Electronic Supplementary Information

Biodegradable supramolecular micelles *via* host-guest interaction of cyclodextrin terminated polypeptides and adamantane terminated polycaprolactones

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1 Materials and methods

All chemicals were purchased from *Sigma Aldrich*, *Alfa Aesar*, *Merck*, *VWR*, *Fluorochem, Carbolution, ABCR*, *Acros Organics*, *Iris Biotech* or *TCI* and used as delivered unless otherwise mentioned. THF was dried using standard laboratory techniques, *n*-pentane was dried over molecular sieves 4 Å. Extra dry DMF was purchased from Acros Organics for polymerisation. Phosphate buffered saline (PBS, 1.47 mM KH_2PO_4, 7.67 mM Na_2HPO_4, 136.9 mM NaCl, 2.7 mM KCl (pH 7.4) was prepared using ultrapure water with a resistance higher than 18 MΩ. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an DPX 300 (Bruker), Avance II 300 (Bruker), Avance II 400 (Bruker) or a DD2 600 instrument (Agilent). Chemical shifts δ in ppm are referenced to the solvent residual peak.

HRMS (ESI) was performed using a MicroTOF ESI (Bruker) and an Orbitrap LTQ XL (Thermo Scientific) and MALDI using Smart Beam TM NdYAG-laser with a wavelength of 355 nm.

IR spectra were recorded on a Digilab FTS 3100 FT-IR (Varian) equipped with a Specac MKII Golden Gate Single Reflection ATR unit.

Gel permeation chromatography (GPC) was carried using DMF (polypeptides) or THF (PCL) as eluent at a flow rate of 1.0 mL/min at 40 °C, on a system consisting a PSS (Polymer Standards Service) SECurity GPC System, a set of two PLgel 5 µm MIXED-C columns (300×7.5 mm, Agilent Technologies). Samples for GPC were prepared in DMF with 0.01 % LiBr or THF and the results were obtained after calibration using PMMA (polypeptides) or polystyrene (PCL) standards.

Dynamic light scattering (DLS) and ζ-potential measurements were carried out on a Nano ZS Zetasizer (Malvern Instruments) at 25 °C and samples were prepared in disposable 1 mL semi-micro PMMA cuvettes (BRAND) or in disposable DTS 1070 capillary cells (Malvern Instruments). Data analysis was performed with Zetasizer Software Version 7.12 (Malvern Instruments) and OriginPro 9.6.0172 (Origin).

Absorbance spectra were recorded using a V-770 spectrophotometer (JASCO) and fluorescence spectra were recorded using a FP 8500 spectrofluorometer (JASCO) with samples prepared in disposable 1 mL PMMA cuvettes.

AFM images were recorded using a Nano Wizard3 (*JPK Instruments*) in tapping mode equipped with a POINTPROBE-PLUS Silicon-SPM-Sensor cantilever (resonance frequency 290-310 kHz, force constant 10–130 N/m, *Nanosensors*) and data was analyzed with *Gwyddion 2.47*. Samples were prepared by drop casting method on freshly cleaved mica surface.

TEM measurements were performed on a JEOL JEM-1400 Plus TEM, operating at an accelerating voltage of 120 kV and a line resolution of 0.2 nm and a point resolution of 0.38 nm. Images were recorded with a CMOS digital camera 16-bit 4096 × 4096 pixel and processed with FIJI open-source software package (*Nature Methods* 2012; doi:10.1038/nmeth.2019**).** For sample preparation, one drop of the particle dispersion ($c = 0.1\ g \cdot L^{-1}$) was deposited on a carbon coated copper grid (400 mesh, Science Services). All samples were stained with 4 % Uranyl acetate solution for 1 h prior to measurements.

2 Experimental procedures

2.1 Synthesis of adamantane-poly-caprolactone (Ad-PCL$_n$)

Ad-PCL$_n$ was synthesised by the ring-opening polymerisation of *ε*-caprolactone monomer with the initiator 1-adamantane methanol (Ad-OH). In a typical procedure, for n = 60, initiator Ad-OH (25.28 mg, 0.146 mmol), catalyst $Sn(Oct)_2$ (59.15 mg, 0.146 mmol) and monomer *ε*-caprolactone (1000 mg, 8.76 mmol) were placed in a flame-dried Schlenk tube. High vacuum was applied to this reaction mixture for 30 min at room temperature, and then heated at 110 °C with continuous stirring for 4 h. The reaction mixture was cooled to room temperature (rt) and the polymer was dissolved in THF and precipitated in cold methanol. The precipitation in methanol was repeated at least twice to obtain pure polymer by redissolving in THF (yield = 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 114H, CH_2), 3.66 (m, 4H, CH_2), 2.30 (t, 116H,

CH_2), 1.64 (m, 240H, CH_2), 1.52 (m, 7H, CH_2, CH), 1.37 (m, 116H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.56, 64.16, 39.29, 36.97, 34.13, 28.36, 25.54, 24.59.

2.2 Synthesis of pentaerythritol-poly-caprolactone (EL-PCL$_n$)

EL-PCL$_n$ was synthesised by the ring-opening polymerisation of ε-caprolactone monomer with the initiator pentaerythritol following the procedure above (yield = 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.10 (s, 8H, CH_2), 4.05 (t, 114H, CH_2), 3.64 (t, 8H, CH_2), 2.30 (t, 120H, CH_2), 1.64 (m, 240H, CH_2), 1.37 (m, 120H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.57, 64.16, 62.64, 34.24, 32.35, 28.36, 25.54, 24.59.

2.3 Synthesis of dipentaerythritol-poly-caprolactone (DEL-PCL$_n$)

DEL-PCL$_n$ was synthesised by the ring-opening polymerisation of ε-caprolactone monomer with the initiator dipentaerythritol following the procedure above (yield = 75 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 136H, CH_2), 3.64 (t, 12H, CH_2), 3.38 (s, 4H, CH_2), 2.30 (t, 136H, CH_2), 1.64 (m, 272H, CH_2), 1.37 (m, 136H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.57, 64.16, 62.63, 34.13, 32.35, 28.36, 25.57, 25.31, 24.69, 24.59.

2.4 Synthesis of tripentaerythritol-poly-caprolactone (TEL-PCL$_n$)

TEL-PCL$_n$ was synthesised by the ring-opening polymerisation of ε-caprolactone monomer with the initiator tripentaerythritol following the procedure above at 150 °C (yield = 75 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 120H, CH_2), 3.63 (t, 16H, CH_2), 3.35 (s, 8H, CH_2), 2.29 (t, 120H, CH_2), 1.64 (m, 240H, CH_2), 1.37 (m, 120H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.57, 64.16, 62.62, 34.12, 32.33, 28.35, 25.53, 25.30, 24.58.

2.5 Synthesis of adamantane-poly-caprolactone-adamantane (Ad-PCL$_n$-Ad)

1-Adamantanecarboxylic acid chloride (29.28 mg, 0.147 mmol) was added to Ad-PCL$_n$ (200 mg, 0.029 mmol) in 10 mL dry DCM under argon atmosphere and then stirred for 18 h at rt. After the completion of the reaction, the polymer was precipitated in cold methanol. The precipitation in methanol was repeated at least twice to obtain pure polymer by redissolving in

DCM (yield = 85 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 114H, CH_2), 3.67 (m, 2H, CH_2), 2.30 (t, 116H, CH_2), 1.99 (m, 6H, CH_2), 1.87 (m, 6H, CH_2), 1.65 (m, 240H, CH_2), 1.52 (m, 7H, CH_2, CH), 1.38 (m, 116H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.54, 64.15, 39.31, 38.87, 36.98, 36.53, 34.13, 28.37, 28.05, 27.97, 25.54, 24.59.

2.6 Synthesis of pentaerythritol-poly-caprolactone-adamantane$_4$ (EL-PCL$_n$-Ad$_4$)

1-Adamantanecarboxylic acid chloride (113.79 mg, 0.572 mmol) was added to EL-PCL$_n$ (200 mg, 0.028 mmol) in 10 mL dry DCM under argon atmosphere and then stirred for 18h at rt. After the completion of the reaction, the polymer was precipitated in cold methanol. The precipitation in methanol was repeated at least twice to obtain pure polymer by redissolving in DCM (yield = 85 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.11 (s, 8H, CH_2), 4.05 (t, 120H, CH_2), 2.30 (t, 120H, CH_2), 2.00 (m, 24H, CH_2), 1.88 (m, 24H, CH_2), 1.65 (m, 252H, CH_2), 1.38 (m, 120H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.54, 64.15, 38.87, 36.53, 34.13, 28.37, 27.97, 25.54, 24.59.

2.7 Synthesis of dipentaerythritol-poly-caprolactone-adamantane$_6$ (DEL-PCL$_n$-Ad$_6$)

1-Adamantanecarboxylic acid chloride (148.72 mg, 0.748 mmol) was added to DEL-PCL$_n$ (200 mg, 0.025 mmol) in 10 mL dry DCM under argon atmosphere and then stirred for 18 h at rt. After the completion of the reaction, the polymer was precipitated in cold methanol. The precipitation in methanol was repeated at least twice to obtain pure polymer by redissolving in DCM (yield = 85 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 148H, CH_2), 3.39 (s, 4H, CH_2), 2.30 (t, 136H, CH_2), 2.00 (m, 36H, CH_2), 1.87 (m, 36H, CH_2), 1.64 (m, 290H, CH_2), 1.37 (m, 136H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.53, 64.14, 38.87, 34.13, 28.36, 27.97, 25.54, 24.59.

2.8 Synthesis of tripentaerythritol-poly-caprolactone-adamantane$_6$ (TEL-PCL$_n$-Ad$_6$)

1-Adamantanecarboxylic acid chloride (198.69 mg, 1.14 mmol) was added to TEL-PCL$_n$ (200 mg, 0.028 mmol) in 10 mL dry DCM under argon atmosphere and then stirred for 18 h at rt. After the completion of the reaction, the polymer was precipitated in cold methanol. The

precipitation in methanol was repeated at least twice to obtain pure polymer by redissolving in DCM (yield = 85 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (t, 136H, CH_2), 3.36 (s, 8H, CH_2), 2.30 (t, 120H, CH_2), 2.00 (m, 48H, CH_2), 1.87 (m, 48H, CH_2), 1.64 (m, 264H, CH_2), 1.37 (m, 120H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.57, 64.16, 38.86, 36.52, 34.13, 28.37, 27.96, 25.54, 24.59.

2.9 Synthesis of *β*-cyclodextrin monotosylate (CD-OTS)

β-Cyclodextrin (5.0 g, 4.41 mmol) was mixed with 110 mL water and heated at 60 °C until it dissolved completely. After the temperature of the reaction mixture was reduced to rt, *p*-toluenesulfonyl)-imidazole (3.9 g, 17.62 mmol) was ground and added, and then stirred for 2 h at rt. A turbid solution was observed. NaOH (2.29 g, 57.27 mmol) in 10 mL water was added to the reaction mixture and stirred for 20 min. Ammonium chloride (6.25 g, 145.38 mmol) was added and stirred until no solid was left in the reaction mixture. The reaction mixture was cooled to 0 °C in ice bath to induce precipitation, the residue was vacuum filtered, and washed with water and acetone multiple times. The solid obtained was redissolved in DMSO and precipitated using acetone, which was again vacuum filtered and washed multiple times with acetone. The solid was dried under high vacuum to obtain CD-OTS as white powder.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 7.76 (d, 2H, ArCH), 7.44 (d, 2H, ArCH), 5.89–5.60 (m, 14H, OH), 4.85–4.75 (m, 7H, CH), 4.55–4.32 (m, 6H, OH), 3.73–3.41 (m, 28H, CH, CH_2), 3.4–3.21 (m, 14H, CH), 2.40 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, DMSO-d_6, δ):133.12, 130.32, 128.02, 102.43, 95.58, 81.98, 73.50, 72.88, 72.81, 72.47, 60.34, 21.64. MALDI: calculated for $C_{49}H_{76}O_{37}S$, 1288.4 and found 1311.49 for $[M+Na]^+$. Yield = 70 %

2.10 Synthesis of *β*-cyclodextrin azide (CD-N_3)

CD-OTS (4.0 g, 3.02 mmol) was placed in a flame-dried Schlenk flask and dissolved in 20 mL dry DMF under argon. NaN_3 (0.98 g, 15 mmol) was added to the reaction mixture and stirred for 2 days at 80 °C. After completion of the reaction, the product was obtained by precipitation in cold acetone and vacuum filtration. The solid obtained was purified again by recrystallisation

in water and precipitation in acetone. After filtration and drying under high vacuum the product was obtained as white solid.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 5.85–5.54 (m, 14H, OH), 4.95–4.75 (m, 7H, CH), 4.59–4.38 (m, 6H, OH), 3.8–3.47 (m, 28H, CH, CH_2), 3.46–3.21 (m, 14H, CH). ^{13}C-NMR (100 MHz, DMSO-d_6, δ): 102.40, 82.01, 73.53, 72.87, 72.68, 72.51, 60.25, 51.57, 31.18. MALDI: Calculated for $C_{42}H_{69}O_{39}N_3$, 1160.0 and found 1183.3 for $[M+Na]^+$. Yield = 80 %

2.11 Synthesis of *β*-cyclodextrin amine (CD-NH_2)

To a solution of CD-N_3 (2.0 g, 1.72 mmol) in 10 mL DMF, PPh_3 (0.6 g, 1.9 mmol) was added and stirred for 2 h at rt. 1 ml water was then added and the reaction mixture was refluxed for 3 h. After the completion of the reaction, the product was precipitated in acetone, filtered, and washed multiple times with acetone. The powder obtained was redissolved in DMSO, precipitated again in acetone, which was then filtered and washed with acetone, to obtain the desired product as white solid after drying under high vacuum.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 5.85–5.52 (m, 14H, OH), 4.95–4.75 (m, 7H, CH), 4.59–4.38 (m, 6H, OH), 3.8–3.47 (m, 28H, CH, CH_2), 3.46–3.21 (m, 14H, CH). ^{13}C-NMR (100 MHz, DMSO-d_6, δ): 102.39, 81.94, 73.51, 72.88, 72.49, 60.37, 31.18. MALDI: Calculated for $C_{42}H_{71}O_{39}N$, 1134.3 and found 1156.35 for $[M+Na]^+$. Yield = 65 %

2.12 Synthesis of *ε*-benzyloxycarbonyl-*L*-lysine-*N*-carboxyanhydride (ZLL-NCA)

Triphosgene (1.5 g, 5.71 mmol) was added to a solution of *ε*-benzyloxycarbonyl-*L*-lysine (4.0 g, 14.27 mmol) in 40 mL of dry THF under argon, stirred at 45 °C until the solution became clear and further for 1 h. 90 % of the solvent was evaporated under reduced pressure at 45 °C and then the product was precipitated by adding to cold, dry *n*-pentane. The white precipitate was vacuum filtered and washed with dry *n*-pentane. The product was further purified by recrystallizing from THF/*n*-pentane to obtain a white powder after drying under high vacuum (yield = 90 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (m, 5H, Ar H), 7.13 (s, 1H, NH), 5.09 (s, 2H, CH_2O), 5.00 (s, 1H, NH), 4.25(t, 1H, CH), 3.19 (t, 1H, CH_2NH), 1.80 (m, 2H, CH_2), 1.52

(m, 4H, CH_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.63, 156.63, 152.24, 136.02, 128.29, 127.94, 127.72, 66.63, 57.13, 39.78, 30.49, 28.79, 20.98. IR (ATR): *v* = 3337 (m), 2941 (m), 1856 (m), 1780 (s), 1695 (m), 1528 (m), 1455 (w), 1260 (m), 1132 (w), 923 (m) cm^{-1}; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{18}N_2O_5$, 329,1216; found, 329.1105.

2.13 Synthesis of *γ*-benzyl-*L*-glutamate-*N*-carboxyanhydride (BLG-NCA)

Triphosgene (1.5 g, 5.06 mmol) was added to a solution of *γ*-benzyl-*L*-glutamate (4.0 g, 12.64 mmol) in 40 mL dry THF under Argon, stirred at 45 °C until the solution was clear and further for 1 h. 90 % of the solvent was evaporated under reduced pressure at 45 °C and then the product was precipitated by adding to cold dry *n*-pentane, washed with dry *n*-pentane. The product was further purified by recrystallizing from THF/*n*-pentane to obtain a white powder after drying under high vacuum (yield = 90 %). ^1H NMR (400 MHz, DMSO-d_6, δ): 7.35 (m, 5H, Ar **H**), 6.65 (s, 1H, N**H**), 5.14 (s, 2H, C**H**$_2$O), 4.38(t, 1H, C**H**), 2.59 (t, 2H, C**H**$_2$ COO), 2.24 (m, 2H, C**H**$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.28, 169.24, 151.73, 135.06, 128.59, 128.48, 128.25, 67.00, 56.80, 29.70, 26.76; IR (ATR): *v* = 3324 (m), 2944 (w), 1857 (m), 1781 (s), 1731 (m), 1357 (w), 1170 (m), 1107 (m), 923 (m) cm^{-1}; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{13}NO_5$, 286.0895; found, 286.0684.

2.14 Synthesis of cyclodextrin-poly- *ε*-benzyloxycarbonyl-*L*-lysine (CD-PZLL$_n$)

CD-PZLL$_n$ was synthesised by ring-opening polymerisation of ZLL-NCA monomer. In a typical procedure for n = 50, ZLL-NCA (0.5 g, 1.6 mmol) monomer was dissolved in 9 mL dry DMF in a Schlenk tube under argon. The initiator CD-NH_2 (46.27 mg, 0.04 mmol) in 1 mL dry DMF was then injected to the solution and then stirred for 2 d at room temperature. The polymer was precipitated in cold diethyl ether, centrifuged to get the product, washed with diethyl ether multiple times. The obtained precipitate was then dissolved in dichloromethane and again precipitated in diethyl ether to obtain the white powdered polymer after centrifugation (yield = 80 %). ^1H-NMR (400 MHz, DMSO-d_6, δ): 8.59-7.71 (b, NH), 7.35-7.07 (b, Ar H), 5.87-5.63 (b, NH, OH), 5.13-4.79 (b, CH_2O, CH), 4.47 (b, OH), 3.97-3.55 (b, CH), 3.44-3.27 (b, CH),

3.0-2.83 (b, CH_2), 2.0-0.94 (b, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 156.77, 136.83, 128.55, 128.13, 128.07, 66.60, 41.00, 29.57, 23.70.

2.15 Synthesis of cyclodextrin-poly-*L*-lysine (CD-PLL$_n$)

Deprotection of CD-PZLL$_n$ gives CD-PLL$_n$. Ad-PZLL$_n$ (200 mg) was dissolved in 2 mL TFA and 0.5 mL HBr (33 % in acetic acid) was added. The reaction mixture was precipitated into an excess of cold diethyl ether after stirring for 1 h at room temperature. The obtained precipitate was washed multiple times with diethyl ether and dried under high vacuum. Further purification by dialysis against water and freeze drying gives the pure product, CD-PLL$_n$, as white powder. ^1H-NMR (400 MHz, D_2O, δ): 4.41-4.2 (b, CH), 4.00-3.52 (b, CH), 3.1-2.98 (b, CH_2), 1.94-1.34 (b, CH_2); ^{13}C NMR (100 MHz, D_2O-d_6, δ): 173.58, 53.36, 39.19, 30.60, 26.34, 22.16.

2.16 Synthesis of cyclodextrin-Poly-*γ*-benzyl-*L*-glutamate (CD-PBLG$_n$)

CD-PBLG$_n$ was synthesised by ring opening polymerisation of BLG-NCA monomer following procedure **2.14**. ^1H-NMR (400 MHz, DMSO-d_6, δ): 8.54-8.00 (b, NH), 7.38-7.14 (b, ArH), 5.88-5.62 (b, OH), 5.13-4.7 (b, CH_2O, CH), 4.47 (b, OH), 4.09-3.78 (b, CH), 3.75-3.5 (b, CH, CH_2), 2.82-1.77 (b, CH_2); ^{13}C-NMR (100 MHz, DMSO-d_6, δ): 173.22, 135.14, 128.61, 129.33, 65.38, 30.79.

2.17 Synthesis of cyclodextrin-poly-*L*-glutamate (CD-PLGn)

Deprotection of the acid groups on the polymer CD-PBLG$_n$ gives CD-PLG$_n$ following the procedure **2.15**. ^1H-NMR (400 MHz, D_2O, δ): 4.35-4.27(t, CH), 4.03-3.51 (CH, CH_2), 2.35-2.16 (m, CH_2), 2.09-1.82 (m, CH_2), ^{13}C-NMR (100 MHz, D_2O, δ): 181.49, 173.47, 53.39, 33.53, 28.04.

2.18 Preparation of cyclodextrin/adamantane supramolecular micelles (CASM$_x^{+/-}$)

For the preparation of 1 mL CASM$_1^-$ with 100 μM CD and Ad, 0.25 mL Ad-PCL$_n$ (400 μM) in DMF was added to CD-PLG$_n$ (133.33 μM) in 0.75 mL aqueous solution under vigorous stirring. After 4 h, this solution was transferred to dialysis membrane with 1KD MWCO, which was

dialysed against water for 1 day. Fresh water was replenished in regular intervals. Similarly, other CASM was prepared with the corresponding polymers.

2.19 Dye loading in $CASM_x^-$

For the preparation of 1 mL dye loaded $CASM_1^-$ with 100 μM CD and Ad, 0.25 mL Ad-PCL_n (400 μM) and 0.1 mg dye (e.g., nile red) in DMF was added to CD-PLG_n (133.33 μM) in 0.75 mL aqueous solution under vigorous stirring. After 4 h, this solution was transferred to dialysis membrane with 1KD MWCO, which was dialysed against water for 1 day. Fresh water was replenished in regular intervals. Similarly, other dye loaded CASM were prepared with the corresponding polymers.

2.20 Biodegradation study

Freshly prepared supramolecular micelles were taken in a vial and 1 mg enzyme (trypsin or esterase from porcine liver) was added to it with slow stirring. After the observation of turbid solution (30 min) DLS was measured. For the nile red loaded micelles, the turbid solution was filtered and then absorbance was measured.

2.21 Bacterial strains and culture conditions

B. subtilis strain DB104 was grown on lysogeny broth (LB) agar and kept at 4 °C. A single isolated colony was picked from this plate, transferred to 3 ml LB broth, and incubated aerobically overnight at 37 °C in a shaker incubator at 180 rpm. The following day, bacteria were suspended in 10 mL of fresh LB medium to an optical density OD_{600} = 0.1 and grown in a flask to an attenuation of approximately OD_{600} = 0.4. Thereafter, the bacterial suspensions were centrifuged at 4000 rpm for 5 min, resuspended in a buffer solution to the final bacterial concentration of approximately $1x10^{-8}$ cells per mL, and used for the experiments.

2.22 Photoinactivation of bacteria

For the irradiation experiments, 1 mL of photosensitiser (PS) stained bacteria with or without 100 mM KI (15 min, 37 °C) was placed in a 24-well plate and irradiated with an LED lamp

(660 ± 24 nm) for a certain duration. A power meter (Solar Meter from Solartech) was used to measure fluence rates regularly. After irradiation, viable bacterial cells were determined by serial dilutions of the bacterial suspension plated on Luria-Bertani agar plates. The number of CFU/ml was calculated using a ProtoCOL automatic colony counter from Synbiosis.

3 Additional experimental data

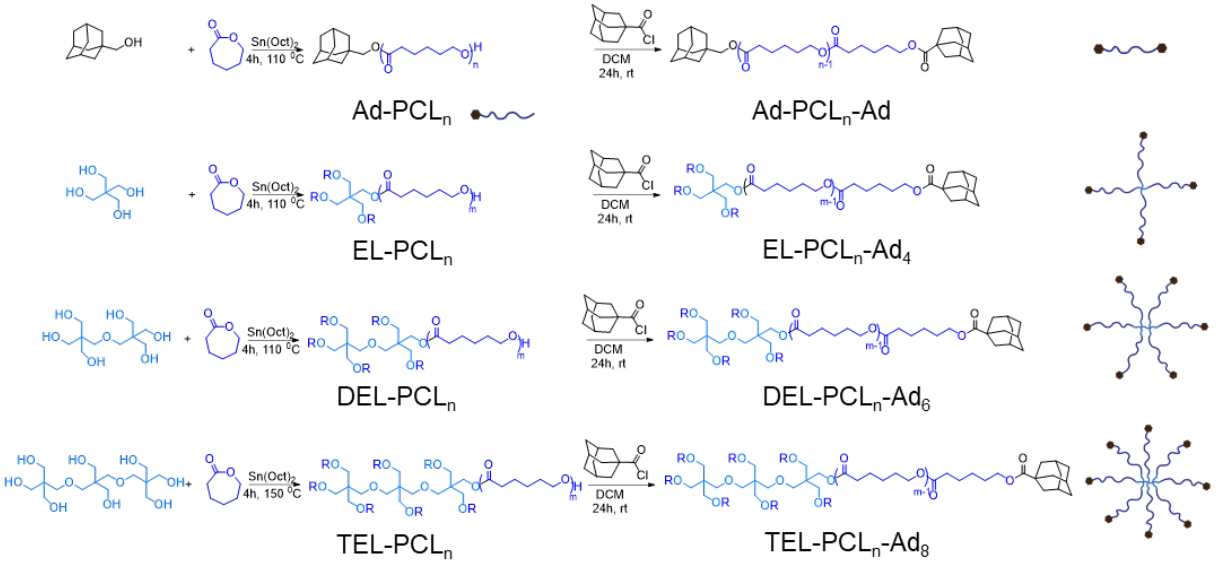


Figure S1: Synthesis scheme of different types of PCL polymers and their end group modification to give Ad terminated PCL. Cartoon representation of PCL polymers with Ad end groups is shown on the right.

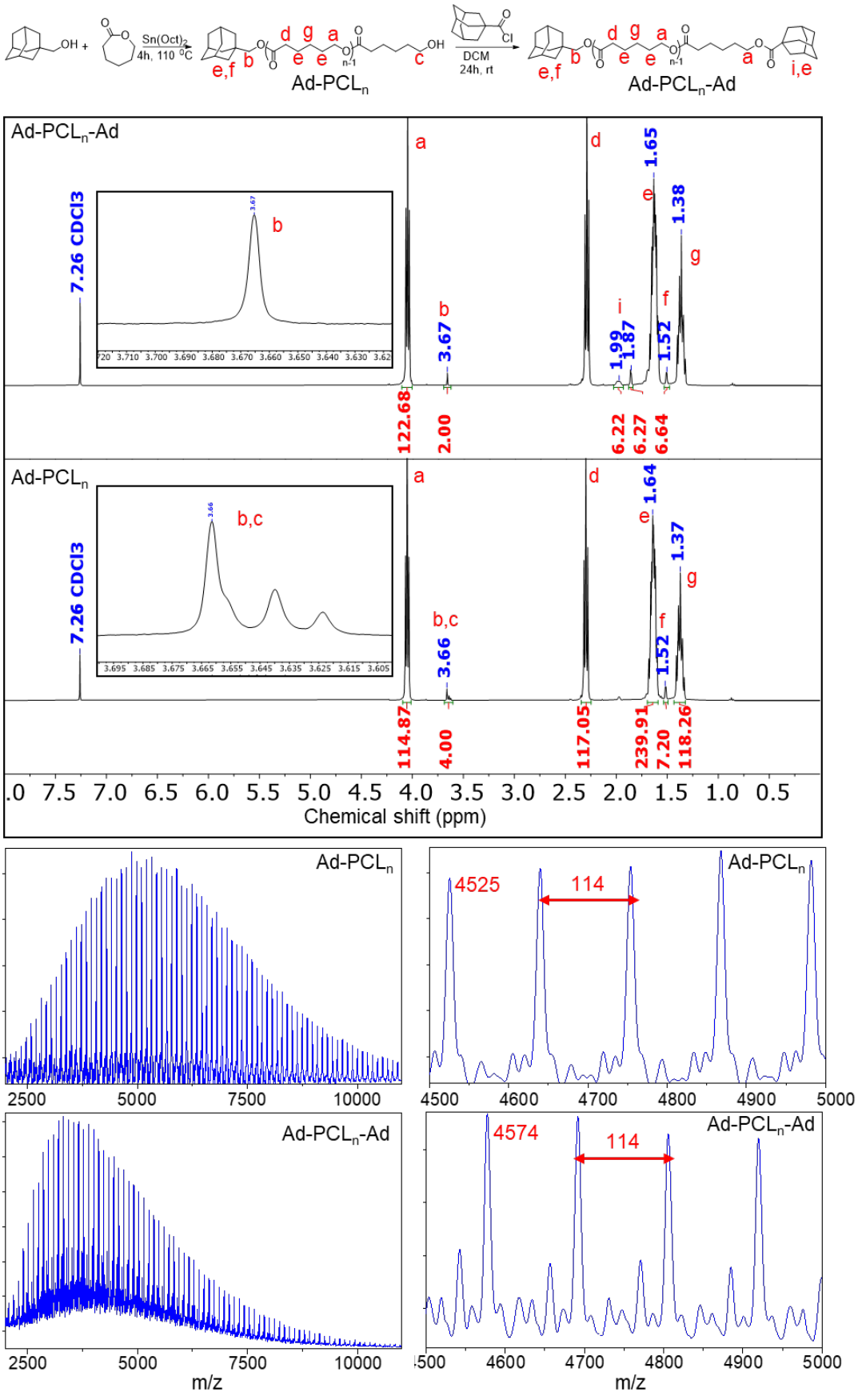


Figure S2: ^{1}H-NMR and MALDI spectra of Ad-PCL$_n$ and Ad-PCL$_n$-Ad

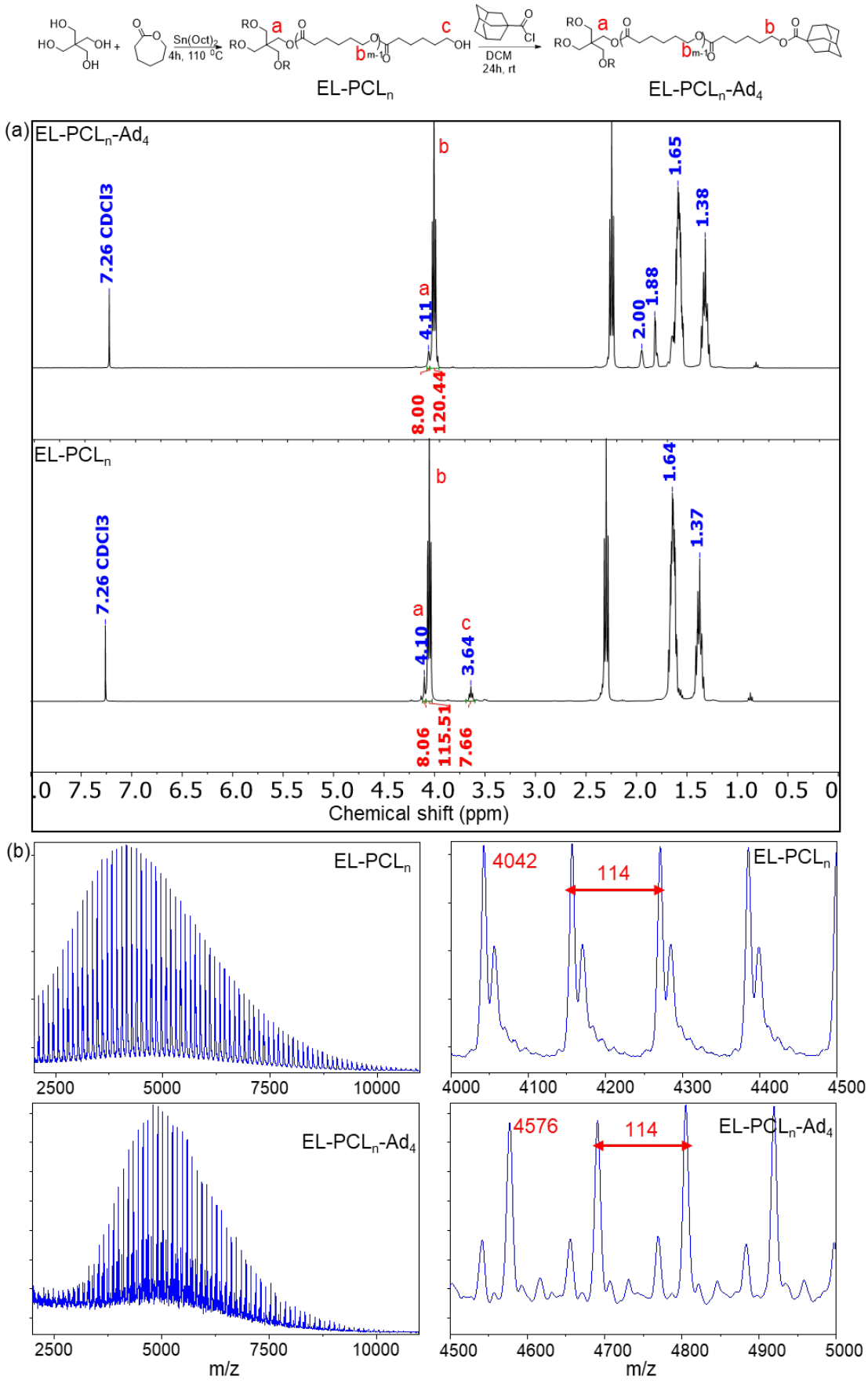


Figure S3: a) ^{1}H-NMR b) MALDI spectra of EL-PCL$_n$ and EL-PCL$_n$-Ad$_4$

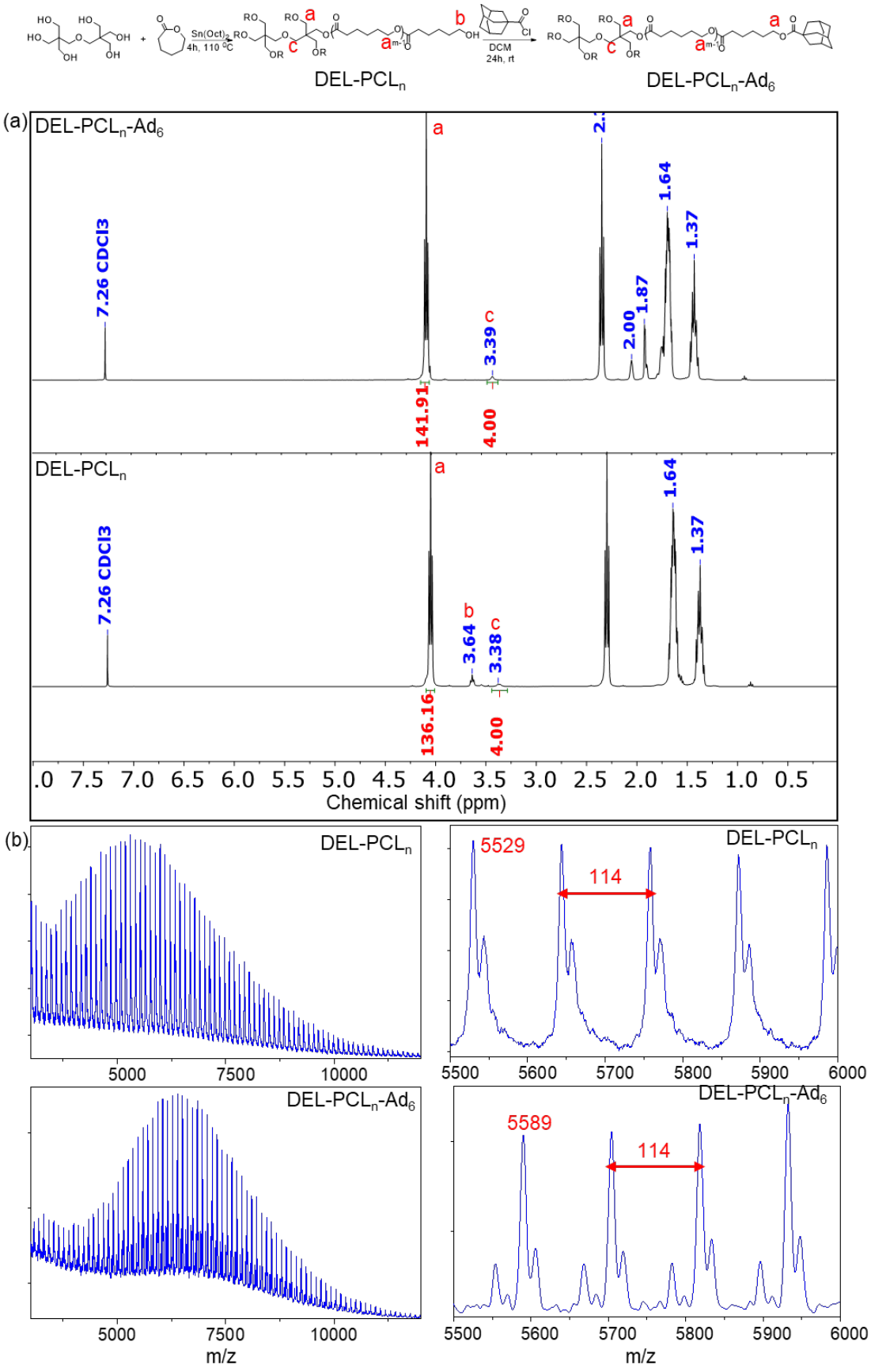


Figure S4: a) ^{1}H-NMR b) MALDI spectra of DEL-PCL$_n$ and DEL-PCL$_n$-Ad$_6$

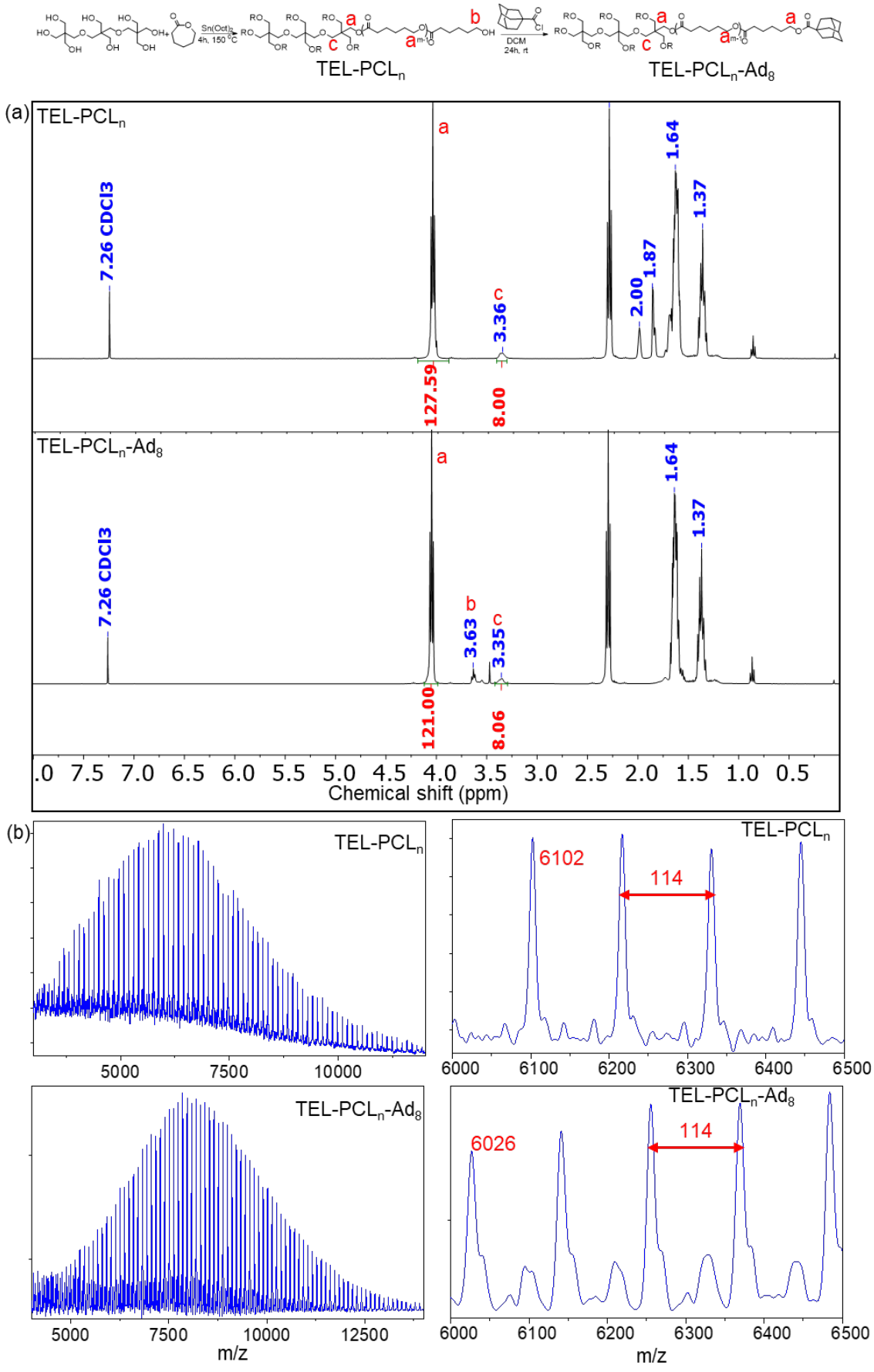


Figure S5: a) ^{1}H-NMR b) MALDI spectra of TEL-PCL$_n$ and TEL-PCL$_n$-Ad$_8$

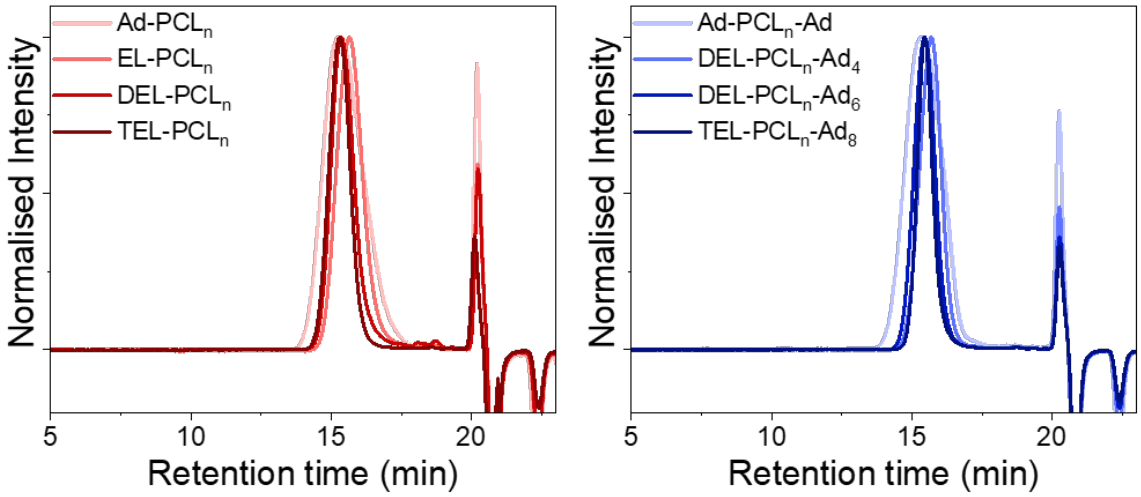


Figure S6: GPC data of all the PCL polymers measured with THF as an eluent.

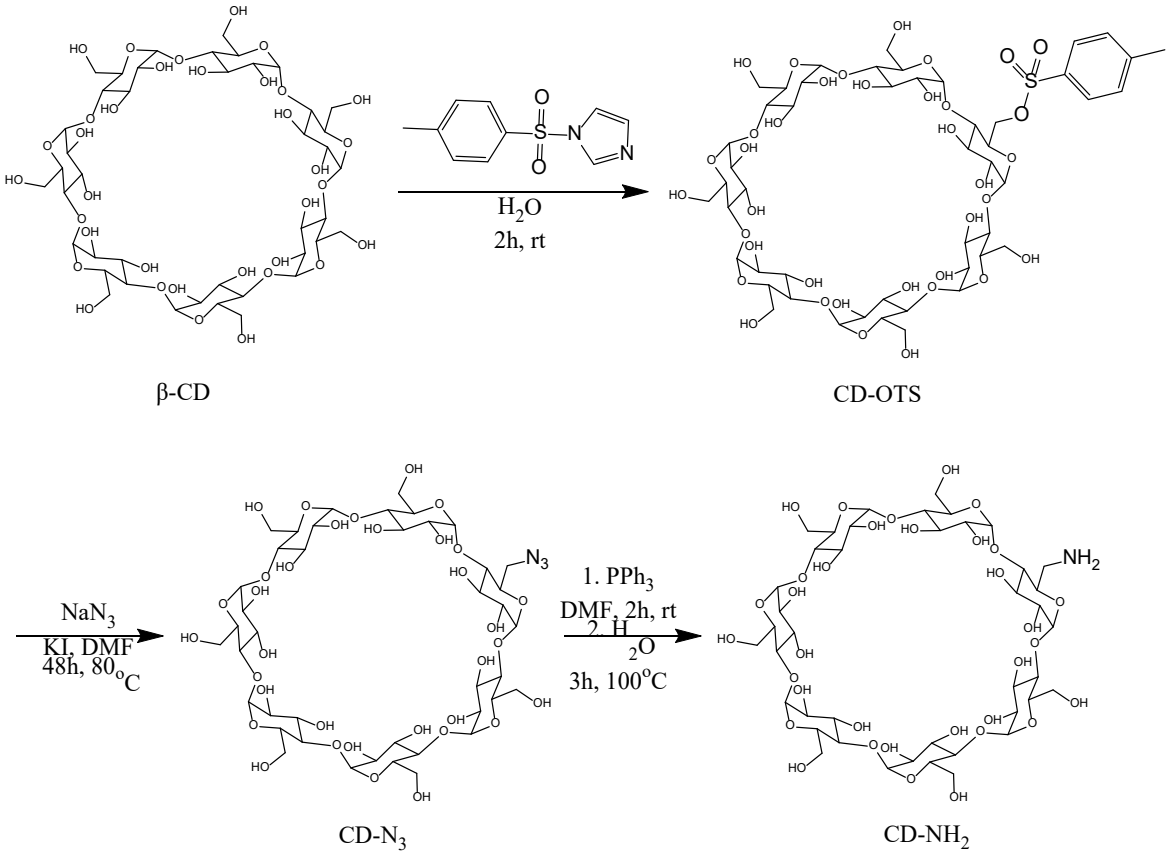


Figure S7: Synthesis of *β*-CD amine (CD-NH_2).

Single amine containing CD initiator *β*-CD amine (CD-NH_2) was synthesised from *β*-CD. Monotosylation of *β*-CD (CD-OTS) was achieved using 1-(*p*-Toluenesulfonyl)imidazole as the tosylating agent, which was confirmed by NMR and MALDI analysis. CD-N_3 was obtained by substitution reaction by NaN_3, and the azide was converted to amine using PPh_3 to obtain CD-NH_2.

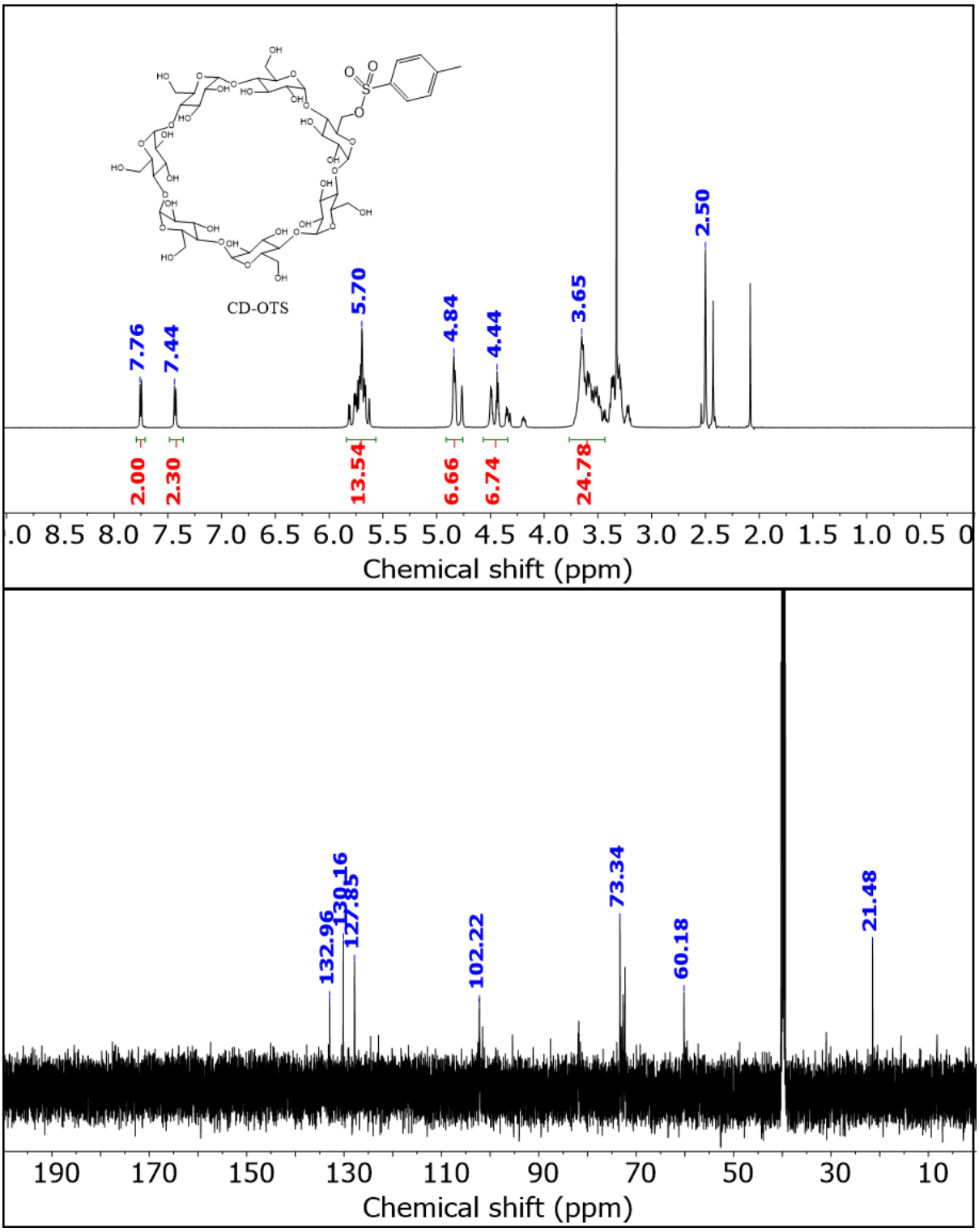


Figure S8: NMR spectra of CD-OTS

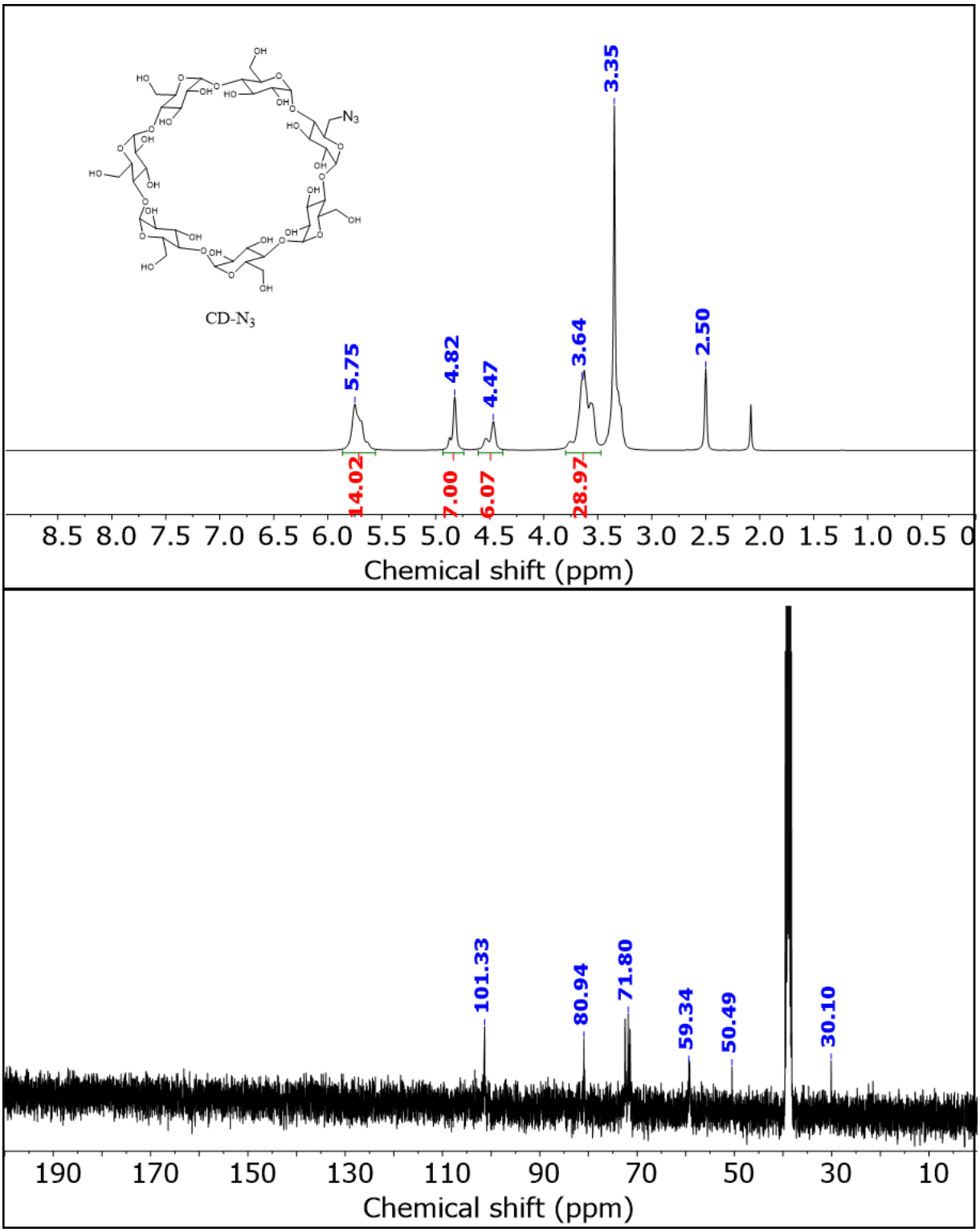


Figure S9: NMR spectra of CD-N_3

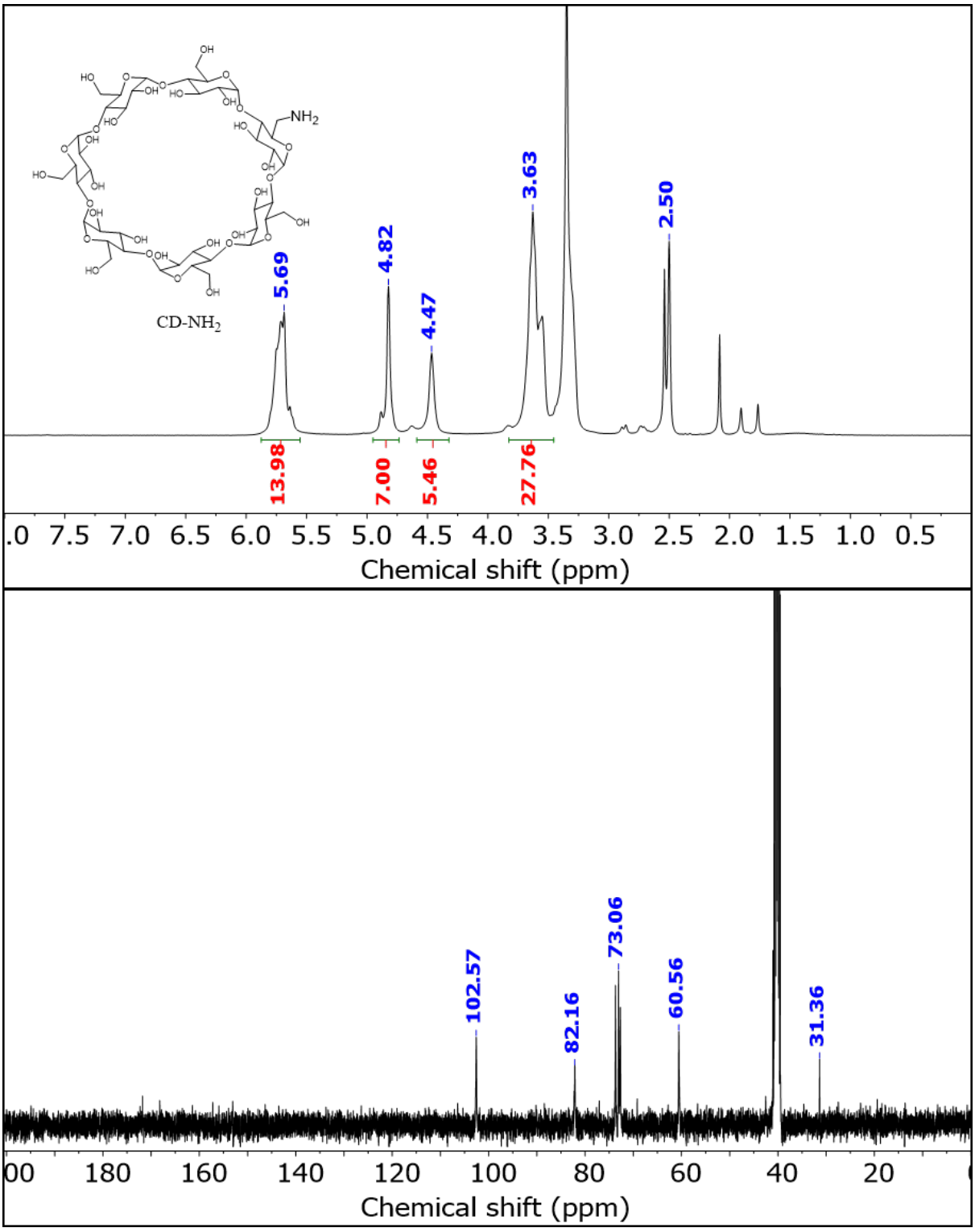


Figure S10: NMR spectra of CD-NH_2

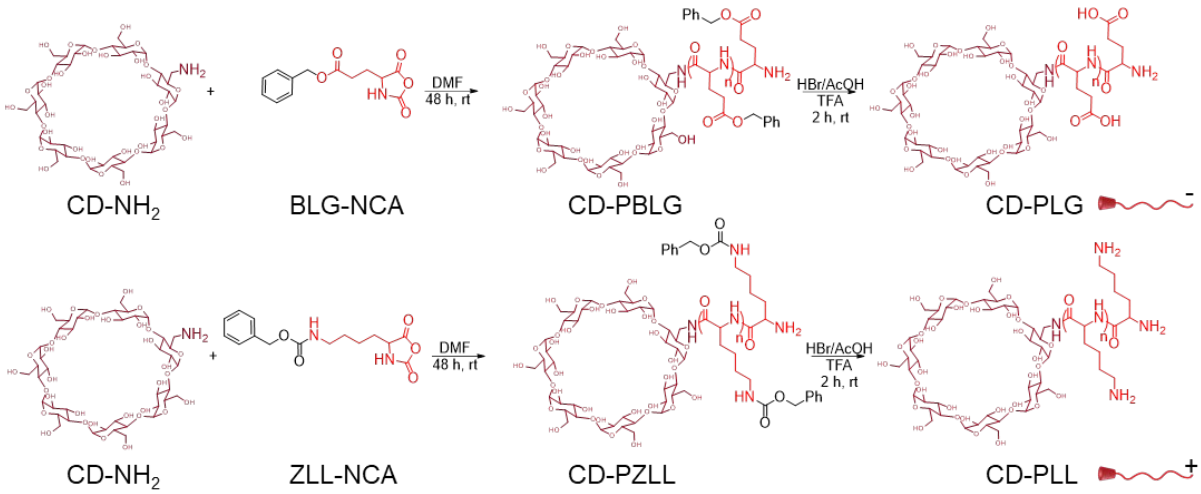


Figure S11: Synthesis of CD-PLG and CD-PLL using NCA polymerisation.

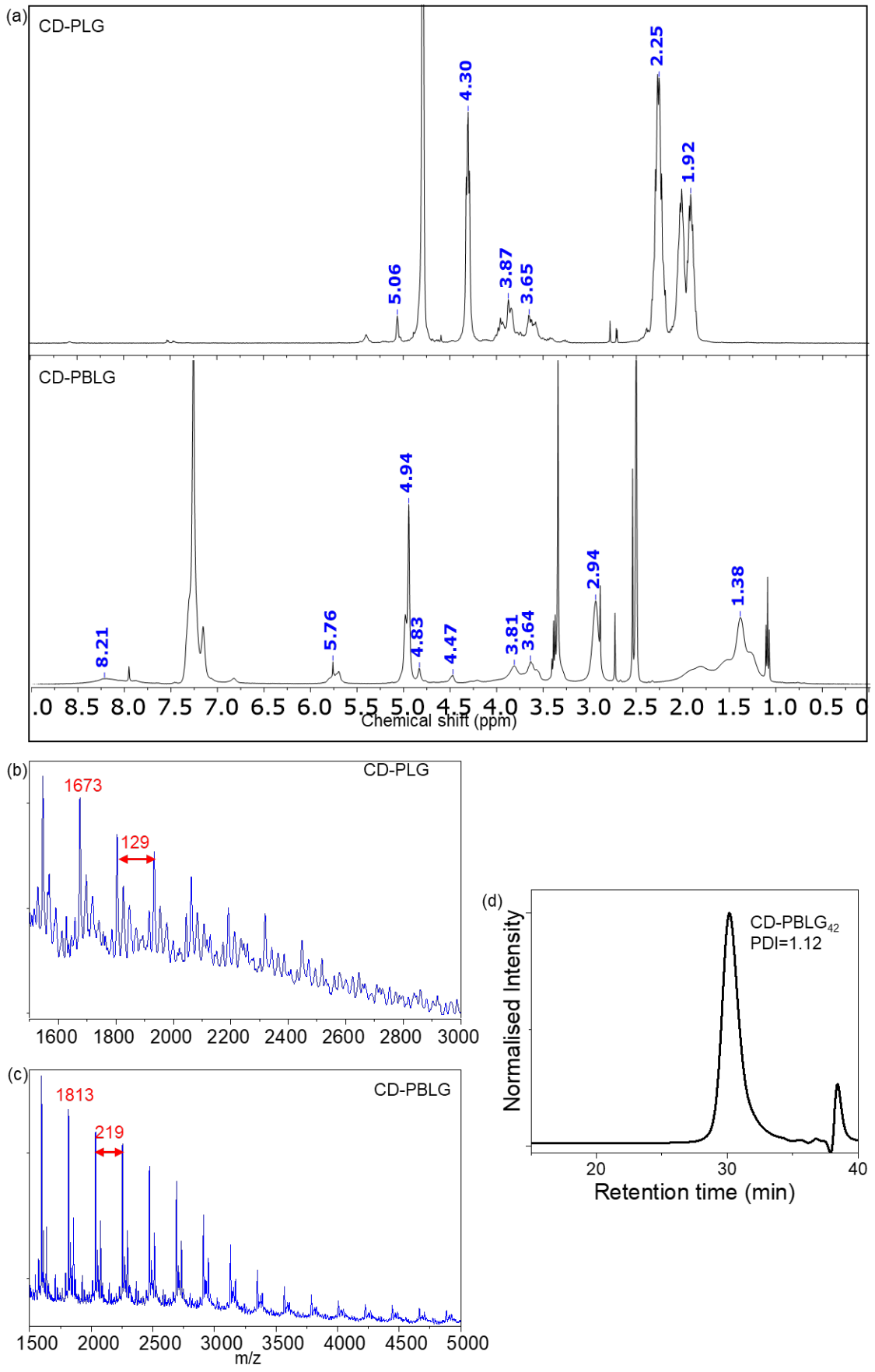


Figure S12: a) ^{1}H-NMR of CD-PLG$_n$ (DMSO-d$_6$) and CD-PBLG$_n$ (D$_2$O), MALDI spectra of b) CD-PLG$_n$, c) CD-PBLG$_n$, d) GPC chromatogram of CD-PBLG$_{42}$.

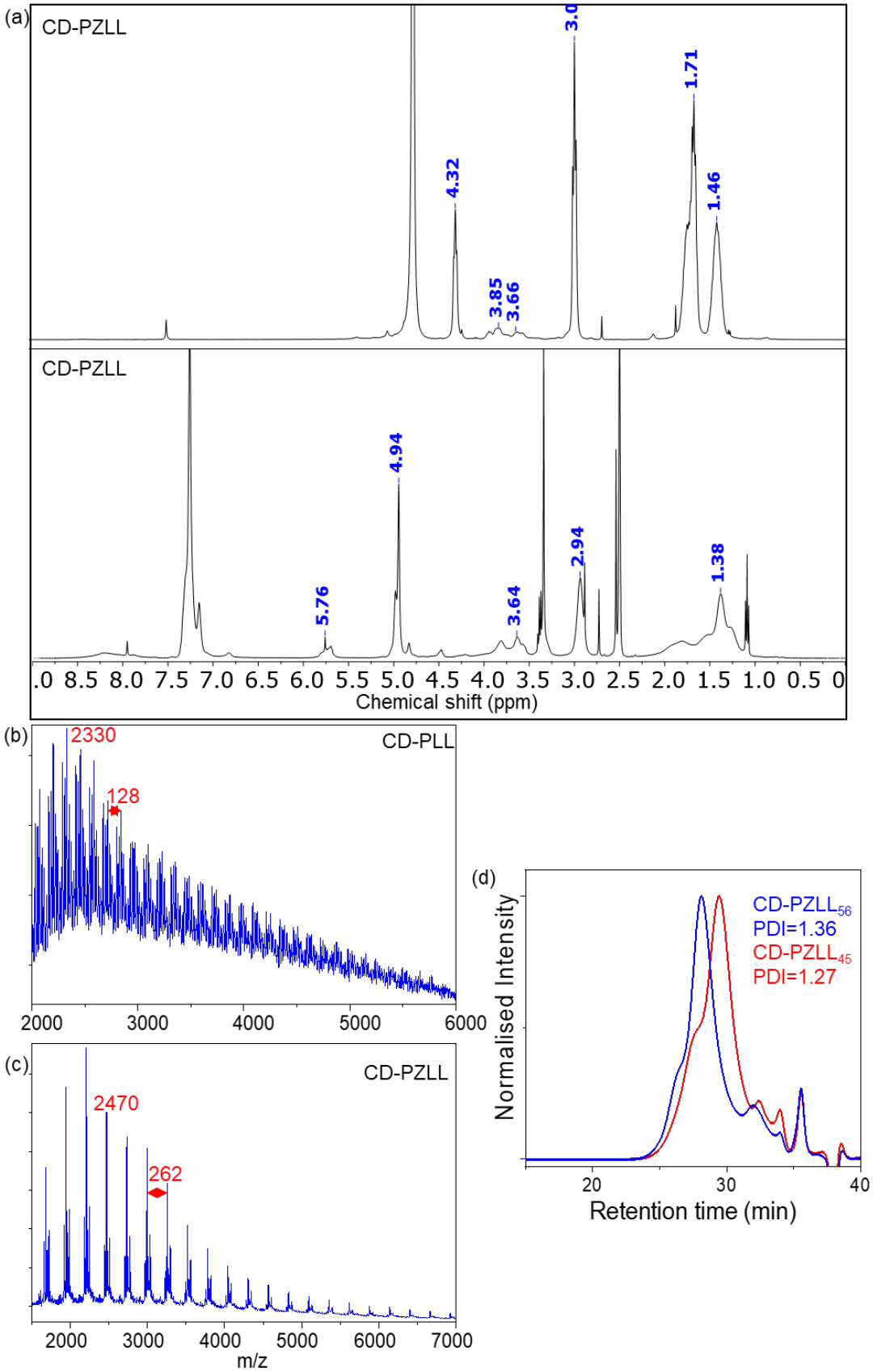


Figure S13: a) ^{1}H-NMR of CD-PZLL$_n$, CD-PLL$_n$. MALDI spectra of b) CD-PLL$_n$, c) CD-PZLL$_n$. d) GPC data of CD-PZLL$_n$.

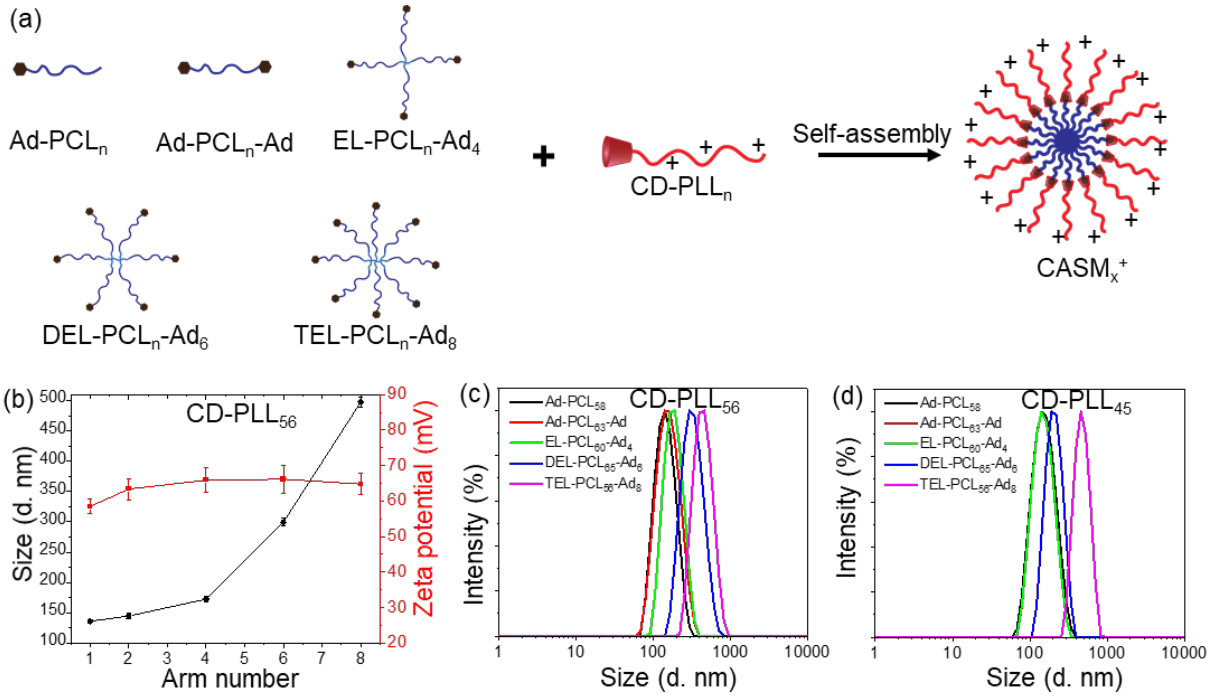


Figure S14: a) Schematic illustration of the formation of CASM$_x^+$ from different hydrophobic components and CD-PLL. b) size and zeta potential obtained with increase in arm number. c,d) DLS data obtained for CASM$_x^+$ with CD-PLL$_{56}$ and CD-PLL$_{45}$.

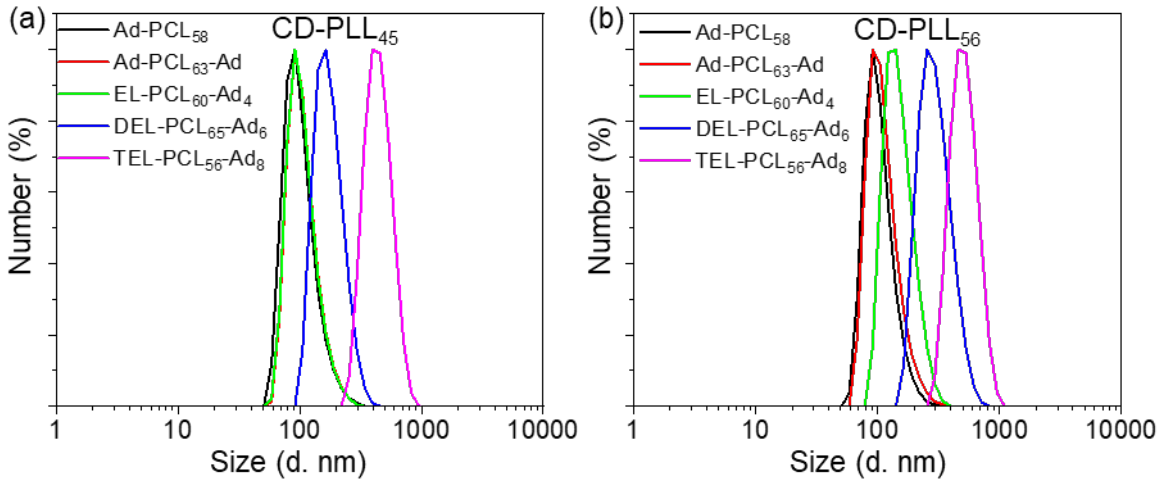


Figure S15: number percent DLS data for a) CASM$_x^+$ formed with CD-PLL$_{45}$ b) CASM$_x^+$ formed with CD-PLL$_{56}$.

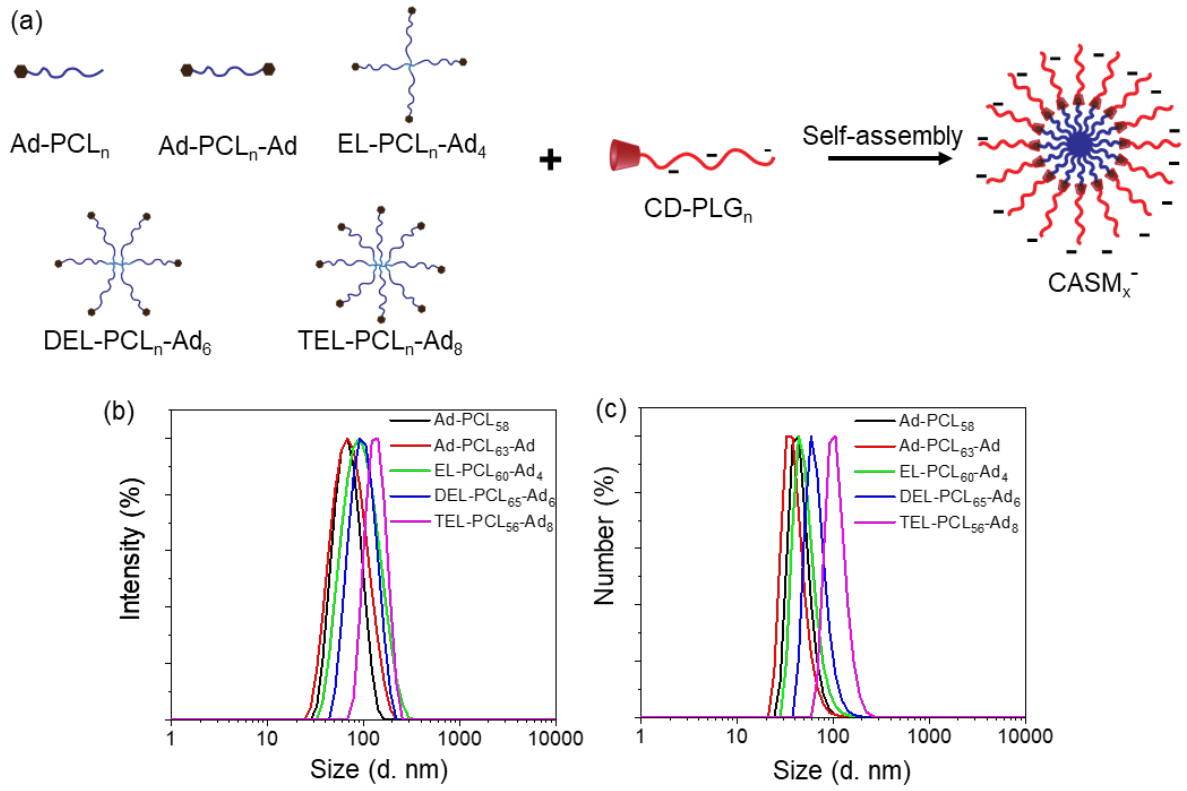


Figure S16: a) Schematic illustration of the formation of $CASM_x^-$ from different hydrophobic component and CD-PLG. b,c) DLS data obtained for $CASM_x^-$ with $CD\text{-}PLG_{42}$.

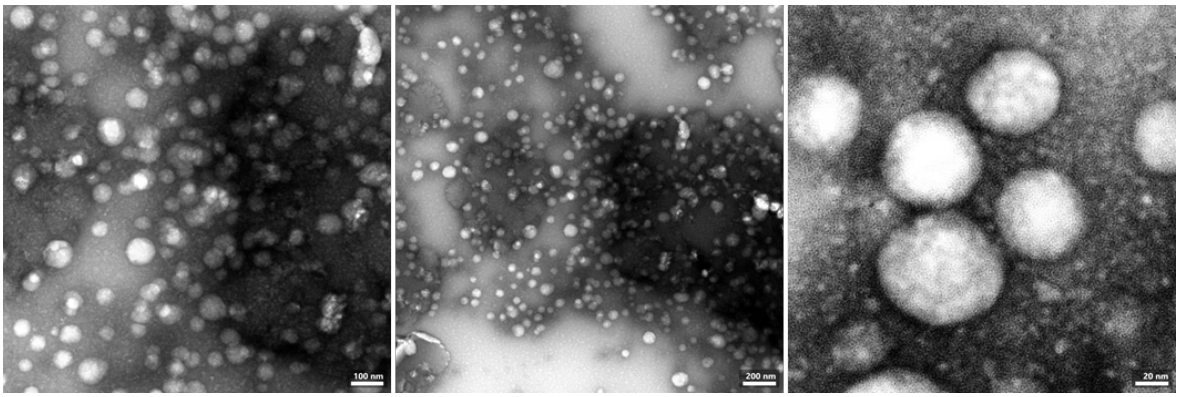


Figure S17: Additional TEM images of $CASM_1^-$

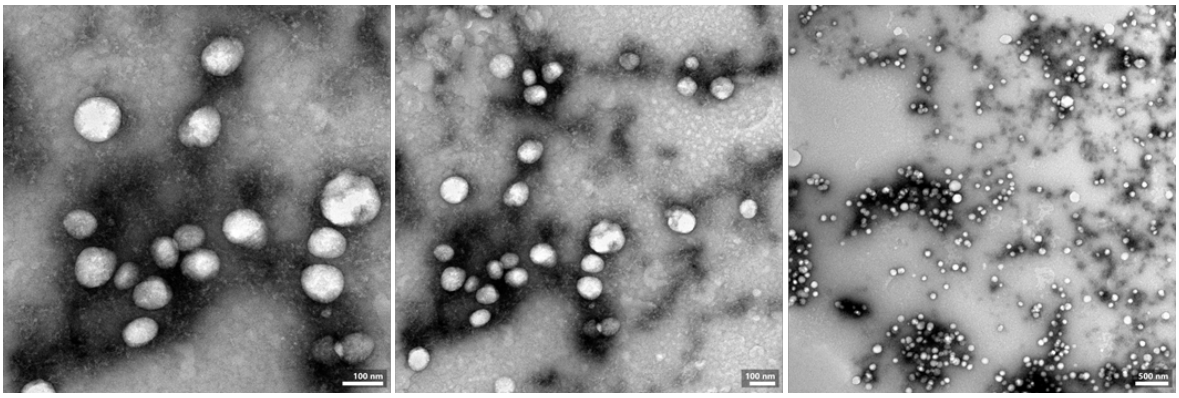
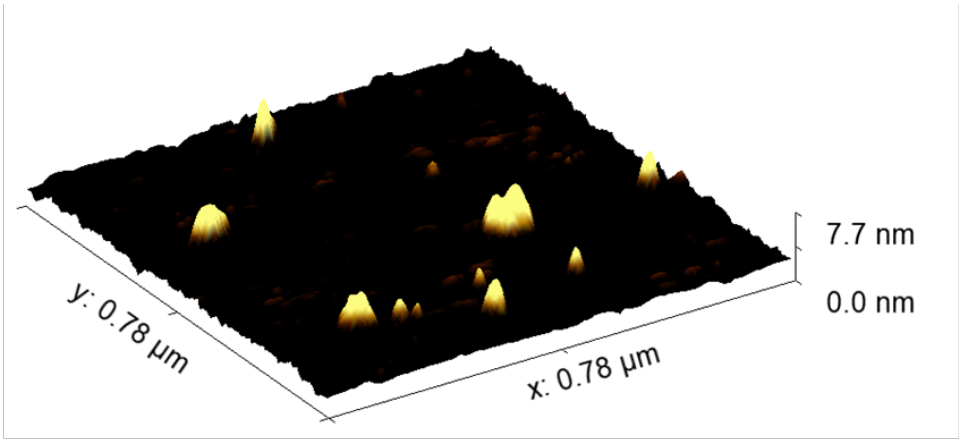


Figure S18: Additional TEM images of $CASM_4^-$



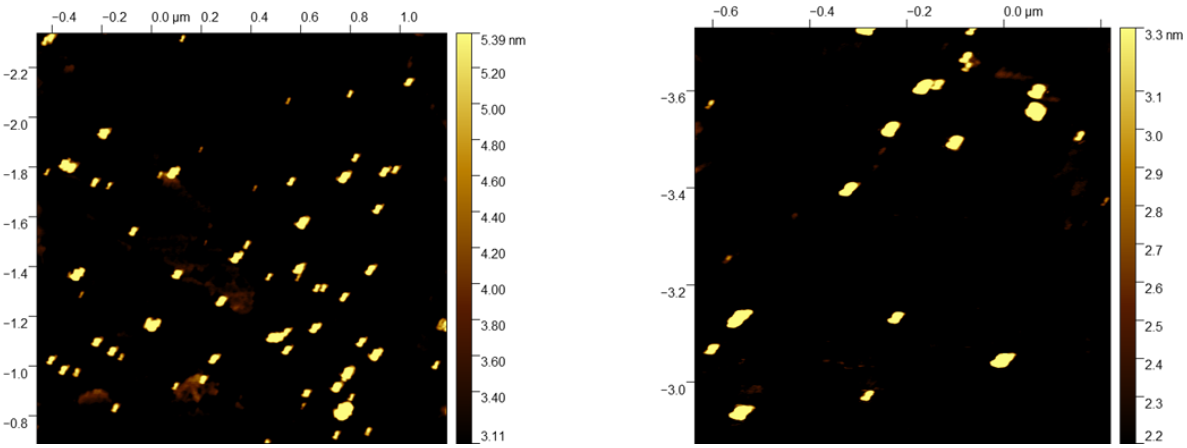


Figure S19: Additional AFM images of $CASM_1^-$

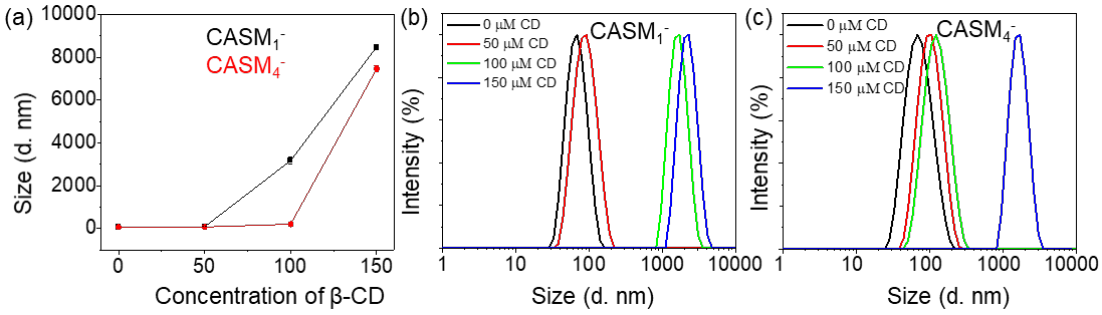


Figure S20: a) Effect of addition of *β*-CD to $CASM_1^-$ and $CASM_4^-$ and b, c) their corresponding DLS data.

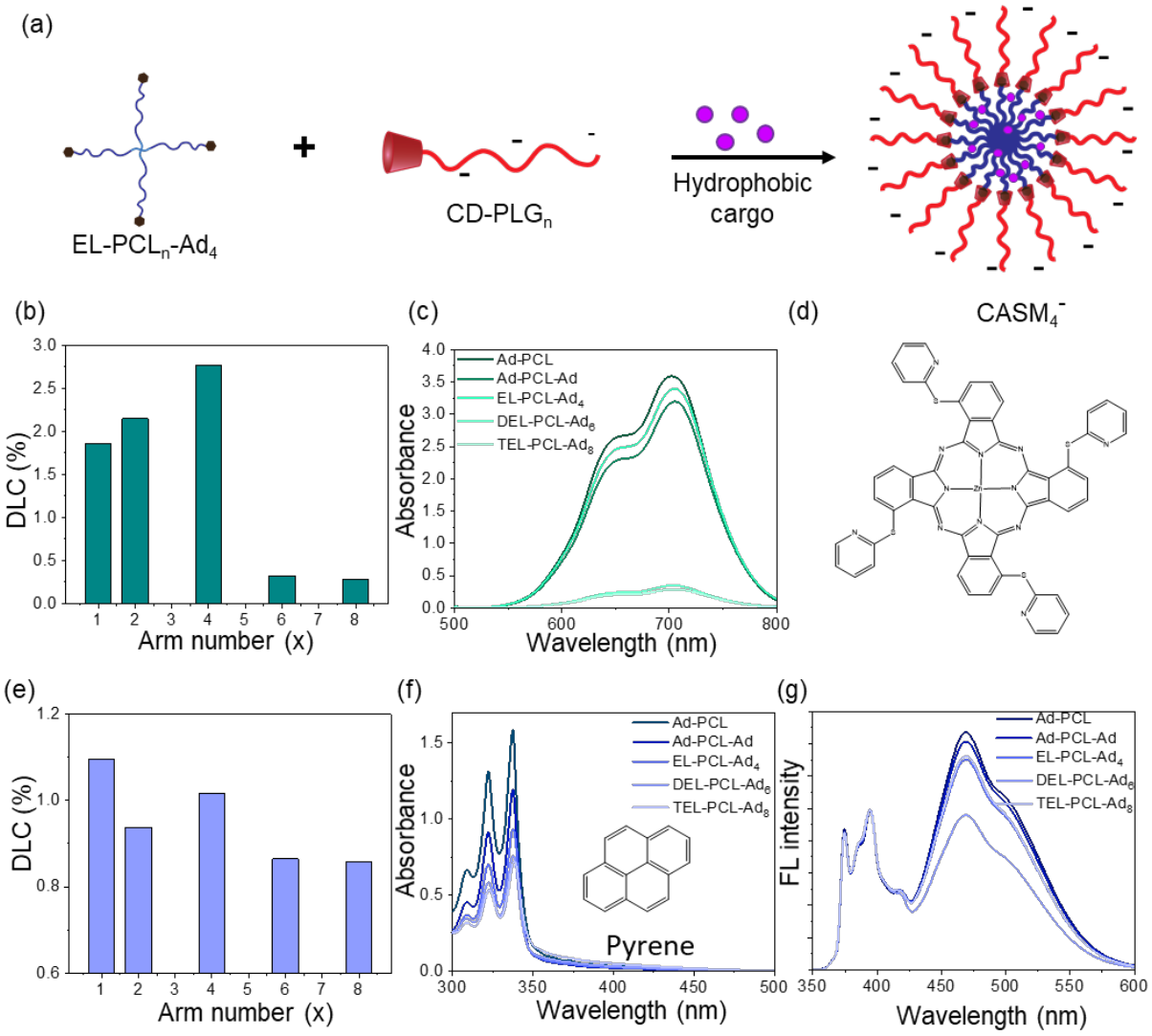


Figure S21: a) Schematic illustration showing the loading of hydrophobic cargo inside the hydrophobic compartment of $CASM_4^-$. b) DLC values calculated for the photosensitiser (PS) loaded $CASM_x^-$, c) corresponding absorbance spectra and d) the chemical structure of PS. e) DLC values calculated for the pyrene loaded $CASM_x^-$, f) corresponding absorbance spectra and g) fluorescence spectra when excited at 337 nm.

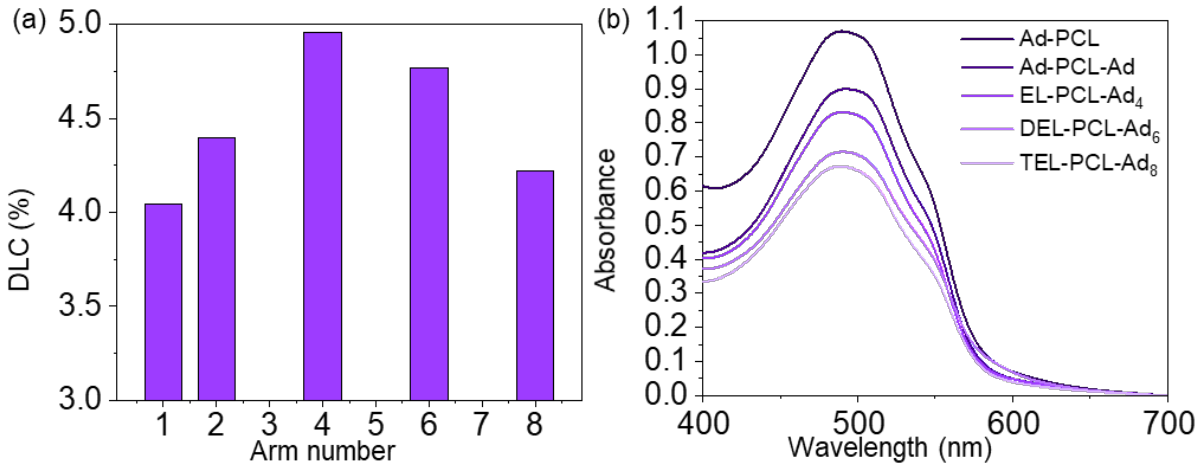


Figure S22: a) DLC values calculated for the DOX loaded $CASM_x^-$, b) corresponding absorbance spectra.

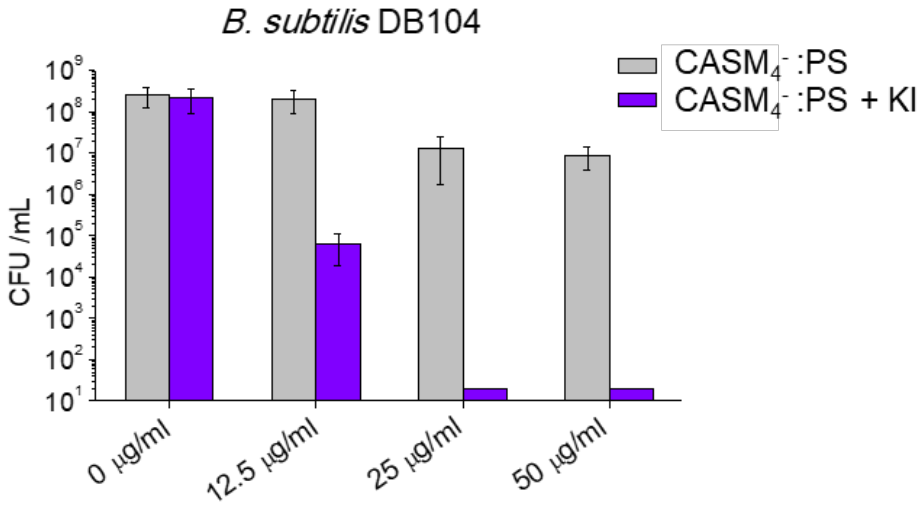


Figure S23: Viability of *B. subtilis* strain DB104 after incubation with corresponding amount of PS encapsulated $CASM_4^-$ ($CASM_4^-$:PS) for 15 min in dark and irradiation with light doses of 54 J/cm^2 (30 min, 30 mW/cm^2). Note the logarithmic y axis. The concentration on x axis indicates the concentration of PS. PS was diluted from a stock solution of 0.1 mg/ml PS. The concentration of in $CASM_4^-$ was approximately 100 µM CD and Ad. The concentration of KI was 100 mM.

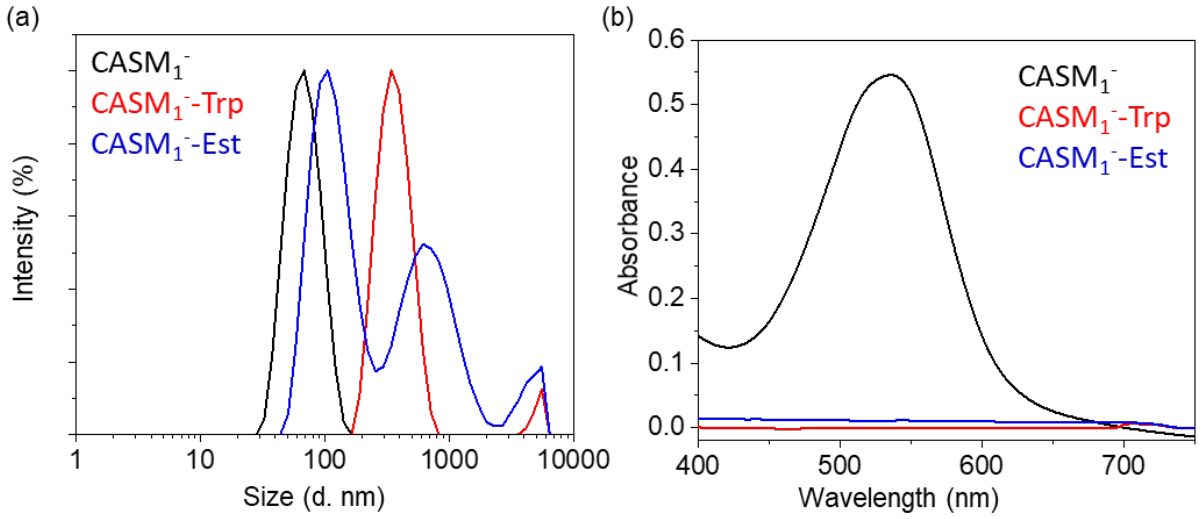


Figure S24: a) DLS data obtained for $CASM_1^-$ treated with esterase (Est) and trypsin (Trp). b) Absorbance spectra of nile red loaded $CASM_1^-$ with and without the treatment with Est and Trp.