Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information for:

Hexamethyl-*p*-Terphenyl Poly(benzimidazolium): A Universal Hydroxide-Conducting Polymer for Energy Conversion Devices

*Andrew G. Wright, Jiantao Fan, Benjamin Britton, Thomas Weissbach, Hsu-Feng Lee, Elizabeth A. Kitching, Timothy J. Peckham, and Steven Holdcroft**

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

EXPERIMENTAL

Materials and chemicals. Chemicals were purchased from Sigma Aldrich unless otherwise noted. Acetic acid (glacial) and potassium iodide (99.0%) were purchased from Caledon Laboratories Ltd.. Mesitoic acid (98%) and 1,4-phenylenediboronic acid (97%) were purchased from Combi-Blocks, Inc.. Ethanol (anhydrous grade) was purchased from Commercial Alcohols. Potassium hydroxide (ACS grade, pellets) was purchased from Macron Fine Chemicals. Dimethylsulfoxide (spectrograde), potassium carbonate (99.0%), potassium chloride (ACS grade), sodium bicarbonate (ACS grade), and hexanes (ACS grade) were purchased from ACP Chemicals Inc.. Methylene chloride (ACS grade, stabilized), silica (230-400 mesh, grade 60), sodium dithionite, acetone (ACS grade), methanol (ACS grade), and sodium chloride (ACS grade) were purchased from Fisher Scientific. Chloroform (ACS grade) and sodium hydroxide (ACS grade) were purchased from BDH. Activated charcoal (G-60) and hydrochloric acid (ACS grade) were purchased from Anachemia. Tetrakis(triphenylphosphine)palladium (99%) was purchased from Strem Chemicals. Dimethylsulfoxide-d_6 (99.9%-D), chloroform-D (99.8%-D), and methylene chloride-d_2 (99.9%-D) were purchased from Cambridge Isotope Laboratories, Inc.. Nuclear magnetic resonance (NMR) spectra were obtained on a 400 or 500 MHz Bruker AVANCE III running IconNMR under Top Spin 2.1. The residual ^{1}H NMR solvent peaks for DMSO-d_6, $CDCl_3$, and CD_2Cl_2 were set to 2.50 ppm, 7.26 ppm, and 5.36 ppm, respectively. The residual ^{13}C NMR solvent peaks for DMSO-d_6 and $CDCl_3$ were set to 39.52 ppm and 77.16 ppm, respectively. All NMR solutions had a solution concentration between 20 and 80 g/L. The conductivity measurements under controlled humidity and temperature were collected in an Espec SH-241 chamber. The 5 L reactor used was a cylindrical jacketed flask (all glass), allowing the temperature to be controlled by a circulation of oil around the reactant mixture, which was generally a different temperature than the measured internal (reactant mixture) temperature. Eaton's reagent was prepared prior to polymerization by stirring P_2O_5 (308.24 g) in methanesulfonic acid (2.5 L) at 120 °C under argon until dissolved, where it was then stored in sealed glass bottles until needed. Deionized water (DI water) was purified to 18.2 MΩ cm using a Millipore Gradient Milli-Q® water purification system. MBIM-I$^-$ (2-mesityl-1,3-dimethyl-1*H*-benzimidazolium iodide) was synthesized according to literature.[1]

Synthesis of 3-bromomesitoic acid (BMA). To the 5 L reactor was added glacial acetic acid (1.0 L) followed by mesitoic acid (225.1 g, 1.37 mol). The circulator temperature was set to 28.0 °C and mechanical stirred at 140 rpm. More glacial acetic acid was added (1.0 L) and stirred for approximately 30 min until the mesitoic acid fully dissolved. Bromine (100 mL, 1.95 mol) was added slowly over 5 min followed by glacial acetic acid (500 mL) to rinse down the sides. After 10 min, the internal temperature was observed to be 10 °C. The red mixture was stirred for

50 min, whereupon the internal temperature returned to approximately 25 °C. The mixture was then transferred by liquid transfer pump and PTFE tubing into 9 L of stirring distilled water (3 x 4 L beakers). The foamy precipitate was collected by vacuum filtration (requiring multiple funnels to collect all solid), compressed with a wide spatula to better dry the solid, and washed with water until white (~2 L total). The cakes were transferred to a 4 L beaker. The solid was recrystallized from approximately 2750 mL of 60% ethanol by boiling and then cooling to room temperature. The fluffy needles were collected by vacuum filtration, washed with room temperature 33% ethanol, and thoroughly dried at 80 °C under vacuum. This resulted in approximately 320 g of white needles. Two of these batches were combined and recrystallized a second time in 2700 mL of 55% ethanol, collected, washed with 33% ethanol, and dried under vacuum at 80 °C to yield 577.5 g of BMA as white fluffy needles (86.6%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 13.33 (s, 1H), 7.09 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 170.02, 138.09, 135.11, 132.86, 132.19, 129.95, 124.45, 23.44, 20.88, 18.71. This procedure was repeated once more. The resulting data is shown in Table S1.

Synthesis of methyl 3-bromomesitoate (BME). Potassium hydroxide pellets (36.0 g, 0.64 mol) were ground with a mortar and pestle to a fine powder and added to a 1 L round-bottom flask followed by DMSO (360 mL). The mixture was vigorously stirred for 30 min. BMA (104.4 g, 0.43 mol) was separately dissolved in DMSO (360 mL) and then added to the basic DMSO mixture, stirring for 15 min at room temperature. Iodomethane (40 mL, 0.64 mol) was then slowly added to the mixture (*exothermic*, temperature was kept below 40 °C) and then stirred closed for 2 h at room temperature. The mixture was then poured into 5 L of stirring ice-water and left stirring at room temperature until all of the ice melted. The precipitate was collected by vacuum filtration, thoroughly washed with water, and dried under vacuum at room temperature for at least 24 h to produce 106.1 g of BME as white crystals (96.4% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 7.12 (s, 1H), 3.85 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H). The above procedure represents a "1.0 Scale". For repeated syntheses, "2.0 Scale" represents the procedure being performed twice simultaneously and the final collected precipitates being combined prior to drying. The resulting data is shown in Table S2. The ^{1}H NMR spectra of BME for each reaction performed are shown in Fig. S4.

Monomer (HMTE) synthesis. To the 5 L reactor was added 1,4-dioxane (2.9 L), BME (150.0 g, 0.58 mol), 1,4-phenylenediboronic acid (48.4 g, 0.29 mol), and 2 M K_2CO_3 (950 mL). The reactor was connected to a water-cooled condenser and the mixture was degassed by bubbling argon through a needle sub-surface for 1 h. The needle was removed and $Pd(PPh_3)_4$ (1.80 g, 0.27% mol per BME) was added under a flow of argon. The circulator temperature was set to 105 °C and the solution was mechanically stirred at 280 rpm for 22 h, where the internal temperature read 89 °C. The dark yellow solution was then cooled to 60 °C and transferred by liquid transfer pump equally into 4 x 4 L beakers, each containing boiling and stirring 43% ethanol (2.62 L, aq.). The mixtures were stirred until they reached room temperature. The dark grey precipitates were collected by vacuum filtration and washed with water. The solid was dissolved in dichloromethane (1.0 L), washed with water (300 mL), and passed through a thick silica pad (~300 g). More dichloromethane (~4 L) was used to flush the silica and the filtrate was then evaporated by rotary evaporation to a pale yellow solid. The solid was then recrystallized in hexanes (5 L) by boiling until dissolved and cooling to -14 °C overnight. The white crystals were collected by vacuum filtration, washed with hexanes (400 mL), and dried under vacuum at 110 °C to yield 68.0 g of HMTE as fluffy, pure white crystals (54% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.15 (s, 4H), 7.00 (s, 2H), 3.92 (s, 6H), 2.33 (s, 6H), 2.03 (dd, $J = 9.0, 4.3$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 171.12, 139.82, 139.07, 137.72, 133.46, 132.82, 132.81, 132.30, 132.28, 129.48, 129.18, 129.17, 52.07, 21.04, 21.00, 19.57, 18.19, 18.15. The above procedure represents a "1.0 Scale". For repeated syntheses, "Scale" represents an appropriately scaled version of all reactants and solvents by that factor. The amount of catalyst used was lowered for each subsequent reaction. The resulting data is shown in Table S3. The ^{1}H NMR spectra of HMTE for each reaction performed are shown in Fig. S5.

Purification of 3,3'-diaminobenzidine (DAB). This procedure was modified from the literature.[2] A 2 L Erlenmeyer flask was filled with distilled water. The water was boiled while bubbling with argon. The bubbling of argon was stopped and then, using an inverted glass funnel, a low flow of argon was kept over the solution for the next steps. The as-received DAB (25.0 g) was added to the boiling water and stirred until dissolved. While boiling the solution, sodium dithionite (0.50 g) was added and stirred for 15 min. Activated charcoal (3.00 g) was then added and boiled for 30 min. The mixture was then quickly vacuum filtered through a hot funnel, producing a colorless filtrate. Argon was flowed through the filter flask and it was then kept sealed in the dark for 18 h. The resulting precipitate was then collected by vacuum filtration, washed with water, and quickly dried under vacuum at 100 °C. The collected recrystallized DAB was stored in the dark under argon until use. The purification process was repeated on more as-received DAB from different companies and the resulting data is shown in Table S4.

Polymerization (HMT-PBI). To a 1 L, 3-neck round-bottom flask was added HMTE (20.0000 g, 46.5 mmol), recrystallized DAB (9.9535 g, 46.5 mmol), and Eaton's reagent (800 mL, self-prepared). Argon was flowed into the flask and out through a $CaCl_2$ drying tube throughout the reaction. This mixture was heated at 120 °C until fully dissolved. After heating at 120 °C for 30 min, the temperature was increased to 140 °C for 20 min. The black solution was then slowly poured into distilled water (3.0 L) with manual stirring to break up the dense fibrous solid that formed. The solid was collected by vacuum filtration on glass fiber and washed with distilled water (1.5 L). The solid was then transferred to fresh distilled water (3.5 L) and the pH was adjusted to ~10 by addition of potassium carbonate (~70 g). The mixture was stirred overnight at room temperature. The solid was collected again, washed with water, boiling water, and acetone, and dried for at least 24 h at 100 °C to yield 26.0 g of HMT-PBI as fibrous solid (103% yield). The overestimated yield is likely due to trace water and acid in the fibrous solid, which will be later discussed. For ^{1}H NMR spectroscopy, HMT-PBI (~13.0 mg) was dissolved in DMSO-d_6 (0.65 mL) by addition of KOD (5 drops of KOD 40 wt% in D_2O) and heating. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 7.76-7.51 (m, 2H), 7.51-7.32 (m, 2H), 7.32-7.15 (m, 4H), 7.16-7.02 (m, 2H), 7.02-6.83 (m, 2H), 2.27-1.91 (m, 12H), 1.91-1.70 (m, 6H). For repeated syntheses, the same method above was used and the resulting data is shown in Table S5. The ^{1}H NMR spectra of HMT-PBI for each reaction performed are shown in Fig. S6.

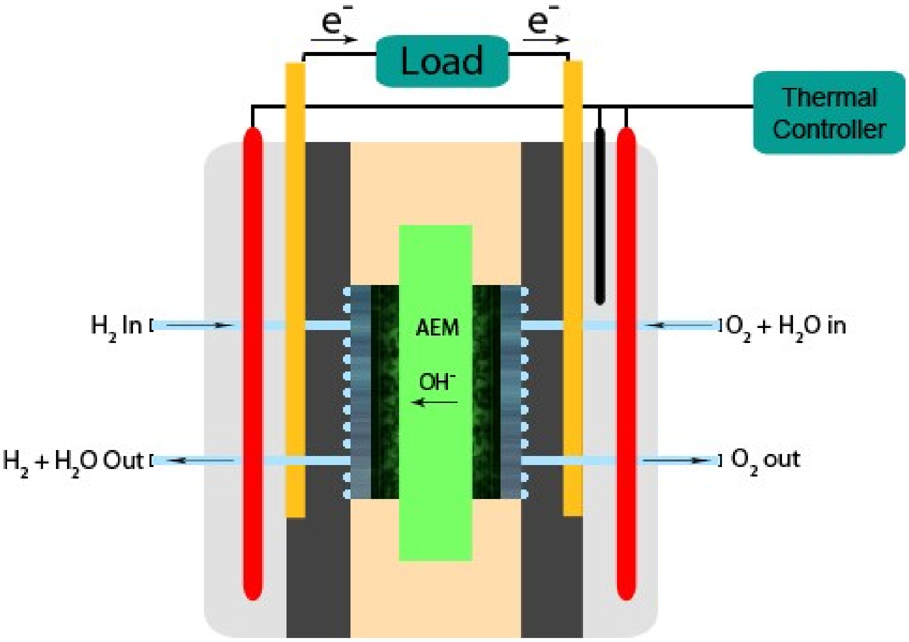
Procedure for ~50% dm HMT-PMBI. To two separate 1 L, 3-neck round-bottom flasks was each added HMT-PBI (30.00 g, 55.1 mmol), DMSO (800 mL), and potassium hydroxide in water (14.00 g KOH in 35 mL H_2O). Each was vigorously stirred and heated at 70 °C for 16 h closed. The viscous dark red/brown mixtures were cooled to room temperature and both were combined by decanting into one 2 L beaker. While manually stirring the mixture with a glass rod, iodomethane (21.0 mL, 337 mmol) was added (exothermic). The dark-coloured mixture was stirred for approximately 5 min until the mixture became a chunky, pale brown sludge. The mixture was then poured equally into 4 x 4 L beakers, each containing distilled water (3 L). To each beaker was then added potassium iodide (5.0 g) and briefly stirred with a glass rod. The precipitate was collected by vacuum filtration and washed with water. The collected cakes were transferred to a clean 4 L beaker and the cakes were beaten to a powder using a metal spatula. This wet solid was then stirred for 16 h in acetone (3 L) with potassium iodide (15.0 g). The solid was collected by vacuum filtration and washed with acetone. The yielded cakes were added to a 1 L container and beaten again to a powder. The solid was dried under vacuum at 80 °C for at least 24 h yielding 58.2 g of 53.7% dm HMT-PMBI as a pale brown powder (88.9% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ: 8.28-7.45 (m, 6.03H), 7.44-7.09 (m, 6.00H), 4.46-3.87 (m, 0.91H), 3.87-3.39 (m, 5.61H), 2.33-1.97 (m, 11.71H), 1.97-1.70 (m, 7.39H). The amount of iodomethane used, the precipitation solvent, and amount of potassium iodide used was varied in subsequent reactions and the resulting data is shown in Table S6. The ^{1}H NMR spectra of ~50% dm HMT-PMBI for each reaction performed are shown in Fig. S7. The dm% was calculated using eqn (S1).

Controlled methylation procedure. To a 1 L round-bottom flask containing dichloromethane (300 mL) was added ~50% dm HMT-PMBI (34.00 g, 51.4% dm) followed by additional dichloromethane (400 mL). The solid was broken up inside with a spatula and the mixture was stirred for 1.5 h until mostly dissolved. Iodomethane (13.0 mL, 209 mmol) was added and the mixture was stirred for 18 h closed at 30 °C. The precipitate was broken up with a spatula and the stirring was continued for 3 h at room temperature. The solvent was evaporated at 44 °C by dynamic vacuum, leaving a strong solid film stuck to the inner glass wall. Methanol was added and heated to dissolve the polymer and then transferred to a large, flat glass dish, using additional methanol to rinse all of the contents into the large dish. The solvent was evaporated in air at room temperature and then under vacuum at 100 °C, yielding one thick 45.6 g brown film of 90.2% dm HMT-PMBI (97.2% yield). The ^{1}H NMR spectra were taken of washed and dried membranes. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 8.97-7.66 (m, 6.15H), 7.66-7.04 (m, 6.00H), 4.30-3.78 (m, 9.57H), 3.78-3.50 (m, 1.16H), 2.44-1.49 (m, 17.88H). For repeated syntheses, the polymer was purified by different methods, such as precipitation into acetone rather than evaporation of dichloromethane. Additionally, if a lower than desired dm% was yielded, such as 86% dm instead of 89% dm, the same procedure could be repeated using DMSO as the solvent and a stoichiometric amount of iodomethane at 30 °C for 18 h. The resulting synthetic data is shown in Table S7. The dm% was calculated using eqn (S1).

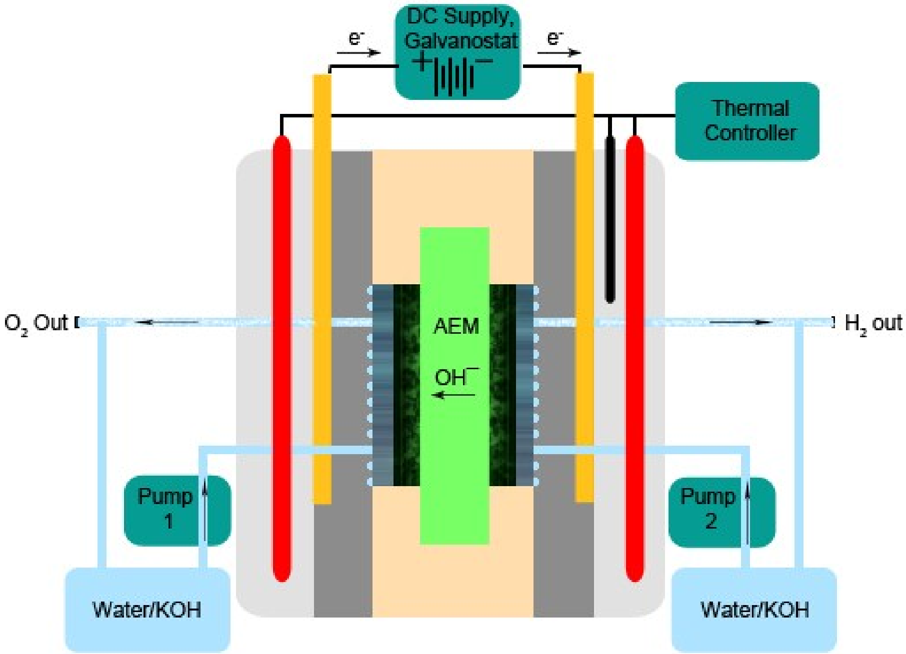
Determination of dm. The degree of methylation (dm) for polymers possessing >55% dm was calculated as previously reported.[3] Specifically, using the baseline corrected (MestReNova, "Full Auto Polynomial Fit") ^{1}H NMR spectrum of >55% dm HMT-PMBI (400 MHz, DMSO-d_6), the integration region 4.30-3.78 ppm was set to 12.00H and the respective integration for 3.78-3.50 ppm was calculated to be x. The dm% was then calculated using eqn (S1).

$$dm\% = 50\left(\frac{1}{1+\frac{x}{6}}\right) + 50 \qquad \text{(S1)}$$

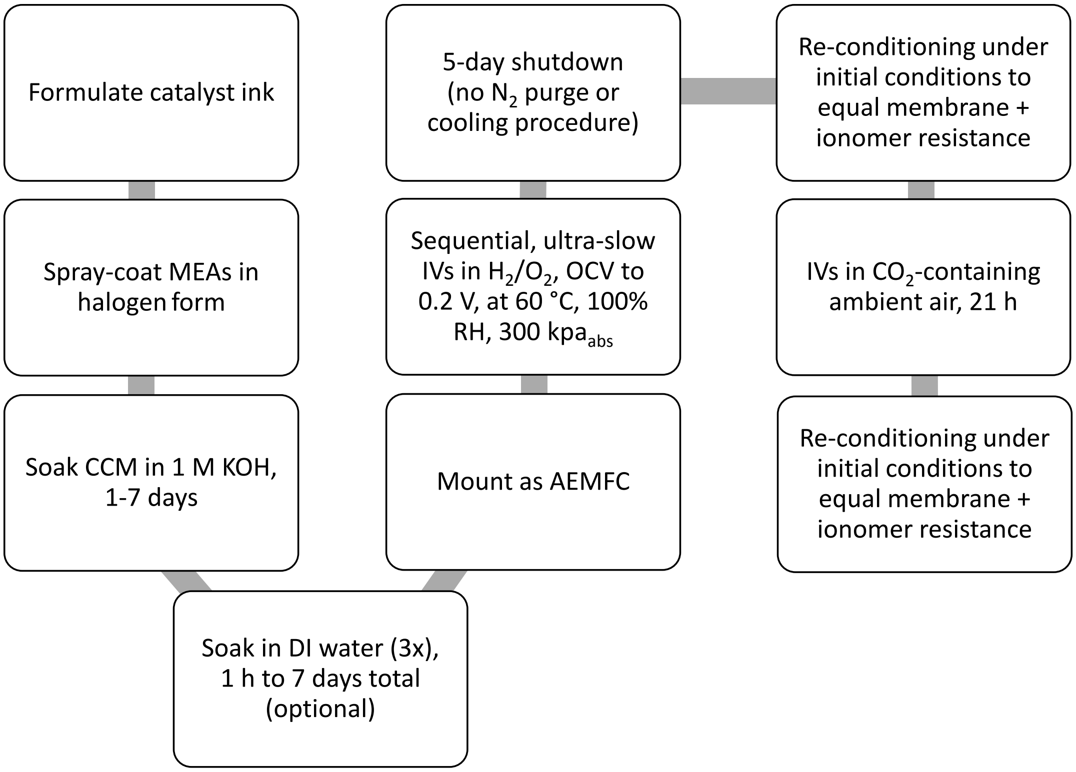
Also using eqn (S1), the dm% for ~50% dm HMT-PMBI was calculated from its ^{1}H NMR spectrum (400 MHz, CD_2Cl_2), where the integration of 4.46-3.87 ppm was set to 12.00H and the respective integration for 3.87-3.39 ppm was calculated to be x. The dm% was then used to calculate the IEC of the materials (eqn (6)), as preliminary measurements revealed that the IEC measured by titration was highly variable, depending upon which method was used to measure it (i.e., Mohr's method vs. acid-base titration) as well as the pre-treatment method (0.5 M vs 2.0 M ion exchange solutions), most likely due to changes in swelling and thus degree of ion exchange. IEC calculated from the degree of methylation, measured by ^{1}H NMR spectroscopy, is highly reproducible, fast, and requires minimal amounts of compound for its measurement.



Scheme S1 Experimental setup of the AEMFC used in this work.



Scheme S2 Experimental setup of the water electrolyzer used in this work.



Scheme S3 The AAEMFC test protocol used in this work, represented as a flow diagram.

AEMFC power density error analysis. All potential data taken at 5 min·pt^{-1} in the polarization curves representing 47.7, 48.9, and 49.2 mW cm^{-2} were paired according to current density (equal fluxes) and subjected to a paired student t-test with $\alpha = 0.005$, rejecting the H_o that difference = 0 in each comparison, statistically determining all three curves representing the three mentioned power densities were indeed different, as the p-values calculated were <0.005 for each pair. This gives a >99.5% confidence that successive improvements between each polarization curve occurred and therefore that the maximum power densities are different. Additionally, when five consecutive polarization curves were taken, the average power density of 45.2 mW cm^{-2} had a standard deviation of ±0.2 mW cm^{-2}, demonstrating that the peak power values of 47.7, 48.9, and 49.2 mW cm^{-2} are significantly different.

Table S1. Yield of BMA for each reaction performed.

Reaction #	Yield (g)	Yield (%)
1	587.6	88.2
2	577.5	86.6

Table S2. Yield of BME and respective reaction scale for each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.0	106.1	96.4
2+3	2.0	218.4	99.2
4+5	2.0	214.8	97.5
6+7	2.0	219.2	99.5
8+9	2.0	218.9	99.4
10+11	2.2	246.3	99.4

Table S3. Yield of HMTE, reaction scale, and amount of $Pd(PPh_3)_4$ used for each reaction performed.

Reaction #	Scale	$Pd(PPh_3)_4$ used (per mol% BME)	Yield (g)	Yield (%)
1	0.80	2.92 g (0.54%)	55.6	55.3
2	1.00	1.80 g (0.27%)	68.0	54.1
3	1.00	1.70 g (0.25%)	70.8	56.4
4	1.00	1.51 g (0.22%)	72.1	57.4
5	1.00	1.01 g (0.15%)	72.2	57.5
6	1.00	0.79 g (0.12%)	68.9	54.9
7	1.00	0.53 g (0.08%)	71.9	57.3
8	1.17	0.77 g (0.10%)	86.3	58.7

Table S4. Yield of DAB after recrystallization and the respective appearance.

Reaction #	Company[a]	DAB used (g)	Yield (g)	Yield (%)	Appearance
1	1	50.0	45.0	90.0	white/sandy sheets
2	1	50.0	42.8	85.6	white/sandy sheets
3	2	50.0	42.7	85.4	long-pointed sandy-sheets
4	2	50.0	42.3	84.6	large sandy-sheets
5	2	50.0	42.5	85.0	small sandy sheets
6	2	50.0	42.6	85.2	very large pointed sandy sheets (glass shards)
7	2	25.0	19.4	77.6	largest pointed yellowish sheets (glass shards)

[a] from which company the DAB was purchased from. Company 1 refers to TCI America and the DAB was received with 98% purity. Company 2 refers to Kindchem (Nanjing) Co., Ltd and the DAB was received with 98% purity.

Table S5. Yield of HMT-PBI with the respective DAB batch used for each reaction performed.

Reaction #	DAB batch	Yield (g)	Yield (%)	Appearance/Notes
1	1	26.0	102.8	off-white fibrous solid
2	1	26.9	106.3	off-white fibrous solid
3	1	25.9	102.4	off-white fibrous solid
4	1+2	25.8	102.0	off-white fibrous solid[a]
5	2	27.2	107.5	off-white fibrous solid[a]
6	2	25.6	101.2	off-white fibrous solid
7	2	26.2	103.5	thick off-white fibers[b]
8	2+3	25.6	101.2	thick white fibrous solid
9	3	25.5	100.8	thick white fibrous solid
10	3	25.4	100.4	thick white fibrous solid
11	3	26.2	103.5	thick white fibrous solid
12	3+4	25.8	102.0	thick white fibrous solid
13	4	25.7	101.6	thick white fibrous solid
14	4	27.3	107.9	thick white fibrous solid[c]
15	4	24.7	97.6	thick white fibrous solid[c]
16	4	25.3	100.0	thick white fibrous solid
17	4+5	25.5	100.8	thin white fibrous solid
18	5	25.5	100.8	thin white fibrous solid
19	5	25.7	101.6	thin white fibrous solid
20	5	25.4	100.4	thin white fibrous solid
21	5+6	25.6	101.2	thin white fibrous solid
22	6	26.2	103.5	very thick white fibrous solid
23	6	25.9	102.4	very thick white fibrous solid
24	6	26.4	104.3	very thick white fibrous solid
25	6+7	25.5	100.8	very thick white fibrous solid
26	7	25.7	101.6	very thick white fibrous solid

[a] turned partially yellow after being left in air overnight when wet in acetone (not immediately dried).

[b] polymer precipitated into ice-water rather than room temperature water.

[c] these two samples were likely accidently mixed when collecting the solid, as they were performed side-by-side. Their average yield is 102.8%, which matches the total overall yield.

Table S6. Yield of ~50% dm HMT-PMBI, reaction scale, amount of iodomethane (MeI) used, and calculated dm% from ^{1}H NMR spectroscopy data for each reaction performed.

Reaction #	Scale	MeI amount used (mL)	Yield (g)	Yield (%)	dm	Appearance
1	0.83	13.8	44.0	79.3	55.6%	pale brown powder[a]
2	1.00	18.5	53.3	83.3	51.4%	pale brown powder[b]
3	1.00	20.0	52.7	79.7	54.9%	pale yellow powder[b]
4	1.00	22.0	54.4	83.1	53.8%	pale yellow powder[c]
5	1.00	22.0	58.6	88.2	55.3%	pale brown powder
6	1.00	22.0	59.6	88.6	56.7%	brown powder
7	1.00	21.0	58.2	88.9	53.7%	pale brown powder
8	1.00	21.0	59.3	88.5	56.2%	brown powder
9	1.00	21.0	58.7	89.1	54.5%	pale brown powder
10	1.00	21.0	58.6	87.6	56.0%	brown powder
11	1.00	21.0	59.1	90.2	53.9%	pale brown powder

[a] polymer was precipitated into water and no potassium iodide was used in the purification process.

[b] polymer was precipitated into methanol and no potassium iodide was used in the purification process.

[c] polymer was precipitated into methanol with potassium iodide. No potassium iodide was used in the acetone purification step.

Table S7. Yield of >55% dm HMT-PMBI, amount of iodomethane (MeI) used, reaction time, and dm% as calculated by ^{1}H NMR spectroscopy data for each reaction performed.

Reaction #	MeI amount used (mL)	Reaction time (h)	Initial dm	Final dm	Yield (g)	Yield (%)
1[a]	10.5/0.6	16/19	55.6%	89.2%	31.6	70.6
2[b]	13.0	18	53.4%	89.4%	37.6	82.2
3	13.0	21	51.4%	90.2%	45.6	97.2
4	13.0	18	54.9%	88.9%	44.2	98.4
5	11.0	17	54.3%	86.5%	43.0	96.8
6	9.0	17	53.8%	82.8%	42.7	98.4
7[c]	18.0	90	55.3%	97.0%	47.2	99.7

[a] this reaction followed a two-step methylation process. The first methylation was performed in DCM for 16 h and the second methylation in DMSO for 19 h. The polymers were collected by precipitation.

[b] polymer was collected by precipitation into acetone containing potassium iodide.

[c] the initial MeI amount was 13.0 mL but was increased to 18.0 mL after 48 h and continued for a total of 90 h.

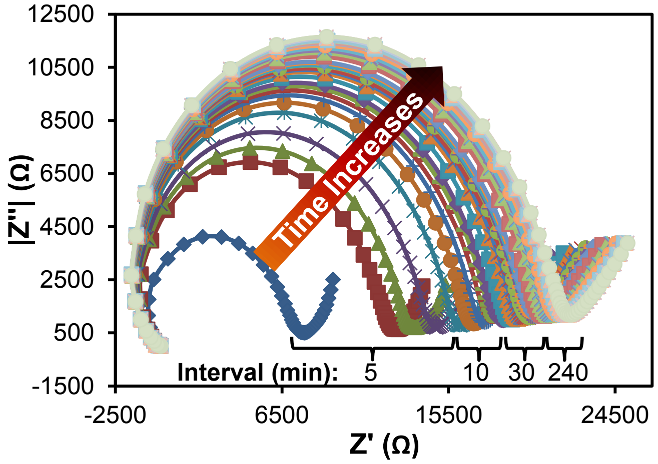


Fig. S1 Measured electrochemical impedance spectroscopy of 89% dm HMT-PMBI (OH^-) at 95% RH and 30 °C in air over time.

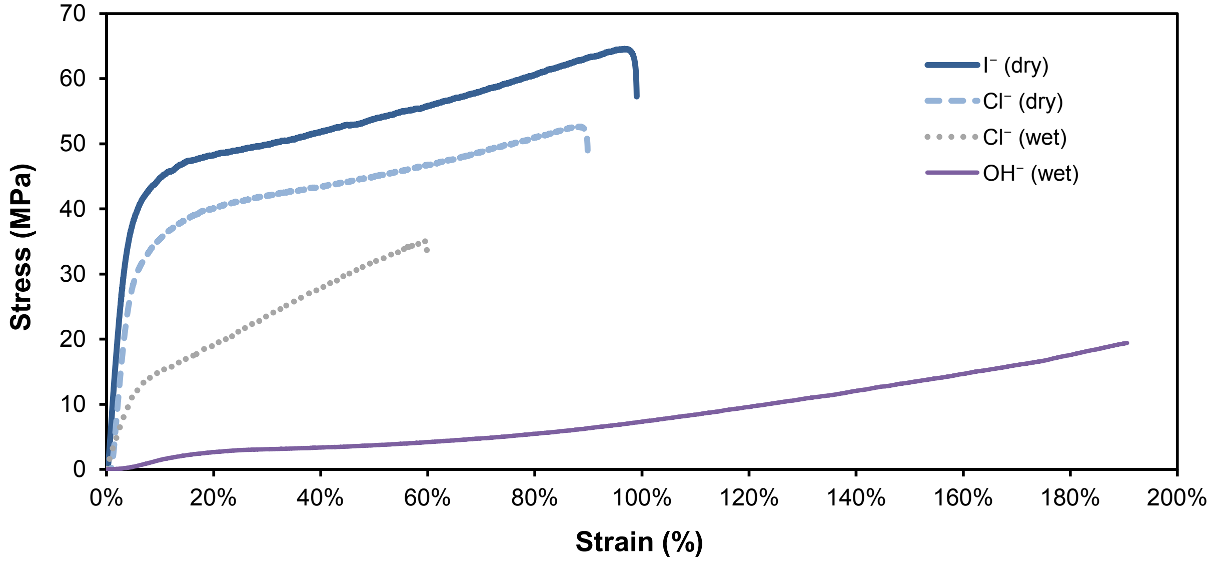


Fig. S2 Mechanical properties of 89% dm HMT-PMBI membranes in different ion forms, such as the as-cast form (I^-, dry), chloride-exchanged wet and dry forms, and hydroxide-exchanged wet form, measured in air.

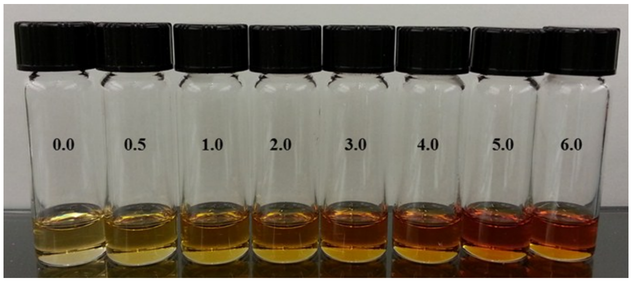


Fig. 3 Photograph of the dissolved HMT-PMBI membranes in DMSO-d_6 after 7 days in various NaOH concentrations (0.0 – 6.0 M) at 80 °C.

^{1}H NMR Spectra:

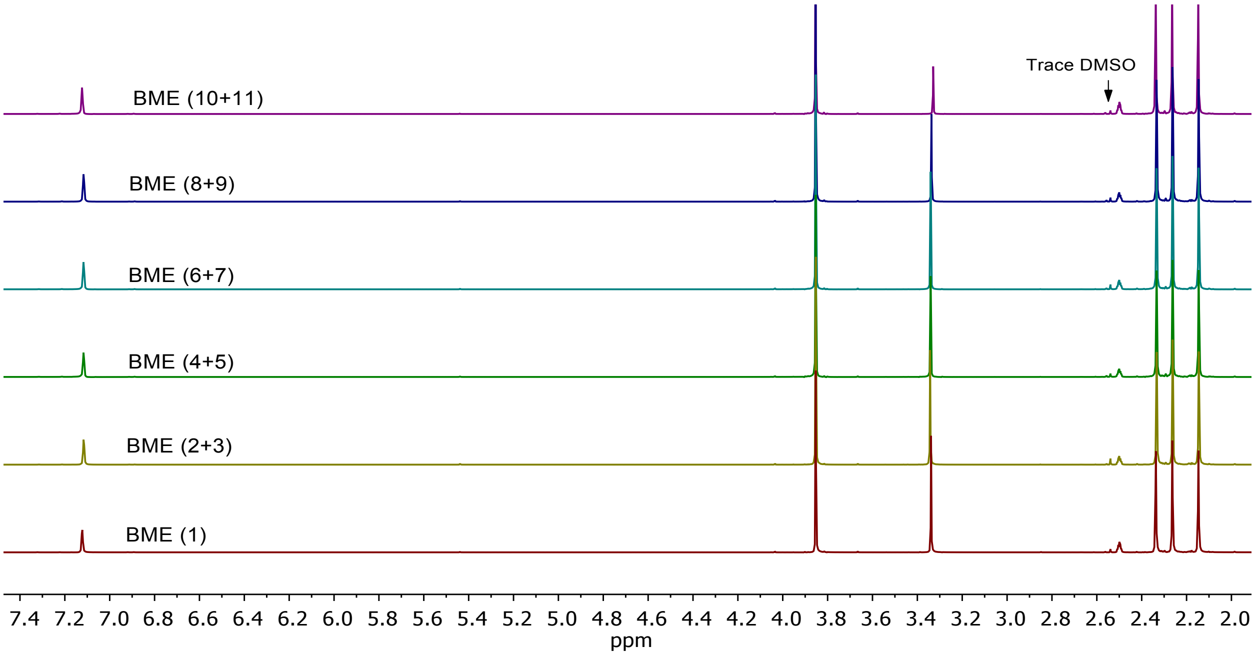


Fig. S4 Stacked ^{1}H NMR spectra (400 MHz, DMSO-d_6) of BME for each reaction performed.

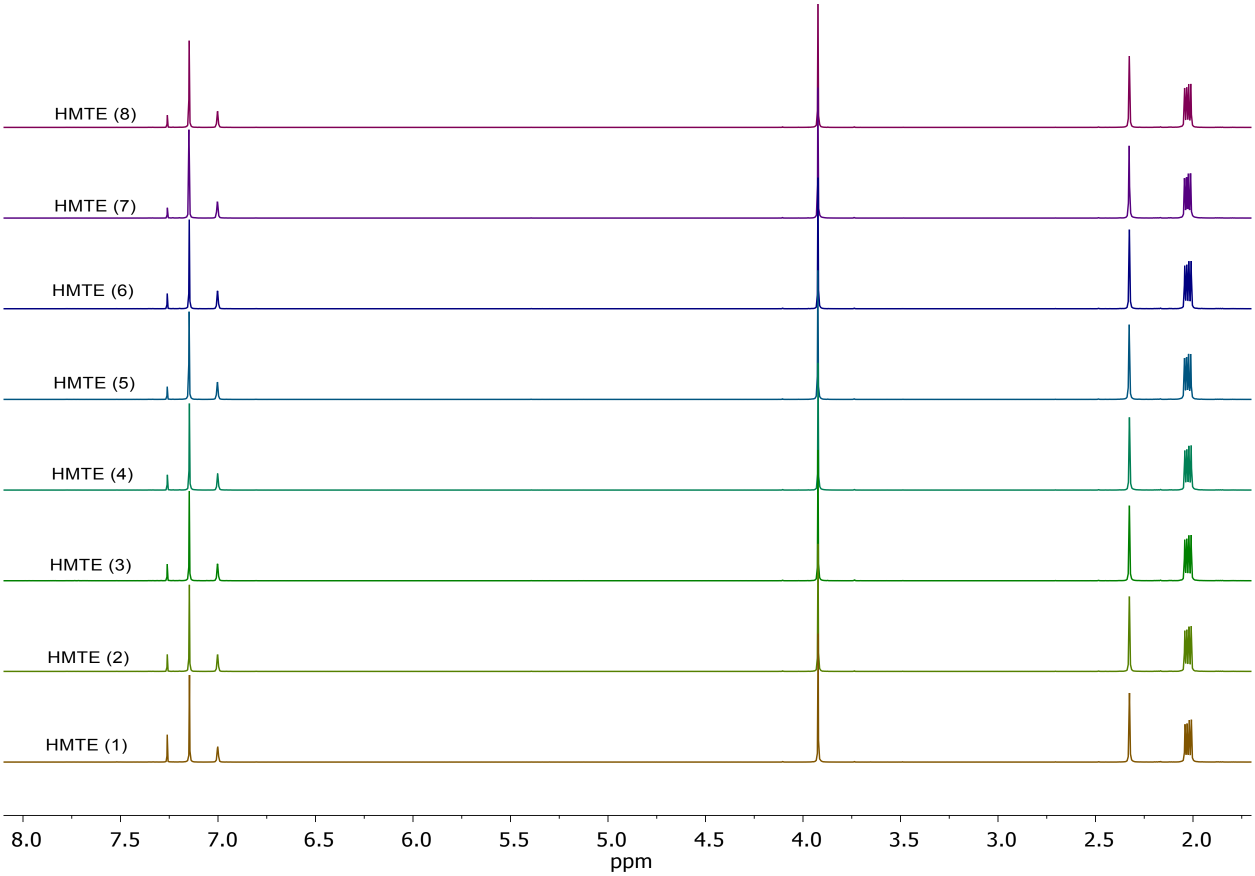


Fig. S5 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$) of HMTE for each reaction performed.

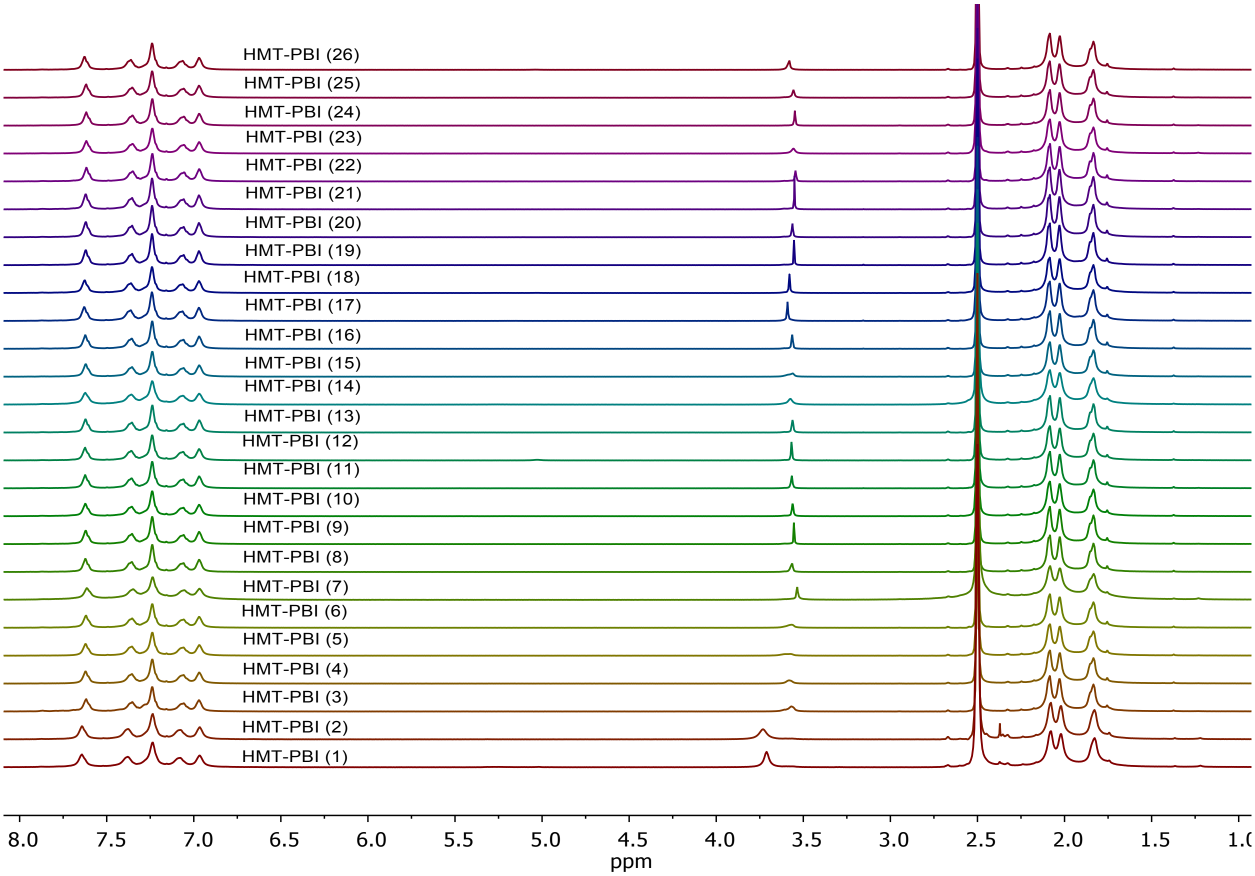


Fig. S6 Stacked ^1H NMR spectra (400 MHz, DMSO-d_6 + 5 drops of 40 wt% KOD in D_2O) of HMT-PBI for each reaction performed.

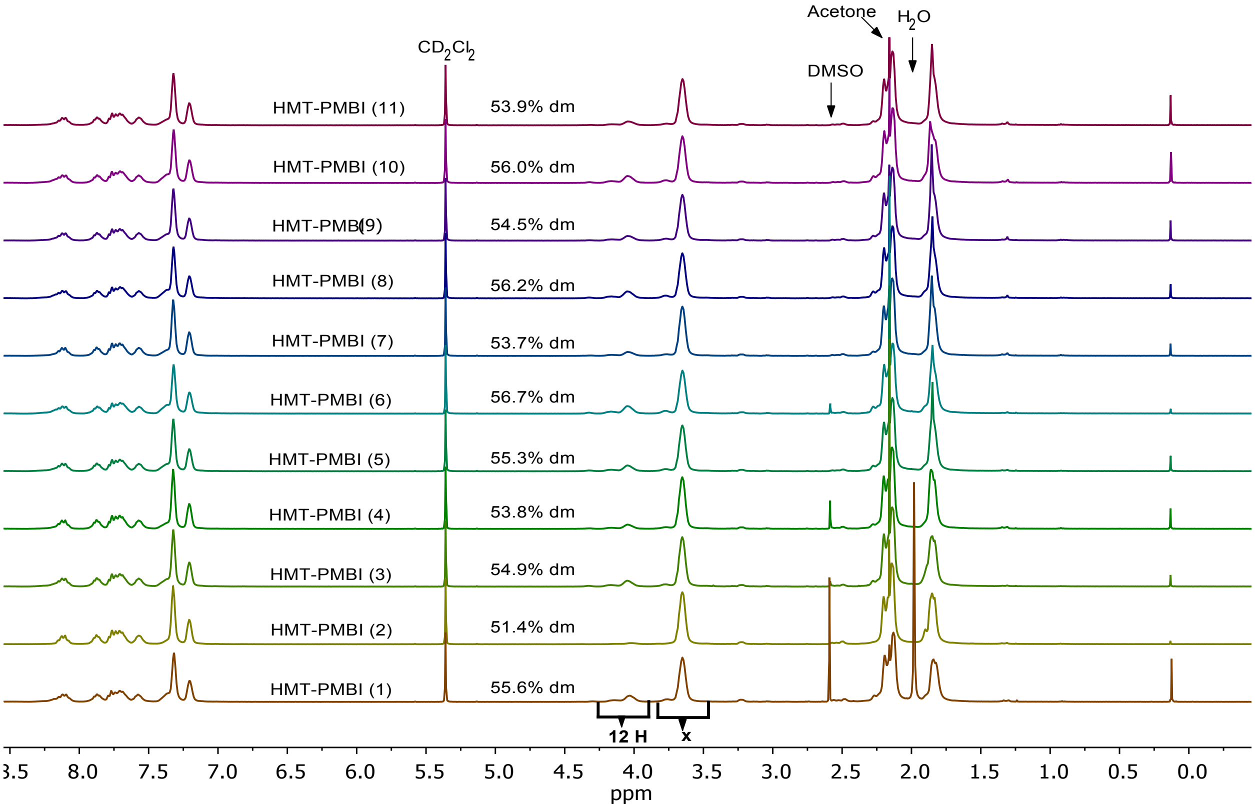


Fig. S7 Stacked ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of ~50% dm HMT-PMBI for each reaction performed.

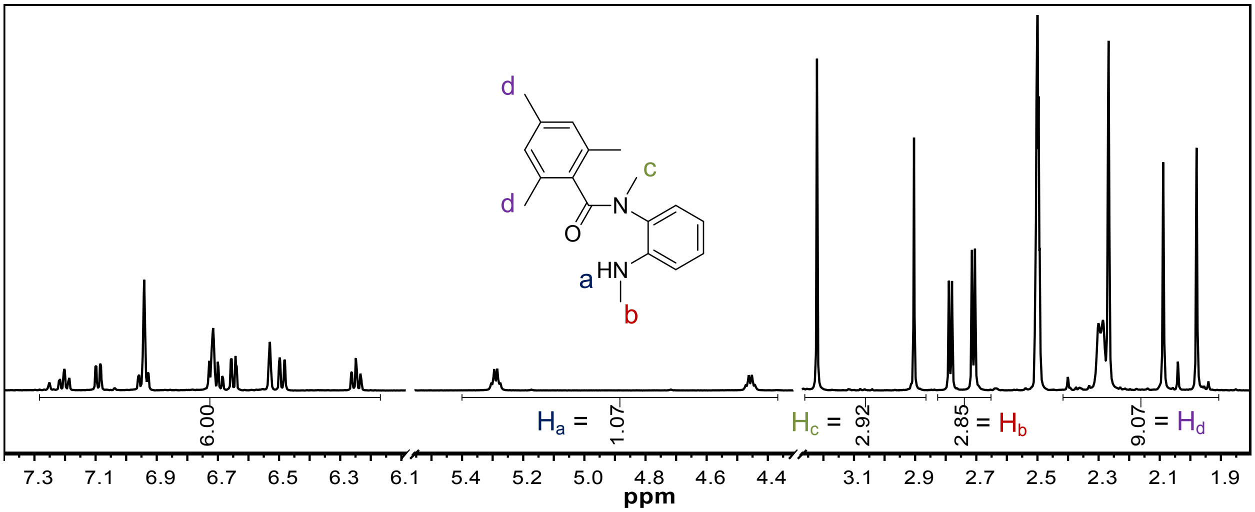


Fig. S8 Selected regions of the solution ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the degraded model compound MBIM-I$^-$ after exposing to 4 M KOH/CH_3OH/H_2O at 80 °C for 7 days. The chemical structure represents one of the suggested isomers that are formed.

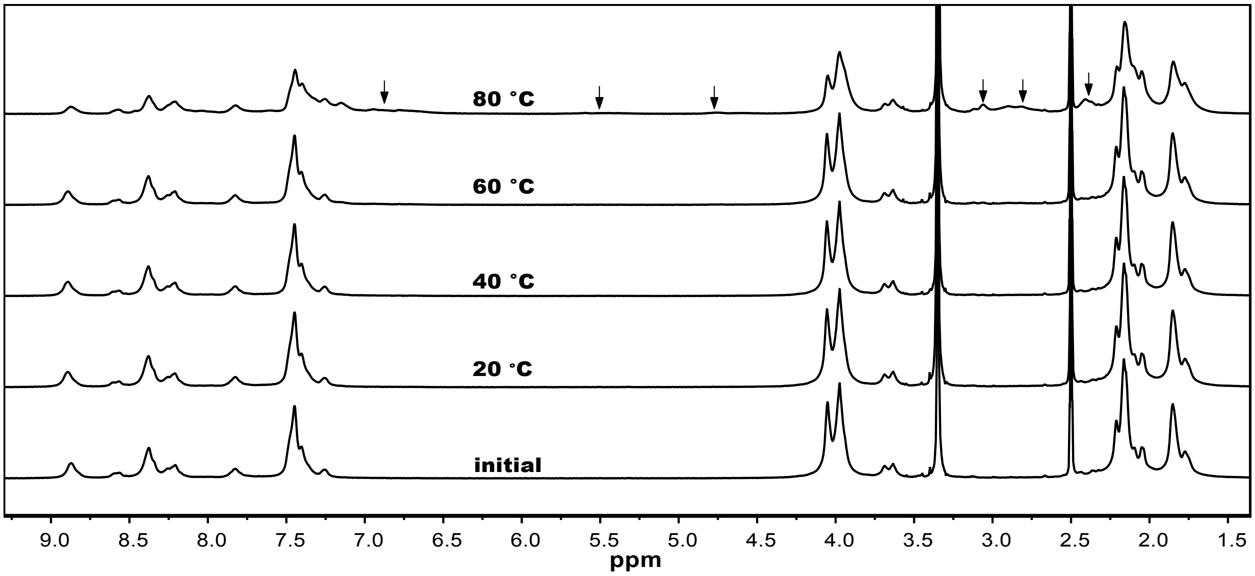


Fig. S9 The corresponding stacked solution ^{1}H NMR spectra (400 MHz, DMSO-d_6) of 89% dm HMT-PMBI in chloride form after membranes were soaked for 7 days in 2 M KOH at various temperatures (as labeled). The arrows show where new peaks are observed.

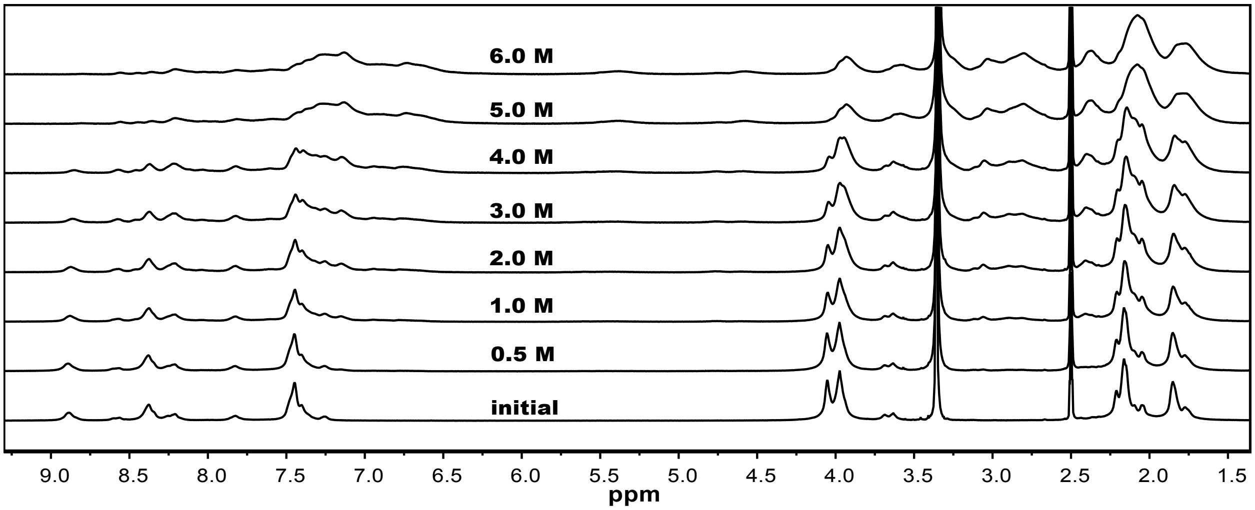


Fig. S10 The corresponding stacked solution ^{1}H NMR spectra (400 MHz, DMSO-d_6) of 89% dm HMT-PMBI in chloride form after membranes were soaked for 7 days in various concentrations of NaOH (as labeled) at 80 °C.

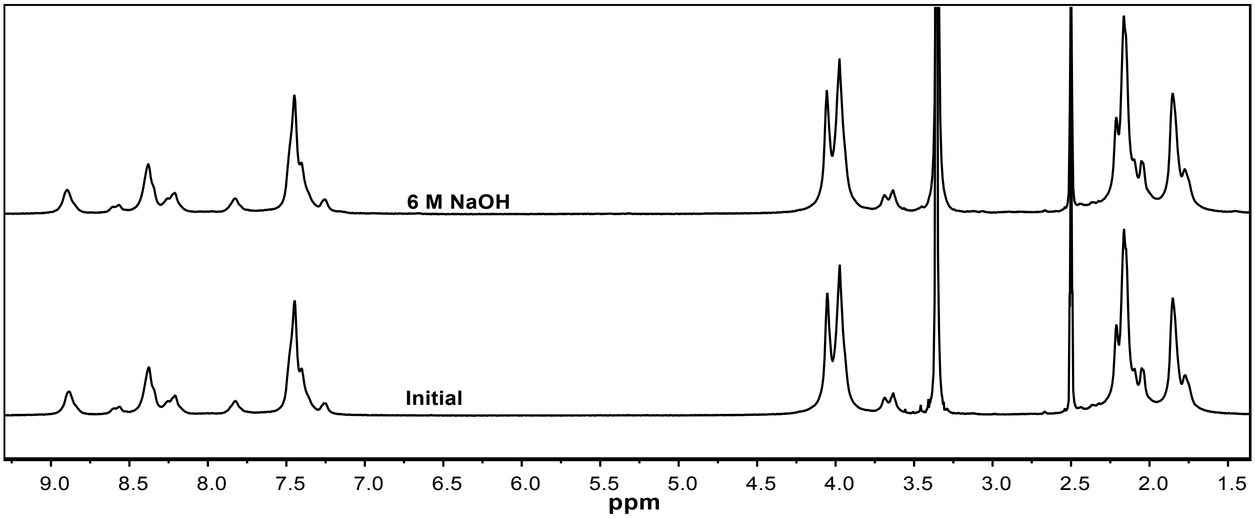


Fig. S11 Stacked solution ^{1}H NMR spectra (400 MHz, DMSO-d_6) of 89% dm HMT-PMBI after 7 days of membrane immersion in 6 M NaOH at room temperature, after being exchanged to chloride form.

REFERENCES

1 A. G. Wright, T. Weissbach and S. Holdcroft, *Angew. Chem. Int. Ed.*, 2016, **55**, 4818–4821.
2 Hoechst Ag, US4433168 A, 1984.
3 A. G. Wright and S. Holdcroft, *ACS Macro Lett.*, 2014, **3**, 444–447.