

Supporting Information

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Synthesis of Polymer-Linked Copper(I) Bis(*N*-Heterocyclic Carbene) Complexes with Linear and Chain Extended Architecture

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1 NMR spectroscopic data

- 1.1 Synthesis of low molecular weight precursor
- 1.2 Synthesis of monovalent, imidazolium end-capped poly(styrene)
- 1.3 Synthesis of bivalent imidazolium end-capped PS
- 1.4 Synthesis of imidazolium containing copolymer
- 1.5 Synthesis of copper(I) bis(NHC) complexes

2 Mass spectrometric data

- 2.1 Linear approach
- 2.2 Chain-extended approach

3 Synthetic tables

4 Chromatograms

5 Network characterization

6 Fluorescence measurements

1 NMR spectroscopic data

1.1 Synthesis of low molecular weight Cu(I) bis(NHC) complex

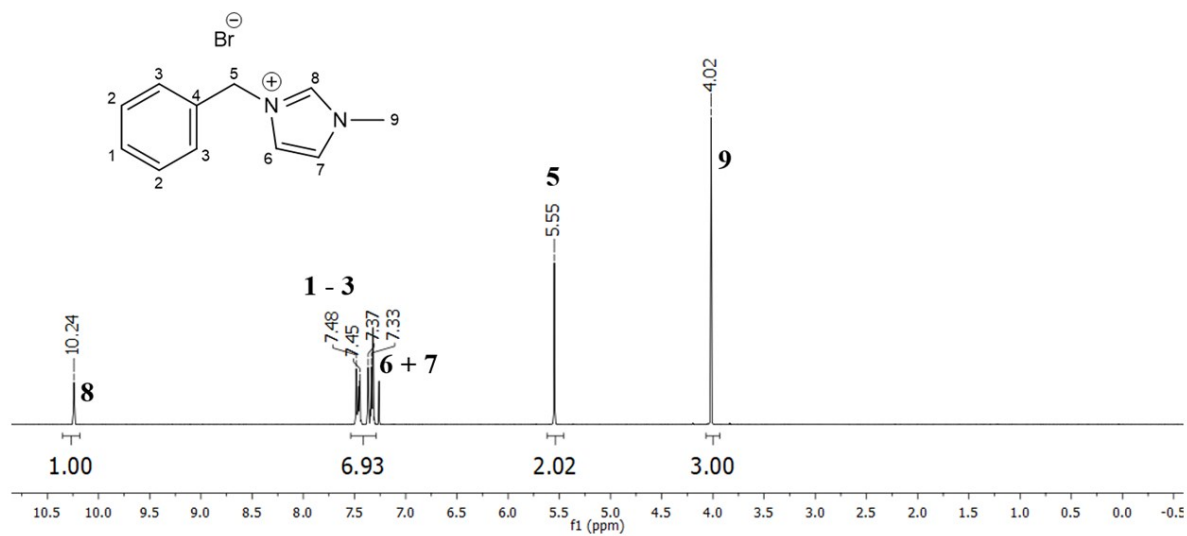


Figure S1. ^1H NMR spectrum of 3-benzyl-1-methylimidazolium bromide (**1**) in CDCl_3 .

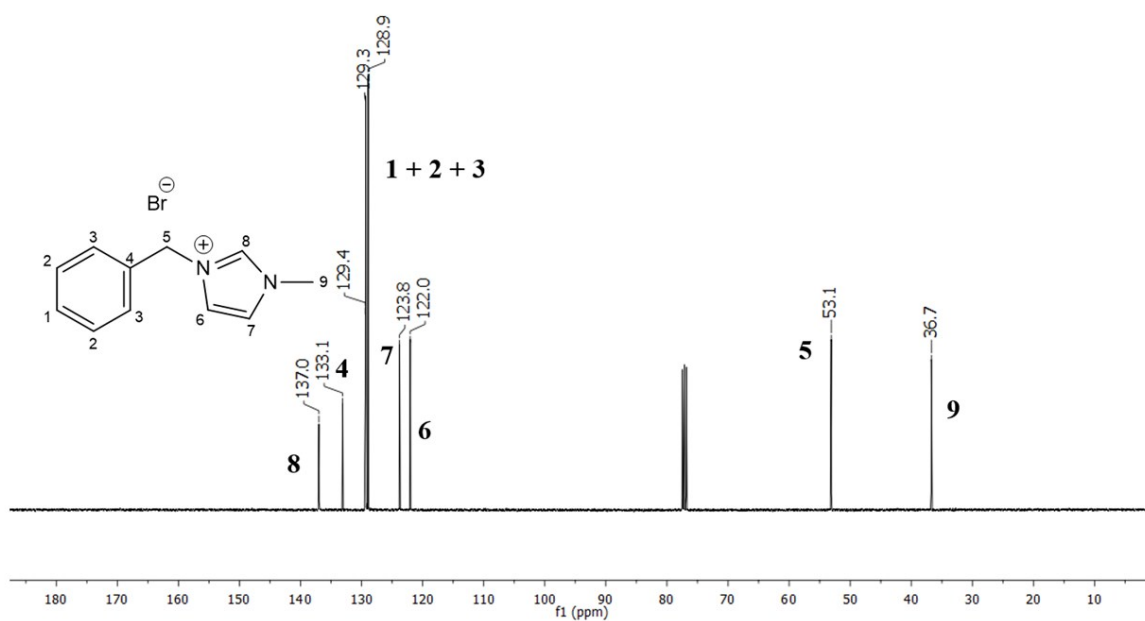


Figure S2. ^{13}C NMR spectrum of 3-benzyl-1-methylimidazolium bromide (**1**) in CDCl_3 .

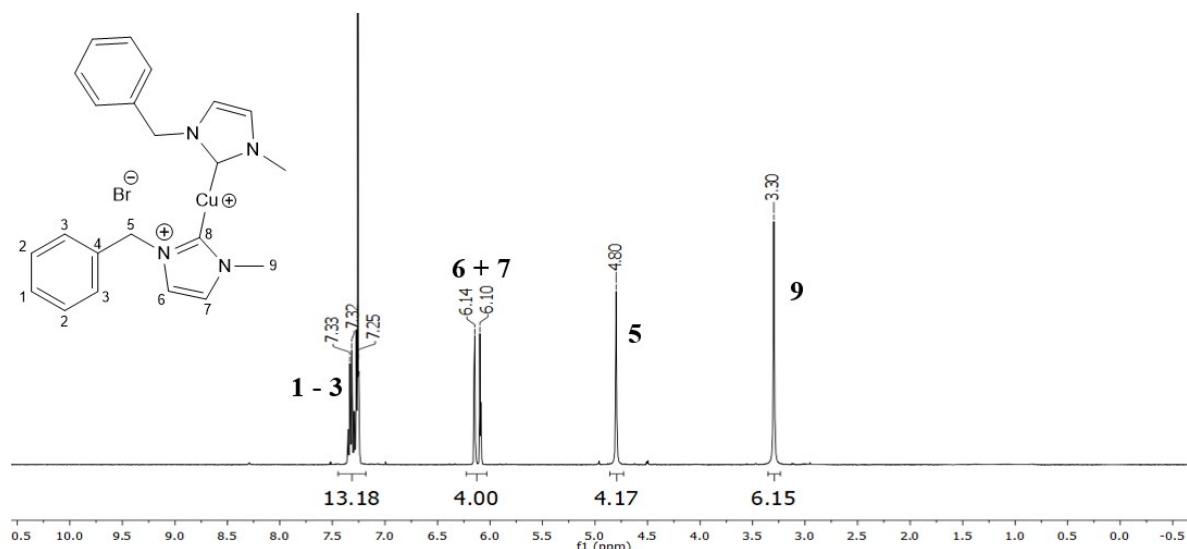


Figure S3. ¹H NMR spectrum of bis(3-benzyl-1-methyl-imidazole-2-yl)copper(I) bromide (**2**) in CDCl₃.

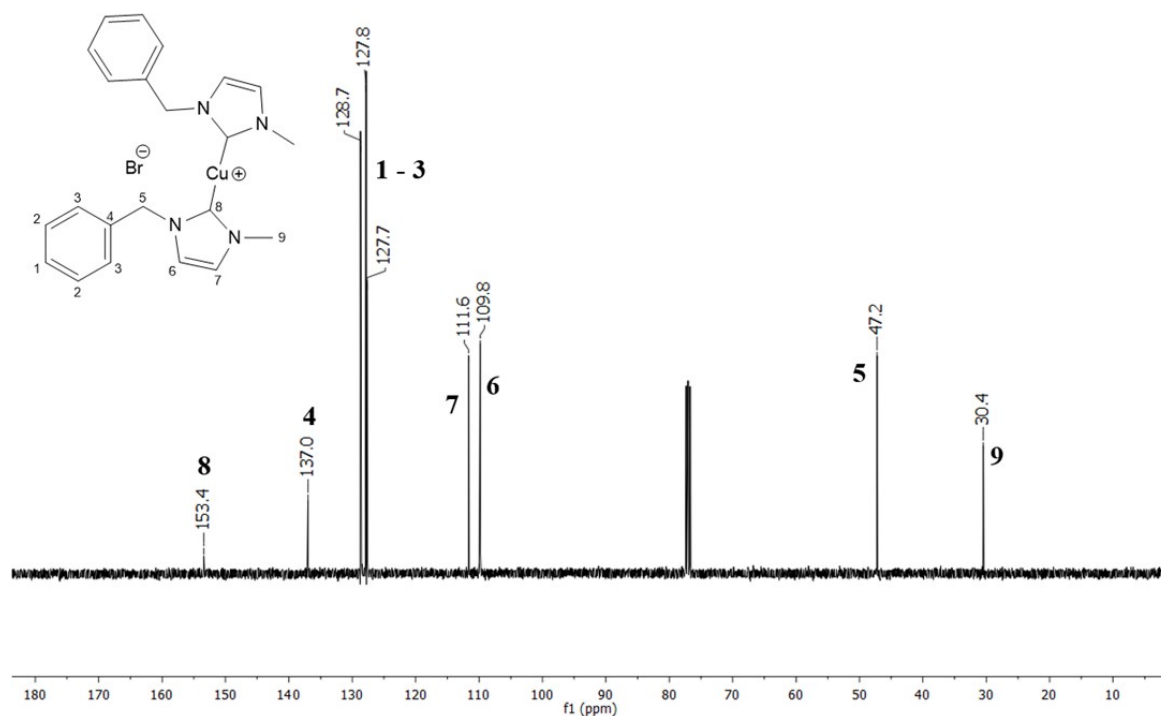


Figure S4. ¹³C NMR spectrum of bis(3-benzyl-1-methyl-imidazole-2-yl)copper(I) bromide (**2**) in CDCl₃.

1.1 Synthesis of monovalent, imidazolium end-capped poly(styrene) (6)

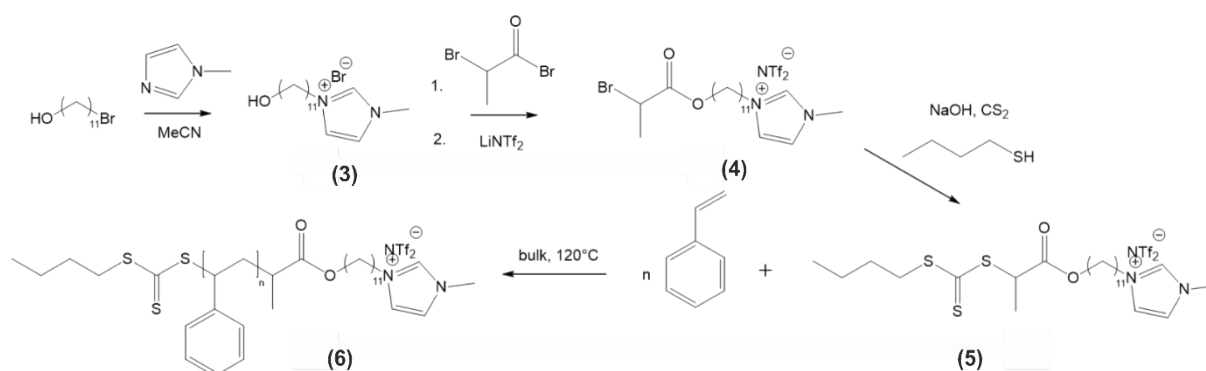


Figure S5. Synthetic route of monovalent poly(styrene) (6).

The chain transfer agent (CTA) **5** for RAFT polymerizations was synthesized in a three step synthesis. First 11-bromoundecan-1-ol was modified with *N*-methylimidazole followed by an esterification reaction with 2-bromopropionic bromide and a subsequent counter ion exchange with NTf_2^- resulting in the bromo substituted ionic liquid 3-(11-(2-bromopropionyloxy)undecyl)-methyl-1-imidazolium bis(trifluoromethane)sulfonimide (**4**) which was well soluble in common organic solvents. The trithiocarbonate group was introduced by a reaction of **4** with butanethiol and carbon disulfide in the presences of sodium hydroxide forming the ionic group end-capped CTA **5** in yields up to 96%. Replacing the 2-methylpropiante compound **4** by a corresponding isobutyrate resulted in low conversion below 10%, presumably due to the shielding effect of the second methyl group during the thio-bromo click reaction.

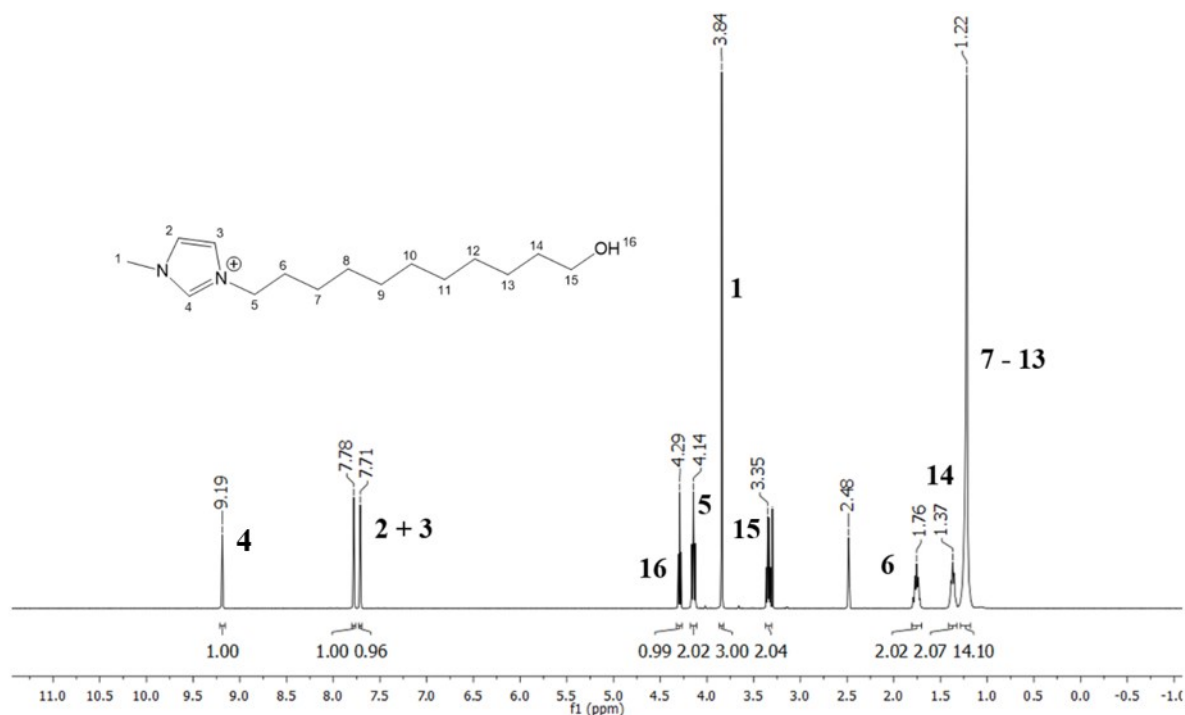


Figure S6. ^1H NMR spectrum of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide (**3**) in $\text{DMSO}-d_6$.

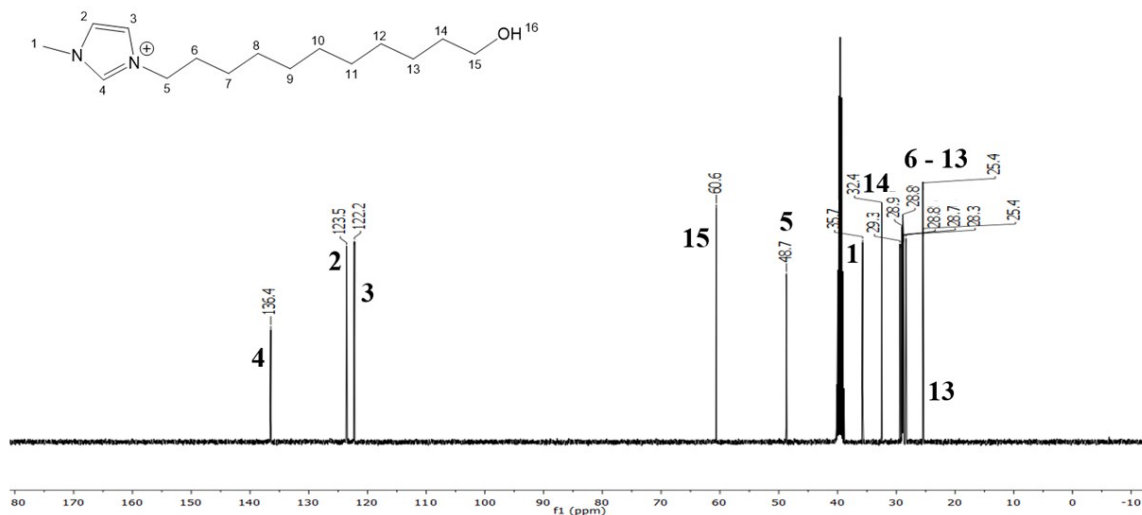


Figure S7. ¹³C NMR spectrum of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide (3) in DMSO-*d*₆.

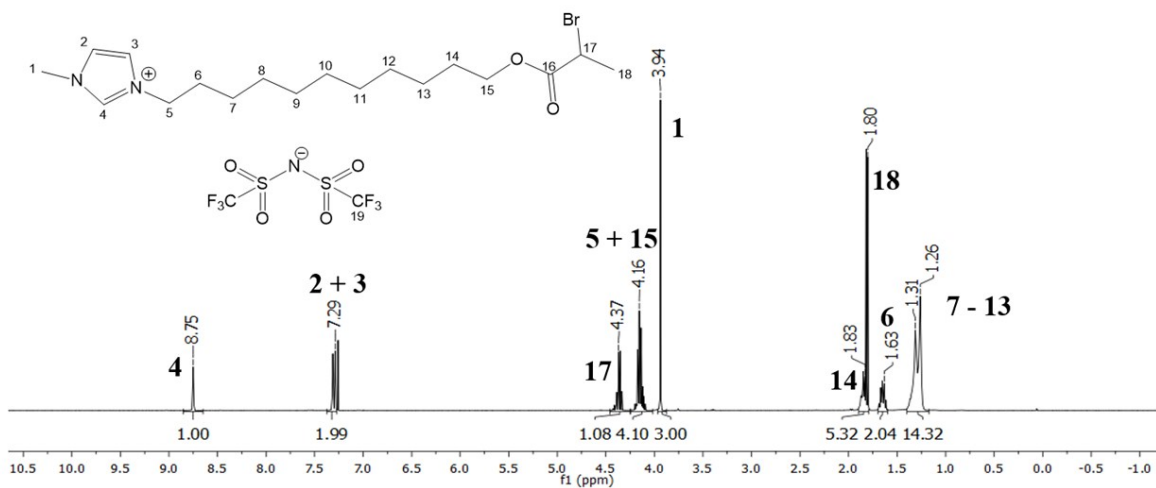


Figure S8. ¹H NMR spectrum of 3-(11-(2-brompropionyloxy)undecyl)-methyl-1-imidazolium bis(trifluoromethane)sulfonimide (4) in CDCl₃.

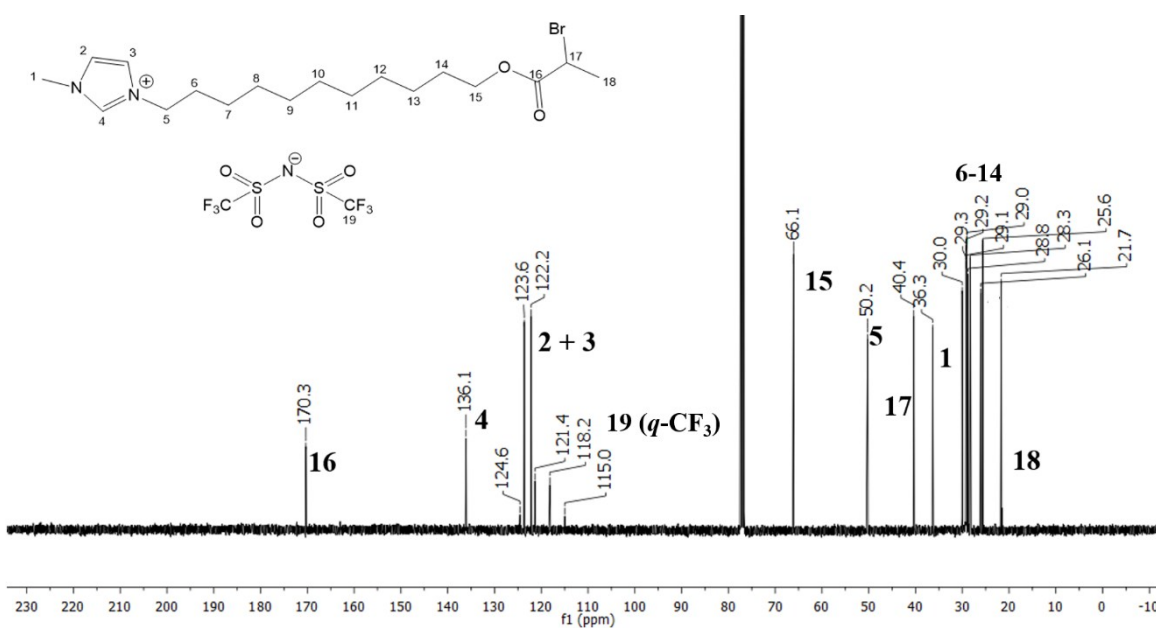


Figure S9. ¹³C NMR spectrum of 3-(11-(2-brompropionyloxy)undecyl)-methyl-1-imidazolium bis(trifluoromethane)sulfonimide (4) in CDCl₃.

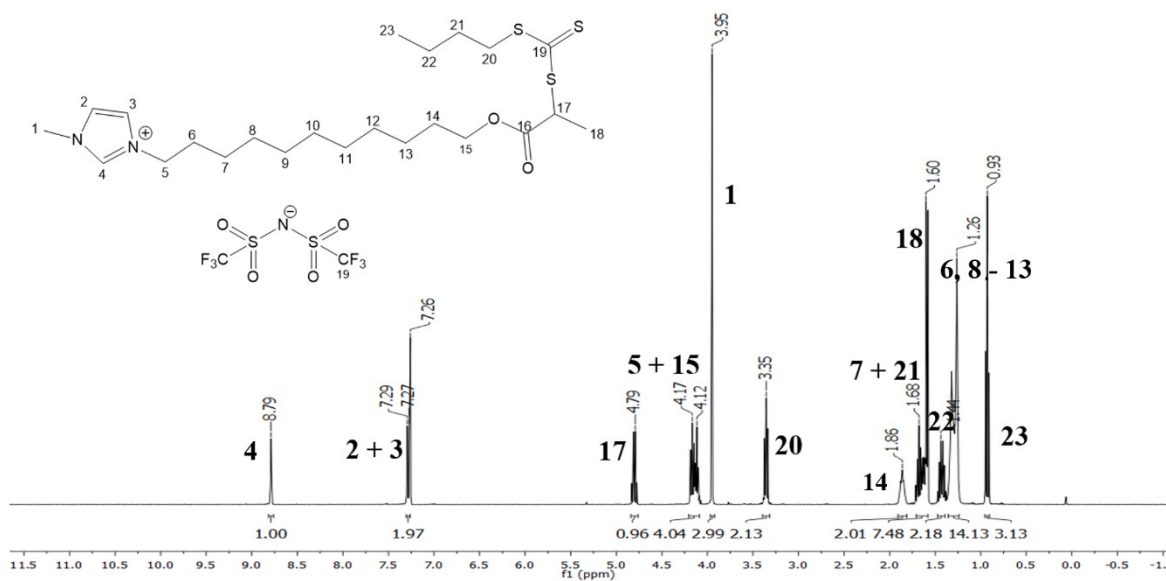


Figure S10. ^1H NMR spectrum of 1-((11-(3-methylimidazolium)undecyloxy)carbonyl)ethyl butyl carbonotrithioate bis(trifluoromethyl)sulfonamide (**5**) in CDCl_3 .

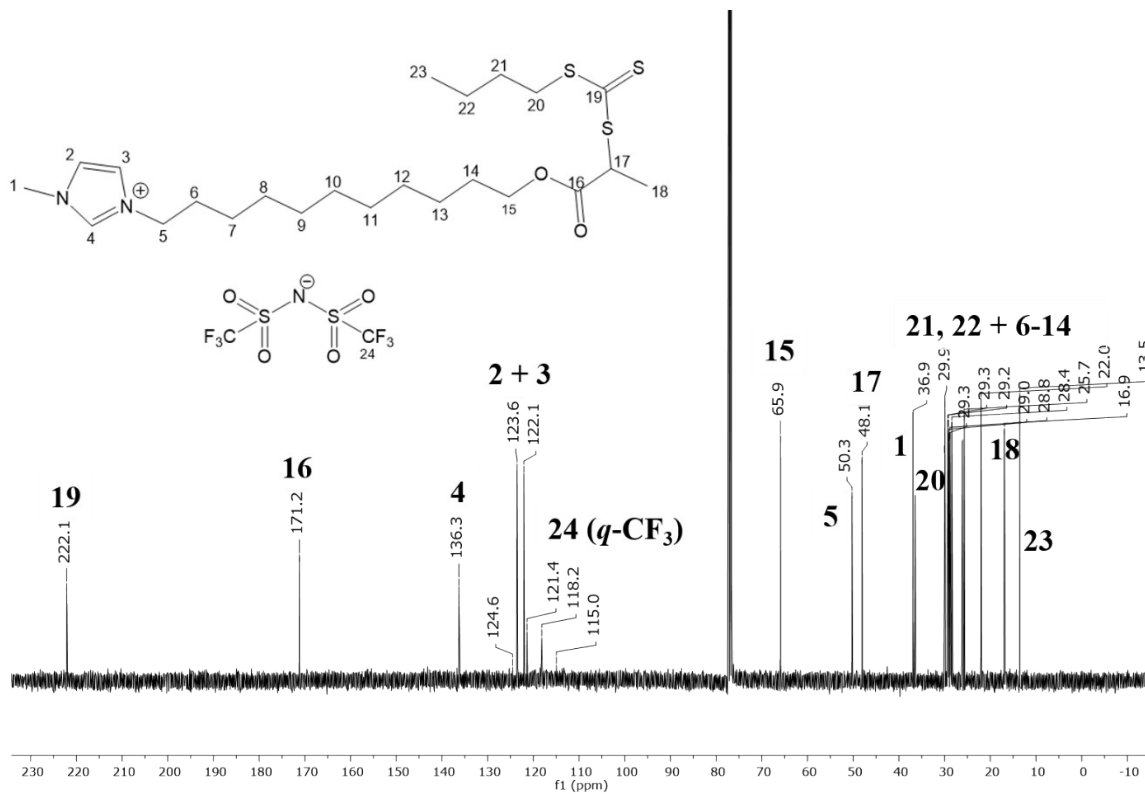


Figure S11. ^{13}C NMR spectrum of 1-((11-(3-methylimidazolium)undecyloxy)carbonyl)ethyl butyl carbonotrithioate bis(trifluoromethyl)sulfonamide (**5**) in CDCl_3 .

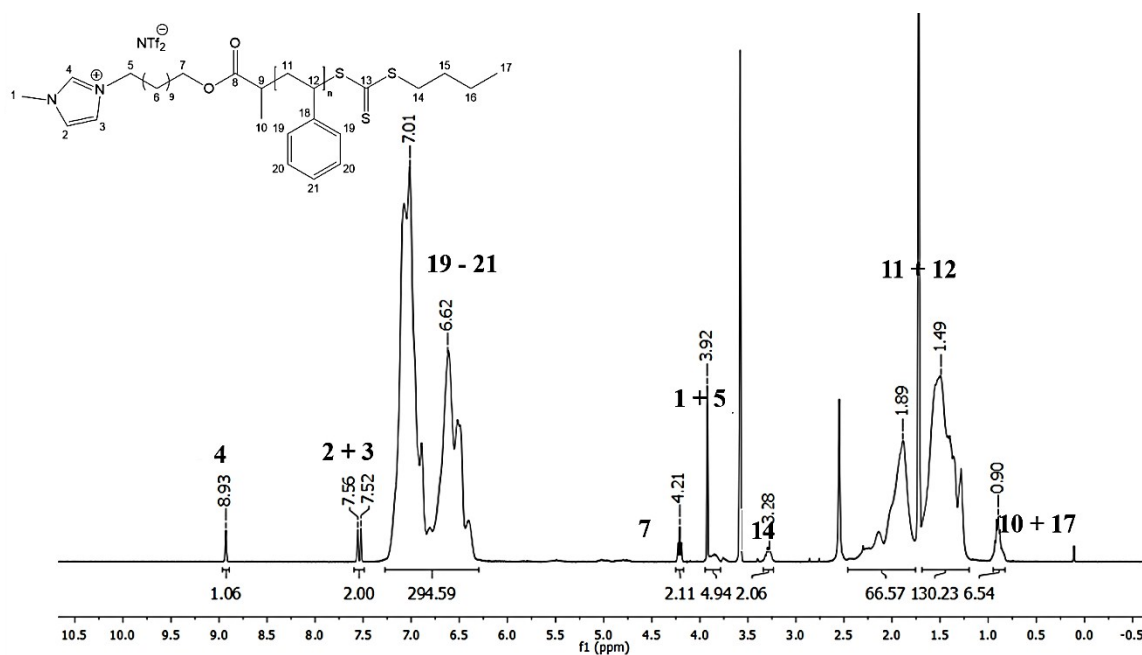


Figure S12. Example for ^1H NMR spectrum of monovalent imidazolium end-capped poly(styrene) (**6**) in $\text{THF-}d_8$.

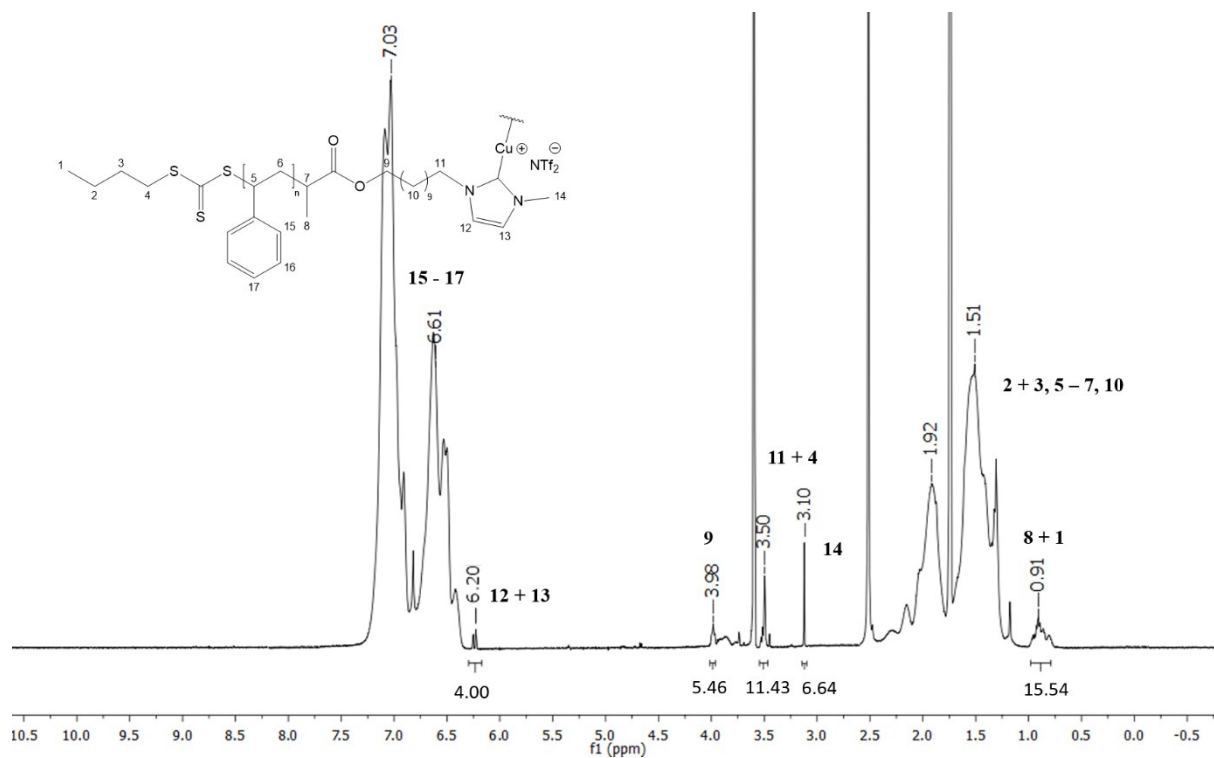


Figure S13. Example for ^1H NMR spectrum of linear poly(styrene) based bis(NHC) copper(I) complex (**7**) in $\text{THF-}d_8$.

1.2 Synthesis of bivalent dithiobenzoate end-capped PS (10)

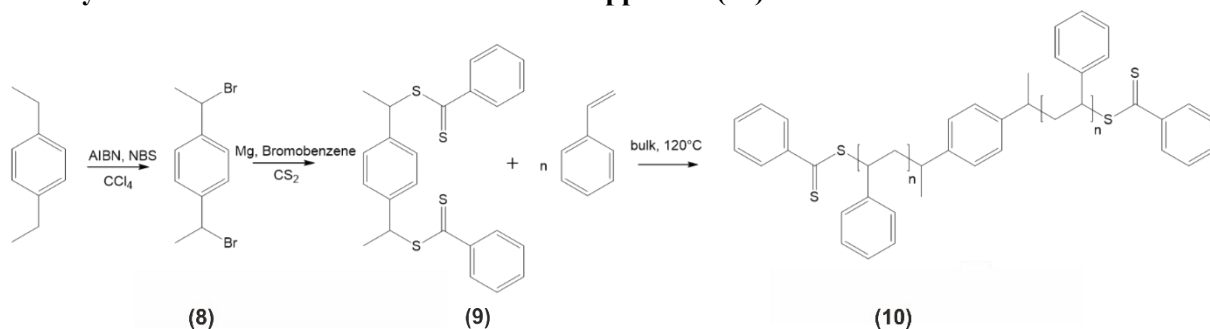


Figure S14. Synthetic route of bivalent poly(styrene) (**8**).

CTA **7** was synthesized by two step synthesis starting from 1,4-diethylbenzene which was modified in a first step by radical bromination with *N*-bromosuccinimide (NBS) yielding 1,4-bis(1-bromoethyl)benzene (**6**). The dithiobenzoate group was introduced in a one pot synthesis of **6** with the *in situ* generated carbon disulfide substituted Grignard product of etched magnesia with bromobenzene, resulting in the required bivalent CTA **7**.

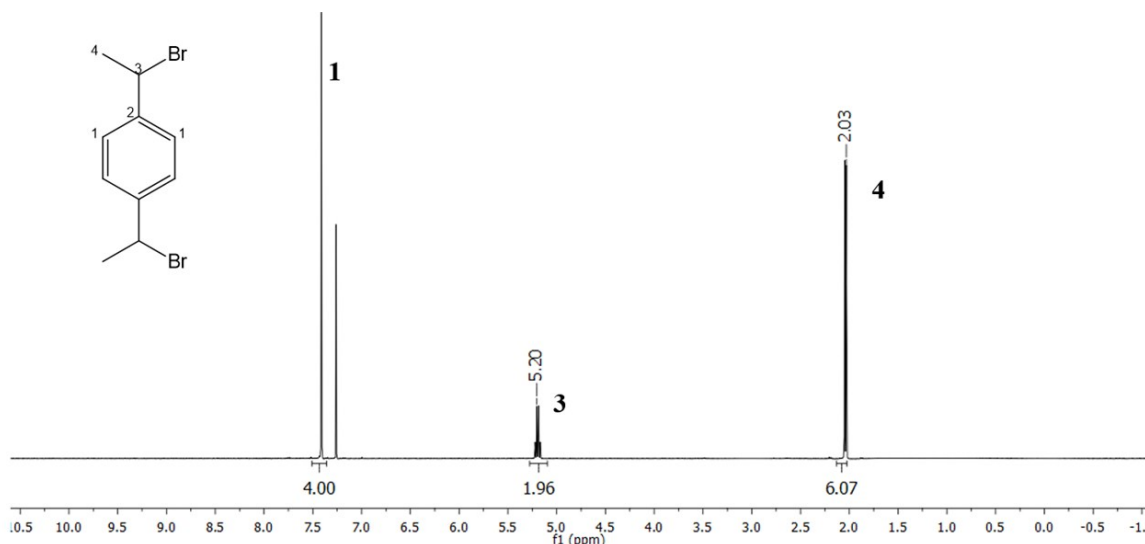


Figure S15. ¹H NMR spectrum of 1,4-bis(1-bromoethyl)benzene (**8**) in CDCl₃.

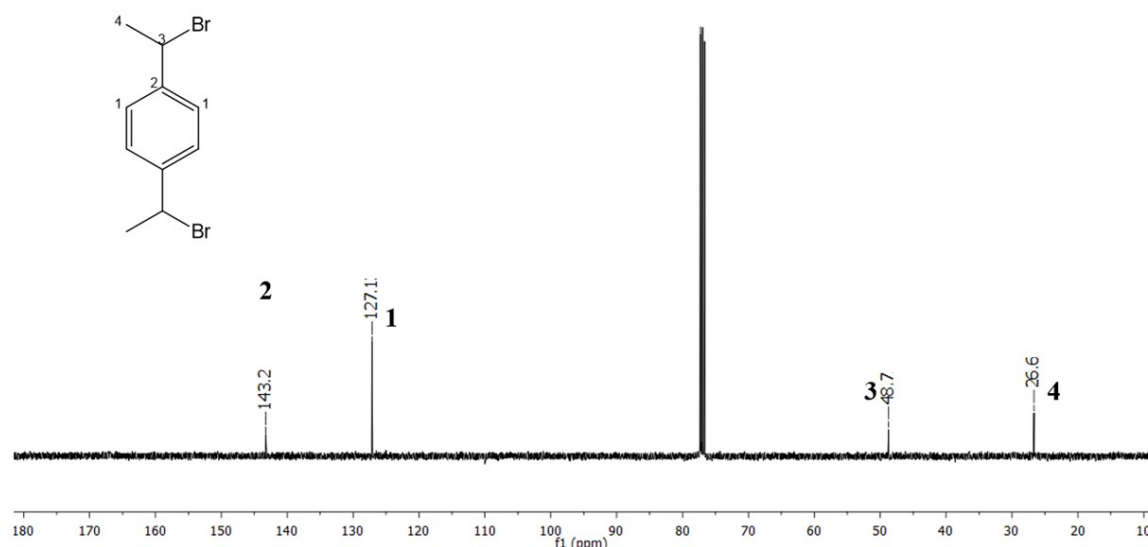


Figure S16. ¹³C NMR spectrum of 1,4-bis(1-bromoethyl)benzene (**8**) in CDCl₃.

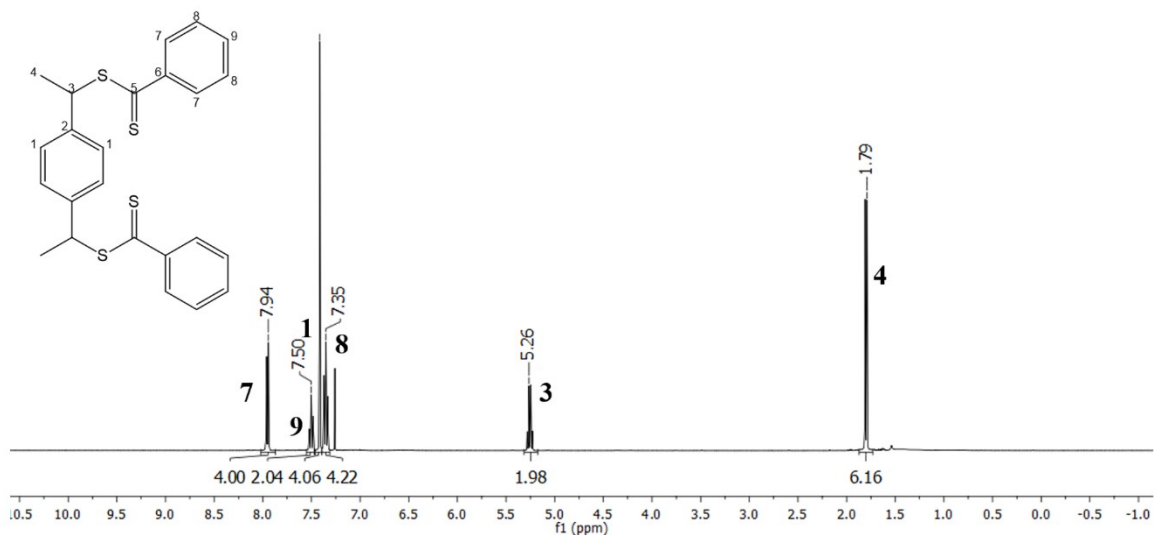


Figure S17. ^1H NMR spectrum of 1,4-phenylene bis(ethane-1,1-diyl) dibenzodithioate (**9**) in CDCl_3 .

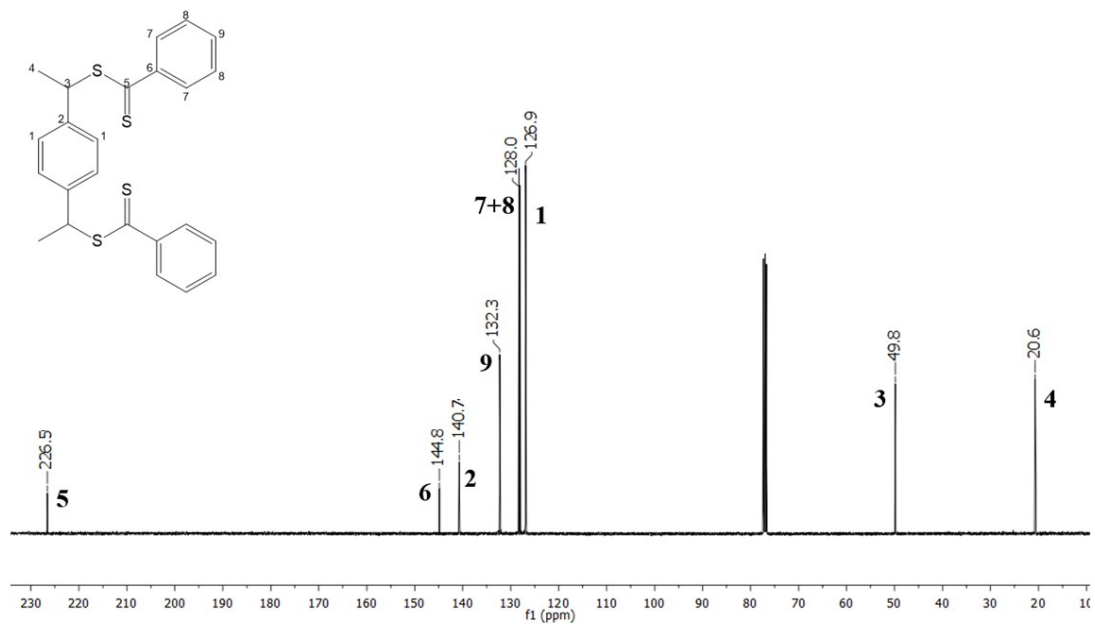


Figure S18. ^{13}C NMR spectrum of 1,4-phenylene bis(ethane-1,1-diyl) dibenzodithioate (**9**) in CDCl_3 .

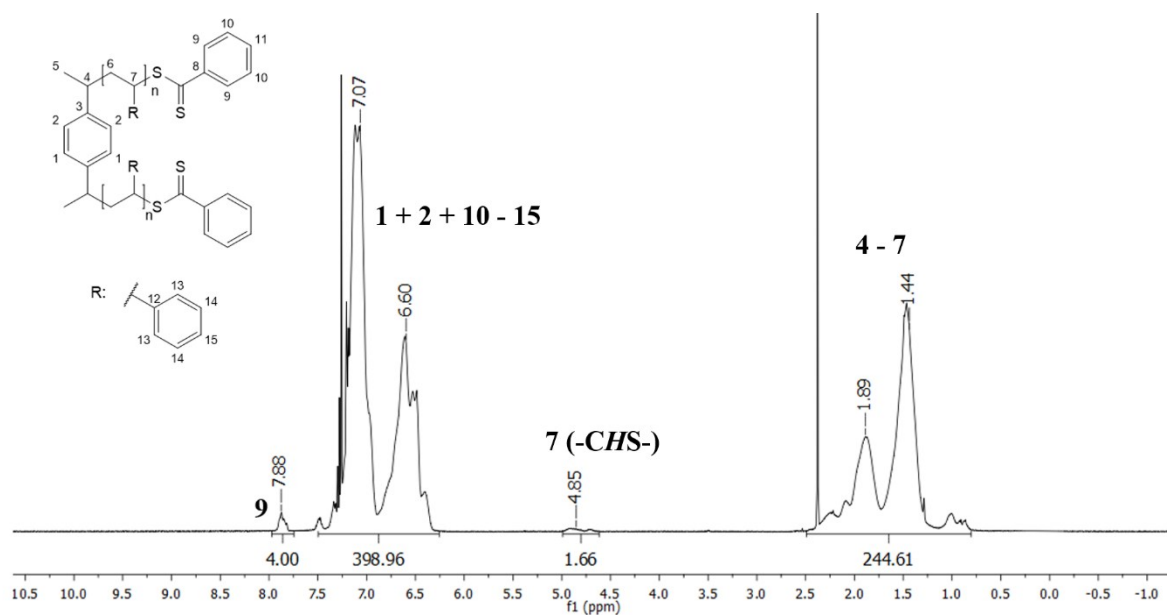


Figure S19. Example of $^1\text{H-NMR}$ spectrum of bivalent dithiobenzoate end-capped poly(styrene) (**10**) in CDCl_3 .

1.3 Synthesis of bivalent imidazolium end-capped PS (**11**)

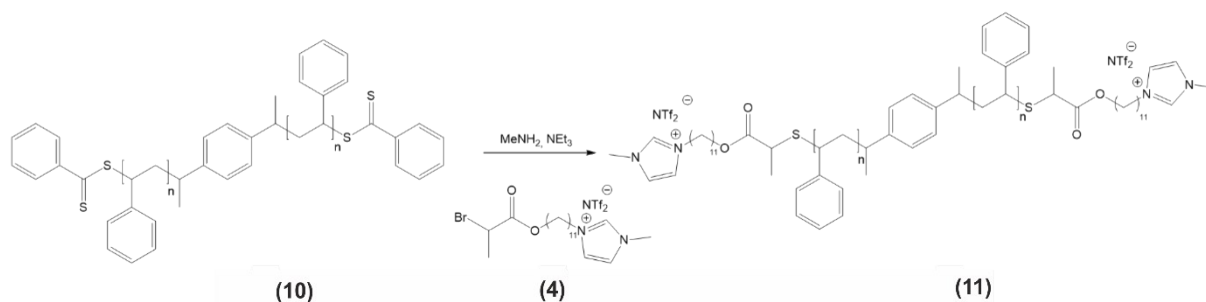


Figure S20. Synthetic route of thio-bromo click reaction (**11**).

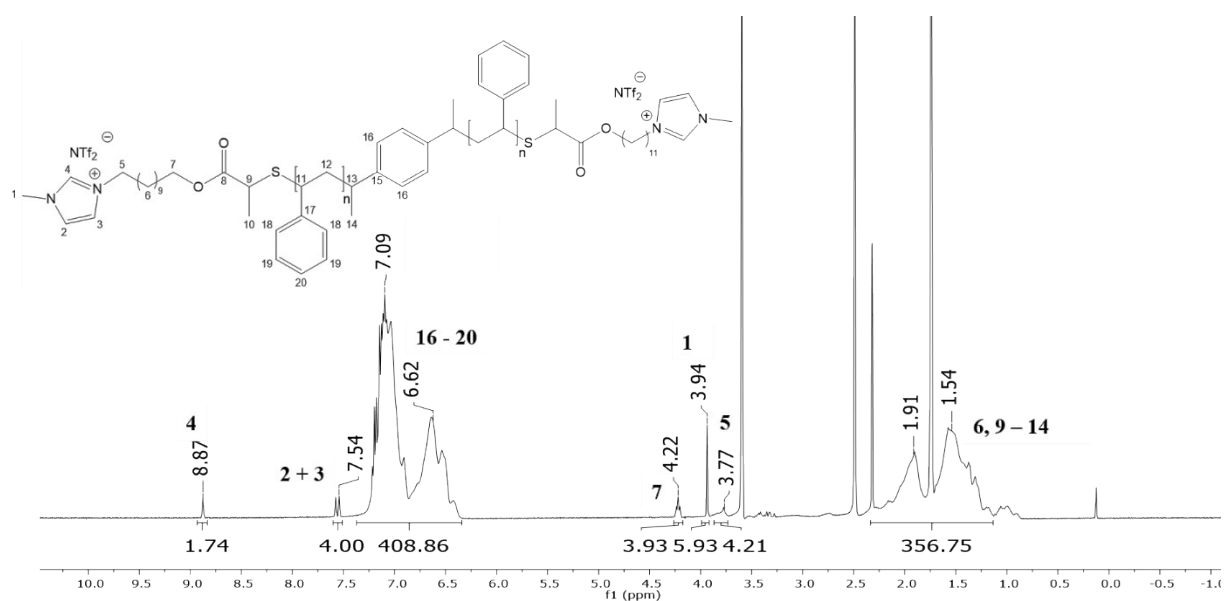


Figure S21. Example for $^1\text{H NMR}$ spectrum of bivalent imidazolium end-capped poly(styrene) (**11**) in $\text{THF-}d_8$.

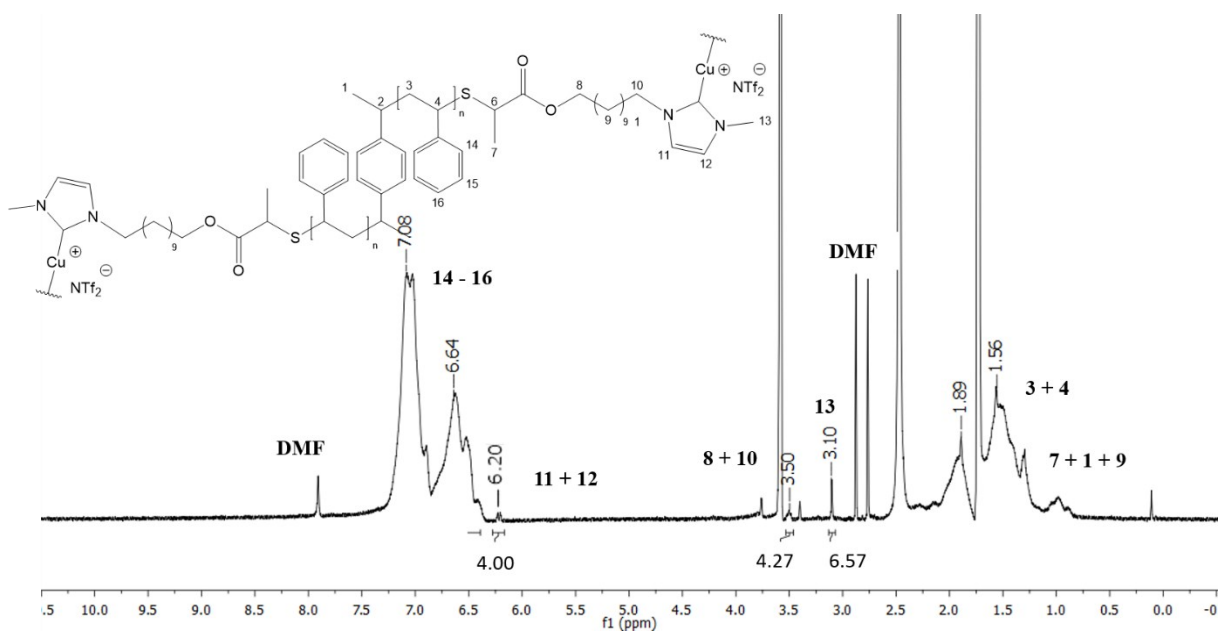


Figure S22. Example for ^1H NMR spectrum of chain extended poly(styrene) based bis(NHC) copper(I) complex (12) in $\text{THF-}d_8$.

2 Mass spectrometric data

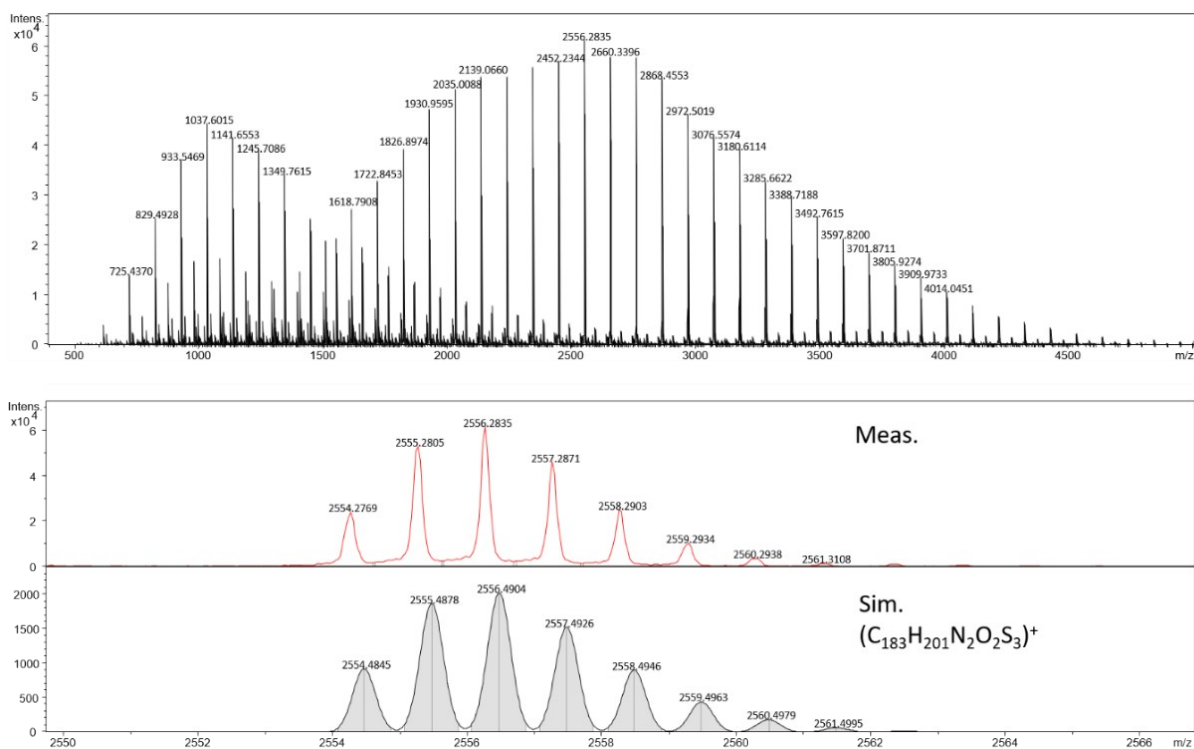


Figure S23. ESI-TOF-MS of monovalent imidazolium end-capped poly(styrene) (6a)

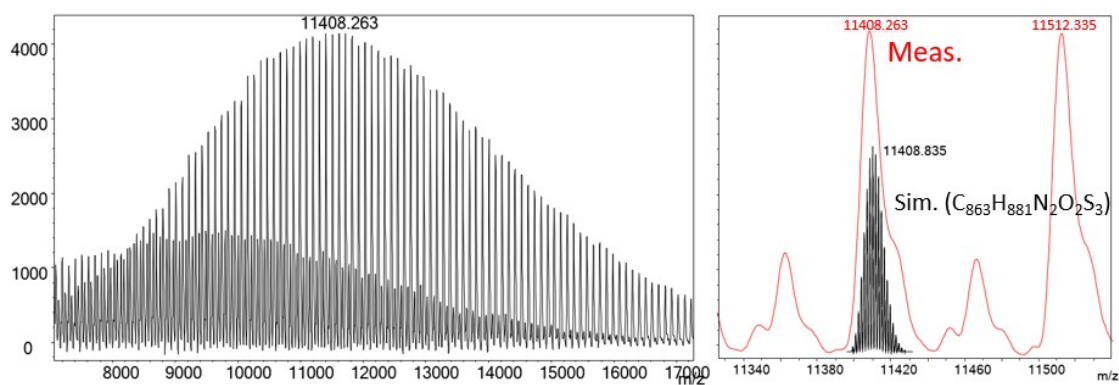


Figure S24. MALDI-TOF-MS of monovalent imidazolium end-capped poly(styrene) (6b).

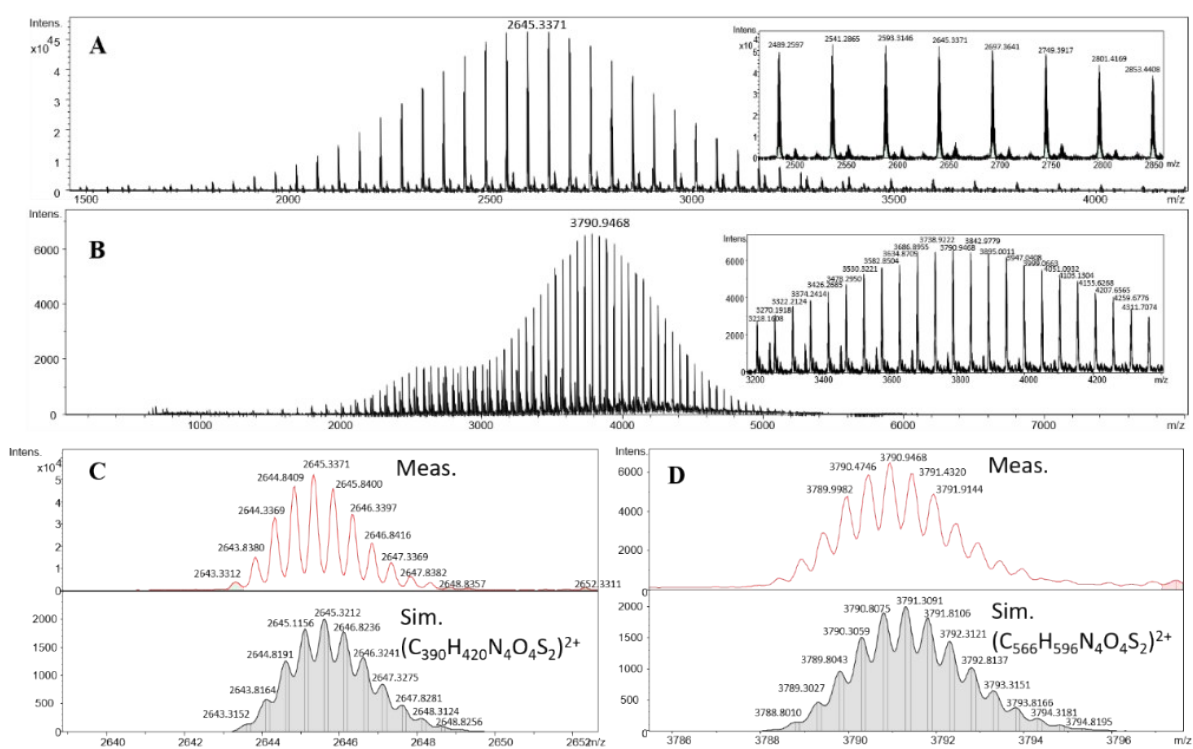


Figure S25. ESI-TOF-MS of bivalent imidazolium end-capped poly(styrene) A (11a), B (11b) and their isotopic pattern C (11a), D (11b).

3 Overview of polymerization and post-modification

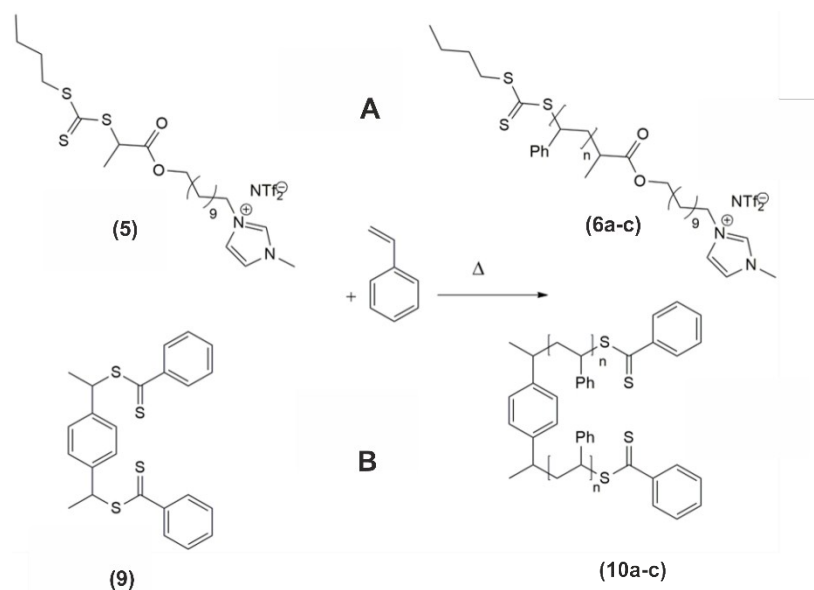


Figure S26. Reaction pathways of monovalent (A) and bivalent (B) poly(styrene) via RAFT.

Table S1. Reaction conditions and characterization data of monovalent and bivalent poly(styrene) via RAFT.

Ent.	compound	CTA	CTA:M	n_{CTA} [mmol]	n_{monomer} [mmol]	Temp [°C]	M_n (GPC) [g mol ⁻¹]	M_n (NMR) [g mol ⁻¹]	PDI	isolated yield [%]
Linear polymers 6										
2	6a		10:500	1.75			5900	6000	1.07	70
3	6b	5	10:1000	0.88	87.4	120	11500	11100	1.17	67
4	6c		10:2500	0.35			25300	26000	1.15	67
Bivalent polymers 10										
5	10a		10: 500	1.75			4400	5000	1.10	37
6	10b	9	10: 750	1.16	87.4	120	9000	8300	1.18	25
7	10c		10:1000	0.87			15500	14800	1.17	13

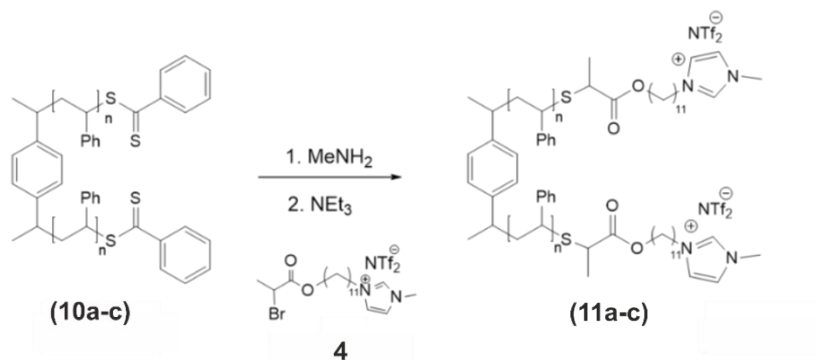


Figure S27. Reaction pathway of bivalent imidazolium end-capped poly(styrene) via thio-bromo click reaction.

Table S2. Characterization data of bivalent imidazolium end-capped poly(styrene) via thio-bromo click reaction

Ent.	compound	precursor	$n_{\text{(precursor)}}$ [mmol]	$n_{\text{(3)}}$ [mmol]	$m_{\text{(3)}}$ [mg]	M_n (GPC) [g mol ⁻¹]	M_n (NMR) [g mol ⁻¹]	PDI	isolated yield [%]
1	11a	10a	0.200	0.880	587	4500	4800	1.12	98
2	11b	10b	0.120	0.528	352	9000	8500	1.15	89
3	11c	10c	0.068	0.299	199	15100	18200	1.17	53

4 Synthesis of Cu(I) bis(NHC)-complexes

Table S3. Reaction conditions Cu(I) bis(NHC)-complexes formation

Ent.	Comp.	Prec.	$n_{\text{(precursor)}}$ [mmol] ^{a)}	$n_{\text{(NaOtBu)}}$ [mmol]	$m_{\text{(NaOtBu)}}$ [mg]	$n_{\text{(Cu-salt)}}$ [mmol]	$m_{\text{(Cu-salt)}}$ [mg]	M_n (precursor) [g mol ⁻¹] ^{b)}	M_n (complex) [g mol ⁻¹] ^{b)}
linear Cu(I) bis(NHC)-complexes									
1	7a	6a	0.080	0.104	09.99	0.040	14.90	5900	12000
2	7b	6b	0.045	0.059	05.62	0.023	08.57	11500	23000
3	7c	6c	0.019	0.025	02.37	0.0095	03.54	25300	50500
Chain extended Cu(I) bis(NHC)-complexes									
4	12a	11a	0.104	0.270	25.99	0.104	38.76	4500	15000
5	12b	11b	0.059	0.153	14.74	0.059	21.99	9000	21500
6	12c	11c	0.027	0.071	06.83	0.027	10.06	15100	31000

^{a)}Determined by using molecular weight via NMR, ^{b)}Determined via GPC (DMF + LiNTf₂) using PS standard calibration

5 Chromatograms

5.1 Concentration dependence of chain extended Bis(NHC)-copper(I) complex synthesis

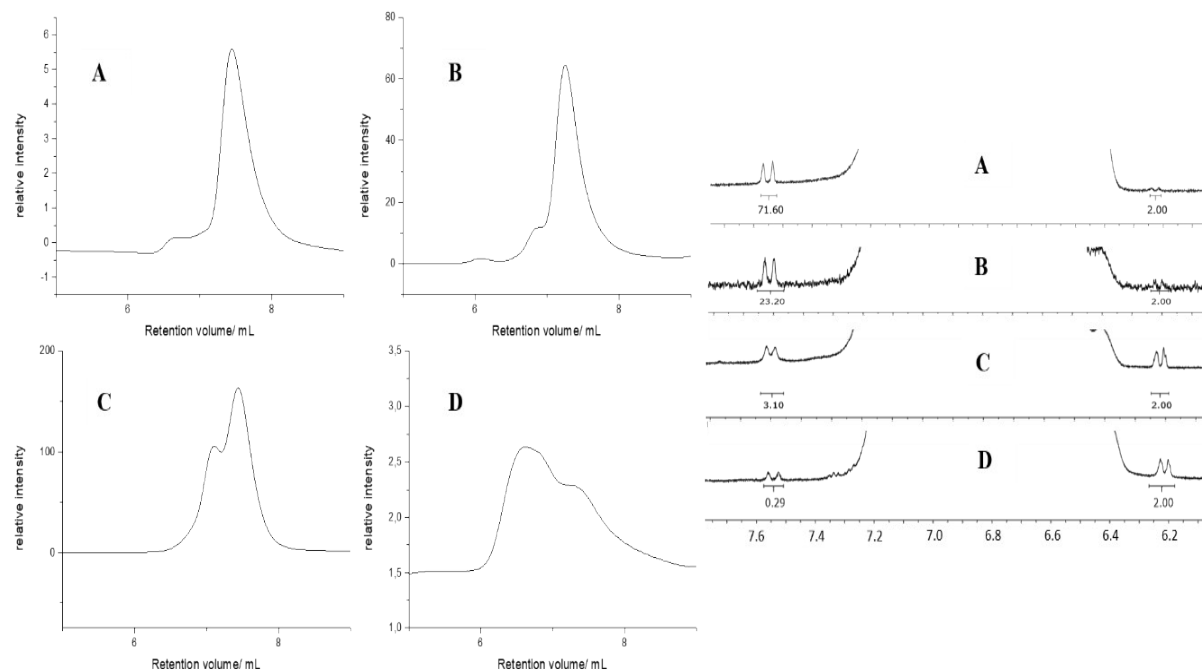


Figure S28. ¹H NMR spectra and GPC investigation proving concentration dependence of chain extension of (**12a**).

Table S4. Conversion in complexation reaction of **11a** using different concentration.

Ent.	Sample	c [mmol * mL ⁻¹]	M_n (GPC) [g mol ⁻¹] 11a	M_n (GPC) [g mol ⁻¹] mixture 12a	\bar{D}	Conversion ^{a)} [%]
1	A	0.02	4500	5000	1.25	5
2	B	0.04		7400	1.30	8
3	C	0.08		9100	1.46	39
4	D	0.15		15000	1.54	87

^{a)}determined via ¹H NMR spectroscopy of the crude reaction mixture by integration of precursor signals at 7.54 ppm and the resonances at 6.25 ppm assigned to the copper(I) bis(NHC) complex

5.2 Preparative GPC

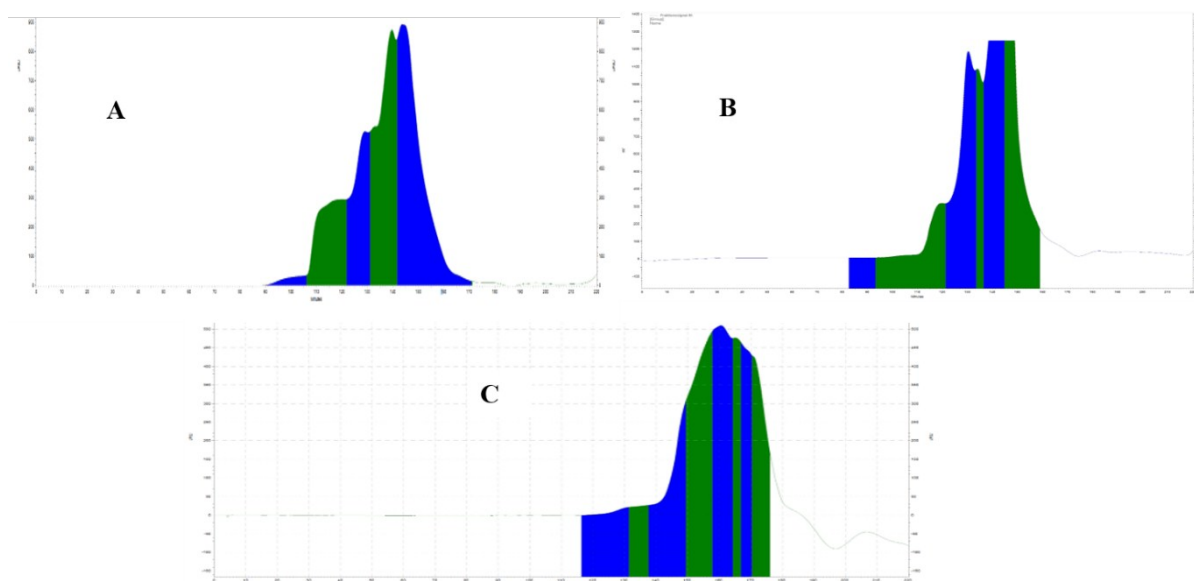


Figure S29. Preparative GPC chromatograms of (A) (12a), (B) (12b) and (C) (12c).

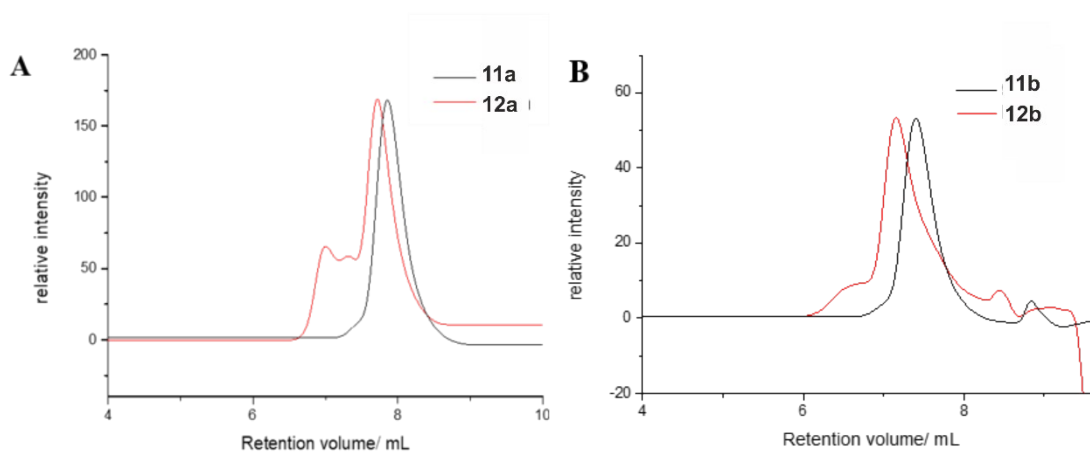


Figure S30. GPC traces of used complex mixtures (12a and 12b).

6 Fluorescence calibration

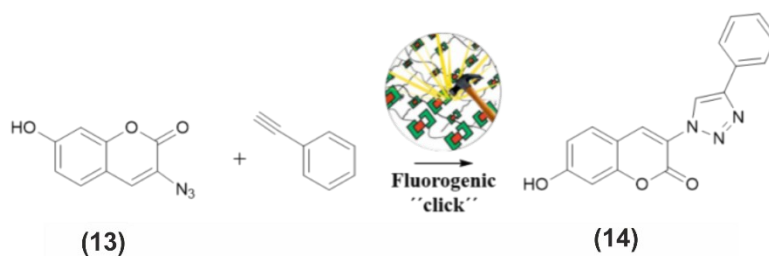


Figure S31. Fluorogenic click reaction of non-fluorescent (10) and phenyl acetylene reacting to highly fluorescent (13).

The calibration of fluorescence spectrometer was done embedding the clicked fluorogenic dye **13** in different concentration of in a high molecular weight PTHF matrix. Fluorescence quenching effects based on the chromaticity of dye were neglected adjusting an overall concentration of coumarin based dyes (**13** + **14**) constant at $1.6 \cdot 10^{-4} \text{ mmol mg}^{-1}$. The experimentally used concentrations ($c_{(14)} = 0, 1.5 \cdot 10^{-4}$

6 , $2.9 \cdot 10^{-6}$, $7.7 \cdot 10^{-6}$, $1.6 \cdot 10^{-5}$, $3.2 \cdot 10^{-5}$, $6.4 \cdot 10^{-5}$ as well as $1.6 \cdot 10^{-4}$ $\text{mmol}_{(13)} \text{mg}_{\text{sample}}^{-1}$) of **14** were adjusted dissolving the PTHF matrix (200 mg, $M_n = 112\,000 \text{ g mol}^{-1}$), the corresponding amounts of **14** and the non-fluorescent dye **13** in dry THF. After the solution becomes homogenous, the solvent was removed under reduced pressure and the sample was brought roughly into a cylindrical form (diameter ~ 13 mm) using spatula and tweezer and was allowed to crystallize for one week into dark. After crystallization the samples were compressed using an automatic hydraulic press together with a 13 mm pellet compression tool applying 10 tons pressure (corresponding to 0.74 GPa) Afterwards the fluorescence intensity was measured at 427 nm after excitation at 360 nm and the obtained fluorescence was fitted versus the concentration to yield **eq1**.

$$I_{\text{Fluorescence}} = 6.01 \cdot 10^6 (\pm 2.94 \cdot 10^5) c_{(13)} + 1.12 \cdot 10^1 (\pm 1.86 \cdot 10^1) \quad (\text{eq1})$$

Table S5. Detailed data for the calibration of the fluorescence intensity versus the concentration of the 7-hydroxy-3-(4-phenyl-1H-[1,2,3]triazole-1-yl)-coumarin (**14**) in a PTHF matrix.

	$c_{(14)}$ [$\text{mmol}_{(13)}/\text{mg}_{\text{sample}}$]	$n_{(14)}$ [mmol]	$m_{(14)}$ [mg]	$n_{(13)}$ [mmol]	$m_{(13)}$ [mg]	$I_{\text{Fluorescence}}$ (427 nm) Sample1 [a.u.]	$I_{\text{Fluorescence}}$ (427 nm) Sample 2 [a.u.]	$I_{\text{Fluorescence}}$ (427 nm) Sample 3 [a.u.]	$I_{\text{Fluorescence}}$ (427 nm) Average [a.u.]
1	0	0	0	$3.4 \cdot 10^{-2}$	6.98	17	17	17	17
2	$1.5 \cdot 10^{-6}$	$3.0 \cdot 10^{-4}$	0.10	$3.4 \cdot 10^{-2}$	6.91	23	24	25	24
3	$2.9 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	0.20	$3.4 \cdot 10^{-2}$	6.85	25	26	26	25
4	$7.7 \cdot 10^{-6}$	$1.6 \cdot 10^{-3}$	0.50	$3.2 \cdot 10^{-2}$	6.65	44	49	49	47
5	$1.6 \cdot 10^{-5}$	$3.2 \cdot 10^{-3}$	1.00	$3.1 \cdot 10^{-2}$	6.31	74	78	88	80
6	$3.2 \cdot 10^{-5}$	$6.6 \cdot 10^{-3}$	2.02	$2.8 \cdot 10^{-2}$	5.63	160	170	182	170
7	$6.4 \cdot 10^{-5}$	$1.3 \cdot 10^{-2}$	4.08	$2.1 \cdot 10^{-2}$	4.26	477	483	510	490
8	$1.6 \cdot 10^{-4}$	$3.4 \cdot 10^{-2}$	10.50	0	0	939	973	989	967

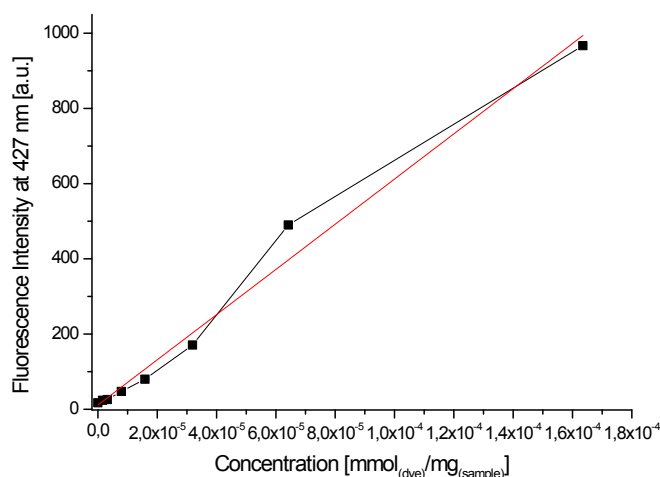


Figure S32. Calibration plot of fluorescence intensity versus the concentration of the clicked dye (**14**) in the polymer matrix.

7 General experimental conditions

Thin-layer chromatography (TLC) was carried out on Merck TLC alumina sheets (silica gel 60 F₂₅₄). Spots on TLC plates were visualized either by UV light with a wavelength of 254 or 366 nm or by oxidizing agents “blue stain” consisting out of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (1 g) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (1 g) dissolved in a mixture of distilled water (90 mL) and concentrated sulphuric acid (6 mL).

Differential scanning calorimetry (DSC) was performed on a 204F1/ASC Phönix from Netzsch (Selb, Germany) using crucibles and lids made of aluminum. Measurements were performed in a temperature range from -20 to 250°C using heating rates of 5, 10, 15 and 20 K min⁻¹. As purge gas, a flow of dry nitrogen (20 mL min⁻¹) was used. For evaluation of data, the Proteus Thermal Analysis Software (Version 5.2.1) was used figuring out an average crystallinity of 65% for the neat pTHF matrix which was marginally shifted to 60 – 62% when click educts were embedded.