Supporting Information

Poly(*N*-alkyl-3,6-carbazole)s via Kumada catalyst transfer polymerization: Impact of Metal-Halogen exchange

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1. Instrumentation

NMR spectra were recorded on a 250, 300, 400 or 600 MHz NMR spectrometer (Bruker AVANCE or Fourier 300) in deuterated solvents at 300 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual solvent signal.[1]

MALDI-ToF MS spectra were measured using an Ultraflex III TOF/TOF (Bruker Daltonics GmbH) equipped with a Nd:YAG laser and a collision cell. The spectra were recorded in the positive reflector or linear mode. Various matrices and additives were applied to optimize the resolution of the obtained spectra. Significant discrimination effects of certain species were not observed by changing the conditions, *e.g.* the use of NaTFA or AgTFA gave similar mass spectra with analogous relative ratios of different species, only varying in the signal to noise ratio. Nevertheless a discrimination of high molar masses is expected.

ESI-Q-TOF MS measurements were executed on a micrOTOF (Bruker Daltonics GmbH) mass spectrometer, which was equipped with an automatic syringe pump for sample injection. The pump was supplied from KD Scientific. It was operated in the positive ion mode. The standard electrospray ion (ESI) source was used to generate ions. Mixtures of dichloromethane and acetonitrile were used as solvent. The ESI-Q-TOF-MS instrument was calibrated in the m/z range 50 to 3,000 using an internal calibration standard (Tunemix solution) which was supplied from Agilent.

Flash column chromatography was carried out on a Biotage Isolera One System using Biotage SNAP Cartridges KP-Sil.

Preparative size exclusion chromatography was either performed by using Bio-Beads (S-X1 or S-X3, dichloromethane) or Toyopearl (HW-55F, dichloromethane/methanol 95/5).

Analytical size exclusion chromatography was performed on the following system:
1. Shimadzu system (controller: SCL-10A VP, degasser: DGU-14A, pump: LC-10AD VP, auto sampler: SIL-10AD VP, oven: Techlab, UV detector: SPD-10AD VP, RI detector: RID-10A, eluent: chloroform/iso-propanol/triethylamine [94:2:4], flow rate: 1 mL/min, temperature: 40 °C, column: PSS SDV pre/lin S column).

2. NMR spectra

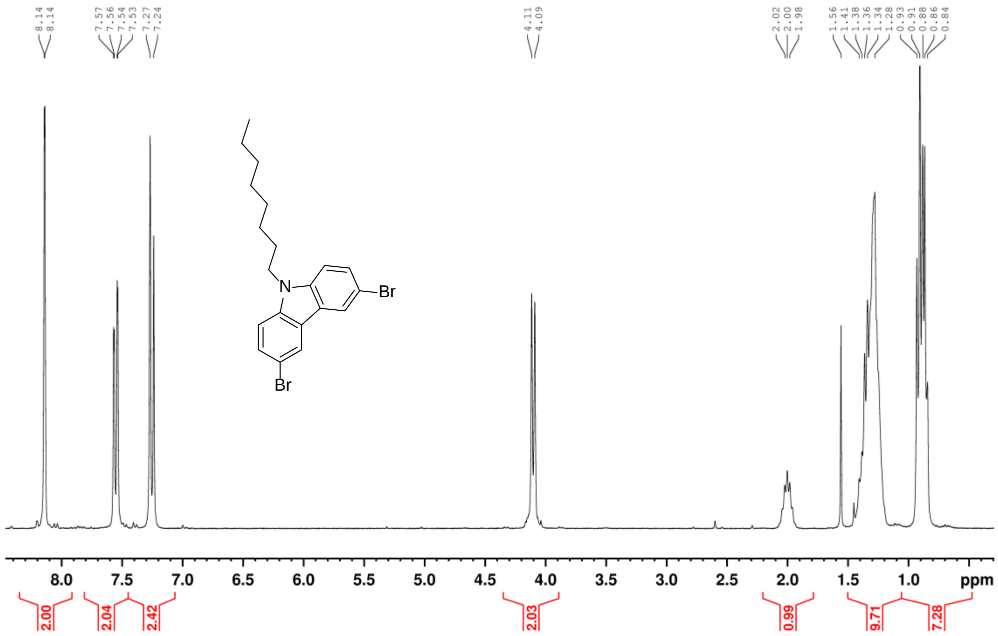


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1**.

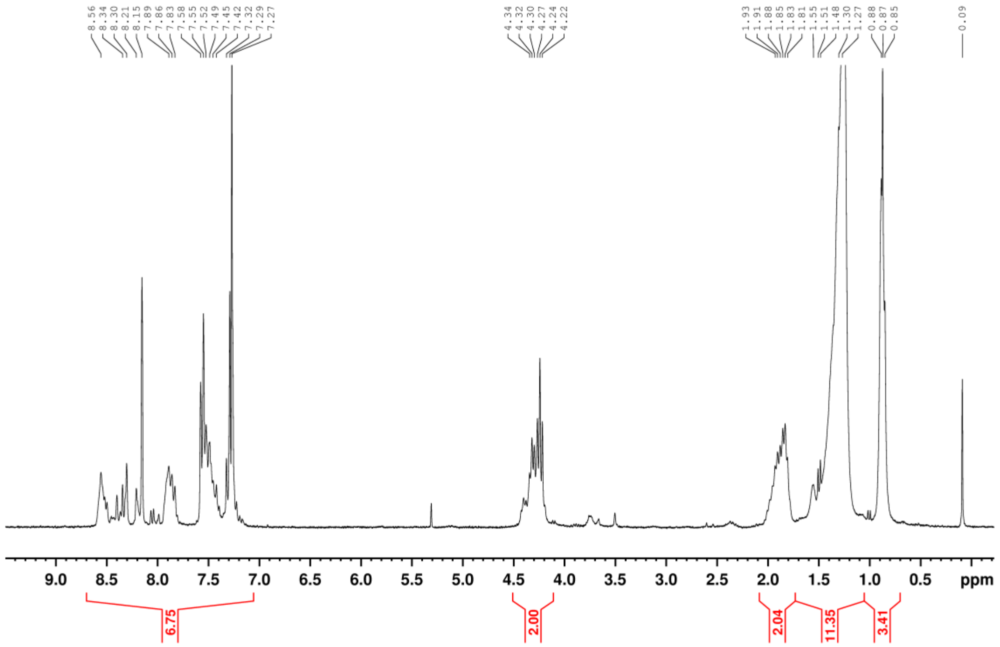


Figure S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **p1**.

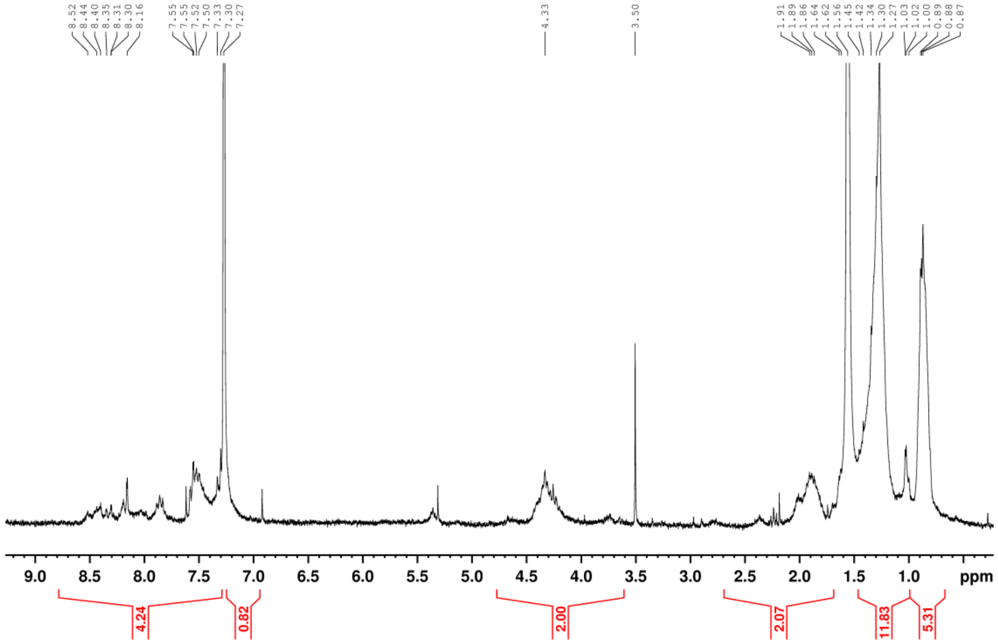


Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **p2**.

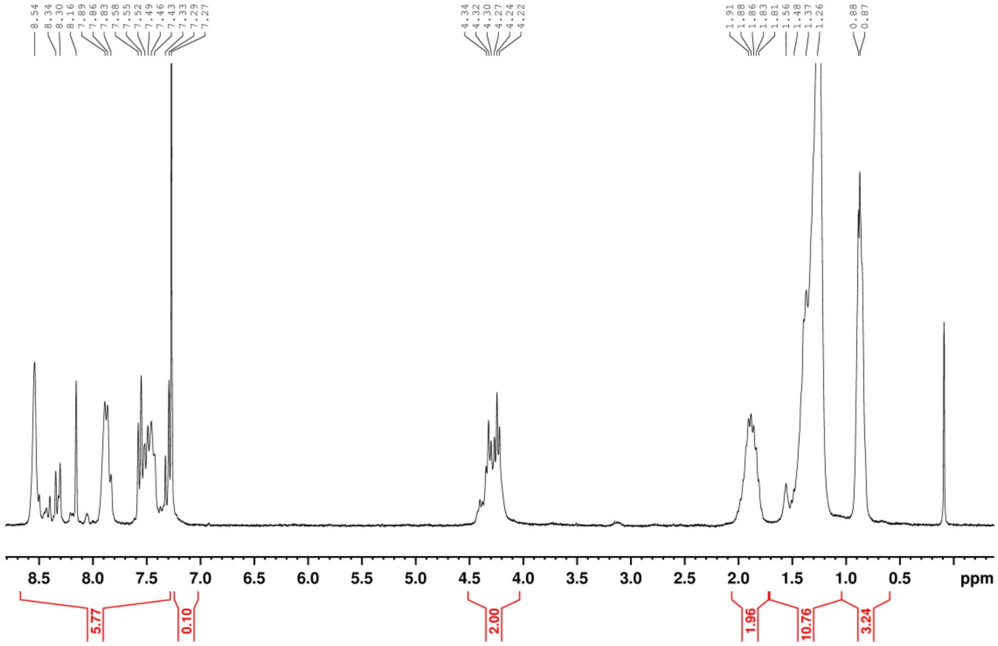


Figure S4. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **p3**.

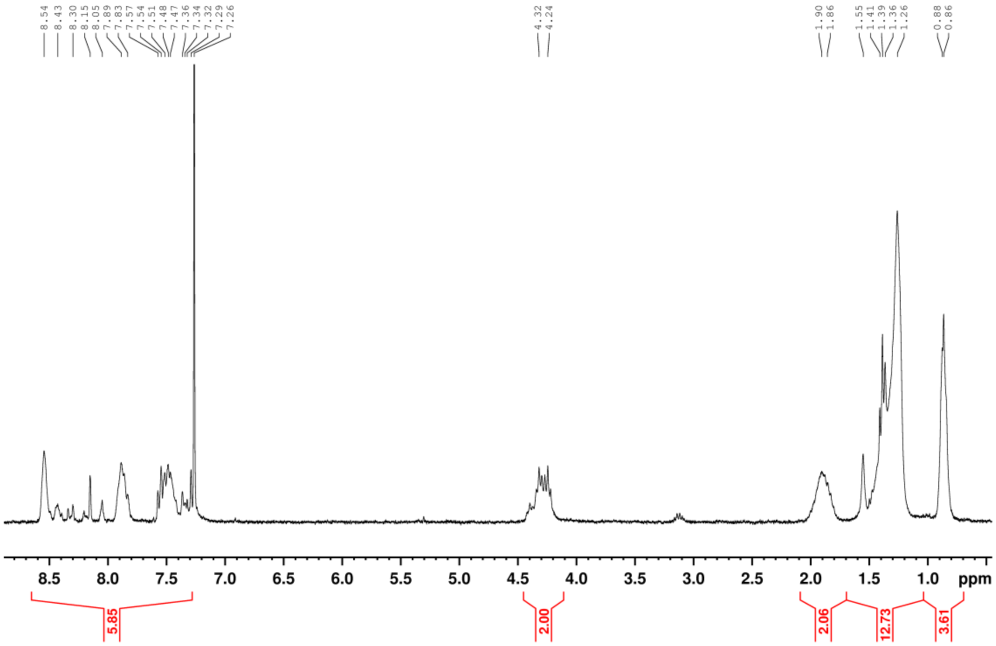


Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **p4**.

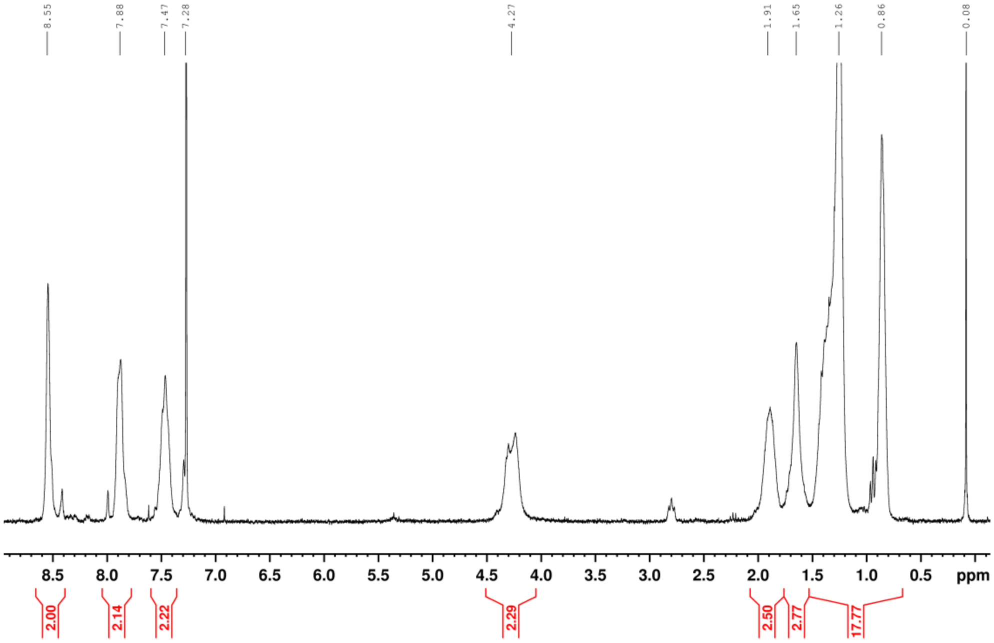


Figure S6. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **p5a**.

3. SEC data

Calibration. Note, that no proper standard SEC calibration is available, so that polystyrene calibration was utilized to estimate the molar mass. It is known, that the apparent molar masses of stiffened polymers, e.g. poly(3,6-carbzole), are systematically overestimated but provide a reasonable value to compare different literature reports.

Influence of quencher on KCTP. The polymerization of **1** was conducted as described in the Experimental Section. At the end of KCTP, two samples were quenched each with HCl or MeOH. No difference was noticed, particularly no chain-chain coupling taken in the case of MeOH, which had been reported for poly(3-hexylthiophene).[2] The result indicates termination during KCTP, so that quenching was performed with (deuterated) methanol in most of the cases.

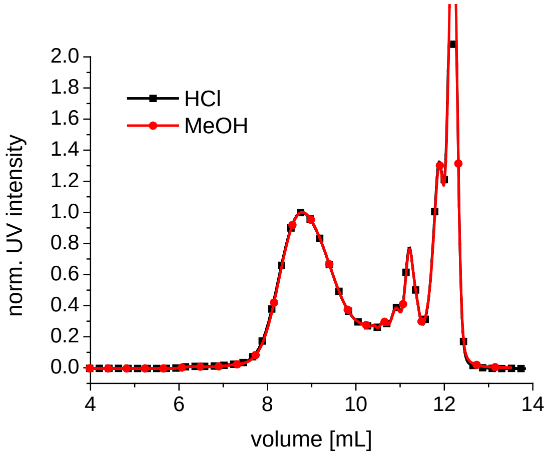


Figure S7. Normalized SEC curves of the test polymerization of **1** (activation with ^{i}PrMgCl) after quenching of one part each with HCl and MeOH are identical, *i.e.* no chain couplings are observed as a result of MeOH addition (Eluent: chloroform/iso-propanol/triethylamine [94:2:4]).

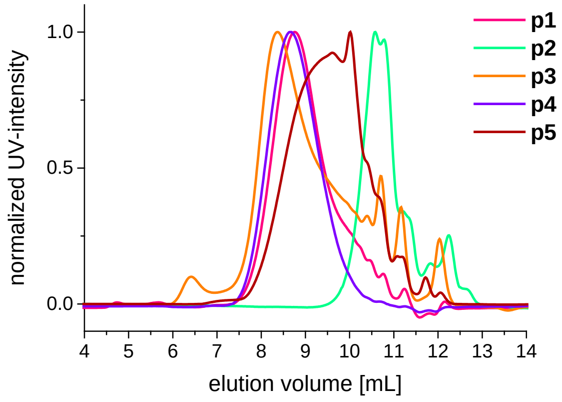


Figure S8. Normalized SEC curves of polymers **p1**–**p5** (Eluent: chloroform/iso-propanol/triethylamine [94:2:4]).

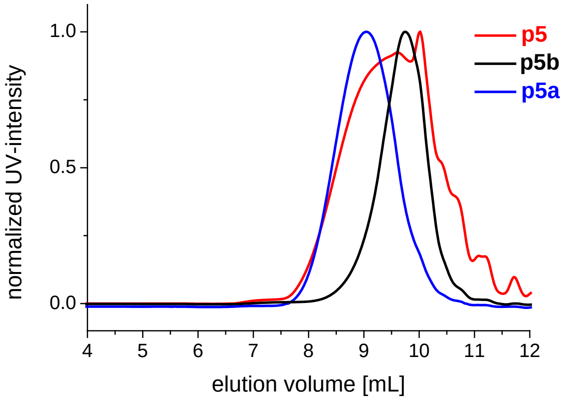


Figure S9. Normalized SEC curves of polymer **p5** and obtained fractions (**p5a** and **p5b**) from precipitation (Eluent: chloroform/iso-propanol/triethylamine [94:2:4]).

4. Mass spectra

Note, that the semi-quantitative analysis of MS intensity data throughout this manuscript is based on the assumption, that specimen with the same degree of polymerization ionize with equal probability, *i.e.* the desorption process is governed by the polymer and the end groups (H, Br, Pr, Bu) have only an inferior impact.

Calibration test. An increasing deviation between experimental and calculated mass values within the series was observed with increasing molar masses.[3-5] Such phenomenon is exemplified for the macrocycle series, which can be unambiguously identified (Figure S8). The comparison between the 4-mer and the 11-mer illustrates the increasing gap between experimental and theoretical values, whereby the characteristic isotope pattern prevails. This phenomena is assigned to known MALDI-ToF challenges, e.g. metastable ion decay, sample inhomogeneity or distorted ionization,[6] occurring for the investigated class of polymers. Though, the deviations should be within the resolution limit of the analyzer ($\Delta m = 0.1 - 0.2$ amu or approximately 50 – 100 ppm). Absolute molecular weights were not recorded as this is not the main focus of the presented work. In summary, chemical structures were assigned on the basis of the (repeating) members within each series and the characteristic isotope pattern, in particular in the presence of bromine (M+2 peak).

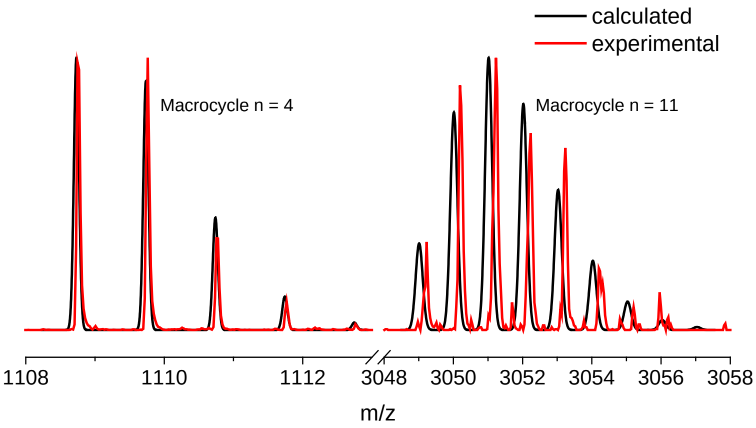


Figure S10. Expansion of MALDI-ToF spectrum of macrocycles (matrix: DCTB + NaTFA) showing the systematic deviation between experimental and calculated values due to calibration artefacts..

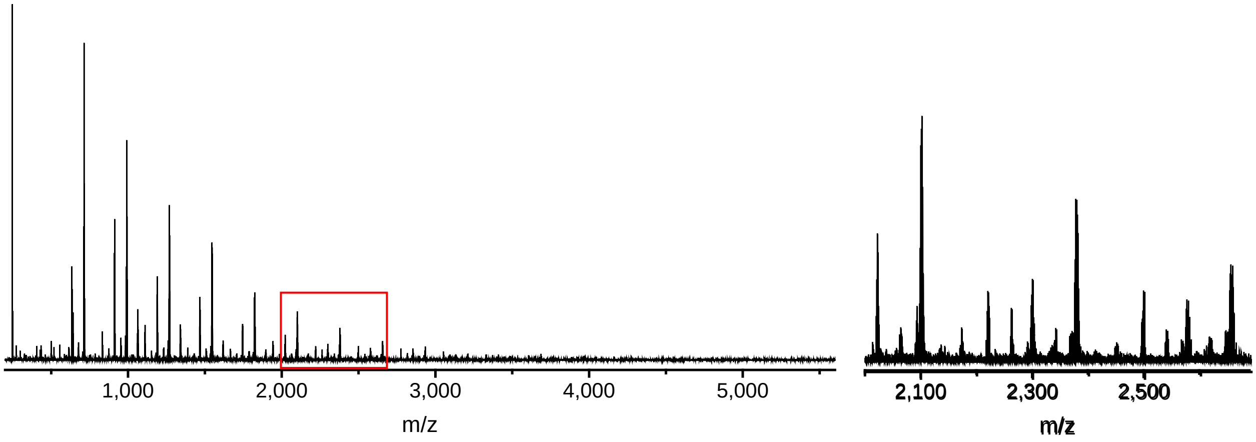
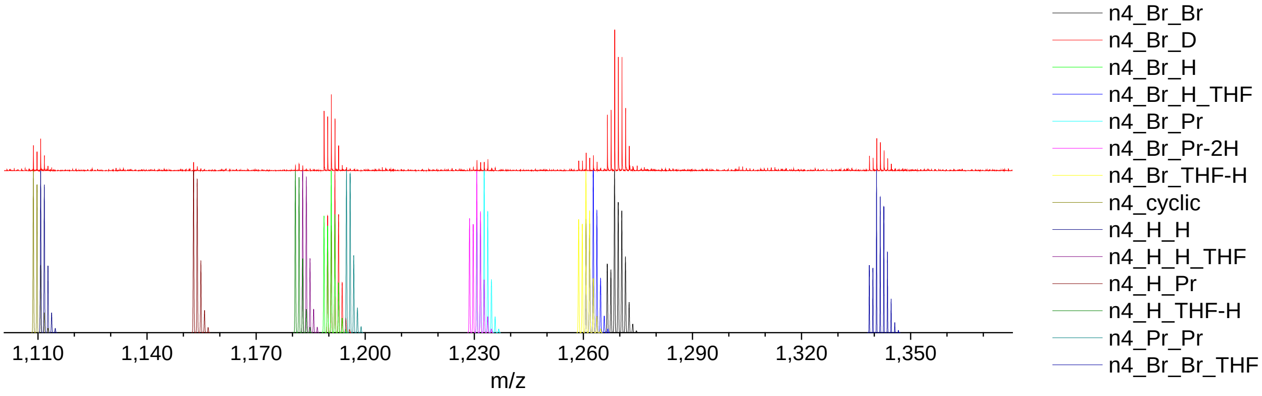


Figure S11. (Left) MALDI-ToF spectrum of **p1** (matrix: DCTB + NaCl) and (right) expansion.



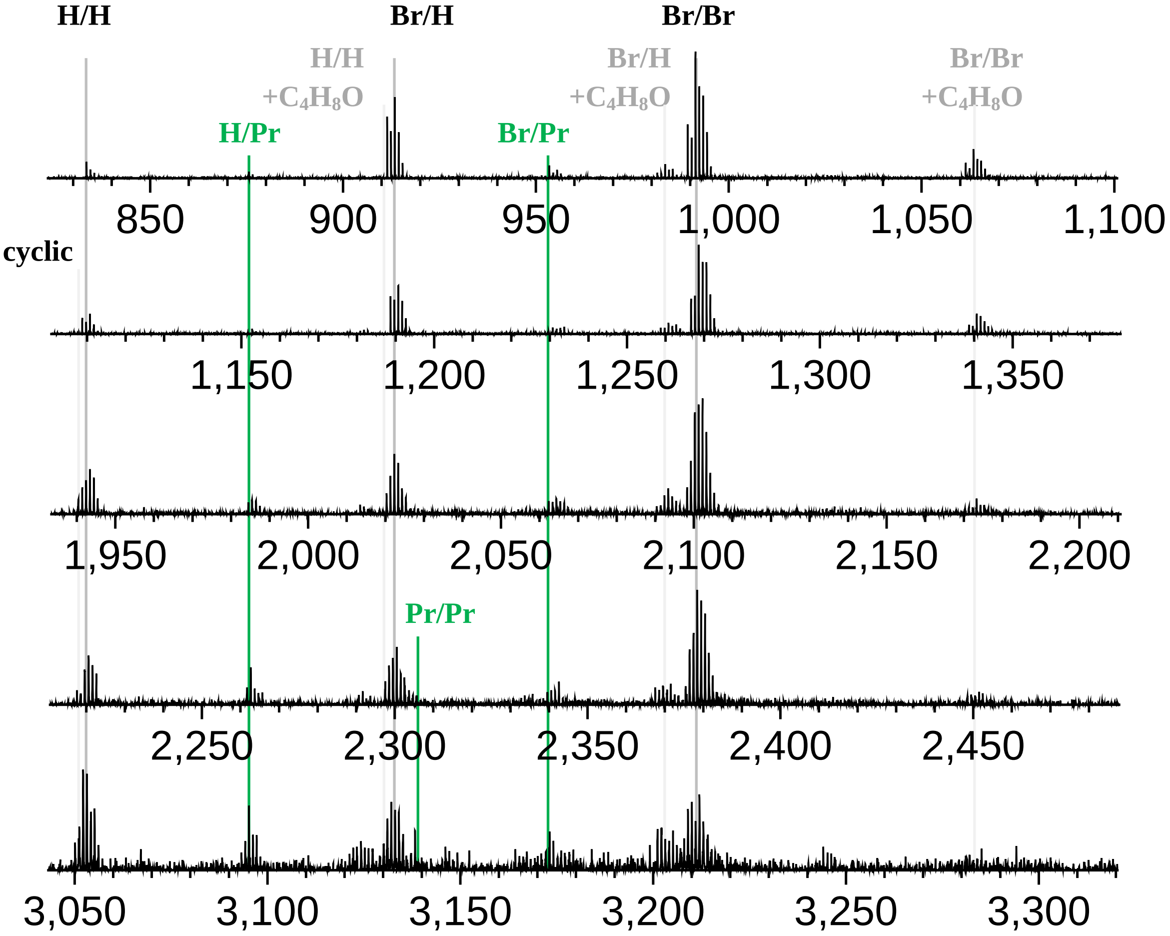


Figure S12. (Top) expansion of 4-mer series with isotope simulation. (Bottom) Comparison of aligned mass spectra of the 3-mer, 4-mer, 7-mer, 8-mer and 11-mer. Calculated (black) and experimental (red) isotopic pattern of various detected polymer series of **p1** (matrix: DCTB + NaCl).

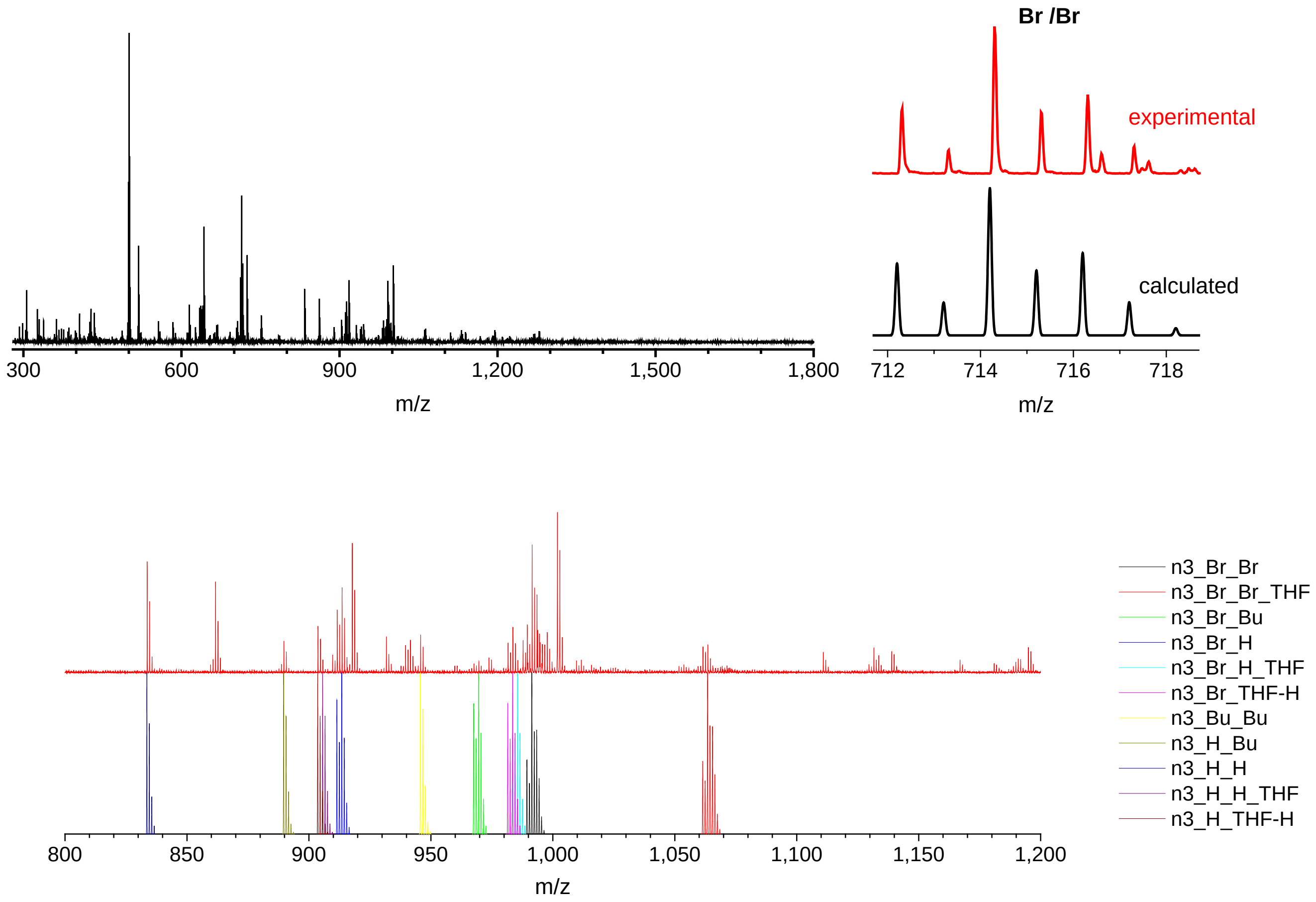


Figure S13. (Top) MALDI-ToF spectrum of **p2** with calculated (black) and experimental (red) isotopic pattern of the di-bromine terminated series (matrix: DCTB + NaCl). (Bottom) Comparison of 4-mer series with isotope simulations.

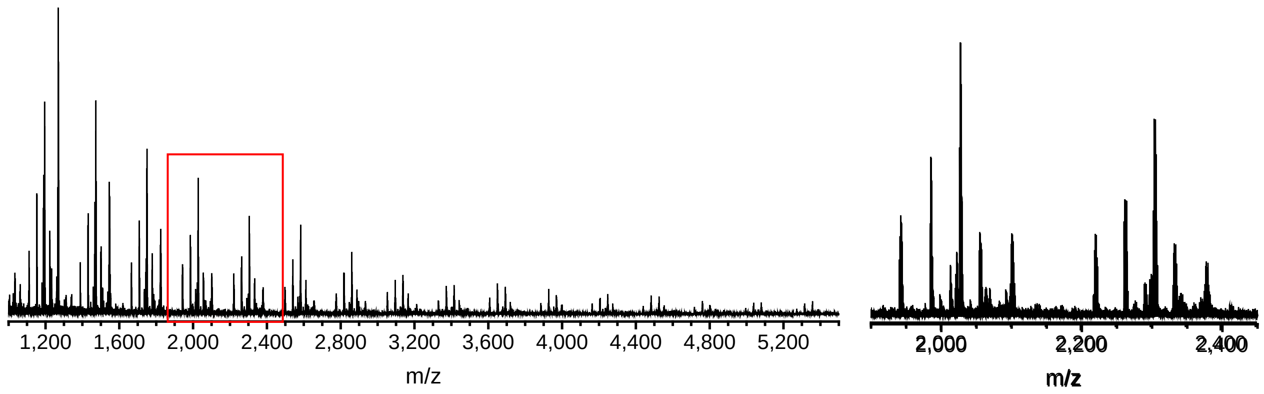


Figure S14. (Left) MALDI-ToF spectrum of **p3** (matrix: DCTB + NaCl) and (right) expansion.

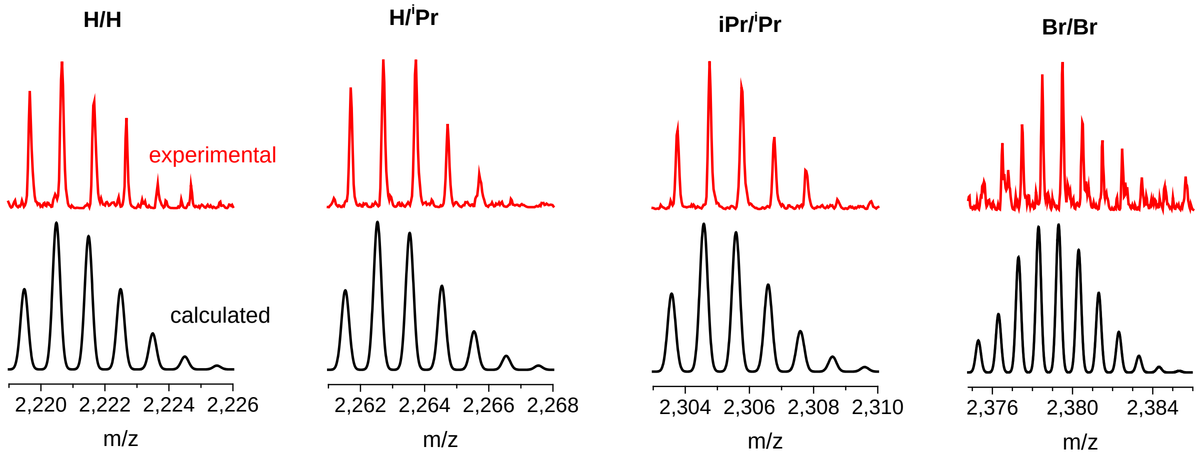


Figure S15. Calculated (black) and experimental (red) isotopic pattern of various detected polymer series of **p3** (matrix: DCTB + NaCl).

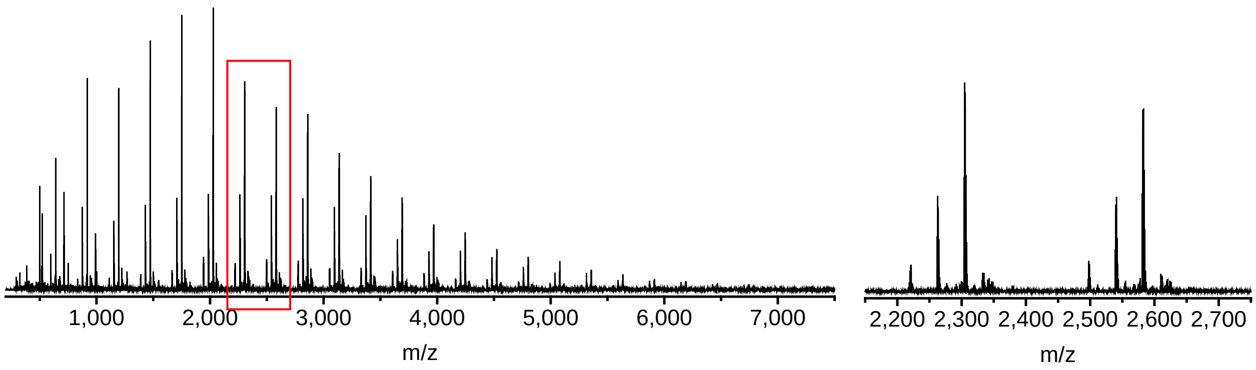


Figure S16. MALDI-ToF spectrum of **p4** (matrix: DCTB + NaCl) and (right) expansion.

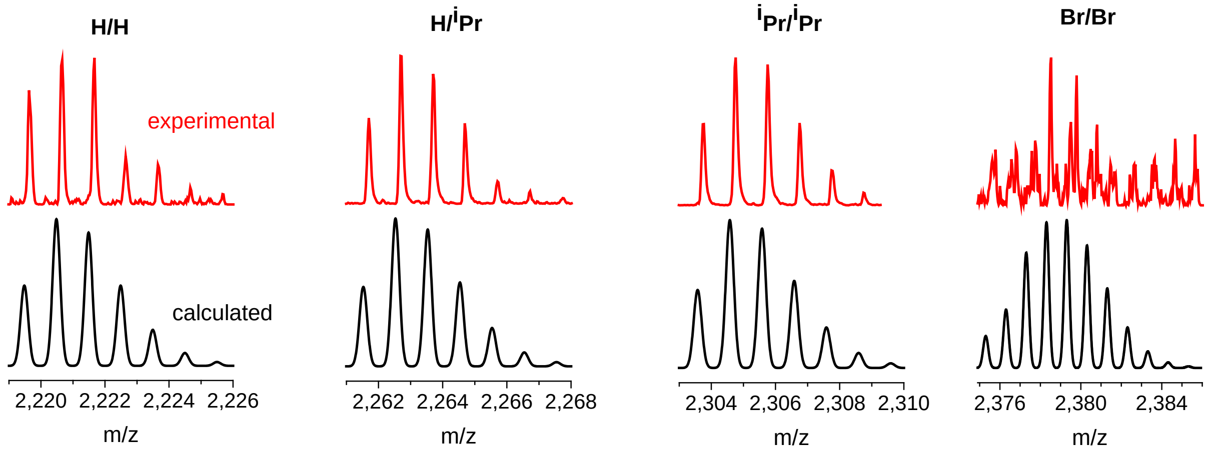


Figure S17. Calculated (black) and experimental (red) isotopic pattern of various detected polymer series of **p4** (matrix: DCTB + NaCl).

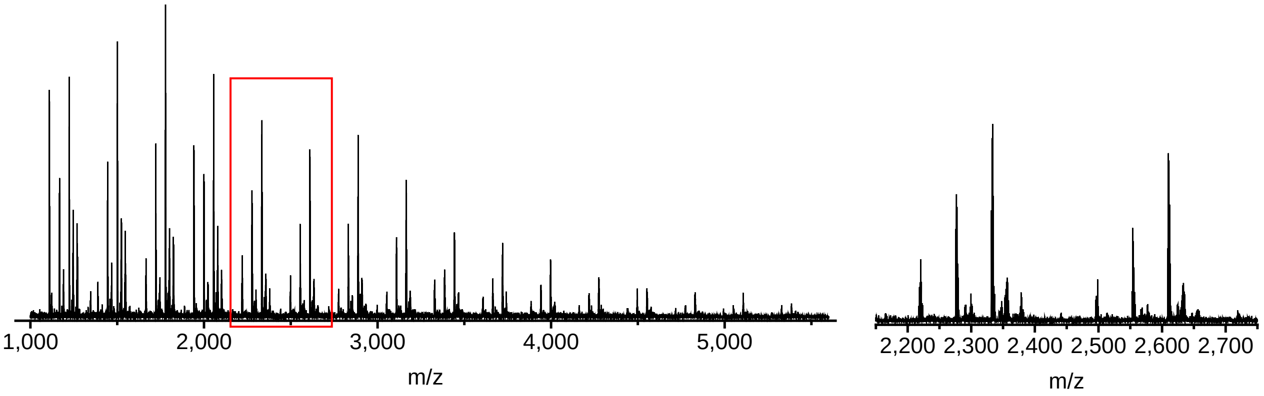


Figure S18. (Left) MALDI-ToF spectrum of **p5a** (matrix: DCTB + NaTFA) and (right) expansion.

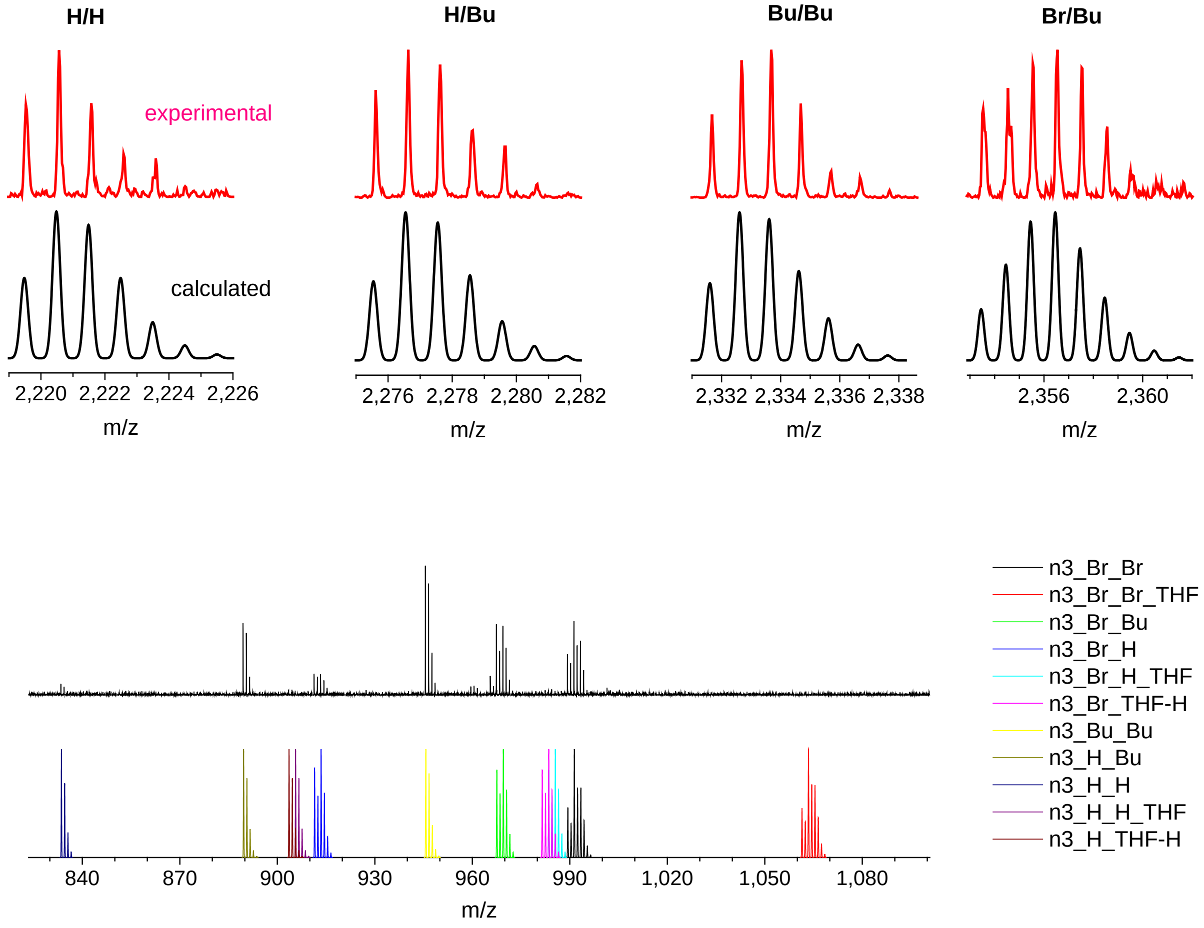


Figure S19. (Top) Calculated (black) and experimental (red) isotopic pattern of various detected polymer series of **p5a** (matrix: DCTB + NaTFA). (Bottom) Comparison of 3-mer series (top) with various end groups (bottom).

References

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176-2179.
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