

Supporting Information

Highly Efficient Mechanochemical Scission of Silver-Carbene Coordination Polymers

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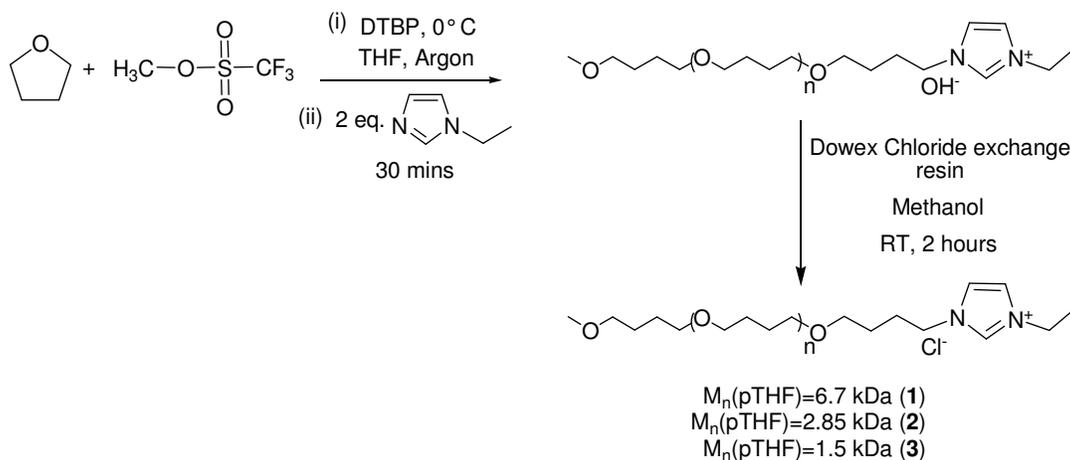
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1. Synthetic Materials and Methods. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker 400 spectrometer in deuterated chloroform or acetone or toluene. Chemical shifts are reported in ppm and referenced to tetramethylsilane and chloroform/acetone (proton and carbon) or toluene. Tetrahydrofuran was distilled from molecular sieves and toluene was distilled from sodium. The solvents used for sonication purposes, were stored under molecular sieves (3 Å) overnight and degassed before use. N-Ethyl methyl imidazole, silver oxide, tetrabutylammoniumhexafluorophosphate, ammonium hexafluorophosphate and methyl trifluoromethanesulfonate (96%) were obtained from Acros. Di-*tert*-butylpyridine (97%) and anhydrous carbon disulfide (>99%) were obtained from Aldrich. Dowex 1x8, 50-100 mesh exchange resin was procured from Acros. Due to the ionic nature of the polymers (**1-4**), size exclusion chromatography analyses could not be performed on these polymers. The molecular weight (M_n) values reported are based on ^1H NMR spectra. The N-ethyl methyl imidazole-Ag complex (**9**) was synthesized according to the method reported in the literature.¹

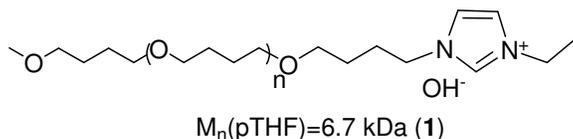
2. Synthesis of N-Ethyl imidazole terminated ω -(methoxy) polytetrahydrofuran (**1-3**)

The N-ethyl imidazole terminated ω -(methoxy) polytetrahydrofurans were synthesized via a cationic ring opening polymerization of tetrahydrofuran initiated by methyl triflate (Scheme S1).² The yield of the polymers obtained ranged from 36-40%.



Scheme S1: Synthesis N-Ethyl imidazole terminated ω -(methoxy) polytetrahydrofurans (**1-3**).

N-Ethyl imidazole terminated ω -(methoxy) polytetrahydrofuran - Anion: OH⁻ (1).

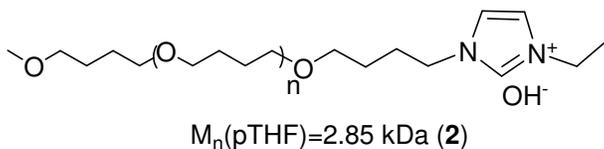


A mixture of 2,6-di-*tert*-butyl-pyridine (0.238 gm, 1.25 mmol) and 30 mL THF was cooled to 0 °C and stirred for 15 minutes under Argon. Methyl trifluoromethane sulfonate (0.406 gm, 2.47 mmol) was added to the mixture and was stirred for 2 hours under argon atmosphere. After 2 hours, the solution was divided equally to two parts. To the first one, 0.44 gm (4.58 mmol) of N-ethyl imidazole dissolved in 5 ml of chloroform was added. After addition, the solution was stirred for 30 mins and left to warm to room temperature. Solvent was removed under vacuo. The reaction mixture was dissolved in 100 ml of ether and kept in the freezer overnight. The resulting solid was filtered and washed with cold ether. The collected solid was dissolved in small amount of chloroform and precipitated into water by stirring overnight. The water was decanted and the polymer was dissolved in chloroform, dried under sodium sulfate, filtered and the solvent evaporated. The polymer was dried overnight in vacuo and obtained as a white solid. ¹H NMR analyses confirmed the end functionalization of the polymer with N-ethyl imidazole.

¹H NMR of **1** (400 MHz, CDCl₃): δ 9.4 (s, 1H, NCHN), 7.27 (d, 2H, J=20 Hz, NCHCHN), 4.35-4.4 (m, 4H, N(CH₂)₂), 3.25-3.5 (m, $n \times 4$ H, CH₂O), 3.23 (s, 3H, OCH₃), 2.01 (q, 2H, J=8 Hz, CH₂CH₂CH₂), 1.45-1.65 (m, $n \times 4$ H, CH₂CH₂O).

M_n calculated from ¹H NMR: 6.7 kDa

N-Ethyl imidazole terminated ω -(methoxy)polytetrahydrofuran (2) – Anion: OH⁻.



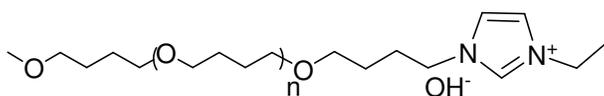
A mixture of 2,6-di-*tert*-butyl-pyridine (0.639 gm, 3.3 mmol) and 10 mL THF was cooled to 0 °C and stirred for 15 minutes under Argon. Methyl trifluoromethane sulfonate (1.015 gm, 6.17 mmol) was added to the mixture and was stirred for 60 min under argon atmosphere. After 60 mins, 1.46 gm (15.19 mmol) of N-ethyl imidazole dissolved in 5 ml of chloroform was added. After addition, the solution was stirred for 30 mins and left to warm to room temperature. Solvent was removed under vacuum. The reaction mixture was dissolved in 100 ml of ether and kept in the freezer overnight. The resulting solid was filtered and washed with cold ether. The collected solid was dissolved in small amount of chloroform and precipitated into water by stirring overnight. The water was decanted and the polymer was dissolved in chloroform, dried under sodium sulfate,

filtered and the solvent evaporated. The polymer was dried overnight in vacuo and obtained as a white solid.

^1H NMR of **2** (400 MHz, CDCl_3): δ 9.4 (s, 1H, NCHN), 7.27 (d, 2H, $J=20$ Hz, NCHCHN), 4.35-4.4 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.25-3.5 (m, $n \times 4$ H, CH_2O), 3.25 (s, 3H, OCH_3), 2.01 (q, 2H, $J=8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.5-1.65 (m, $n \times 4$ H, $\text{CH}_2\text{CH}_2\text{O}$).

M_n calculated from ^1H NMR: 2.85 kDa

N-Ethyl imidazole terminated ω -(methoxy)polytetrahydrofuran – Anion (OH^-) (**3**).



$M_n(\text{pTHF})=1.5$ kDa (**3**)

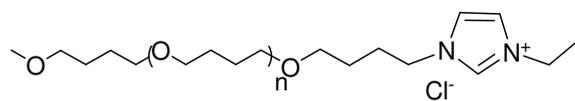
A mixture of 2,6-di-*tert*-butyl-pyridine (0.639 gm, 3.3 mmol) and 10 mL THF was cooled to 0 °C and stirred for 15 minutes under Argon. Methyl trifluoromethane sulfonate (1.015 gm, 6.17 mmol) was added to the mixture and was stirred for 15 mins under argon atmosphere. After 15 mins, 1.46 gm (15.19 mmol) of N-ethyl imidazole dissolved in 5 ml of chloroform was added. After addition, the solution was stirred for 30 mins and left to warm to room temperature. Solvent was removed under vacuo. The reaction mixture was dissolved in 100 ml of ether and kept in the freezer overnight. The resulting solid was filtered and washed with cold ether. The collected solid was dissolved in small amount of chloroform and precipitated into water by stirring overnight. The water was decanted and the polymer was dissolved in chloroform, dried under sodium sulfate, filtered and the solvent evaporated. The polymer was dried overnight in vacuo and obtained as a white solid.

^1H NMR of **3** (400 MHz, CDCl_3): δ 9.4 (s, 1H, NCHN), 7.28 (d, 2H, $J=20$ Hz, NCHCHN), 4.3-4.4 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.35-3.5 (m, $n \times 4$ H, CH_2O), 3.25 (s, 3H, OCH_3), 2.01 (q, 2H, $J=8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.55-1.65 (m, $n \times 4$ H, $\text{CH}_2\text{CH}_2\text{O}$).

M_n calculated from ^1H NMR: 1.5 kDa

3. Procedure for anion exchange to chloride

The polymers were dissolved in methanol and stirred with the Dowex chloride exchange resin for 30 mins. The solution was then filtered, the solvent was evaporated and the polymers were dried under vacuum to obtain chloride exchanged polymers as a white solid.

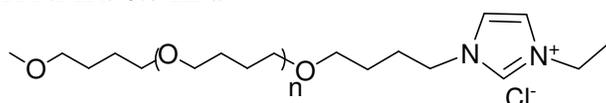


$M_n(\text{pTHF})=6.7 \text{ kDa (1)}$

^1H NMR of **1** (400 MHz, CDCl_3): δ 11.1 (s, 1H, NCHN), 7.25 (d, 2H, $J=20 \text{ Hz}$, NCHCHN), 4.35-4.4 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.25-3.5 (m, $n \times 4\text{H}$, CH_2O), 3.23 (s, 3H, OCH_3), 2.01 (q, 2H, $J=8 \text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.45-1.65 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$).

^{13}C NMR of **1** (125.6 MHz, CDCl_3): δ 138.2 (s, NCHN), 121.6 (s, NCHCHN), 120.73 (s, NCHCHN), 70.4-70.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 58.4 (s, OCH_3), 49.8 (s, NCH_2CH_2), 45.2 (s, NCH_2CH_3), 26.1-26.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 15.5 (s, NCH_2CH_3).

M_n calculated from ^1H NMR: 6.7 kDa

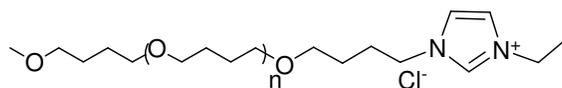


$M_n(\text{pTHF})=2.85 \text{ kDa (2)}$

^1H NMR of **2** (400 MHz, CDCl_3): δ 11.15 (s, 1H, NCHN), 7.23 (d, 2H, $J=20 \text{ Hz}$, NCHCHN), 4.41-4.45 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.25-3.5 (m, $n \times 4\text{H}$, CH_2O), 3.25 (s, 3H, OCH_3), 2.01 (q, 2H, $J=8 \text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.5-1.65 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$).

^{13}C NMR of **2** (125.6 MHz, CDCl_3): δ 138.2 (s, NCHN), 121.6 (s, NCHCHN), 120.73 (s, NCHCHN), 70.4-70.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 58.4 (s, OCH_3), 49.8 (s, NCH_2CH_2), 45.2 (s, NCH_2CH_3), 26.1-26.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 15.5 (s, NCH_2CH_3).

M_n calculated from ^1H NMR: 2.85 kDa



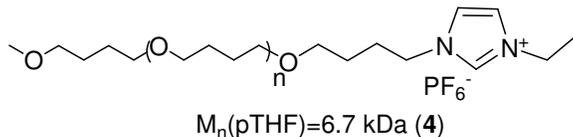
$M_n(\text{pTHF})=1.5 \text{ kDa (3)}$

^1H NMR of **3** (400 MHz, CDCl_3): δ 11.1 (s, 1H, NCHN), 7.2 (d, 2H, $J=20 \text{ Hz}$, NCHCHN), 4.4-4.45 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.35-3.5 (m, $n \times 4\text{H}$, CH_2O), 3.25 (s, 3H, OCH_3), 2.01 (q, 3H, $J=8 \text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.55-1.65 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$).

^{13}C NMR of **3** (125.6 MHz, CDCl_3): δ 138.2 (s, NCHN), 121.6 (s, NCHCHN), 120.73 (s, NCHCHN), 70.4-70.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 58.4 (s, OCH_3), 49.8 (s, NCH_2CH_2), 45.2 (s, NCH_2CH_3), 26.1-26.6 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$), 15.5 (s, NCH_2CH_3).

M_n calculated from ^1H NMR: 1.5 kDa

4. Procedure for anion exchange to hexafluorophosphate



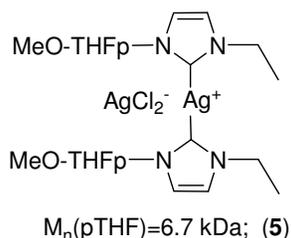
The chloride counter anion polymer was taken in 5 ml of methanol and stirred for 1 hour with 1.1 eq of ammonium hexafluorophosphate. After stirring, the solvent was removed, the polymer redissolved in chloroform, filtered and solvent removed. ^1H NMR confirmed anion exchange to hexafluorophosphate anion.

^1H NMR of **4** (400 MHz, CDCl_3): δ 8.7 (s, 1H, NCHN), 7.15 (d, 2H, $J=20 \text{ Hz}$, NCHCHN), 4.2-4.25 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.25-3.5 (m, $n \times 4\text{H}$, CH_2O), 3.25 (s, 3H, OCH_3), 1.98 (t, 2H, $J=8 \text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.45-1.65 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$).

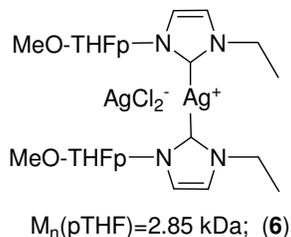
M_n calculated from ^1H NMR: 6.7 kDa

5. Synthesis of silver(I) based coordination polymers (5-7)

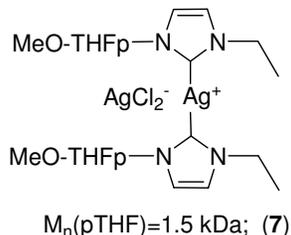
The silver(I) based coordination polymers were synthesized according to literature reports.³ The polymers were stirred with 0.55 eq. of silver oxide in dichloromethane at room temperature for 18 hours. Analysis by ^1H NMR after filtration through celite confirmed the formation of silver-NHC complexes.



^1H NMR of **5** (400 MHz, CDCl_3): δ 6.99 (d, 2H, $J=8 \text{ Hz}$, NCHCHN), 4.18-4.2 (m, 4H, $\text{N}(\text{CH}_2)_2$), 3.25-3.5 (m, $n \times 4\text{H}$, CH_2O), 3.25 (s, 3H, OCH_3), 1.4 (t, 3H, $J=8 \text{ Hz}$, CH_2CH_3), 1.45-1.65 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$).

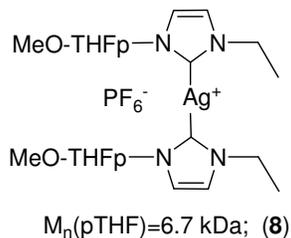


¹H NMR of **6** (400 MHz, acetone d₆): δ 7.41 (d, 2H, J= 8 Hz, NCHCHN), 4.2-4.22 (m, 4H, N(CH₂)₂), 3.25-3.5 (m, n × 4H, CH₂O), 3.25 (s, 3H, OCH₃), 1.4 (t, 3H, J= 8 Hz, CH₂CH₃), 1.45-1.65 (m, n × 4H, CH₂CH₂O).



¹H NMR of **7** (400 MHz, CDCl₃): δ 6.99 (d, 2H, J= 8 Hz, NCHCHN), 4.18-4.2 (m, 4H, N(CH₂)₂), 3.25-3.5 (m, n × 4H, CH₂O), 3.25 (s, 3H, OCH₃), 1.41 (t, 3H, J= 8 Hz, CH₂CH₃), 1.45-1.65 (m, n × 4H, CH₂CH₂O).

6. Synthesis of silver(I) based coordination polymer (**8**)



The silver(I) based coordination polymers were synthesized according to literature reports.⁴ The polymer (93 mg, 0.013 mmol) was stirred with 0.55 eq. of silver oxide (1.79 mg, 0.007 mmol) in dichloromethane in the presence of tetrabutylammonium phosphate (1 mg) and 1 ml of 1N NaOH at room temperature for 18 hours. After stirring, the organic layer was taken out, filtered through celite and analysed by ¹H NMR.

¹H NMR of **8** (400 MHz, CDCl₃): δ 7.15 (d, 2H, J= 8 Hz, NCHCHN), 4.18-4.2 (m, 4H, N(CH₂)₂), 3.25-3.5 (m, n × 4H, CH₂O), 3.25 (s, 3H, OCH₃), 1.9 (t, 3H, CH₂CH₃), 1.45-1.65 (m, n × 4H, CH₂CH₂O).

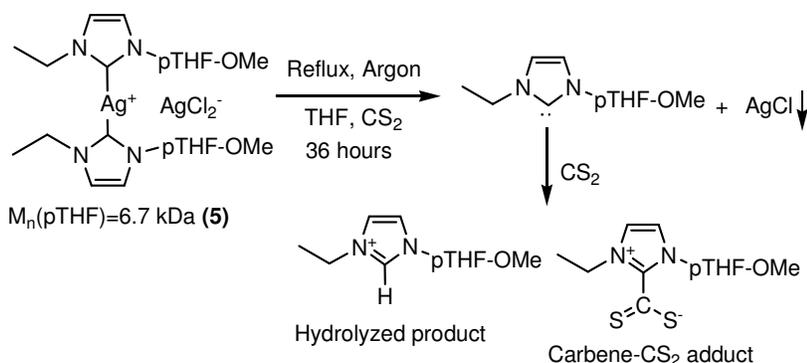
7. General procedure for sonication experiments

Sonication experiments were carried out with a Sonics VCX 500 Watt Ultrasonic processor purchased from Sonics and Materials Inc. A 13 mm probe was used at a frequency of 20 kHz, at 39% of the maximum amplitude of 125 μm. The sonication was performed in a water cooled glass vessel under inert Argon atmosphere. The internal temperature of the sonication vessel was measured during sonication using a thermometer and was found to be around ~27°C.

For a typical experiment, 15 mg (corresponds to 1.5 g/L) of the coordination polymers (**5-8**) were taken in 10 ml of toluene/acetonitrile/acetone in a water cooled glass vessel and sonicated under argon atmosphere in the presence of 1% (v/v) of carbon disulfide and/or 0.1% (v/v) of water. After sonication, the solvent was removed and the ^1H NMR of the sonicated sample was recorded in acetone d_6 . The amount of conversion was determined by integrating the peaks corresponding to that of the complex and the broken polymer.

For time dependent sonication experiments, 15 mg of the polymer complex (**5** and **8**) was taken in 10 ml of acetonitrile/toluene each time and sonicated under argon in the presence of 1% (v/v) of carbon disulfide and/or 0.1% (v/v) of water. After sonication, the solvent was removed and the ^1H NMR of the sonicated sample was recorded in acetone d_6 . The amount of conversion was determined by integrating the peaks corresponding to that of the complex and the broken polymer.

8. Synthesis of carbene- CS_2 adduct from the coordination polymer silver complex (**5**)



Scheme S2: Thermal induced scission of coordination polymer **5** in the presence of carbon disulfide.

10 mg of coordination polymer (**5**) was taken in 10 ml of THF and 3 ml of carbon disulfide and refluxed under argon atmosphere for 36 hours. After 36 hours, the solvent was removed and ^1H NMR of the crude reaction mixture was recorded in acetone d_6 . Analysis of NMR indicated the formation of carbene- CS_2 adduct and hydrolyzed product in the ratio 54:46. The NMR of the crude reaction mixture is provided in Figure S1.

9. Analyses of stability of carbene- CS_2 adduct

In order to analyze the stability of carbene- CS_2 adduct to the presence of water, the crude product obtained from the above reaction was taken in acetone d_6 and to this, 10 μl and 30 μl of water was added and ^1H NMR was recorded. Addition of water did not change the ratio of carbene- CS_2 and hydrolyzed product (54:46).

The stability of the carbene CS₂ adduct towards ultrasonication was also studied by taking the crude reaction mixture in toluene and acetonitrile and sonicating for 10 mins under Argon using the same reaction condition as that of the scission experiments. The ratios of the carbene-CS₂ adduct and hydrolyzed product did not change upon sonication suggesting that carbene-CS₂ adduct is stable under sonication.

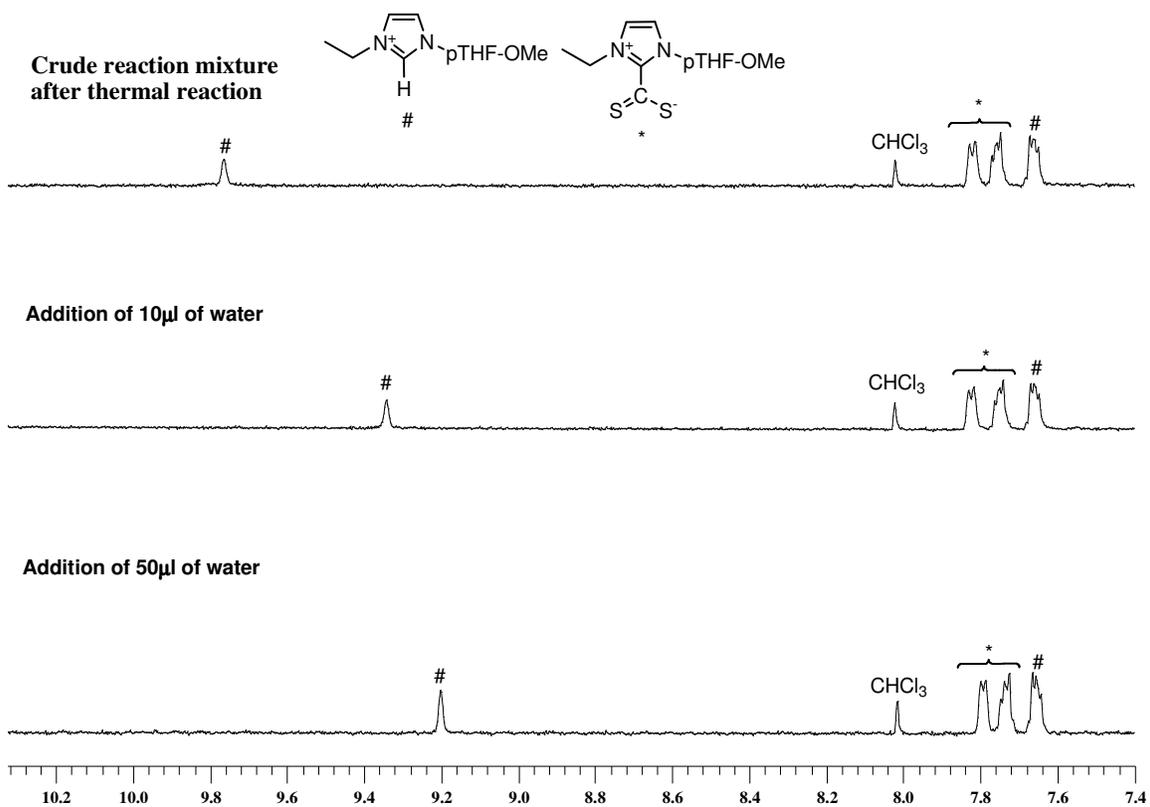


Figure S1: The ¹H NMR (acetone d₆) of the crude reaction mixture after thermal reaction and after addition of 10 µl and 50µl of water respectively.

10. ^1H NMR of N-ethyl imidazole terminated polymers (1-4)

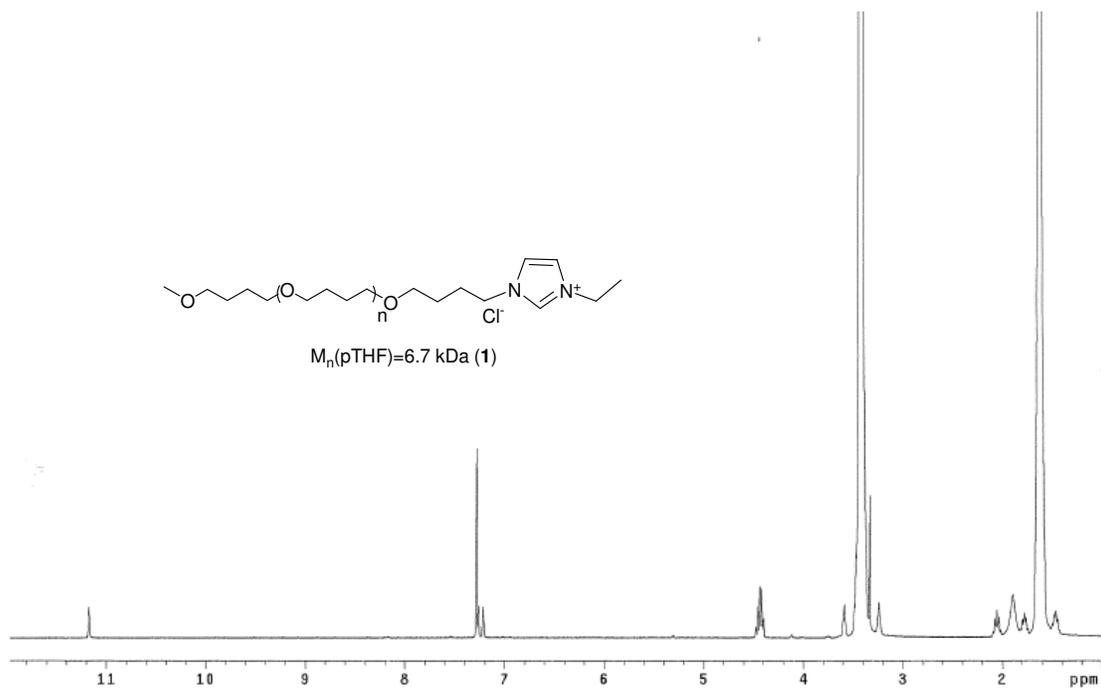


Figure S2: The ^1H NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (1) in CDCl_3 .

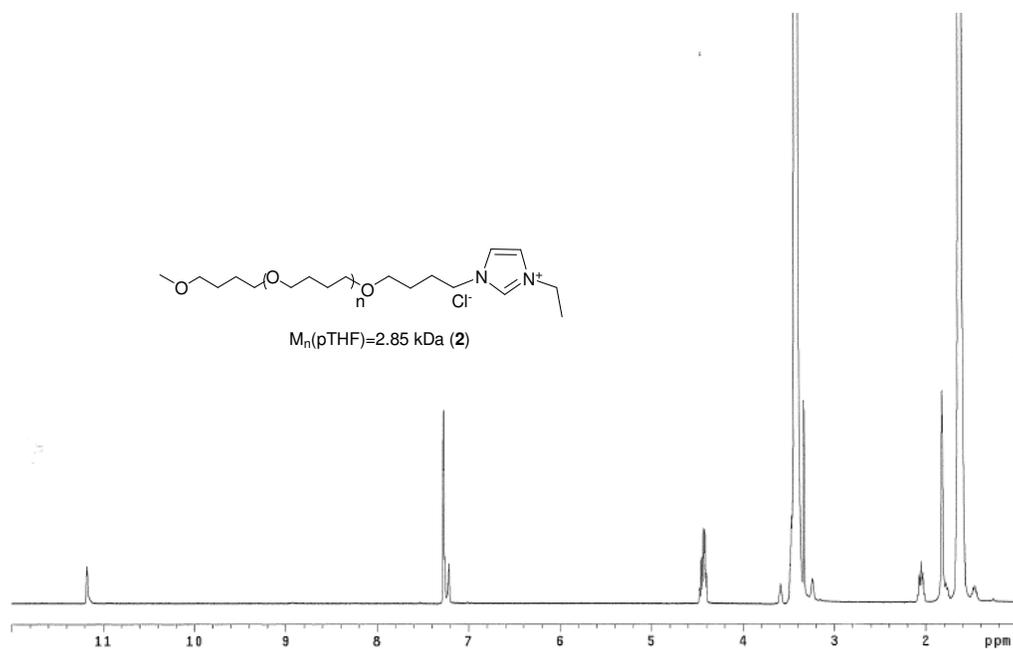


Figure S3: The ^1H NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (2) in CDCl_3 .

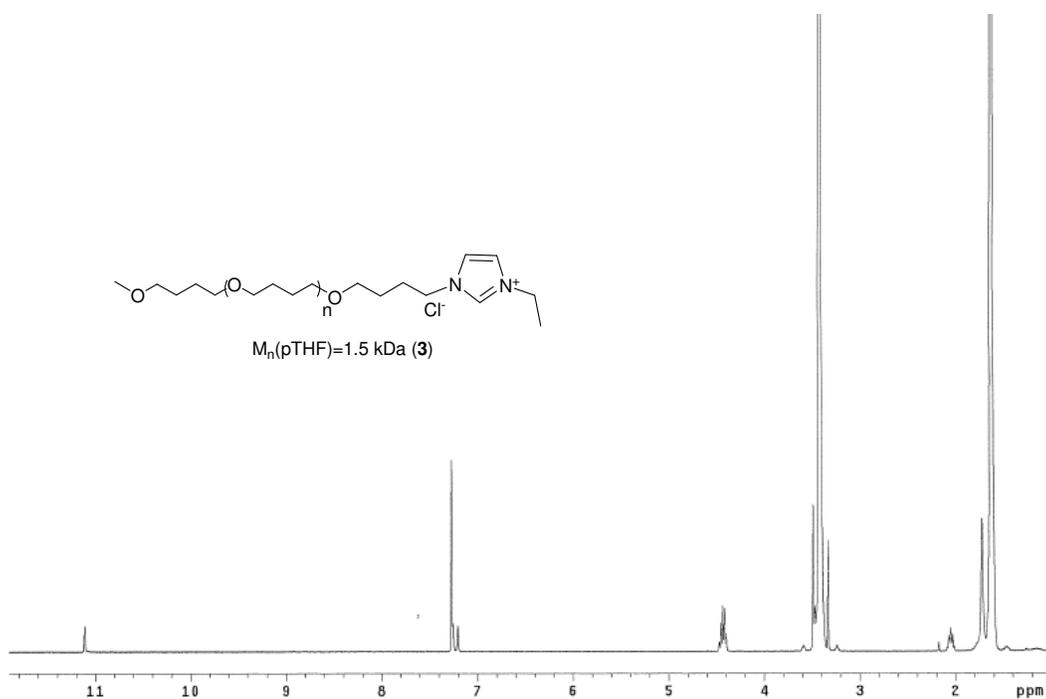


Figure S4: The ^1H NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (**3**) in CDCl_3 .

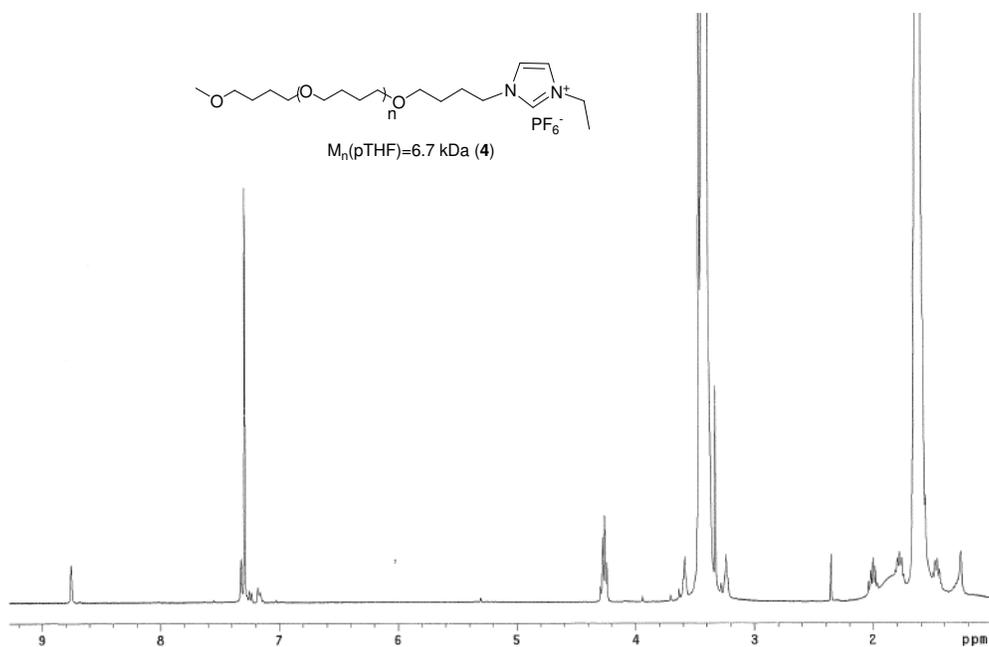


Figure S5: The ^1H NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (**4**) in CDCl_3 .

11. ^{13}C NMR of N-ethyl imidazole terminated polymers (1-3)

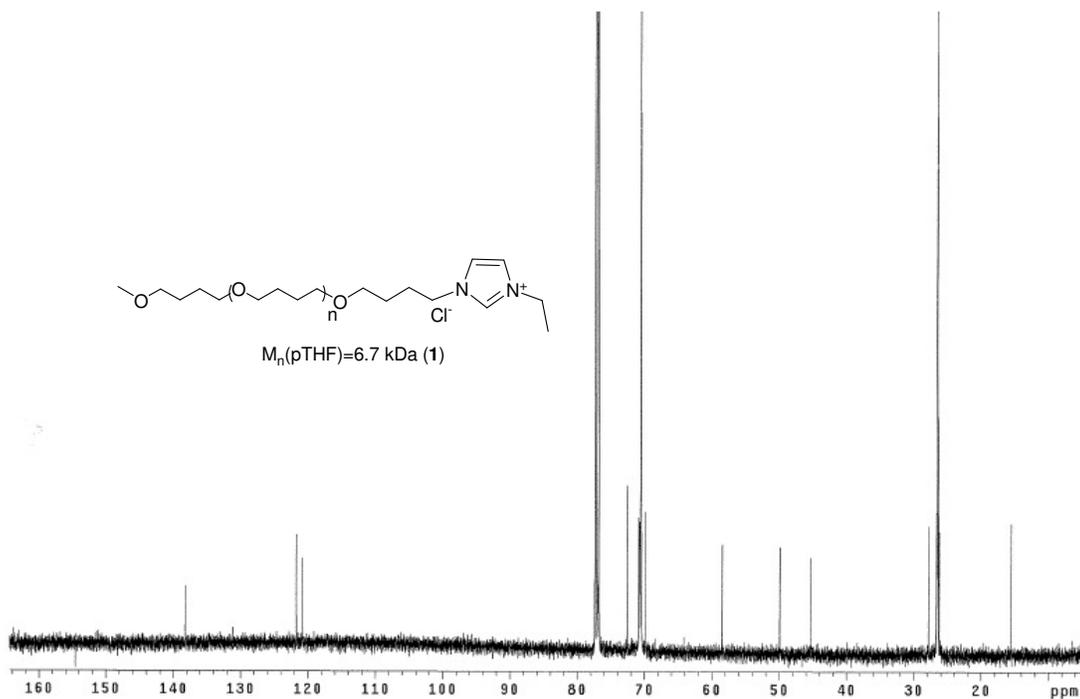


Figure S6: The ^{13}C NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (1) in CDCl₃.

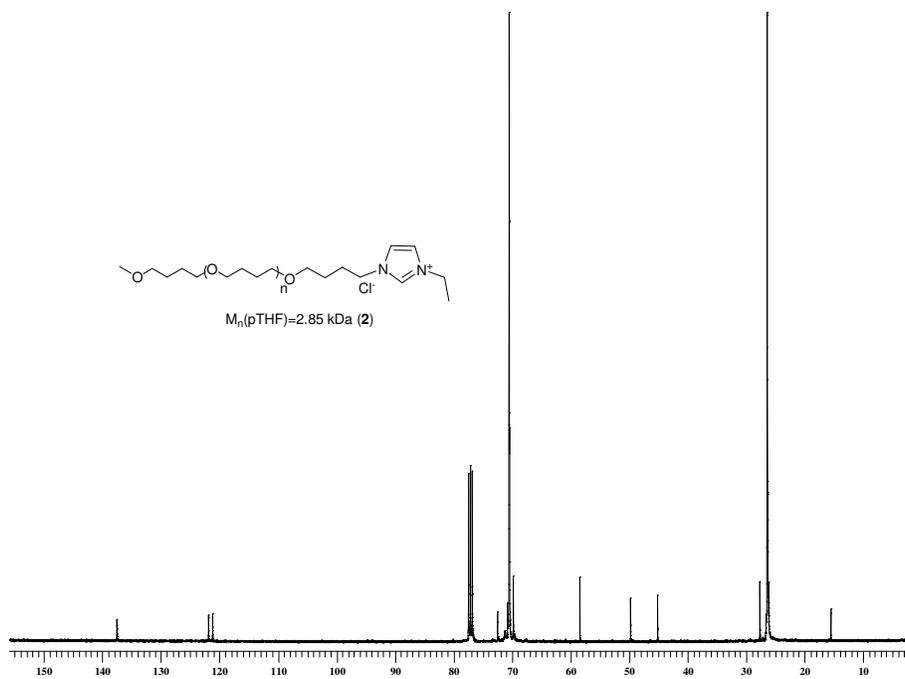


Figure S7: The ^{13}C NMR spectrum of N-ethyl imidazole terminated polytetrahydrofuran (2) in CDCl₃.

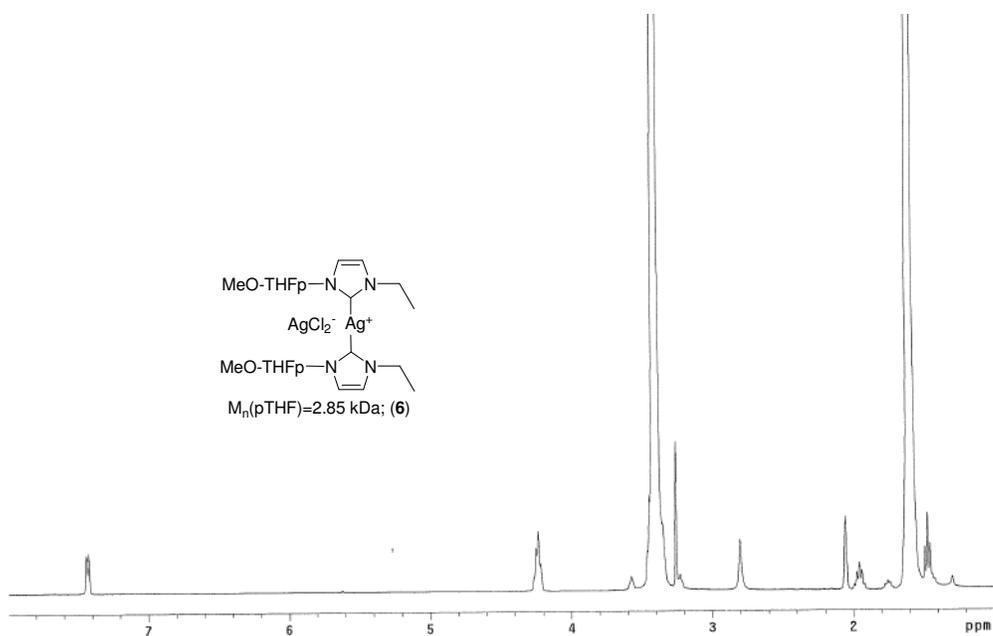


Figure S10: The ^1H NMR spectrum of coordination polymer **(6)** in acetone d_6 .

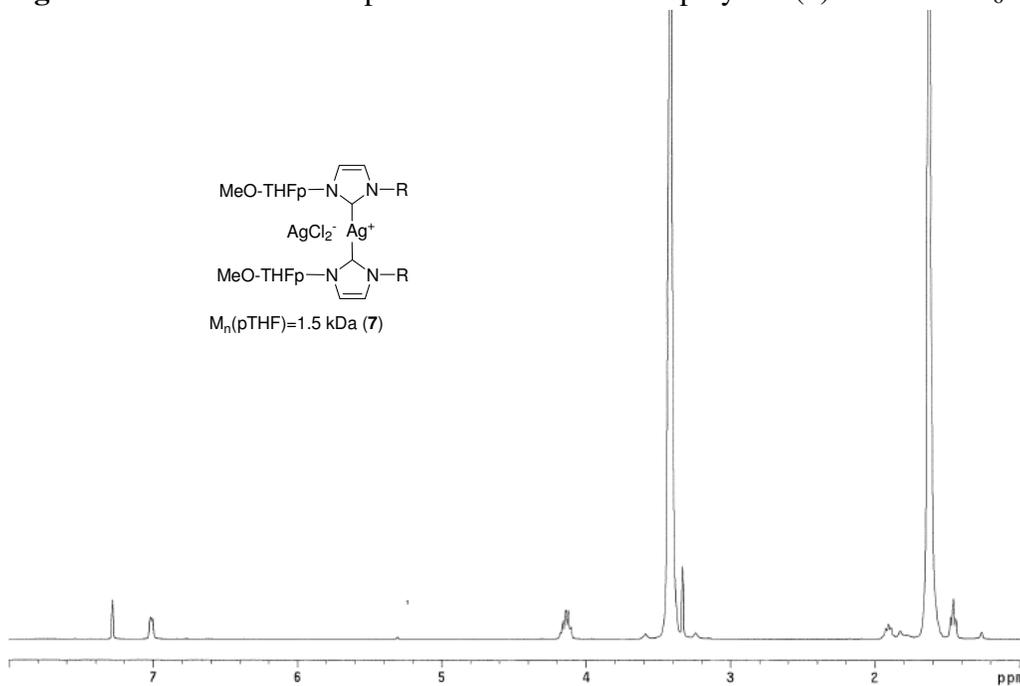


Figure S11: The ^1H NMR spectrum of coordination polymer **(7)** in CDCl_3 .

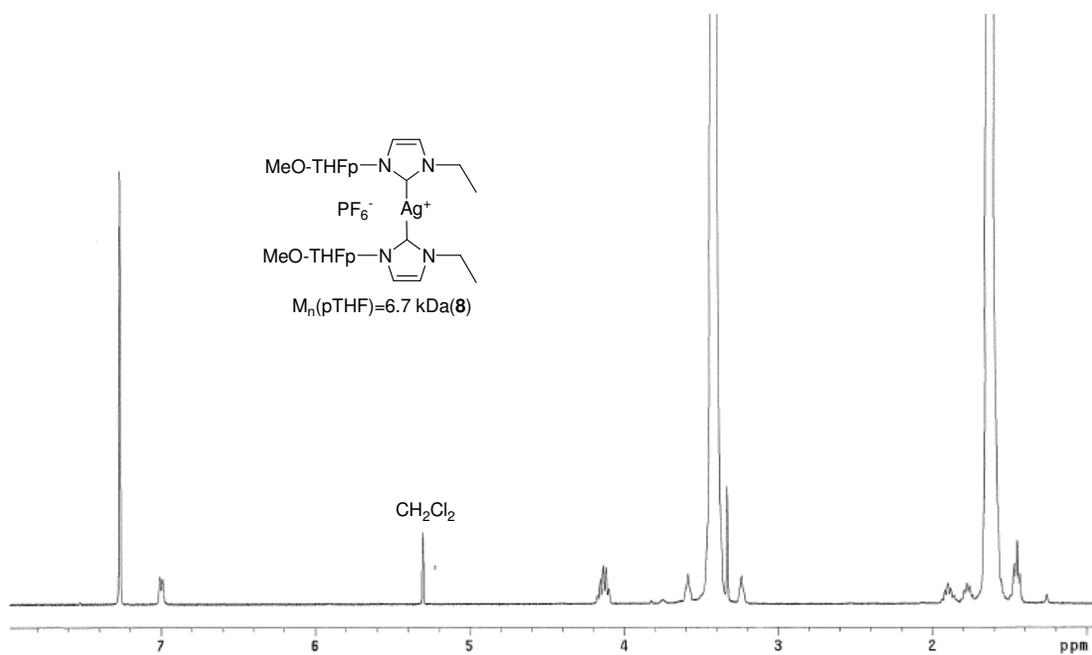


Figure S12: The ^1H NMR spectrum of coordination polymer (**8**) in CDCl_3 .

13. ^1H NMR spectra of the sonicated coordination polymers solution.

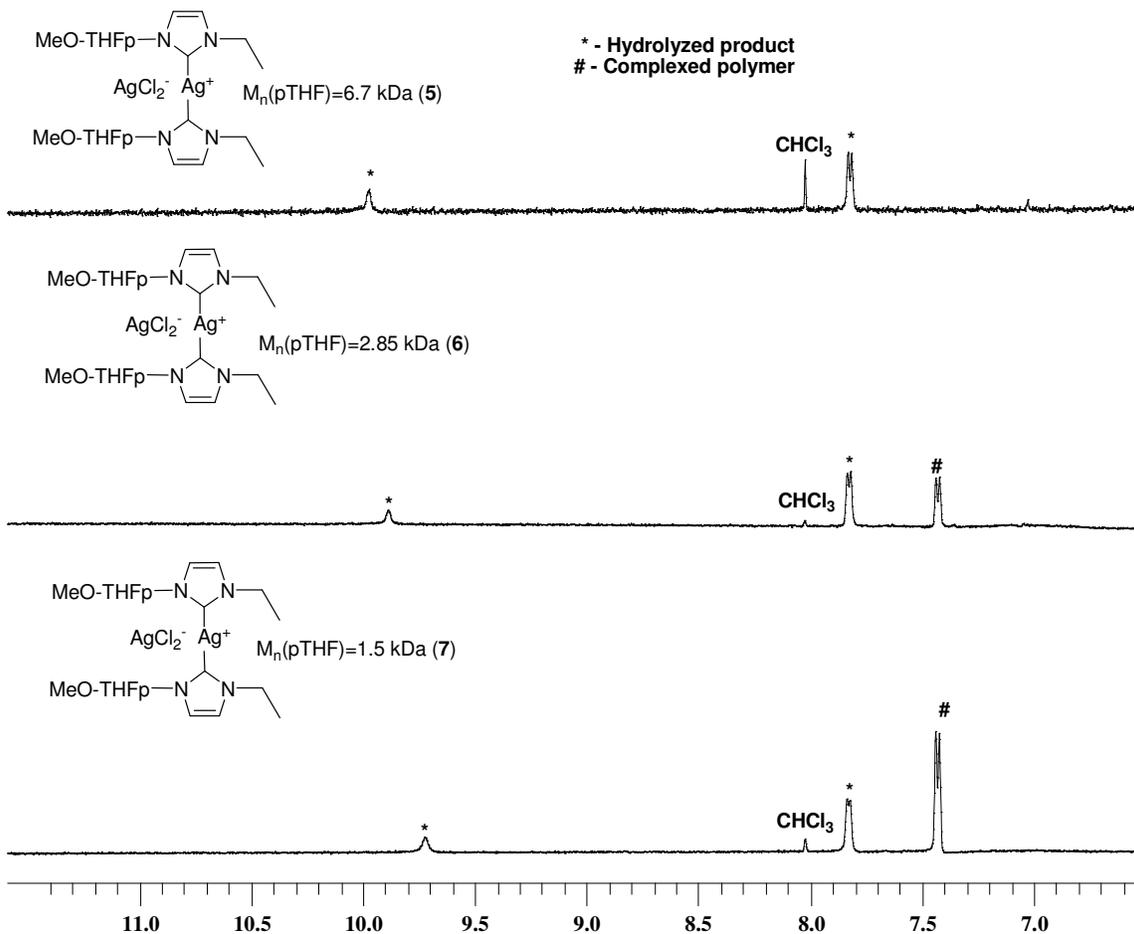


Figure S13: The ^1H NMR in acetone d_6 showing the aromatic region of the samples obtained after ultrasonication induced scission of coordination polymers (5-7) in acetonitrile in presence of 1% of carbon disulfide (sonication time=10 mins).

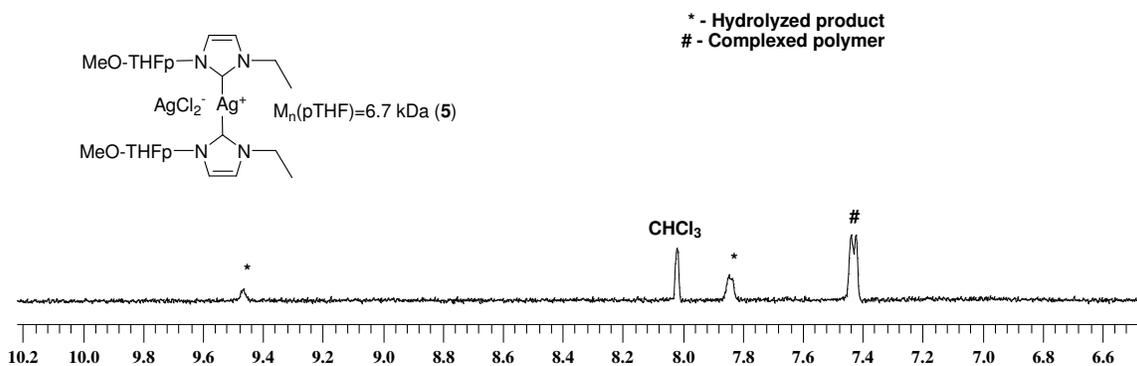


Figure S14: The ^1H NMR (acetone d_6) showing the aromatic region of the samples obtained after ultrasonication induced scission of coordination polymers (5) in acetonitrile in presence of 1% of carbon disulfide (sonication time = 1 min).

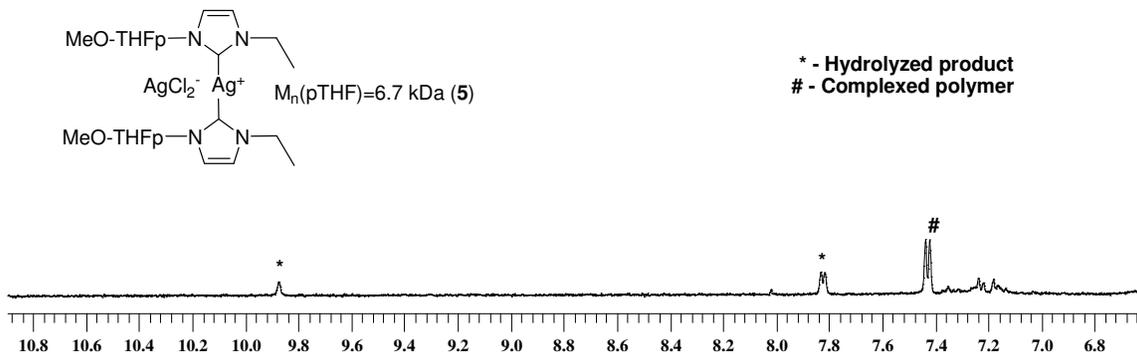


Figure S15: The ^1H NMR (acetone d_6) showing the aromatic region of the samples obtained after ultrasonication induced scission of coordination polymers (5) in toluene in presence of 1% of carbon disulfide (sonication time = 10 min).

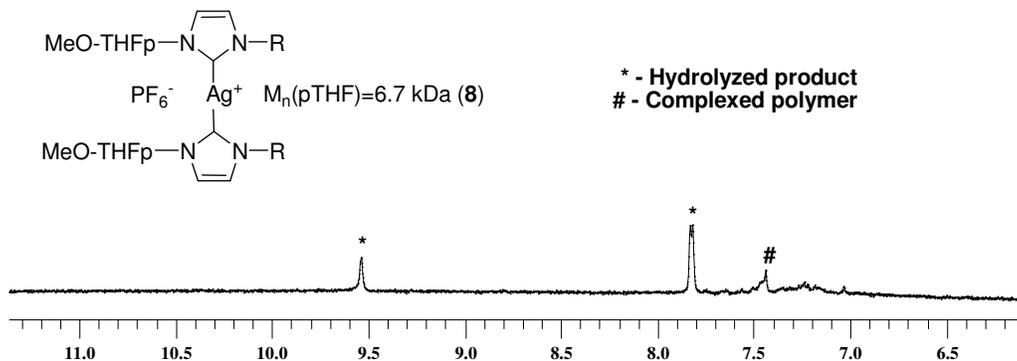


Figure S16: The ^1H NMR (acetone d_6) showing the aromatic region of the samples obtained after ultrasonication induced scission of coordination polymers (8) in toluene in presence of 1% of carbon disulfide (sonication time = 10 min).

14. References

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