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## Supporting Information for:

# Tetraarylborate polymer networks as single-ion conducting solid electrolytes

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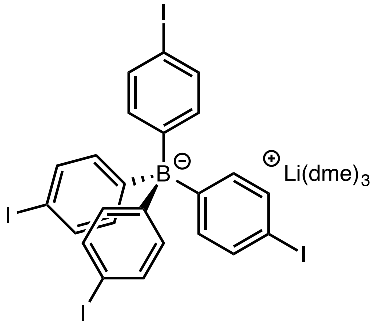
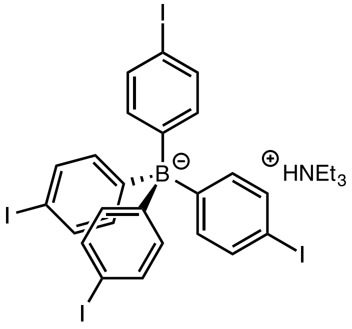
## General Information

All reagents were purchased from commercial sources and used without further purification. MeOH, toluene, and $CH_3CN$ were purchased from commercial sources and purified using a custom-built alumina-column based solvent purification system. Anhydrous DMSO and DMF were purchased from Sigma-Aldrich and used as received. Other solvents were purchased from commercial sources and dried over activated 3Å molecular sieves. NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using a standard $^1H\{^{13}C, ^{15}N\}$ Z-PFG probe with a 20 Hz sample spin rate, or on a Bruker AMX-400 Avance 400 MHz spectrometer without spinning, or on a Bruker AV-600 Avance III spectrometer without spinning. Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer using 75 mg samples degassed at 90 °C for 24 h and backfilled with $N_2$. $N_2$ isotherms were generated by incremental exposure to ultra high purity nitrogen up to 1 atm in a liquid nitrogen (77 K) bath and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). Scanning electron micrographs for polymer **16** were obtained on a LEO 1550 FESEM (Keck SEM) operating at 200 kV and a working distance of 3 mm. Samples were prepared by adsorption onto a silicon wafer, which was then attached to a flat aluminum platform sample holder. The sample was then placed directly into the instrument. No metal coating was applied. Scanning electron micrographs for polymers **11a** and **11b** were obtained on a FEI/Phillips XL30 SEM after gold sputtering. Elemental analyses were performed at the University of California, Berkeley Microanalytical Laboratory.

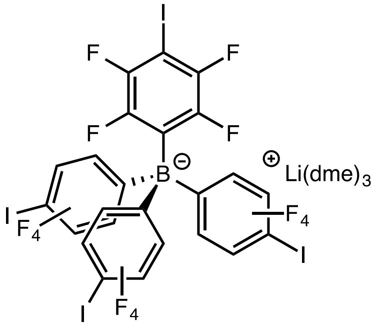
## Monomer Synthesis



**Tris(1,2-dimethoxyethane)lithium tetrakis(4-iodophenyl)borate** (**6**) was synthesized according to a minor modification of the procedure of Wuest.[1] 1,4-diiodobenzene (36.0 g, 109.1 mmol) was dissolved in 500 mL anhydrous diethyl ether under nitrogen atmosphere, and was cooled to approximately –15 ºC in a dry ice/ethylene glycol bath. *n*-Butyllithium (68 mL, 1.6 M in hexanes, 108.8 mmol) was added dropwise, and the solution was left to stir for an additional 20 minutes. Next, boron trifluoride diethyl etherate (2.7 mL, 21.9 mmol) was added dropwise, and the reaction was left to slowly warm to room temperature overnight. In the morning, the solution was concentrated to approximately 100 mL total volume, filtered, and rinsed with a small amount of diethyl ether. The solid obtained was suspended in acetone (100 mL), filtered through Celite, which was washed with additional acetone (25 mL), and concentrated. The crude material was dissolved in the minimal amount of hot 1,2-dimethoxyethane, and was then precipitated with the addition of hexanes, collected by filtration and dried *in vacuo* to yield the desired material (18.0 g, 16.4 mmol, 75% yield), with $^1H$ NMR consistent with the previous report.[1] $^1H$ NMR (400 MHz, DMSO-$d_6$): δ 7.27 (d, 8H, $J$ = 8.0 Hz), 6.87-6.82 (m, 8H), 3.39 (s, 12H), 3.20 (s, 18H).



**Triethylammonium tetrakis(4-iodophenyl)borate (8).** Tris(1,2-dimethoxyethane)lithium tetrakis(4-iodophenyl)borate (5.50 g, 5.0 mmol) was dissolved in the minimum amount of a water/methanol mixture (1:1 v/v) at room temperature. An aqueous solution of triethylamine (700 µL $NEt_3$ in 30 mL $H_2O$) was added in one portion, causing immediate precipitation. The suspension was left to stand overnight, then it was filtered and dried under high vacuum to deliver the desired material (4.58 g, 4.95 mmol). $^1$H NMR analysis showed the complete disappearance of signals associated with the 1,2-dimethoxyethane groups, which were replaced by the triethylammonium cation signals. $^1$H NMR (400 MHz, DMSO-$d_6$): δ $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.30 (d, 8H $J$ = 8.0 Hz), 6.91-6.85 (m, 8H), 3.09 (q, 6H, $J$ = 7.3 Hz), 1.16 (t, 9H, $J$ = 7.3 Hz).



**Tris(1,2-dimethoxyethane)lithium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate (18).** 1,4-diiodotetrafluorobenzene (2.00 g, 4.98 mmol) was dissolved in anhydrous diethyl ether (25 mL) and cooled to –78 ºC. Next, *n*-butyllithium (2.0 mL, 2.35 M solution in hexanes, 4.7 mmol) was added dropwise and the reaction was left to stir at -78 ºC for 90 minutes, at which point boron trichloride (1.1 mL, 1.0M solution in heptanes) was added dropwise. The reaction was left to slowly warm to room temperature overnight, then was quenched by the dropwise addition of an aqueous lithium chloride solution (0.1 M, 10 mL). The resulting suspension was diluted with more diethyl ether, rinsed with water (3 x 25 mL), then dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude material was dissolved in the minimal amount of hot 1,2-dimethoxyethane and precipitate by the addition of hexanes to deliver the intermediate product, presumed to be tris(1,2-dimethoxyethane)lithium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate in analogy with that reported above (830 mg, 62% yield). $^1$H NMR (400 MHz, Acetone-$d_6$) δ 3.43 (s, 12H), 3.26 (s, 18H). $^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -126.88 (d, $J$ = 16.9 Hz), -128.40 – -130.58 (m).

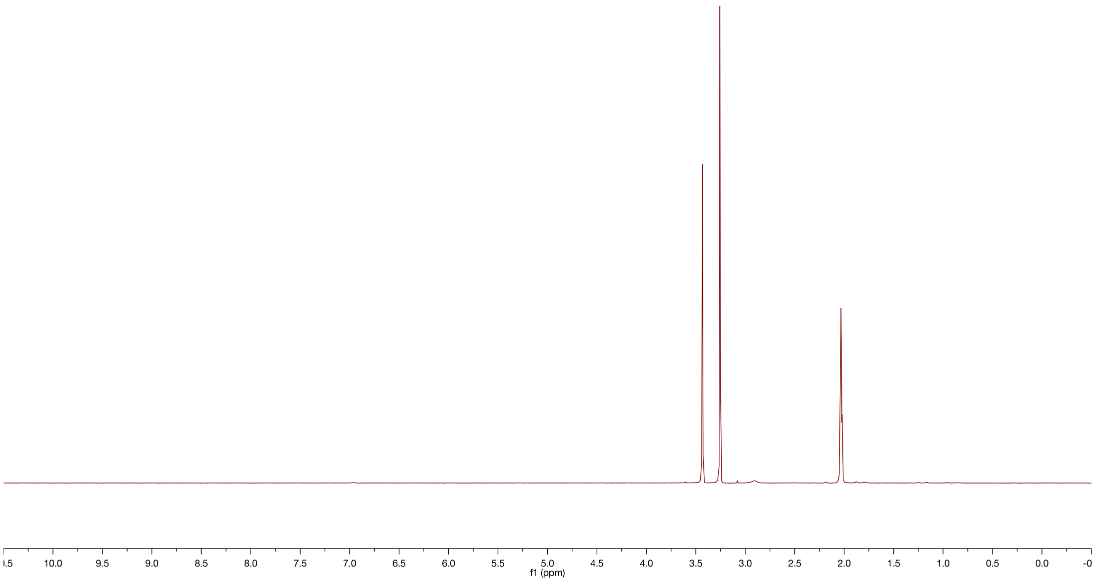


**Figure S1.** $^{1}$H NMR spectrum of compound **18**.

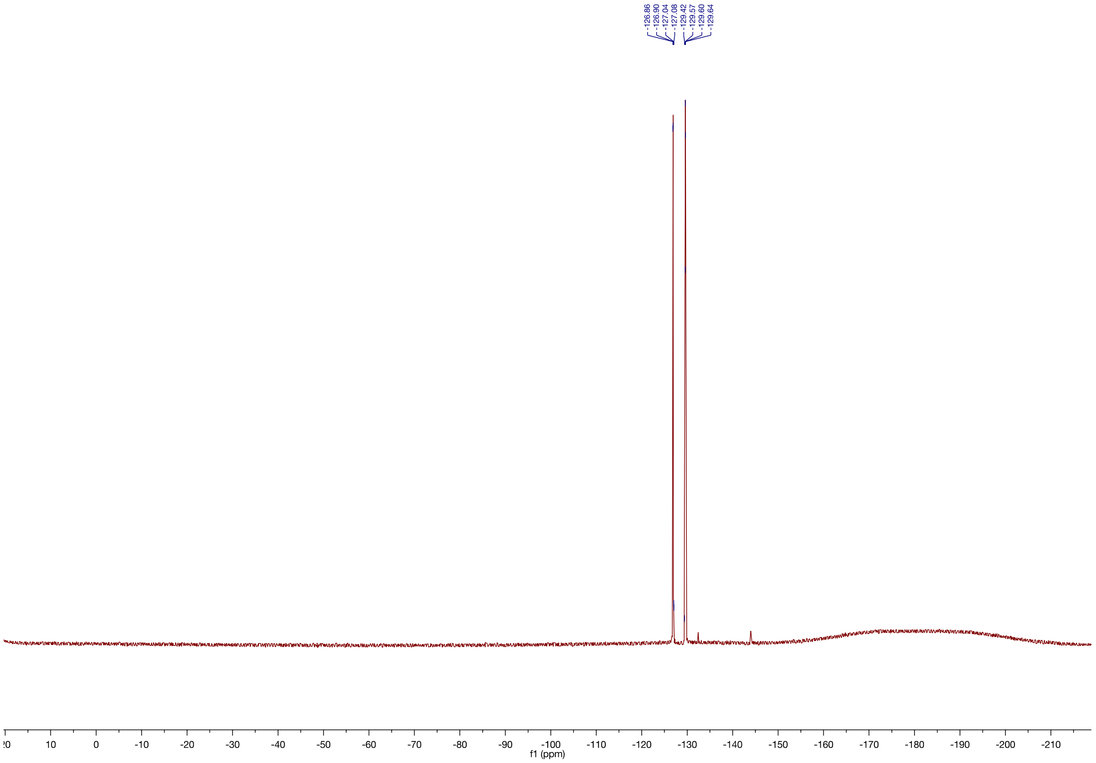
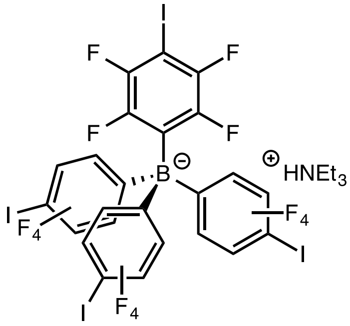


**Figure S2**. $^{19}$F NMR spectrum of compound **18**.



**Triethylammonium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate (12)** Tris(1,2dimethoxyethane)lithium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate (2.08 g, 1.50 mmol) was dissolved in the minimal amount of a water/methanol mixture (1:1 v/v) at room temperature. An aqueous solution of triethylamine (210 µL in 9 mL $H_2O$) was added in one portion, and the resulting suspension was left to stand overnight. In the morning, the material was obtained by filtration and dried *in vacuo* to deliver the desired material (1.54 g, 1.27 mmol, 85% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): δ 3.09 (q, 6H, *J* = 7.3 Hz,), 1.17 (t, *J* = 9H, 7.3 Hz). $^{13}$C NMR (600 MHz, $CDCl_3$): δ 148.1, 146.0. $^{19}$F NMR (376.4 MHz, DMSO-$d_6$): δ -125.7, -129.5. Elemental analysis for $C_{30}H_{16}BF_{16}I_4N$ calculated: 29.71% C, 1.33 % H, 1.15% N. Found: 29.58% C, 1.08% H, 1.12% N.

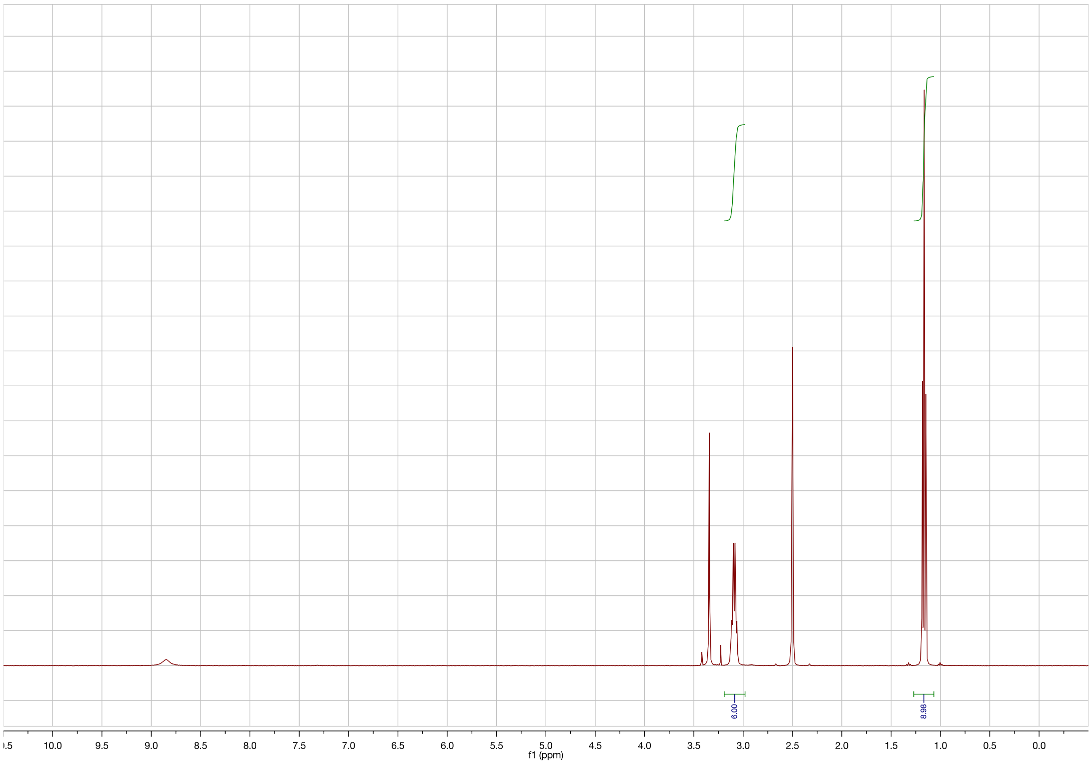


**Figure S3.** $^1$H NMR spectra of compound **12.**

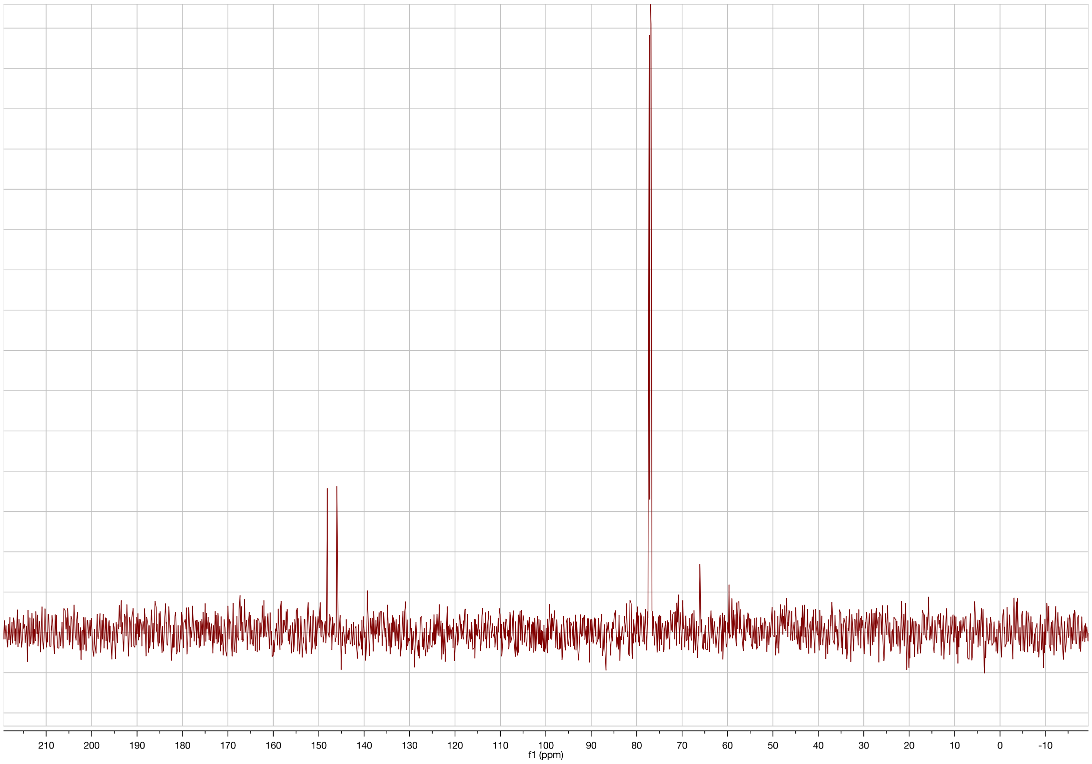


**Figure S4.** Fluorine-decoupled $^{13}$C NMR spectrum of compound **12.**

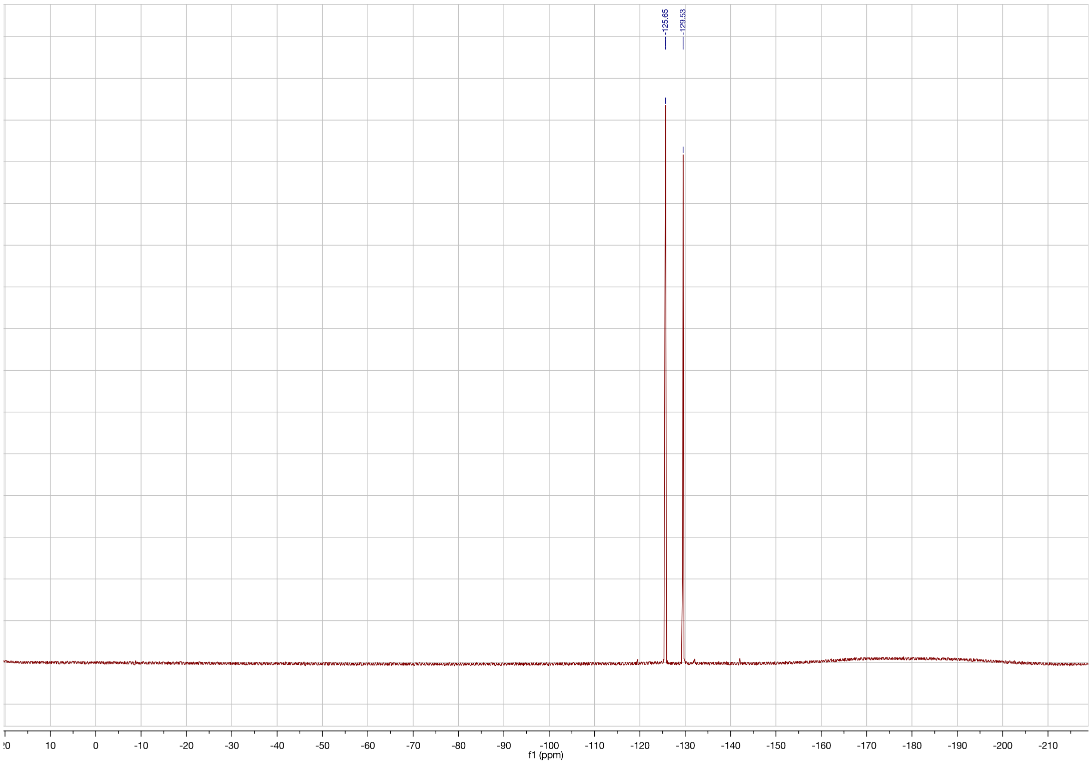


**Figure S5.** $^{19}$F NMR spectrum of compound **12.**

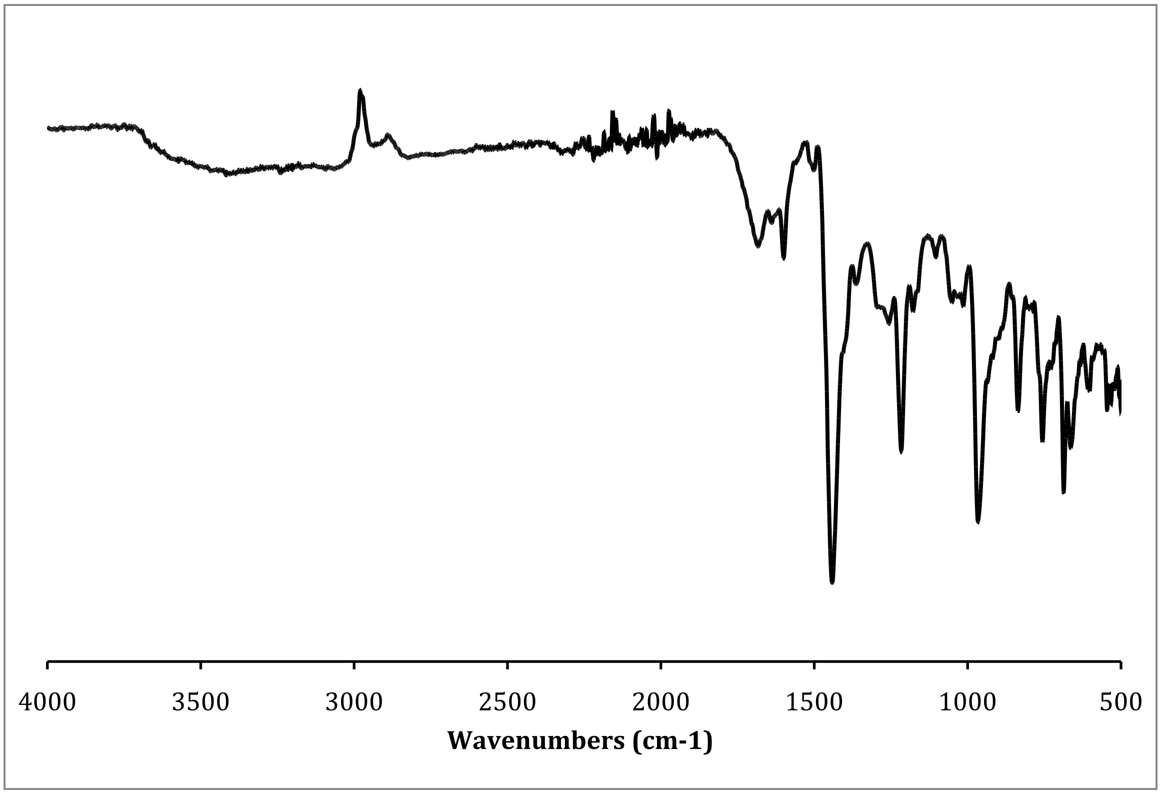
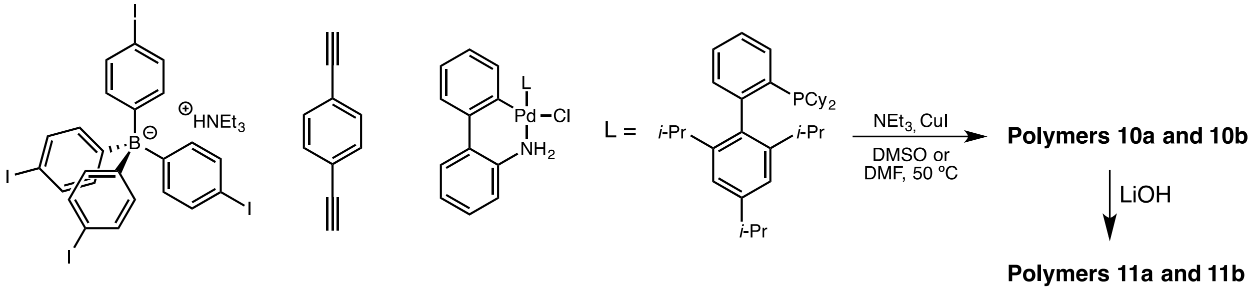


**Figure S6.** FT-IR spectrum of compound **12.**



**Polymers 11a and 11b**. Triethylammonium tetrakis(4-iodophenyl)borate (462 mg, 0.5 mmol), 1,4-diethynylbenzene (127 mg, 1.01 mmol), copper iodide (19 mg, 20 mol% compared to borate) and the second generation XPhos palladium precatalyst (20 mg, 5 mol% compared to borate) were charged in an oven-dried 40 mL septum capped vial under nitrogen. Degassed solvent (DMSO for **10a**, DMF for **10b**, 10 mL) were added, followed by freshly distilled (over KOH) triethylamine (835 $\mu$L, 6 mmol). The punctures in the septum were sealed with melted Parafilm, and the reaction was heated with stirring at 65 ºC for 72 hours. During this time, the reaction mixture solidified into a malleable gel. The gel was extracted from the vial with the aid of a spatula, and placed onto filter paper over vacuum. Every ten minutes, acetone (50 mL) was added, and the gel slowly collapsed to a free flowing powder over the course of ten solvent exchanges to deliver the intermediate polymers **10a** and **10b**, which contained triethylammonium counterions, as suggested by the significant amount of nitrogen present by elemental analysis (>1%). Triethylammonium cations were exchanged for lithium in both powders through the following process: the polymer sample was suspended in anhydrous methanol (24 mL) in a 40 mL septum capped vial, to which lithium hydroxide was added (75 mg). The vial was heated to 50 ºC for twelve hours, at which point, the methanol was removed by syringe. A fresh quantity of methanol (24 mL) was added, along with additional lithium hydroxide (50 mg). The vial again was heated to 50 ºC for twelve hours, at which point the methanol was removed by syringe. A final quantity of fresh methanol (24 mL) was added, along with the final portion of lithium hydroxide (25 mg). The vial was heated to 50 ºC for twelve hours, at which point the solid polymer was recovered by filtration and allowed to air-dry over vacuum for 15 minutes.

The air-dried solids were then heated in water (24 mL) at 80 ºC for two hours and collected by filtration. Excess water was rinsed off with anhydrous methanol, and the resulting solid was suspended in anhydrous methanol (24 mL) at 60 ºC for two hours, filtered, and suspended in fresh anhydrous methanol (24 mL) for a second two hour period at 60 ºC. Next, the polymers were suspended in 1:1 anhydrous MeOH:THF (24 mL total) and pure anhydrous THF (2 x 24 mL cycles), with all soakings performed for two hours at 60 ºC. After the final filtration, the obtained polymer samples were dried under high vacuum at 100 ºC for 12 hours to deliver polymers **11a** (196.1 mg) and **11b** (207.9 mg). Elemental analysis for $[C_{44}H_{24}BLi]_\infty$ with 0–4 THF molecules coordinated to lithium: 83.91–92.65% C, 4.24–6.57% H, 0.0% N. Found for polymer **11a**: 85.15 %C, 5.09% H, no nitrogen detected (<0.2%). Found for polymer **11b**: 82.80% C, 5.0% H, 0.33% N. The difference in FT-IR spectra observed between polymers **11a** and **11b** was no greater than that observed for different synthetic batches of either polymer.

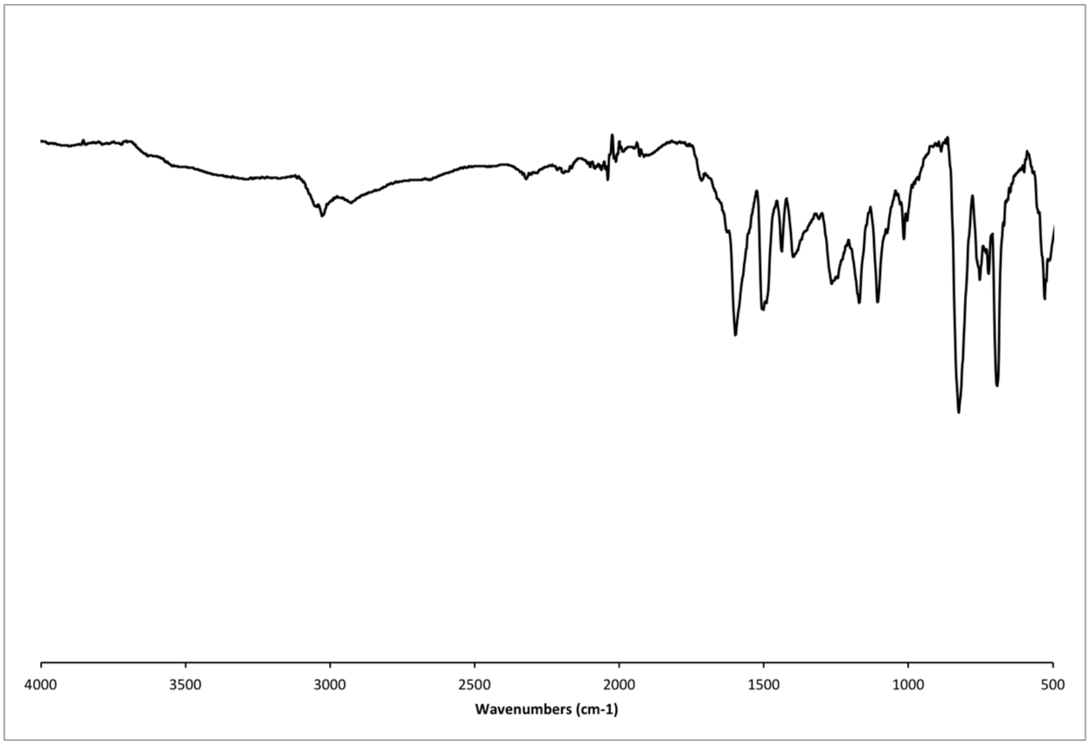


**Figure S7**. Represenatitive FTIR spectrum for polymers **11a/b**. The particular spectrum shown is for polymer **11b**.

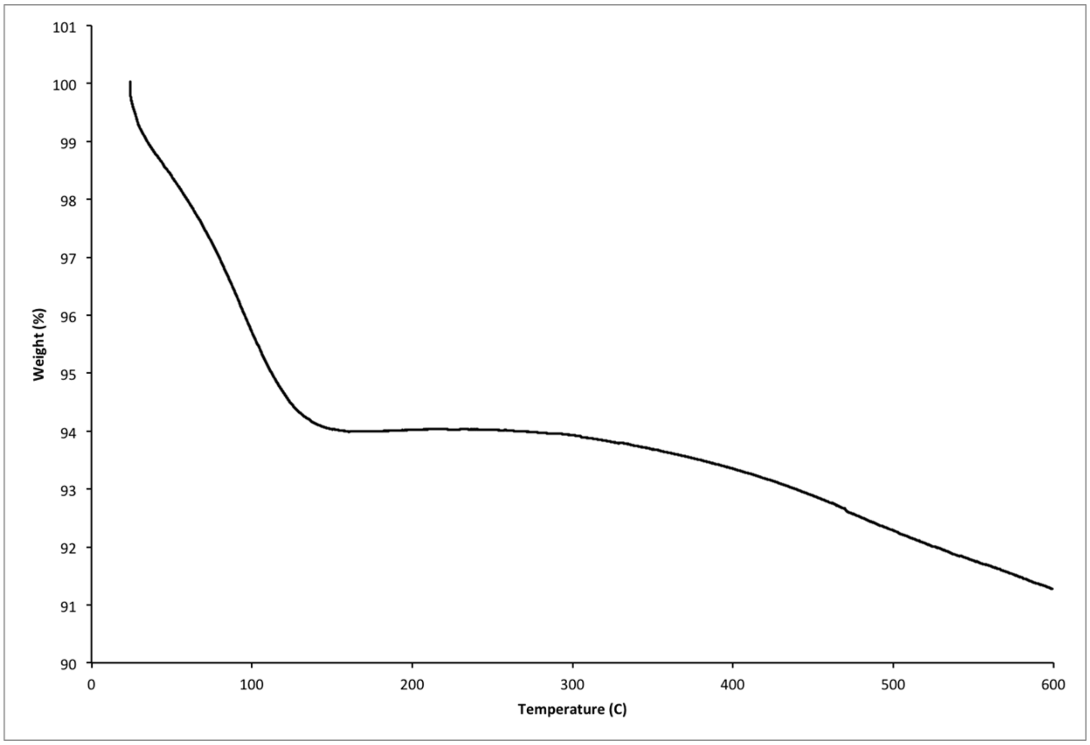
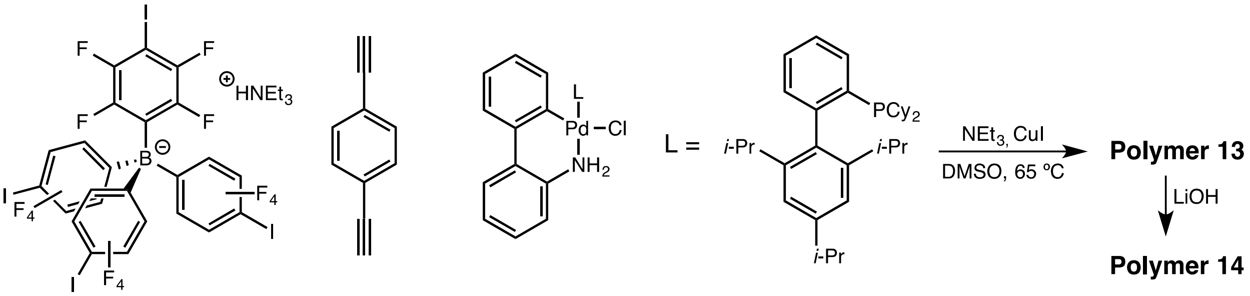


**Figure S8.** Representative thermal gravimetric analysis for polymers **11a/b** using a linear 1 ºC/min heating rate up to 600 ºC. The particular measurement shown is from polymer **11a**.



**Polymer 14**. Triethylammonium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate (606 mg, 0.5 mmol), 1,4-diethynylbenzene (127 mg, 1.01 mmol), copper iodide (19 mg, 20 mol% compared to borate) and the second generation XPhos palladium precatalyst (20 mg, 5 mol% compared to borate) were charged in an oven-dried 40 mL septum capped vial under nitrogen. Degassed DMSO (10 mL) was added, followed by freshly distilled (over KOH) triethylamine (835 µL, 6 mmol). The punctures in the septum were sealed with melted Parafilm, and the reaction was heated with stirring at 65 ºC for 72 hours. During this time, the reaction mixture solidified into a malleable gel. The gel was extracted from the vial with the aid of a spatula, and placed onto filter paper over vacuum. Every ten minutes, acetone (50 mL) was added, and the gel slowly collapsed to a free flowing powder over the course of ten solvent exchanges to deliver the intermediate polymer **13**, which contained triethylammonium counterions, as suggested by the significant amount of nitrogen present by elemental analysis (>1%). Triethylammonium cations were

exchanged for lithium in both powders through the following process: the polymer sample was suspended in anhydrous methanol (24 mL) in a 40 mL septum capped vial, to which lithium hydroxide was added (75 mg). The vial was heated to 50 ºC for twelve hours, at which point, the methanol was removed by syringe. A fresh quantity of methanol (24 mL) was added, along with additional lithium hydroxide (50 mg). The vial again was heated to 50 ºC for twelve hours, at which point the methanol was removed by syringe. A final quantity of fresh methanol (24 mL) was added, along with the final portion of lithium hydroxide (25 mg). The vial was heated to 50 ºC for twelve hours, at which point the solid polymer was recovered by filtration and allowed to air-dry over vacuum for 15 minutes.

The air-dried solids were then heated in water (24 mL) at 80 ºC for two hours and collected by filtration. Excess water was rinsed off with anhydrous methanol, and the resulting solid was suspended in anhydrous methanol (24 mL) at 60 ºC for two hours, filtered, and suspended in fresh anhydrous methanol (24 mL) for a second two hour period at 60 ºC. Next, the polymers were suspended in 1:1 anhydrous MeOH:THF (24 mL total) and pure anhydrous THF (2 x 24 mL cycles), with all soakings performed for two hours at 60 ºC. After the final filtration, the obtained polymer samples were dried under high vacuum at 100 ºC for 12 hours to deliver polymer **14** (349.2 mg). Elemental analysis for $[C_{44}H_8F_{16}BLi]_\infty$ with 0–4 THF molecules coordinated: 61.58-62.85% C, 0.94-3.52% H, 0% N. Found 60.44% C, 2.50% H, no nitrogen detected.

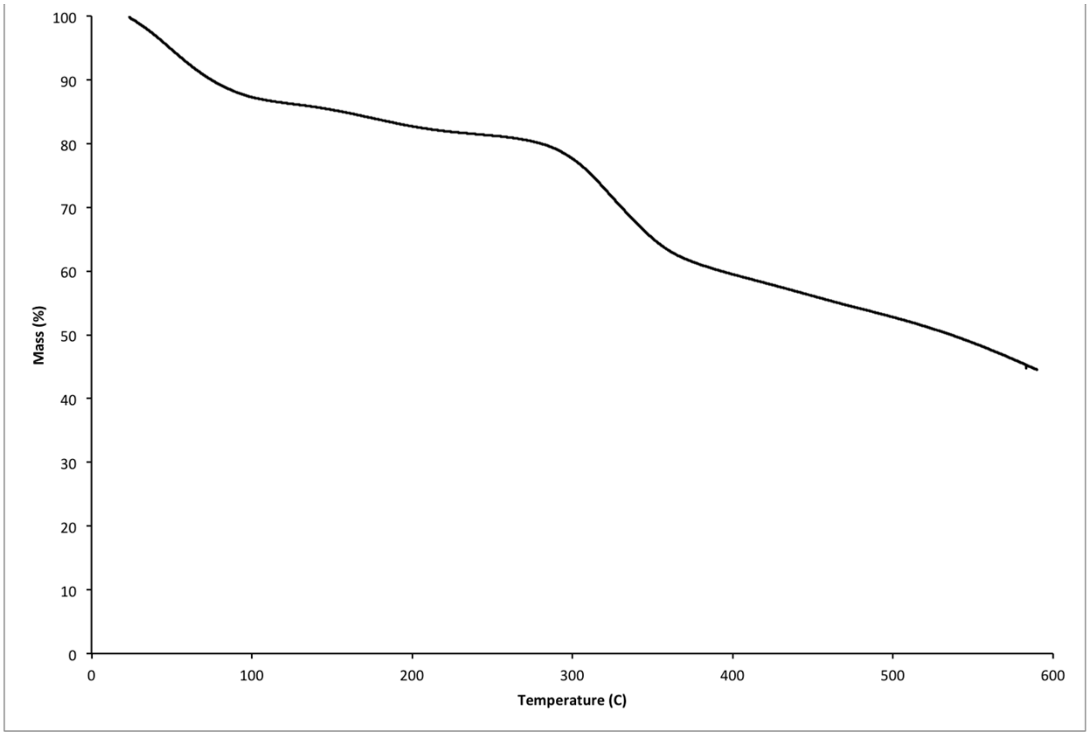


**Figure S9.** Thermal gravimetric analysis of polymer **14** using a linear 1 ºC/min heating rate up to 600 ºC.

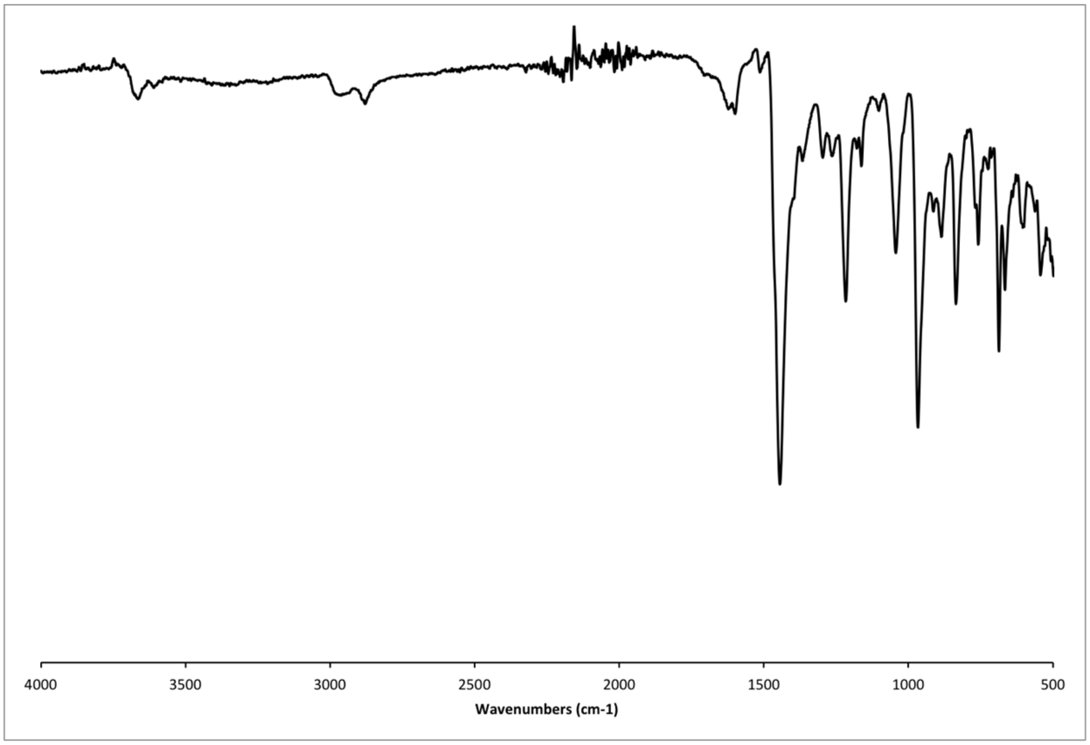
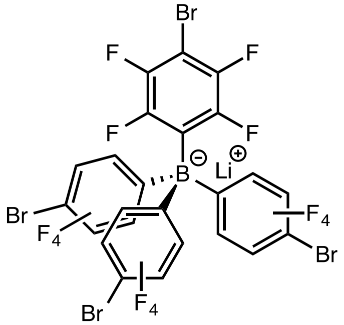
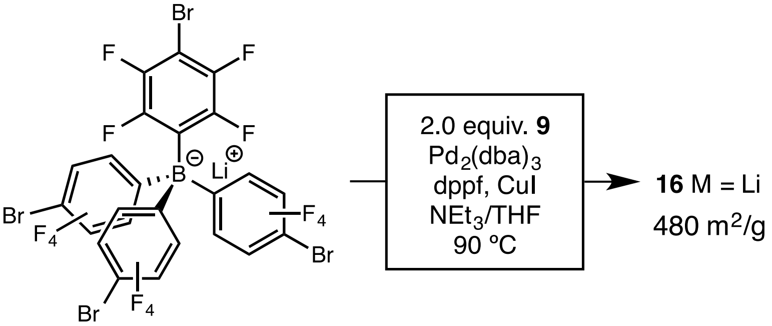


**Figure S10.** FTIR spectrum of polymer **14**.



**Lithium tetrakis(4-bromo-2,3,5,6-tetrafluorophenyl)borate (15)** was Compound **2** was prepared by modifying a previously reported procedure.[2] 1,4-dibromotetrafluorobenzene (10.0 g, 32.5 mmol) was dissolved in anhydrous diethyl ether (180 mL) in a flame-dried round bottom flask and stirred at -78 °C under a $N_2$ atmosphere. To this solution, n-BuLi (2.5 M in hexane, 32.5 mmol, 13.0 mL) was added via syringe under $N_2$ over 30 min, and the mixture was stirred at -78 °C for 1 h. A $BCl_3$ solution (1M in hexane, 8.0 mL, 8.0 mmol) was added dropwise under $N_2$ at -78 °C, and the mixture was stirred at this temperature for 1.5 h, then warmed to room temperature for 12 h. The reaction was quenched with $H_2O$ (100 mL), and the organic layer was separated. The aqueous layer was extracted twice with $Et_2O$, and the combined organic layers were dried over $Mg_2SO_4$ and filtered. After removing the solvent under vacuum, the resulting oil was purified by column chromatography ($SiO_2$, 10:90 MeOH : $CH_2Cl_2$) to provide a colorless oil, which was then dried at 160 °C overnight to give compound **2** (6.5 g, 86% Yield) as a white powder. Solution $^{19}$F and $^{13}$C NMR, and FT-IR spectra matched a previous report.[2]



**Polymer 16**. A flame-dried round bottom flask was charged with compound **2** (2.0 g, 2.15 mmol), 1,4-diethynylbenzene (0.54 g, 4.3 mmol), CuI (0.05 g, 0.24 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.36 g, 0.65 mmol), $Et_3N$ (30 mL) and anhydrous THF (30 mL) under a $N_2$ atmosphere. The mixture was degassed by three freeze-pump-thaw degassing cycles, after which $Pd_2(dba)_3$ (0.12 g, 0.13 mmol) was added. The mixture was again degassed by two freeze-pump-thaw cycles. The suspension was stirred at room temperature for 10 min and then heated to 85 °C for 3 d. An orange solid was formed, which was isolated and washed several times with $H_2O$, MeOH, and $CH_2Cl_2$. After activation by soaking in $CH_2Cl_2$ (2 x 200 mL) for 2 h and drying under vacuum overnight, polymer **16** (840 mg, 46% yield) was obtained as a fine orange powder. Polymer **16** (200 mg) was immersed in a $LiPF_6$ solution in $CH_3CN$ (15 mL, 0.2 M) and stirred for 4 h. The solution was removed carefully and the remaining polymer was washed several times with anhydrous $CH_3CN$. This procedure was repeated 3 times. The suspension was filtered and the solid was washed with anhydrous $CH_3CN$ (3 x 15 mL), anhydrous THF (3 x 15 mL), and anhydrous $CH_2Cl_2$ (2 x 15 mL). The solid was finally dried under vacuum overnight.

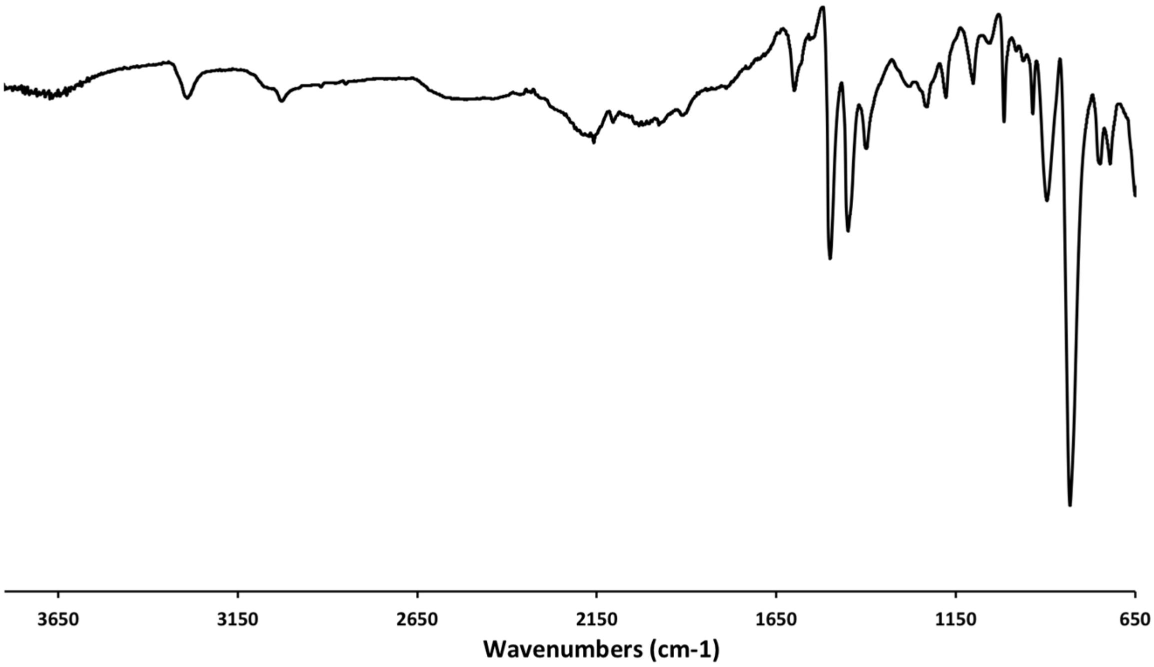


**Figure S11**. FT-IR spectrum of polymer **16**.

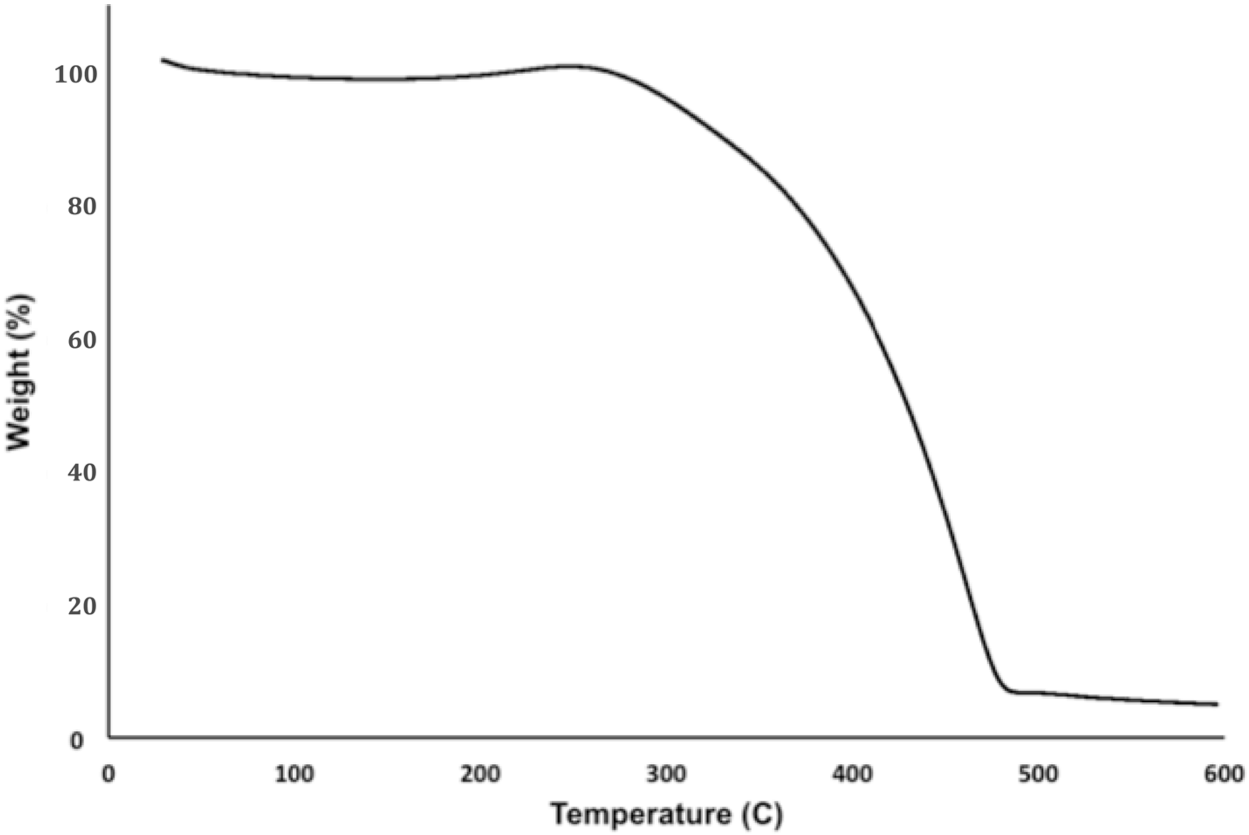


**Figure S12**. Thermal gravimetric analysis of polymer **16** using a linear 10 ºC/min ramp method up to 600 ºC.

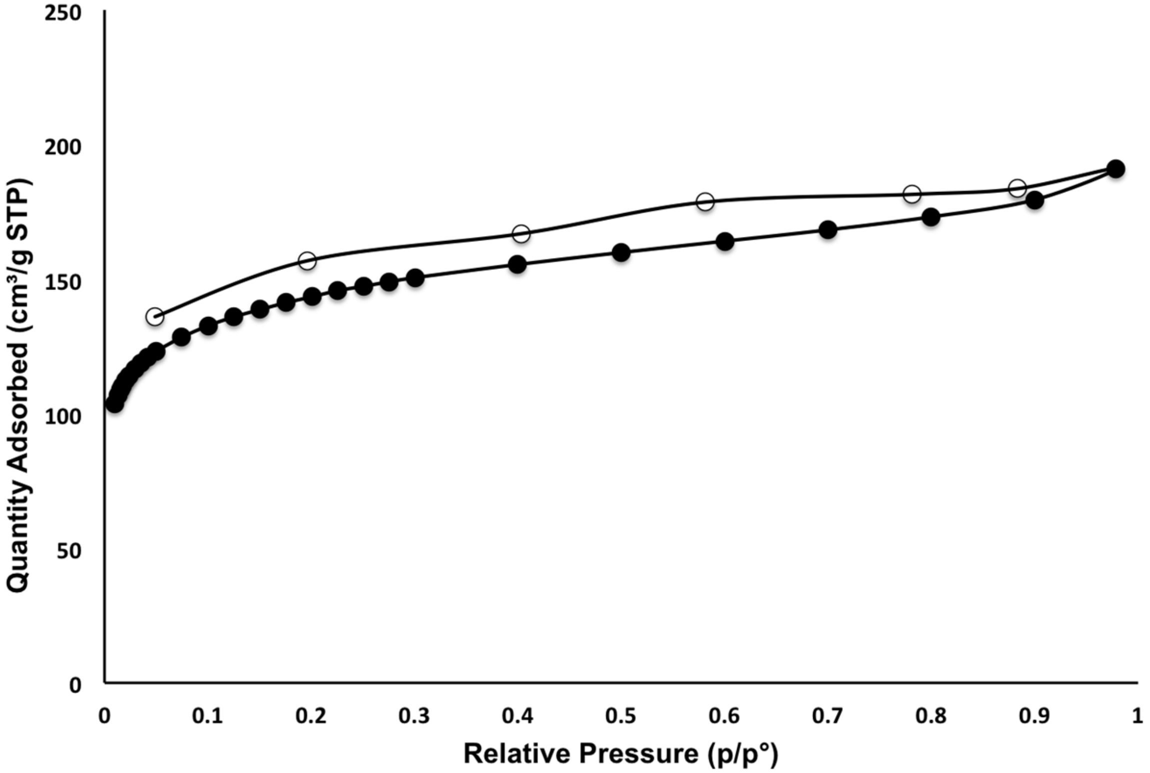


**Figure S13.** $N_2$ adsorption isotherm (77 K) of **16** after enrichment using $LiPF_6$ in $CH_3CN$. Adsorption: closed circles; Desorption: open circles.

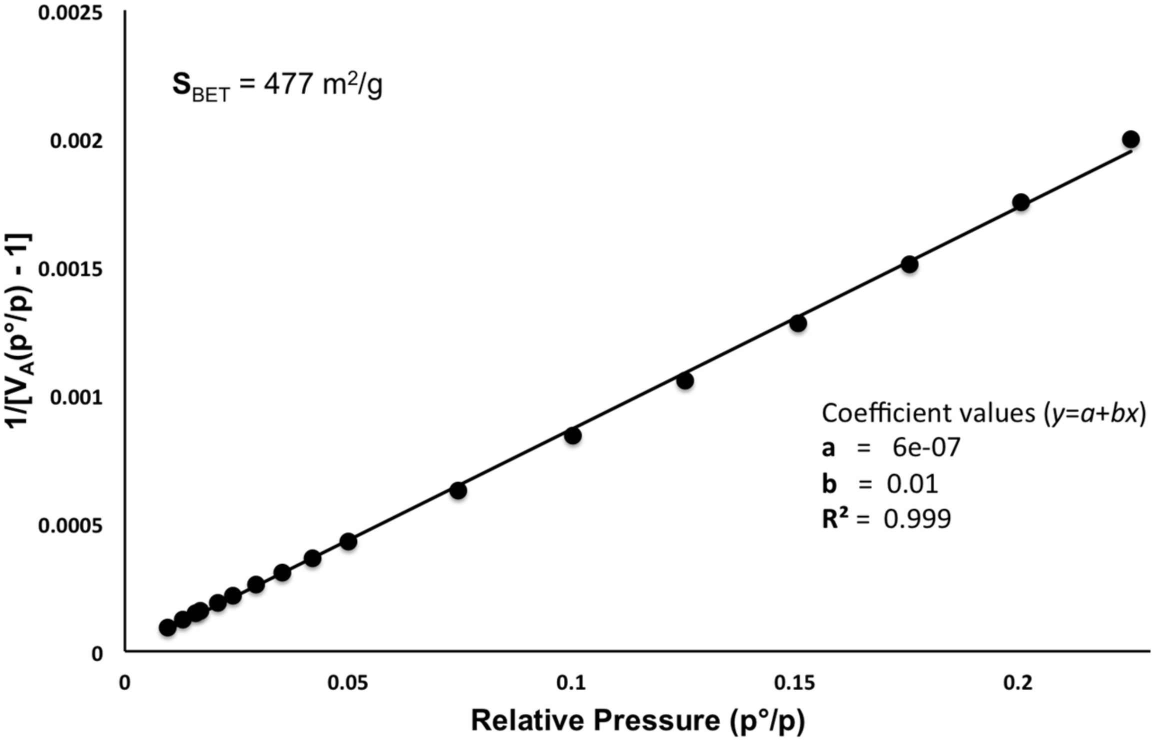
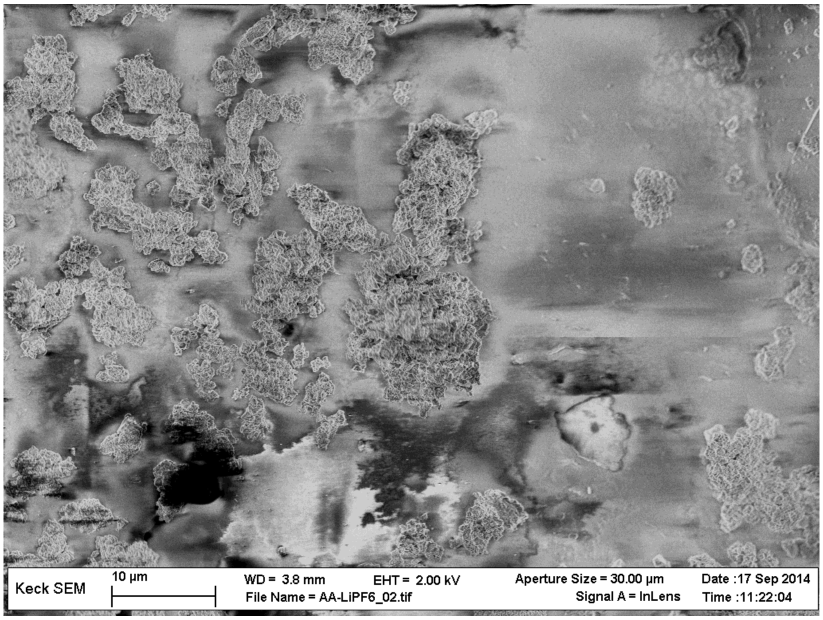


**Figure S14.** BET surface area plot of **16** after enrichment using $LiPF_6$ in $CH_3CN$.



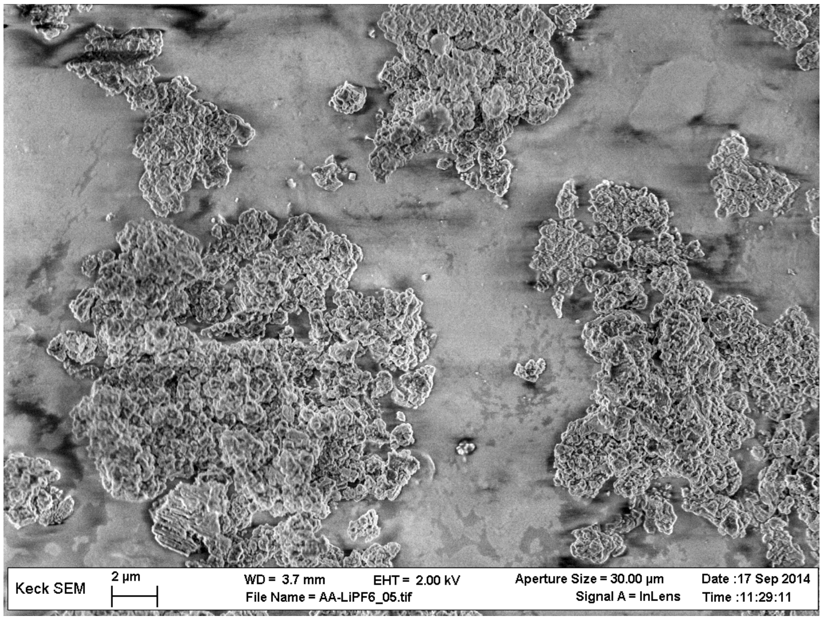


**Figure S15.** SEM images of as-synthesized polymer **16**.

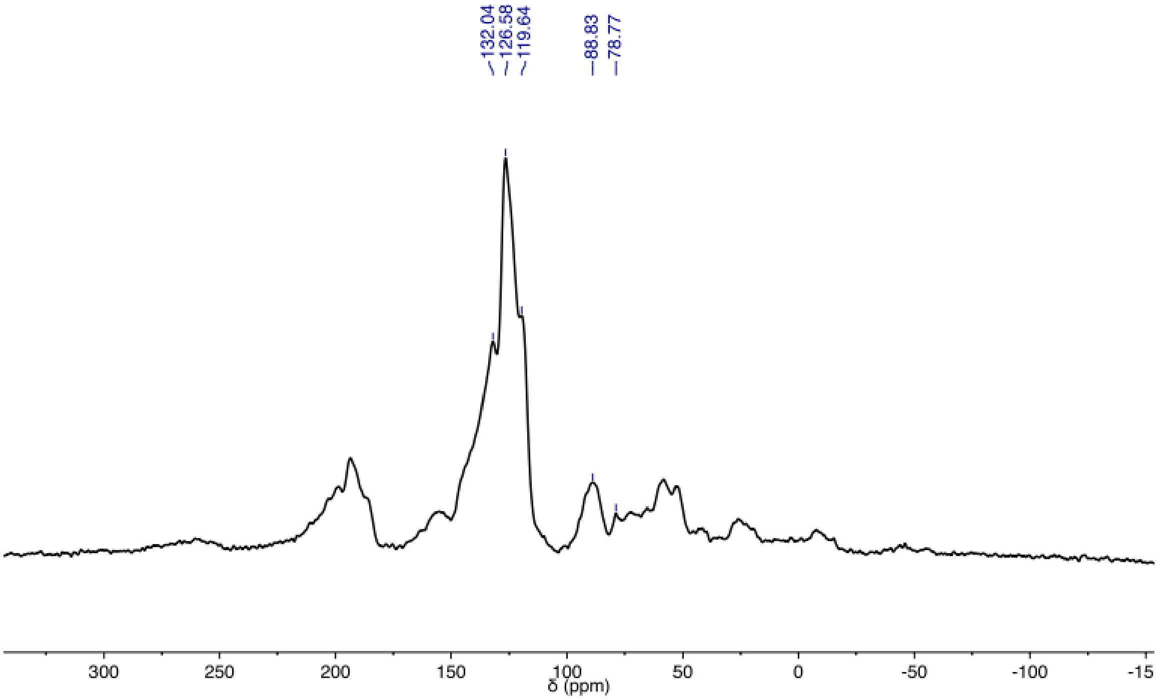


**Figure S16**. $^{13}$C-MAS ssNMR of polymer **16**.

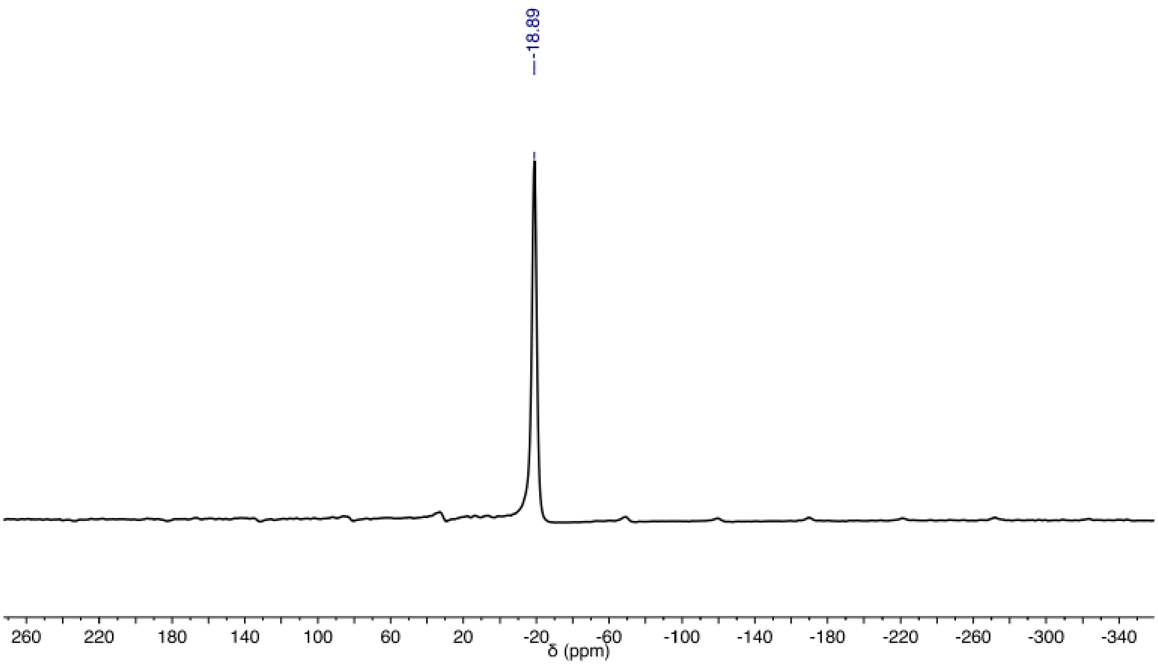


**Figure S17**. $^{11}$B-MAS ssNMR of polymer **16**.

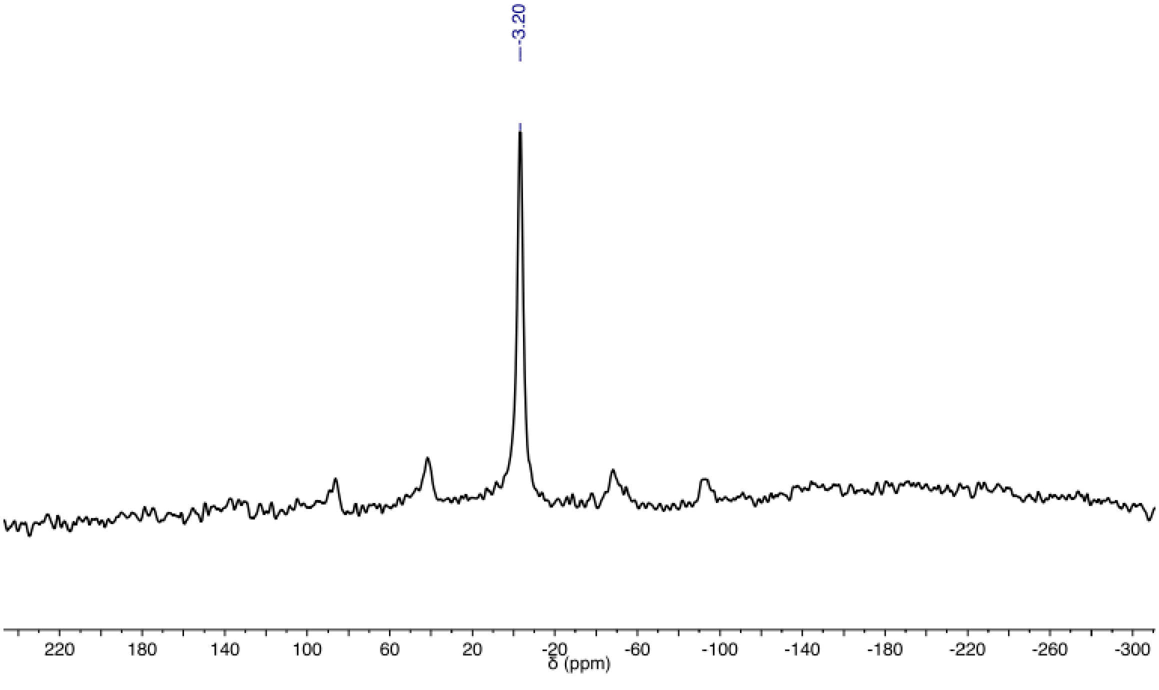
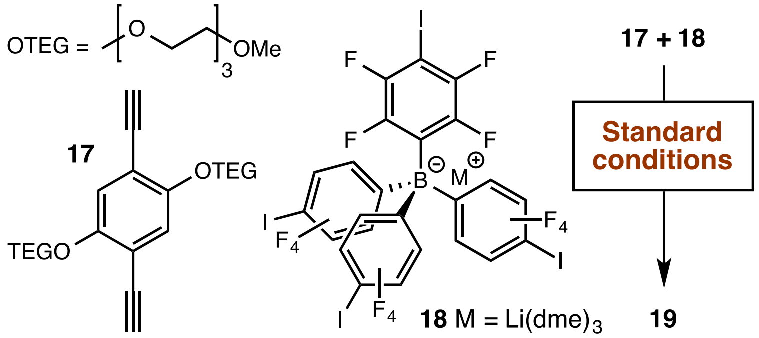


**Figure S18**. $^{7}$Li-MAS ssNMR of polymer **16**.



**Polymer 19**. The required bis-alkyne linker was prepared according to the literature procedure.[3] The lithium borate required was an intermediate obtained from the synthesis of **12** (see above). The polymerization conditions were identical to those described for polymer **14**: Tris(1,2-dimethyoxyethane)lithium tetrakis(4-iodo-2,3,5,6-tetrafluorophenyl)borate (300 mg, 0.216 mmol), 1,4-diethynyl-2,5-bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzene (196 mg, 0.435 mmol), copper iodide (8 mg, 20 mol% compared to borate) and the second generation XPhos palladium precatalyst (8.6 mg, 5 mol% compared to borate) were charged in an oven-dried 40 mL septum capped vial under nitrogen. Degassed DMSO (5 mL) was added, followed by freshly distilled (over KOH) triethylamine (360 µL, 2.58 mmol). The punctures in the septum were sealed with melted Parafilm, and the reaction was heated with stirring at 65 ºC for 72 hours. During this time, the reaction mixture solidified into a malleable gel. An additional portion of DMSO (16 mL) was added to aid transfer. The gel was extracted from the vial with the aid of a spatula, and placed onto filter paper over vacuum. Every ten minutes, acetone (50 mL) was added, and the gel slowly collapsed to a free flowing powder over the course of ten solvent exchanges to deliver the intermediate polymer **19**. As some triethylammonium cations could have been generated under the reaction conditions, the same exchange procedure was again applied: the polymer sample was suspended in anhydrous methanol (24 mL) in a 40 mL septum capped vial, to which lithium hydroxide was added (75 mg). The vial was heated to 50 ºC for twelve hours, at which point, the methanol was removed by syringe. A fresh quantity of methanol (24 mL) was added, along with additional lithium hydroxide (50 mg). The vial again was heated to 50 ºC for twelve hours, at which point the methanol was removed by syringe. A final quantity of fresh methanol (24 mL) was added, along with the final portion of lithium hydroxide (25 mg). The vial was heated to 50 ºC for twelve hours, at which point the solid polymer was recovered by filtration and allowed to air-dry over vacuum for 15 minutes.

The air-dried solids were then heated in water (24 mL) at 80 ºC for two hours and collected by filtration. Excess water was rinsed off with anhydrous methanol, and the resulting solid was suspended in anhydrous methanol (24 mL) at 60 ºC for two hours, filtered, and suspended in fresh anhydrous methanol (24 mL) for a second two hour period at 60 ºC. Next, the polymers were suspended in 1:1 anhydrous MeOH:THF (24 mL total) and pure anhydrous THF (2 x 24 mL cycles), with all soakings performed for two hours at 60 ºC. After the final filtration, the obtained polymer samples were dried under high vacuum at 100 ºC for 12 hours to deliver polymer **19**. Elemental analysis for $[C_{72}H_{64}O_{16}F_{16}BLi]_\infty$ calculated: 57.38% C, 4.28% H, 0% N. Found 55.11% C, 4.48% H, no nitrogen detected.

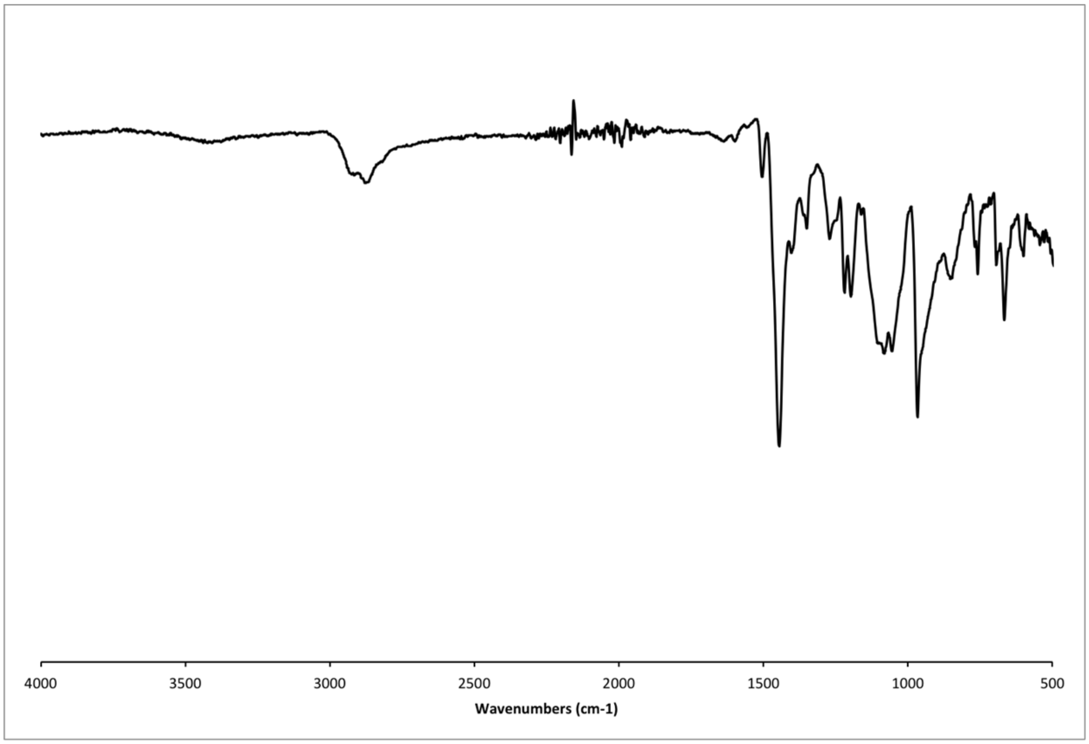


**Figure S19**. FT-IR spectrum of polymer **19**.

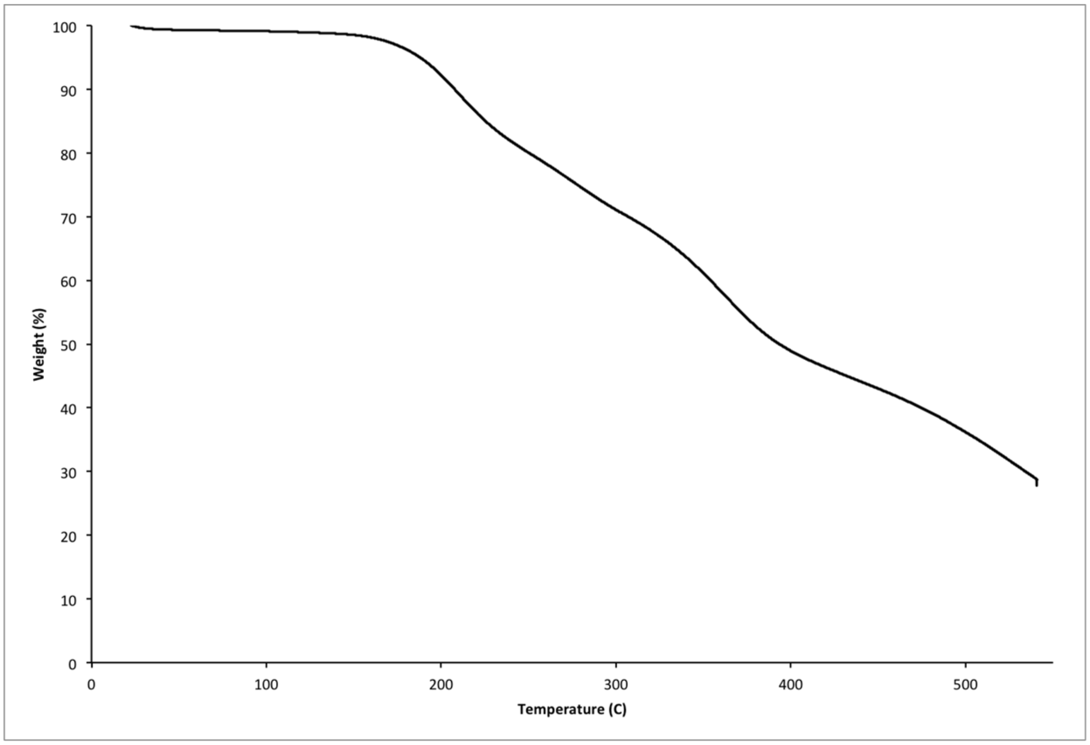


**Figure S20**. Thermal gravimetric analysis of polymer **19** using a linear 1 ºC/min heating rate up to 540 ºC.

## Ionic Conductivity Measurements

Polymer samples were prepared for measurement of ionic conductivity in the following way: A sample of the solid polymer (50-100 mg) was transferred into a nitrogen-filled glovebag, and was suspended under anhydrous propylene glycol (5 mL) for 72 hours, at which point they were filtered under nitrogen atmosphere and allowed to dry under flowing nitrogen for ten minutes, at which point, they were free-flowing solids.

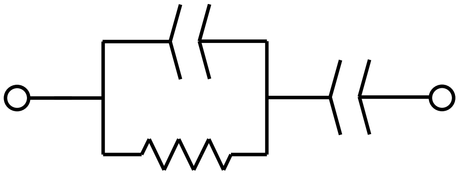
The samples were then transferred to an argon-filled glovebox. A Garolite washer that had a thickness of one millimeter and a 3.88 mm diameter hole bored in the center was taped onto a polished stainless steel disk using Kapton tape. The solid polymer of interest was loaded into the center of the washer, a thin sheet of polypropylene was placed over the top, and the sample was mechanically compressed with a hydraulic press, at a load of approximately 5,000 lbs. The thickness of the sample was measured after the completion of the AC impedance spectra with the use of a digital thickness gauge accurate to 0.1 µm. The pellets used for the data displayed in this publication had the following thicknesses: polymer **11a** = 0.971 mm, polymer **14** = 1.080 mm, polymer **16** = 1.029 mm, polymer **19** = 1.020 mm.

The stainless steel/Garolite/sample disk was then loaded into a custom-built test cell and capped with a second stainless steel monolith that had also been polished to a mirror finish. The monolith and washer functioned as blocking electrodes for the experiment. Pellet contact was maintained between two stainless steel electrodes with a compressed 15-lb spring.

All electrochemical characterization of completed on an electrochemical impedance spectroscopy capable Bio-Logic VMP-3 multipotentiostat. Impedance spectra were collected between 1 MHz and 10 Hz at 100 mV ac and the temperature was determined with a K-type thermocouple. Data recorded at 10 mV ac displayed an essentially identical frequency response. Ionic conductivity was calculated by fitting the frequency response curve to the model circuit in Scheme S1 using the freeware package EC-Lab by Bio-logic inc. From the refined cell resistance, $R_{bulk}$, the ionic conductivity was calculated with Equation 1.

$$\sigma_{bulk} = \frac{A}{R_{bulk} l} \qquad (1)$$

Here, $l$ is the pellet thickness, A is the electrode area and $\sigma_{bulk}$ is the bulk ionic conductivity of the sample in S $cm^{-1}$. Variable temperature conductivity data was fit to the Stokes-Einstein relation in order to determine the energy of activation.[3]



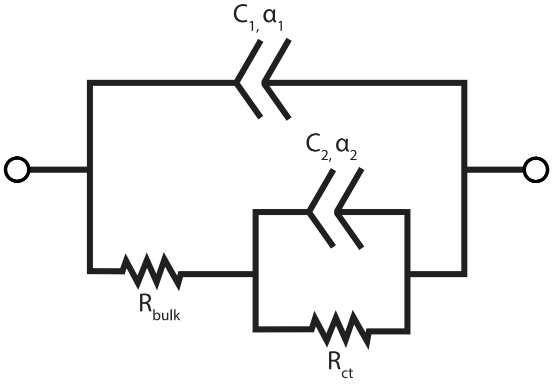
**Scheme S1:** Model circuit used to fit impedance spectra of electrolytes collected on blocking stainless steel electrodes. The resistor in parallel with the constant phase elements represents $R_{bulk}$.

*Transference number determination*

Transference numbers were determined in an identical cell and the same pellets with polished lithium metal smashed onto the stainless steel current collectors. A 300 mV dc voltage was applied across the pellet and the current response was recorded as a function of time for 20 minutes. An impedance spectrum was recorded immediately before the voltage step and at the end of the step. The transference number was then calculated as previously reported (Equation 2).[4]

$$t_{+} = \frac{I^{s}(\Delta V - I^{0}R^{0})}{I^{0}(\Delta V - I^{s}R^{s})} \quad (2)$$

In Equation 2, $t_+$ is the transference number, $I^s$ is the steady state current, ΔV is the dc voltage applied across the cell, $I^0$ is the initial current following the voltage step, $R^0$ is the charge transfer resistance for lithium reduction/oxidation measured by impedance spectroscopy before the voltage step, $I^s$ is the steady state current measured at the end of the voltage step, and $R^s$ is the resistance for lithium reduction/oxidation at the end of the voltage step. The cell resistances were determined by fitting the collected impedance spectra to the model circuit in Scheme 2 using the freeware package EC-Lab.



**Scheme S2:** Model circuit used to fit impedance spectra collected on non-blocking lithium metal electrodes. $R_{ct}$ was used to determine $R^0$ and $R^s$ in the transference number calculation.

## Cyclic Voltammetry (CV) and Impedance Stability on Lithium Foil:

In order to rigorously prevent carbonate vaporization form interfering with measurements a custom build air tight three-electrode cell was contructed using a 1/8 inch diameter Swagelok PFA union tee and Ti or SS plugs machined to fit snugly. For CV experiments, lithium metal of smeared onto the counter and reference electrodes and polished to a mirror finish. A pellet of the sample was packed inside the cell and the three electrodes were inserted. The working electrodes tested were titanium and stainless steel. The cells were heated overnight at 90 °C to obtain a stable lithium electrolyte interface. CV's were also collected at

90 °C, and an IR drop determination (single point impedance) was conducted before measurement. The sweep rate was constant across all experiments, 5 mV/s. All data was collect using the Bio-Logic's software package EC-LAB

Stability on lithium electrodes was measured over time at room temperature in the same cell. The counter and reference electrodes were shorted and the working electrode was placed opposite in the union tee to form a linear cell geometry. The third electrode was inserted to make the cell air tight but not used. Quartz fiber was added to the end of this current collector such that it was not in electrical contact with the sample. All data was collect using the Bio-Logic's software package EC-LAB. A two-point impedance spectrum (1 MHz to 1 Hz) was collected every hour for 200 hours. All spectra where fit to the model circuit in Scheme S2 and conductance was reports as the sum of the resistive components.

## References

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