# Supporting Information

## Environmentally Sensitive Luminescence Reveals Spatial Confinement, Dynamics and Their Molecular Weight Dependence in a Polymer Glass

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# Contents

## S0. General considerations

All manipulations unless stated otherwise were performed using Schlenk or glovebox techniques under dry argon atmosphere. Anhydrous solvents were dispensed from an solvent purification system manufactured by INERT (USA) and degassed prior to use. Anhydrous deuterated solvents were purchased from Eurisotop, degassed and stored over 4Å molecular sieves. Methyl acrylate was passed through alumina plug, degassed and used immediately. AIBN initiator was recrystallized from warm diethyl ether before use. All other chemicals unless noted otherwise were purchased from major commercial suppliers (TCI Europe and Sigma-Aldrich) and used without purification.

**Instrumentation and methods:**

NMR spectra were measured on Agilent 400-MR DD2 spectrometer. LCMS measurements were performed using LTQ XL spectrometer equipped with Shimadzu HPLC setup operating at 0.2 mL/min flow rate with water/MeCN mobile phase containing 0.1%$_{vol}$ formic acid and Discovery C18 column. Gel permeation chromatography (GPC) measurements were performed using Shimadzu HPLC setup equipped with Agilent PLGel column operating at 40°C with THF as the mobile phase supplied at 1 mL/min flow rate. Quantification was performed using refractive index detector, the apparatus was calibrated using ReadyCal PMMA standards. Differential Scanning Calorimetry measurements were performed in crimped Al sample pans using a TA DSC250 and Perkin Elmer Pyris Diamond DSC apparatus operating at 20 °C/min ramp rate in dry nitrogen. Samples were conditioned at 75°C before the measurement for at least 10 minutes and subsequent 1$^{st}$ and 2$^{nd}$ heating curves were used to obtain average $T_g$ value.

NOTE: an onset point was used as a measure of bulk $T_g$ throughout this work. We,, however, note the ongoing debate that conventional $T_g$ is more accurately characterized as a midpoint on cooling, while the value used herein is often named fictive temperature or fictive $T_g$. See Ref 1 for additional information.

**Photophysical characterization**

The **photoluminescence measurements** were performed using Ocean Optics HDX spectrometer integrated in a free space optics assembly with excitation at 405 nm delivered by a ThorLabs laser module (CPS405).

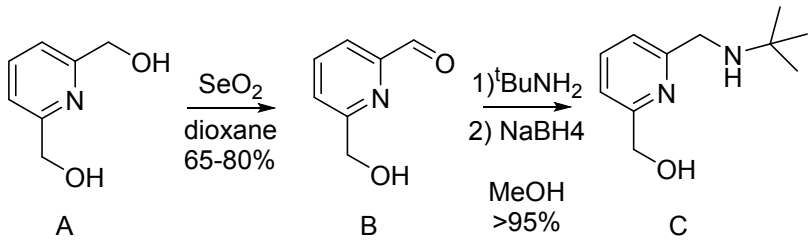
**IMPORTANT NOTE**: The response of spectrometer was calibrated using reference light source (Ocean Optics, HL-3P-CAL) to deliver accurate absolute spectral intensity measurements. See the example of the influence on the processing routine below in S3.

Heating and cooling was performed in a modified Linkam THMS 600 stage flushed with nitrogen throughout the experiment to prevent icing.

**Confocal microscopy** measurements were performed using Leica SP8 DIVE apparatus using polymer samples drop cast on cover slips and treated as described below in S3.

## S1. Synthesis and compound characterization

**Macrocyclic ligand $N_4^{tButBuOH}$:**




Commercial pyridine dimethanol **A** (TCI) was converted to monoaldehyde **B** following the literature procedure[2] that can be scaled up to 100 mmol. Oily **B** was found to solidify overtime without impairing its reactivity. All compounds described in this multistep synthesis were used without additional purification that was performed after the final cyclisation step.

Aminoalcohol **C**: 8.13 g of solidified aldehyde **B** (1eq., 59.3 mmol) were loaded in a round bottom flask containing 100 mL absolute methanol. No exclusion or air or moisture was necessary. The suspension was stirred vigorously and tert-butyl amine (2eq., 12.47 mL, 118.68 mmol) was added to the flask at room temperature in one portion. Within 20 minutes suspended aldehyde dissolved and IR indicated the consumption of the starting aldehyde. To the clear solution, solid $NaBH_4$ (3.6 g, ca. 1.6 eq.) was added in three portions over the period of 15 minutes and the bubbling solution was allowed to stir for additional 2 hours. Upon completion, reaction mixture was carefully (gas evolution!) quenched with saturated sodium bicarbonate solution (50 mL), diluted with water twofold and extracted with chloroform (5x50 mL). Combined organic phase was dried with potassium carbonate and concentrated to give 11.3 g of clear oil (>99%) that was used without additional purification.

**$^1$H NMR** (400 MHz, $CDCl_3$)*:* δ 7.62 (t, $^3J_{HH}$ = 7.7 Hz, 1H, py-p-CH), 7.24 (d, $^3J_{HH}$ = 7.8 Hz, 1H, py-o-CH), 7.08 (d, $^3J_{HH}$ = 7.7 Hz, 1H, py-o-CH), 4.71 (s, 2H, -$CH_2$-OH), 3.88 (s, 2H, -$CH_2$-NH$^t$Bu), 1.19 (s, 9H, $^t$Bu).

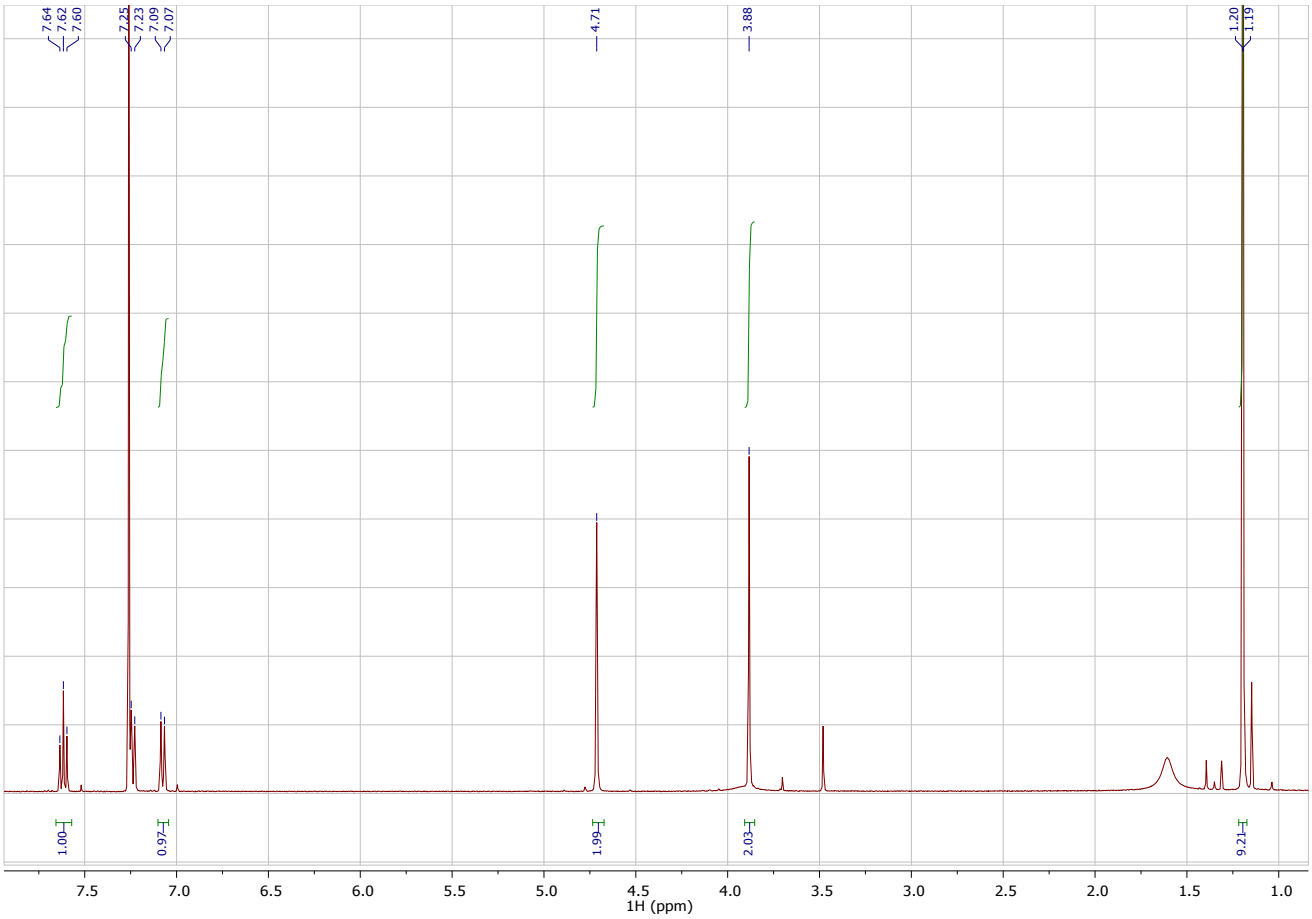
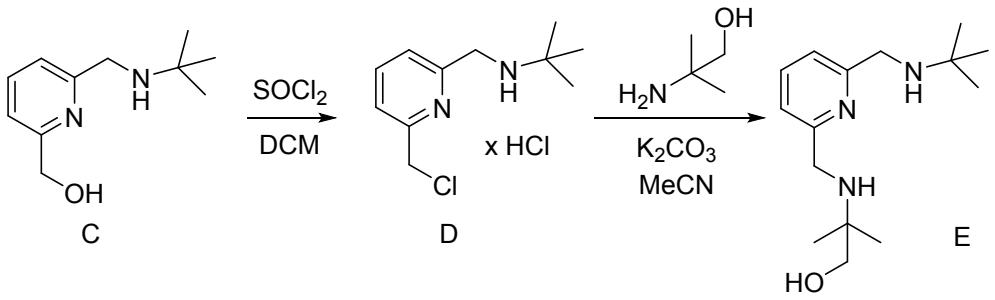



**Figure S1.** $^{1}H$ NMR spectrum of animoalcohol **C** in $CDCl_3$




Synthesis of aminoalcohol **E**:

Chloromethyl amine **D**: To 12 g (61.85 mmol) of amino alcohol **C** dissolved in anhydrous dichloromethane (60 mL), thionyl chloride (2 eq, 14.71 g, 8.97 mL, ca 123.7 mmol) were added dropwise using syringe over the period of three minutes under Ar flow. Reaction mixture was capped with oil bubbler and allowed to stir for 1.5 hours when NMR indicated the completion of reaction. Volatile compounds were removed by distillation under static vacuum into a liquid nitrogen cooled trap. Remainder of thionyl chloride was removed by two co-evaporations with 15 mL toluene done similarly, using distillation into the cold trap. This treatment yielded waxy solid that was further co-evaporated with acetonitrile to remove

trace amounts of water. Resulting product **D** was a hydrochloride salt that was used without isolation for the next step. NMR data below is presented for the hydrochloride salt in $D_2O$.

**$^1$H NMR** (400 MHz, $D_2O$): δ 7.97 (t, $^3J_{HH}$ = 7.8 Hz, 1H, py-p-CH), 7.62 (d, $^3J_{HH}$ = 7.8 Hz, 1H, py-o-CH), 7.51 ($^3J_{HH}$, J = 7.8 Hz, 1H, py-o-CH), 4.77 (s, 2H, -$CH_2$-Cl), 4.40 (s, 2H, -$CH_2$-$NH_2^+$-$^t$Bu), 1.48 (s, 9H).

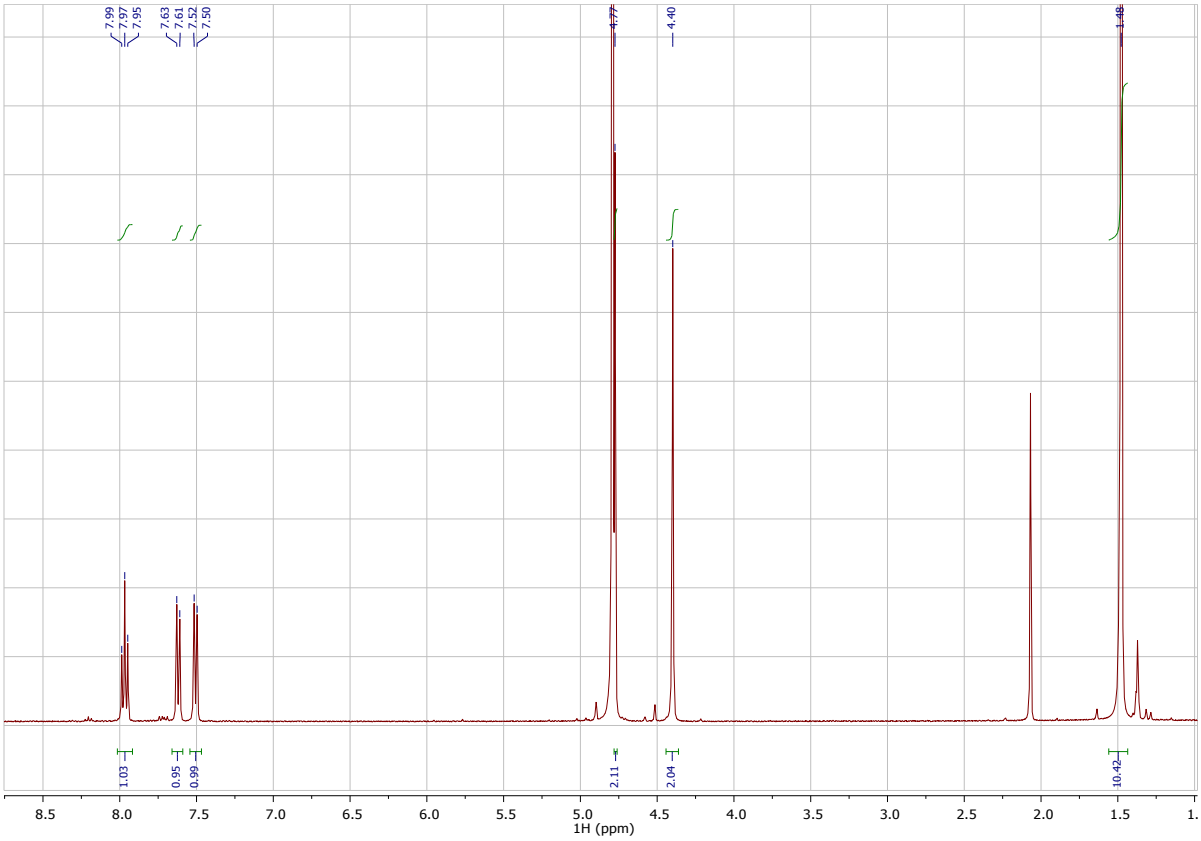



**Figure S2.** $^1$H NMR spectrum of hydrochloride salt **D** in $D_2O$

If necessary, the neutral **D** can be isolated in the following way: A portion of wax obtained as described above is dissolved in water, cooled down to 0°C and neutralized with saturated sodium bicarbonate solution. Aqueous phase is extracted three times with chloroform and organic phase is dried with solid $K_2CO_3$ and concentrated on the rotary evaporator while maintaining the bath temperature below 40°C to prevent alkylation side reactions. Neutralized compound **D** is obtained as clear oil that can be stored in the freezer (-20°C) for two days before notable degradation occurs. Due to the lack of long term stability, compound **D** was handled exclusively as HCl salt in all synthesis steps. NMR data for neutral **D** is given below:

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.65 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, py-p-CH), 7.30 (m, 2H, overlap of two doublets, py-o-CH), 4.64 (s, 2H, -$CH_2$-Cl), 3.88 (s, 2H, -$CH_2$-NH$^{t}$Bu), 1.18 (s, 9H, $^{t}$Bu).

**$^{13}$C NMR** (100 MHz, CDCl3, all singlets): δ 160.46, 155.85, 137.38, 121.58, 120.72, 50.56, 48.31, 46.83, 29.09.

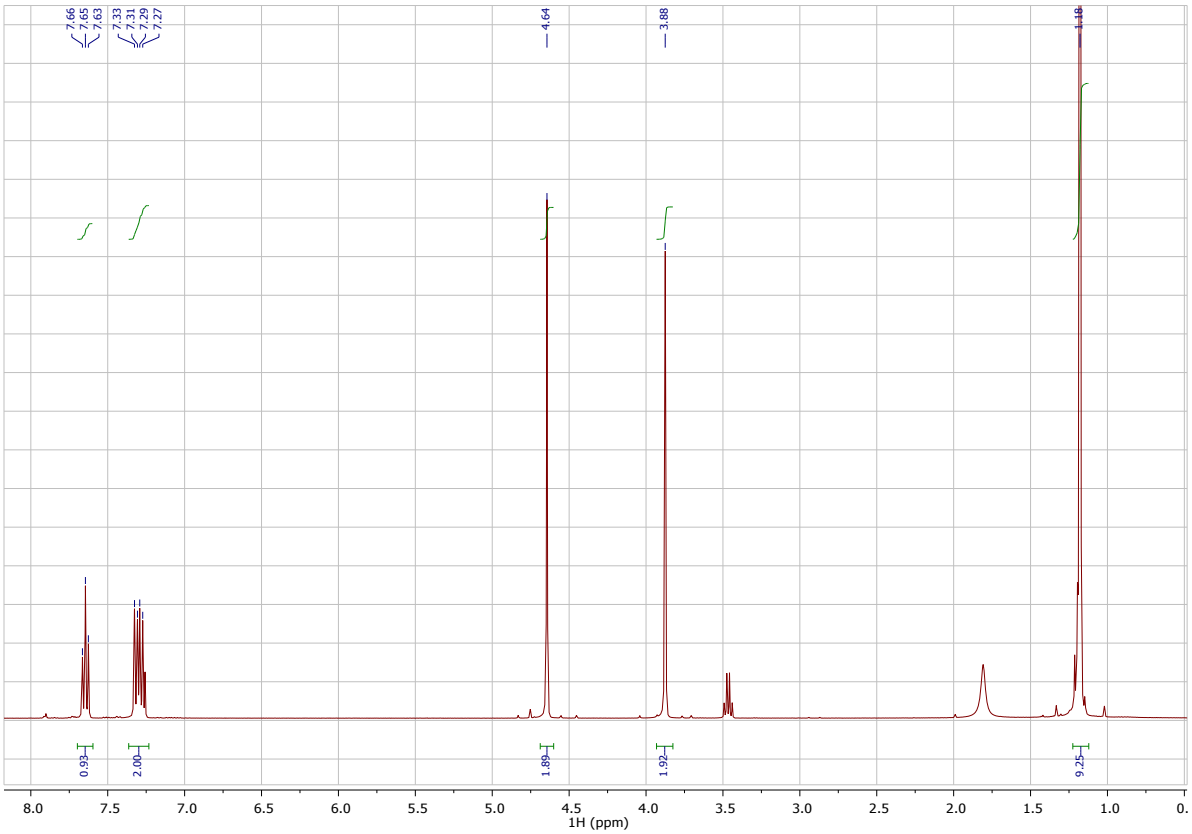



**Figure S3.** $^{1}$H NMR spectrum of neutral **D** in $CDCl_3$

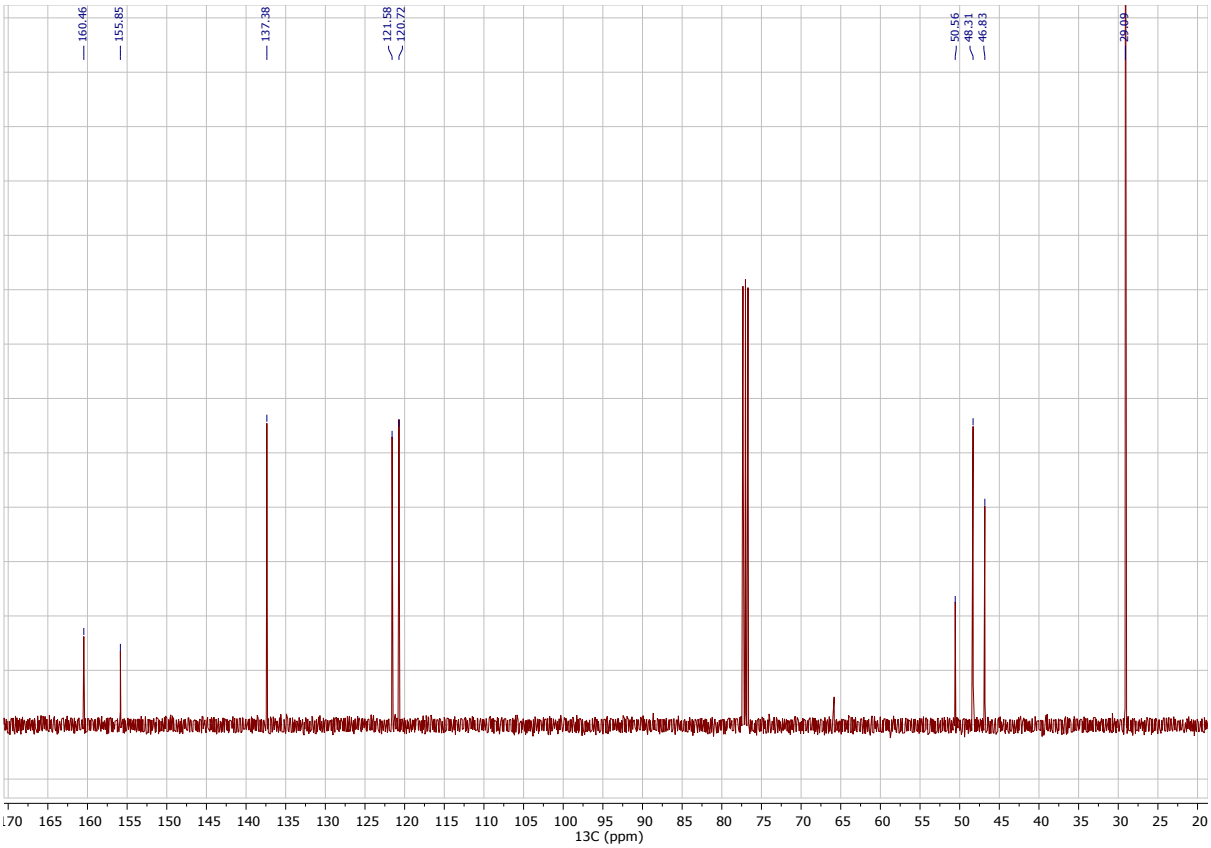



**Figure S4.** $^{13}C$ NMR spectrum of neutral **D** in $CDCl_3$

Aminoalcohol **E**: To the waxy solid **D** obtained as described above in hydrochloride form (ca. 61.85 mmol) was added 200 mL acetonitrile and a milky suspension was stirred for 5 minutes. A portion of solid finely ground $K_2CO_3$ (25.6 g, ca 3 eq.) was added to this suspension at 0°C and the reaction mixture was allowed to stir for 15 minutes to neutralize the HCl bound to compound **D**. Further, an aliquot of 2-amino-2-methyl-1-propanol (55 g, ca. 10 eq) was molten using heatgun (60°C) and slowly poured into the reaction mixture cooled to 0°C.

NOTE: Care should be taken to cool down reaction mixture as addition of amine to protonated compound **D** was found to be highly exothermic and resulted in notable degradation.

After amine addition, reaction mixture was heated at 80°C for 8 hours and filtered to remove undissolved inorganic solids. Acetonitrile was removed using rotary evaporator and resulting thick oil was dissolved in water (200 mL) and extracted with chloroform (5x75 mL) leaving the majority of aminomethyl propanol in the aqueous phase. Organic phase was further washed with small (!) portions of water (3x5 mL) and brine (5 mL), dried over solid $K_2CO_3$ and concentrated to give thick oil weighing 17.68 g that was used for final synthetic step without additional purification.

NOTE: In case of notable degradation, target compound **E** can be distilled using short path distillation apparatus at 180°C (bath temperature) under vacuum (ca. 0.3 mbar). Distillation is efficient in removing oligomerized byproducts, however traces of unreacted aminomethyl propanol are more conveniently removed by extraction of chloroform solution of **E** with small portions of water.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.57 (t, $^3J_{HH}$ = 7.7 Hz, 1H, py-p-CH), 7.24 (d, 1H, overlap with chloroform, py-o-CH), 7.09 (d, $^3J_{HH}$ = 7.7 Hz, 1H, py-o-CH), 3.87 and 3.84 (both s, both 2H, -$CH_2$-NHR), 3.34 (s, 2H, -$C(CH_3)_2$-C***H***$_2$-OH), 1.18 (s, 9H, $^t$Bu), 1.13 (s, 6H, -C(C***H***$_3$)$_2$-$CH_2$-OH).

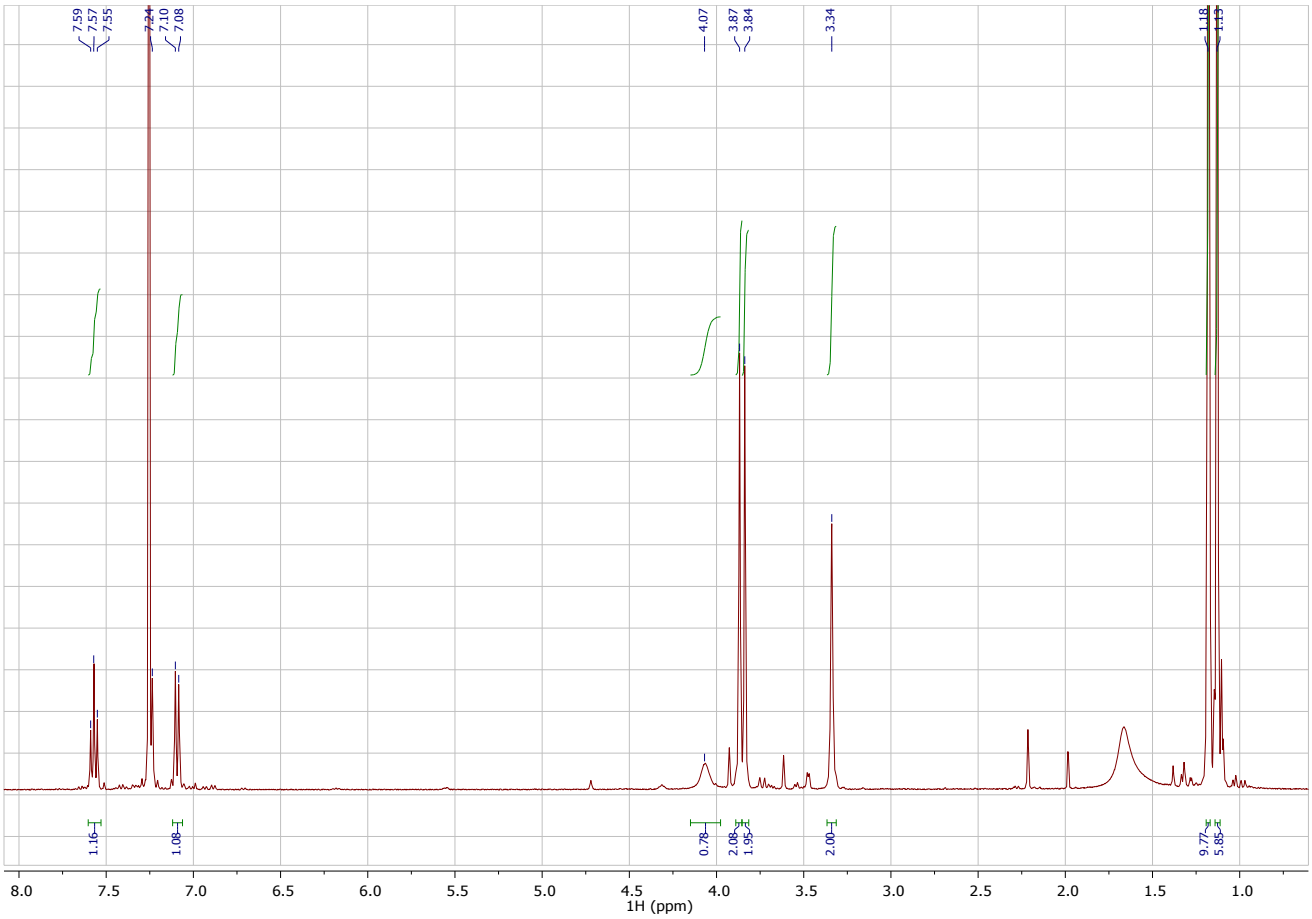
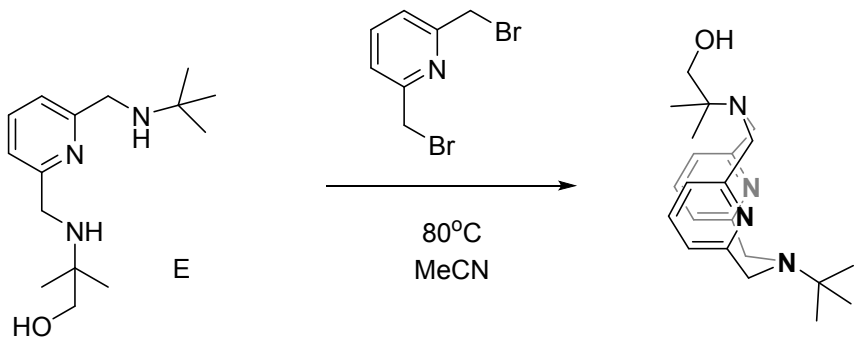



**Figure S5.** $^1$H NMR spectrum of crude **E** in $CDCl_3$

Macrocycle $\mathbf{N_4^{tButBuOH}}$:




17 g of aminoalcohol **E** (64.1 mmol) prepared as above was dissolved in 10 mL acetonitrile and set aside. Separately, solution of 2,6-bis(bromomethyl)pyridine (16.27 g, 61.4 mmol) was prepared in 65 mL warm acetonitrile. Solutions were quickly mixed and transferred to a dropping funnel fixed onto a round bottom flask containing suspension of 19.5 g $Na_2CO_3$ (183.9 mmol, ca. 2.85 eq) in 300 mL of acetonitrile preheated to 80°C. Solution of both compounds was added to the carbonate suspension dropwise over a period of 40 minutes and allowed to stir further at 80°C for three hours. During the addition, milky suspension forms and reaction mixture becomes notably turbid overtime.

Reaction mixture was further cooled to 0°C and worked up as follows:

Acetonitrile mother liquor, isolated by filtration, contained unreacted bromomethyl pyridine and trace amounts of target compound. Evaporation of acetonitrile yields thick oily residue that was set aside.

Filter cake residue was suspended in chloroform and shaken with water to remove inorganic salts. Chloroform fractions were concentrated to yield thick wax that was treated with 150 mL water and concentrated HCl (36%) until nearly complete dissolution occurred. This typically requires 65 mmol of HCl with final solution pH=3. Solution was further passed through paper filter, diluted to ca 250 mL and treated with solid potassium carbonate upon vigorous stirring until pH=8-9. This results in the formation of stable milky emulsion and deposition of heavy wax on the vessel walls. The wax was analysed by NMR spectroscopy and contained no target macrocycle. Contents of the vessel were carefully transferred to the separatory funnel making sure to discard waxy residues and transfer the emulsion phase exclusively. Emulsion was further extracted with chloroform (4x100 mL) and the organic phases were combined, dried over $K_2CO_3$ and concentrated on the rotary evaporator. The resulting paste was triturated with diethyl ether (2x15mL) to remove coloured impurities, rinsed with pentane and dried under vacuum to yield very fine white powder of target compound (4.78 g). Additional portion of the product can be recovered by repeated extraction

($CHCl_3$, 4x50 mL) of the remaining aqueous emulsion once after treatment of the latter with 2M NaOH till pH 12. This yields additional 1.4 g of target compound not requiring washing with ether or pentane.

Concentrated acetonitrile mother liquor and ether washings can be subjected to identical repeated workup to yield small portions of product.

Combined yield: 6.18 g (27.35 %)

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.05 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-Py-C***H***), 6.72 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-Py-C***H***), 6.55 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-Py-C***H***), 3.98 (broad s, 8H Py-C***H***$_2$-), 3.62 (d, $^3J_{HH}$ = 5.6 Hz, 2H, N-C(($CH_3$)$_2$(C***H***$_2$OH))), 1.97 (s, 1H, -O***H***), 1.32 (s, 9H, -tBu-C***H***$_3$), 1.30 (s, 6H, N-C((C***H***$_3$)$_2$($CH_2OH$))).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 160.39(s, Py-$C_{quart}$), 158.77(s, Py-$C_{quart}$), 135.39(s, Py-$C_{para}$), 122.11(s, Py-$C_{meta}$), 120.55(s, Py-$C_{meta}$), 69.75(s, -***C***$H_2$-OH), 59.29(s, -***C***-($CH_3$)$_2$($CH_2OH$)), 58.54(s, Py-***C***$H_2$-), 56.07(s, -***C***-($CH_3$)$_3$), 55.94(s, Py-***C***$H_2$-), 28.00(s, $^t$Bu-***C***$H_3$), 23.51(s, -C-(***C***$H_3$)$_2$($CH_2OH$)).

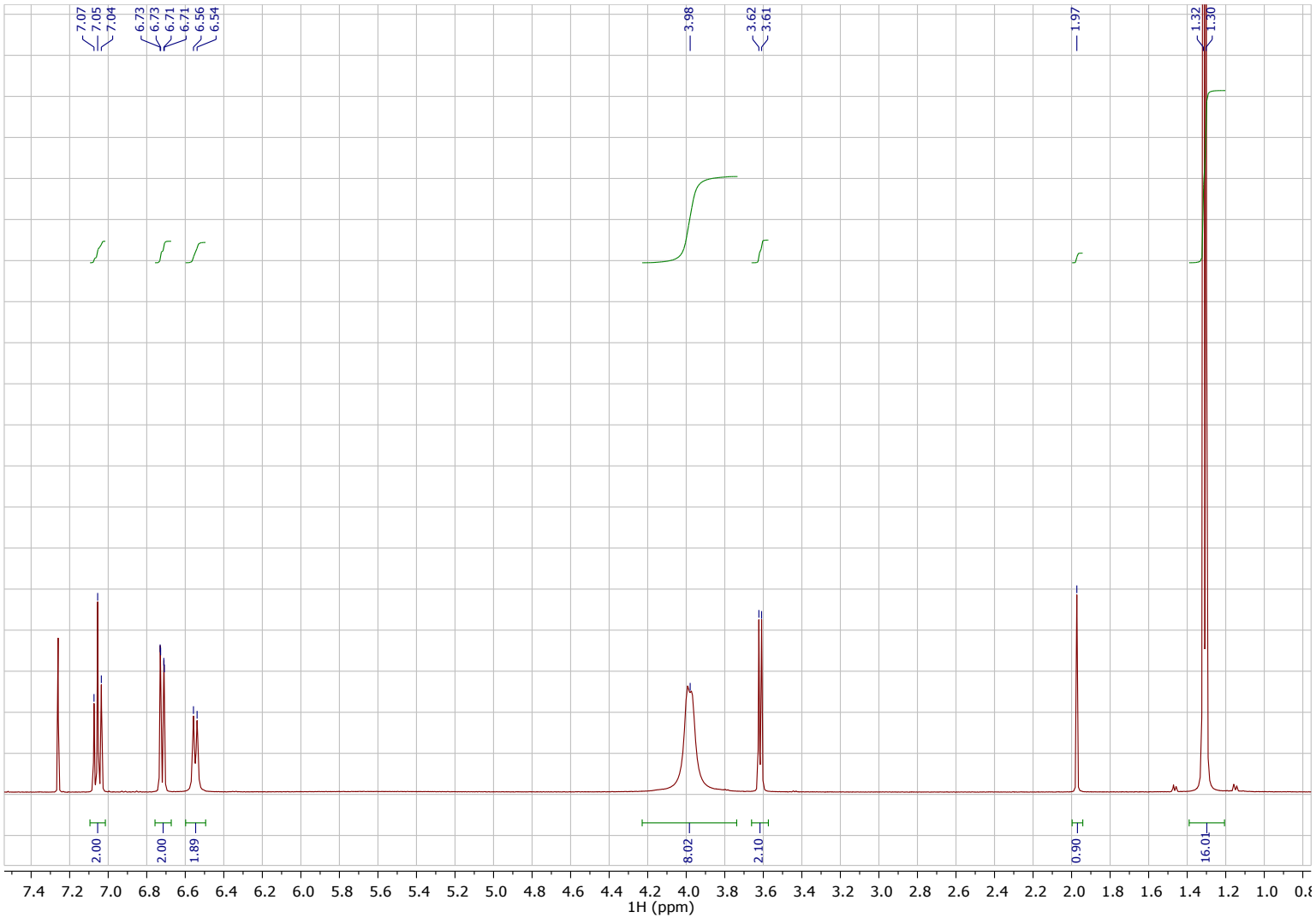



**Figure S6.** $^{1}$H NMR spectrum of $\mathbf{N_4^{tButBuOH}}$ in $CDCl_3$ .

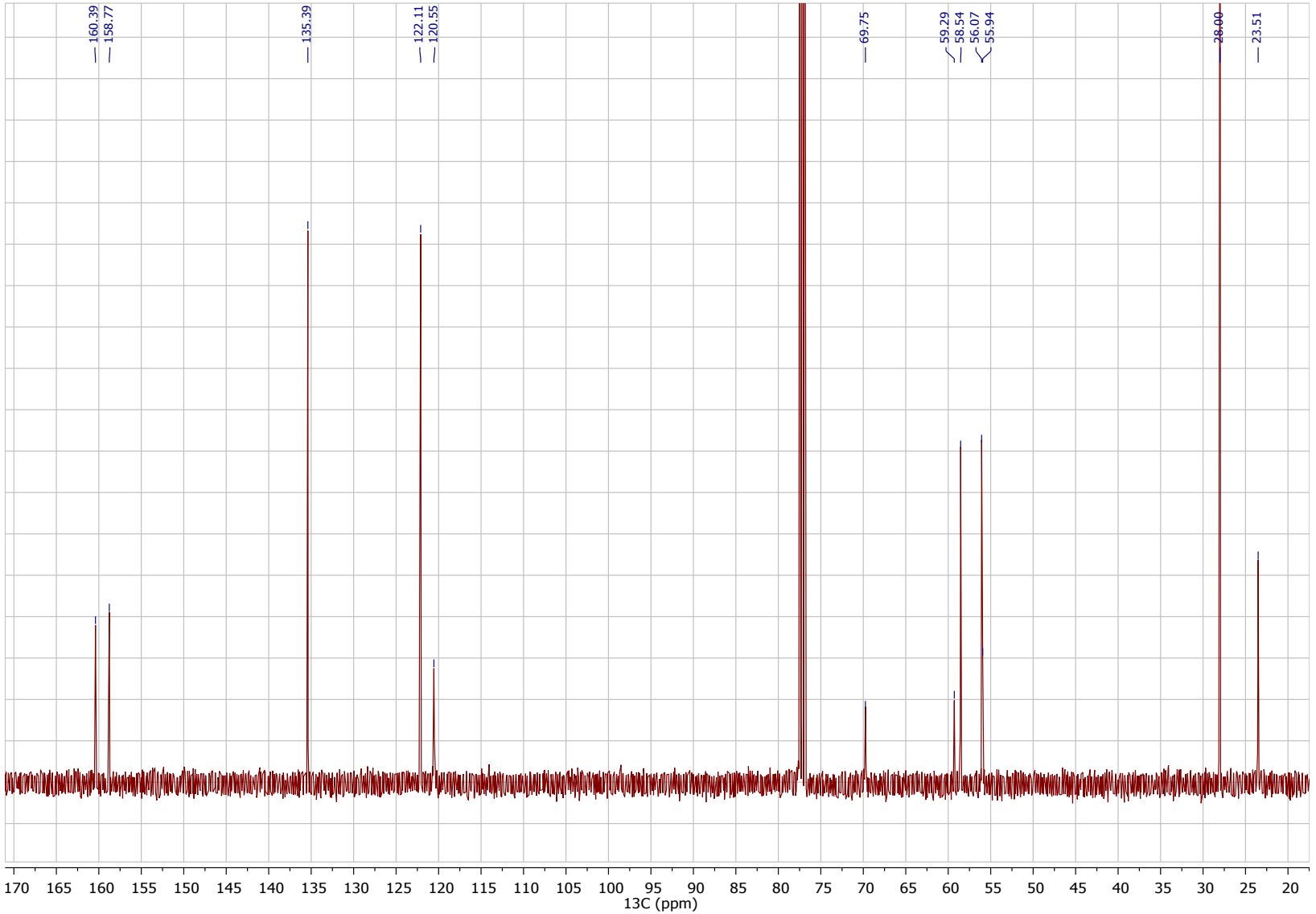



**Figure S7.** $^{13}C$ NMR spectrum of $\mathbf{N_4^{tButBuOH}}$ in $CDCl_3$.

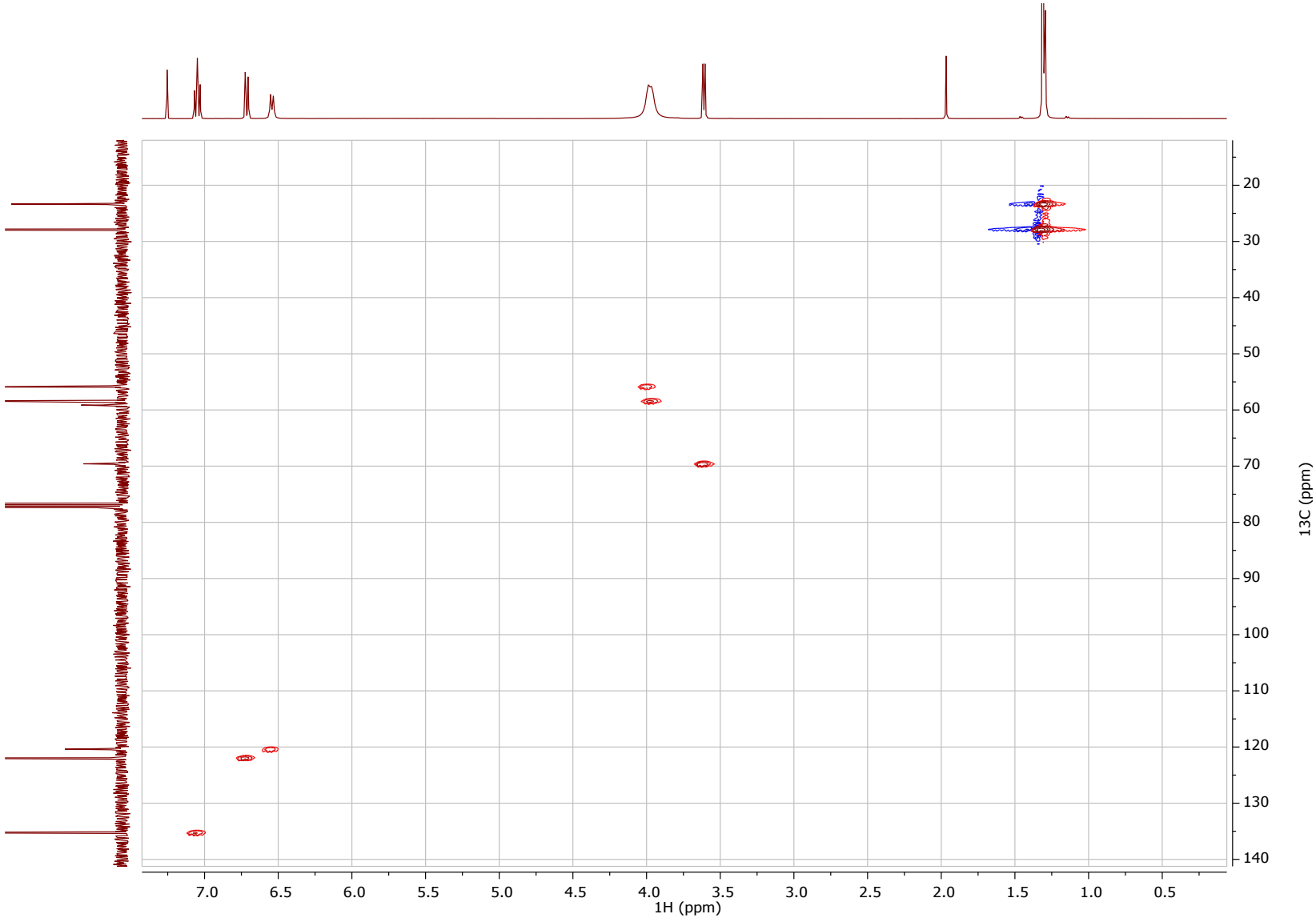



**Figure S8.** gHMQC spectrum of $\mathbf{N_4^{tButBuOH}}$ in $CDCl_3$.

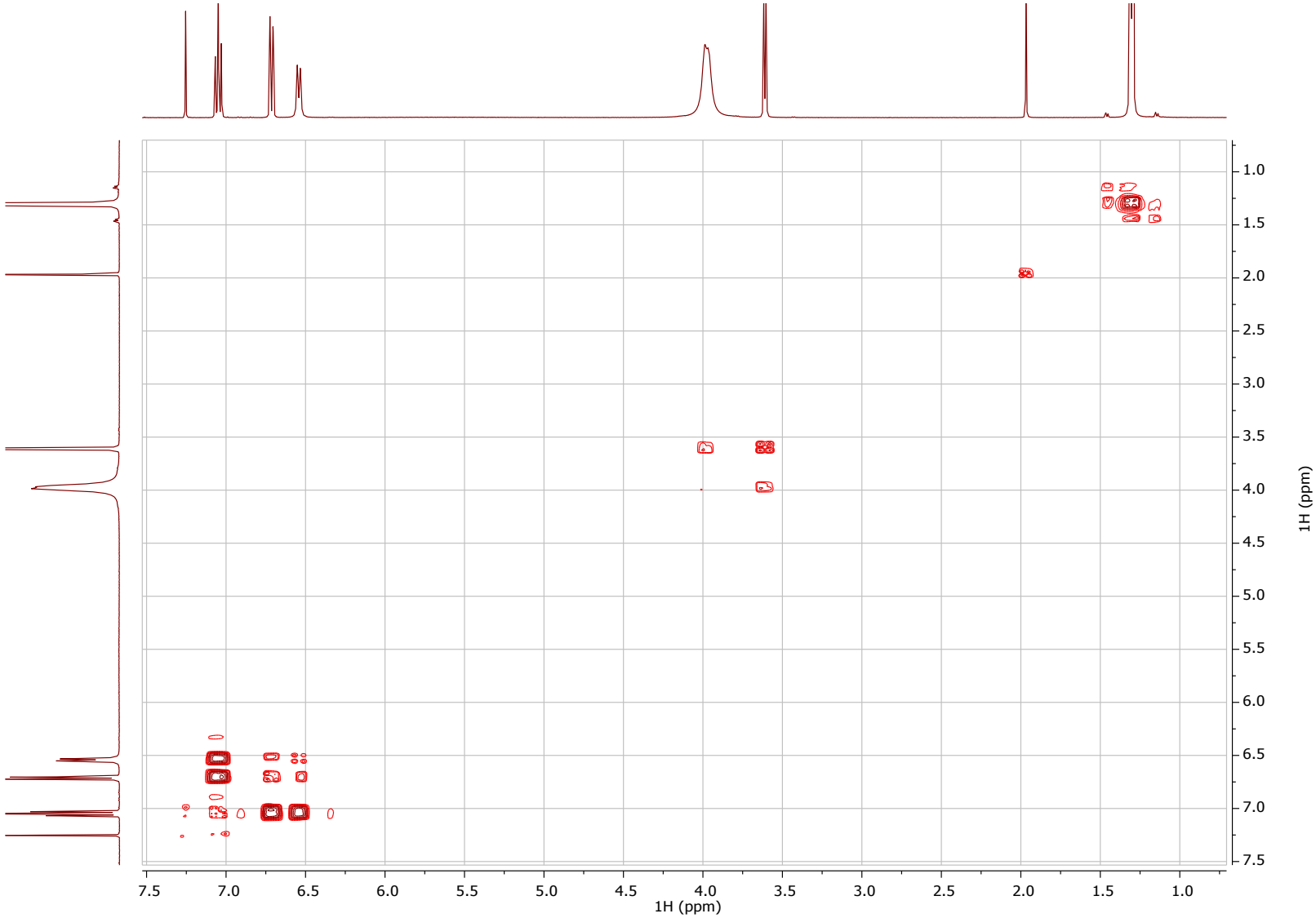
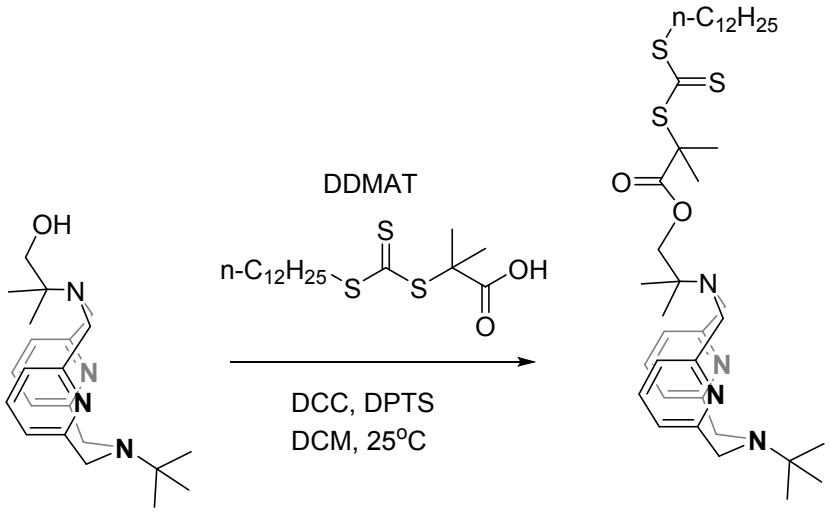



**Figure S9.** gCOSY spectrum of $\mathbf{N_4^{tButBuOH}}$ in $CDCl_3$.

**Synthesis of RAFT chain transfer agent (CTA-$N_4$):**




140 mg of macrocycle $\mathbf{N_4^{tButBuOH}}$ (380 μmol) were combined with DDMAT[3] (152 mg, 1.1 eq., 417 μmol), DPTS[4] catalyst (1 eq., 111 mg) in dry dichloromethane (5mL). The mixture was stirred until a homogeneous clear solution formed and solution of DCC (117 mg, 1.5 eq.) in 2 mL dichloromethane was added to the mixture in one portion at room temperature under argon. Within 30 minutes white precipitate forms and reaction mixture is allowed to stir overnight at room temperature. Upon completion, suspension was filtered and yellow organic fraction was shaken with 1N HCl followed by saturated sodium bicarbonate and brine. This treatment produces more white solid suspended in the organic phase that was treated with sodium sulfate, filtered and concentrated to dryness on the rotary evaporator to produce thick waxy solid. The solid was further purified by column chromatography on silica eluting with dichloromethane to remove neutral contaminations and DDMAT decomposition products followed by DCM/$NEt_3$ (100/1) to elute a yellow band containing the target compound. Combined fractions were concentrated in vacuo and recrystallized from pentane at -20°C to produce pale yellow microcrystalline powder of target compound. Yield: 120 mg (44%).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 6.91 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-Py-C***H***), 6.70 (m, overlap of two doublets, 4H, both *m*-Py-C***H***), 4.19 (s, 2H, N-C(($CH_3$)$_2$(C***H***$_2$ODDMAT))), 4.11 (apparent d, 8H, Py-C***H***$_2$-), 3.15 (t, J = 7.5 Hz, 2H, -S-C***H***$_2$-n$C_{11}H_{24}$), 1.66 (s, 6H, -O-C(O)-C(C***H***$_3$)$_2$-S-), 1.46 (q, 2H, -S-$CH_2$-C***H***$_2$-n$C_{10}H_{22}$), 1.40 – 1.03 (m, overlap of $^t$Bu-C***H***$_3$, N-C((C***H***$_3$)$_2$($CH_2$ODDMAT)) and 9 counts of -C***H***$_2$- groups of C12 tail, 6H+ 9H + 18H), 0.92 (t, J = 6.7 Hz, 3H, C12 tail, terminal -C***H***$_3$).

**$^{13}$C NMR** (101 MHz, $C_6D_6$) δ 221.89 (trithiocarbonate $\boldsymbol{C}_q$), 172.07 (carbonyl $R_2\boldsymbol{C}$=O), 159.64 and 159.40 (py-$C_{2,6}$), 134.70 (py-$C_4$), 121.46 and 121.32 (py-$C_{3,5}$), 71.29 ($N_4$ N-C($(CH_3)_2$($\boldsymbol{C}H_2$ODDMAT), 57.87 and 57.62 (py-$\boldsymbol{C}H_2$-), 57.34, 55.96 and 55.21 ($\boldsymbol{C}_q$ of DDMAT and $^t$Bu of N4 macrocycle), 36.66 (-S-$\boldsymbol{C}H_2$-n$C_{11}H_{24}$), 31.95 (*), 29.70 (*), 29.60 (*), 29.45(*), 29.42(*), 29.07(*), 28.80 (-S-$CH_2$-$\boldsymbol{C}H_2$-n$C_{10}H_{22}$), 27.26(*), 25.12 (DDMAT – C($\boldsymbol{C}H_3)_2$-), 23.93(*), 22.73(*), 13.98 (DDMAT terminal $\boldsymbol{C}H_3$).

(*) remaining resonances of $^t$Bu fragment $CH_3$ groups and $C_{12}$ chain of DDMAT

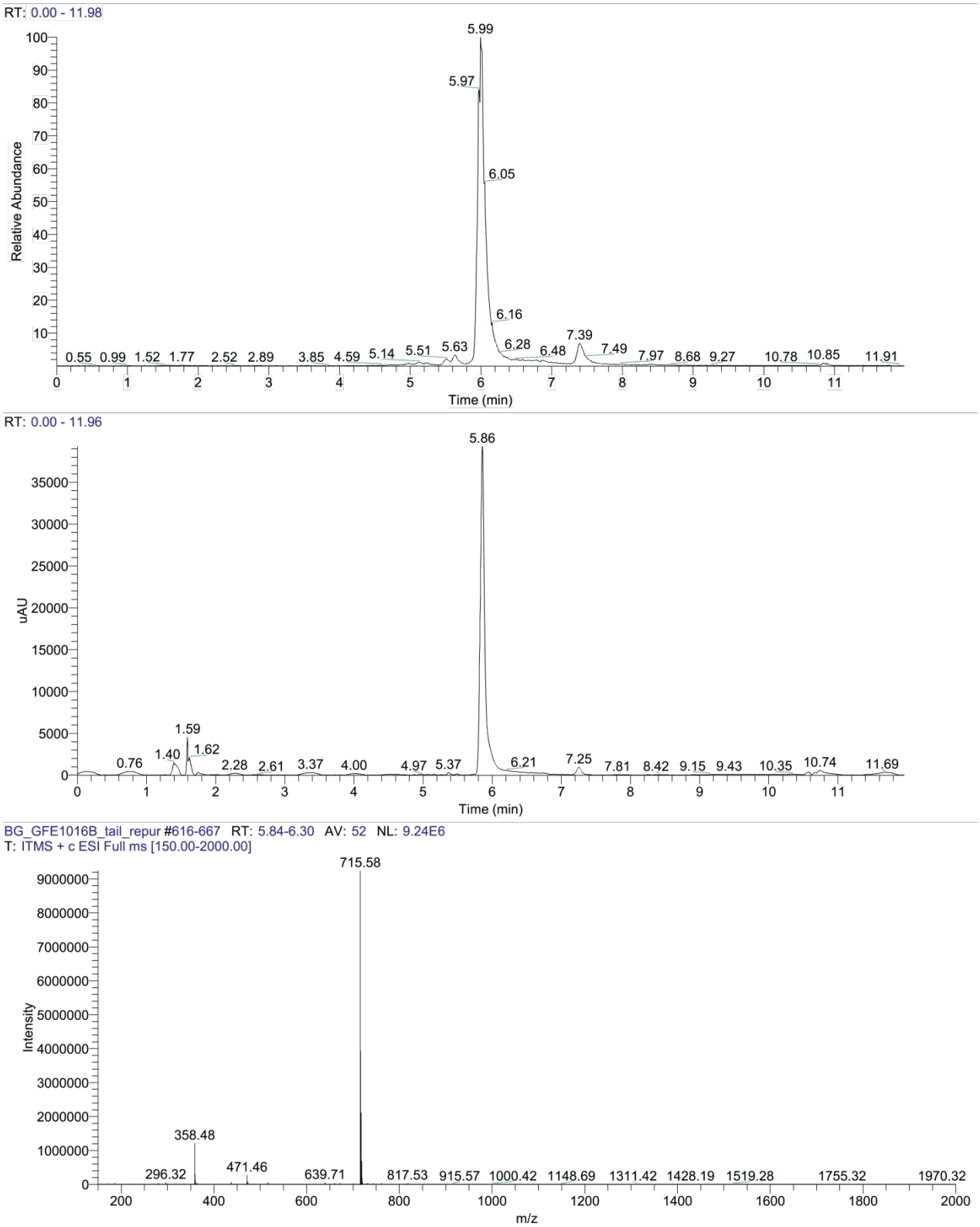



**Figure S10.** LC-MS data for **RAFT CTA-$N_4$**.

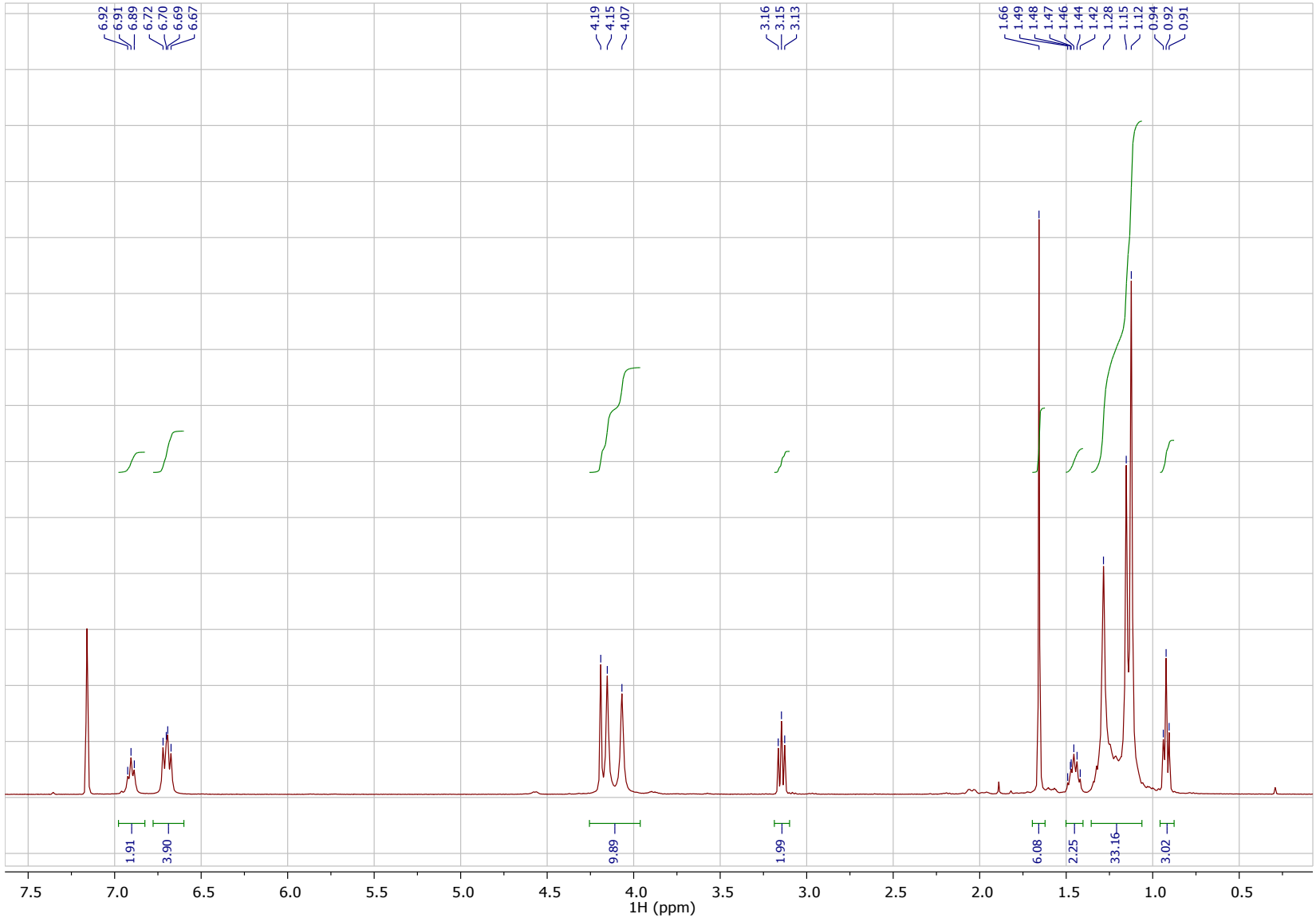



**Figure S11.** $^{1}$H NMR spectrum of **RAFT CTA-N$_4$** in $C_6D_6$ .

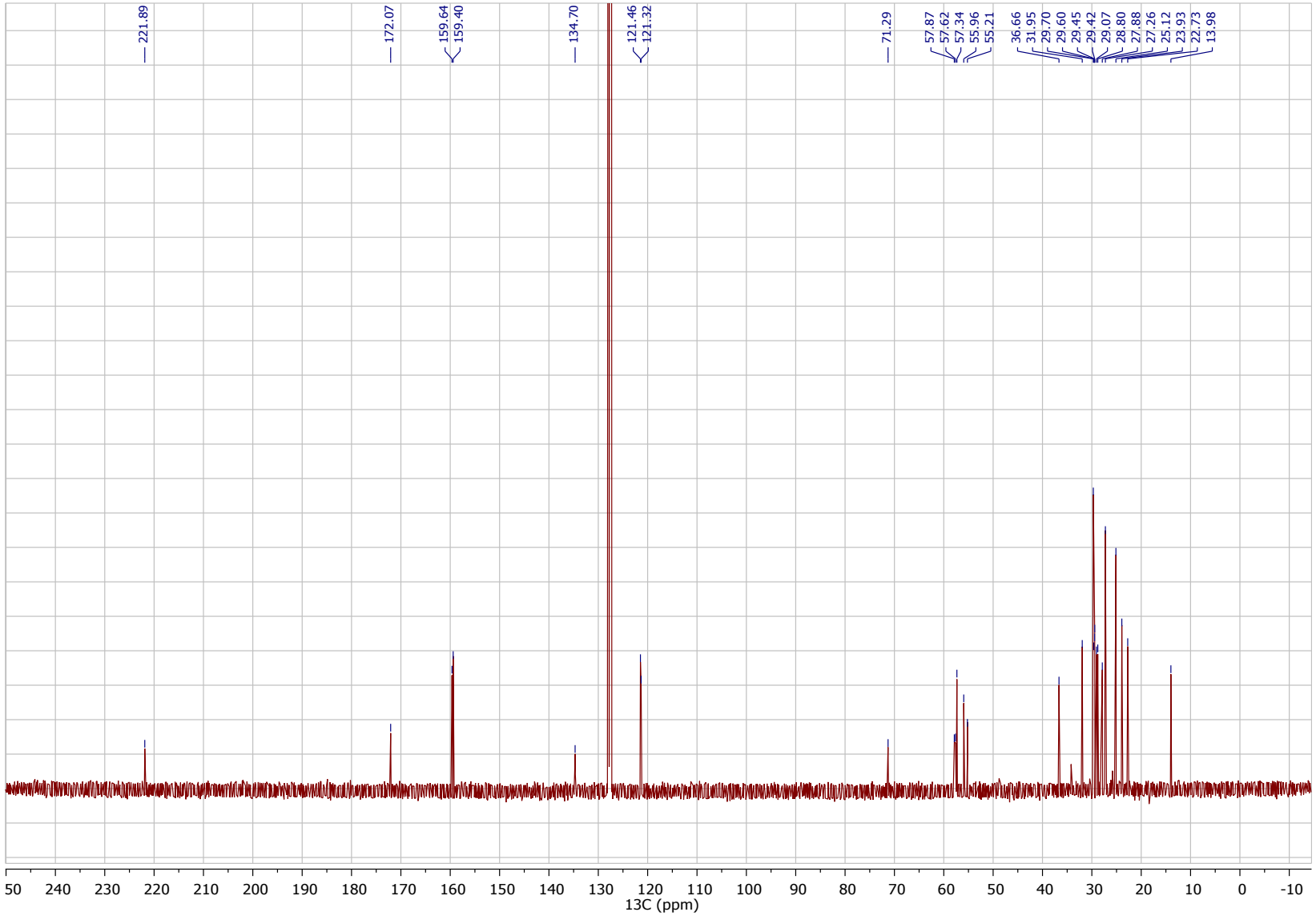



**Figure S12.** $^{13}C$ NMR spectrum of **RAFT CTA-$N_4$** in $C_6D_6$.

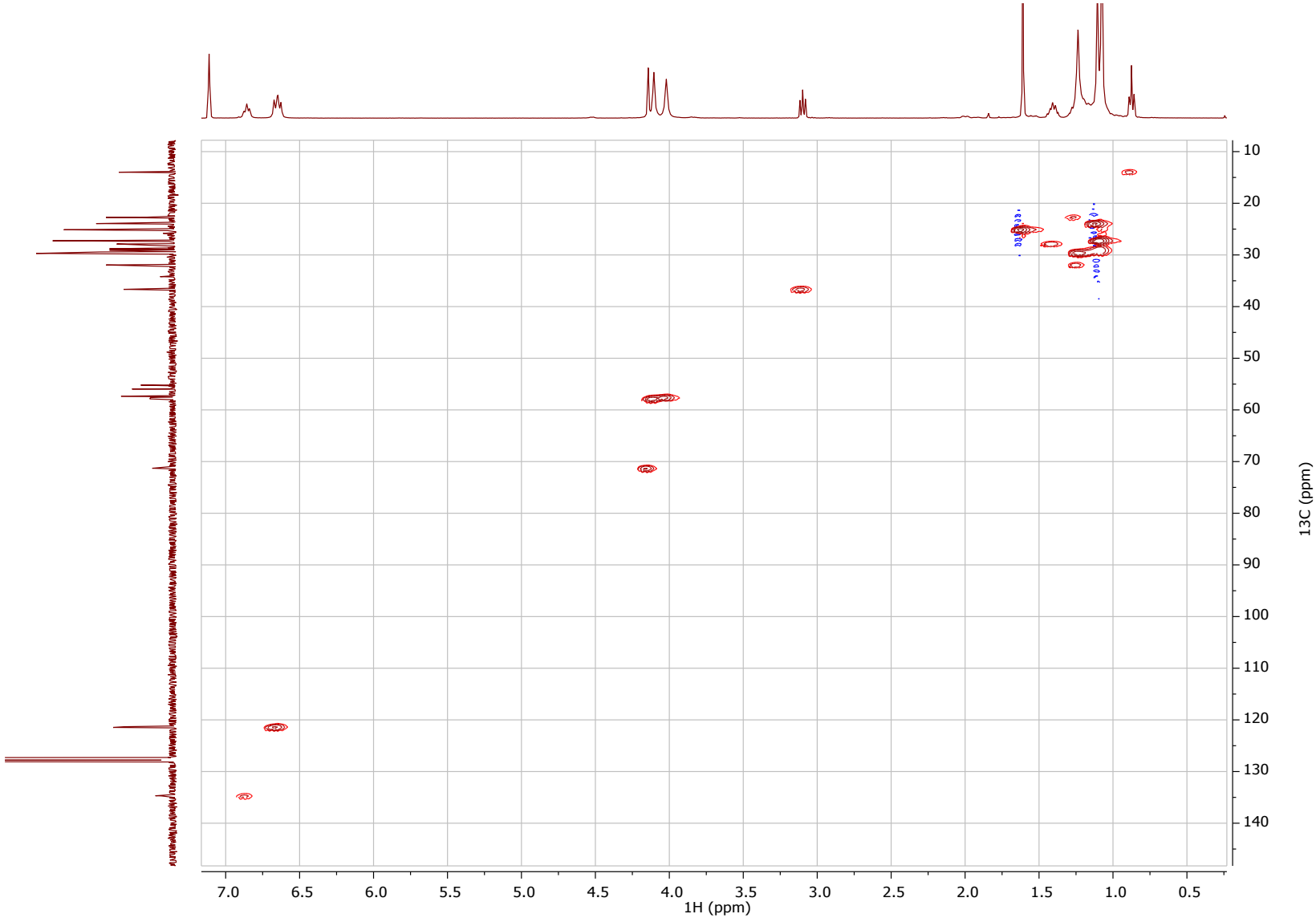
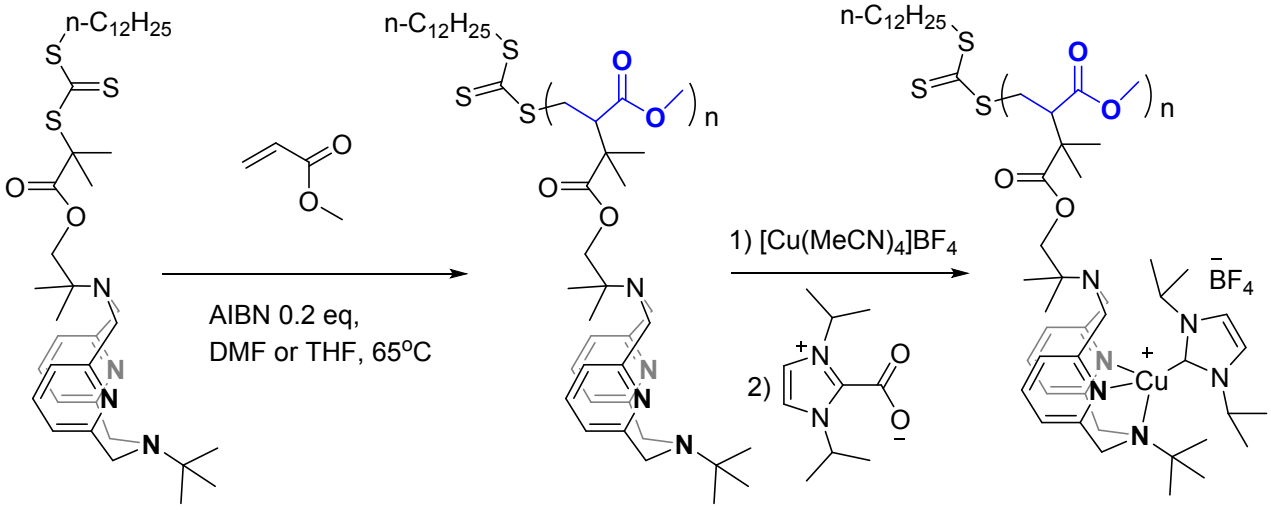



**Figure S13.** gHSQC NMR spectrum of **RAFT CTA-$N_4$** in $C_6D_6$.

**Polymer synthesis:**




**NMR tube scale polymerization and metallation procedure:**

The following procedure describes the NMR follow up of polymerization and subsequent metallation of 3.9 kDa sample with the synthesis conditions for remaining polymers given below in Table S1.

10 mg of **RAFT CTA-N$_4$** (13.98 µmol) were combined with AIBN (0.2 eq., 0.4 mg) and methyl acrylate (63.37 µL, RAFT/M=1/50). An aliquot of THF-d8 (250 µL) was added and NMR spectrum was recorded (A, Figure S1.14 below). The tube was heated at 65 °C for 6 hours and polymerization took place as indicated by the consumption of starting material (86% conversion) evident from the NMR spectrum (B, Figure S1.14). At this point, a sample for GPC analysis and calorimetry was withdrawn from the tube and metalation of the material was performed.

To this polymer solution, 1 eq. of [Cu(MeCN)$_4$]BF$_4$ was added as solution in deuterated acetonitrile (14 µmol in 100 µL) and the tube was shaken. Colour changed from pale yellow to orange and equivalent amount of 1,3-di-isopropylimidazolium-2-carboxylate (14 µmol in 100 µL MeCN) was added, reaction mixture changed colour to yellow and NMR spectrum was recorded (C, Figure S1.14 below) to confirm the formation of Cu complex.

Analysis of 2D data (Figure S1.15) was consistent with complexation and in line with previous studies on similar small molecule complexes with BF$_4$ and BARF counter ions[5-6]. Formation of copper complexes with BARF counterion was performed similarly using [Cu(MeCN)$_4$]BArF metal precursor instead.[5]

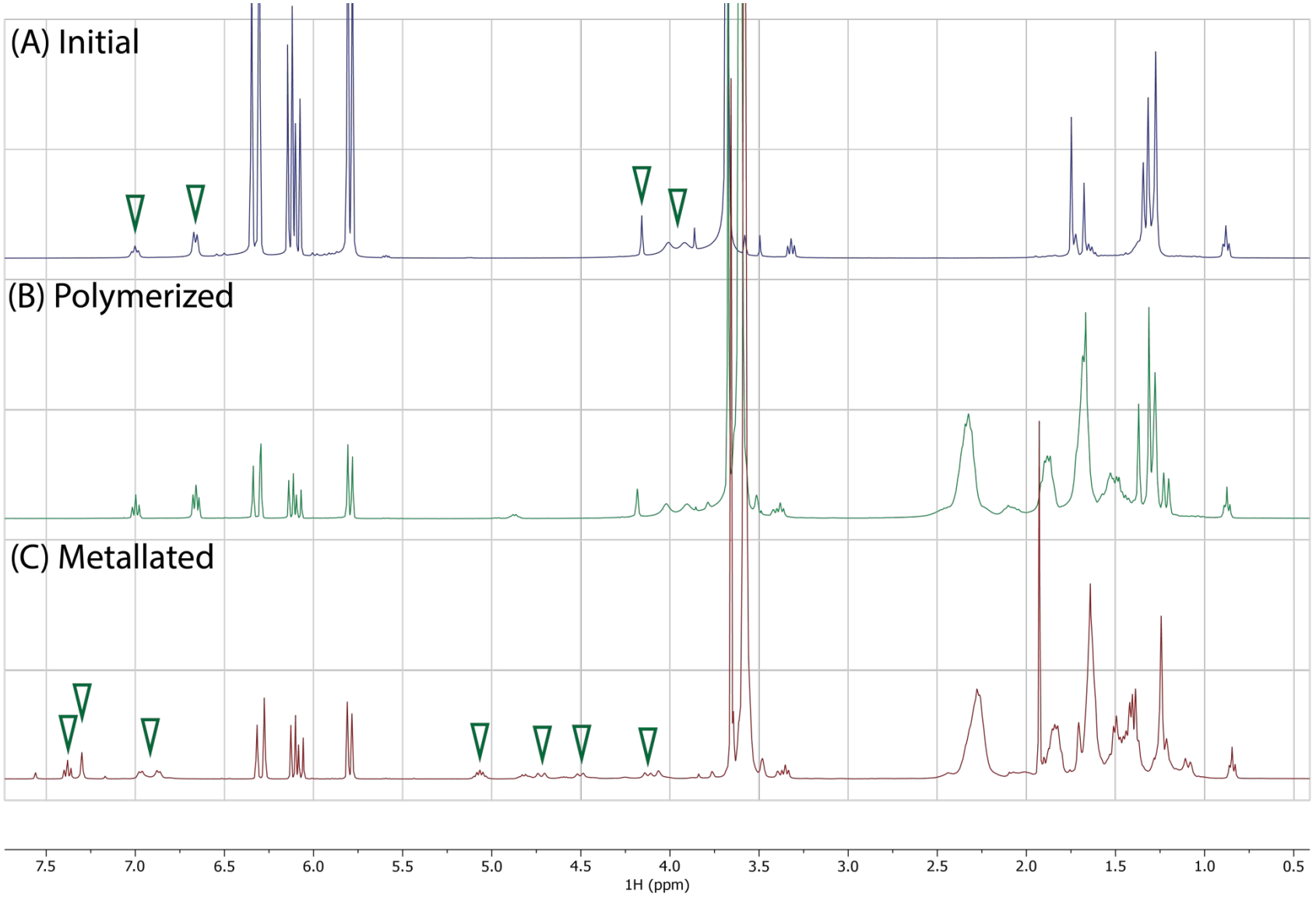



**Figure S14.** $^{1}H$ NMR follow up of polymerization and metalation of 3.9 kDa sample in THF-d8. Triangles indicate $N_4$ macrocycle resonances.

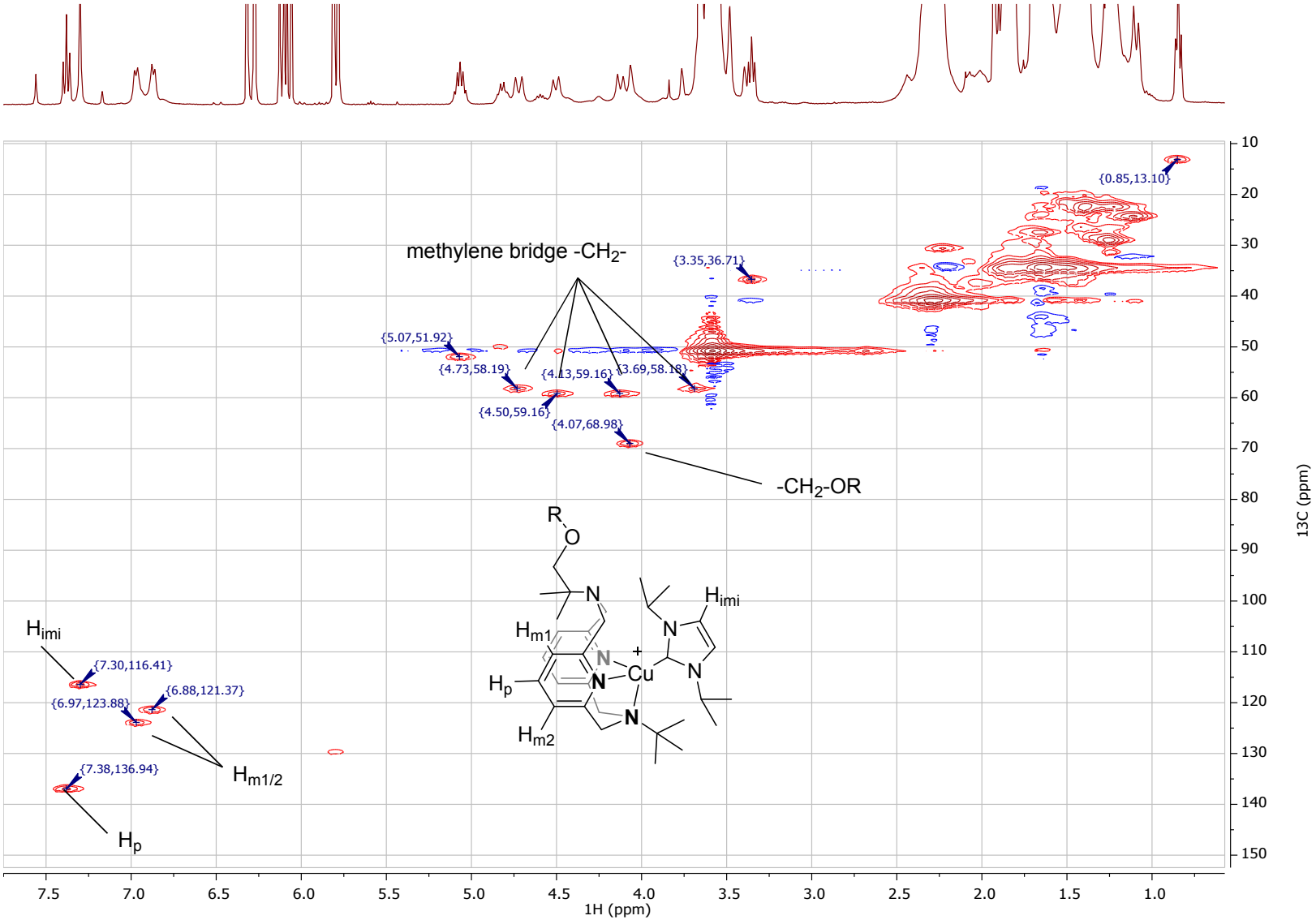



**Figure S15.** gHMQC spectrum of metallated 3.9 kDa sample in THF-$d_8$. Resonances of Cu complex labelled.

**General procedure for large scale polymerization:**

Having confirmed the adequacy of the synthesis strategy we performed the remaining polymerization reactions separately using conditions indicated in Table S1. Typical procedure:

A sample of RAFT agent and AIBN combined as stock solutions in DMF at the ratio of RAFT/AIBN=1/0.2 were added to and methyl acrylate monomer in a glass vial in the glovebox. Additional DMF was added to the mixture and the vial was capped with air tight PTFE lined cap and warmed to 65 °C overnight. Upon completion of polymerizations all samples appeared as soft non flowing pale yellow lumps. Dichloromethane was added to polymer samples to partially dissolve them and the volatile organic compounds including unreacted monomer and DMF were removed in vacuo using rotary evaporator. This treatment was followed by an overnight drying in the vacuum oven (10-15 mbar) at 65°C. Resulting polymers were stored in the glovebox under Ar and metallated using the procedure described above. Outcome of metalation was verified using NMR spectroscopy.

**Blank pMA samples:** were prepared using the procedure described above using DDMAT methyl ester (methyl 2-(dodecylthiocarbonothioylthio)2-methylpropionate)[7] as a chain transfer agent to exclude the presence of carboxylic acid groups that can affect probe molecule in blended materials.

Blends of blank pMA with $CuN_4$ probes with $BF_4$ and BARF counterions were prepared using 100 mg of the polymer dissolved in DCM containing 0.5 and 1 mg of the Cu probe for $BF_4$ and BARF correspondingly. Solutions were mixed thoroughly, drop cast and vacuum dried before tested as outlined above. GPC data for the blank pMA samples is given in Figure S1.16B below

**IMPORTANT NOTE on $M_n$ and end group analysis:**

NMR spectroscopy was used to confirm ligand incorporation as in the case of the tube-scale synthesis (See Figures S1.17-1.20 for related spectra).
While analysis of end group chemistry using NMR is reliable we found it inaccurate for analysing absolute ligand content by comparing integration of end group resonances to those of the main chain functionalities due to the limited dynamic range of the instrument incapable of resolving end group species present is low concentrations in high $M_n$ samples.

Alternatively a reliable value can be obtained using $M_n$ data from GPC given below. Additional verification can be performed using NMR spectroscopy data collected with internal standard, e.g. benzene, present in amounts similar to those of the end groups.

**Table S1.** Synthesis conditions and properties of pMA samples

| No. | Mn, kDa | PDI | Monomer: RAFT:AIBN | T, °C | MA, µL | Solvent, µL |
|---|---|---|---|---|---|---|
| **1** | **3.9** | **1.2** | **50/1/0.2** | **65** | **63.37** | **THF-$d_8$, 400[a]** |
| **2** | **8.2** | **1.37** | **100/1/0.2** | **65** | **300.56** | **DMF, 100** |
| **3** | **13** | **1.45** | **150/1/0.2** | **65** | **253** | **THF-$d_8$, 400[a]** |
| **4** | **17.5** | **1.60** | **200/1/0.2** | **65** | **1065** | **DMF, 650** |
| **5** | **26.9** | **1.59** | **400/1/0.2** | **65** | **1065** | **DMF, 650** |
| **6** | **52.7** | **1.64** | **600/1/0.2** | **65** | **799** | **DMF, 650** |

[a] NMR tube scale reaction

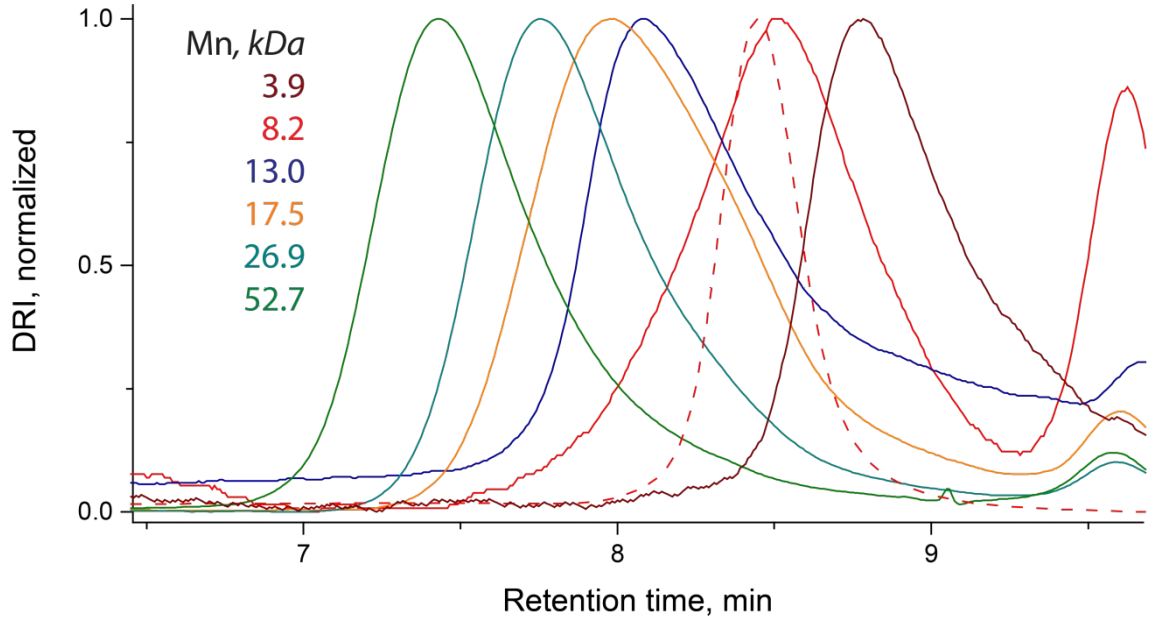



**Figure S16 A.** GPC traces of end-labelled polymers. Dashed line is for the blank pMA sample used in dilution experiments.

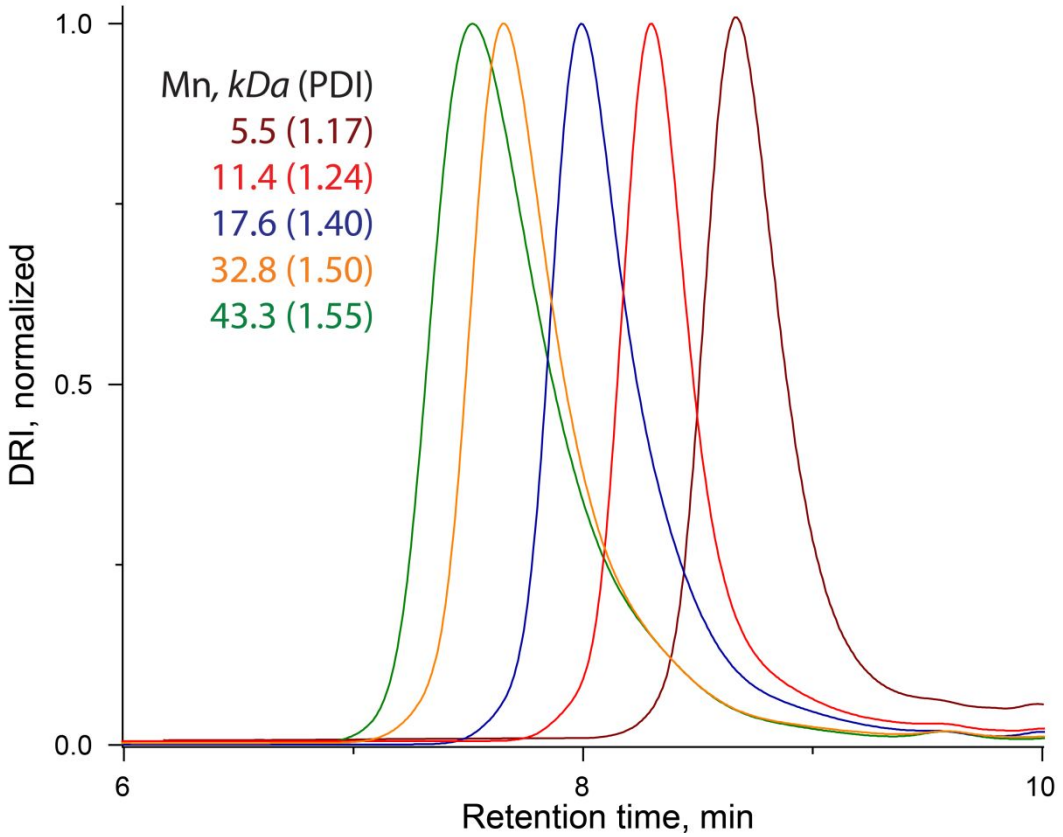



**Figure S16 B.** GPC traces of blank pMA sample used in $CuN_4$ blending experiments.

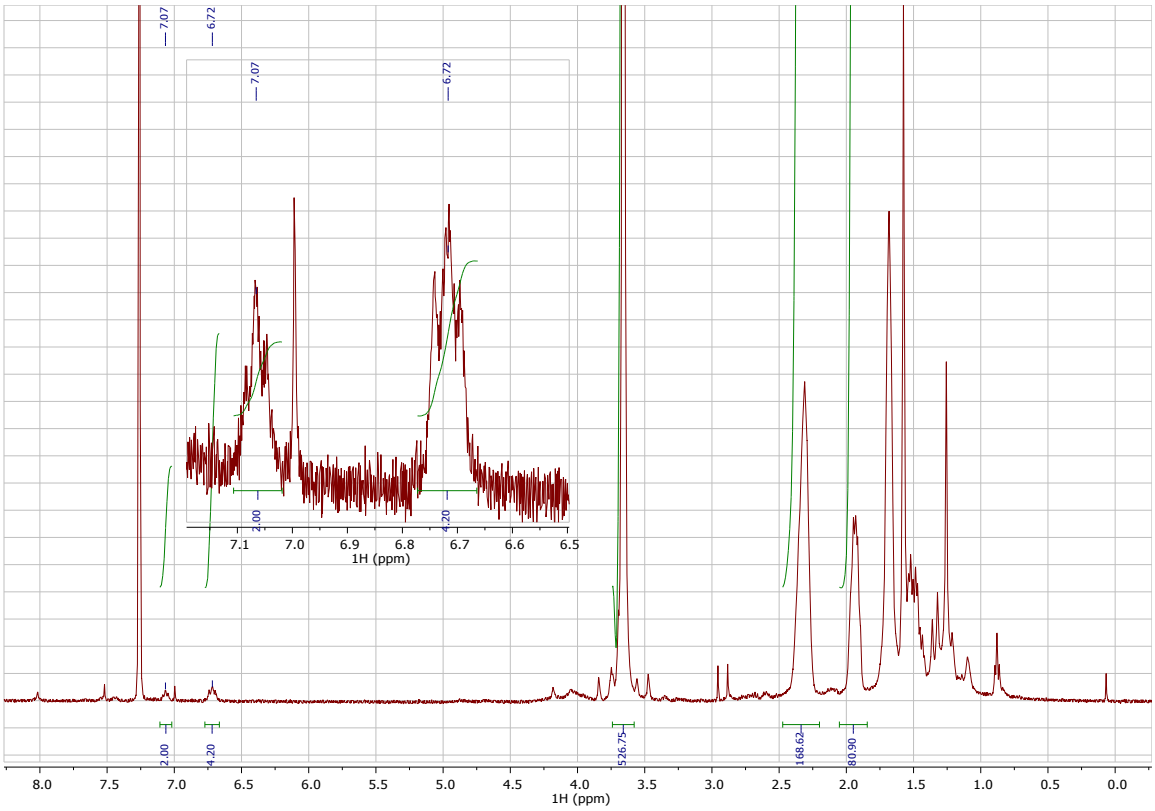



**Figure S17.** $^1$H NMR spectrum of 8.2 kDa pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle.

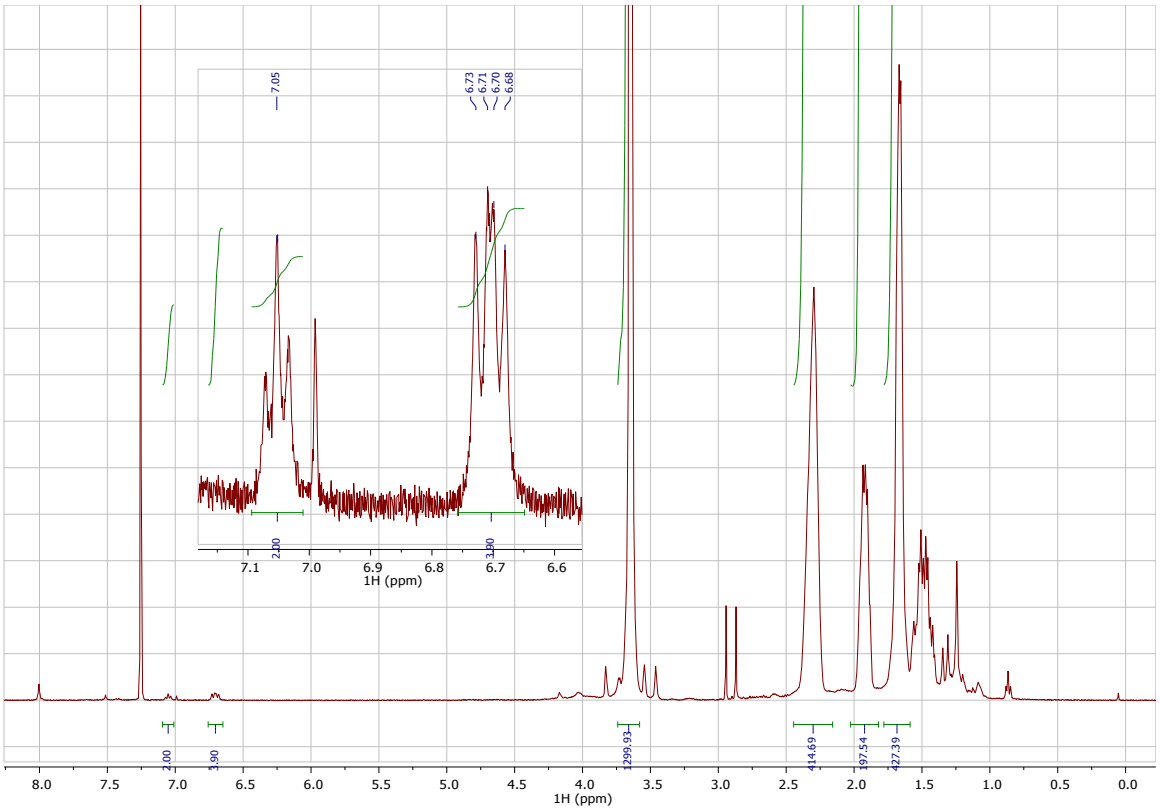



**Figure S18.** $^{1}$H NMR spectrum of 17.5 kDa pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle.

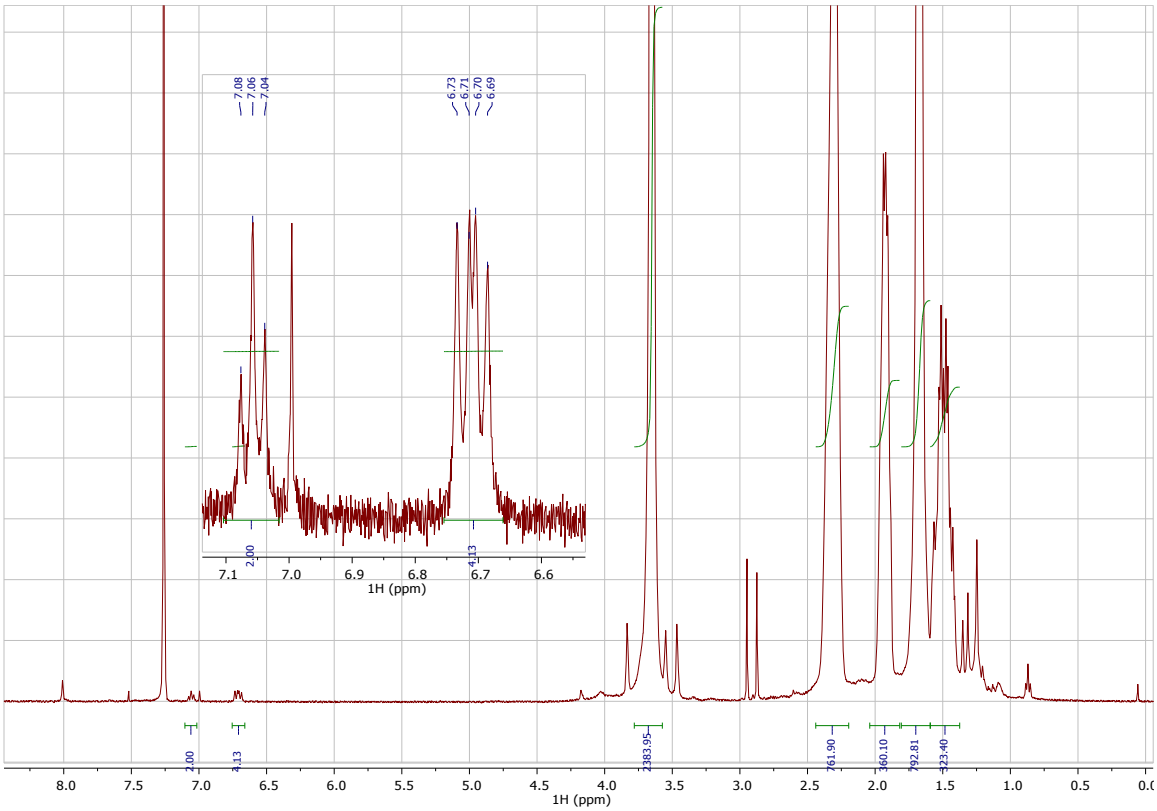



**Figure S19.** $^{1}$H NMR spectrum of 26.9 kDa pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle.

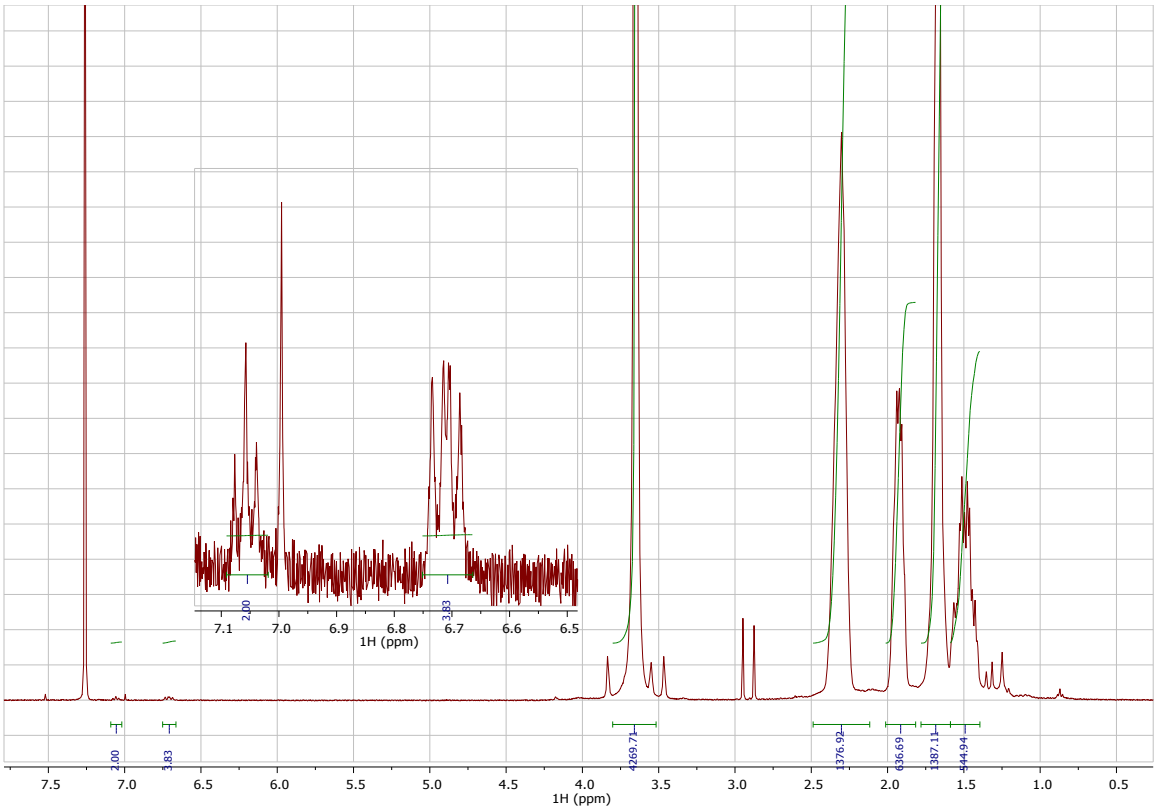



**Figure S20.** $^{1}$H NMR spectrum of 52.7 kDa pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle.

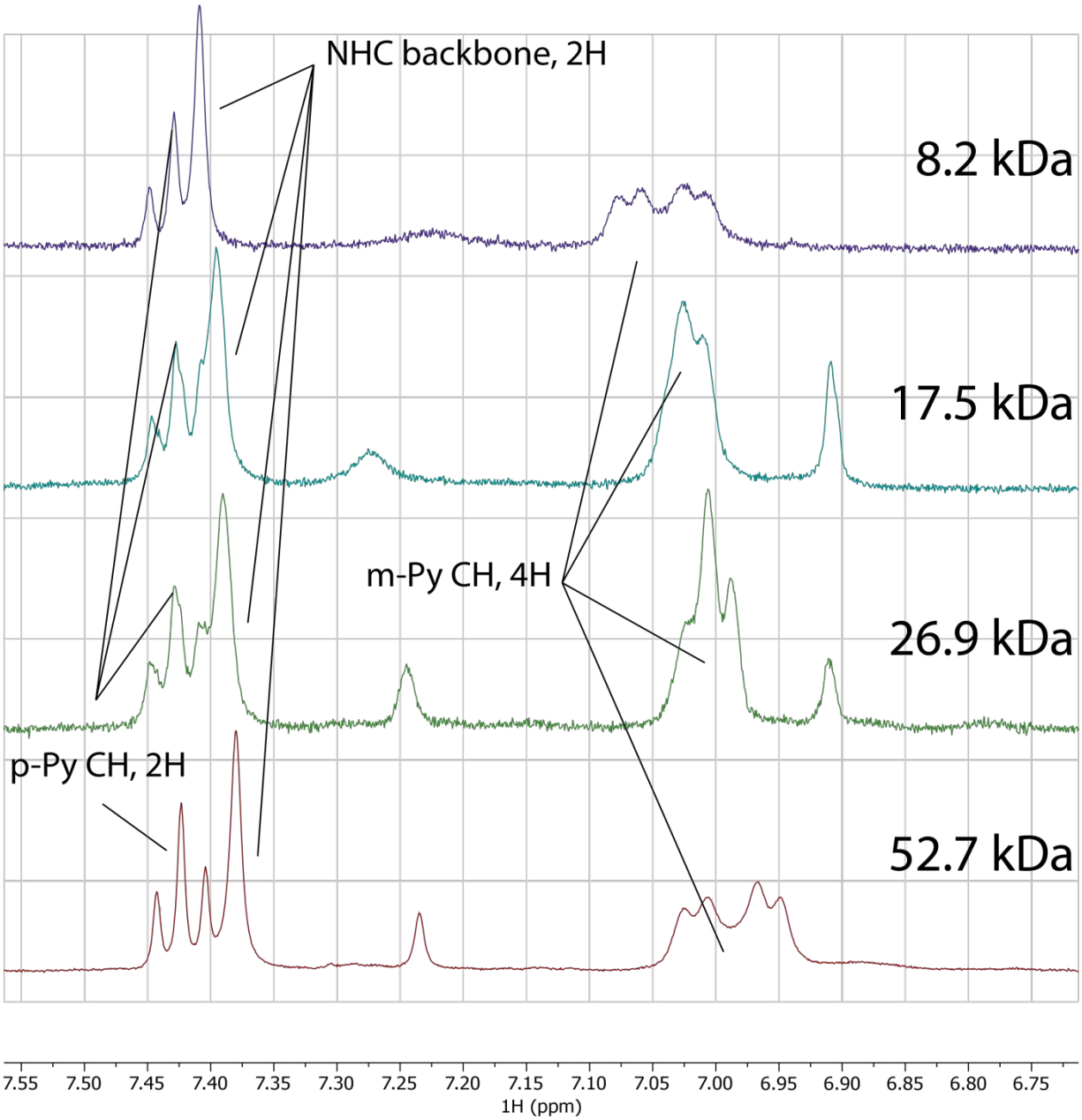



**Figure S21.** Section of $^{1}$H NMR spectra of metallated polymers prepared using general procedure in DMF. Counterion - $BF_4$.Measurements performed in protic THF with THF-$d_8$ reference capillary.

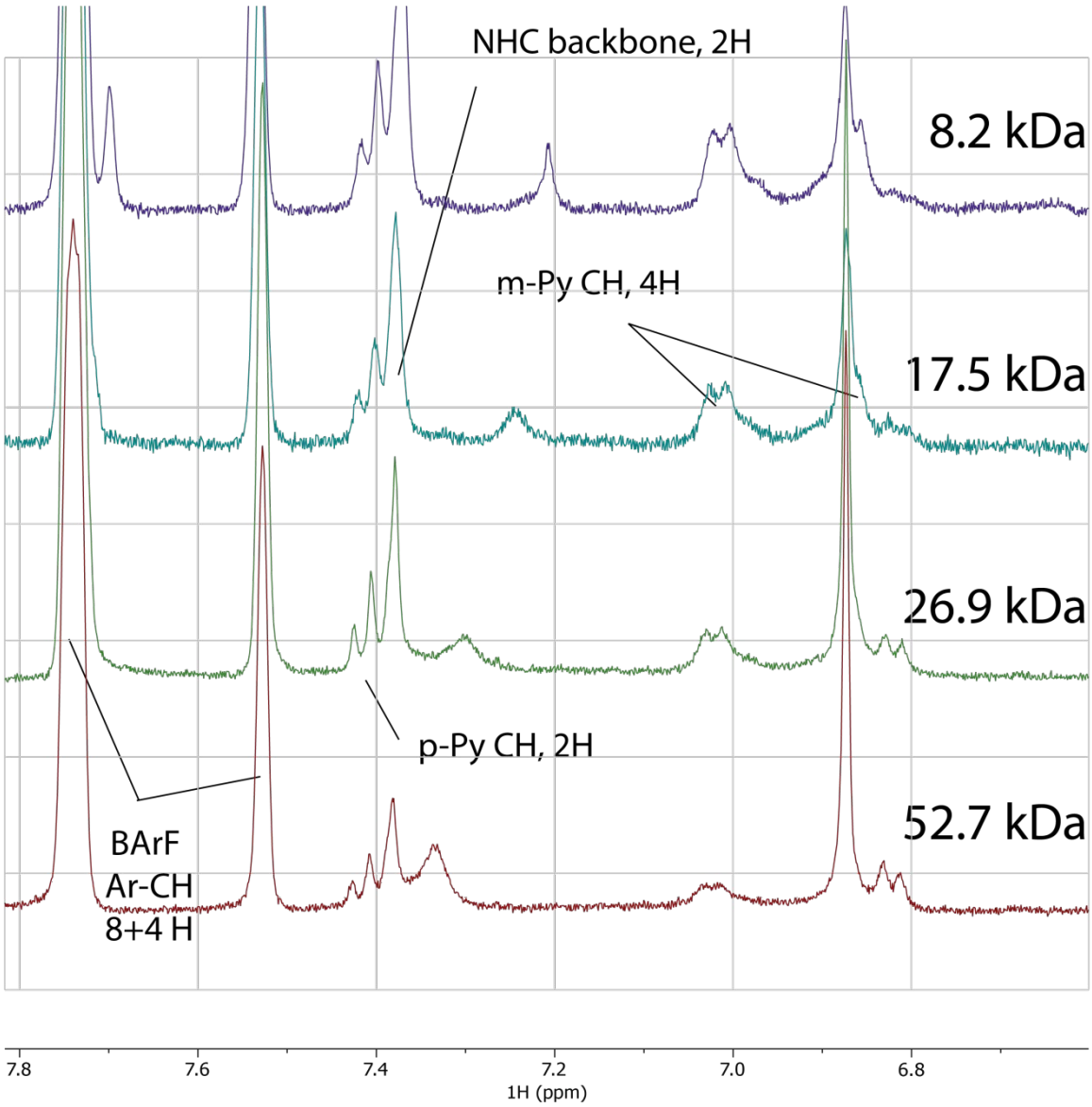
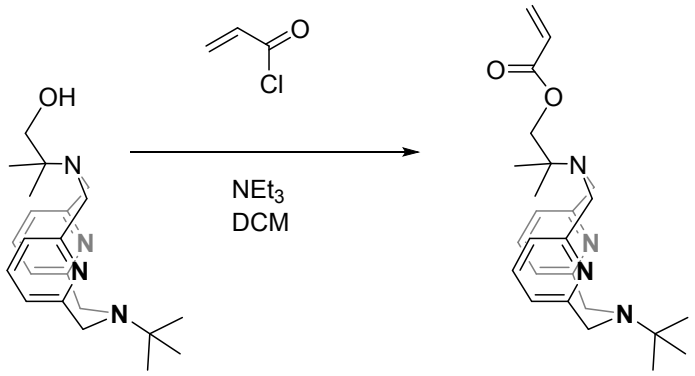



**Figure S22.** Section of $^{1}$H NMR spectra of metallated polymers prepared using general procedure in DMF. Counterion – BArF. Measurements performed in protic THF with THF-$d_8$ reference capillary.

**Preparation of the randomly labelled pMA samples.**

**Monomer synthesis:**




**$N_4$ acrylate** was prepared in the following way: 480 mg of macrocycle **$N_4^{tButBuOH}$** (1.3 mmol, preparation above) were dissolved in dry dichloromethane (5mL) containing ca 363 µL trimethylamine (2 eq., 2.61 mmol). Solution was cooled to 0°C and 115.5 µL of distilled acryloyl chloride (1.43 mmol, 1.15 eq.) were added in one portion. Solution turned pale yellow, was allowed to warm to room temperature and stirred for 1 hour to complete the reaction.

Upon completion, 5 mL of water was added in air, followed by saturated sodium bicarbonate solution and reaction mixture was extracted with DCM (4x25 mL) and combined organic extract was dried over sodium sulphate containing 100 mg Norit carbon to remove coloured impurities. Evaporation of DCM and trituration of resulting oil with cold pentane yields 410 mg of $N_4$ acrylate as tan solid (74.7%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.06 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-Py-C***H***), 6.71 (m, overlap of two doublets, 4H, both *m*-Py-C***H***), 6.47 (d, $^3J_{HH}$ = 17.3 Hz, 1H, -CH=C***H*****$_2$**), 6.31 – 6.10 (m, 1H, -C***H***=$CH_2$), 5.88 (d, $^3J_{HH}$ = 10.4 Hz, 1H, -CH=C***H*****$_2$**), 4.30 (s, 2H, -C***H*****$_2$**-O-Acr), 4.02 (br apparent d, 8H, Py-C***H***$_2$-), 1.39 (s, 6H, -C(C***H*****$_3$**$)_2$-), 1.31 (s, 9H, $^t$Bu-C***H*****$_3$**).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.18 (carbonyl $R_2$***C***=O), 159.45 and 158.86 (py-$C_{2,6}$), 135.27 (py-$C_4$), 130.95 (acrylate –CH=***C***$H_2$), 128.50 (acrylate –***C***H=$CH_2$), 122.04 and 121.79 (py-$C_{3,5}$), 69.63 (-***C***$H_2$OAcr), 57.95 and 55.84 ($^t$Bu quaternary ***C***), 57.84 and 57.72 (py-***C***$H_2$-), 27.70 ($^t$Bu-***C***$H_3$), 24.23 (-N-C((***C***$H_3$$)_2$($CH_2$OAcr).

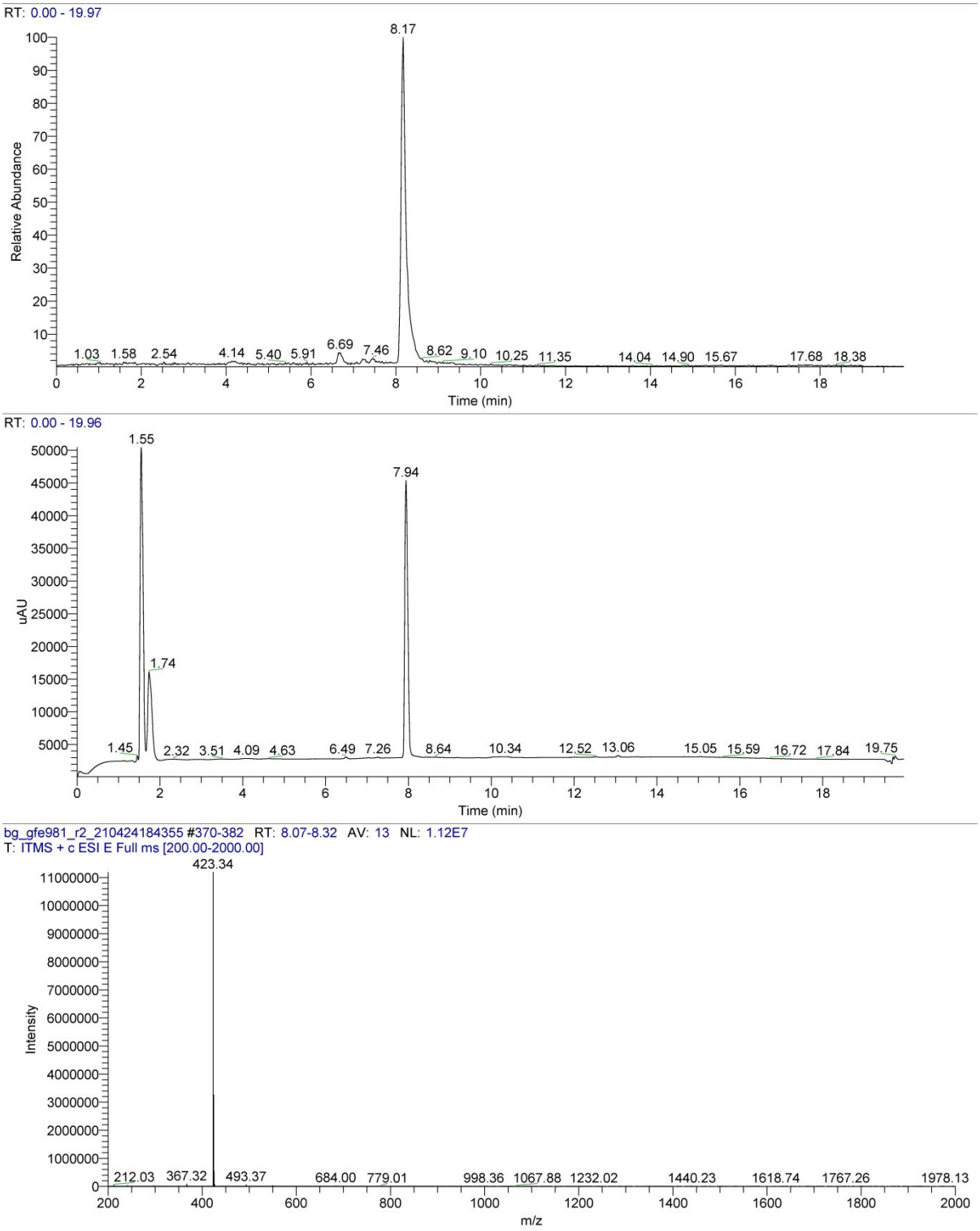



**Figure S23.** LC-MS data for **$N_4$ acrylate**

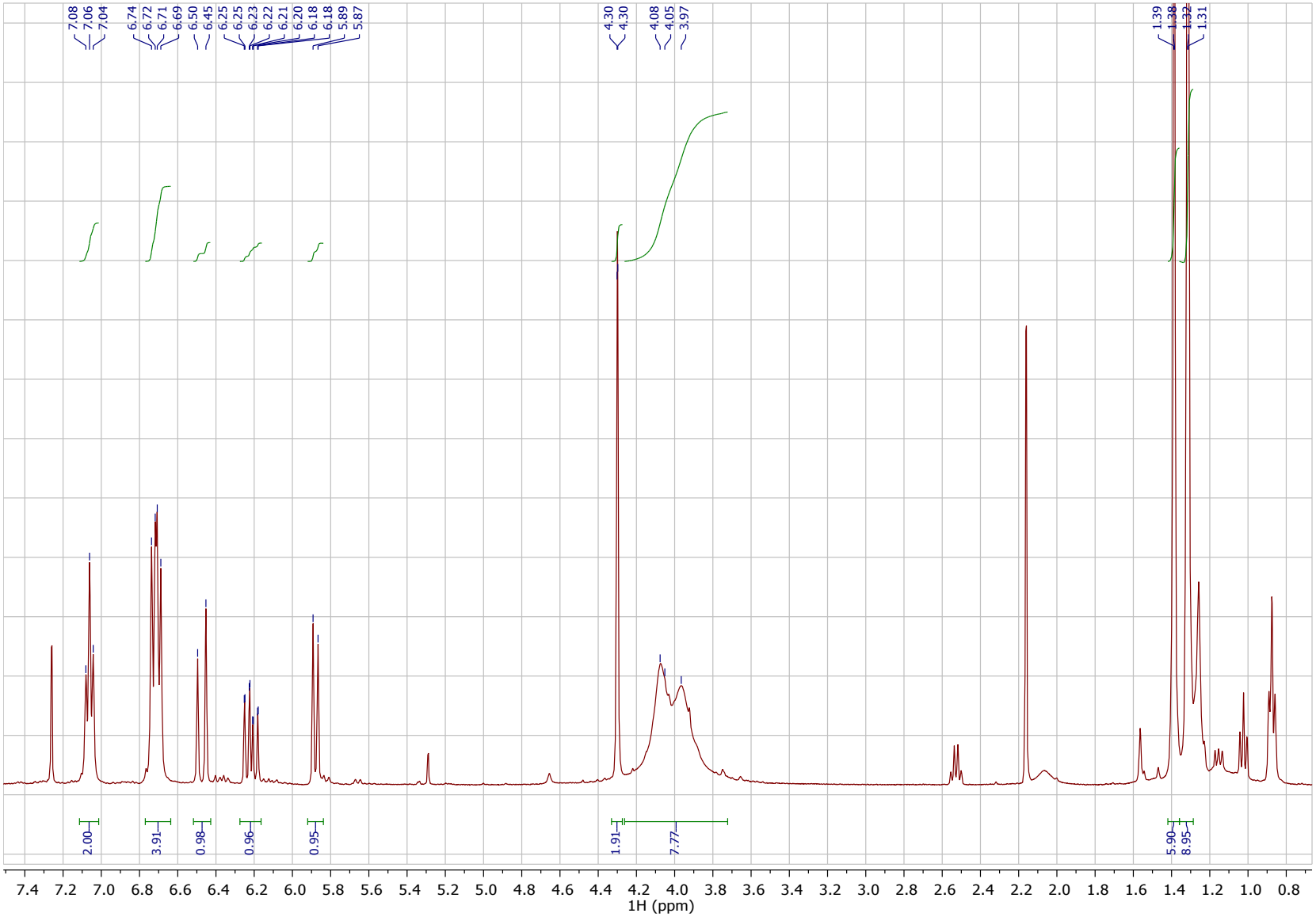



**Figure S24.** $^{1}$H NMR spectrum of **$N_4$ acrylate** in $CDCl_3$

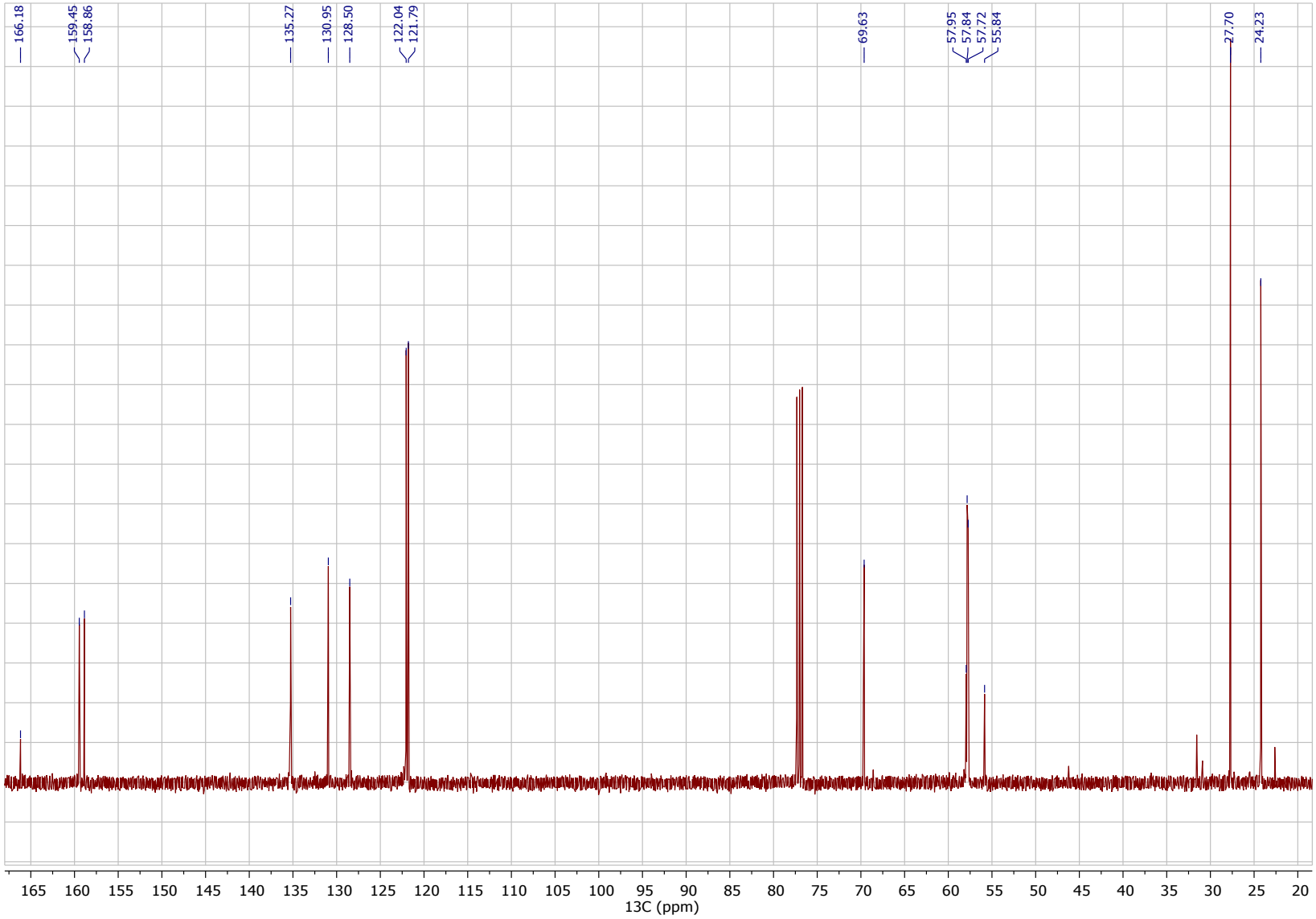



**Figure S25.** $^{13}C$ NMR spectrum of **$N_4$ acrylate** in $CDCl_3$

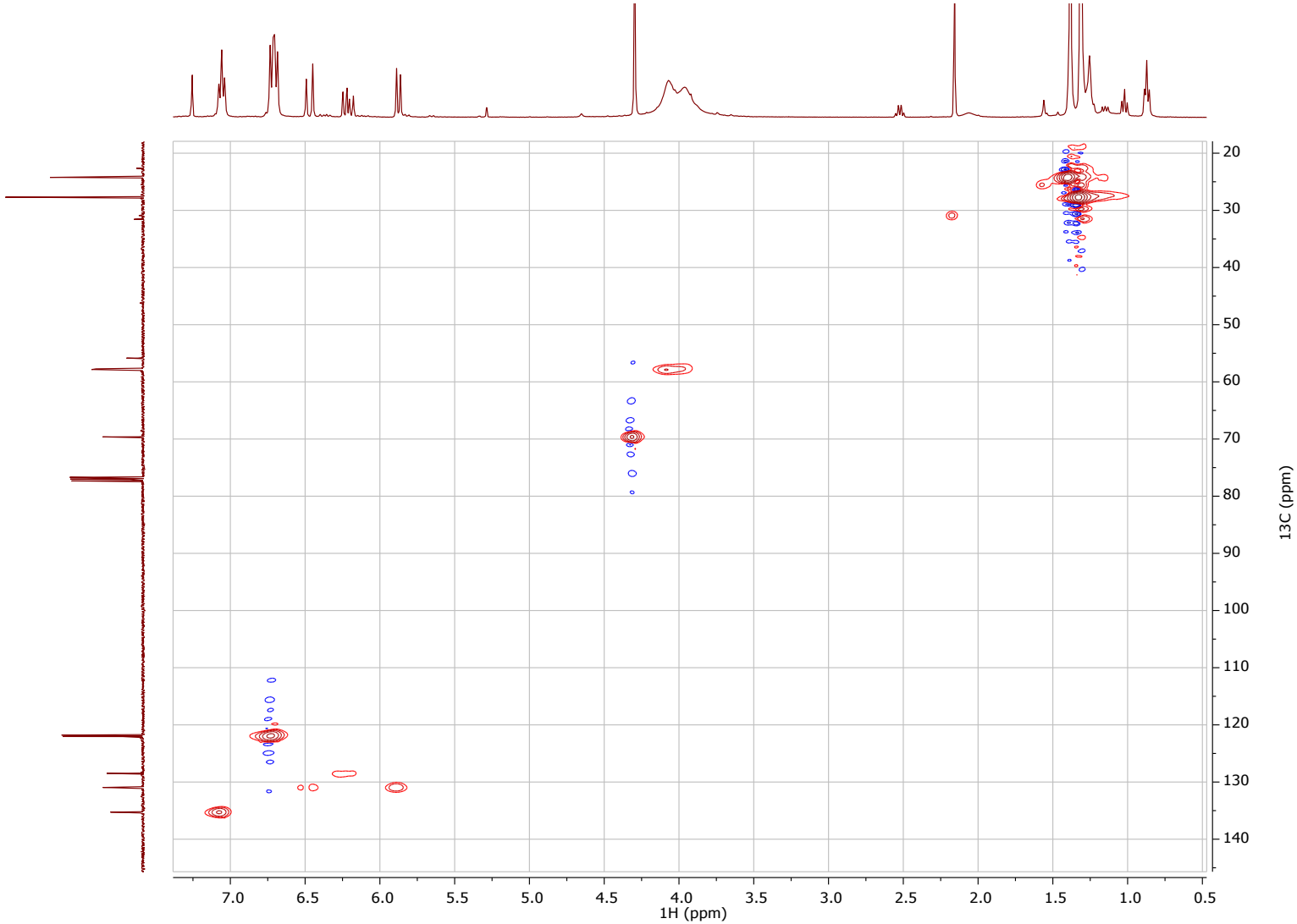



**Figure S26.** HMQC spectrum of **$N_4$ acrylate** in $CDCl_3$

**Polymer synthesis and metalation:**

All polymers were prepared with N4 ligand loaded at 20 μmol/g pMA. Mn variation was set by the amount of CTA used in co-polymerization.

The stock of $N_4$ acrylate monomer in methyl acrylate (20 μmol/g MA: 36.2 g N4 acrylate in 4.5 mL MA) and cyanomethyl dodecyl trithiocarbonate (stock in THF-$d_8$, 122.62 mg in 700μL) as a RAFT CTA. Ratios and loadings are indicated in the table below. Small amount of THF-$d_8$ was added and reaction mixture was sealed in a J. Young tube and placed under blue LED light (455 nm) overnight. NMR reported >95% monomer conversion in all cases and the resulting polymer was recovered from the tubes by dissolving in chloroform and evaporating all volatiles. See representative $^1$H NMR spectrum below.

**Table S2.** Synthesis conditions and properties of pMA samples copolymerized with $N_4$ acrylate

| **No.** | **Mn, kDa** | **PDI** | **MA:CTA molar ratio** | **CTA, mg** | **MA, mL** | **Solvent, μL** |
|---|---|---|---|---|---|---|
| **1** | **8.6** | **1.10** | **75/1** | **70.07** | **1.5** | **THF-$d_8$, 500** |
| **2** | **17.2** | **1.15** | **150/1** | **35.04** | **1.5** | **THF-$d_8$, 400** |
| **3** | **34.1** | **1.13** | **300/1** | **17.52** | **1.5** | **THF-$d_8$, 500** |

Randomly labelled pMA was metallated is procedure identical to that used for end-labelled polymers. Identical NMR spectra were obtained (See data below).

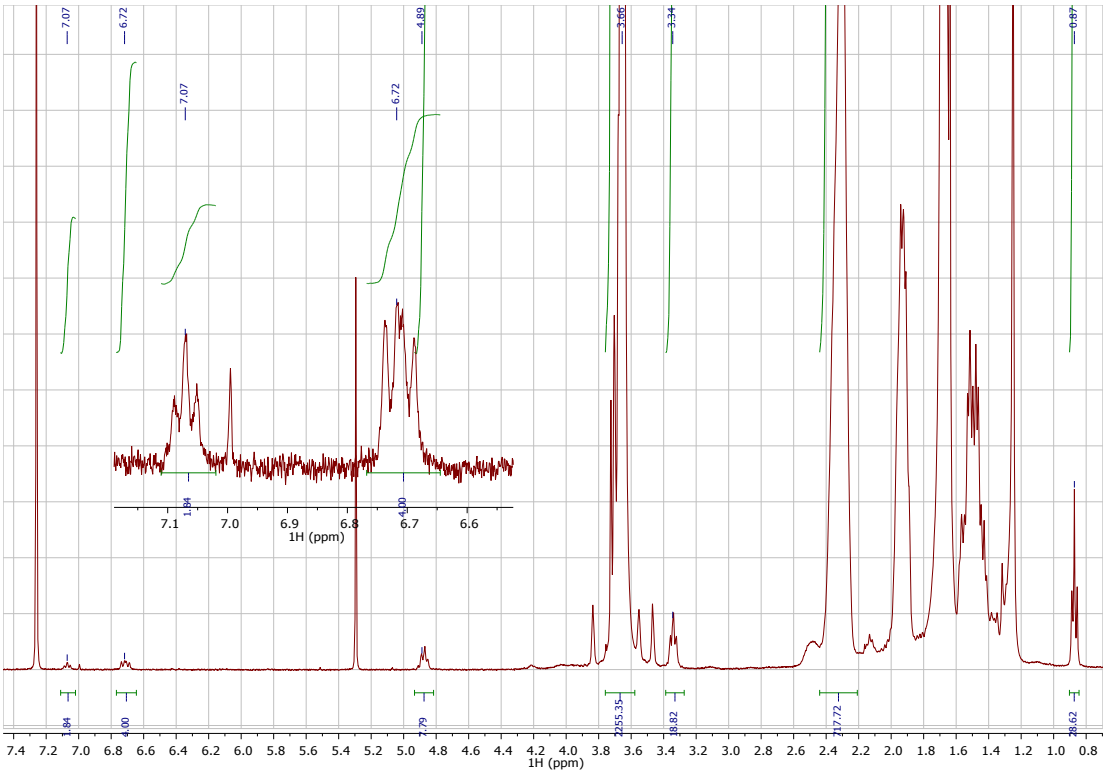



**Figure S27.** $^{1}$H NMR spectrum of 8.6 kDa randomly labelled pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle. Integration reports $N_4$:CTA ratio of 7.79 vs loaded 7.74

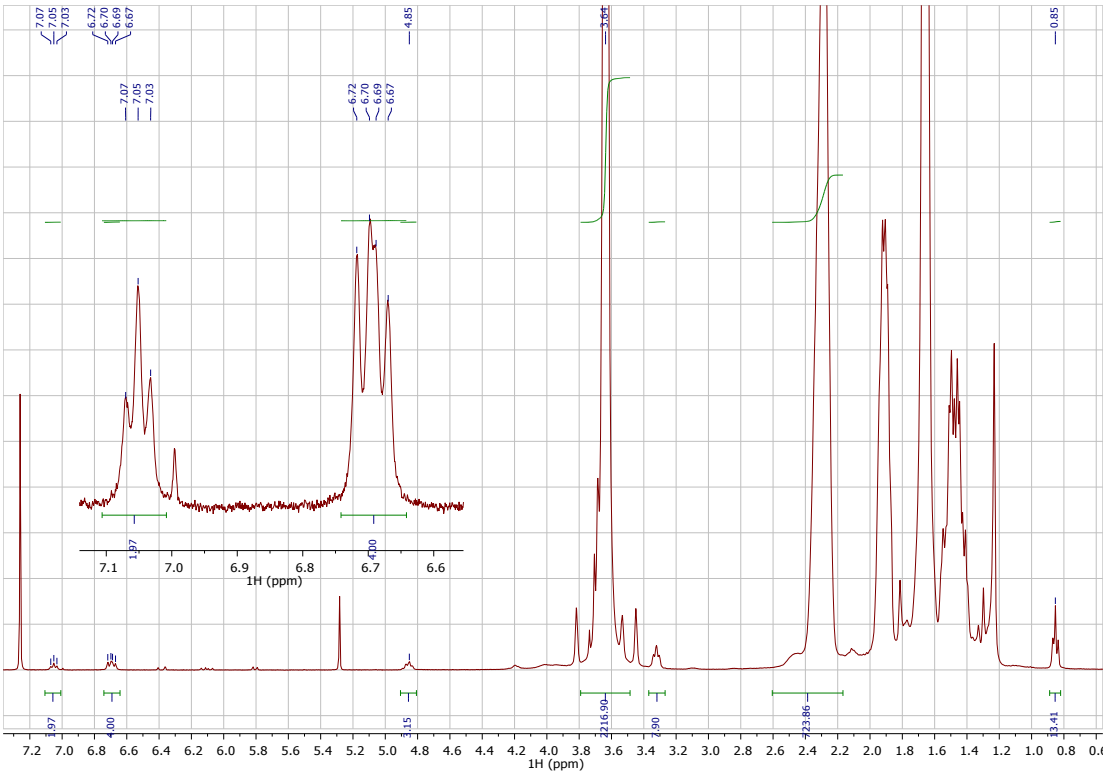



**Figure S28.** $^{1}$H NMR spectrum of 17.2 kDa randomly labelled pMA sample before metalation in $CDCl_3$. Insert shows the resonances of $\mathbf{N_4}$ macrocycle. Integration reports $N_4$:CTA ratio of 3.55 vs loaded 3.87

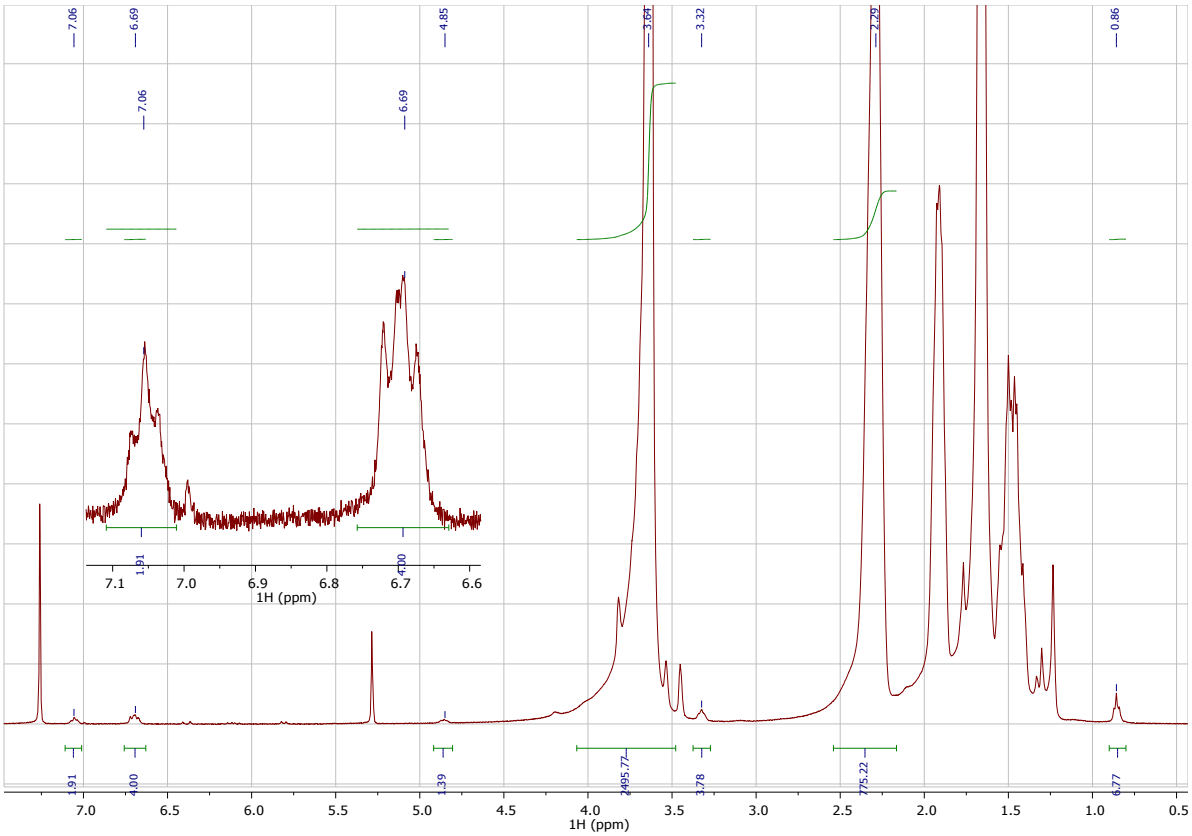



**Figure S29.** $^{1}$H NMR spectrum of 34.1 kDa randomly labelled pMA sample before metalation in $CDCl_3$. Insert shows the resonances of **$N_4$** macrocycle. Integration reports $N_4$:CTA ratio of 1.64 vs loaded 1.93

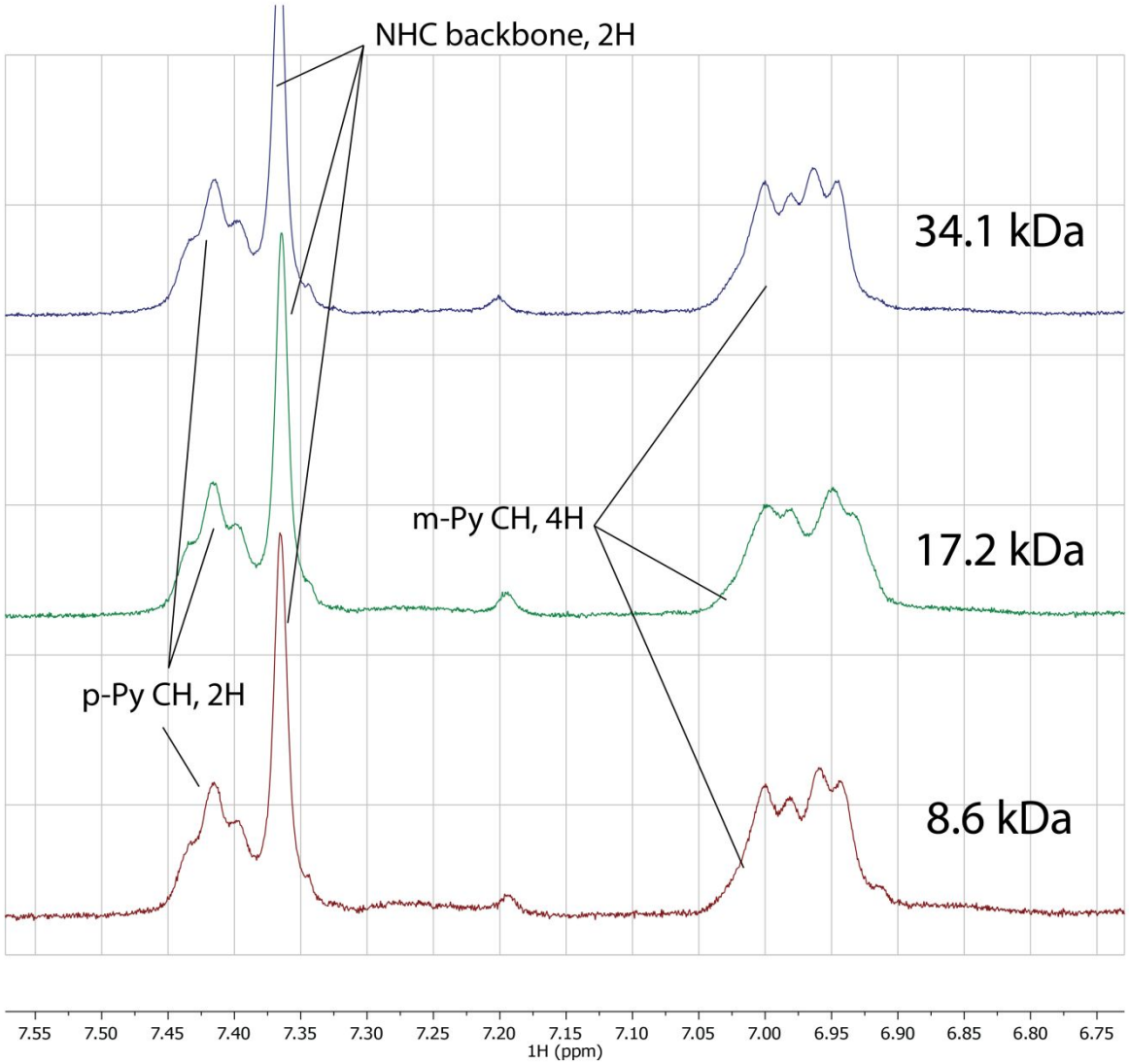



**Figure S30.** Section of $^{1}$H NMR spectra of metallated randomly labelled polymers. Counterion – $BF_4$. Measurements performed in protic THF with THF-$d_8$ reference capillary.

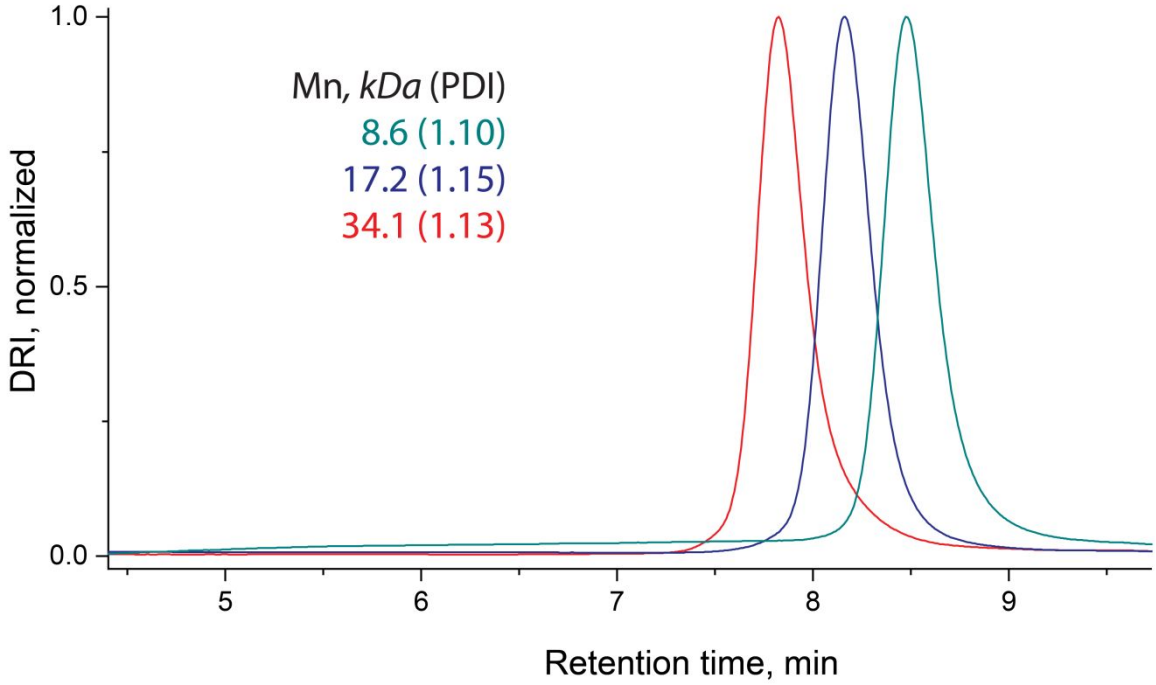



**Figure S31.** GPC traces for $N_4$-pMA copolymer

## S2. Photoluminescence, structural and thermal data

All polymer samples were vacuum dried for at least 12 hours before characterization and further annealed at 75°C to erase thermal history before PL measurements and calorimetry experiments.

**Temperature dependent photoluminescence spectra** were recorded with an interval of 15° upwards of -90°C.

**IMPORTANT NOTE:** Raw spectrometer output was used to analyse spectral intensity ratio defined as count ratio at 530 vs 610 nm and used in all ratiometry plots. The obtained value was later corrected for instrument sensitivity using absolute irradiance calibration. An example of the processing routine is given below in Figure S2.1. Representative temperature dependence of the whole spectrum is shown in Figure 2C of the manuscript.

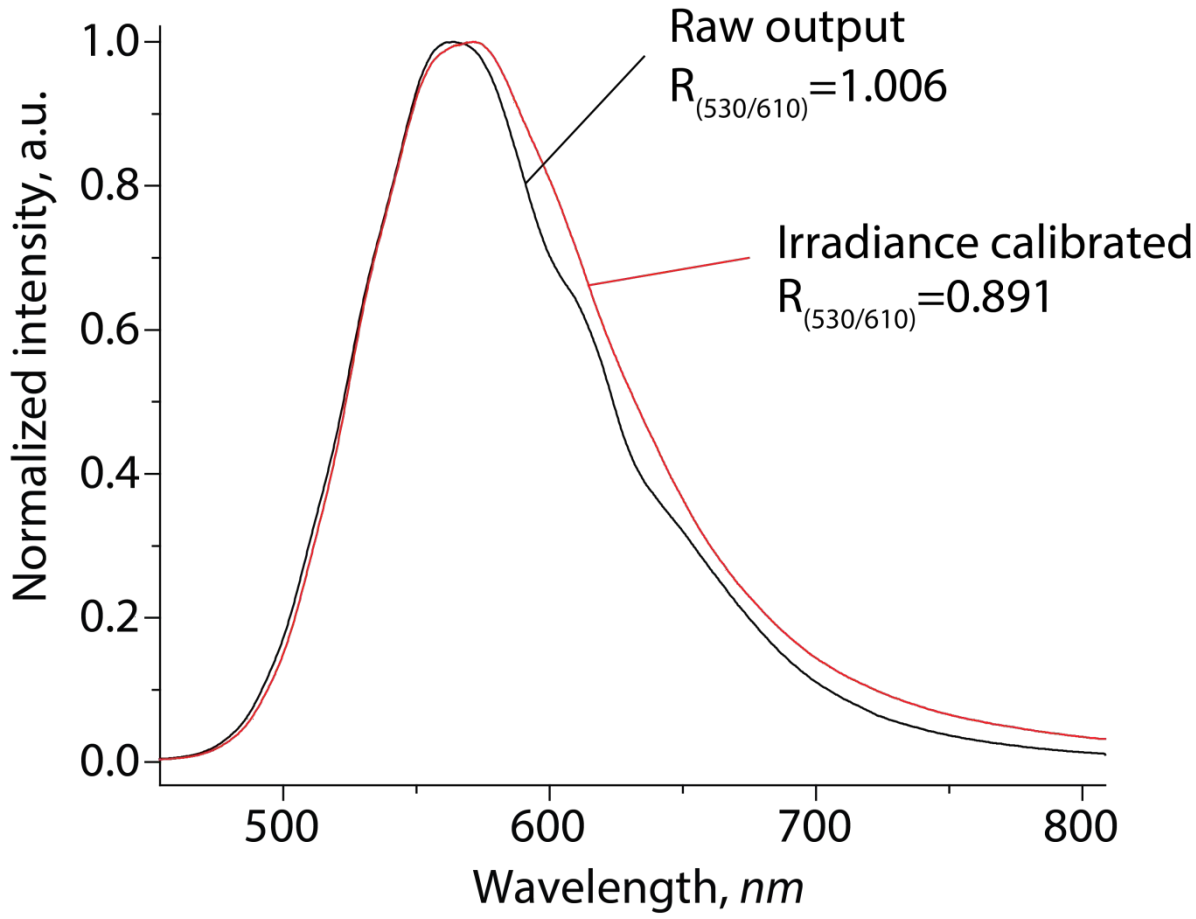



**Figure S32.** Comparison between PL spectra before and after absolute irradiance calibration and impact on ratiometry data.

**Transition temperature analysis:**

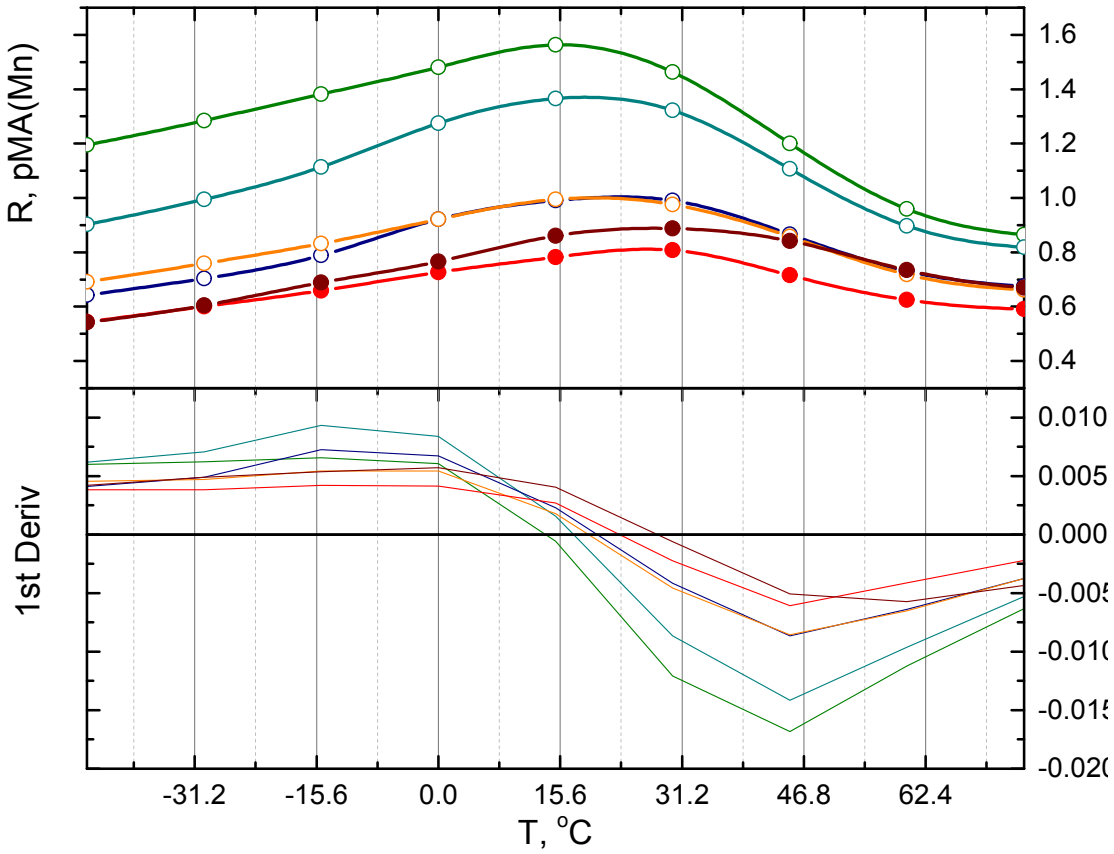



**Figure S33.** Example of processing of ratiometry data shown in Figure 3A of the manuscript and 1st derivative plot used to determine the curve maxima.

$T_g$(PL) values were estimated from ratiometry data as a zero of the 1st derivative of the ratiometry curve. See Figure S2.2 for data given in Figure 2 of the manuscript.

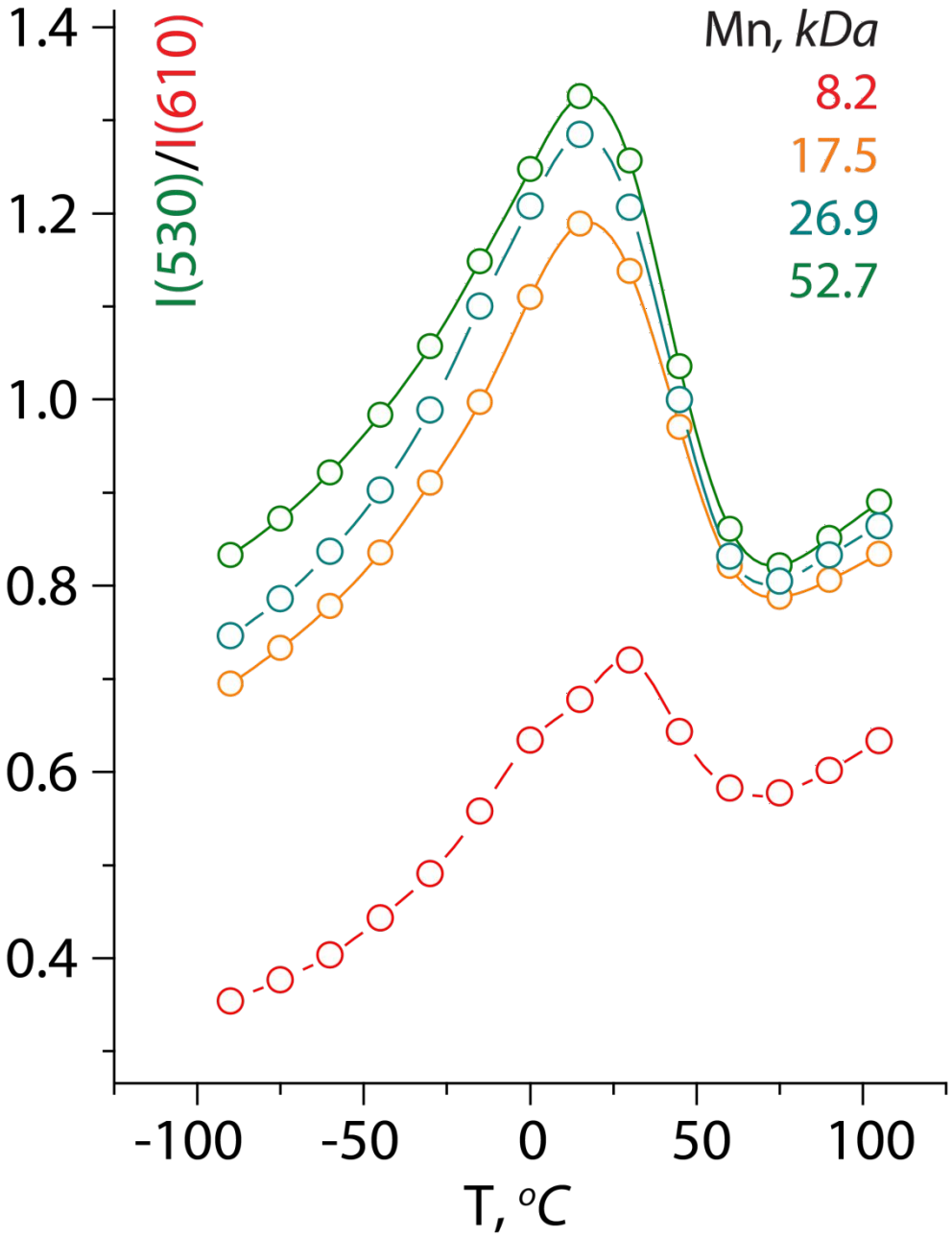



**Figure S34.** Ratiometry data for end-labelled pMA samples containing 2nm BArF probe. Transition temperature data shown in Figure 3 of the manuscript.

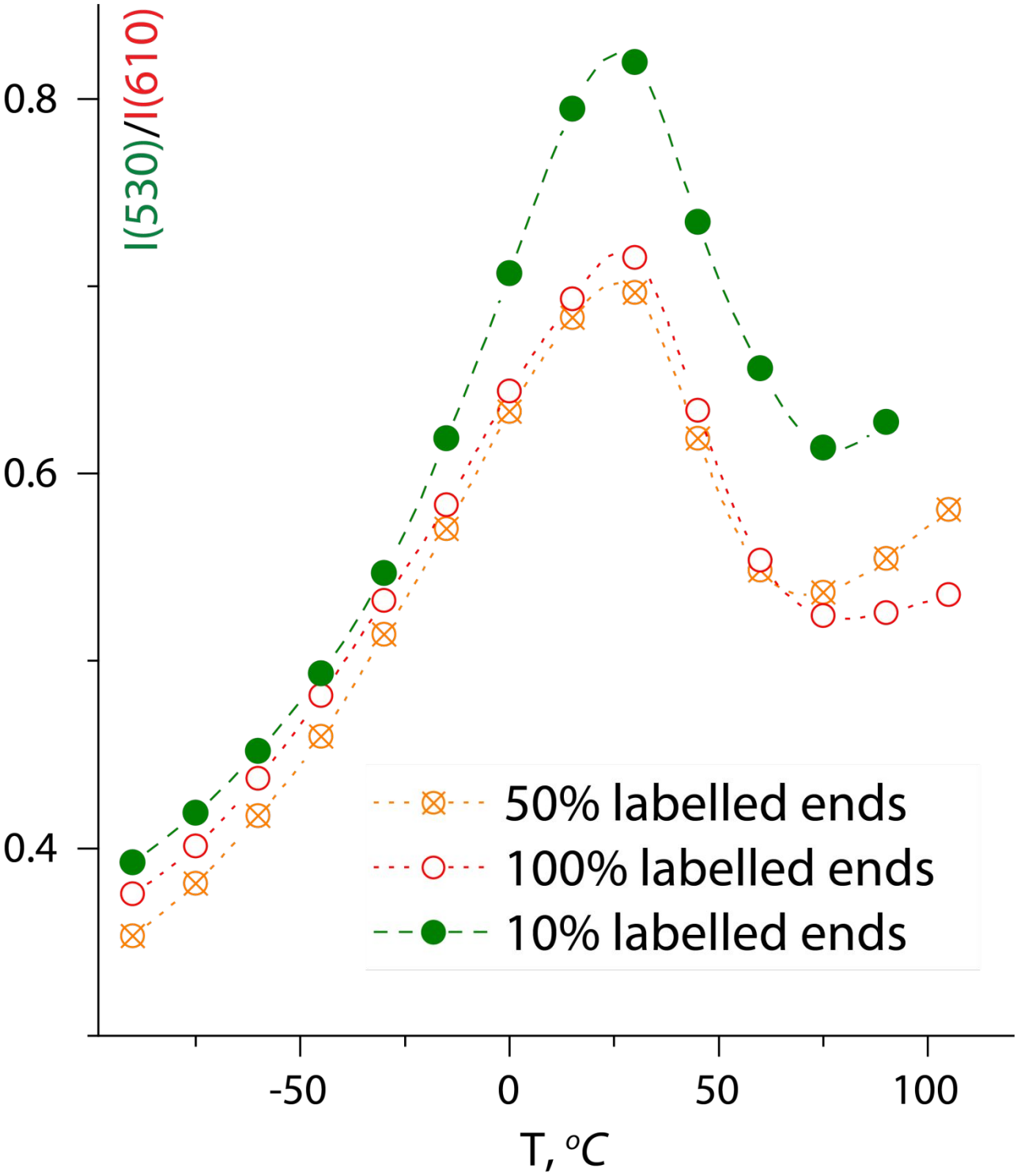



**Figure S35.** Ratiometry data for end-labelled pMA samples containing $BF_4$ probe at multiple dilution level. Parent 8.2 kDa end labelled sample was diluted with blank polymer of Mn=9.46 kDa prepared as described above

**DCS data for neutral and charged pMA samples.**

| Sample | Tg onset 1, °C | Tg onset 2, °C |
|---|---|---|
| Neutral series pMA-$N_4$ | | |
| 3.9 kDa | -4.74 | -4.15 |
| 8.2 kDa | 6.42 | 6.57 |
| 13 kDa | 9.39 | 9.40 |
| 17.5 kDa | 9.77 | 9.79 |
| 26.9 kDa | 14.57 | 14.37 |
| 52.7 kDa | 16.37 | 16.79 |
| $BF_4$ counterion series, pMA-$CuN_4$ | | |
| 3.9 kDa | 10.12 | 10.74 |
| 8.2 kDa | 12.61 | 12.68 |
| 13 kDa | 10.75 | 10.80 |
| 17.5 kDa | 11.83 | 11.66 |
| 26.9 kDa | 12.24 | 13.19 |
| 52.7 kDa | 16.08 | 16.35 |
| BArF counterion series, pMA-$CuN_4$-BArF | | |
| 8.2 kDa | 11.37 | 11.83 |
| 17.5 kDa | 15.25 | 15.37 |
| 26.9 kDa | 15.52 | 15.47 |
| 52.7 kDa | 15.52 | 15.18 |
| $CuN_4$/pMA blends, $BF_4$ counterion | | |
| 5.5 kDa | 1.81 | 1.90 |
| 11.5 kDa | 8.56 | 8.57 |
| 17.6 kDa | 10.49 | 10.55 |
| 32.8 kDa | 14.23 | 14.34 |
| 43.3 kDa | 12.78 | 12.85 |
| $CuN_4$ randomly labelled pMA, $BF_4$ counterion | | |
| 8.6 kDa | -3.50 | -3.47 |
| 17.2 kDa | 2.03 | 1.99 |
| 34.1 kDa | 8.68 | 8.54 |

**Table S3.** Tg data for duplicate measurements of neutral pMA samples and those metallated with Cu complex with different counterions.

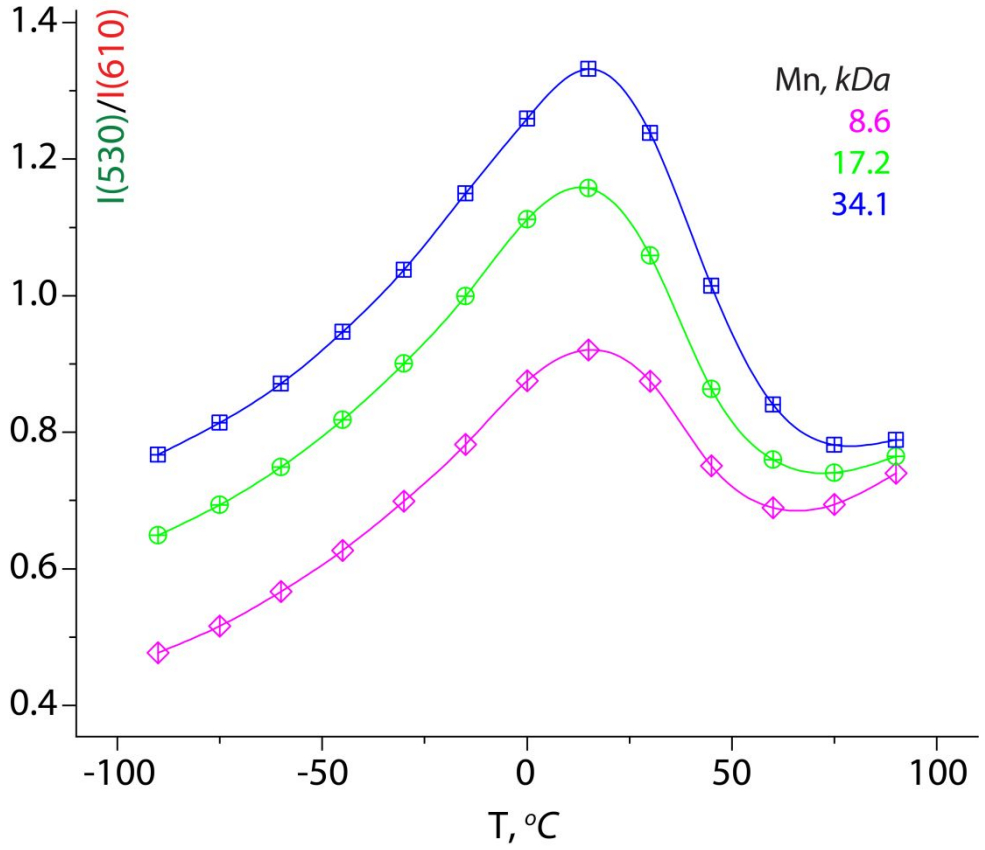



**Figure S36.** Ratiometry data for randomly labelled pMA samples (pMA-$N_4$ copolymer) containing $BF_4$ probe

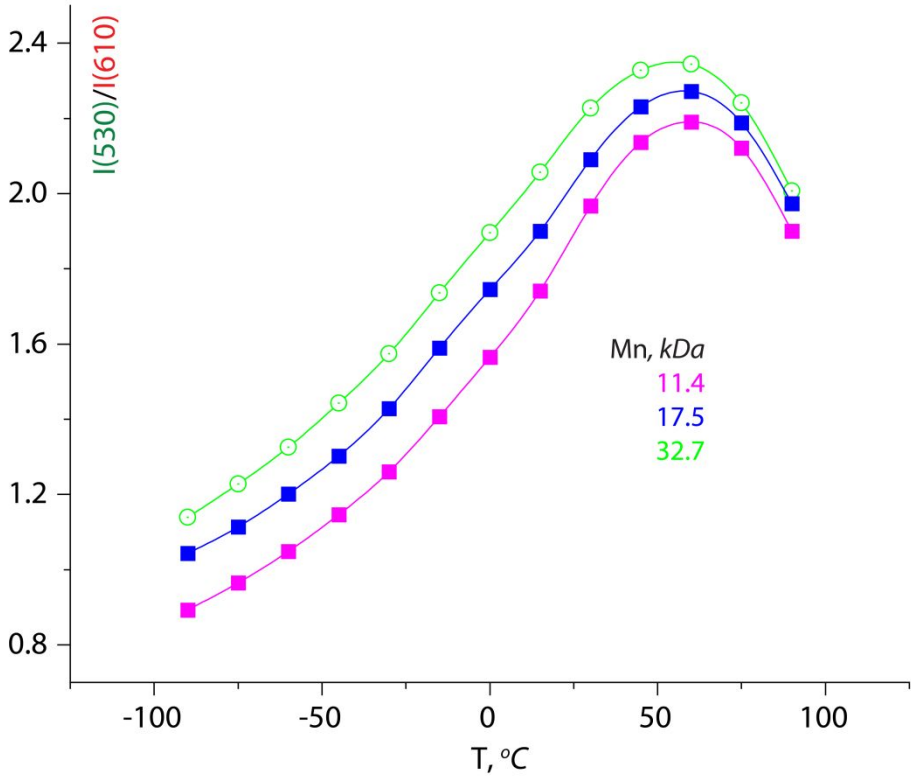



**Figure S37.** Ratiometry data for $CuN_4$-BARF probe freely dispersed in pMA

**Microscopy data.**

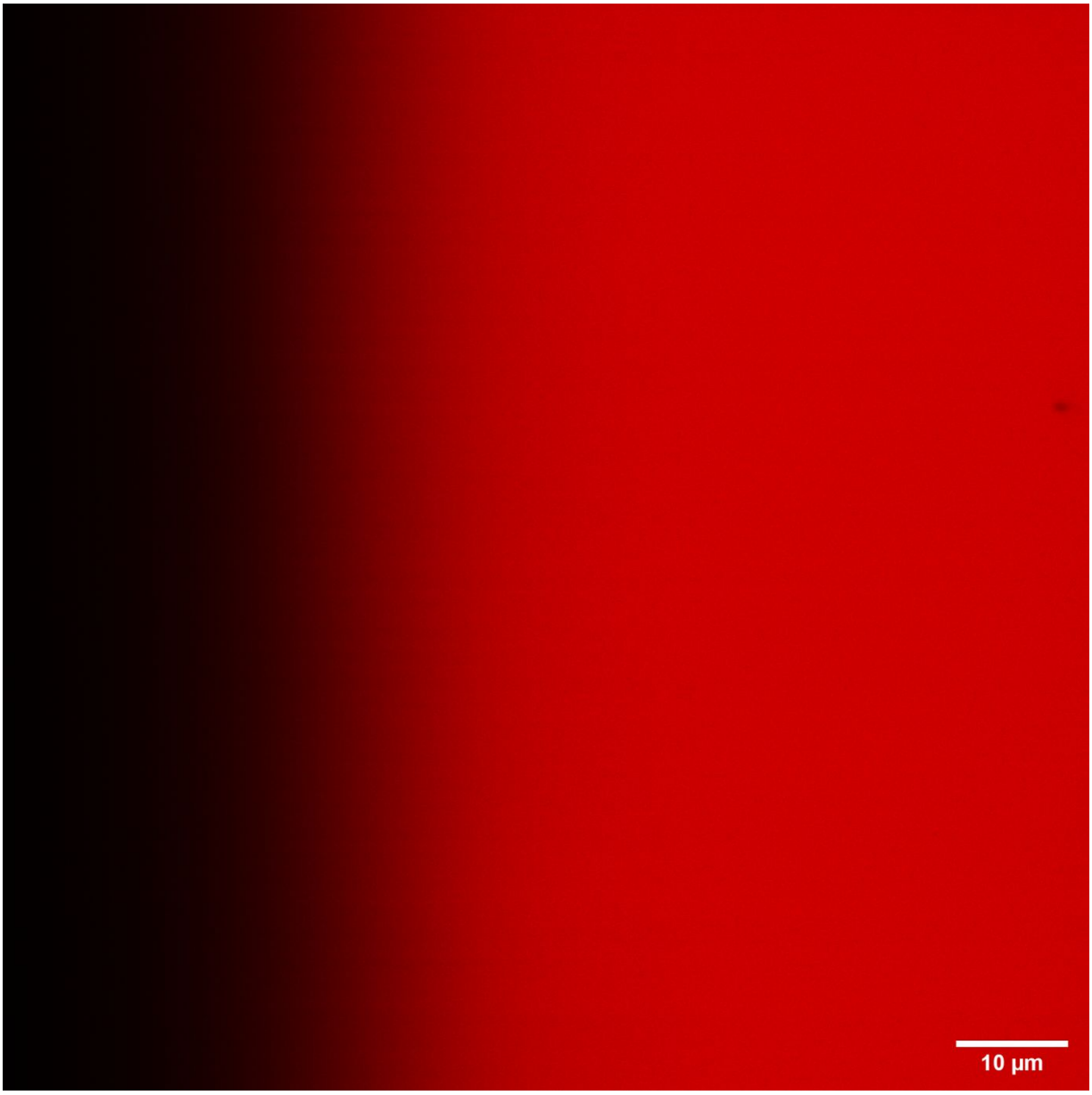



**Figure S38.** Laser scanning confocal microscopy image for end-labelled pMA sample of Mn=8.2 kDa. Excitation by multiphoton source at 800 nm, emission detection range 550-580 nm.

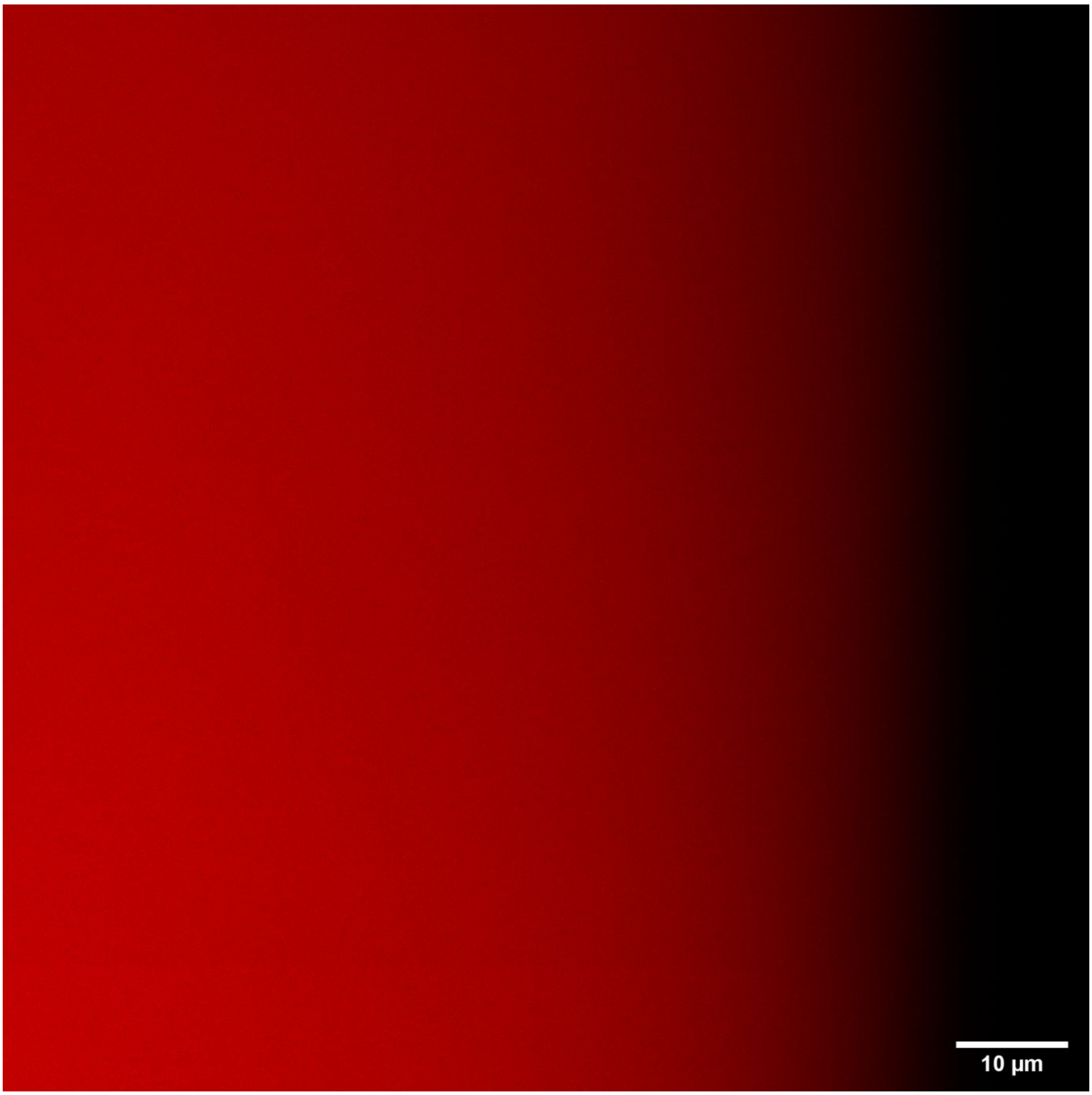



**Figure S39.** Laser scanning confocal microscopy image for end-labelled pMA sample of Mn=52.7 kDa. Excitation by multiphoton source at 800 nm, emission detection range 550-580 nm.

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