Sulfo-Phenylated Polyphenylenes Containing Sterically-Hindered Pyridines

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Materials and instruments

Materials

Triethylamine (99%, Anachemia Science), 1,4-dibromonaphthalene (98%), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (95%) and 1-Bromo-4-iodobenzene (98%) were purchased from Combi-Blocks, Inc. Acetone, dichloromethane (DCM), diethyl ether (reagent grade) methanol (MeOH), petroleum ether (PE), potassium carbonate (K₂CO₃, reagent grade), tetrahydrofuran (THF) were purchased from Thermo Fisher Scientific. n-butanol, dichloroethane (DCE), dimethyl sulfoxide (DMSO), ethyl acetate (EtOAc) and potassium hydroxyde (KOH, reagent grade) were purchased from Caledon Laboratories Ltd. Nitrobenzene (ACS reagent, >99%), trimethylsilyl chlorosulfonate (99%), 2, 5-dibromopyridine (98%), 4′-Bromoacetophenone (98%), phenylboronic acid (95%), tetrakis(triphenylphosphine)palladium(0) (98%), n-Butyllithium solution (2.5 M in hexane), benzaldehyde and 4,4′-diiodobiphenyl (technical grade, 90%) were purchased from Sigma Aldrich Canada Co. Dimethylformamide (DMF, anhydrous HPLC grade) was purchased from J&K Scientific. Anhydrous ethanol was purchased from Commercial Alcohols. Diphenylphosphineferrocene palladium dichloride (97%) was purchased from Strem Chemicals, Inc. 1,3-(diphenyl)propan-2-one (98%), bisbenzyl (98%), 1,3,5-tribromobenzene (98%) and trimethylsilylethynyl (98%) were purchased from Tokyo Chemical Industry Co., Ltd. America. Diphenylphosphine palladium dichloride (98%) was purchased from Strem Chemicals, Inc. Copper iodide (99.9%) was purchased from Santa Cruz Biotechnology, Inc. Chemicals and organic solvents were used as received except THF was dried with sodium using benzophenone as the indicator.
**Instruments**

A Bruker AVANCE III 500 MHz equipped with a 5 mm TXI Inverse probe at room temperature (T = 298 K) was used to record $^1$H and $^{13}$C NMR. Mass spectra were recorded for all molecules on an AB Sciex 4000 Q TRAP spectrometer (ESI mode). High resolution mass spectroscopy measurements were performed on a LC-TOF instrument from Agilent Technologies in positive APPI mode. Molecular ion (M⁺) or protonated molecular ions (M+H)⁺ were used for empirical formula confirmation, and were done at the Centre Régional de Spectrometry de Masse de l’Université de Montréal. Gel permeation chromatography analysis was conducted using Water HPLC HR 5, HR 4 and HR 3 columns using HPLC grade DMF (containing 0.10 M LiBr) as eluent. Polystyrene samples, purchased from Waters Associates Inc., were used as standards for the calibration. Thermogravimetric analysis (TGA) measurements were performed on a PerkinElmer STA6000 heating at a rate of 10 °C per minute from 23 °C to 800 °C under nitrogen atmosphere to assess thermal stability of polymers. Infrared spectra were recorded using a Perkin Elmer UATR FT-IR spectrometer, scanning previously dried membrane samples 100x. Samples were folded to obtain an average thickness of 300 ± 50 μm, after which they were measured.
Synthetic pathways

Synthesis of BTCS-TEA diene monomer

Scheme S1. Synthesis of diene monomer BTCS-TEA. Reagents and conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, TEA, 50 °C, overnight; (b) I$_2$, DMSO, 155 °C, overnight; (c) dibenzyl ketone, KOH, refluxing, 45 min; (d) TMS-OSO$_2$-Cl, DCE, overnight; (e) n-BuOH, TEA. TEA = triethylamine, THF = tetrahydrofuran.
**Scheme S2.** Synthesis of dienophile monomers **TPPy** and **TPP**. Reagents and conditions: (a) Trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, TEA, 50 °C, overnight; (b) benzaldehyde, KOH, NH₄OH, EtOH, RT, 3 d; (c) Trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, TEA, RT, overnight; (d) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, n-BuLi, THF, -78 °C, 1 h; (e) phenylboronic acid, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O, 90 °C, overnight; (f) 13, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O, 90 °C, overnight; (g) K₂CO₃, Et₂O/MeOH, RT, 1h. TEA = triethylamine, THF = tetrahydrofuran.
Scheme S3. Synthesis of polymer sTPPPP-H⁺ and sTPPyPP-H⁺.

Synthetic procedures

Synthesis of 1,4-bis(phenylethynyl)benzene (3)

1,4-diiodobenzene (16.5 g, 50 mmol), phenylacetylene (12.1 mL, 110 mmol), and Pd(PPh₃)₂Cl₂ (36 mg, 0.05 mmol) were dissolved in 122 mL diethylamine under N₂. To the solution was added CuI (19 mg, 0.1 mmol) and the mixture was stirred at 50 °C overnight. After cooling the solution to room temperature, the volatiles were removed in vacuo. The crude solid product was sequentially washed with saturated ammonium chloride solution, 1M HCl and MeOH. A gray solid (12.2 g, 88%) was recovered after air-drying and used in the next step without further
purification. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.54-7.58 (m, 8H), 7.40-7.37 (m, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 131.62, 131.51, 128.41, 128.35, 123.15, 123.10, 91.23, 89.11;

Figure S1. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3
**Synthesis of 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (4)**

Compound 4 was synthesized according to a previously reported literature. To a solution of 1,4-bis(phenylethynyl)benzene (10.8 g, 38.8 mmol) in 186 mL DMSO was added Iodine (19.71 g, 77.6 mmol). The reaction was stirred at 155 °C for 14 h. After cooling to room temperature, the mixture was poured into 1.0 L of 1% Na$_2$S$_2$O$_3$ solution. The residue was filtered, washed with water and dissolved in dichloromethane. The solution was washed with Na$_2$S$_2$O$_3$ solution and water in an extraction funnel, dried with magnesium sulfate and passed through a short silica gel column. The volatiles were removed *in vacuo*. The crude product was recrystallized by ethyl acetate/hexanes (1:2) to afford yellow needle-like crystals (10.0 g, 75.0%). 1H NMR (CDCl$_3$, 400 MHz)
MHz) δ 8.14 (s, 4H), 8.00 (d, 4H), 7.71 (t, 2H), 7.55 (t, 4H); **¹³C NMR (CDCl₃, 100 MHz)** δ 193.36, 193.21, 137.19, 135.18, 132.65, 130.22, 129.95, 129.13;

**Figure S3.** **¹H NMR spectrum (CDCl₃, 400 MHz)** of 4
Figure S4. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 4

Synthesis of 4,4'-(1,4-phenylene)bis(2,3,5-triphenylcyclopenta-2,4-dien-1-one) (5)

Compound 5 was synthesized according to a previously reported literature.$^2$ 1,3-(diphenyl)propan-2-one (4.57 g, 21.74 mmol) and 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (3.54 g, 10.35 mmol) were dissolved in 172 mL ethanol at 80 °C. To the resulting solution was added KOH (1.16 g, 20.7 mmol) in 5 mL ethanol dropwise via an additional funnel. The reaction was stirred at 80 °C for additional 45 min and then cooled at 0 °C for 2 h. The precipitate was filtered, washed with cold ethanol and further purified via recrystallization from dichloromethane. After drying in vacuo overnight a dark purple solid was obtained (5.8 g, 81.2%). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) δ 7.29-7.21 (m, 26H), 6.94 (d, 4H), 6.80 (s, 4H); $^{13}$C
**NMR (CD$_2$Cl$_2$, 100 MHz)** $\delta$ 200.60, 154.93, 154.67, 134.12, 133.51, 131.41, 131.26, 130.66, 130.60, 129.77, 129.51, 129.05, 128.53, 128.12, 128.07, 126.19, 125.93;

**Figure S5.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 5
Figure S6. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 5

Synthesis of tetra(para-sulfonated) bistetrcyclone (6)

Compound 6 was synthesized according to a previously reported literature.$^3$ To a solution of 4,4'-(1,4-phenylene)bis(2,3,5-triphenylcyclopenta-2,4-dien-1-one) (4.00 g, 5.8 mmol) in 300 mL degassed dichloroethane was slowly added trimethylsilyl chlorosulfonate (16.02 mL, 104.4 mmol) in 8 mL dichloroethane via an addition funnel. The reaction was stirred under Ar at room temperature overnight. 5.0 mL ethanol was added to the mixture to quench the reaction and the solution was stirred at room temperature for additional 4 h. The mixture was poured into 1.5 L diethyl ether. The precipitate was filtered, washed with diethyl ether and dried in vacuo to afford a dark red powder (5.0 g, 86.2%). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 7.50-7.46 (q, 8H), 7.33 (t, 2H), 7.25 (t, 4H), 7.14 (d, 4H), 7.07 (d, 4H), 6.92 (d, 4H), 6.86 (s, 4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ...
100 MHz) δ 199.38, 154.79, 154.63, 147.14, 147.08, 133.18, 132.08, 130.57, 130.23, 129.19, 
128.96, 128.79, 128.63, 128.13, 125.26, 125.21, 124.44, 124.15;

**Figure S7.** $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of 6
Figure S8. $^{13}$C NMR spectrum (DMSO-$d_6$, 100 MHz) of 6

Synthesis of tetra triethylammonium tetra(para-sulfonated) bistetracyclone (7)

Compound 7 was synthesized according to a previously reported literature. To a solution of tetra(para-sulfonated) bistetracyclone (5.0 g, 4.95 mmol) in $n$-butanol (200 mL) was added triethylamine (100 mL). The mixture was stirred at ambient temperature overnight, then filtered. The obtained solid was washed with ethyl acetate three times. A dark red solid (5.6 g, 80.0%) was obtained after drying in a vacuum oven at 60 °C overnight. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.51 (q, 8H), 7.34 (t, 2H), 7.27 (t, 4H), 7.14 (d, 4H), 7.08 (d, 4H), 6.93 (d, 4H), 6.86 (s, 4H), 3.10 (q, 24H), 1.18 (t, 36H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 199.40, 154.76, 154.58, 147.26, 147.24, 132.08, 131.13, 130.50, 130.12, 129.16, 129.04, 128.92, 128.78, 128.61, 128.11, 125.24, 125.19, 124.44, 124.15, 45.76, 8.63;
Figure S9. $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of 7
Figure S10. $^{13}$C NMR spectrum (DMSO-$d_6$, 100 MHz) of 7

Synthesis of 1-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (9)

Compound 9 was synthesized according to previous literature procedures with some modifications. 4,5 1-(4-Bromophenyl)ethan-1-one (19.705 g, 100 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (701 mg, 1 mmol) and trimethylsilylacetylene (18 mL, 120 mmol) were dissolved in a mixed solvent of 70 mL trimethylamine and 120 mL THF under N$_2$. To the solution was added CuI (381 mg, 2 mmol). The mixture was stirred at 50 °C for 18 h. After cooling to room temperature, the volatiles were removed in vacuo. The crude product was purified via flash column chromatography (dichloromethane/hexanes = 1 : 20). A light yellow oil (18.0 g, 83.3%) was obtained. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.84 (d, 2H), 7.50 (d, 2H), 2.54 (s, 3H), 0.25 (s, 9H);
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 196.85, 136.43, 131.97, 129.73, 128.02, 104.05, 97.98, 26.40, -0.21; HRMS (El) m/z calculated for C$_{13}$H$_{17}$OSi$^+$ (M + H$^+$) 271.1049, found 217.1040.

Figure S11. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 9
Figure S12. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 9

Synthesis of 2,6-bis(4-ethynylphenyl)-4-phenylpyridine (10)

Compound 10 was synthesized according to a previous literature procedure which was slightly modified. To a solution of benzaldehyde (1.33 g, 12.5 mmol) in 62.5 mL ethanol was added 1-(4-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (5.41 g, 25 mmol). Then ammonium hydroxide (36.3 mL, 29.3%) and KOH pellets (1.41 g, 25 mmol) were added to the mixture. The reaction was stirred at ambient temperature for 3 days. The crude solid was collected via filtration and washed with ethanol. Purification by flash chromatography (dichloromethane/hexanes = 1 : 3) gave a white powder (0.8 g, 18.0%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.20 (d, 4H), 7.92 (s, 2H), 7.76 (d, 4H), 7.67 (d, 4H), 7.58-7.50 (m, 3H), 3.12 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 156. HRMS (EI) $m/z$ calculated for C$_{27}$H$_{18}$N$^+$ (M + H$^+$) 356.1439, found 356.1449
Figure S13. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 10
Figure S14. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 10

Synthesis of ((4-bromophenyl)ethynyl)trimethylsilane (12)

Compound 13 was synthesized according to a previous literature procedure which was slightly modified.\textsuperscript{7} 1-bromo-4-iodobenzene (8.49 g, 30 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (42 mg, 0.6 mmol) and trimethylsilylacetylene (4.7 mL, 33 mmol) were dissolved in a mixed solvent of 50 mL trimethylamine and 120 mL THF under Ar. To the solution was added CuI (229 mg, 1.2 mmol). The mixture was stirred at RT for 18 h, then the volatiles were removed \textit{in vacuo}. The crude product was purified via flash column chromatography (hexanes). A white solid (5.8 g, 76.3\%) was obtained. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.45 (d, 2H), 7.34 (d, 2H), 0.27 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 133.34, 131.44, 122.70, 122.17, 103.87, 95.57, -0.15. HRMS (EI) $m/z$ calculated for C$_{11}$H$_{13}$BrSi$^+$ (M$^+$) 251.9970, found 251.9085
Figure S15. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 12
Figure S16. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 12

Synthesis of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)silane (13)

Compound 13 was synthesized according to a previous literature procedure which was slightly modified.$^8$ To a solution of ((4-bromophenyl)ethyl)trimethylsilane (2.53 g, 10 mmol) in 60 mL anhydrous THF was added n-BuLi (2.5 M in hexane, 5.2 mL, 13 mmol) dropwise manually over 30 min under Ar at -78 °C. The resulting mixture was stirred for 1 h, after which 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.2 mL, 30 mmol) was added dropwise into the solution and the mixture was allowed to warm to RT while stirring overnight. 100 mL of 1 M H$_2$SO$_4$ was added to quench the reaction and the mixture was vigorously stirred for another 2 h. The product was extracted with diethyl ether (50 mL x 2). The organic layer was separated and
washed with brine and water three times each. Purification via flash column chromatography (dichloromethane/hexanes = 1 : 4) yielded the target product as a white solid (600 mg, 20.0%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.75 (d, 2H), 7.48 (d, 2H), 1.37 (s, 12H), 0.27 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 134.41, 131.06, 125.78, 105.22, 95.49, 83.91, 24.85, -0.09. HRMS (EI) $m/z$ calculated for C$_{17}$H$_{26}$BO$_2$Si$^+$ (M$^+$) 301.1795, found 301.1788.

Figure S17. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 13
Compound 15 was synthesized according to a previous literature procedure with slight modifications.\textsuperscript{9} 1,3,5-tribromobenzene (3.75 g, 11.9 mmol) and phenylboronic acid (1.22 g, 10.0 mmol) were dissolved in 30 mL THF under Ar. To the solution was added 2M Na\textsubscript{2}CO\textsubscript{3} (10 mL) and Pd(PPh\textsubscript{3})\textsubscript{4} (231 mg, 0.2 mmol). The reaction was refluxed under Ar overnight. After cooling the reaction to RT, diethyl ether (20 mL x 2) was added to extract the product. The organic layer was separated and washed with brine and water three times each. The organic layer was dried with MgSO\textsubscript{4}. After removal of the volatiles \textit{in vacuo}, the product was further purified via flash column chromatography (hexanes) to yield a colorless oil (1.5 g, 47.6\%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) $\delta$ 7.68 (d, 2H), 7.46 (t, 1H), 7.55 (m, 2H), 7.48 (m, 2H), 7.43 (t, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) of 13
100 MHz) δ144.82, 138.37, 138.36, 132.58, 128.99, 128.44, 127.08, 123.26. **HRMS (EI) m/z** calculated for C_{12}H_{8}Br_{2}^{+} (M^{+}) 310.8894, found 310.9108.

**Figure S19.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 15
Figure S20. $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 15

Synthesis of ((5'-phenyl-[1,1':3,1''-terphenyl]-4,4''-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (16)

3,5-Dibromo-1,1'-biphenyl (125 mg, 0.4 mmol) and trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)silane (288 mg, 0.96 mmol) were dissolved in 10 mL THF under Ar. To the solution was added 2M Na$_2$CO$_3$ (5 mL) and Pd(PPh$_3$)$_4$ (30 mg, 0.02 mmol). The mixture was refluxed under Ar overnight. After cooling the reaction to RT, diethyl ether (10 mL x 2) was added to extract the product. The organic layer was separated and washed with brine and water three times each. The organic layer was dried with MgSO$_4$. After removal of the volatiles *in vacuo*, the product was further purified via flash column chromatography (dichloromethane/hexanes = 1 : 3) to yield a colorless oil (61.1 mg, 30.3%). $^{1}$H NMR (CDCl$_3$, 100 MHz):
400 MHz) δ 7.78 (d, 2H), 7.77 (t, 1H), 7.70-7.72 (d, 2H), 7.66-7.88 (d, 4H), 7.60-7.62 (d, 4H), 7.52 (t, 2H), 7.43 (t, 1H), 0.32 (s, 18H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 142.65, 141.56, 140.92, 132.46, 142.45, 128.85, 127.67, 127.33, 127.03, 125.33, 124.73, 122.51, 104.92, 95.14, -0.02.

**HRMS (El) m/z** calculated for C$_{34}$H$_{34}$Si$_2$ $^+$ (M$^+$) 498.2194, found 498.2192.

**Figure S21.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 16
**Figure S22.** $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 16

**Synthesis of 4,4'-diethynyl-5'-phenyl-1,1':3',1''-terphenyl (17)**

To a solution of ((5'-phenyl-[1,1':3',1''-terphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (61.0 mg, 0.122 mmol) dissolved in 10 mL diethyl ether and 20 mL methanol was added K$_2$CO$_3$ (170 mg, 1.22 mmol). The mixture was stirred at RT for 1 h. Diethyl ether (10 mL) was added to extract the product and the organic layer was separated, washed with brine and water, and dried with MgSO$_4$. Removal of the volatiles *in vacuo* gave a white solid (43 mg, 99.2%), which was used for the following reaction without further purification. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.20 (d, 4H), 7.92 (s, 2H), 7.77 (d, 2H), 7.67 (d, 4H), 7.57-7.53 (m, 6H), 3.18 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 142.70, 141.54, 141.32, 140.83, 132.64, 128.88,
127.71, 127.32, 127.18, 125.43, 124.84, 121.48, 83.45, 77.92. **HRMS** (El) m/z calculated for C_{28}H_{19}^+ (M + H^+) 355.1481, found 355.1472.

**Figure S23.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 17
General procedure A: synthesis of sulfonated polymers with triethylammonium salts (polymer-HNEt$_3^+$)

The two polymers were synthesized and purified according to previous literature procedures.$^2, 3$ Monomer BTCS-TEA (7) and the appropriate dienophile monomer were mixed in nitrobenzene under Ar. The mixture was first stirred at R.T for 10 min and heated at 180 °C for 3 d. After cooling to room temperature, ethyl acetate was added to the reaction and the mixture was refluxed for 4 h. The precipitate was filtered and washed with ethyl acetate. The polymer precipitate was then dissolved in DMSO at 80 °C, and re-precipitated into ethyl acetate. Filtration and drying under vacuum at 80 °C overnight yielded the final polymer product.

**Figure S24.** $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 17
General procedure B: conversion from sulfonate triethylammonium salts (Polymer-HNEt$_3^+$) to sulfonic acids (Polymer-H$^+$)

To a solution of Polymer-HNEt$_3^+$ in methanol was slowly added NaOH in methanol. The mixture was stirred at room temperature for 48 h. Polymer-Na$^+$ was filtered, washed with methanol and dried under vacuum, then suspended in water. To said mixture of Polymer-Na$^+$ in water was added 2 M $\text{H}_2\text{SO}_4$. After stirring at room temperature for 24 h, filtration, and drying in vacuo overnight, the Polymer-H$^+$ was obtained.

Synthesis of polymer sTPPyPP-H$^+$

Following general procedure A, monomer 7 (849.0 mg, 0.6 mmol) and dienophile monomer 10 (214 mg, 0.6 mmol) were mixed in 40 mL nitrobenzene. The polymer (sTPPyPP-HNEt$_3^+$) was dried in a vacuum oven overnight to afford a dark brown solid (1.03 g, 99.9%).$^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 8.9 (s, 4H), 8.25-6.46 (m, 47H), 3.01 (q, 24H), 1.25 (t, 36H). GPC Analysis: Mn = 82 kDa, Mw = 181 kDa, $\bar{D} = 2.23$. 
Figure S25. $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of polymer sTPyPP-HNEt$_3^+$

Following general procedure B, to a solution of sTPyPP-HNEt$_3^+$ (1.0 g) in 60 mL methanol was slowly added a solution of NaOH in methanol (4.0 g NaOH, 20 mL methanol) the polymer of Na$^+$ form was isolated via filtration. The obtained sTPyPP-Na$^+$ was suspended in 40 mL water and combined with 40 mL of 2 M H$_2$SO$_4$. After filtration, sTPyPP-H$^+$ was dried in vacuo to afford a gray powder (620.0 mg, 78.7%). $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 8.45-6.46 (m, 47H). GPC Analysis: Mn = 115 kDa, Mw = 295 kDa, $\mathcal{D} = 2.56$. 
Figure S26. $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of polymer sTPyPP-HNEt$_3^+$

Synthesis of polymer sTPPPP-H$^+$

Following general procedure A, monomer 7 (320.9 mg, 0.227 mmol) and dienophile monomer 17 (81.9 mg, 0.231 mmol) were mixed in 18 mL nitrobenzene. The polymer (sTPPPP-HNEt$_3^+$) was dried in a vacuum oven overnight to afford a brown solid (351 mg, 90.2%). $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 9.00 (s, 4H), 8.25-6.0 (m, 48H), 3.01 (q, 24H), 1.25 (t, 36H).
Figure S27. $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of polymer sTPPPP-HNEt$_3^+$

Following general procedure B, to a solution of sTPPPP-HNEt$_3^+$ (300.0 mg) in 16 mL methanol was slowly added a solution of NaOH in methanol (1.6 g NaOH, 5 mL methanol) and the polymer of Na$^+$ form was isolated via filtration. The obtained sTPPPP-Na$^+$ was suspended in in 15 mL water and combined with 15 mL of 2 M H$_2$SO$_4$. After filtration, sTPPPP-H$^+$ was dried in vacuo to afford a gray powder (213.0 mg, 71.6%). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 8.25-6.0 (m, 48H).
Figure S28. $^1$H NMR spectrum (DMSO-$d_6$, 400 MHz) of polymer $s$TPPPP-$H^+$

Methods

Mechanical strength measurements
Figure S29 Strain vs. Stress curves under ambient condition

TGA Measurements
Figure S30 TGA curves for sTPPPP-H⁺ and sTPPyPP-H⁺
Fuel Cell Characterizations

The catalyst inks for fuel cell tests were prepared via the following method:

Water was used to wet Pt/C powder (TKK TEC-10E50E: 46.4wt% Pt on graphitized carbon) well, after which methanol was added to achieve a desired mixture (MeOH: H$_2$O = 3:1). Nafion® D520 ionomer was added dropwise to the stirring mixture to obtain 1% solids containing 30wt% ionomer and 70wt% Pt/C. The resulting catalyst ink was then deposited via spray coater (Sono-Tek ExactaCoat SC) onto the membrane surface at 60°C for an electrode area of 5cm$^2$, yielding a catalyst coated membrane (CCM): 0.4mg/cm$^2$ Pt/C was deposited on the cathode and 0.2mg/cm$^2$ Pt/C was deposited on the anode. The CCMs were then sandwiched between conventional GDLs (Sigracet 24BC) and laid between Teflon gaskets with thicknesses allowing for 20 to 30% GDL compression by a torque wrench set to 50 in-lbs.

The fuel cell performances for membranes were evaluated using a single cell fuel cell test station (Teledyne Medusa RD, Model 890CL, Scribner Assoc. Inc.). Conditioning was achieved by increasing current at 25 mA/cm$^2$ increments, followed by 2 ohmic-region polarization curves and a 10 h constant voltage held at 0.5 V to obtain stable conditioned performance. The polarization experiments were performed at 80 °C, 100% (anode/cathode), 95% (anode/cathode), 90% (anode/cathode), 100%/90% (anode/cathode) and 50% (anode/cathode) relative humidity (RH), 0.5/0.25 slpm set flows (increases somewhat at high current density), varied stoichiometry, O$_2$/H$_2$ or air/H$_2$. Polarizations were done consecutively with conditioning period under the different RH conditions. After running the polarization at 50% RH, an experiment at 100 % RH was repeated to examine the recoverability of sTPPyPP-H$^+$. The IV curves for evaluating the recoverability is shown in Figure S32. Starting at open circuit voltage (OCV), the current was gradually increased from 0.2 A at a rate of 0.01 A min$^{-1}$, then from 0.5 A to 1.5 A at 0.1 A min$^{-1}$.
and finally from 2 A to 15 A at 0.2 A min$^{-1}$. When the current or voltage reached 15 A or 0.25 V, the polarization was complete and the potential was returned to OCV for 2 min. This process was repeated 13 to 15 times at the different RH conditions, for roughly 25 h in total. After the described conditioning and polarizations were done for sTPPyPP-H$^+$, the accelerated stress test (AST) was then followed according to DOE protocols. The conditions when OCV was held was 90 °C, 30% RH at anode and cathode, zero backpressure under H$_2$/Air at gas flows and 1000/1000 stoichiometry, 0.07/0.17 slpm for the 5 cm$^2$ cells. The PFSA reference was equilibrated to these AST conditions without prior conditioning or any polarization experiments. However, gas crossover tests by CA were conducted at desired intervals for the PFSA sample.

Electrochemical data was obtained after allowing the OCV to settle to 0.150 V under 0.5/0.5 SLPM N$_2$/H$_2$, 80 °C, 100% RH. A PAR VersaStat potentiostat/gain phase analyzer was used to measure chronoamperometry (CA), linear-sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) for electrochemical catalyst surface area (ECSA). CA was a series of potential holds from 0 to 0.5 V in 30 second, 0.1 V steps. Hydrogen crossover current was determined from the average current held at 0.5 V. LSV was obtained via a 2 mV s$^{-1}$ potential sweep from OCV to 0.6 V. EIS was obtained using a 0.45 V bias and a 10 V AC sweep from 1 to $10^5$ Hz.

CV was performed at a rate of 50 mV s$^{-1}$, where 0.4 V was the initial potential with 0.01 V and 0.8 V as the vertex potentials. ECSA was calculated from averaging integrated hydrogen adsorption and desorption peaks. C$_{dl}$ was obtained from the gap distance between the forward scan and the reverse scan from 0.35 to 0.55 V in the voltammogram.
**Figure S31.** (Left) *In situ* polarization (left axis, solid) and power density (right axis, open), and (Right) Resistance of N-211, N-212, sTPPPP-H⁺ and sTPPyPP-H⁺ under H₂/O₂. Conditions were 80 °C, 100% RH, 0.5/1.0 slpm anode/cathode gas flows, zero backpressure.
**Figure S32.** *In situ* polarization (left axis, solid) and power density (right axis, open) of sTPPyPP-H⁺ at different RHs using H₂/O₂. Conditions were 80 °C, 100/95/90/50% RH, 0.5/1.0 slpm anode/cathode gas flows, zero backpressure.
Figure S33. *In situ* polarization (left axis, solid) and power density (right axis, open) of sTPPPP-H⁺ at different RHs using H₂/O₂. Conditions were 80 °C, 100/95/90/50% RH, 0.5/1.0 slpm anode/cathode gas flows, zero backpressure.
**Figure S34.** *In situ* polarization (left axis, solid) and power density (right axis, open) of sTPPyPP-H⁺ and sTPPPP-H⁺ before and after 50% RH polarization using H₂/O₂. Conditions were 80 °C, 100% RH, 0.5/1.0 slpm anode/cathode gas flows, zero backpressure.
Figure S35. The fit small angle X-ray scattering spectra of hydrated sTPyPP-H⁺ and sTPPPP-H⁺.
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