before reacting. The DMF was then ejected from the resin with the assistance of vacuum. (without completely drying it) The resin was then swelled with a solution of ascorbic acid (26 mg), indene (86 mg, 0.74 mmol), *N*-phenyl maleimide (128 mg, 0.74 mmol) and ZnTPP (~0.9 mg) in DMF (0.4 mL) with the components dissolved in that order. The resin was then left to agitate for 24 h under blue LED irradiation. (>95% conversion – in order to collect an NMR sample, it was necessary to rinse the leftover resin with DCM, collect the filtrate and concentrate under vacuum) After washing the resin with DMF (5 x 3 mL) and DCM (5 x 3 mL), the product was then cleaved by swelling the resin in a solution of trifluoroacetic acid in DCM (50:50 v/v) and then agitated for 1 h at ambient temperature. The filtrate was then collected and dried under a stream of nitrogen, then under high vacuum.

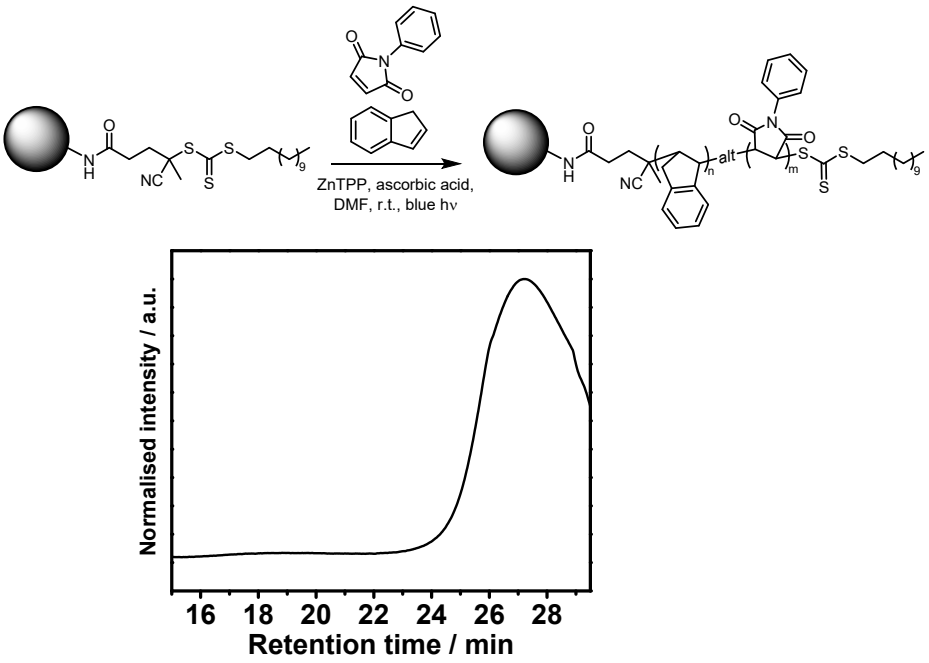



**Figure S13.** GPC elugram (DMAc, 1 mL $min^{-1}$, 50 °C) of the product from the alternating copolymerisation of indene and *N*-phenylmaleimide on-resin ($M_n$= 8000 g $mol^{-1}$, Đ= 1.32)

*Synthesis of poly(2-azido-3-hydroxypropyl methacrylate)*

Poly(2-azido-3-hydroxypropyl methacrylate) was made by a multi-step route to show that solid-phase synthesis could be used in this way, avoiding dialysis or precipitation steps.

The homopolymerisation of glycidyl methacrylate (GMA) was performed as follows:

CDTPA-functional rink amide resin (10 mg, 2.19 mmol $g^{-1}$) was swelled in DMF (2 mL) for 15 min prior to reacting. The DMF was then ejected from the resin with the assistance of vacuum. (without completely drying it) The resin was then swelled in a solution of ascorbic acid (56 mg), GMA (42 mg, 0.3 mmol) and ZnTPP (~0.1 mg) in DMF (0.3 mL) with the components dissolved in that order. The resin was then left to agitate for 24 h under blue LED irradiation.

(93% conversion) After washing the resin with DMF (5 x 2 mL) and DCM (5 x 2 mL), the product was then cleaved by swelling the resin in a solution of trifluoroacetic acid in DCM (50:50 v/v) and then agitated for 1 h at ambient temperature. The filtrate was then collected and dried under a stream of nitrogen, then under high vacuum.

The subsequent azidation was performed by the following procedure. Sodium azide (10 mg) was suspended in a solution of ammonium chloride (10 mg) in DMF (3 mL) with large particles broken up by irradiation under an ultrasonic bath. The mixture was then added to the resin obtained from the previous step (divided into two Eppendorf tubes because the total reaction volume exceeded that of one tube) and the suspension was left to agitate in an incubating shaker at 50 °C for 24 h.

After washing and drying the resin, the polymer was cleaved using the general method described in the Experimental section.

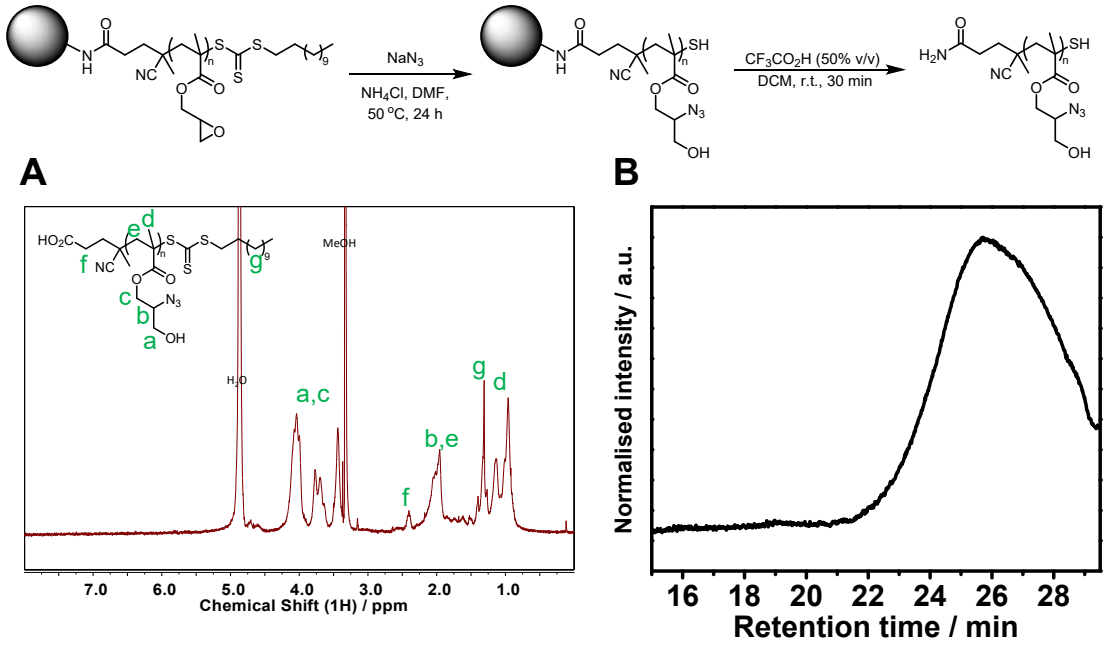



**Figure S14.** Synthesis of poly(2-azido-3-hydroxypropyl methacrylate) on-resin with NMR spectrum (400 MHz, $CDCl_3$) (A) and GPC elugram (DMAc, 50 °C, 1 mL $min^{-1}$), $M_{n,\ vs\ PSt}$ = 10,800 g $mol^{-1}$, Đ= 1.27 (B)

Being able to characterise the product by liquid-phase characterisation means such as NMR or GPC indicates that minimal cross-linking occurred upon final treatment with acid, indirectly demonstrating a successful azidation.

It must also be noted that from the presence of the dodecyl resonance in the $^1H$ NMR data, the trithiocarbonate group might still be intact in the polymer which would be unusual given it was exposed to a strong nucleophile in sodium azide. It is possible that this resonance could originate from a disulphide bond formation between the resulting dodecanethiol and the thiol-terminal polymer.

## Static nanospray ionisation mass spectrometry (nESI-MS) data

The following analyses were performed on samples after cleavage, without a chromatography component.

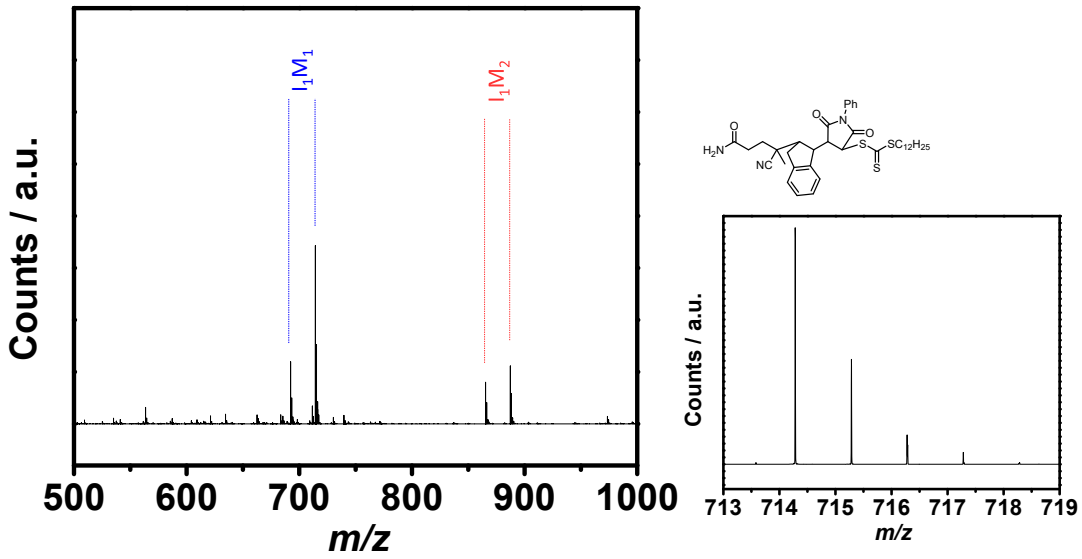



**Figure S15.** nESI-MS data (MeCN) of the apparent 2-mer with assignments and a zoom-in of the peaks corresponding to the structure drawn. (I – indene, M – *N*-phenylmaleimide) Peaks corresponding to both the H+ and Na+ charge states are grouped as the same species.

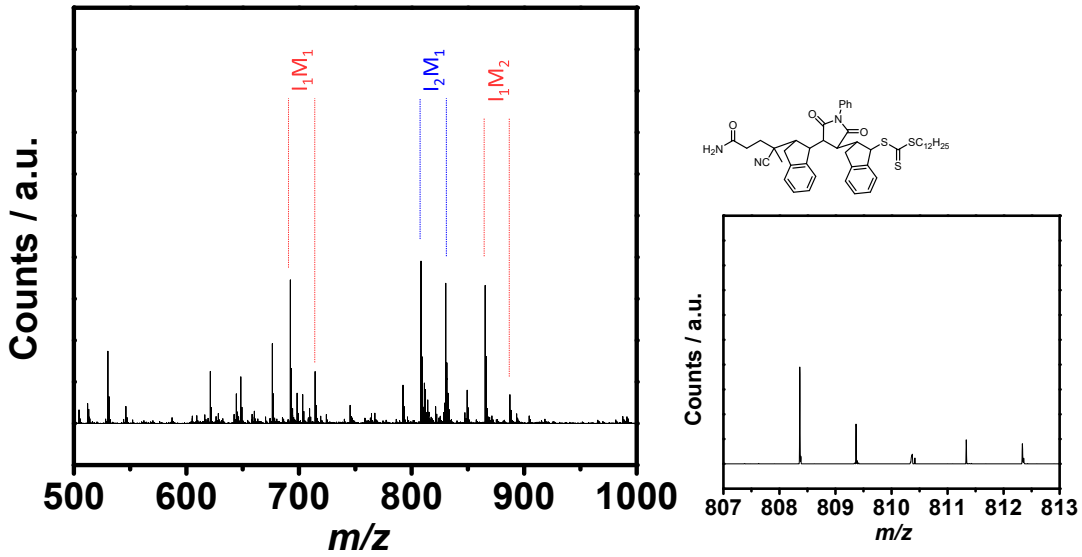



**Figure S16.** nESI-MS data (MeCN) of the apparent 3-mer with assignments and a zoom-in of the peaks corresponding to the structure drawn. (I – indene, M – *N*-phenylmaleimide) Peaks corresponding to both the H+ and Na+ charge states are grouped as the same species.

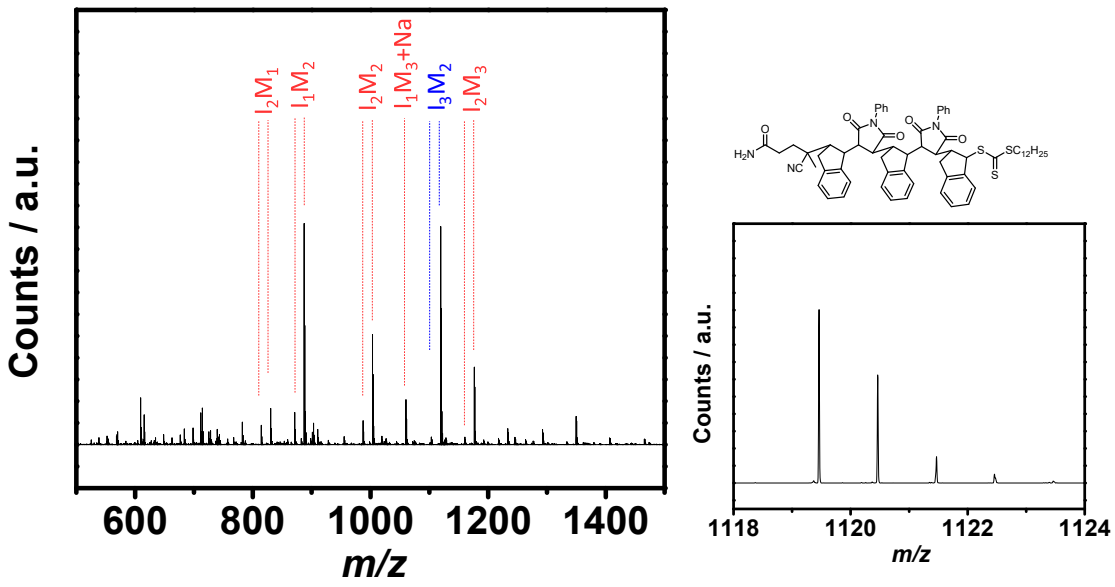



**Figure S17.** nESI-MS data (MeCN) of the apparent 5-mer with assignments and a zoom-in of the peaks corresponding to the structure drawn. (I – indene, M – *N*-phenylmaleimide) Peaks corresponding to both the H+ and Na+ charge states are grouped as the same species.

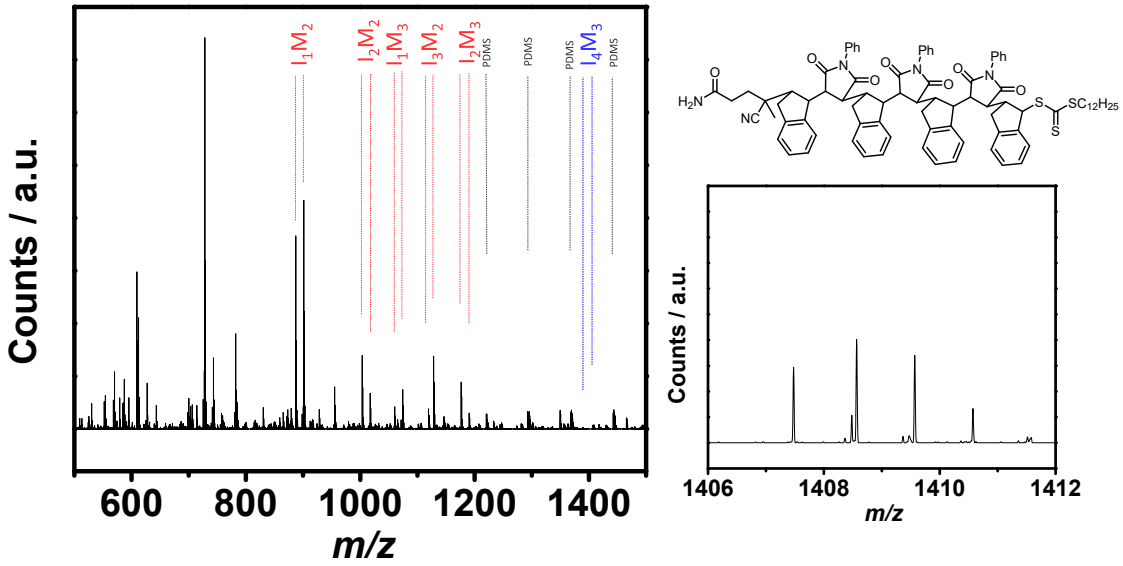



**Figure S18.** nESI-MS data (MeCN) of the apparent 7-mer with assignments and a zoom-in of the peaks corresponding to the structure drawn. (I – indene, M – *N*-phenylmaleimide) Peaks corresponding to both the H+ and Na+ charge states are grouped as the same species.

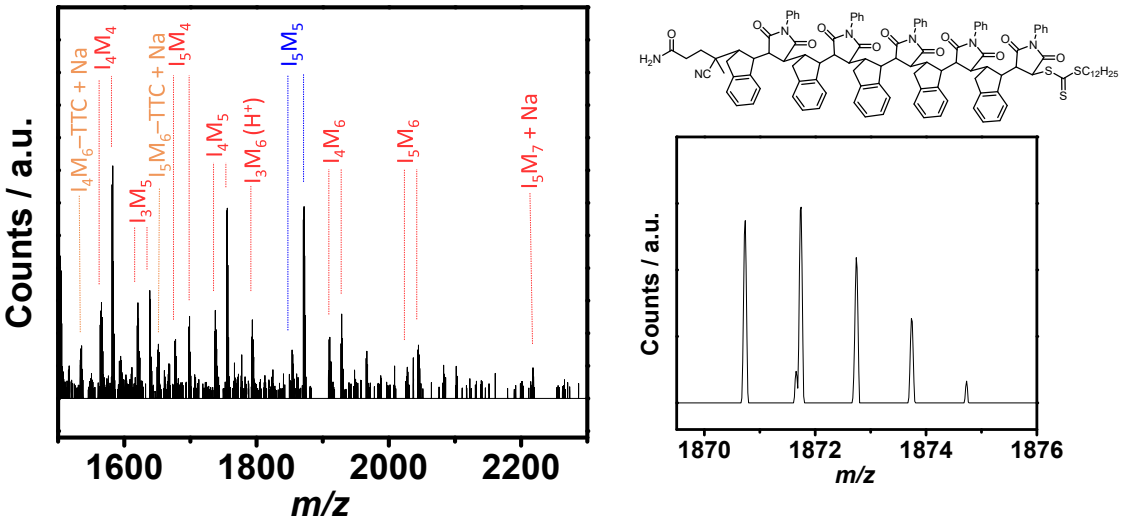



**Figure S19.** nESI-MS data (MeCN) of the apparent 10-mer with assignments and a zoom-in of the peaks corresponding to the structure drawn. (I – indene, M – *N*-phenylmaleimide) Peaks corresponding to both the H+ and Na+ charge states are grouped as the same species unless otherwise specified.

## Ultrahigh performance liquid chromatography – atmospheric pressure chemical ionisation mass spectrometry (UHPLC–MS) data

The following analyses were performed on samples after cleavage, with the mass spectrometry data collected at a selected column retention time.

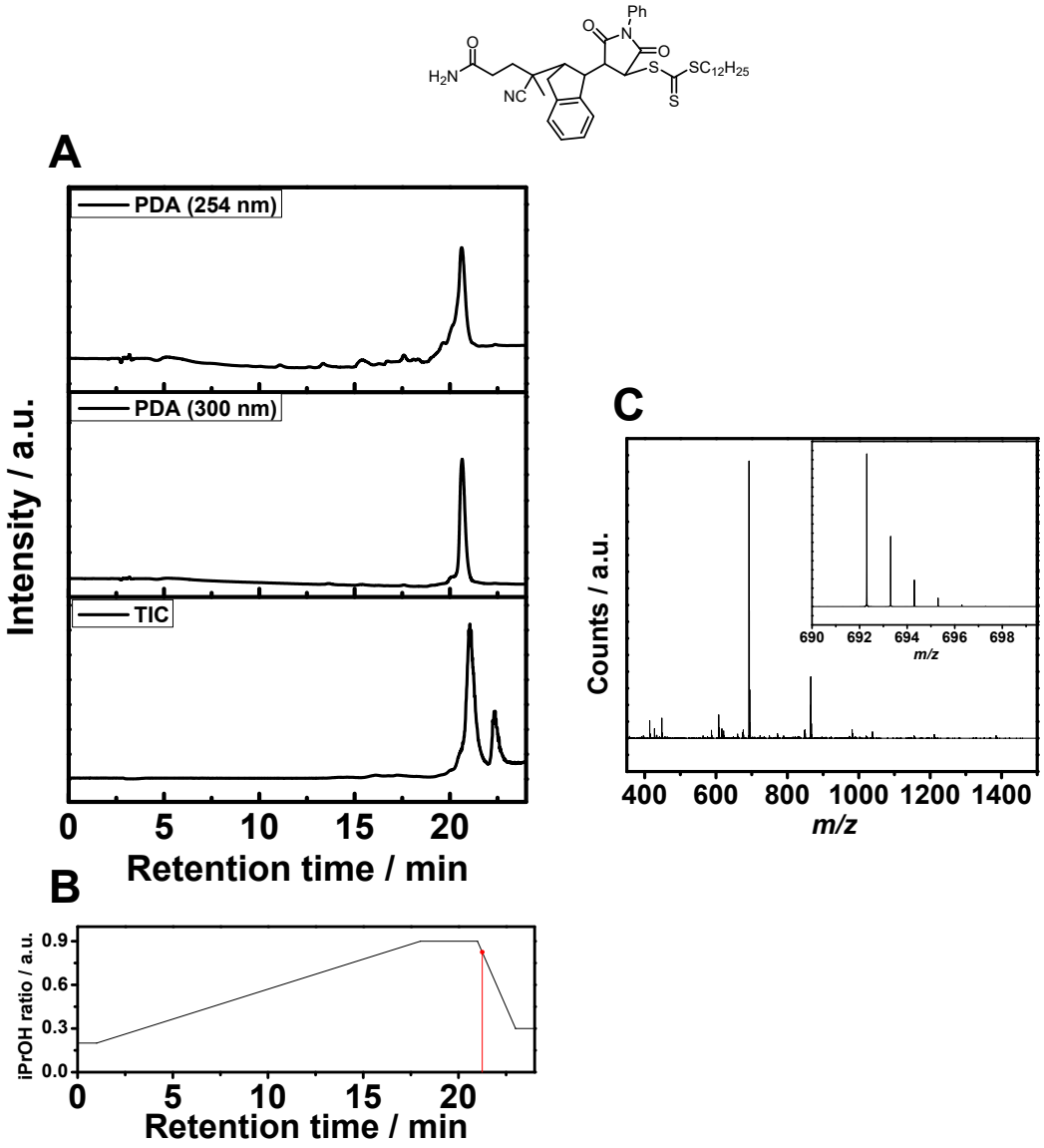



**Figure S20.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 °C) of the apparent 2-mer (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B) and the APCI–MS data from 21.25 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C).

**Table S2.** Assignment of key peaks in the mass spectrum from Figure S20C (CDTPAm – CDTPA modified to the primary amide, Ind – indene, PhMal – *N*-phenylmaleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 21.25 | *692.30, 693.31, 694.30, 695.30* | *CDTPAm+(Ind)$_1$+(PhMal)$_1$ (H$^+$)* |
| | 865.35, 866.35, 867.35, 868.35 | CDTPAm+(Ind)$_1$+(PhMal)$_2$ (H$^+$) |

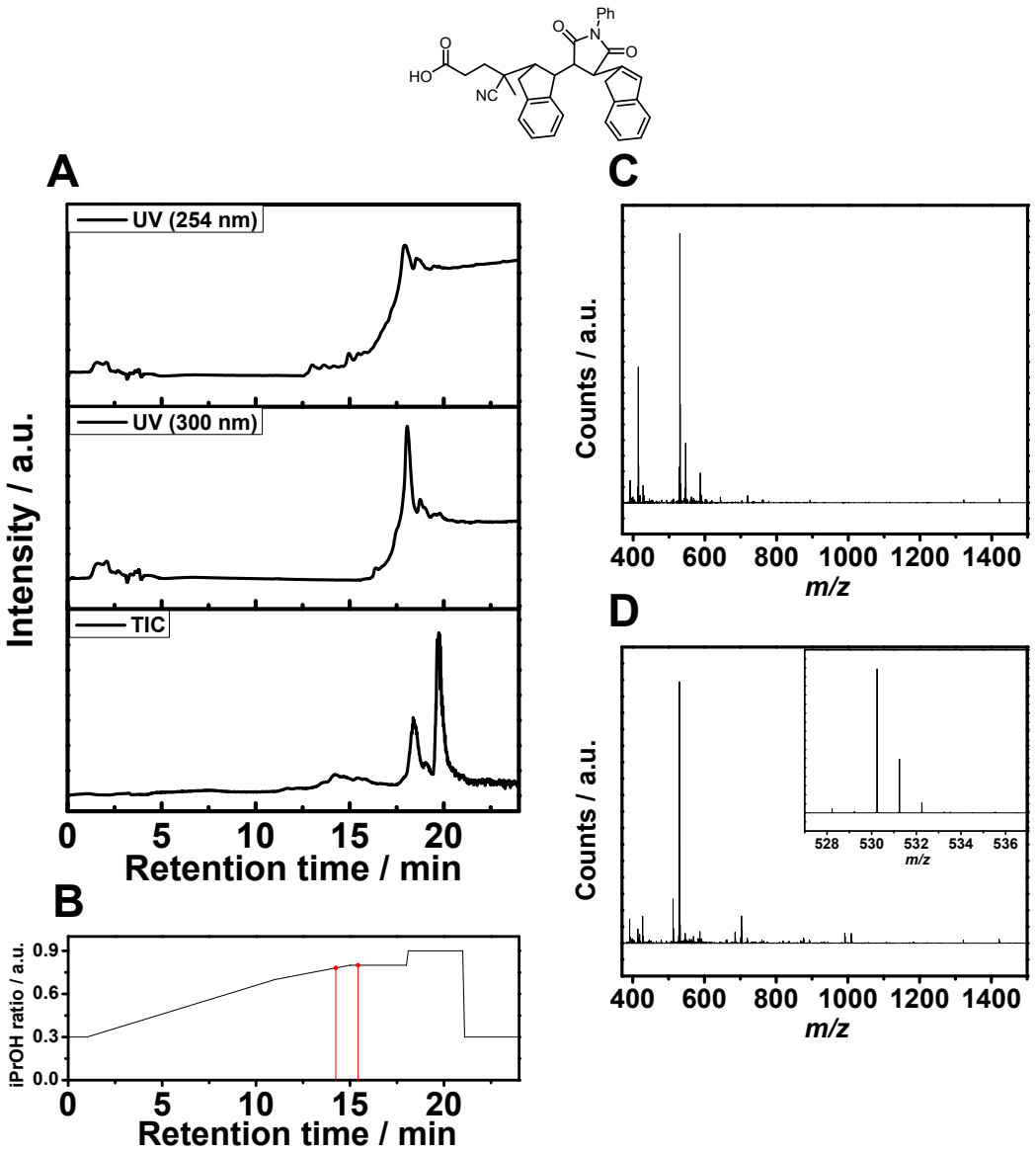



**Figure S21.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 °C) apparent 3-mer (elimination product MS shown here) (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 14.24 min retention time (C), the APCI–MS data from 15.43 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C)

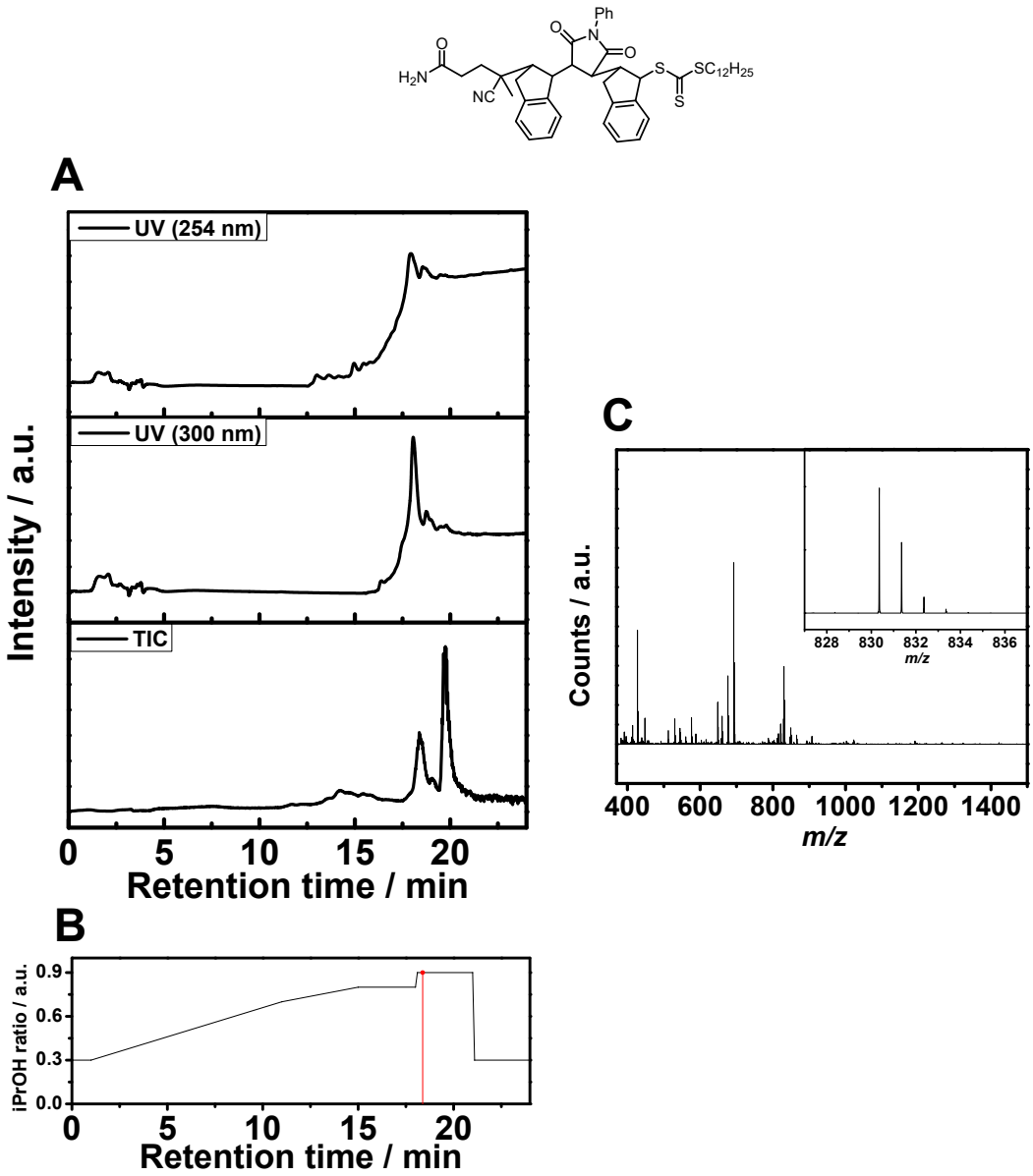



**Figure S22.** UHPLC–MS elugrams ($^{i}$PrOH–water, 0.4 mL min$^{-1}$, 25 $^{o}$C) of the apparent 3-mer (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 18.38 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C)

**Table S3.** Assignment of key peaks in the mass spectra from Figure S21C, Figure S21D, Figure S22C and Figure S22D (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, PhMal – *N*-phenylmaleimide).

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 14.24 | 414.18, 415.18, 416.18 | CDTPA-TTC+$(Ind)_1$+$(PhMal)_1$ ($H^+$) |
| 15.43 | *530.24, 531.25, 532.25* | *CDTPA-TTC+$(Ind)_2$+$(PhMal)_1$ ($H^+$)* |
| | 703.29, 704.29, 705.29 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_2$ ($H^+$) |
| 18.38 | 576.24, 577.24, 578.24 | CDTPAm+$(PhMal)_1$ ($H^+$) |
| | 692.30, 693.30, 694.31, 695.29 | CDTPAm+$(Ind)_1$+$(PhMal)_1$ ($H^+$) |

| | | |
|---|---|---|
| | 830.36, 831.35, 832.36, 833.36 | CDTPAm+(Ind)$_2$+(PhMal)$_1$ (Na$^+$) |

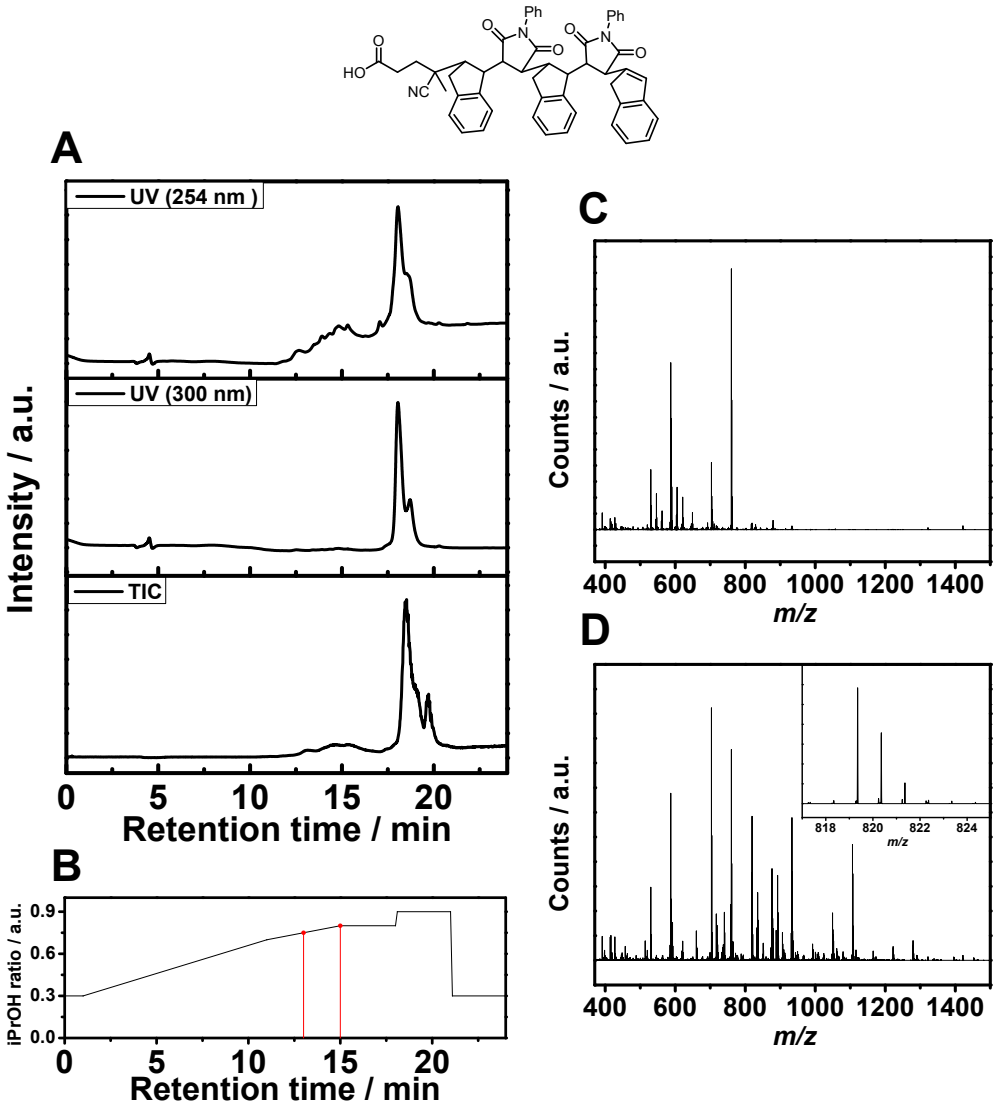



**Figure S23.** UHPLC–MS elugrams ($^i$PrOH–water, 0.4 mL min$^{-1}$, 25 $^o$C) of the apparent 5-mer (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 13.00 min retention time (C) and the APCI–MS data from 15.00 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (D)

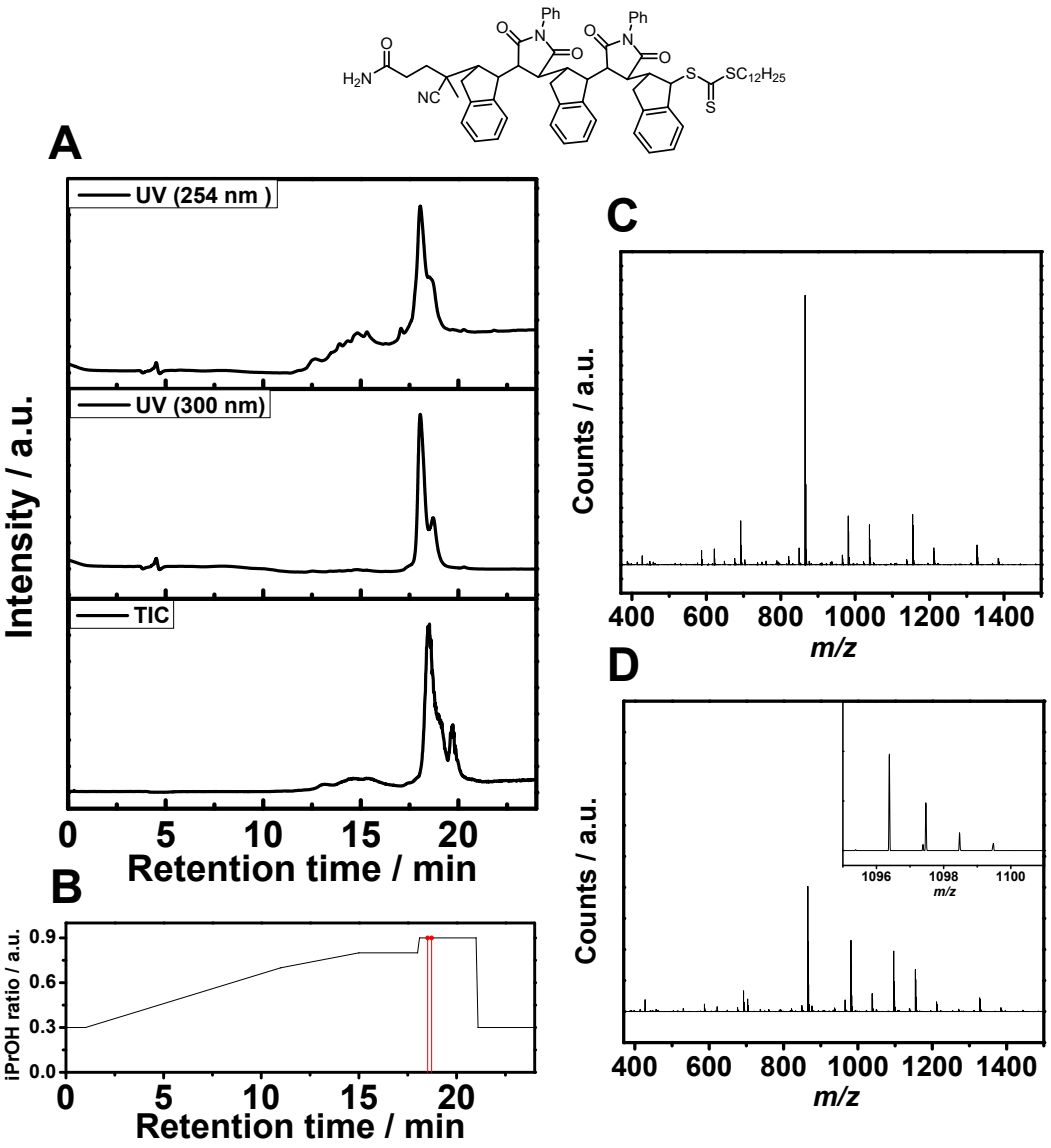



**Figure S24.** UHPLC–MS elugrams (ⁱPrOH–water, 0.4 mL min$^{-1}$, 25 °C) of the apparent 5-mer (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 18.52 min retention time (C) and the APCI–MS data from 18.73 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (D)

**Table S4.** Assignment of key peaks in the mass spectra from Figure S23C, Figure S23D, Figure S24C and Figure S24D (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, PhMal – *N*-phenylmaleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 13.00 | 530.24, 531.24, 532.24 | CDTPA-TTC+$(PhMal)_3$ ($H^+$) |
| | 587.23, 588.23, 589.24 | CDTPA-TTC+$(Ind)_1$+$(PhMal)_2$ ($H^+$) |
| | 703.29, 704.29, 705.30 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_2$ ($H^+$) |
| | 760.27, 761.27, 762.27 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_3$ ($H^+$) |
| 15.00 | *819.35, 820.35, 821.35* | *CDTPA-TTC+$(Ind)_3$+$(PhMal)_2$ ($H^+$)* |
| | 876.34, 879.34, 878.34 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_3$ ($H^+$) |

| | | |
|---|---|---|
| | 933.32, 934.32, 935.33 | CDTPA-TTC+$(Ind)_1$+$(PhMal)_4$ ($H^+$) |
| 18.52 | 865.35, 866.36, 867.36 | CDTPAm+$(Ind)_1$+$(PhMal)_2$ ($H^+$) |
| | 981.41, 982.41, 983.41 | CDTPAm+$(Ind)_2$+$(PhMal)_2$ ($H^+$) |
| | 1038.39, 1039.40, 1040.40 | CDTPAm+$(Ind)_1$+$(PhMal)_3$ ($H^+$) |
| | 1153.46, 1154.46, 1155.47, 1156.46 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ ($H^+$) |
| | 1327.51, 1328.51, 1329.49, 1330.50 | CDTPAm+$(Ind)_2$+$(PhMal)_4$ ($H^+$) |
| 18.73 | *1096.39, 1097.38, 1098.38* | *CDTPAm+$(Ind)_3$+$(PhMal)_2$ ($H^+$)* |

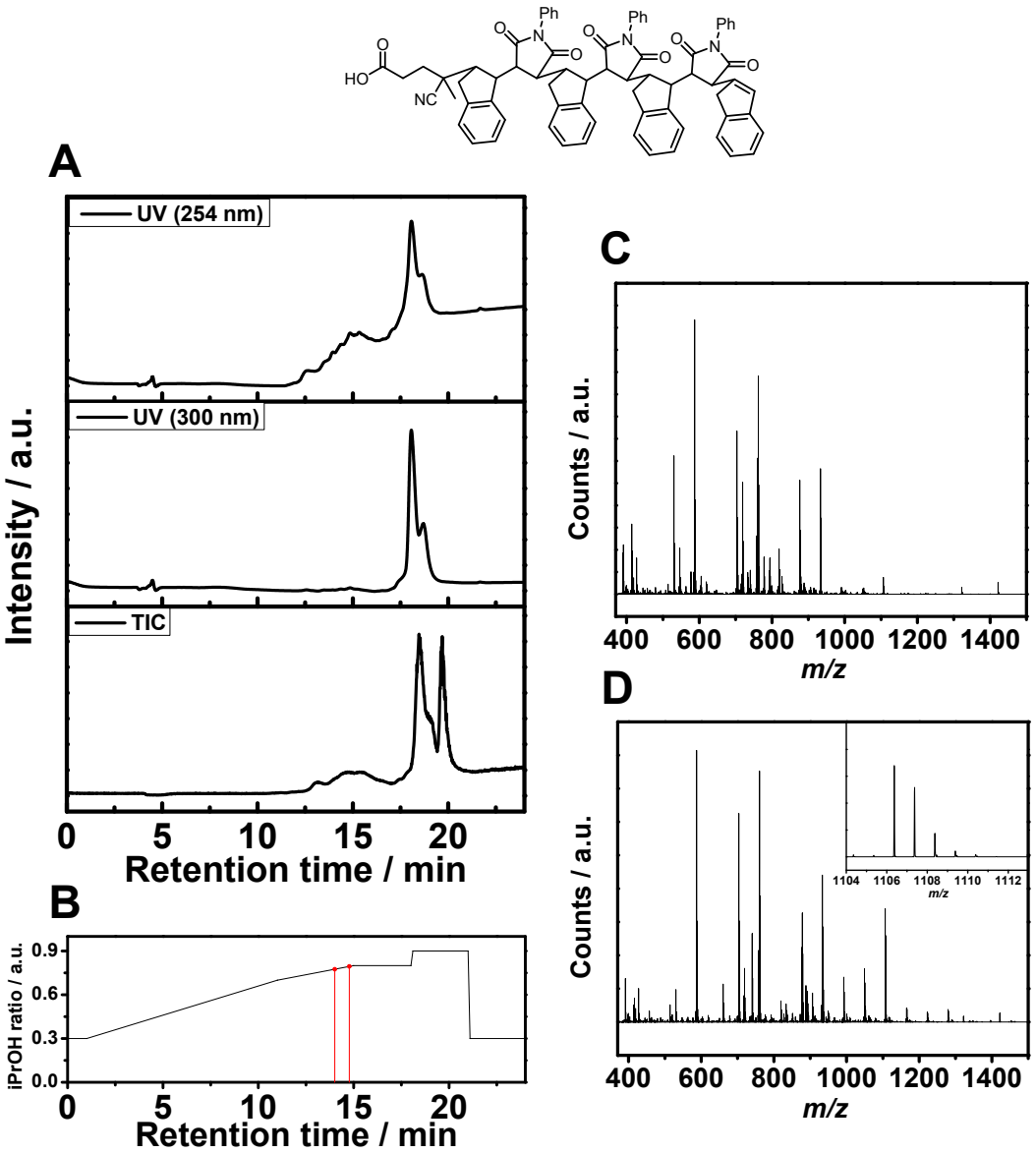



**Figure S25.** UHPLC–MS elugrams ($^i$PrOH–water, 0.4 mL min$^{-1}$, 25 $^o$C) of the apparent 7-mer (A), the relevant isopropanol–water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 14.01 min retention time (C) and the APCI–MS data from 14.77 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (D)

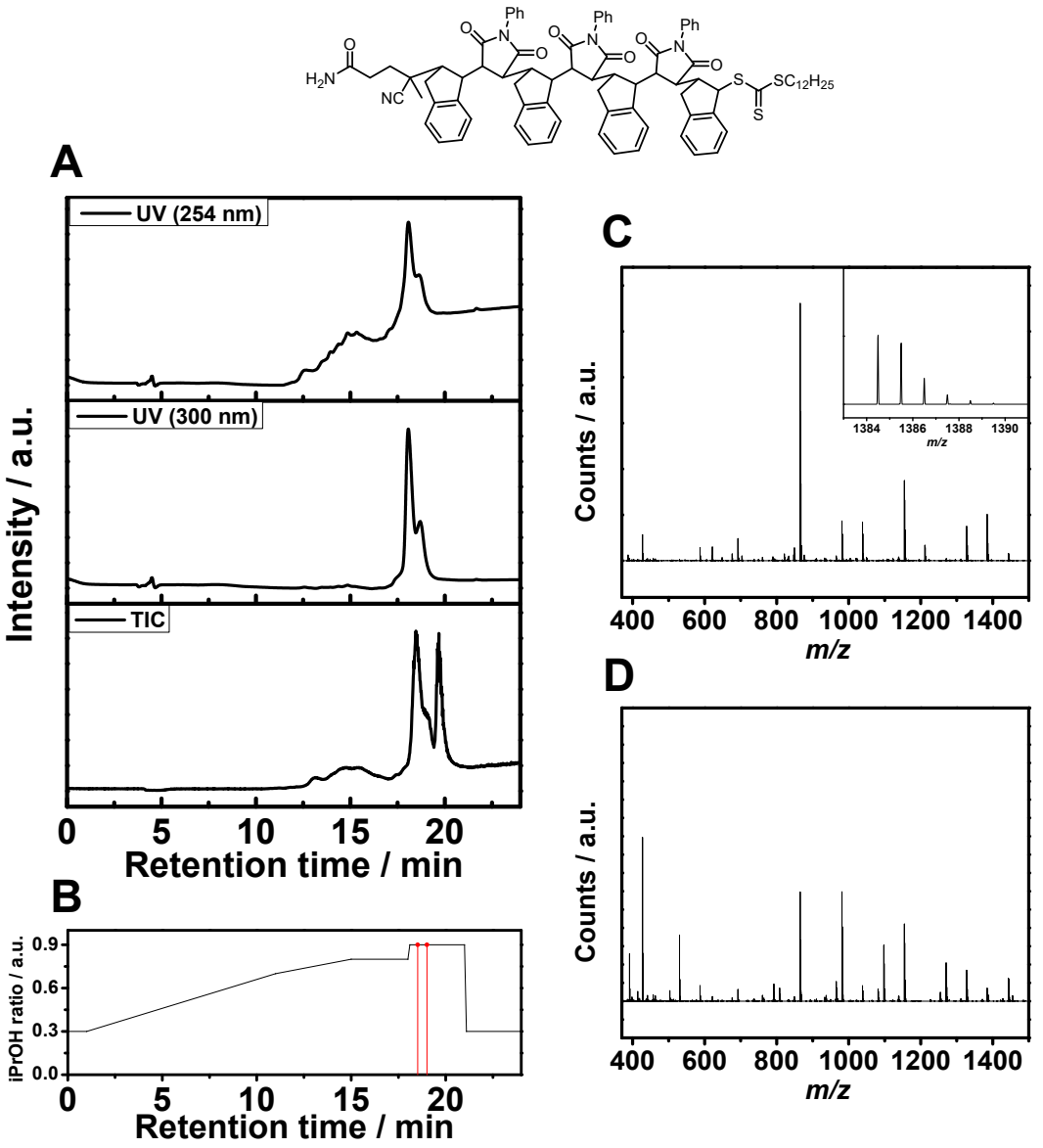



**Figure S26.** UHPLC–MS elugrams ($^{i}$PrOH–water, 0.4 mL min$^{-1}$, 25 $^{o}$C) of the apparent 7-mer (A), the relevant isopropanol–water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 18.50 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C) and the APCI–MS data from 19.01 min retention time (D)

**Table S5.** Assignment of key peaks in the mass spectra from Figure S25C, Figure S25D, Figure S26C and Figure S26D (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, PhMal – *N*-phenylmaleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 14.01 | 530.24, 531.24, 532.25 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_1$ $(H^+)$ |
| | 587.23, 588.23, 589.24 | CDTPA-TTC+$(Ind)_1$+$(PhMal)_2$ $(H^+)$ |
| | 703.29, 704.29, 705.30 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_2$ $(H^+)$ |
| | 762.29, 763.29, 764.29 | CDTPA-TTC+$(Ind)_4$+$(PhMal)_1$ $(H^+)$ |
| | 819.35, 820.36, 821.36 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_2$ $(H^+)$ |
| | 876.34, 879.34, 878.34 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_3$ $(H^+)$ |
| | 933.32, 934.32, 935.33 | CDTPA-TTC+$(Ind)_1$+$(PhMal)_4$ $(H^+)$ |
| 14.77 | 878.35, 879.36, 880.36 | CDTPA-TTC+$(Ind)_5$+$(PhMal)_1$ $(H^+)$ |
| | 1049.38, 1050.38, 1051.38 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_4$ $(H^+)$ |
| | *1106.37, 1107.37, 1108.37* | *CDTPA-TTC+$(Ind)_4$+$(PhMal)_3$ $(H^+)$* |
| 18.50 | 865.35, 866.36, 867.36 | CDTPAm+$(Ind)_1$+$(PhMal)_2$ $(H^+)$ |
| | 981.41, 982.42, 983.41 | CDTPAm+$(Ind)_2$+$(PhMal)_2$ $(H^+)$ |
| | 1038.39, 1039.39, 1040.40 | CDTPAm+$(Ind)_1$+$(PhMal)_3$ $(H^+)$ |
| | 1154.46, 1155.46, 1156.46 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ $(H^+)$ |
| | 1211.44, 1212.44, 1213.44, 1214.44 | CDTPAm+$(Ind)_1$+$(PhMal)_4$ $(H^+)$ |
| | 1327.50, 1328.50, 1329.51, 1330.51 | CDTPAm+$(Ind)_2$+$(PhMal)_4$ $(H^+)$ |
| | *1384.50, 1385.49, 1386.50, 1387.51* | *CDTPAm+$(Ind)_4$+$(PhMal)_3$ $(H^+)$* |
| 19.01 | 1097.47, 1098.48, 1099.48 | CDTPAm+$(Ind)_3$+$(PhMal)_2$ $(H^+)$ |
| | 1270.52, 1271.52, 1272.52, 1273.51 | CDTPAm+$(Ind)_3$+$(PhMal)_3$ $(H^+)$ |
| | 1443.58, 1444.56, 1445.57, 1446.57 | CDTPAm+$(Ind)_3$+$(PhMal)_4$ $(H^+)$ |
| | 1500.56, 1501.53, 1502.57, 1503.58 | CDTPAm+$(Ind)_3$+$(PhMal)_4$ $(H^+)$ |

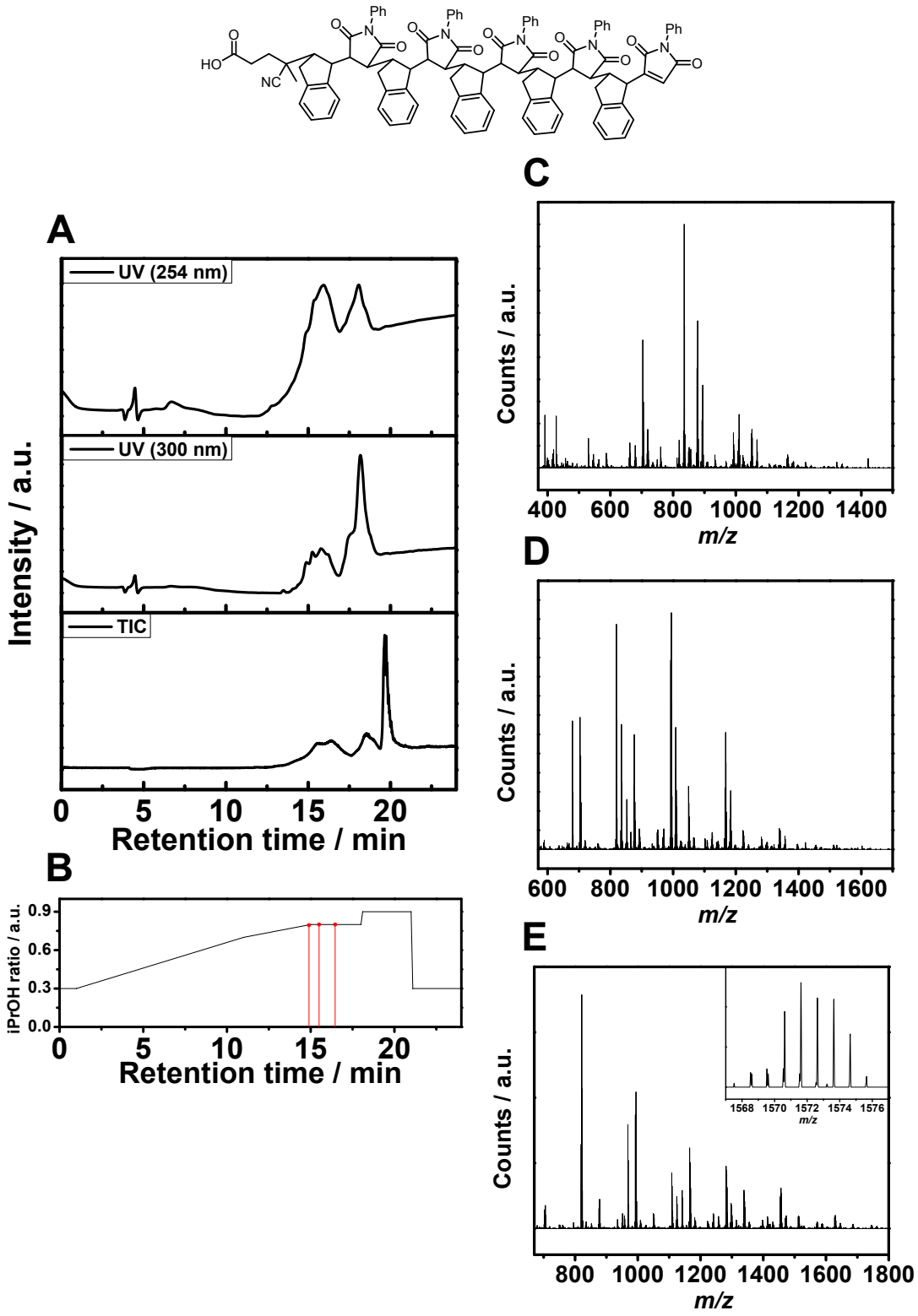



**Figure S27.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 $^{o}$C) of the apparent 10-mer (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 14.92 min retention time (C), the APCI–MS data from 15.55 min retention time (D) and the APCI–MS data from 16.46 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (E)

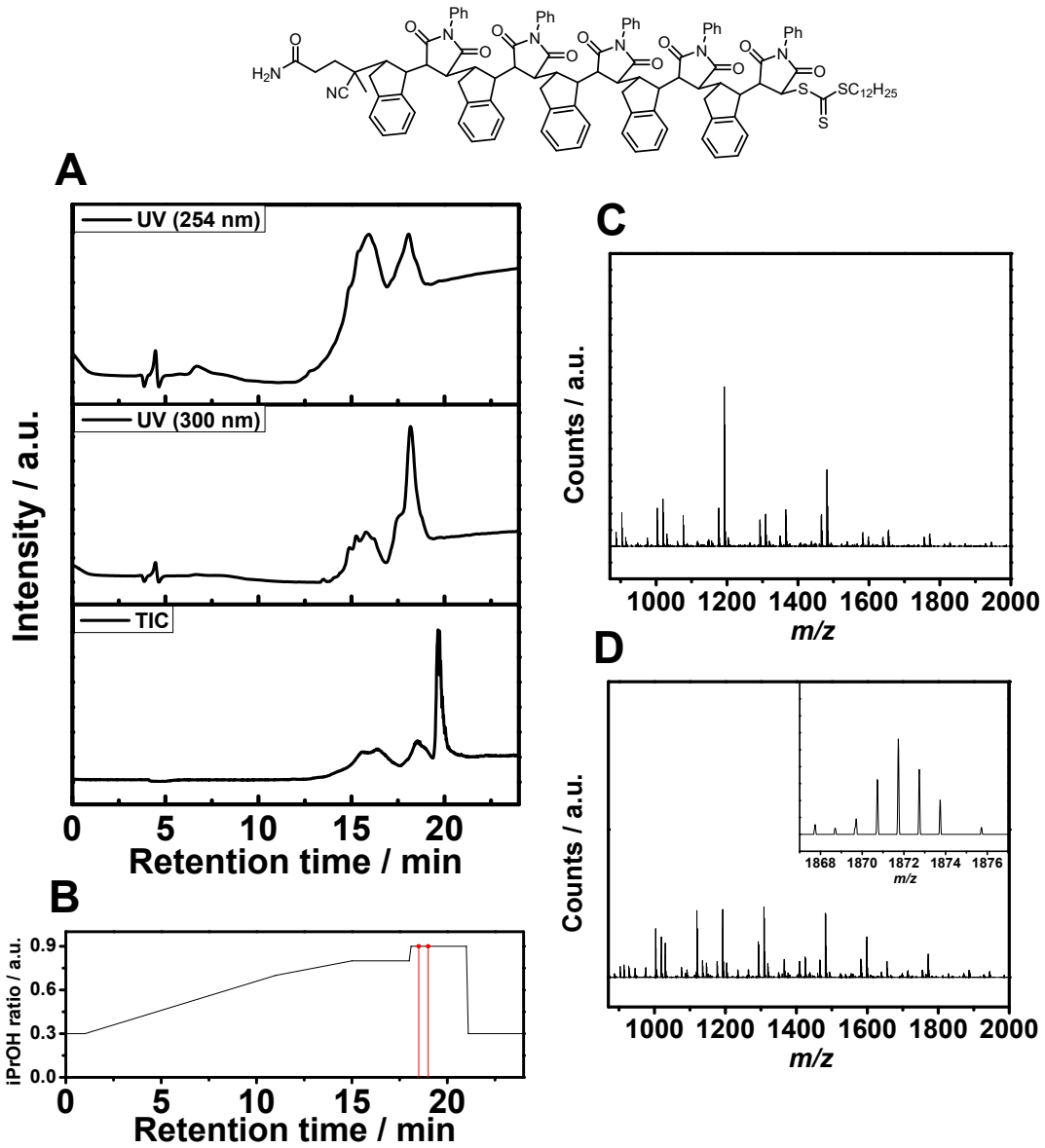



**Figure S28.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 $^{o}$C) of the apparent 10-mer (A), the relevant isopropanol–water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 18.57 min retention time (C) and the APCI-MS data from 19.00 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (D)

**Table S6.** Assignment of key peaks in the mass spectra from Figure S27C, Figure S27D, Figure S27E, Figure S28C and Figure S28D (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, Ph-Mal – *N*-phenylmaleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 14.92 | 703.29, 704.29, 705.30 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_2$ ($H^+$) |
| | 878.35, 879.35, 880.35 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_1$ ($H^+$) |
| | 1051.40, 1052.40, 1053.40 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_4$ ($H^+$) |
| 15.55 | 819.35, 820.35, 821.35 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_2$ ($H^+$) |
| | 876.35, 879.35, 880.35 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_3$ ($H^+$) |
| | 992.41, 993.41, 994.41 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_3$ ($H^+$) |
| | 1049.38, 1050.38, 1051.38 | CDTPA-TTC+$(Ind)_2$+$(PhMal)_4$ ($H^+$) |
| | 1167.46, 1168.46, 1169.46 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_4$ ($H^+$) |
| 16.46 | 1109.49, 1110.49, 1111.49 | CDTPA-TTC+$(Ind)_4$+$(PhMal)_3$ ($H^+$) |
| | 1283.51, 1284.51, 1285.51 | CDTPA-TTC+$(Ind)_4$+$(PhMal)_4$ ($H^+$) |
| | 1337.50, 1338.50, 1340.50, 1341.50 | CDTPA-TTC+$(Ind)_3$+$(PhMal)_5$ ($H^+$) |
| | 1455.57, 1456.57, 1457.57, 1458.57 | CDTPA-TTC+$(Ind)_4$+$(PhMal)_5$ ($H^+$) |
| | *1572.63, 1573.63, 1574.63, 1575.63* | *CDTPA-TTC+$(Ind)_5$+$(PhMal)_5$ ($H^+$)* |
| | 1628.61, 1629.61, 1630.61, 1631.61 | CDTPA-TTC+$(Ind)_4$+$(PhMal)_6$ ($H^+$) |
| 18.57 | 1003.40, 1004.40, 1005.41, 1019.38, 1020.38, 1021.39 | CDTPAm+$(Ind)_2$+$(PhMal)_2$ ($Na^+$, $K^+$) |
| | 1076.37, 1077.37, 1078.38 | CDTPAm+$(Ind)_1$+$(PhMal)_3$ ($K^+$) |
| | 1176.45, 1177.46, 1178.47, 1192.43, 1193.43, 1194.43, 1195.43 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ ($Na^+$, $K^+$) |
| | 1292.52, 1293.52, 1294.51, 1295.52, 1308.50, 1309.49, 1310.49, 1311.49 | CDTPAm+$(Ind)_3$+$(PhMal)_3$ ($Na^+$, $K^+$) |
| | 1349.50, 1350.49, 1351.49, 1352.50, 1365.47, 1366.48, 1367.47, 1368.48 | CDTPAm+$(Ind)_2$+$(PhMal)_4$ ($Na^+$, $K^+$) |
| | 1465.55, 1466.55, 1467.57, 1468.60, 1481.53, 1482.53, 1483.55, 1484.55 | CDTPAm+$(Ind)_3$+$(PhMal)_4$ ($Na^+$, $K^+$) |
| | 1581.63, 1582.62, 1583.63, 1584.63, 1597.60, 1598.60, 1599.59, 1600.60 | CDTPAm+$(Ind)_4$+$(PhMal)_4$ ($Na^+$, $K^+$) |
| 19.00 | 1119.46, 1120.47, 1121.47 | CDTPAm+$(Ind)_3$+$(PhMal)_2$ ($Na^+$) |
| | 1203.41, 1204.41, 1205.44 | CDTPAm+$(Ind)_1$+$(PhMal)_3$ ($Na^+$) |
| | 1319.48, 1320.47, 1321.48, 1322.49 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ ($Na^+$) |
| | 1408.58, 1409.58, 1410.58, 1411.59, 1424.55, 1425.56, 1426.56, 1427.55 | CDTPAm+$(Ind)_4$+$(PhMal)_3$ ($Na^+$, $K^+$) |
| | 1654.58, 1655.60, 1656.61, 1657.56 | CDTPAm+$(Ind)_3$+$(PhMal)_5$ ($K^+$) |
| | 1770.60, 1771.65, 1772.66, 1773.64 | CDTPAm+$(Ind)_4$+$(PhMal)_5$ ($K^+$) |
| | *1870.72, 1871.74, 1872.73, 1873.75, 1886.71, 1887.73, 1888.72, 1889.70* | *CDTPAm+$(Ind)_5$+$(PhMal)_5$ ($Na^+$, $K^+$)* |
| | 1927.74, 1928.72, 1929.68, 1930.77 1943.67, 1944.69, 1945.71, 1946.70 | CDTPAm+$(Ind)_4$+$(PhMal)_6$ ($Na^+$, $K^+$) |

The consistent observation of earlier elution peaks which didn't absorb at 300 nm and showed losses of mass units of 278.53 seemed to correspond with elimination of the trithiocarbonate.

When triisopropylsilane was added as a cation scavenger during the quenching, there was some evidence of an abatement of the acidolytic elimination in the 5-mer sample (*i.e.,* similar to Figure S23 and Figure S24)

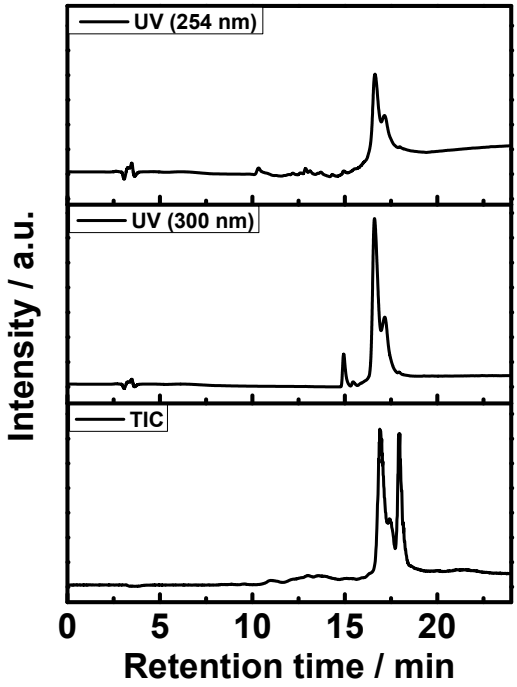



**Figure S29.** UHPLC–MS elugrams ($^{i}$PrOH–water, 0.4 mL min$^{-1}$, 25 $^{o}$C) of the apparent 5-mer upon adding TIPS in the cleavage solution. (compare elugrams with Figure S23 and S24)

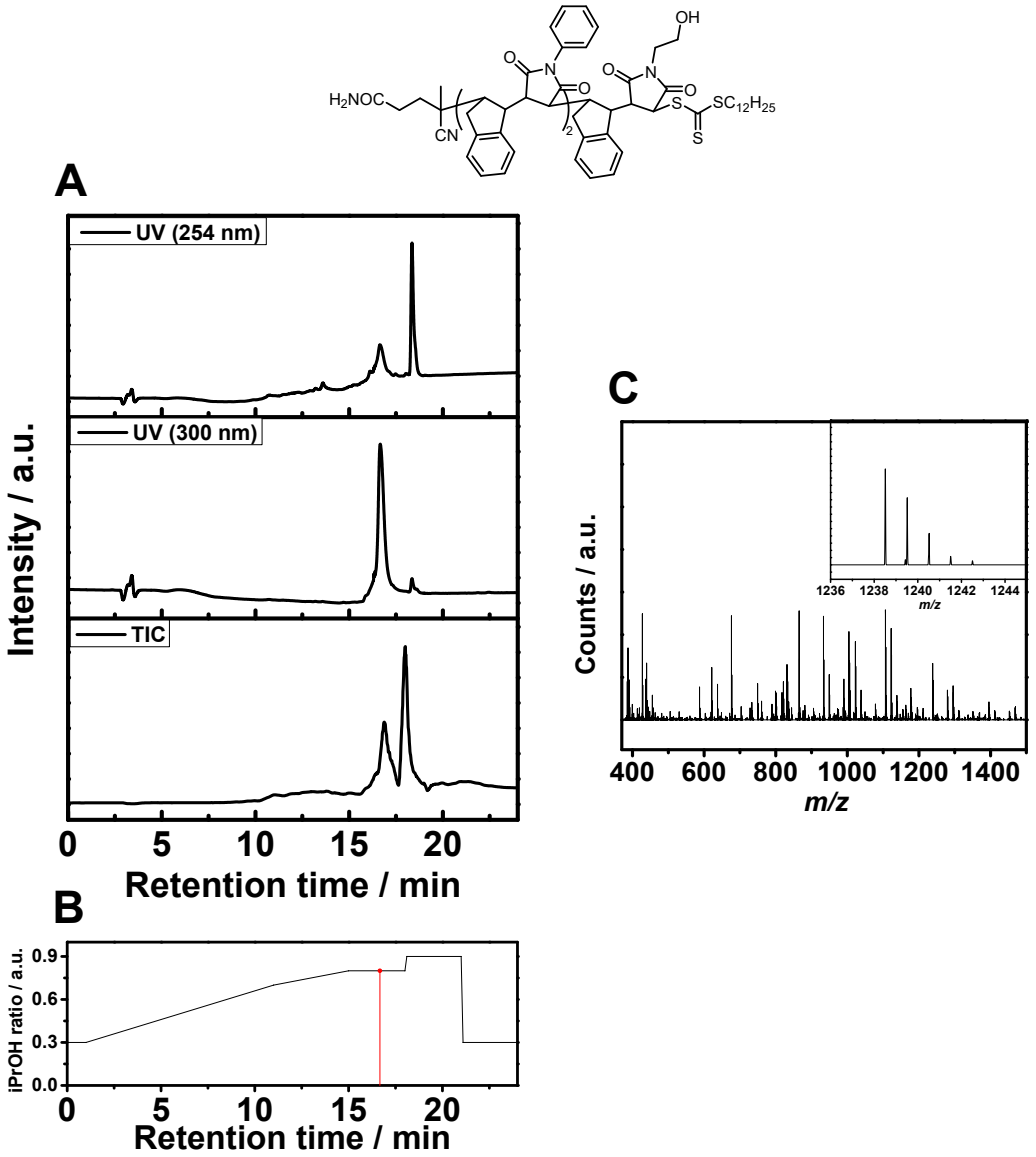



**Figure S30.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 °C) of the apparent 6-mer with *N*-hydroxyethyl maleimide added at the 6$^{th}$ position (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 16.67 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C)

**Table S7.** Assignment of key peaks in the mass spectrum from Figure S30C (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, Ph-Mal – phenyl maleimide, $C_2H_4OH$-Mal – *N*-hydroxyethyl maleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 17.57 | 1122.44, 1123.44, 1124.44, 1125.44 | CDTPAm+$(Ind)_2$+$(PhMal)_2$+ $(C_2H_4OH\text{-}Mal)_1$ ($H^+$) |
| | 1177.45, 1178.45, 1179.44, 1180.45 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ ($Na^+$) |
| | *1238.51, 1239.51, 1240.53, 1241.52* | *CDTPAm+$(Ind)_3$+$(PhMal)_2$+ $(C_2H_4OH\text{-}Mal)_1$ ($H^+$)* |
| | 1295.50, 1296.51, 1297.50, 1297.52 | CDTPAm+$(Ind)_2$+$(PhMal)_3$+ $(C_2H_4OH\text{-}Mal)_1$ ($H^+$) |

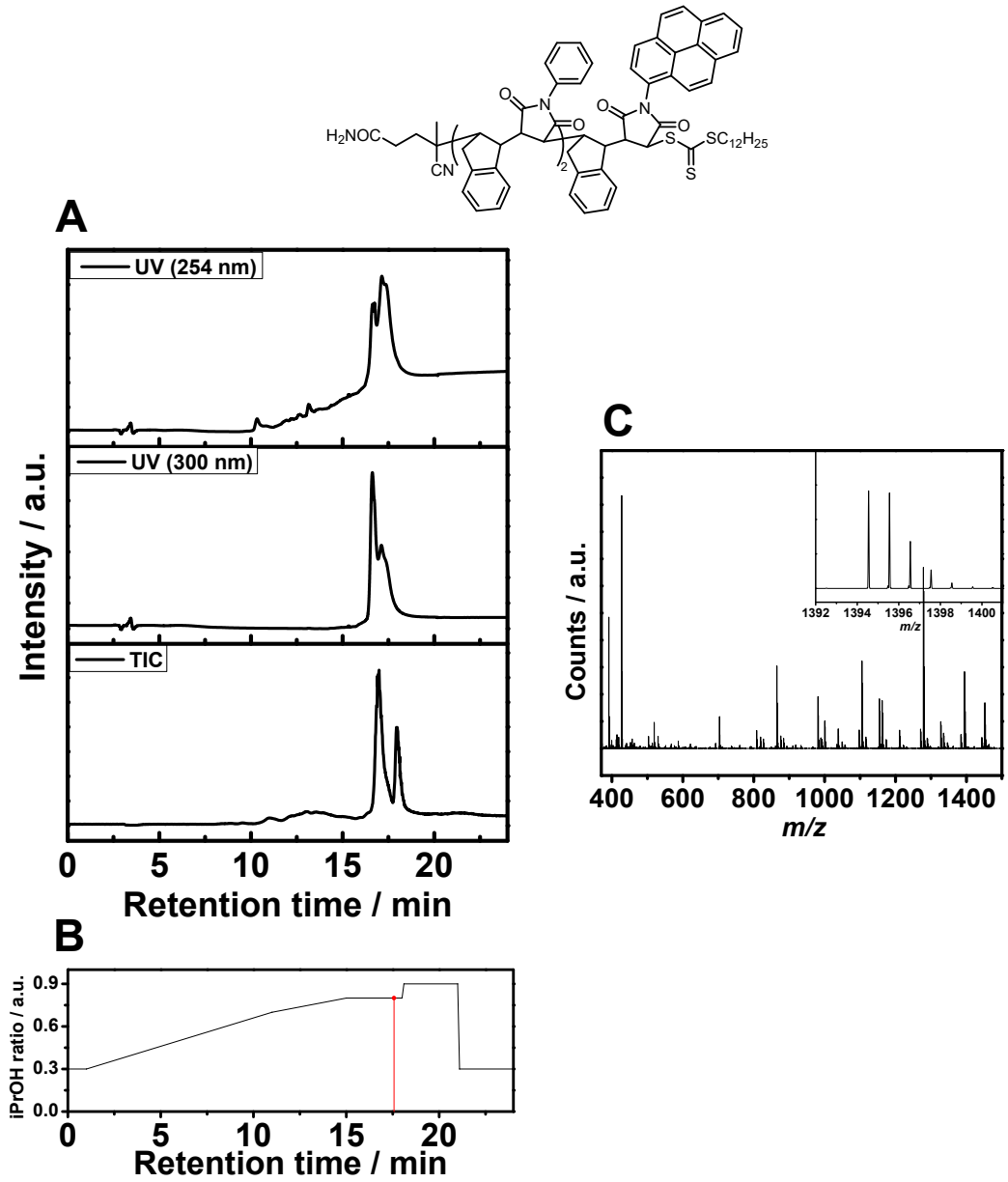



**Figure S31.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL min$^{-1}$, 25 °C) of the apparent 6-mer with *N*-(1-pyrenyl)maleimide added at the 6$^{th}$ position (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 17.57 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C)

**Table S8.** Assignment of key peaks in the mass spectrum from Figure S31C (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, Ph-Mal – *N*-phenylmaleimide, PyMal – *N*-(1-pyrenyl)maleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 17.57 | 1105.44, 1106.45, 1107.44 | CDTPAm+$(Ind)_2$+$(PhMal)_1$+ $(Py\text{-}Mal)_1$ ($H^+$) |
| | 1154.46, 1155.46, 1156.46 | CDTPAm+$(Ind)_2$+$(PhMal)_3$ ($H^+$) |
| | 1162.42, 1163.43, 1164.44 | CDTPAm+$(Ind)_1$+$(PhMal)_2$+ $(Py\text{-}Mal)_1$ ($H^+$) |

| | | |
|---|---|---|
| | 1278.49, 1279.51, 1280.49, 1281.47 | CDTPAm+$(Ind)_2$+$(PhMal)_2$+ $(Py\text{-}Mal)_1$ ($H^+$) |
| | 1384.49, 1385.49, 1386.51, 1387.51 | CDTPAm+$(Ind)_4$+$(PhMal)_3$ ($H^+$) |
| | *1394.55, 1395.55, 1396.55, 1397.56* | *CDTPAm+$(Ind)_3$+$(PhMal)_2$+ $(Py\text{-}Mal)_1$ ($H^+$)* |
| | 1451.53, 1452.53, 1453.54, 1454.53 | CDTPAm+$(Ind)_2$+$(PhMal)_3$+ $(Py\text{-}Mal)_1$ ($H^+$) |
| | 1567.59, 1568.61, 1569.60, 1570.60 | CDTPAm+$(Ind)_3$+$(PhMal)_3$+ $(PyMal)_1$ ($H^+$) |

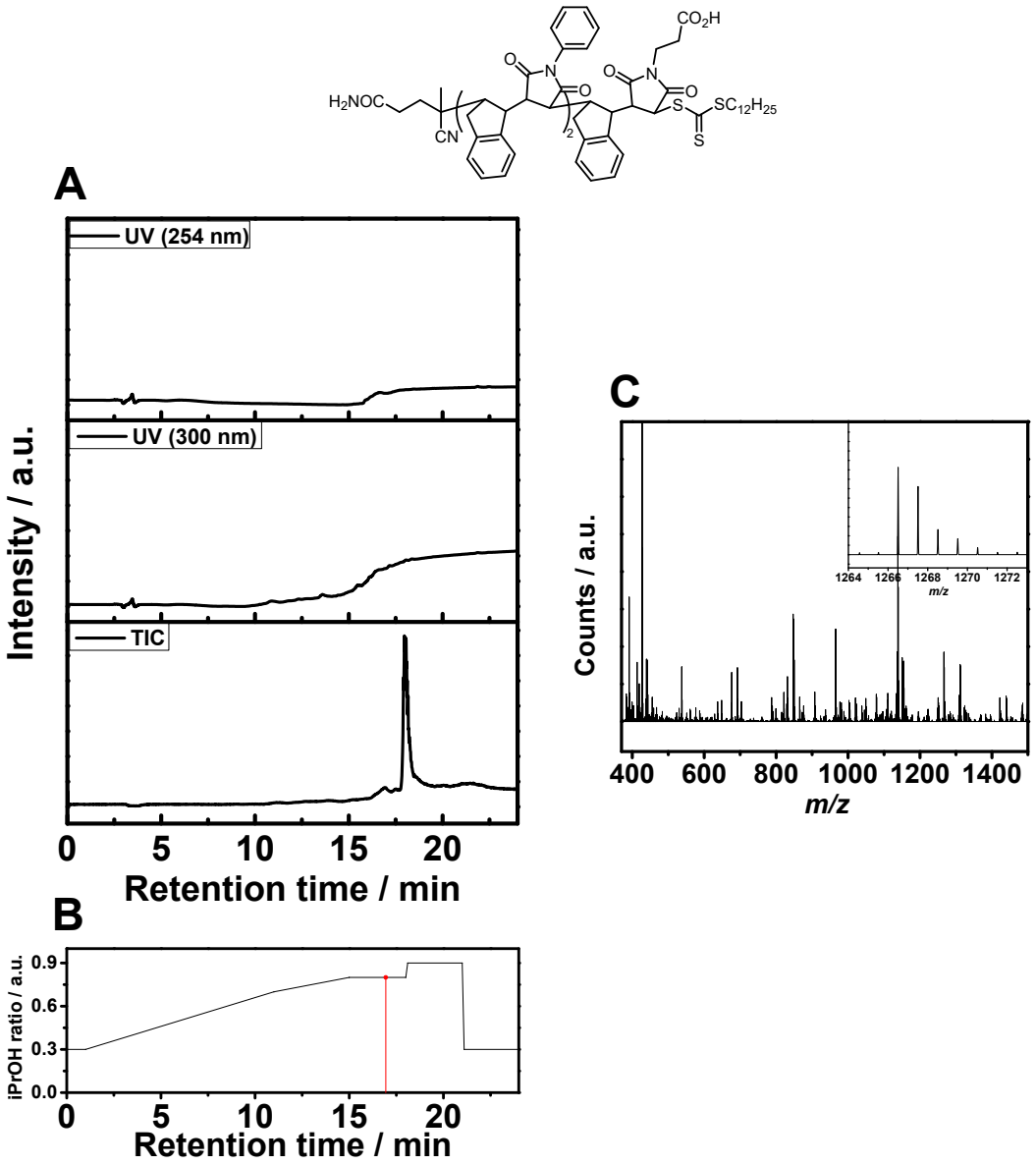



**Figure S32.** UHPLC–MS elugrams (*i*PrOH–water, 0.4 mL $min^{-1}$, 25 °C) of the apparent 6-mer with β-alanyl maleimide added at the 6th position (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 16.28 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C)

**Table S9.** Assignment of key peaks in the mass spectrum from Figure S32 (CDTPAm – CDTPA modified to the amide, TTC – dodecyltrithiocarbonate, Ind – indene, Ph-Mal – phenyl maleimide, $C_2H_4CO_2H$-Mal – β-alanyl maleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 17.57 | 1150.44 | CDTPAm+$(Ind)_{\mathbf{2}}$+$(PhMal)_{\mathbf{2}}$+ $(C_2H_4CO_2H\text{-}Mal)_{\mathbf{1}}$ ($H^+$) |
| | 1154.45 | CDTPAm+$(Ind)_{\mathbf{2}}$+$(PhMal)_{\mathbf{1}}$+ $(C_2H_4CO_2H\text{-}Mal)_{\mathbf{2}}$ ($H^+$) |
| | *1266.50, 1267.52, 1268.51, 1269.50* | *CDTPAm+$(Ind)_{\mathbf{3}}$+$(PhMal)_{\mathbf{2}}$+ $(C_2H_4CO_2H\text{-}Mal)_{\mathbf{1}}$ ($H^+$)* |

A peak at 965.42 along with peaks corresponding to adding PhMal to this (1138.47 and 1311.53) could not be identified.

## Synthesis on chlorotrityl (CTC) resins

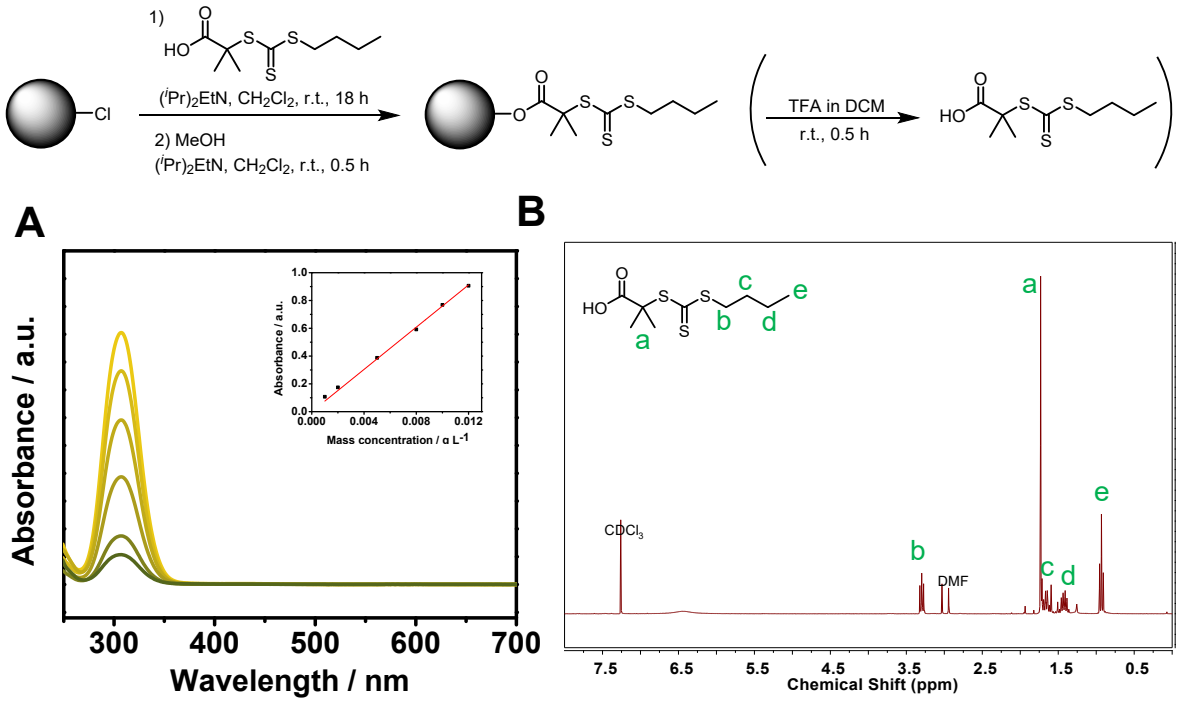



**Figure S33.** Immobilisation of BDMAT on CTC resin by methods detailed in the Experimental. UV-visible spectrophotometry (TFA in DCM, 10% v/v) calibrating BDMAT concentration to absorbance at 310 nm (y = ax, a = 72.7 ± 1.2, $R^2$ = 0.99) (A), $^1$H NMR spectrum (400 MHz, $CDCl_3$) of the cleavage product of BDMAT from CTC resin (B).

Through the addition of resin (0.05 mg mL-1, *via* dilution) to the cleavage solution, the stoichiometry was determined to be 1.56 mmol $g^{-1}$.

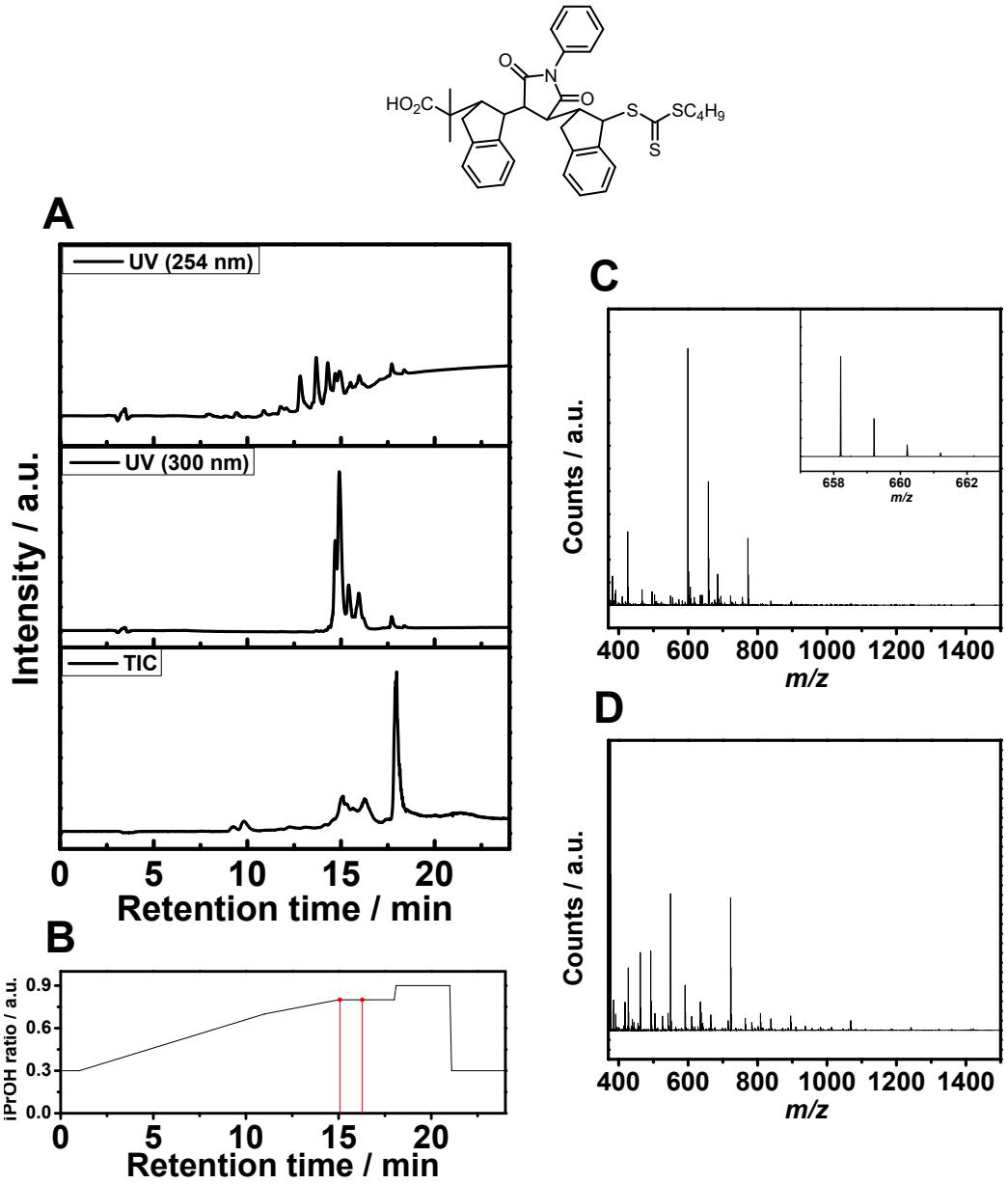



**Figure S34.** UHPLC–MS elugrams (*i*PrOH-water, 0.4 mL min$^{-1}$, 25 °C) of the apparent 3-mer (made from BDMAT immobilized on CTC resin) (A), the relevant isopropanol-water gradient used in the run (with the selected TIC time point for analysis – red) (B), the APCI–MS data from 15.07 min retention time (with the insert corresponding to a zoom-in of the peaks corresponding to the structure drawn above) (C), the APCI–MS data from 16.28 min retention time (D).

**Table S10.** Assignment of key peaks in the mass spectra from Figure S34C and Figure S34D, (TTC – dodecyltrithiocarbonate, Ind – indene, PhMal – *N*-phenylmaleimide)

| Retention time (min) | APCI–MS peaks (*m/z*) | Assigned adduct |
|---|---|---|
| 15.07 | 426.08, 427.08, 428.08 | BDMAT+$(PhMal)_1$ ($H^+$) |
| | 599.13, 600.13, 601.13 | BDMAT+$(PhMal)_2$ ($H^+$) |
| | *658.21, 659.21, 660.21* | *BDMAT+$(Ind)_2$+$(PhMal)_1$ ($H^+$)* |
| | 772.18, 773.18, 774.17 | BDMAT+$(PhMal)_3$ ($H^+$) |

| | | |
|---|---|---|
| 16.28 | 376.15, 377.16, 378.16 | BDMAT-TTC+$(Ind)_1$+$(PhMal)_1$ ($H^+$) |
| | *492.21, 493.21, 494.21* | *BDMAT-TTC+$(Ind)_2$+$(PhMal)_1$ ($H^+$)* |
| | 549.20, 550.21, 551.20 | BDMAT-TTC+$(Ind)_1$+$(PhMal)_2$ ($H^+$) |
| | 722.25, 723.24, 724.25 | BDMAT-TTC+$(Ind)_1$+$(PhMal)_3$ ($H^+$) |

It must be noted that in this sample, the trithiocarbonate elimination adducts eluted later than the main product.