

Supporting Information for

Microwave-assisted Diels-Alder polycondensation of proton conducting poly(phenylene)s.

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List of Schemes

Scheme S1: The overall syntheses of a) monomer **TEAsBTC** and b) monomer **BP-L**. The amount of reagents used (u) and products yielded (y) represent a total over multiple reactions performed for each step. Yield percentages are reported as the averages and standard deviations of all reaction batches performed.

Scheme S2: Synthesis of intermediate **3**.

Scheme S3: Synthesis of intermediate **4**, 1,4-bisbenzil.

Scheme S4: Synthesis of **BTC**.

Scheme S5: Synthesis of **sBTC**.

Scheme S6: Synthesis of **TEAsBTC**.

Scheme S7: Synthesis of intermediate **8**.

Scheme S8: Synthesis of **BP-L**.

Scheme S9: Microwave-assisted or traditional oil bath synthesis of **sPPB-HNEt₃⁺**.

Scheme S10: Synthesis of **sPPB-H⁺**.

Scheme S11: The overall, up-scaled cation exchange from **sPPB-HNEt₃⁺** to **sPPB-H⁺**. The amount of reagents used (u) and products yielded (y) represent a total over multiple reactions performed for each step. Yield percentages are reported as the averages and standard deviations of all reaction batches performed.

Scheme S12: Preparation and separation of **sPPB-HNEt₃⁺_{Sol'n}** and **sPPB-HNEt₃⁺_{PreC}** during polymer syntheses.

Scheme S13: A representative Diels-Alder condensation reaction showing both possible isomers produced.

List of Figures

Figure S1: ^1H NMR of intermediate **3**.

Figure S2: ^{13}C NMR of intermediate **3**.

Figure S3: Intermediate **3** following reaction workup.

Figure S4: ^1H NMR of intermediate **4**.

Figure S5: ^{13}C NMR of intermediate **4**.

Figure S6: ^1H NMR of compound **BTC**.

Figure S7: ^{13}C NMR of compound **BTC**.

Figure S8: **BTC** following reaction workup.

Figure S9: ^1H NMR of compound **sBTC**.

Figure S10: ^{13}C NMR of compound **sBTC**.

Figure S11: Large scale synthesis of **sBTC**.

Figure S12: ^1H NMR of monomer **TEAsBTC**.

Figure S13: ^{13}C NMR of monomer **TEAsBTC**.

Figure S14: **TEAsBTC** following reaction workup.

Figure S15: ^1H NMR of compound **8**.

Figure S16: ^{13}C NMR of compound **8**.

Figure S17: Compound **8** obtained from ethanol recrystallization.

Figure S18: ^1H NMR of monomer **BP-L**.

Figure S19: ^{13}C NMR of monomer **BP-L**.

Figure S20: Microwave report for the synthesis of **sPPB-HNEt₃⁺_{MW}** described above.

Figure S21: ^1H NMR of polymer **sPPB-HNEt₃⁺** prepared by traditional oil bath (top) or microwave-assisted (bottom) methods. The inset depicts the aromatic regions of both spectra.

Figure S22: ^1H NMR of polymer **sPPB-HNEt₃⁺_{sol'n}** prepared via MWAS. The inset highlights the three predominant apparent singlets and their relative integrals (to one another) attributed to the 4 polymer core aromatic protons, H_{Core} , observed in three different chemical environments due to differing backbone arrangements: *p-p*, *m-m*, and *m-p* (left to right).³

Figure S23: ^1H NMR of polymer **sPPB-H⁺** prepared from **sPPB-HNEt₃⁺_{Trad}** (top) or **sPPB-HNEt₃⁺_{MW}** (bottom). The inset depicts the aromatic regions of both spectra.

Figure S24: Microwave experiment setup schematics for (a) pressurized experiments, performed using between 1 and 12 EasyPrep Plus vessels (4 pictured); and (b) Open vessel, larger batch experiments, performed in up to 3 L round bottom flasks (pictured, containing ~1.4 L H₂O for illustrative purposes only) equipped with a glass probe adapter.

Figure S25: CEM EasyPrep Plus pressure reactor vessel setup schematic.⁵ The control vessel is shown. All other reaction vessels were charged with identical stir bars and quantities of reagents and solvent, but did not possess a sapphire thermowell, nut, or nut plug.

Figure S26: Representative temperature vs. inputted microwave power vs. time plot for a 2 h MW reaction performed on a 1 g scale in 20 mL nitrobenzene at 195 °C.

Figure S27: Thermal experiment setup schematics depicting: (a) A 1 L experiment setup containing ~650 mL H₂O (for illustrative purposes only) highlighting the approximate internal solvent level of a reaction with respect to approximate oil levels, and the approximate probe location with respect to the reaction vessel and oil bath (for illustrative purposes only, actual probe visible in the back in a similar position), and; (b) A reaction vessel wrapped in four layers of aluminum foil insulation prepared for thermal polymerization.

Figure S28: ^1H NMR spectra of nitrobenzene (a) as received from commercial sources, prior to reaction use; (b) following polymerization and subsequent recycling twice; and (c) following polymerization and recycling five times.

Figure S29: Tensile stress-strain properties of **sPPB-H⁺**,¹ **sPPB-H⁺_{Trad}**, **sPPB-H⁺_{MW}**, and NR-211¹ membrane samples.

Figure S30: ^1H NMR spectra (DMSO-D₆) of **sPPB-H⁺_{MW}** polymer membranes before (red), following 1 h (green), and following 3 h (blue) exposure time to Fenton's reagent. The superimposed aromatic regions of each spectrum are shown in the inset. The H₂O/H₃O⁺ peak is typically located between 3.5 and 6.5 ppm.

Figure S31: ^1H NMR spectra (DMSO-D₆) of **sPPB-H⁺_{Trad}** polymer membranes before (red), following 1 h (green), and following 3 h (blue) exposure time to Fenton's reagent. The superimposed aromatic regions of each spectrum are shown in the inset. The H₂O/H₃O⁺ peak is typically located between 3.5 and 6.5 ppm.

List of Tables

Table S1: Reaction parameters for syntheses of intermediate **3**.

Table S2: Yields of intermediate **3**, and respective relative scale of each reaction performed.

Table S3: Yields of intermediate **4**, and respective relative scale of each reaction performed.

Table S4: Reaction parameters for **BTC** syntheses.

Table S5: Yields of **BTC**, and respective relative scale of each reaction performed.

Table S6: Yields of **sBTC**, and respective relative scale of each reaction performed.

Table S7: Yields of **TEAsBTC**, and respective relative scale of each reaction performed.

Table S8: Reaction parameters for intermediate **8**.

Table S9: Yields of intermediate **8**, and respective relative scale of each reaction performed.

Table S10: Reaction parameters for **BP-L** syntheses.

Table S11: Yields of **BP.L**, and respective relative scale of each reaction performed.

Table S12: Yields of **sPPB-HNEt₃⁺_{MW}**, and respective relative scale of each reaction.

Table S13: Reaction parameters for traditional **sPPB-HNEt₃⁺_{Trad}** syntheses (via oil bath).

Table S14: Yields of **sPPB-HNEt₃⁺_{Trad}**, and respective relative scale of each reaction.

Table S15: Yields of **sPPB-H⁺_{Trad}**, and respective relative scale of each reaction.

Table S16: Yields of **sPPB-H⁺_{MW}**, and respective relative scale of each reaction.

Table S17: Results of MW-assisted **sPPB-HNEt₃⁺** syntheses run between 1 – 5 h at 160 – 220 °C.

Table S18: GPC analyses of **sPPB-HNEt₃⁺_{sol'n}** from polymerizations run between 1 – 5 h at 160 – 220 °C.

Table S19: GPC analyses of **sPPB-HNEt₃⁺_{prec}** or **sPPB-HNEt₃⁺_{insoluble}** from polymerizations run between 1 – 5 h at 160 – 220 °C.

Table S20: Yields of MW-assisted **sPPB-HNEt₃⁺** syntheses run between 1 – 5 h at 160 – 220 °C.

Table S21: Proton conductivity values measured for assessed polymers at 30 °C and various RH.

Table S22: Proton conductivity values measured for assessed polymers at 80 °C and various RH.

Table S23: Polymer regiochemistry data and corresponding ratios for **sPPB-HNEt₃⁺_{MW}**.

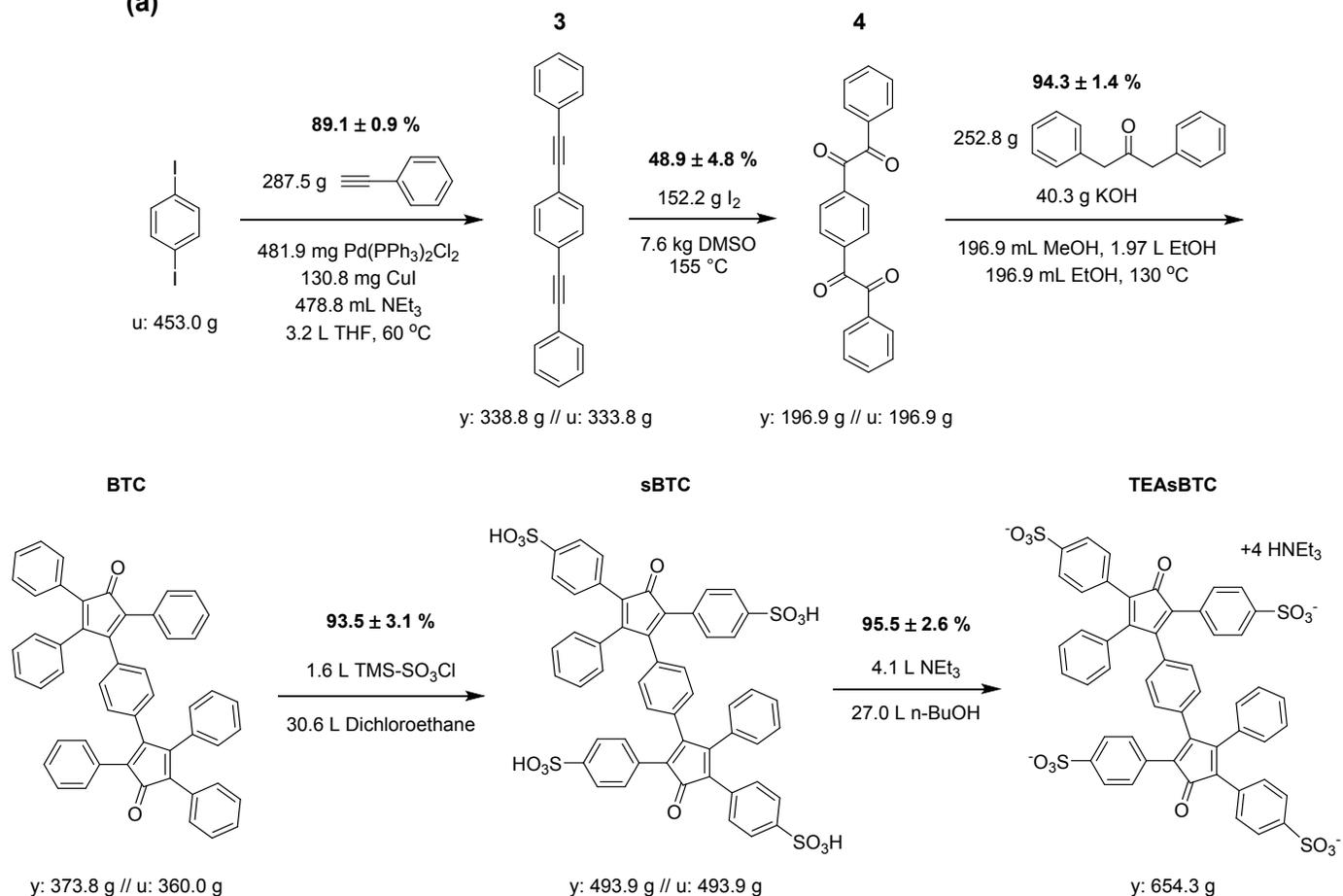
Table S24: Polymer regiochemistry data and corresponding ratios for **sPPB-HNEt₃⁺_{Trad}**.

Materials

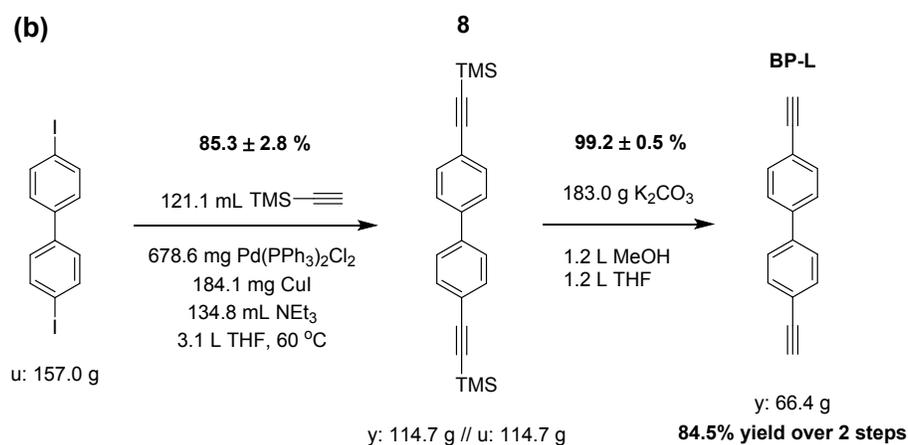
Triethylamine (NEt_3 , 99%), activated charcoal (G-60), and hydrochloric acid (HCl, ACS reagent, 36.5-38% content) were purchased from Anachemia Science. 1,4-diodobenzene (98%) and phenylacetylene (98%) were purchased from Combi-Blocks Inc., and used without purification. Acetone (Certified ACS), dichloromethane (DCM, Certified ACS stabilized), methanol (MeOH, reagent grade), pentane (reagent grade), ethyl acetate (Certified ACS), silica gel (S825-1, 230-400 mesh, grade 60), anhydrous magnesium sulfate (MgSO_4 , Certified Powder), and Celite™ (545 Filter aid, not Acid-washed powder) were purchased from Fisher Scientific. Nitrobenzene (PhNO_2 , 98%, reagent plus), dimethylformamide (DMF, Chromatosolv® HPCL grade), trimethylsilylchlorosulfonate ($\text{TMSO-SO}_2\text{-Cl}$, 99%), and lithium bromide (LiBr, ReagentPlus®, >99%) were purchased from Sigma-Aldrich Canada Co. Nitrobenzene was degassed with argon prior to each use. All other compounds were used without any further purification. Ethanol (EtOH, 99%) was purchased from Commercial Alcohols. Trimethylsilylacetylene (lot number 003013I12J) was purchased from Oakwood Chemicals. Diethyl ether anhydrous (Et_2O , ACS reagent) and potassium carbonate anhydrous (K_2CO_3 , ACS grade) were purchased from ACF Montreal. Chloroform (CHCl_3 , ACS grade), dimethylsulfoxide (DMSO, ACS grade), sodium hydroxide (NaOH, ACS grade) and iodine (I_2 , analytical reagent) were purchased from BDH. Petroleum ether (reagent grade), *n*-butanol (*n*-BuOH, reagent grade), potassium hydroxide (KOH, reagent grade, min 85%), sulfuric acid (H_2SO_4 , reagent grade, 95-98%), potassium carbonate anhydrous (K_2CO_3 , Reagent ACS, min 99%), and tetrahydrofuran (THF, ACS grade) were purchased from Caledon Laboratory Chemical. 1,3-diphenylacetone (ACS reagent, 98%) was purchased from Tokyo Chemical Industry Co., Ltd. Argon (PP 4.8) was purchased from Praxair. Diphenylphosphine palladium dichloride ($\text{Pd}(\text{P}(\text{phi})_3)_2\text{Cl}_2$, 97%) and copper(I) iodide (>99.9%) were purchased from Strem Chemicals. Finally, dimethylsulfoxide- d_6 (D, 99.9%), acetone- d_6 (D, 99.9%), and methylene chloride- d_2 (D, 99.8%, CD_2Cl_2) were purchased from Cambridge Isotope Laboratories, Inc.

Synthesis

(a)

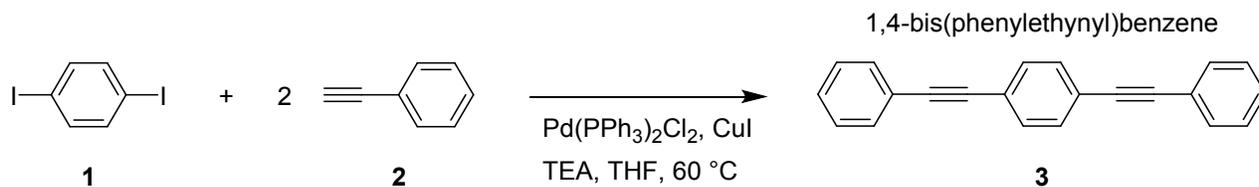


(b)



Scheme S1: The overall syntheses of a) monomer **TEAsBTC** and b) monomer **BP-L**. The amount of reagents used (u) and products yielded (y) represent a total over multiple reactions performed for each step. Yield percentages are reported as the averages and standard deviations of all reaction batches performed.

Intermediate 3: 1,4-bis(phenylethynyl)benzene



Scheme S2: Synthesis of intermediate **3**.

Table S1: Reaction parameters for syntheses of intermediate **3**.

Parameters	Previous	Current
Scale	5.0 g	≤ 253.0 g
Pd cat.	5 mol% = 532 mg	0.05 mol% = 269 mg
Cu cat.	5 mol% = 144 mg	0.05 mol% = 73 mg
Solvent	50x v/w – HNEt ₂	8x v/w – THF/Triethylamine
Yield	90-95%	89.1 ± 0.9%
Purity (¹ H NMR approximation)	≥99%	≥95%

Table S2: Yields of intermediate **3**, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	38.0	90.1%
2	3.00	112.5	88.9%
3	5.06	188.3	88.2%
Total		338.8	89.1 ± 0.9%

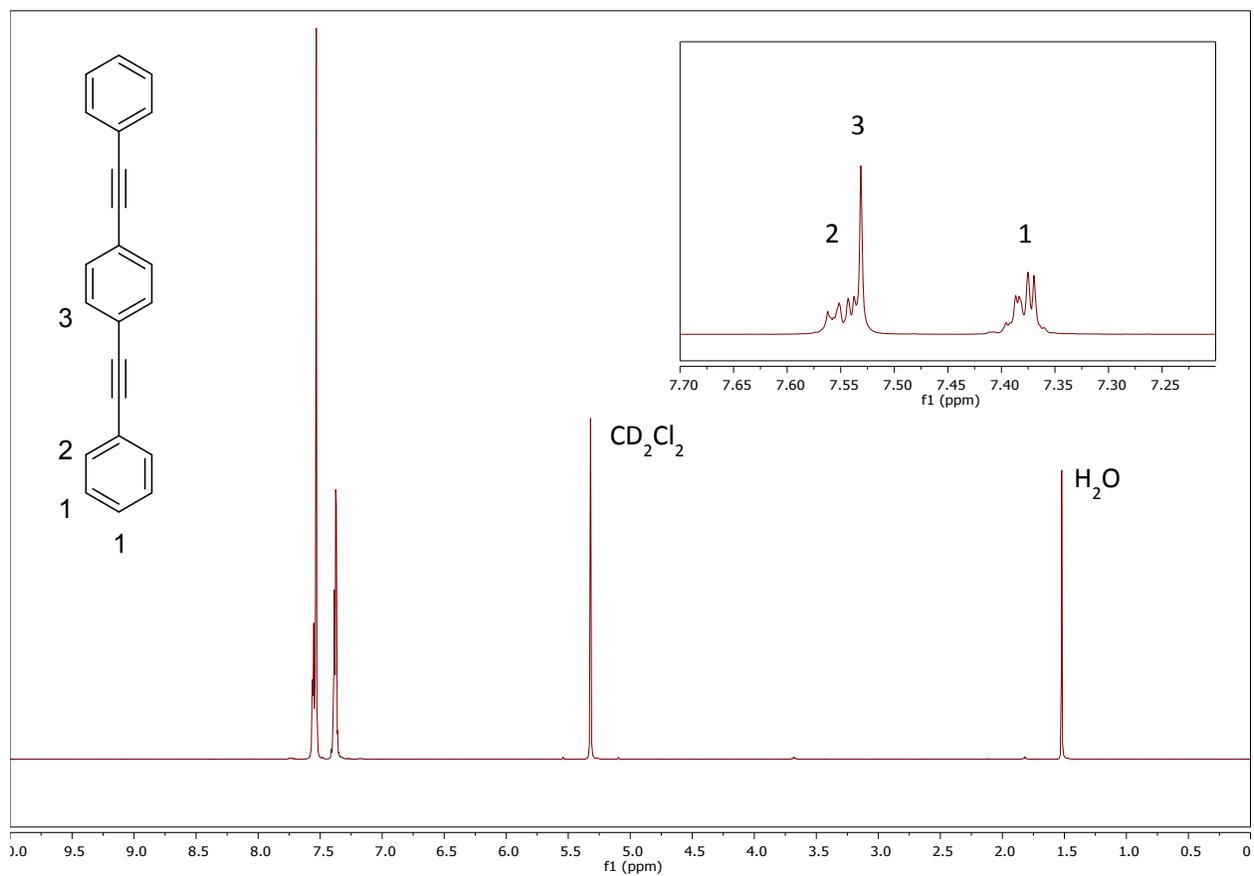


Figure S1: ^1H NMR of intermediate **3**.

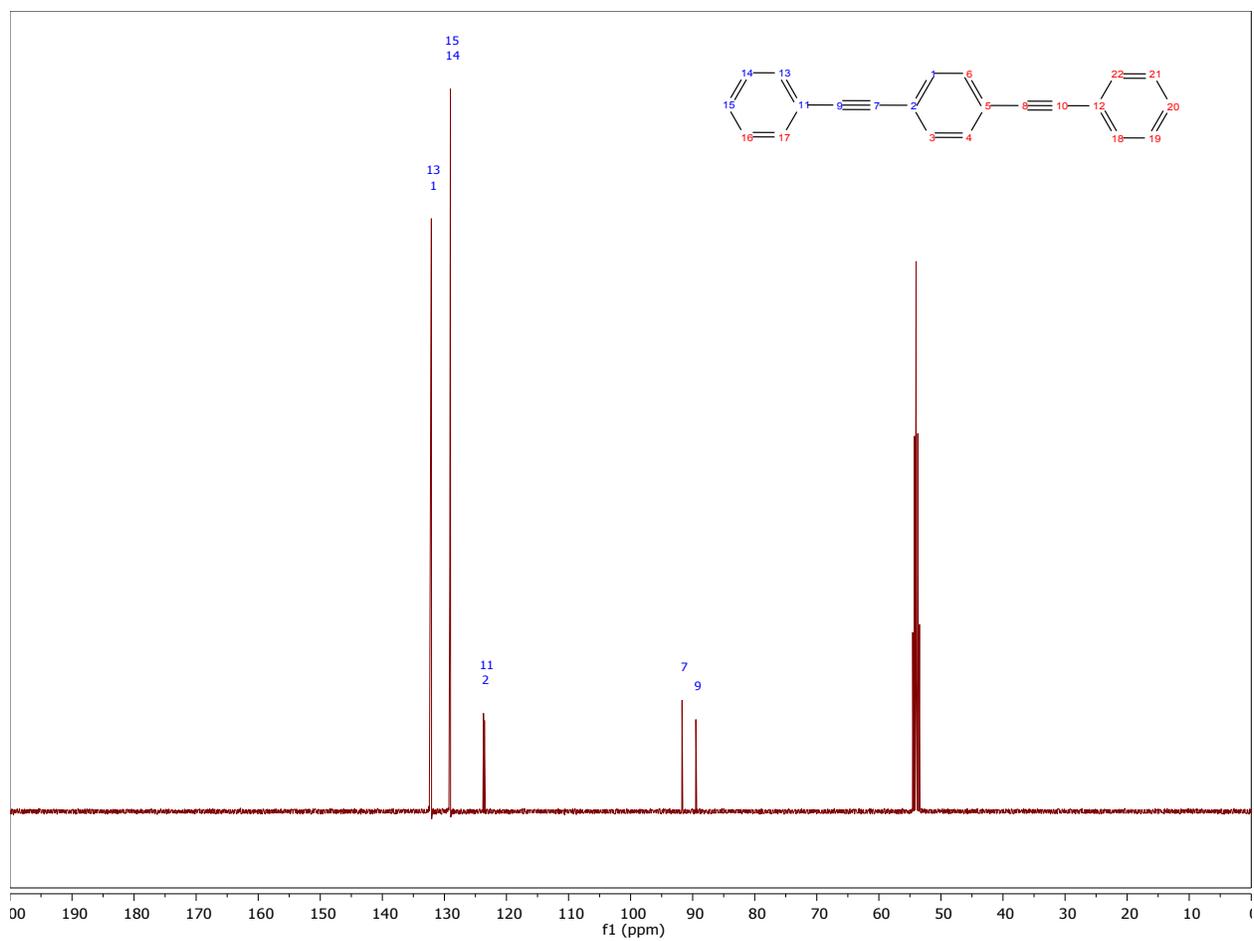


Figure S2: ¹³C NMR of intermediate **3**.

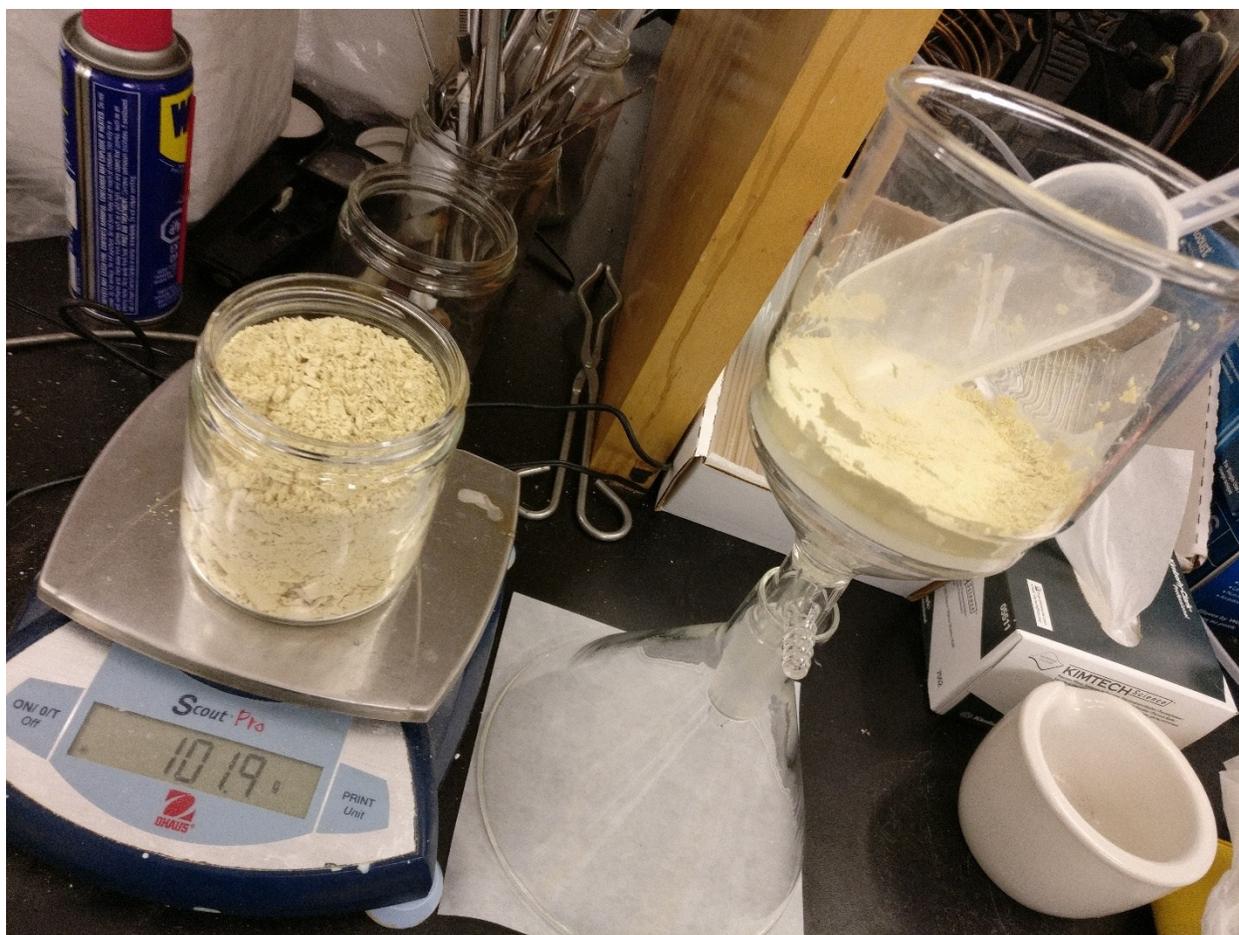
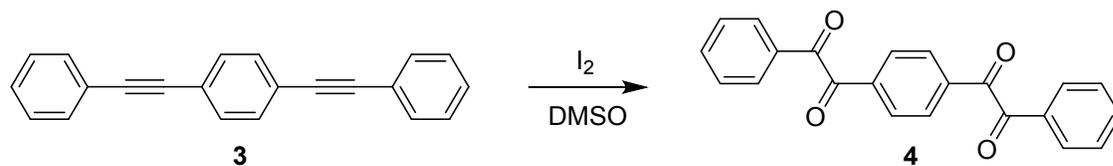


Figure S3: Intermediate **3** following reaction workup.

Intermediate 4: 1,4-bisbenzil



Scheme S3: Synthesis of intermediate 4, 1,4-bisbenzil.

Table S3: Yields of intermediate 4, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	28.5	57.9%
2	1.04	23.6	46.3%
3	2.09	46.0	44.7%
4	2.09	47.4	46.0%
5	1.00	24.3	49.4%
6	1.13	27.1	49.0%
Total		196.9	48.9 ± 4.8%

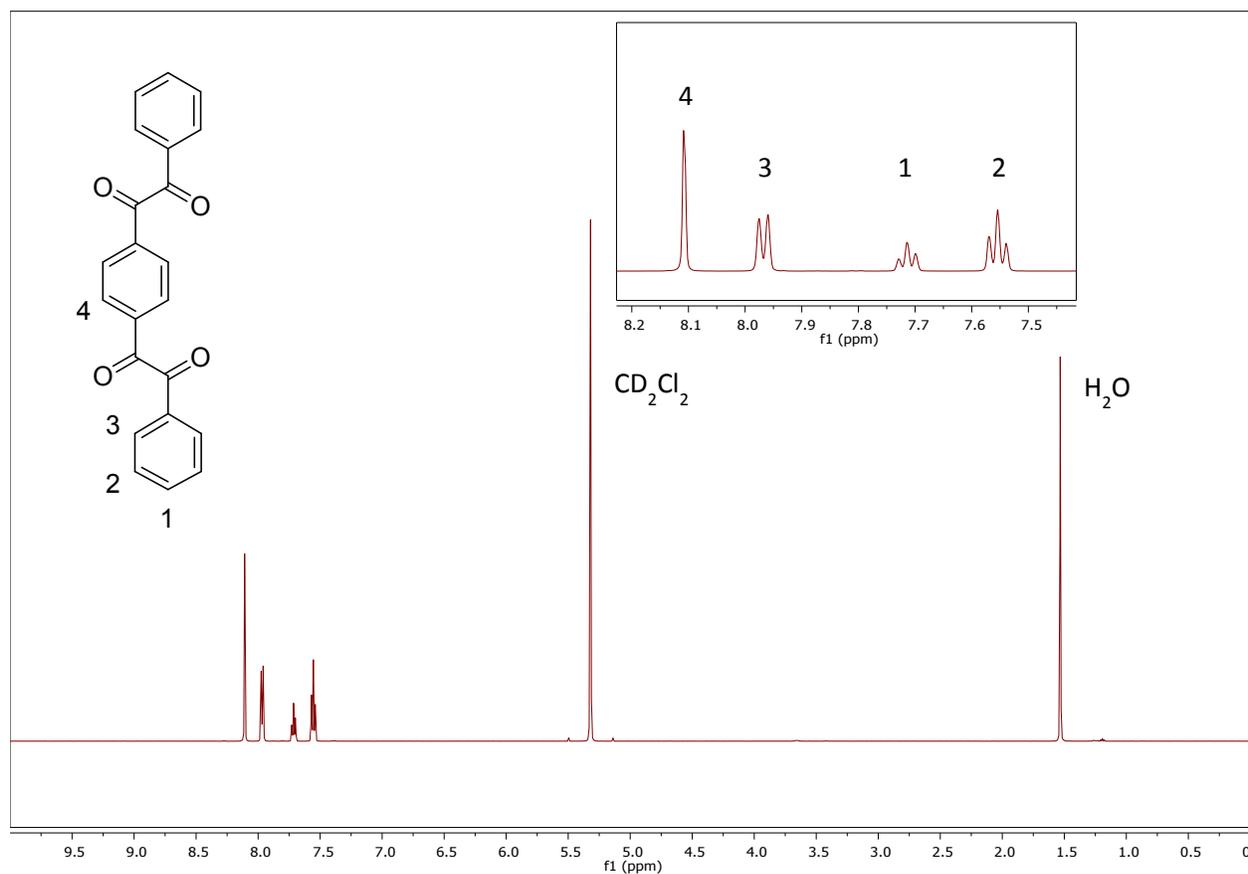


Figure S4: 1H NMR of intermediate 4.

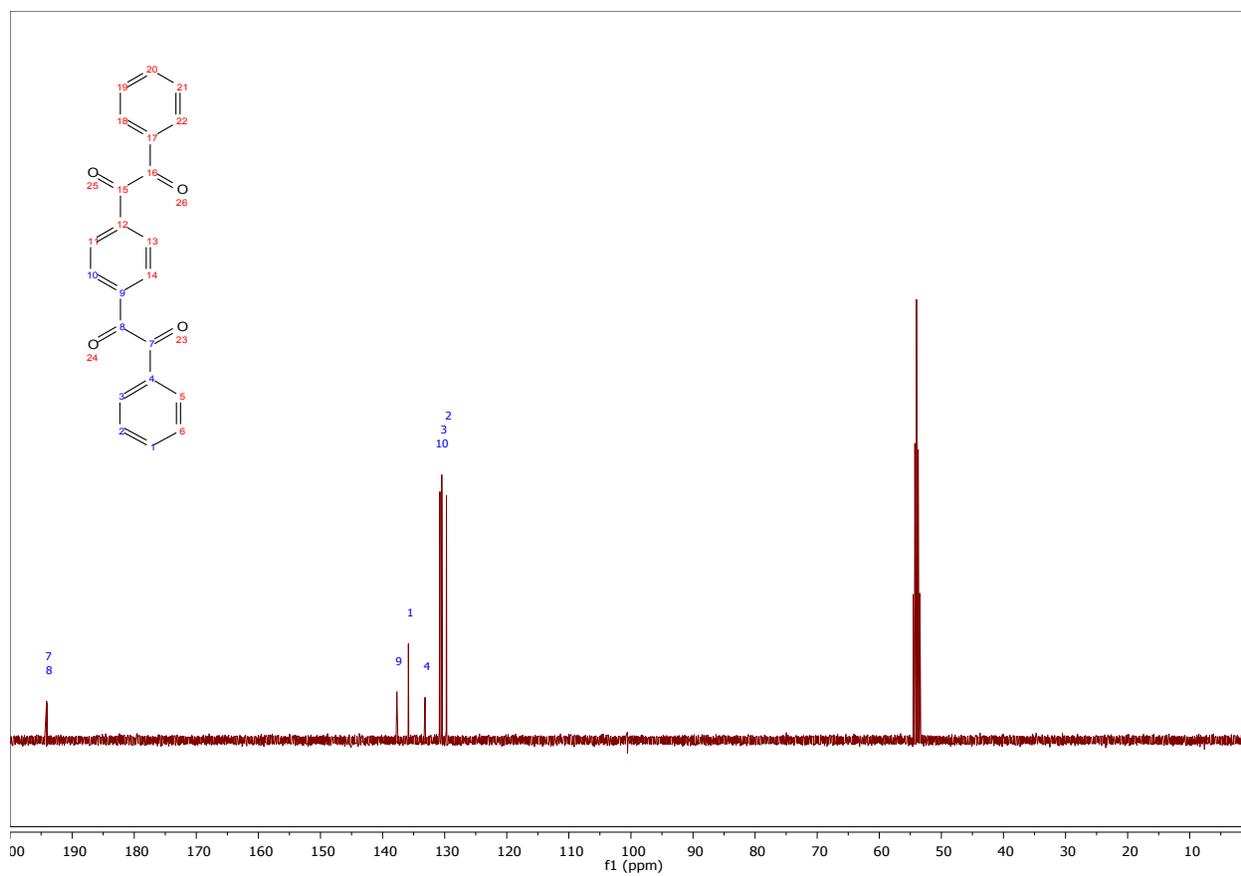
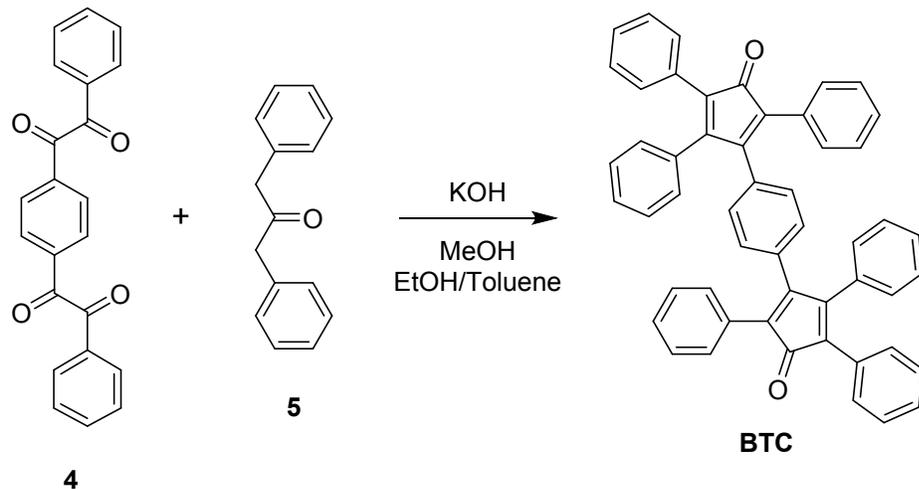


Figure S5: ¹³C NMR of intermediate 4.

Compound BTC: 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene



Scheme S4: Synthesis of **BTC**.

Table S4: Reaction parameters for **BTC** syntheses.

Parameters	Previous ¹	Current
Scale	≤ 6.5 g	≤ 71.0 g
Solvent	EtOH	1:10:1 MeOH:EtOH:Toluene
Solvent ratio	60-100x v/w	12x v/w
Yield	67-70%	94.3 ± 1.4%
Purity (¹ H NMR approximation)	≥99%	≥90%

Table S5: Yields of **BTC**, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	62.0	94.6%
2	1.41	89.0	96.2%
3	1.46	89.0	92.9%
4	2.18	133.8	93.5%
Total		373.8	94.3 ± 1.4%

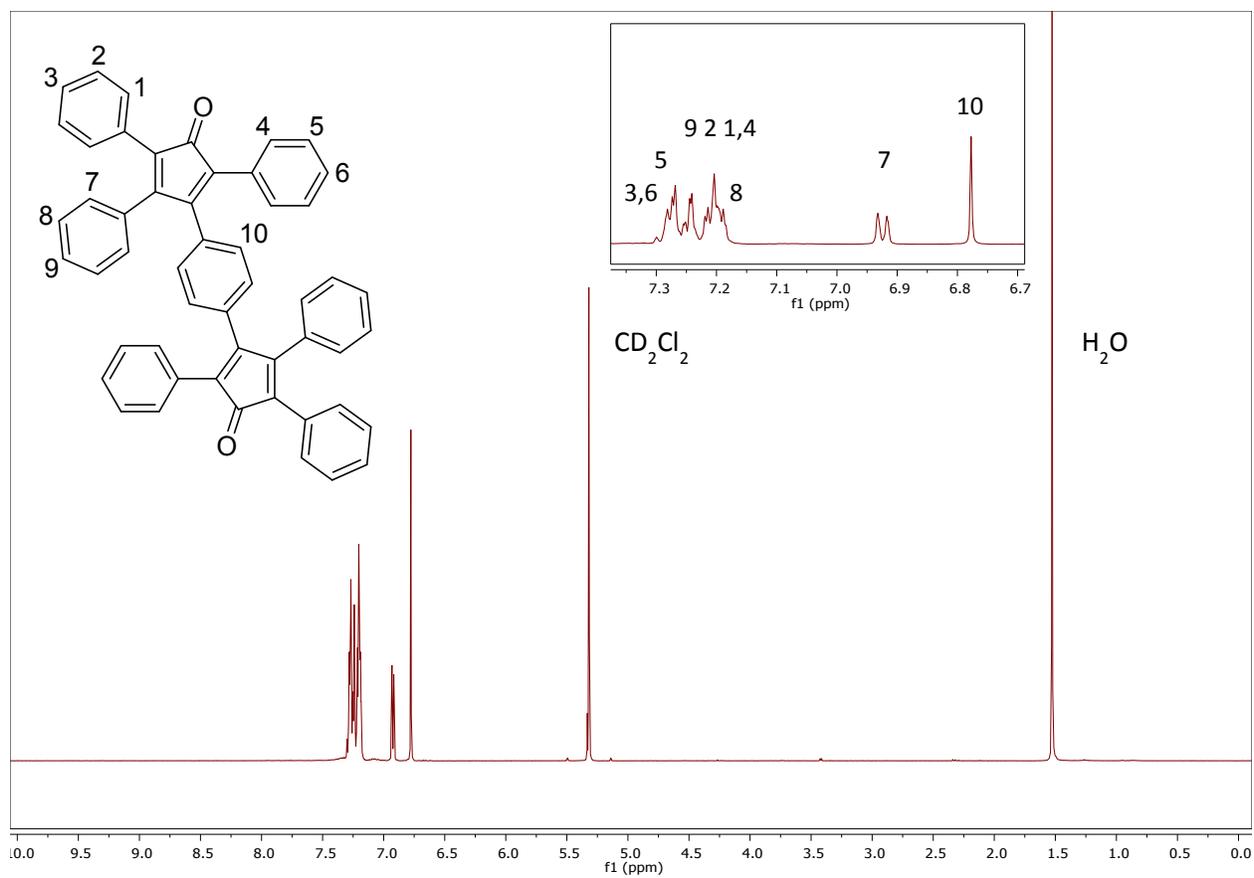


Figure S6: ^1H NMR of compound BTC.

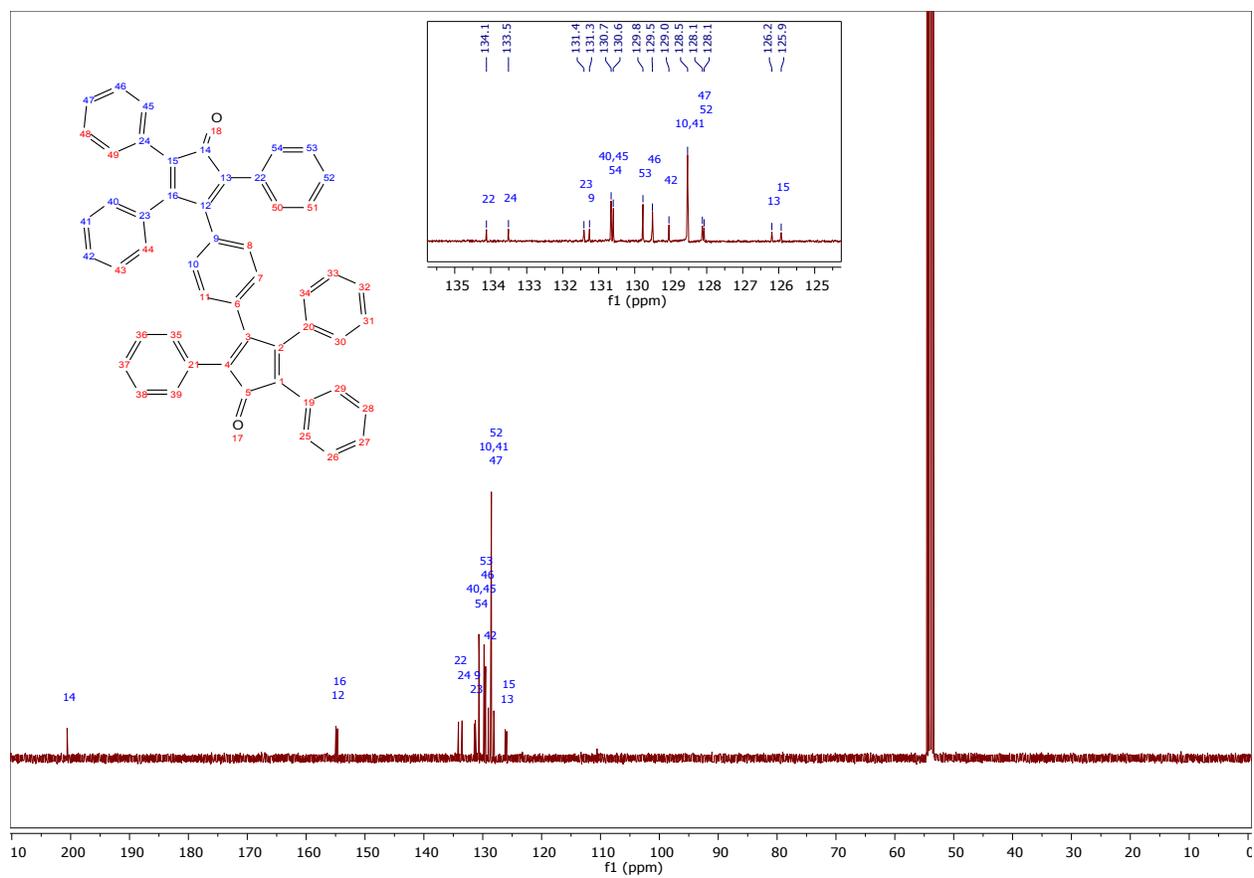
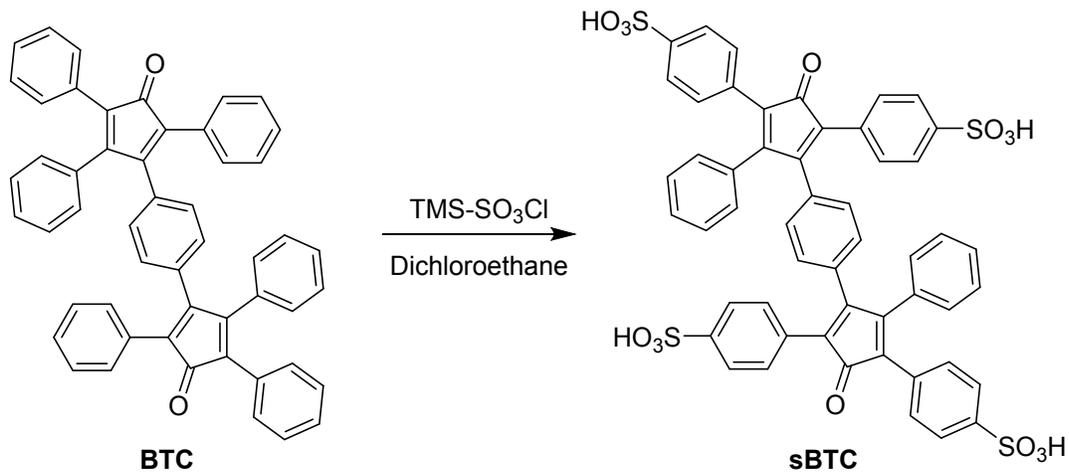


Figure S7: ^{13}C NMR of compound BTC.



Figure S8: BTC following reaction workup.

Compound sBTC: Tetra(para-sulfonated) bistetracyclone



Scheme S5: Synthesis of sBTC.

Table S6: Yields of sBTC, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	13.4	91.6%
2	5.00	70.5	96.3%
3	5.00	65.0	88.8%
4	5.00	68.5	93.6%
5	5.00	70.0	95.7%
6	5.00	69.8	95.4%
7	5.00	65.8	89.9%
8	5.00	70.9	96.9%
Total		493.9	93.5 ± 3.1%

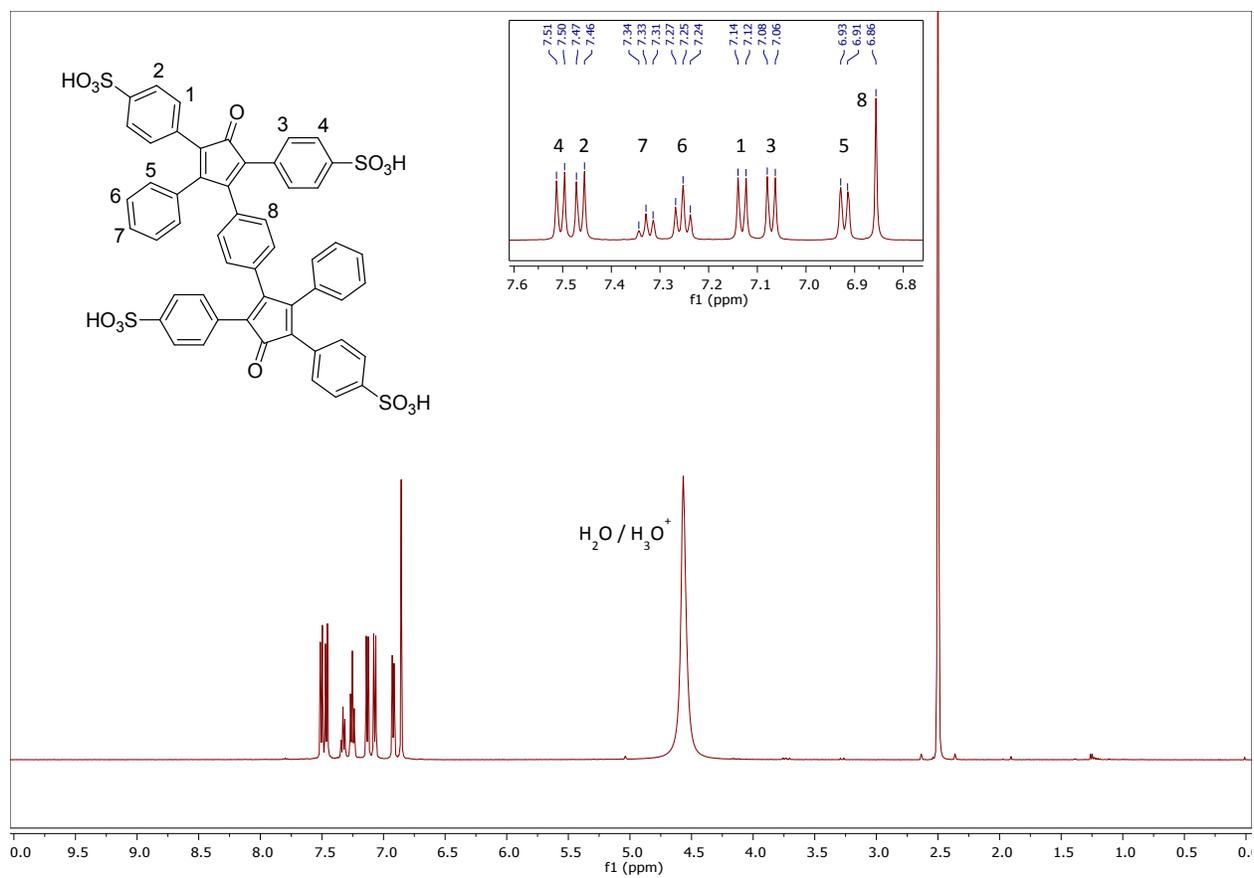


Figure S9: ¹H NMR of compound sBTC.

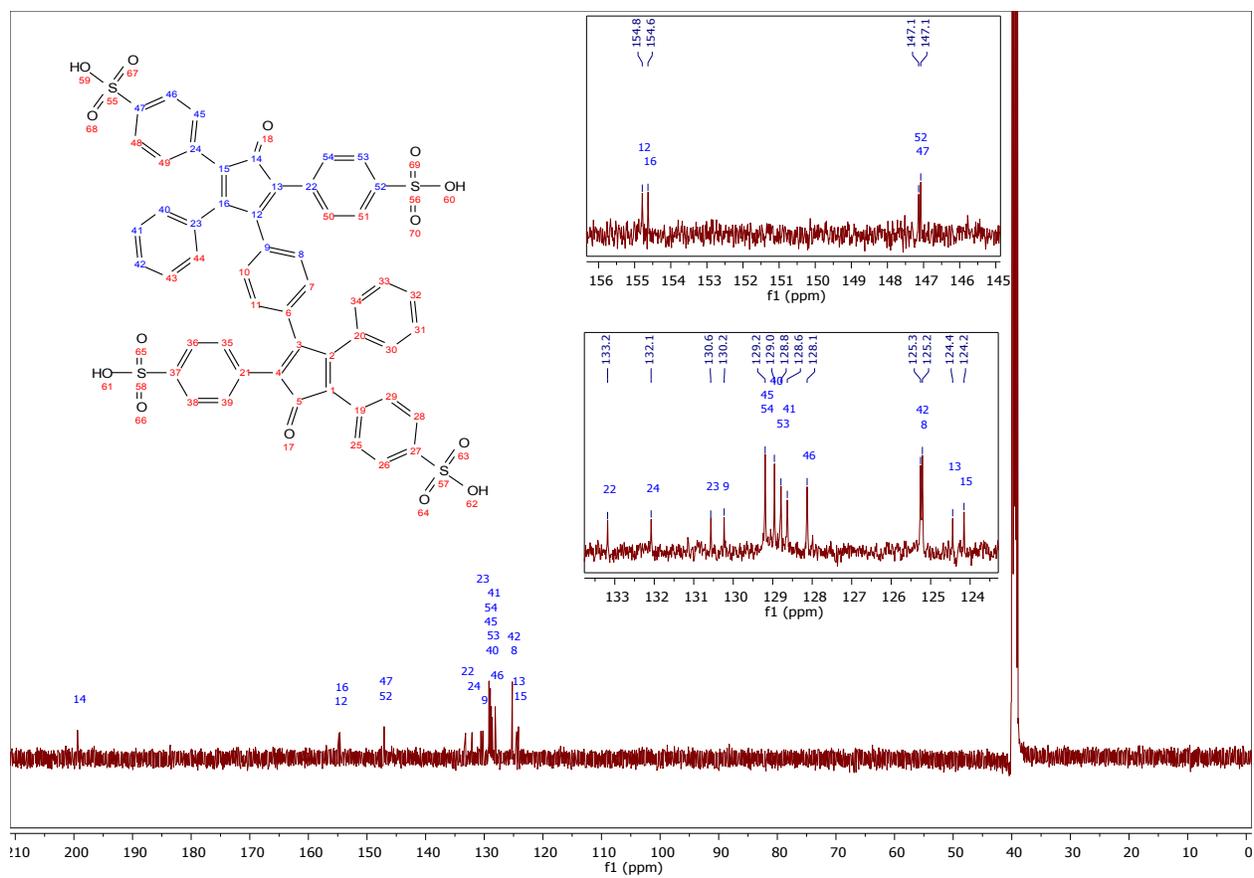


Figure S10: ^{13}C NMR of compound sBTC.

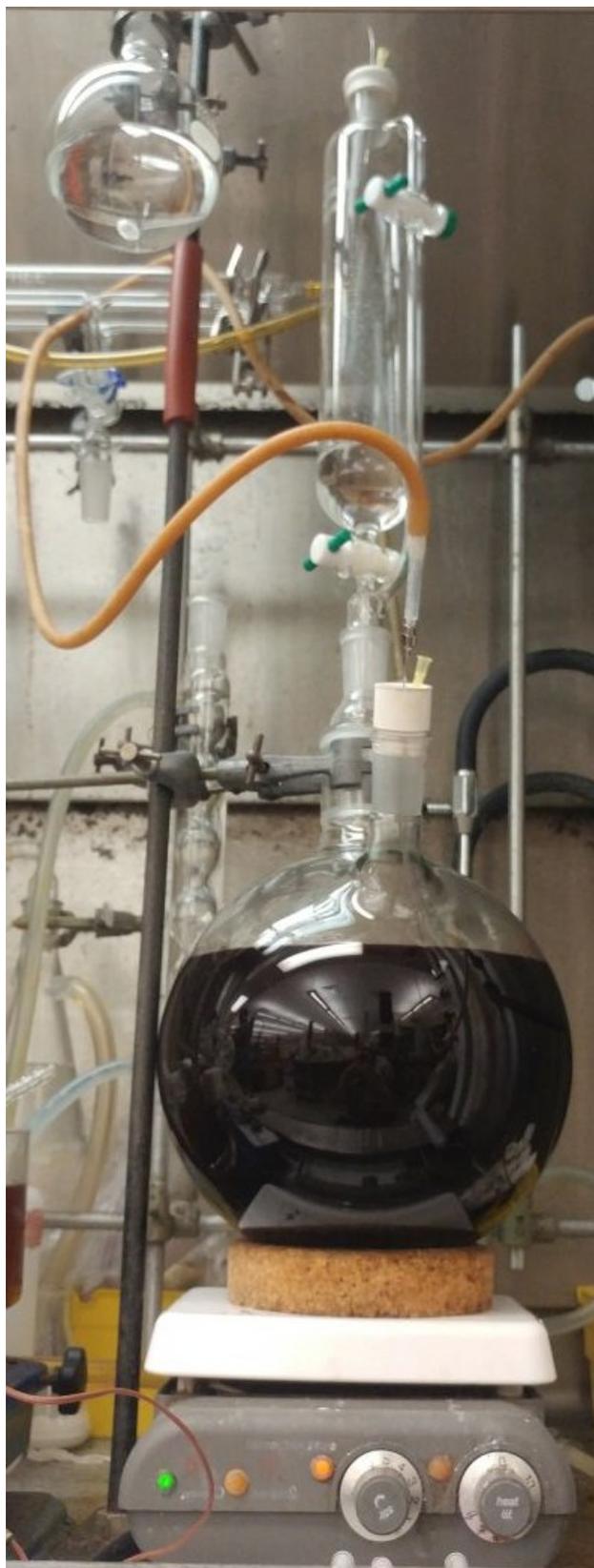
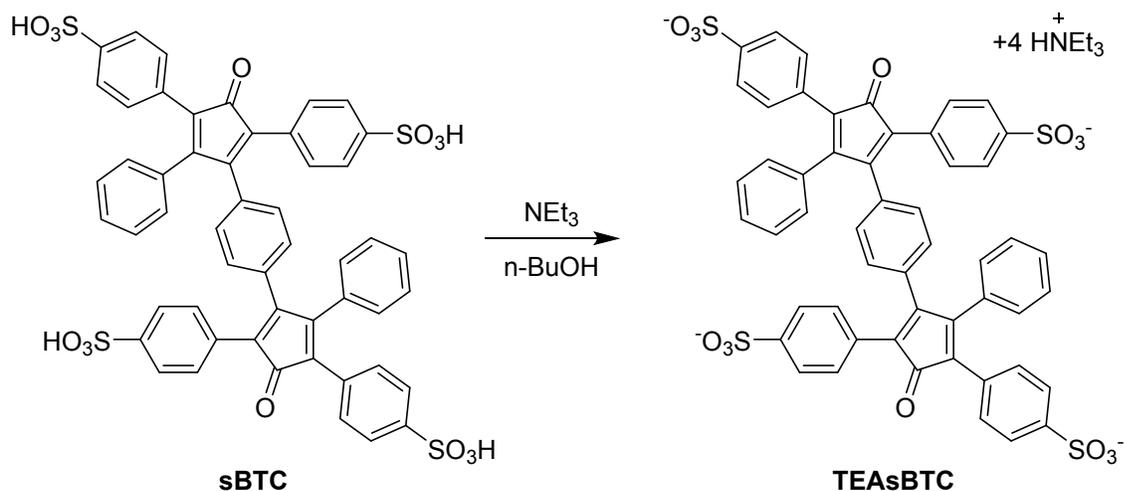


Figure S11: Large scale synthesis of sBTC.

Monomer TEAsBTC: Tetra triethylammonium tetra(para-sulfonated) bistetracyclone



Scheme S6: Synthesis of TEAsBTC.

Table S7: Yields of TEAsBTC, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	18.2	97.7%
2	5.15	92.3	96.2%
3	4.89	87.1	95.7%
4	5.10	87.6	92.3%
5	5.23	90.0	92.3%
6	4.76	87.5	98.7%
7	5.68	103.6	98.0%
8	5.06	88.0	93.4%
Total		654.3	95.5 ± 2.6%

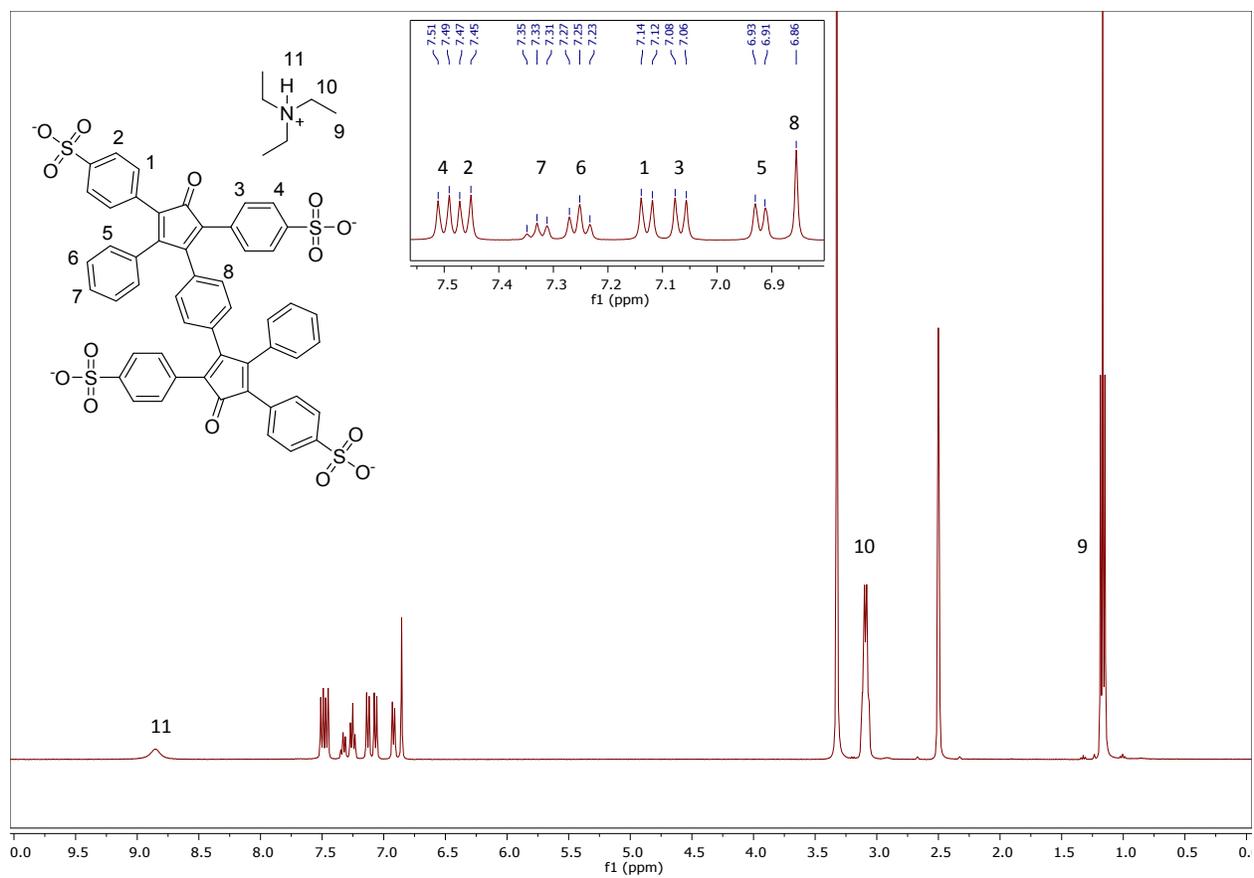


Figure S12: ¹H NMR of monomer TEAsBTC.

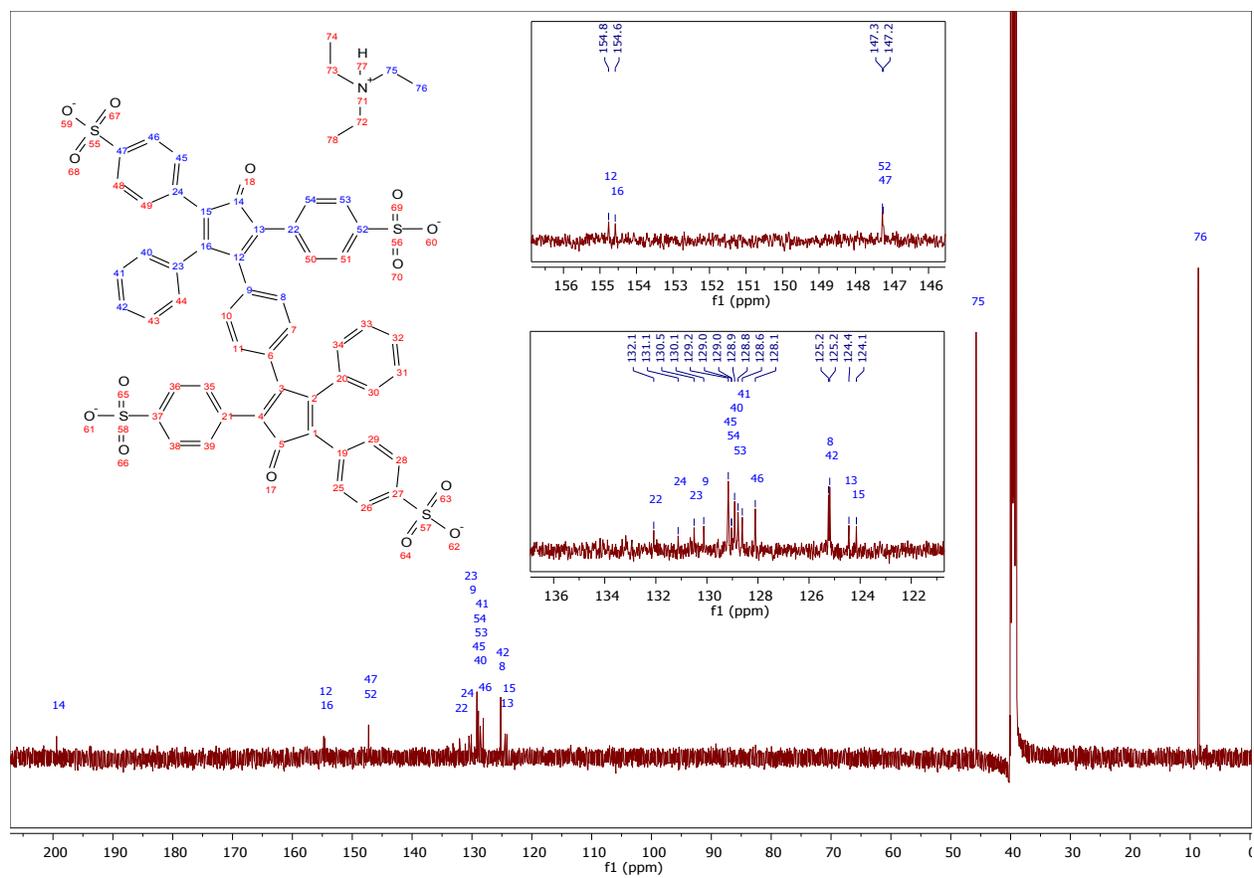


Figure S13: ^{13}C NMR of monomer TEAsBTC.



Figure S14: TEAsBTC following reaction workup.

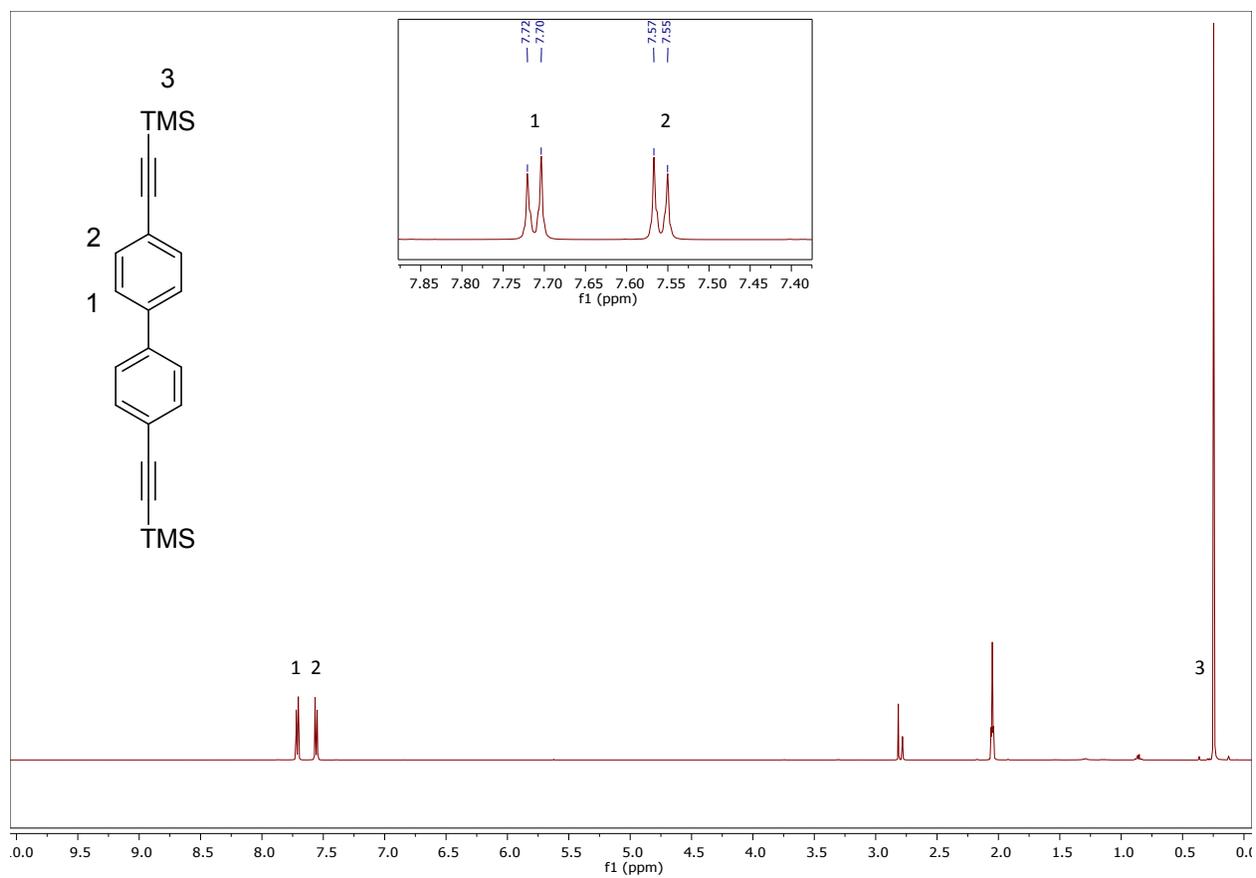


Figure S15: ¹H NMR of compound 8.

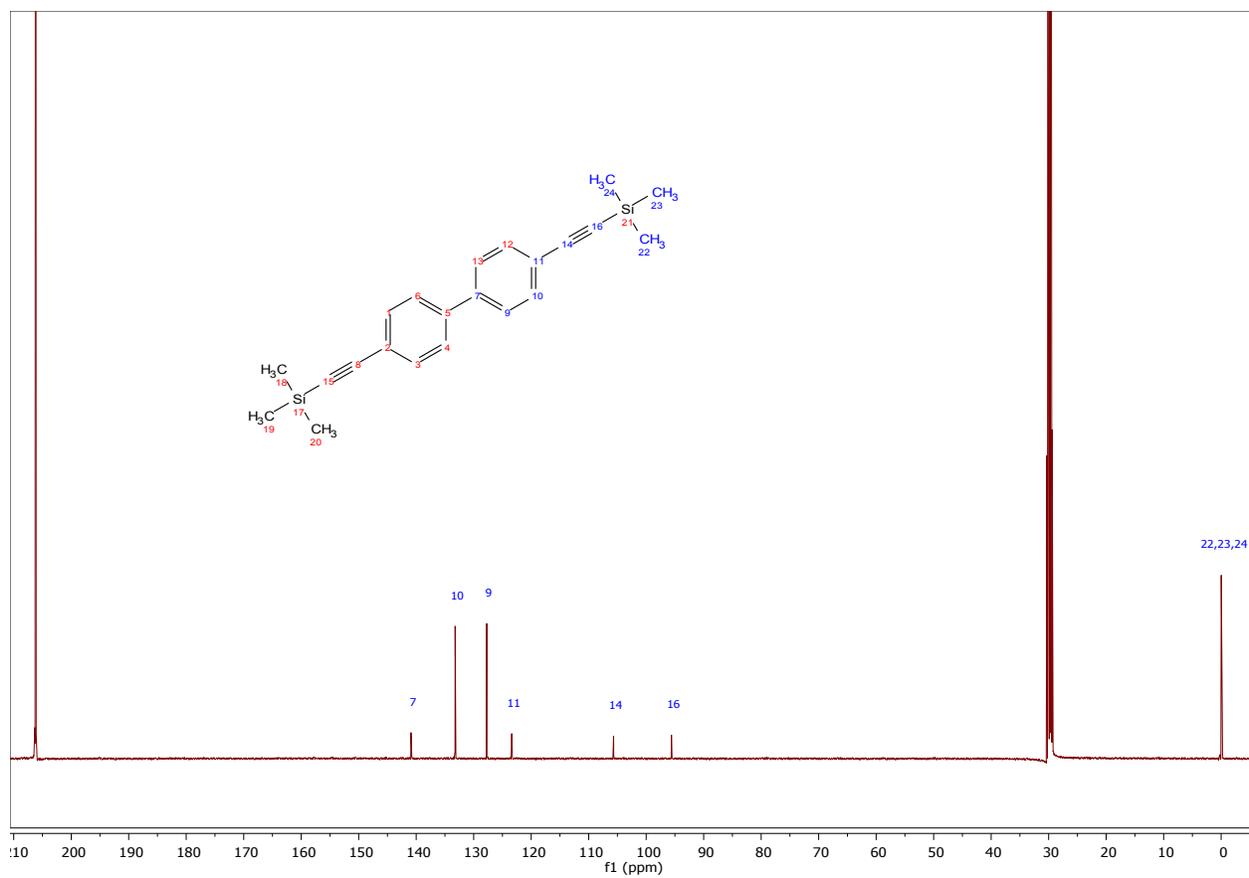
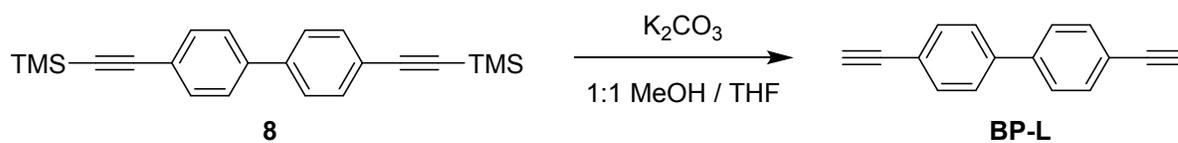


Figure S16: ¹³C NMR of compound **8**.



Figure S17: Compound **8** obtained from ethanol recrystallization.

Monomer BP-L: 4,4'-diethynyl-*p*-biphenyl



Scheme S8: Synthesis of **BP-L**.

Table S10: Reaction parameters for **BP-L** syntheses.

Parameters	Previous	Optimized
Scale	3 g	3 g
K ₂ CO ₃ used	10 eq.	4 eq.
Solvent	3:1 THF:MeOH	1:1 THF:MeOH
Solvent ratio	60x v/w	20x v/w
Yield	76-99%	Quantitative
Purity (¹ H NMR approximation)	≥99%	≥99%

Table S11: Yields of **BP-L**, and respective relative scale of each reaction performed.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	2.9	99.4%
2	1.88	5.5	99.4%
3	3.82	11.0	98.7%
4	5.98	17.2	98.6%
5	10.26	29.9	99.8%
	Total	66.4	99.2 ± 0.5%

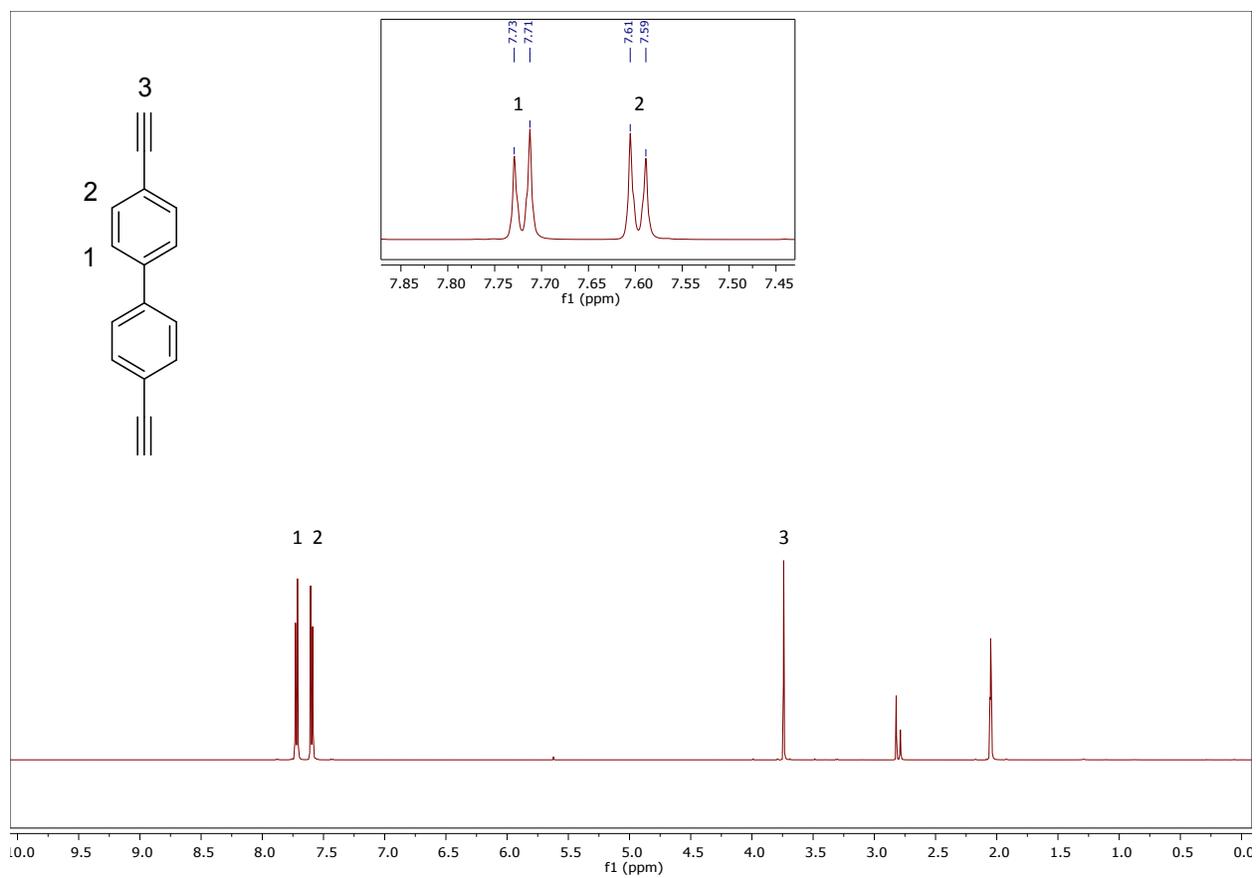


Figure S18: ¹H NMR of monomer BP-L.

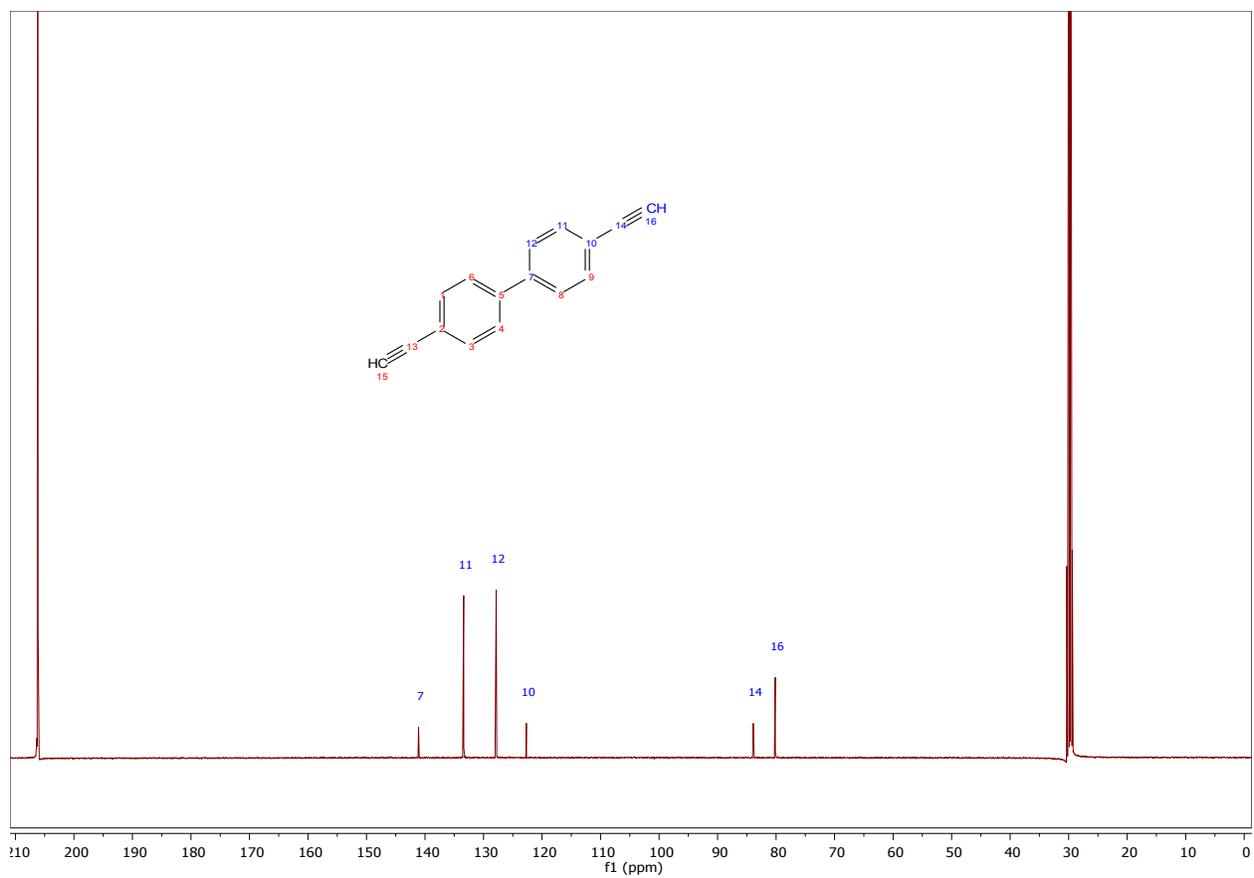
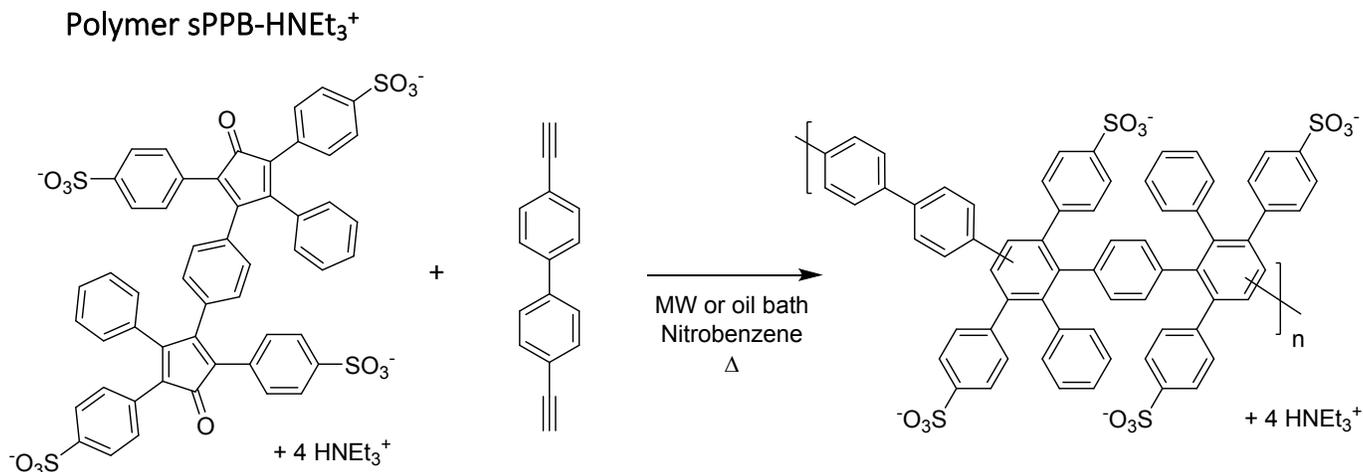


Figure S19: ^{13}C NMR of monomer **BP-L**.



Scheme S9: Microwave-assisted or traditional oil bath synthesis of **sPPB-HNEt₃⁺**.

All traditionally heated syntheses reported herein were performed in oil baths, which were found to provide more uniform reaction heating than previously utilized sand baths. The maximum scale achievable using available heating instruments and oil baths was limited to 1 L.

Table S12: Yields of **sPPB-HNEt₃⁺_{MW}**, and respective relative scale of each reaction.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	3.0	99.6%
2	1.62	4.6	95.4%
3	1.63	4.7	96.9%
4	1.62	4.6	96.3%
5	3.10	9.2	99.7%
6	7.17	21.3	99.8%
7	13.83	41.1	99.9%
8	25.61	75.6	99.3%
Total		163.9	98.4 ± 1.8%

Table S13: Reaction parameters for traditional **sPPB-HNEt₃⁺_{Trad}** syntheses (via oil bath).

Parameters	Previous ¹	Optimized
Scale	≤ 1.0 g	≤ 34.5 g
Solvent	Nitrobenzene	Nitrobenzene
Solvent ratio	10-40x v/w	20x v/w
Temperature	215 °C	180 °C
Yield	85-95%	99.0 ± 0.7%
M _w (Đ)	138-175 kDa (1.57-2.82)	448-501 kDa (1.93-2.42)

Table S14: Yields of **sPPB-HNEt₃⁺_{Trad}**, and respective relative scale of each reaction.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	3.0	98.7%
2	1.03	3.0	96.2%
3	2.16	6.2	96.2%
4	10.18	31.4	103.2% ^a
5	8.95	27.4	102.5% ^a
6	10.21	30.6	100.1% ^a
7	10.21	30.4	99.8%
8	6.34	19.0	100.3% ^a
9	9.33	27.6	99.1%
10	12.74	37.9	99.4%
11	12.73	37.3	98.1%
Total		253.7	99.4 ± 2.5%

^a The excess yields obtained are likely due to residual DMSO² and nitrobenzene^{3,4} (see ¹H NMR spectra for **sPPB-HNEt₃⁺**) contained within the obtained polymer fibers, which is difficult to fully remove even with extensive vacuum oven drying.²

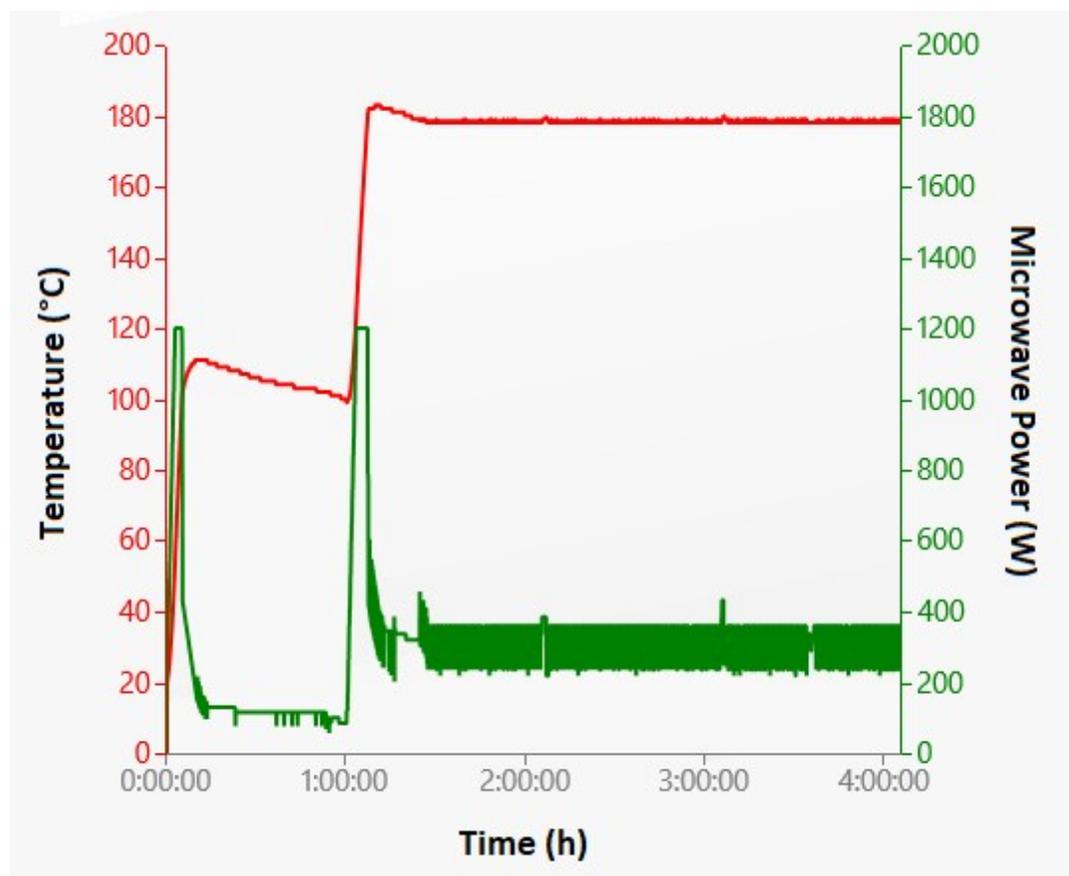


Figure S20: Microwave report for the synthesis of **sPPB-HNEt₃⁺_{MW}**.

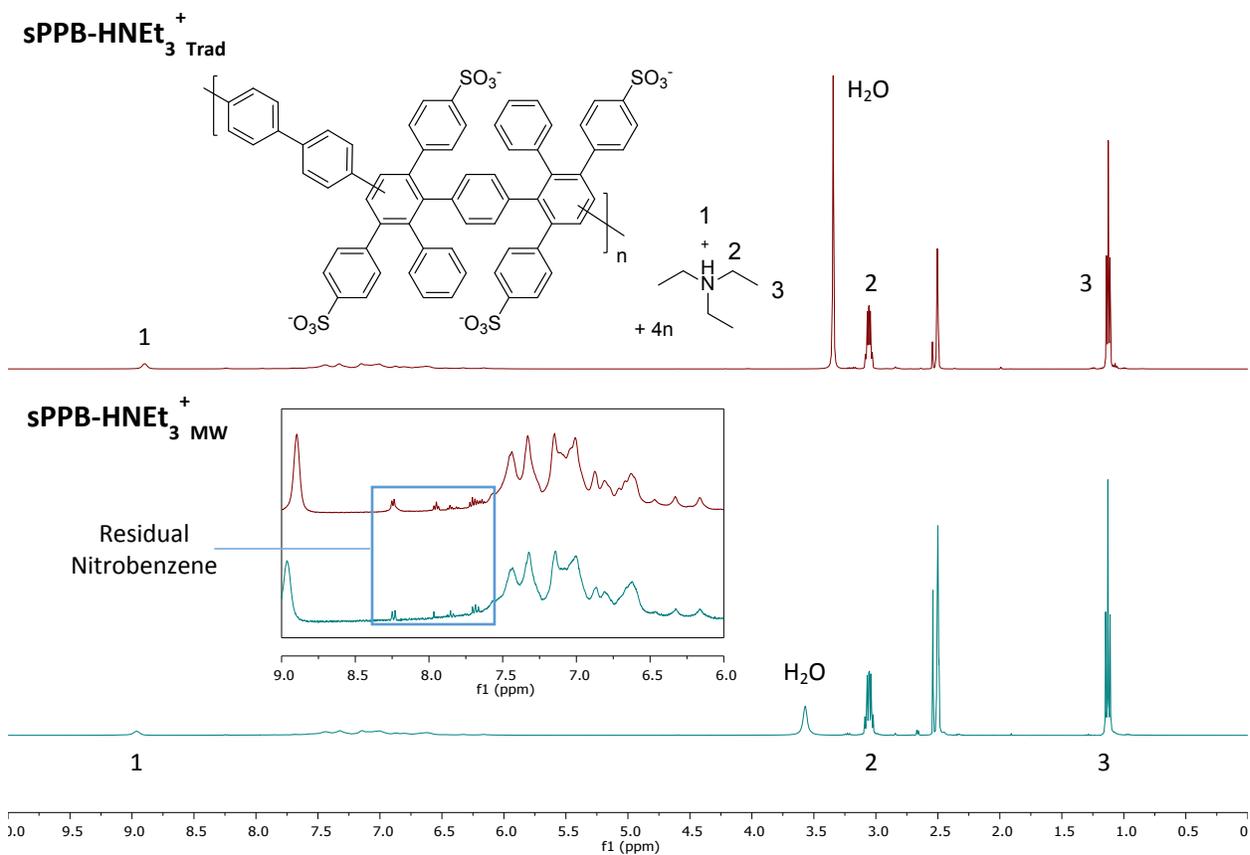


Figure S21: ¹H NMR of polymer **sPPB-HNEt₃⁺** prepared by traditional oil bath (top) or microwave-assisted (bottom) methods. The inset depicts the aromatic regions of both spectra.

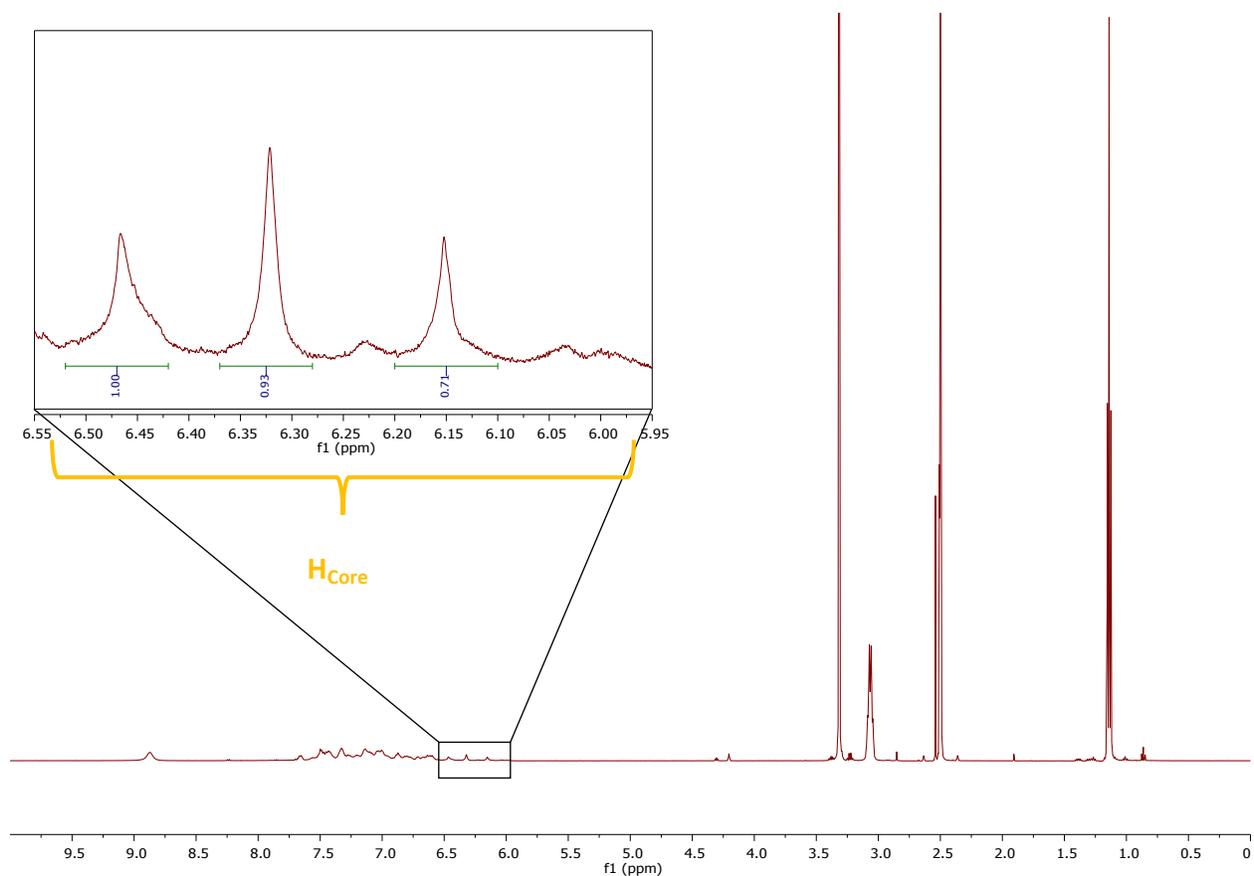
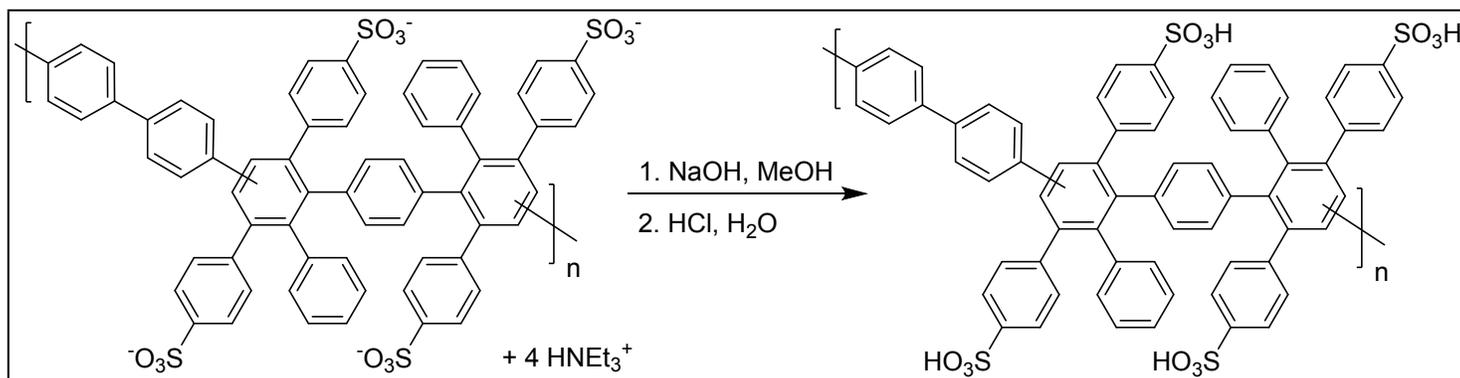


Figure S22: ^1H NMR of polymer $\text{sBPB-HNET}_3^+\text{sol}'\text{n}$ prepared via MWAS. The inset highlights the three predominant apparent singlets and their relative integrals (to one another) attributed to the 4 polymer core aromatic protons, H_{Core} , observed in three different chemical environments due to differing backbone arrangements: *p-p*, *m-m*, and *m-p* (left to right).³

Polymer sPPB-H⁺



Scheme S10: Synthesis of sPPB-H⁺.

sPPB-HNEt₃⁺_{prec} (28.00 g, 17.925 mmol of repeating unit) was dissolved in methanol (1.23 L) in a 3 L round bottom flask with vigorous stirring at room temperature, then 2 M NaOH (448 mL in methanol) was added dropwise. Upon formation of precipitate, the solution was stirred for an addition 12 h, then the reaction was evaporated. To the resulting brown solid was added DI H₂O (1.1 L), and the resulting slurry was stirred to uniformity. 2 M HCl (1.1 L) was then added dropwise to the suspension, ensuring a pH of ≤1 was achieved, and the resulting mixture was stirred for 12 h, filtrated, and the polymer precipitate washed thrice with water. Drying under vacuum overnight at 80 °C yielded the pure product as a dark brown chunky solid (20.57 g, 17.774 mmol of repeating unit, 99.2%).

¹H NMR (500 MHz, DMSO-D₆) δ (ppm): 6.02-7.60 (m, 40H), 4.19 (s, H₂O/H₃O⁺). Data agree with previously published results.¹

GPC Analysis: M_n = 235,600 g mol⁻¹, M_w = 452,000 g mol⁻¹, Đ = 1.92.

Table S15: Yields of sPPB-H⁺_{Trad}, and respective relative scale of each reaction.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	21.0	99.6%
2	0.93	19.5	99.5%
3	0.98	20.6	99.2%
4	1.40	29.1	98.7%
5	1.60	33.1	98.2%
6	1.59	33.2	98.7%
7	1.13	23.7	99.7%
Total		180.2	99.1 ± 0.5%

Table S16: Yields of **sPPB-H⁺_{MW}**, and respective relative scale of each reaction.

Reaction #	Scale	Yield (g)	Yield (%)
1	1.00	7.8	99.6%
2	1.79	14.0	99.5%
3	5.32	40.0	95.6%
4	2.84	22.0	98.3%
Total		83.9	98.2 ± 1.9%

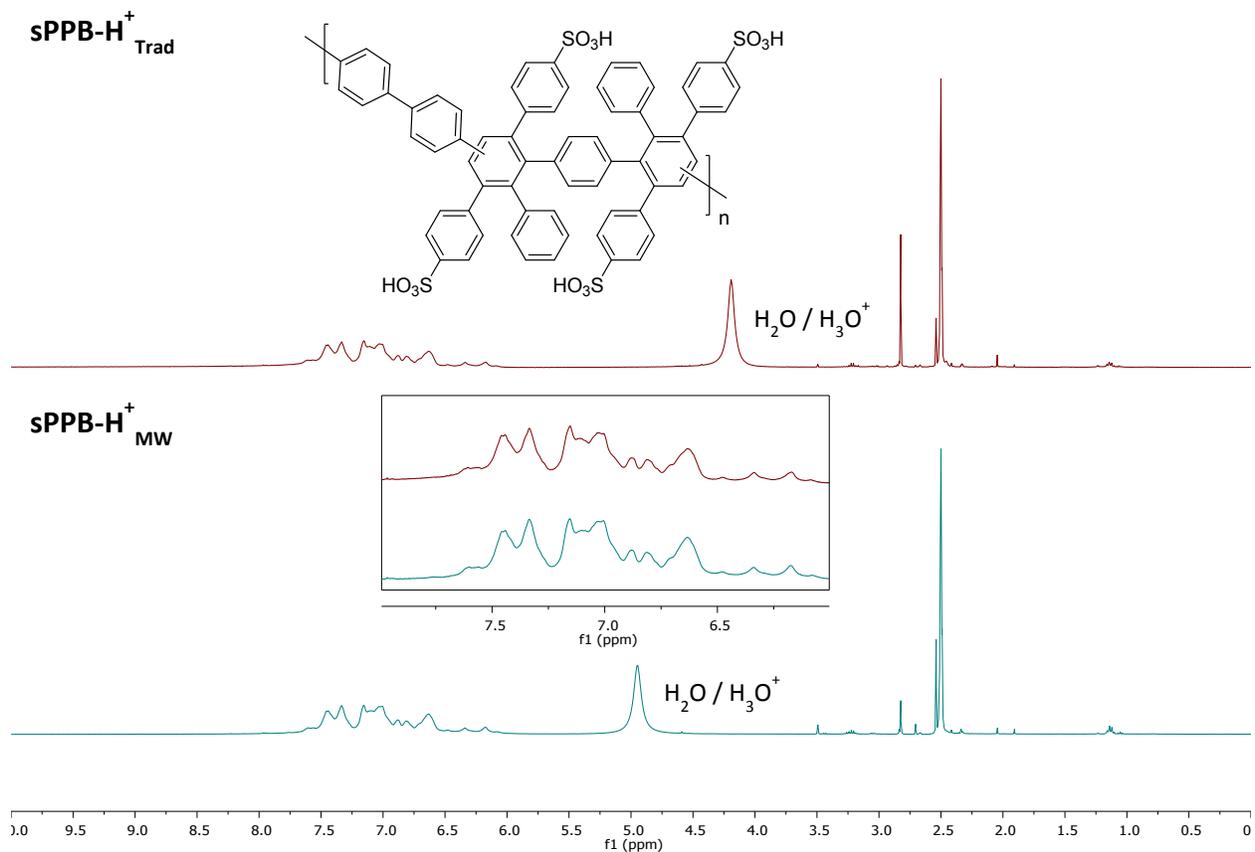
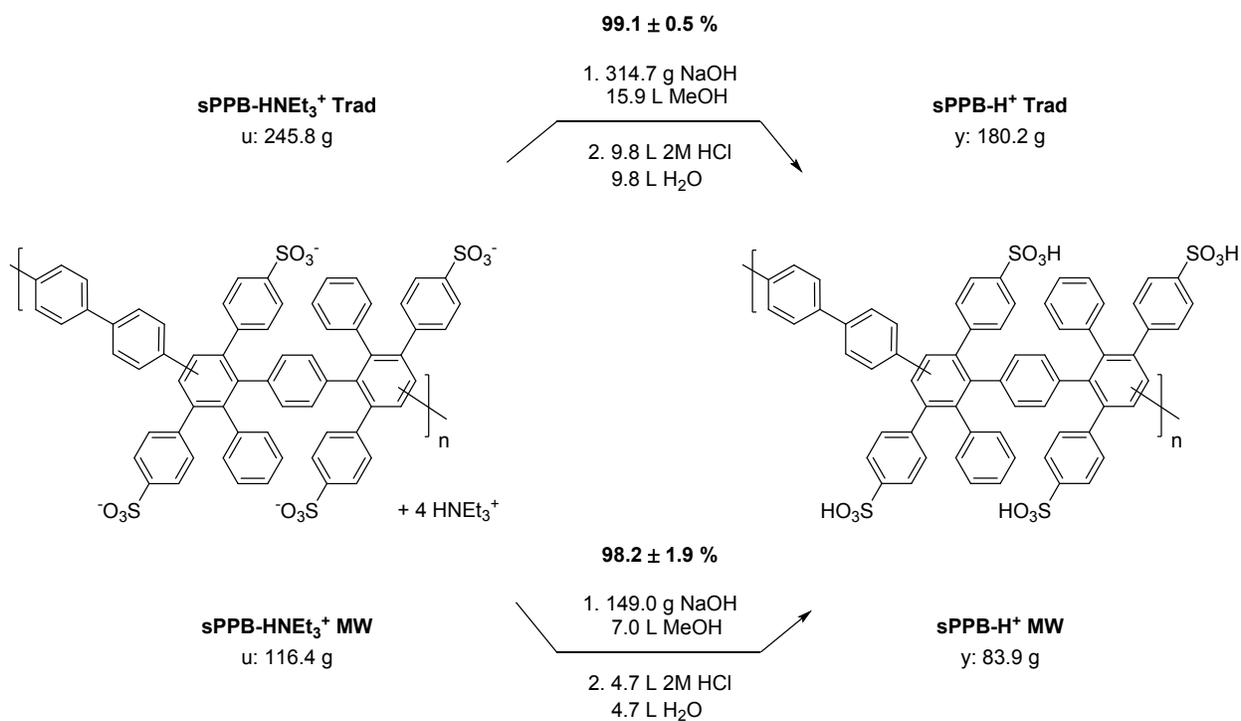


Figure S23: ¹H NMR of polymer **sPPB-H⁺** prepared from **sPPB-HNET₃⁺_{Trad}** (top) or **sPPB-HNET₃⁺_{MW}** (bottom). The inset depicts the aromatic regions of both spectra.



Scheme S11: The overall, up-scaled cation exchange from **sPPB-HNEt₃⁺** to **sPPB-H⁺**. The amount of reagents used (u) and products yielded (y) represent a total over multiple reactions performed for each step. Yield percentages are reported as the averages and standard deviations of all reaction batches performed.

Microwave Optimization

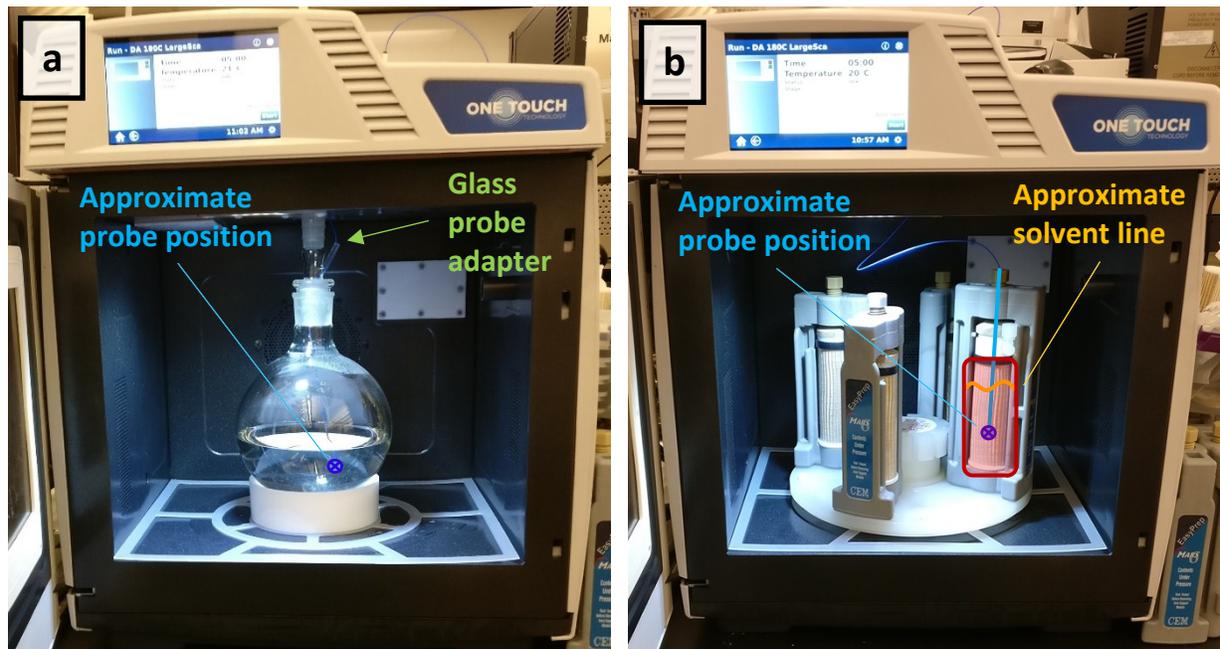


Figure S24: Microwave experiment setup schematics for (a) pressurized experiments, performed using between 1 and 12 EasyPrep Plus vessels (4 pictured); and (b) Open vessel, larger batch experiments, performed in up to 3 L round bottom flasks (pictured, containing ~1.4 L H₂O for illustrative purposes only) equipped with a glass probe adapter.

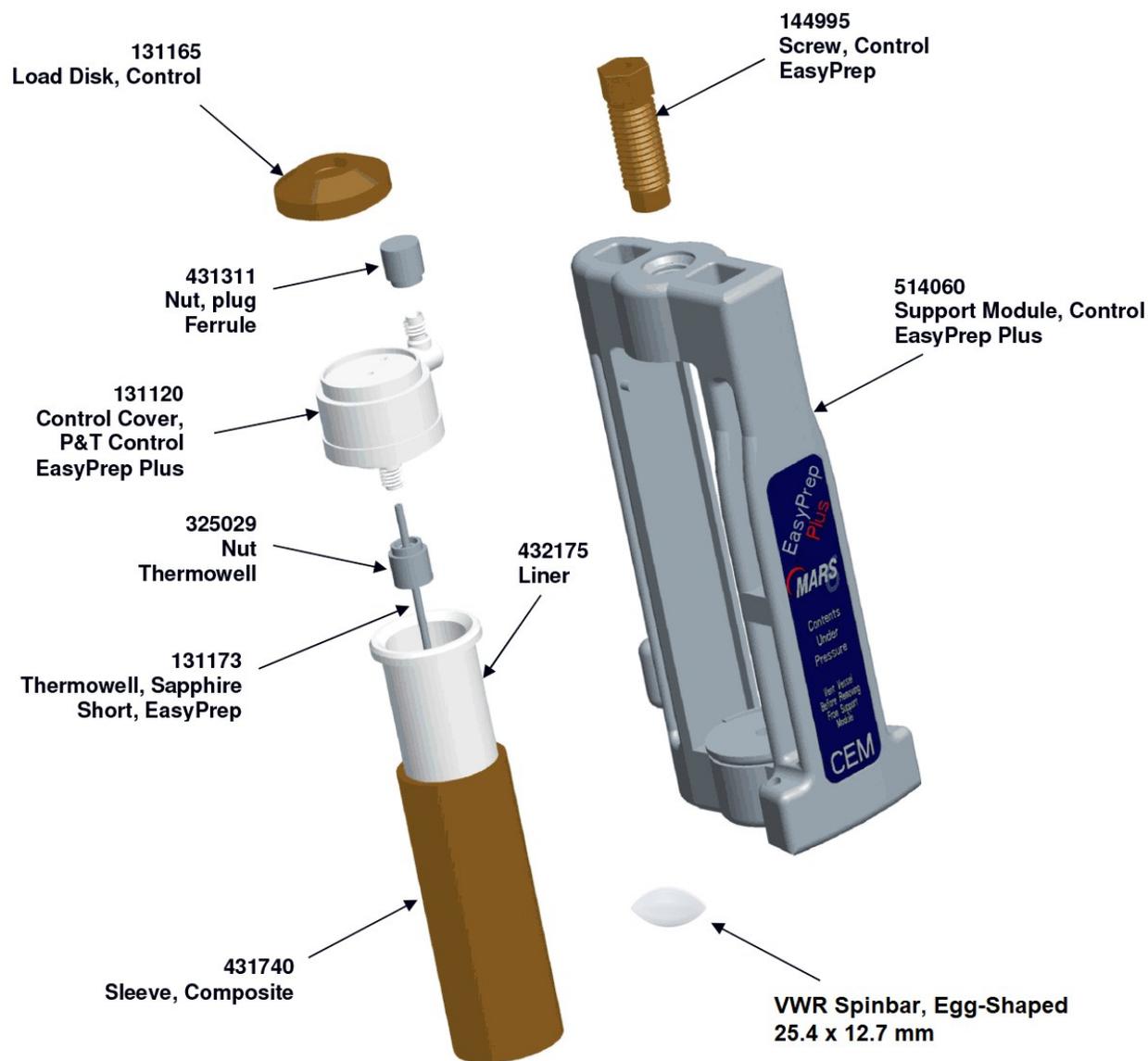


Figure S25: CEM EasyPrep Plus pressure reactor vessel setup schematic.⁵ The control vessel is shown. All other reaction vessels were charged with identical stir bars and quantities of reagents and solvent, but did not possess a sapphire thermowell, nut, or nut plug.

Each reaction was initially stirred at 100 °C for 20 min to facilitate reaction medium homogeneity. After completion, each reaction was precipitated into excess acetone. Precipitations were filtered through a medium frit sintered glass Buchner funnel, and dried under vacuum overnight at 80 °C to yield the final polymeric products. Data are summarized in Table 1.

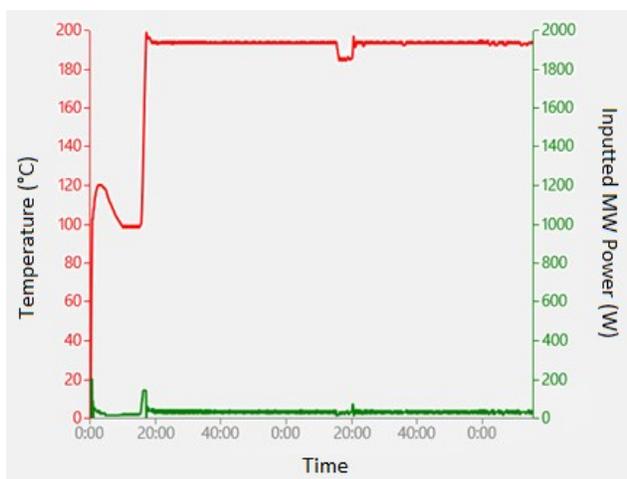


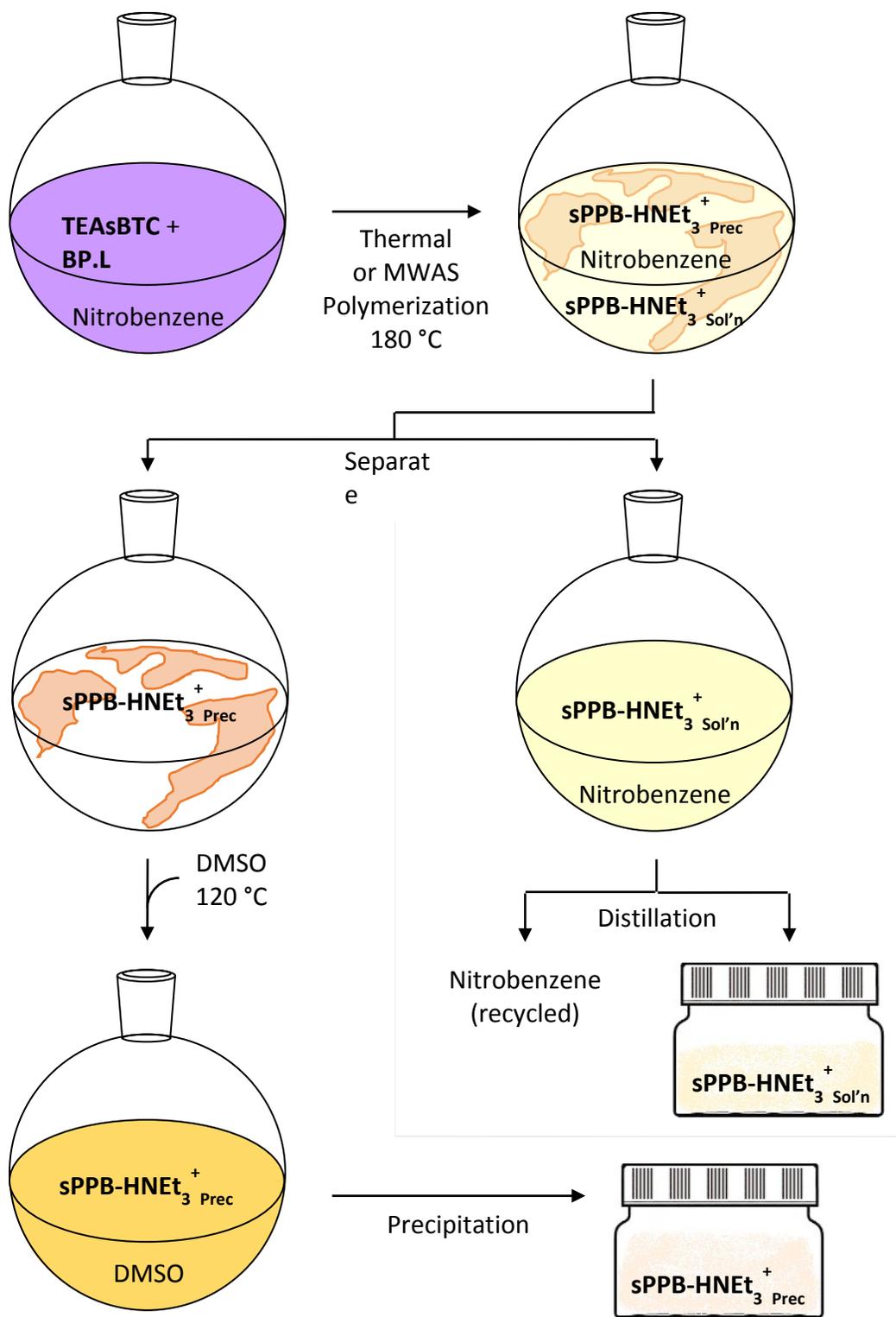
Figure S26: Representative temperature vs. inputted microwave power vs. time plot for a 2 h MW reaction performed on a 1 g scale in 20 mL nitrobenzene at 195 °C.

Increasing reaction times yielded polymers with increasing molecular weights (M_w) when reactions were performed in nitrobenzene, although material obtained was dark and difficult to subsequently dissolve. GPC in DMF (0.01 M LiBr) of polymers prepared in DMSO and sulfolane showed low M_w product which also possessed fairly low dispersities (\mathcal{D}). Reactions performed in DMF and ethylene glycol failed to yield polymer product.

For any given temperature, 5 identical reactions were set up in individual, identical vessels, and equipped to a carousel within the microwave reactor. After a 20 min mixing phase at 100 °C to facilitate reaction medium homogeneity, reactions were heated to the desired temperature, and periodically removed from the microwave reactor according to their specified reaction time. Mixing phase microwave parameters were 100 °C, 2 min ramp time, 20 min hold at 600 W max power. Reaction phase microwave parameters were variable temperatures, as indicated, with a 5 min ramp time up to 300 min hold at 800 W max power. All reactions were

performed on a 1 g scale, using monomer ratio **BP-L/TEAsBTC** = 1.015; and solvent ratio = 20x volume/weight of monomers.

Once complete, reactions were removed from the microwave reactor, depressurized, and allowed to cool for 30 min at ambient conditions. Each reaction was decanted into stirring acetone (ca. 300 mL). Oftentimes, this process resulted in formation of a precipitate in the stirring solvent, which was collected by suction filtration in a medium frit sintered glass Buchner funnel, washed thrice with additional acetone, dried at 80 °C under vacuum overnight. Through this process, **sPPB-HNet₃⁺_{sol'n}** was obtained, which was attributed to lower molecular weight oligomers which were retained for further analysis. Additionally, amber-colored gel-like precipitates were often observed adhered to reactor walls. These precipitates were rinsed thrice with acetone to help remove residual nitrobenzene, air dried, and dissolved in their respective reactor vessels in DMSO (30 mL) under microwave conditions (5 min ramp, 55 min hold at 150 °C, 600 W max power). The resulting orange polymer solutions were poured onto large surface area glass dishes and heated at 86 °C overnight to evaporate DMSO. The polymer membranes obtained from this process were then soaked in water (3 x 8 h), dried at 80 °C under vacuum overnight. Through this process, **sPPB-HNet₃⁺_{prec}** was obtained, which was attributed to higher molecular weight polymer agglomerates and retained for further analysis. This general process is depicted in Scheme S12. In instances where the microwave dissolution process was unsuccessful in dissolving polymer materials adhered to reactor walls, the polymeric dispersions were poured into stirring acetone (300 mL) and collected by suction filtration in a medium frit sintered glass Buchner funnel. After being washed thrice with additional acetone and dried at 80 °C under vacuum overnight, **sPPB-HNet₃⁺_{insoluble}** was obtained.



Scheme S12: Preparation and separation of $\text{sPPB-HNEt}_3^+_{\text{Sol'n}}$ and $\text{sPPB-HNEt}_3^+_{\text{Prec}}$ during polymer syntheses.

Qualitative observations from this reaction work-up process are detailed in Table S17. Reaction yields, given as sums of isolated solutions, precipitates, and insoluble matter, are outlined in Table S20. Strong trends were observed in increasing reaction time with decreasing reaction solution yields, which corresponds to lower molecular weight oligomers that remain soluble in the nitrobenzene solvent system throughout the reaction process. Complimentary to this observation, reaction precipitate yields increased with increasing reaction time, as did overall reaction yields. All polymers from reaction solutions **sPPB-HNEt₃⁺_{sol'n}**, precipitates **sPPB-HNEt₃⁺_{prec}**, and insoluble matter **sPPB-HNEt₃⁺_{insoluble}** collected (Table S17) were characterized by GPC in DMF (0.01 M LiBr) to assess optimal synthesis conditions for achieving soluble polymers with high molecular weight. Data are outlined in Tables S18 and S19.

Table S17: Results of MW-assisted **sPPB-HNEt₃⁺** syntheses run between 1 – 5 h at 160 – 220 °C.

Reaction time	Reaction temperature			
	160 °C	180 °C	200 °C	220 °C
1 h	Solution	Solution Precipitate	Solution Insoluble matter	Solution Insoluble matter
2 h	Solution Precipitate	Solution Precipitate	Solution Insoluble matter	Solution Insoluble matter
3 h	Solution Precipitate	Solution Precipitate	Solution Insoluble matter	Insoluble matter
4 h	Solution Precipitate	Solution Precipitate	Solution Insoluble matter	Insoluble matter
5 h	Solution Precipitate	Solution Insoluble matter	Insoluble matter	Insoluble matter

Table S18: GPC analyses of **sPPB-HNEt₃⁺_{sol'n}** from polymerizations run between 1 – 5 h at 160 – 220 °C.

Reaction time	Reaction material	M_w in Daltons (Đ)			
		Reaction temperature			
		160 °C	180 °C	200 °C	220 °C
1 h	Reaction solution	26,000 (1.15)	21,600 (1.08)	15,400 (1.04)	23,200 (1.10)
2 h		26,200 (1.09)	26,100 (1.15)	18,200 (1.06)	21,600 (1.11)
3 h		26,700 (1.18)	24,400 (1.17)	19,300 (1.04)	N/A
4 h		26,300 (1.19)	24,700 (1.16)	20,200 (1.10)	N/A
5 h		27,000 (1.18)	21,100 (1.13)	18,500 (1.05)	N/A

Table S19: GPC analyses of $\text{sPPB-HNet}_3^+_{\text{prec}}$ or $\text{sPPB-HNet}_3^+_{\text{insoluble}}$ from polymerizations run between 1 – 5 h at 160 – 220 °C.

Reaction time	Reaction material	M_w in Daltons (D)			
		Reaction temperature			
		160 °C	180 °C	200 °C	220 °C
1 h	Reaction precipitate	62,600 (1.05)*	213,500 (2.43)	19,100 (1.04)	64,800 (1.32)
2 h		122,200 (1.57)	295,500 (2.69)	20,900 (1.09)	96,600 (1.90)
3 h		181,200 (1.98)	317,100 (2.36)	24,900 (1.04)	N/A
4 h		272,400 (2.75)	326,200 (2.41)	67,900 (1.50)	N/A
5 h		295,600 (2.84)	245,300 (3.04)	65,800 (1.50)	N/A

Table S20: Yields of MW-assisted sPPB-HNet_3^+ syntheses run between 1 – 5 h at 160 – 220 °C.

Reaction time	Reaction material	Reaction yields (%)			
		Reaction temperature			
		160 °C	180 °C	200 °C	220 °C
1 h	Solution	94.2*	28.9	7.2	8.6
	Precipitate		66.1		
	Insoluble matter			87.1	86.8
	Overall Yield	94.2	95.0	94.2	95.3
2 h	Solution	27.0	26.2	6.1	7.8
	Precipitate	68.3	70.6		
	Insoluble matter			90.1	89.9
	Overall Yield	95.6	96.8	96.3	97.7
3 h	Solution	23.9	17.1	4.2	N/A
	Precipitate	71.6	78.9		
	Insoluble matter			92.1	
	Overall Yield	95.4	96.0	96.3	N/A
4 h	Solution	18.9	17.0	2.1	N/A
	Precipitate	76.5	81.7		
	Insoluble matter			94.9	
	Overall Yield	95.4	98.6	97.0	N/A
5 h	Solution	18.9	9.2		N/A
	Precipitate	72.6	82.2		
	Insoluble matter		7.0	97.9	
	Overall Yield	96.5	98.4	97.9	N/A

* Although no polymer precipitate was isolated from the reaction performed at 160 °C for 1 h, two distinct peaks were observed during GPC characterization. There were attributed to shorter, lower M_w (see Table S18), and longer, higher M_w (see table S19) oligomeric products.

Thermal Experiments

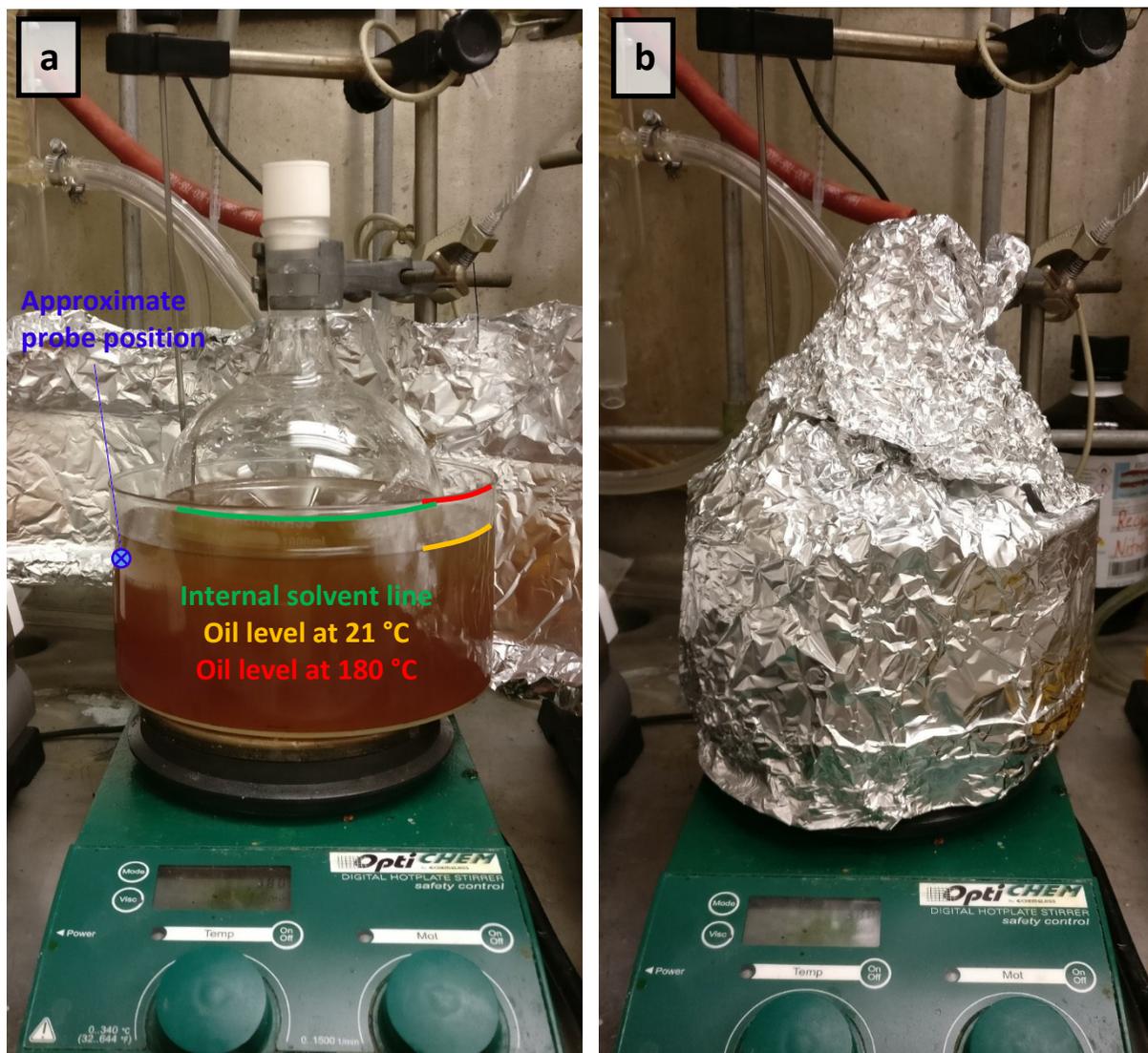


Figure S27: Thermal experiment setup schematics depicting: (a) A 1 L experiment setup containing ~650 mL H₂O (for illustrative purposes only) highlighting the approximate internal solvent level of a reaction with respect to approximate oil levels, and the approximate probe location with respect to the reaction vessel and oil bath (for illustrative purposes only, actual probe visible in the back in a similar position), and; (b) A reaction vessel wrapped in four layers of aluminum foil insulation prepared for thermal polymerization.

Solvent Recycling

The simplistic nature (two reagents, no catalysts or additives) of the Diels-Alder polymerization in this work allowed for exercising green chemistry principles through recycling of the reaction solvent. Both monomers **TEAsBTC** and **BP-L**, and respective polymer product **sPPB-HNEt₃⁺** are stable solids at temperatures ≤ 200 °C,^{3,1} and thus remain in the original distillation flask as solid residues, allowing for bulk recyclability of the nitrobenzene solvent. ¹H NMR spectra in CD₂Cl₂ of the pure solvent (a), compared to its recycled counterpart following two (b) and five (c) reactions are shown in Figure S28. Data show no difference in the purity of the solvent before or after recycling. Each time, over 90% of the solvent used for reaction was successfully recovered. The remaining nitrobenzene likely remains absorbed within the polymeric precipitates **sPPB-HNEt₃⁺_{prec}** observed along reactor walls following reaction.

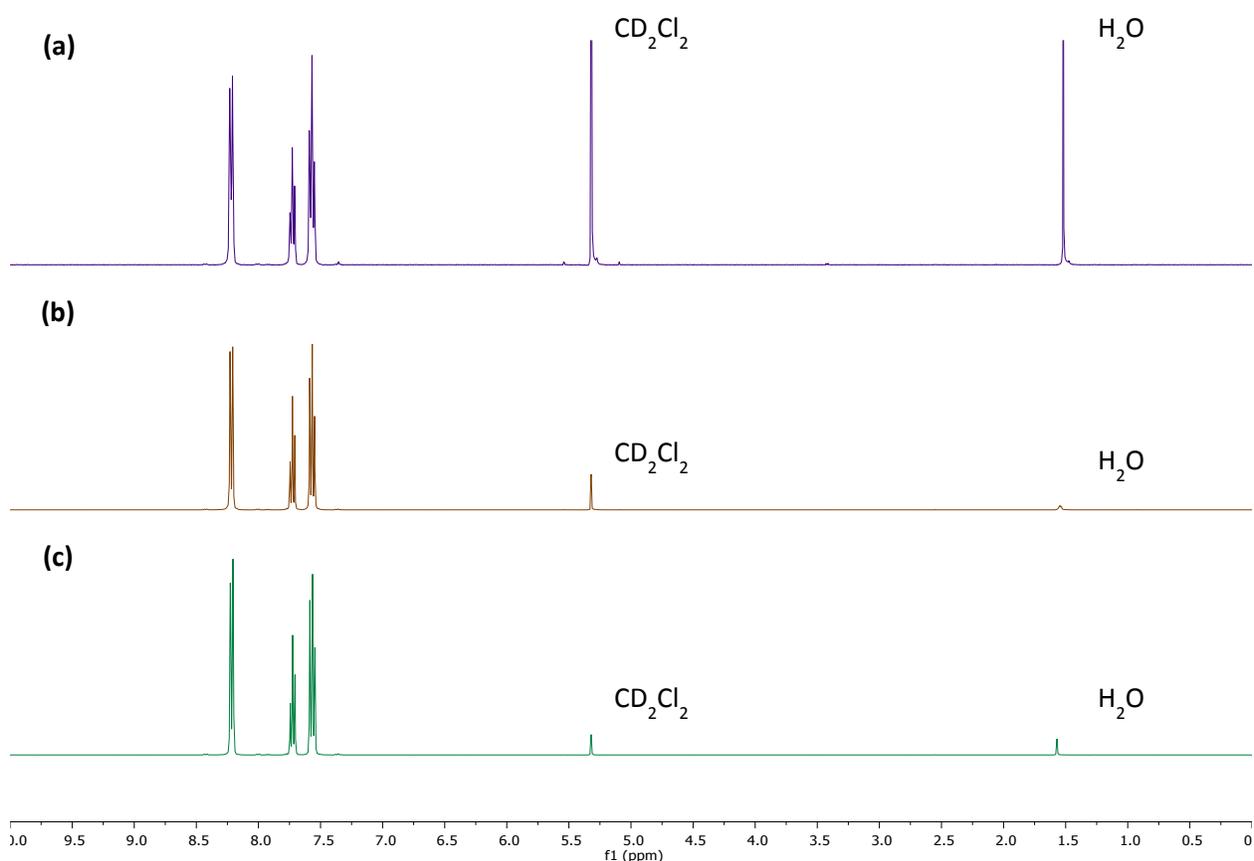


Figure S28: ¹H NMR spectra of nitrobenzene (a) as received from commercial sources, prior to reaction use; (b) following polymerization and subsequent recycling twice; and (c) following polymerization and recycling five times.

Membrane Preparation

Casting

Polymers membranes were prepared via casting acidic polymers **sPPB-H_{MW}⁺** and **sPPB-H_{Trad}⁺** from DMSO solutions (7.5% w/w) onto glass plates using a K202 Control Coater casting table and RK PrintCoat Instrument Ltd. adjustable casting blade at a height of 420 μm . After heating at 86 °C for 12 h, polymer membranes were removed from the glass plates, washed in 1 M H₂SO₄ (24 h) and DI H₂O (3 x 8 h), and dried under vacuum at 80 °C overnight.

Characterization

NMR

¹H and ¹³C NMR spectra were obtained using either: a) Bruker AVANCE III 500 MHz running IconNMR under TopSpin 2.1 equipped with a 5mm TXI Inverse ¹H/¹³C/¹⁹F probe; or b) Bruker AVANCE III 400 MHz running IconNMR under TopSpin 2.1 equipped with a 5mm BBOF plus ATM probe, as indicated.

GPC

Size exclusion chromatography (gel permeation chromatography, GPC) data was obtained using Water HPLC HR 5, HR 4 and HR 3 columns eluting HPLC grade DMF containing 0.01 M LiBr. Calibrations were performed using polystyrene standards purchased from Waters Associates Inc.

Water Uptake, Water Content and Dimensional Stability

Water uptake, content, and volumetric expansion (dimensional stability) measurements were obtained by comparing the fully hydrated versus fully dried masses and dimensions of minimum 3 membrane samples per polymer examined. In any given case below, the subscript “wet” denotes a fully hydrated parameter (eg. mass, m_{wet}), and the subscript “dry” denotes a fully dried parameter (eg. mass, m_{dry}). Fully hydrated measurements were obtained by soaking membrane samples in DI H₂O for 24 hours. Samples were then wiped dry using dust-free laboratory wipes and immediately weighed, measured with a micrometer and scanned immersed in water to obtain their fully hydrated masses (m_{wet}), thicknesses (th_{wet}), and planar

areas (A_{wet}), respectively. Fully dried measurements were obtained by drying membrane samples in a vacuum oven at 80 °C for 24 hours. After cooling to room temperature under vacuum, the samples were removed and immediately weighed, measured with a micrometer and scanned to obtain their fully dried masses (m_{dry}), thicknesses (th_{dry}), and planar areas (A_{dry}), respectively. In all cases, sample parameters were measured a minimum of 3 times each, per sample, to reduce the effects of compounded instrumental error. Error is reported as the standard deviation.

Membrane sample water uptake (WU) and water content (WC) were calculated using Equations S1 and S2, respectively. The dry and wet volumes of a membrane sample (V_{dry} and V_{wet} respectively) were calculated using Equation S3, which were used to determine overall membrane volumetric expansion (VE%) as per Equation S4.

$$(S1) \quad WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \qquad (S2) \quad WC = \frac{m_{wet} - m_{dry}}{m_{wet}} \times 100\%$$

$$(S3) \quad V_{dry} = A_{dry} \times th_{dry} \qquad (S4) \quad VE\% = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\%$$

Mechanical Strength Measurements

Barbell-shaped samples were cut from polymer membranes equilibrated at ambient conditions for minimum 24 hours, averaging 25 μm thickness, using a standard ASTM D638 type IV specimen cutting die. Measurements were performed on an Instron 3344 Series single column system operating with a crosshead speed of 5 mm min^{-1} . All data reported are averages of minimum three samples measured per membrane, with error reported as the standard deviation. The tensile strength, Young's modulus, and elongation at break of each polymer examined are reported in Table 4. Representative tensile stress-strain curves for each polymer examined are shown in Figure S29.

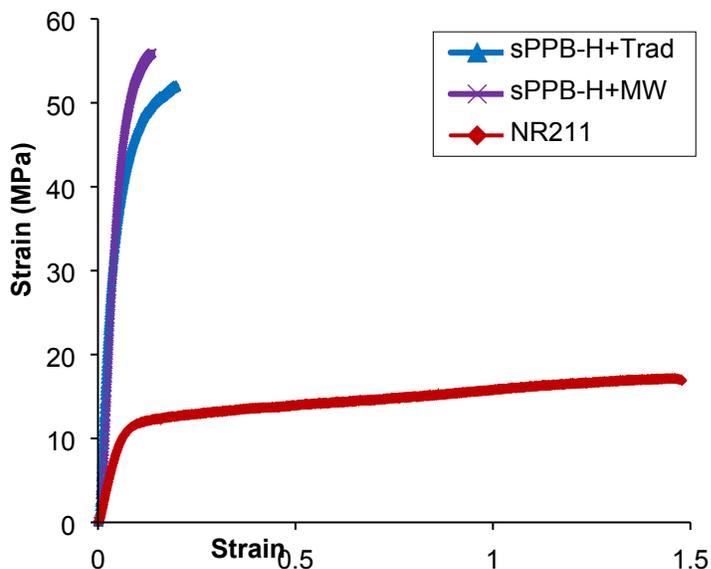


Figure S29: Tensile stress-strain properties of examined polymer membrane samples.

Oxidative Stability

Polymer membrane samples were subject to Fenton's reagent (3 ppm Fe^{2+} , 3% H_2O_2) to evaluate *ex-situ* oxidative stability. A typical trial involved fastening a series of membrane samples (ca. 2 x 2 cm) with known masses (m_{dry}) to Teflon anchors using perfluorinated fishing line, as described previously.⁶ Each sample was then placed into a preheated (to 80 °C) H_2O_2 solution in DI H_2O (>3.0%), to which was added concentrated (300 ppm) ferrous solution in DI H_2O until the desired solution concentration for each was reached. New ferrous solutions were prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for each oxidative stability test performed. Samples were periodically removed from the test solutions and washed in 1 M HCl (24 h) and DI H_2O (3 x 8 h). Residual masses (m_{res}) were obtained by drying under vacuum at 80 °C for 24 h, cooling to room temperature under vacuum, and weighing immediately following removal from the vacuum oven. Once massed, samples were further characterized by ^1H NMR in DMSO-D_6 (Figures S30 and S31). Sample remaining masses were calculated according to Equation S5. Each remaining mass reported corresponds to an average of minimum 3 samples, with error reported as the standard deviation.

$$(S5) \text{ Weight \% remaining} = \frac{m_{\text{res}}}{m_{\text{dry}}} \times 100\%$$

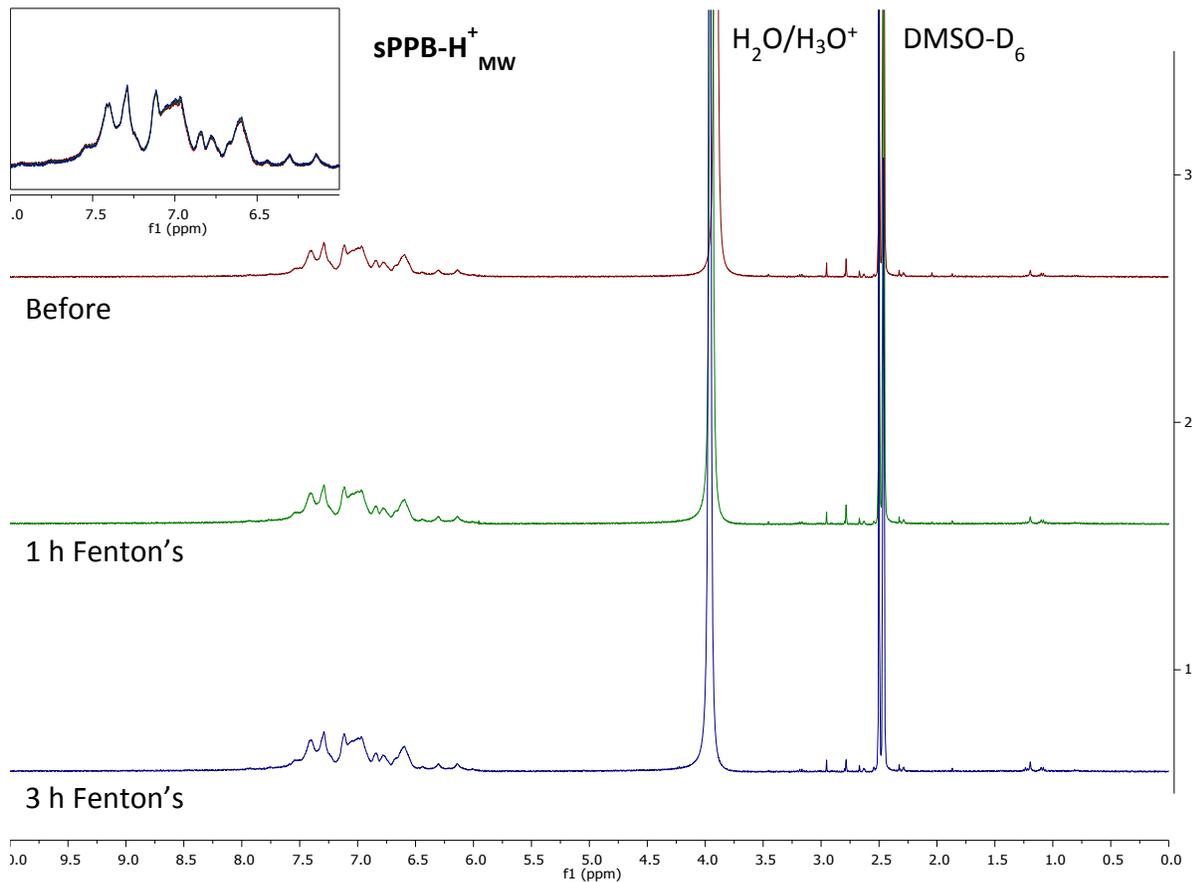


Figure S30: ¹H NMR spectra (DMSO-D₆) of sPPB-H⁺_{MW} polymer membranes before (red), following 1 h (green), and following 3 h (blue) exposure time to Fenton's reagent. The superimposed aromatic regions of each spectrum are shown in the inset. The H₂O/H₃O⁺ peak is typically located between 3.5 and 6.5 ppm.

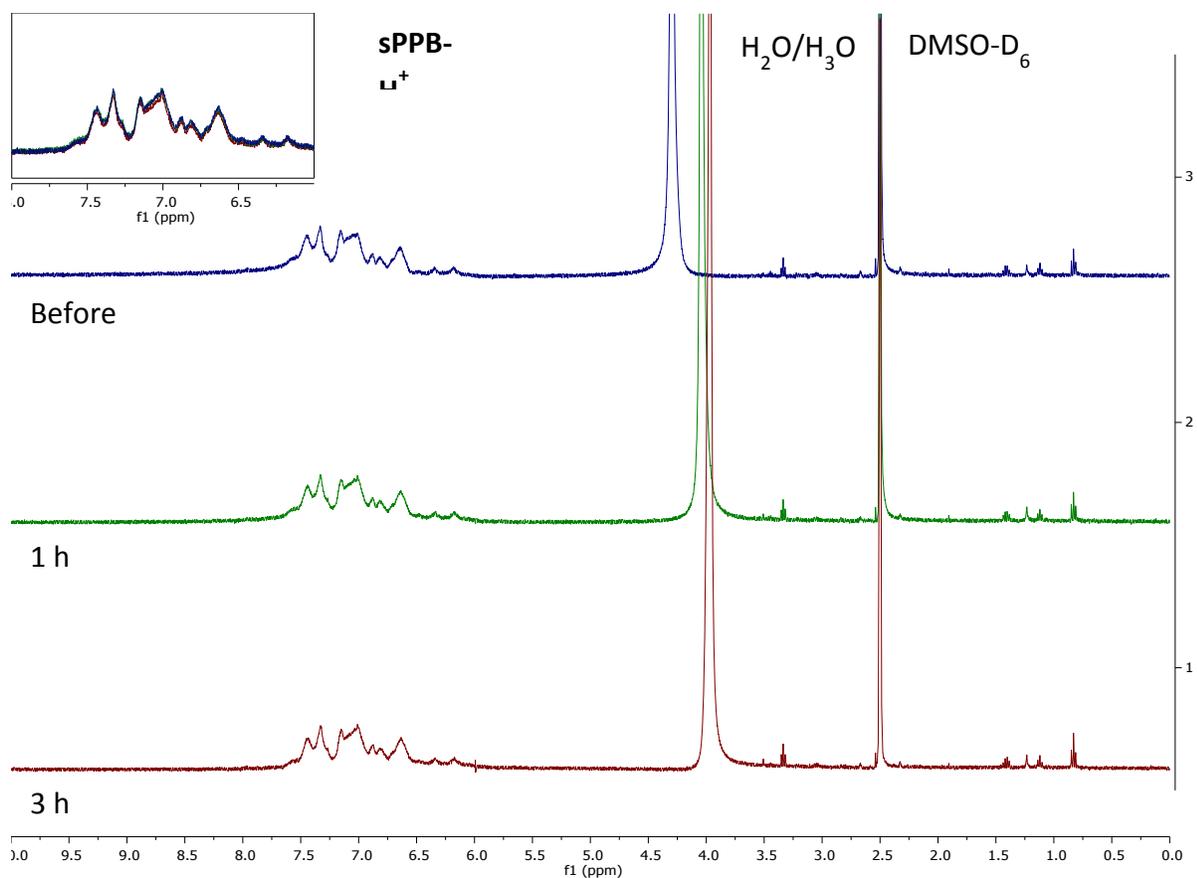


Figure S31: ^1H NMR spectra (DMSO-D_6) of sPPB-H^+ Trad polymer membranes before (red), following 1 h (green), and following 3 h (blue) exposure time to Fenton's reagent. The superimposed aromatic regions of each spectrum are shown in the inset. The $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ peak is typically located between 3.5 and 6.5 ppm.

Shear and Inherent Viscosity Measurements

Polymer effective shear viscosities were assessed using an Anton Paar MCR 102 Rheometer fitted with a standard cup and concentric cylinder bob geometry. Polymer casting solutions (7.5% w/w in DMSO) were held at 25 °C during measurements and assessed either: a) as viscoelastic fluids using a shear rate ramping logarithmically from $d(\gamma) \cdot dt^{-1} = 0.01$ Hz to 100 Hz with point durations ramping logarithmically from 100 to 0.05 s, or b) in low viscosity mode using a shear rate ramping linearly from $d(\gamma) \cdot dt^{-1} = 1$ to 100 Hz with point durations ramping linearly from 10 to 1 s. Data were analyzed using a Carreau-Yasuda regression model or Newton's law of viscosity, respectively. Relative solution viscosity ($\eta_{relative}$) was calculated using Equation S6, where $\eta_{solution}$ and $\eta_{solvent}$ are the measured shear viscosities of the polymer solution and pure solvent, respectively. From this was calculated inherent viscosity ($\eta_{inherent}$) using Equation S7, where c is the concentration of assessed polymer solutions in $g\ dL^{-1}$.

$$(S6) \eta_{relative} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$$(S7) \eta_{inherent} = \frac{\ln_{10}(\eta_{relative})}{c}$$

Ion Exchange Capacity (IEC)

Ion exchange capacities (IECs) for each polymer were determined by acid base titration experiments using a Metrohm 848 Titrino Plus automatic titrator equipped with a standardized titrant (0.01 M NaOH solution, Sigma Aldrich), as previously described.¹ All values reported are an average of minimum three samples per polymer examined, with error reported as the respective standard deviations. Experimental IEC (IEC_{xp} , meq. g^{-1}) was calculated according to Equation S8, where V_t is the volume and C_t is the concentration of standardized titrant required to neutralize an acidic solution obtained from a membrane sample of m_{dry} mass. Theoretical IEC (IEC_{th} , meq. g^{-1}) was determined using Equation S9, where MW is the molecular weight of one polymeric repeat unit, and n_{SO_3H} is the moles of sulfonic acid moieties present therein.

$$(S8) IEC_{xp} = \frac{V_t \times C_t}{m_{dry}}$$

$$(S9) IEC_{th} = \frac{n_{SO_3H}}{MW}$$

Water Sorption (λ) and Analytical Acid Concentration [SO_3H]

The number of water molecules per acid functional group λ ($mol\ H_2O \cdot mol^{-1}\ SO_3H$) was calculated using Equation S10, where MW_{H_2O} corresponds to the molecular weight of pure H_2O ,

WU to the calculated water uptake (%) of a membrane sample (see Equation S1), and IEC_{xp} to the experimental IEC of said membrane sample (see Equation S8). Analytical acid concentration of hydrated membranes, $[SO_3H]$ ($\text{mmol } SO_3H \cdot \text{cm}^{-3}_{\text{membrane}}$), was calculated using Equation S11, where m_{dry} is the fully dry mass of a membrane sample, V_{wet} is its fully hydrated volume (see Equation S3), and IEC_{xp} is its experimentally determined IEC.

$$(S10) \quad \lambda = 10 \times \frac{WU}{MW_{H2O} \times IEC_{xp}} \quad (S11) \quad [-SO_3H] = \frac{m_{dry}}{V_{wet}} \times IEC_{xp}$$

Proton Conductivity (σ_{H+}) and Effective Proton Mobility (μ_{eff})

Proton conductivity was measured via AC impedance spectroscopy using a Solartron 1260 frequency response analyzer (FRA) incorporating conductivity cells with a two electrode configuration. A 100 mV sinusoidal AC potential operating over a frequency range of 10 MHz – 100 Hz was utilized. Temperature and humidity controlled proton conductivity measurements were performed in an Espec model SH-241 humidity chamber, as previously detailed.¹ Measurements series were performed between 30 and 95% RH, at 30 and 80 °C. Data was fit to a Randles equivalent circuit to calculate sample ionic resistance (R_p), which was used in conjunction with sample cross-sectional area (A_{xs} , cm^2) and the distance between cell electrodes (L , cm) to calculate proton conductivity (σ_{H+}) using Equation S12. Sample cross-sectional area was calculated from respective width (W , cm) and thickness (th , cm).¹ Effective proton mobility at a given set of conditions (eg. 80 °C, 95% RH, see Table 3) was calculated according to Equation S13, where σ_{H+} is the proton conductivity of a membrane sample measured at those conditions, $[SO_3H]$ is its analytical acid concentration (see Equation S11), and F is the Faraday constant (96485 C mol^{-1}).

$$(S12) \quad \sigma_{H+} = \frac{L}{R_p \times A_{xs}} \quad (S13) \quad \mu_{eff} = \frac{\sigma_{H+}}{F \times [-SO_3H]}$$

Table S21: Proton conductivity values measured for assessed polymers at 30 °C and various RH.

Relative humidity (RH)	σ_{H^+} 30 °C (mS cm ⁻¹)		
	sPPB-H ⁺ _{MW}	sPPB-H ⁺ _{Trad}	NR211
95%	136.6	144.1	78.5
90%	94.1	91.3	49.4
80%	53.5	53.9	N/A
70%	32.2	37.0	12.6
60%	19.5	23.2	N/A
50%	11.4	14.2	1.7
40%	6.2	7.7	N/A
30%	3.4	4.1	0.1

Table S22: Proton conductivity values measured for assessed polymers at 80 °C and various RH.

Relative humidity (RH)	σ_{H^+} 80 °C (mS cm ⁻¹)		
	sPPB-H ⁺ _{MW}	sPPB-H ⁺ _{Trad}	NR211
95%	181.9	186.2	113.0
90%	121.1	120.4	67.9
80%	66.2	66.8	N/A
70%	39.4	44.0	31.2
60%	24.2	28.3	N/A
50%	14.4	17.2	14.7
40%	8.0	9.6	N/A
30%	4.3	5.0	13.3

Fuel Cell Characterization

Catalyst inks were prepared using PFSA ionomer (Nafion[®] D520) and Pt/C catalyst powder (TKK TEC-10E50E, comprising 46.4 wt% Pt on graphitized carbon). The catalyst powder was suspended in H₂O, after which H₂O and MeOH were added in succession. The resulting solution was stirred rapidly, and ionomer solution was added dropwise until a final mixture containing 1 wt% solids in 1:3 H₂O:MeOH was obtained. Of this 1 wt% solids, 30 wt% was ionomer and 70wt% was Pt/C catalyst powder. Catalyst inks were deposited onto membrane surfaces atop a vacuum plate held at 60 or 80 °C in the case of hydrocarbon or PFSA membranes, respectively, using an ultrasonicated spray coater (Sono-Tek ExactaCoat SC) to give a final electrode area of 5 cm², yielding catalyst coated membranes (CCMs). In all cases reported, catalyst loadings were 0.4 mg Pt · cm⁻² for anode and cathode. The resulting CCMs were mounted into fuel cell hardware using commercial gas diffusion layers (GDLs) with microporous layers (Sigracet 24BC) and Silicon-Fibreglass gasketing (~380 μm total gasketing) to achieve a final GDL compression of 20-30% at 5.6 N·m (50 in·lbs) torque.

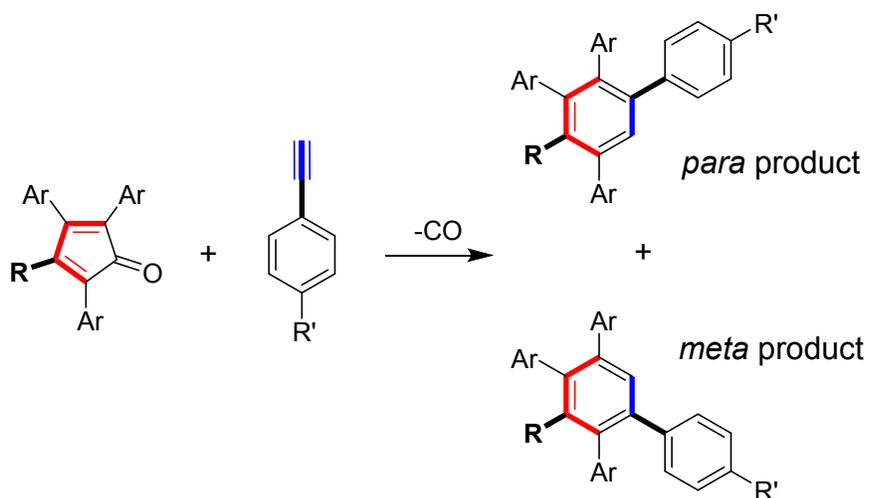
PFSA membrane substrates were Nafion[®] 212 (50 ± 1 μm) or Nafion[®] 211 (25 ± 1 μm), as indicated. Hydrocarbon membrane substrates were sPPB-H⁺ (33 ± 2 μm), sPPB-H⁺_{Trad} (24 ± 2 μm), or sPPB-H⁺_{MW} (28 ± 2 μm), as indicated. Thicknesses of membrane samples were measured 5x (corners and center) by micrometer and averaged. The error is the standard deviation of said measurements.

In-situ fuel cell (FC) characterizations were performed on a fuel cell testing station (Teledyne Medusa RD, Model 890CL, Scribner Assoc. Inc.). Cells were conditioned via recurring current increases (50 mA cm⁻² increments from 400 mA cm⁻² to 3A cm⁻²) to a 0.50 V hold until consistent performance was obtained (ca. 12 h). Polarization data were obtained at 80 °C under H₂/O₂ (0.5/1.0 slpm) or H₂/Air (0.5/1.0 slpm), varied stoichiometry, zero backpressure, and varying anode/cathode relative humidity (RH): 100%/100%, 90%/90%, or 50%/50%, as indicated.

Electrochemical characterizations were performed on cells equilibrated under H₂/N₂ (0.5/0.5 slpm) at 80 °C and 100% RH to a steady potential of ≤0.15 V. Electrochemical

impedance spectroscopy (EIS), linear-sweep voltammetry (LSV), and cyclic voltammetry (CV), as indicated, were performed on a combined potentiostat and frequency response analyzer (PARSTAT, Princeton Applied Research) using previously described methods.^{1,3} Ramped voltammetry was performed using 100 mV steps from 0 to 600 mV at 30 seconds steps⁻¹. Fuel crossover current was calculated from the average measured current density at 500 mV during the latter 50% (15 s) of the potential hold. LSV, executed from low equilibrated potential to 600 mV sweeping at a rate of 2 mV s⁻¹, was used to monitor potential electrical shorting.

Additional Information



Scheme S13: A representative Diels-Alder condensation reaction showing both possible isomers produced.

Polymer regiochemistry ratios (*para* – *para*, *meta* – *meta*, and *meta* – *para*) were calculated according to Equation S14, in which the *p-p* ratio is used as an example.

$$(S14) \%p - p = \frac{p - p_{integration}}{\sum p - p, m - m, m - p_{integrations}} \times 100\%$$

Table S23: Polymer regiochemistry data and corresponding ratios for **sPPB-HNEt₃⁺_{MW}**.

Sample	<i>para</i> - <i>para</i>		<i>meta</i> - <i>meta</i>		<i>meta</i> - <i>para</i>	
	6.52 - 6.42 ppm		6.37 - 6.28 ppm		6.20 - 6.10 ppm	
	Integration	%	Integration	%	Integration	%
MW 1	1.00	38.6%	0.94	36.1%	0.66	25.3%
MW 2	1.00	39.3%	0.93	36.3%	0.62	24.4%
MW 3	1.00	38.7%	0.93	36.1%	0.65	25.2%
Average	1.00	38.8%	0.93	36.2%	0.67	25.0%
$\sigma_{\bar{x}}$	0.00	0.4%	0.01	0.1%	0.05	0.5%

Table S24: Polymer regiochemistry data and corresponding ratios for **sPPB-HNEt₃⁺_{Trad}**.

Sample	<i>para</i> - <i>para</i>		<i>meta</i> - <i>meta</i>		<i>meta</i> - <i>para</i>	
	6.52 - 6.42 ppm		6.37 - 6.28 ppm		6.20 - 6.10 ppm	
	Integration	%	Integration	%	Integration	%
Trad 1	1.00	30.4%	1.21	36.9%	1.08	32.7%
Trad 2	1.00	32.8%	1.14	37.4%	0.91	29.8%
Trad 3	1.00	31.8%	1.16	36.7%	0.99	31.5%
Average	1.00	31.7%	1.11	37.0%	0.90	31.3%
$\sigma_{\bar{x}}$	0.00	1.2%	0.04	0.4%	0.09	1.5%

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