Supporting Information

for

Vinyl iodide containing polymers directly prepared via an iodo-yne polymerization

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A) Model reaction of 1-octyne and diiodoperfluorohexane



Figure S1: Diiodoperfluorohexane and 1-Octyne model system for polymerization. **A)** Reaction scheme of model system that gives a mix of diastereomers. **B)** High resolution GCMS of diastereomers. **C)** ¹H-NMR demonstrating nearly quantitative conversion of 1-octyne and diiodoperfluorohexane. **D)** ¹⁹F-NMR demonstrating nearly quantitative conversion of 1-octyne and diiodoperfluorohexane.



Purified Polymer - 2.3 grams, 94 % Yield

Figure S2: Time lapse of large scale polymerization of diiodoperfluorohexane and 1,9-decadiyne. Purified polymer yielded 2.3 grams, a 94% yield.



Figure S3: Comparison of iodo-yne polymer molecular weight calculation through different SEC anaylsis conditions. All molecular weight data was calculated through refractive index signal. **A)** SEC performed with THF as an eluent at 39 °C with a flowrate of 0.9 mL/min at 6900 PSI. The instrument was calibrated with a set of low dispersity polystyrene standards. **B)** SEC performed with THF as eluent at 50 °C with a flowrate of 0.7 mL/min. The instrument was calibrated with a set of low dispersity polystyrene standards. **C)** SEC performed with DMSO as eluent at 65 °C with a flowrate of 0.3 mL/min. The instrument was calibrated with a flowrate of 0.3 mL/min. The instrument was calibrated with a set of low dispersity poly SEC performed with DMSO as eluent at 65 °C with a flowrate of 0.3 mL/min. The instrument was calibrated with a set of low dispersity poly (methyl methacrylate) standards. **D)** SEC performed with DMF + 0.1% LiBr as eluent at 50 °C with a flowrate of 1.0 mL/min. The instrument was calibrated with a set of low dispersity polystyrene standards.



Figure S4: Soxhlet fractionation of polymer **3** and analysis via differential scanning calorimetry. **A**) Scheme representing Soxhlet extraction of THF soluble polymer **3**. **B**) Differential scanning calorimetry comparison of iodo-yne polymer **3** before and after Soxhlet purification in THF. Polymer **3** before Soxhlet purification (middle, black), the THF soluble fraction of polymer **3** (bottom, blue) and the THF insoluble fraction of polymer **3** (top, red).



Figure S5: NMR analysis of polymer **3** following exposure to heat, light, or prolonged shelf life. **A**) ¹H-NMR. **B**) ¹⁹F-NMR.



Figure S6: Characterization of polymer **3** treated with Pd(PPh₃)₄. **A)** Infrared spectroscopy (IR) spectra of polymer **3** before (black, top) and after (red, bottom) treatment. **B)** Enhanced region of the identical infrared spectroscopy (IR) spectra in **A**, revealing complete loss of terminal alkyne C-H stretch due to reaction between vinyl iodide groups and terminal alkyne groups.



Figure S7: Reaction scheme of AIBN initiated thiol-yne addition of butanethiol to polymer **3** to give polymer **4**. Both possible end groups are shown at the polymer termini to demonstrate the reactions of each functionality. The polymer mixture likely also includes polymers with two terminal perfluoroiodides or two terminal alkynes.

A) Workflow of polymer purification



B) Stacked ¹H-NMR of pure Polymer 5 and the concentrated work-up solution



Figure S8: Optimization of purification conditions of the Sonogashira coupling to give polymer **5**. **A)** Unoptimized purification conditions to give polymer **5** in 51% yield (top, method A) and the optimized conditions which gave polymer **5** in 74% yield (bottom, method B). **B)** Stacked ¹H-NMR of the purified polymer **5** (top) and the concentrated methanol work-up containing 1-octyne, triphenylphosphine, diisopropylammonium chloride, and extracted polymer **5** (bottom).



Figure S9: Small molecule analog to investigate the phenol coupling. Small molecule **s3** when reacted with phenol and copper iodide employing dimethylglycine as the ligand to give the phenol coupled product **s4** as the major product, with a small amount of ene-yne **s5** formed as a by-product.

Polymer 5:



Polymer 6:



Polymer 8:



| C₅H₁₁

Polymer 9:



Polymer 10:



Figure S10: Representation of polymers synthesized in Table 2.



Figure S11: Thermal analysis of polymers **3** and **11**. **A)** Thermal gravimetric analysis (TGA) of polymers **3** (black) and **11** (red) under oxygen, showing an increase in thermal stability following elimination of the iodide with tetramethyl guanidine. **B)** Differential scanning calorimetry (DSC) of polymers **3** (black) and **11** (red) indicating a minor change in the glass transition temperature (T_g).

A) ¹H-NMR



Figure S12: Use of 365 nm light to isomerize the olefin generated via iodo-yne polymerization. Polymer sample was irradiated while swollen in toluene solution at a concentration of 100 mg/mL. A) ¹H-NMR comparing polymer **3** that had not been irradiated with light (top) and polymer **3** that had been irradiated with light (bottom). B) ¹⁹F-NMR comparing polymer **3** that had not been irradiated with light (bottom).



Figure S13: Overlaid ¹⁹F-NMR spectra comparing the elimination of vinyl iodide with and without irradiation of 365 nm light. ¹⁹F-NMR of polymer **11** that was synthesized with tetramethyl guanidine as a base, without 365 nm light (top) and ¹⁹F-NMR of polymer **11** that was synthesized with tetramethyl guanidine as a base, with illumination via 365 nm light throughout the reaction (bottom).

General experimental procedures:

Chemical reagents were purchased from Sigma-Aldrich, Alfa Aesar, Fisher Scientific, or Acros Organics and used without purification unless noted otherwise. No unexpected or unusually high safety hazards were encountered. Anhydrous and deoxygenated solvents toluene (PhMe), tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (MeCN), and dimethylformamide (DMF) were dispensed from a Grubb's-type Phoenix Solvent Drving System¹. Thin laver chromatography was performed using Silica Gel 60 F254 (EMD Millipore) plates. Flash chromatography was executed with technical grade silica gel with 60 Å pores and 40-63 µm mesh particle size (Sorbtech Technologies). Solvent was removed under reduced pressure with a Büchi Rotovapor with a Welch self-cleaning dry vacuum pump and further dried with a Welch DuoSeal pump. Bath sonication was performed using a Branson 3800 ultrasonic cleaner. Nuclear magnetic resonance (¹H-NMR, ¹³C-NMR, and ¹⁹F-NMR) spectra were taken on Bruker Avance 500 (¹H-NMR and ¹³C-NMR) or AV-300 (¹⁹F-NMR) instruments and processed with MestReNova software. All ¹H, ¹³C, and ¹⁹F NMR spectra are reported in ppm and relative to residual solvent signals (¹H, ¹³C). Fluorine NMR were reported with trifluoroacetic acid as the reference peak as an external standard. Size exclusion chromatography (SEC), unless otherwise noted, was conducted on a Shimadzu prominence-I LC-2030C high performance liquid chromatography (HPLC) system with a UV detector and connected to a Wyatt Dawn Heleos-II light scattering detector and Wyatt Optilab T-rEX refractive index detector, one MZ Analysentechnik GPC-Precolumn 50 x 8.0 mm MZ-Gel SDplus Linear LS 5µm pore, and two MZ Analysentechnik GPC-column 300 x 8.0 mm MZ-Gel SDplus Linear LS 5µm pore. Eluent was THF at 50 °C (flow rate: 0.70 mL/ min). Calibration was performed using near monodisperse polystyrene PS standards from Polymer Laboratories. Differential scanning calorimetry measurements were taken on a PerkinElmer DSC. Thermal gravimetric analysis was performed on a PerkinElmer Pyris Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer. Mass spectra (Electron impact (EI)) were collected on an Agilent 7890B-7520 Quadrupole Time-of-Flight GC/MS. Irradiation with light was performed with BI365 nm Inspection UV LED lamp, purchased from Risk reactor (Output power density >5000µW/cm² at 15" (38 cm), voltage range 90-265V ac, output power: 3*325 mW at 365 nm peak). Centrifugation was performed on a Thermo Scientific Sorvall ST 16 Centrifuge. All sonication was done in a Branson M-Series Model 3800 120V bath sonicator. For probe sonication, a QSonica (Q125) sonicator was used.

Abbreviations: AIBN = azoisobutyronitrile; DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene; DCM = dichloromethane; DMF = dimethylformamide; DMSO = dimethylsulfoxide; DSC = differential scanning calorimetry; Et_2O = diethyl ether; MeCN = acetonitrile ; MeOH = methanol; PhMe = toluene; SEC = size exclusion chromatography; TGA = thermal gravimetric analysis; THF = tetrahydrofuran; TMG = tetramethylguanine

SEC prep/procedures:

THF HPLC instrument: Size exclusion chromatography (SEC) was conducted on a Shimadzu prominence-I LC-2030C high performance liquid chromatography (HPLC) system with a UV detector and connected to a Wyatt Dawn Heleos-II light scattering detector and Wyatt Optilab T-

rEX refractive index detector. Calibration was performed using near monodisperse polystyrene standards from Polymer Laboratories. Polymer samples were dissolved in THF (5 mg/mL) and stirred at 50 °C for 1 hour. Polymer solutions were filtered through 0.2 micron PTFE filter and 50 μ L were then run through one MZ Analysentechnik GPC-Precolumn 50 x 8.0 mm MZ-Gel SDplus Linear LS 5 μ m pore, and two MZ Analysentechnik GPC-column 300 x 8.0 mm MZ-Gel SDplus Linear LS 5 μ m pore columns at 50 °C with an eluent rate of 0.7mL/min. Unless otherwise noted, UV absorbance was used for molecular weight determination.

DMSO HPLC instrument: Size exclusion chromatography (SEC) was conducted on a Shimadzu prominence-I LC-2030C high performance liquid chromatography (HPLC) system with a UV detector and connected to a Wyatt Dawn Heleos-II light scattering detector and Wyatt Optilab T-rEX refractive index detector. Calibration was performed using near monodisperse poly(methyl-methacrylate) PMMA standards from Polymer Laboratories. Polymer samples were dissolved in DMSO (5 mg/mL) and stirred at 100 °C for 1 hour. Polymer solutions were filtered through 0.2 micron PTFE filter and 50 μ L were then run through one Agilent PLgel guard column D, and an Agilent PLgel 10 μ m mixed B columns at 65 °C with a flow rate at 0.35 mL/min. Unless otherwise noted, RI signal was used for molecular weight determination.

DMF HPLC instrument: Size exclusion chromatography (SEC) was conducted on a Waters Alliance HPLC System, 2695 Separation Module high performance liquid chromatography (HPLC) system with a Waters 2414 Differential Refractometer (RI) and Waters 2998 Photodiode Array Detector (PDA). Calibration was performed using near monodisperse polystyrene standards from Polymer Laboratories. Polymer samples were dissolved in DMF (5 mg/mL) and stirred at 85 °C for 1 hour. Polymer solutions were filtered through 0.2 micron PTFE filter and 40 μ L were then run through 2 Tosoh TSKgel Super HM-M columns at 50 °C with a flow rate at 0.30 mL/min. Unless otherwise noted, RI signal was used for molecular weight determination.

THF UPLC instrument: Size exclusion chromatography (SEC) was conducted on a Waters Acquity APC ultra-high performance liquid chromatography (UPLC) system with an ACQUITY UPLC PDA Detector and an ACQUITY UPLC Refractive Index Detector. Calibration was performed using near monodisperse polystyrene standards from Polymer Laboratories. Polymer samples were dissolved in THF (5 mg/mL) and stirred at 50 °C for 1 hour. Polymer solutions were filtered through 0.2 micron PTFE filter and 25 μ L were then run through Three Acquity APC XT Columns (45 + 200 + 450 pore sizes) at 39 °C with a flow rate at 0.9 mL/min with a column pressure of 6900 PSI. Unless otherwise noted, RI signal was used for molecular weight determination.

TGA prep/procedures: Polymer samples (5–10 mg) were placed in a calibrated ceramic container and the temperature was raised to 100 °C. After a delay of 1 minute to remove residual solvent, the weight of the sample was re-recorded, and the temperature was raised to 650 °C at a rate of 20 °C/min. The resulting data were then normalized to % weight loss of sample. Unless otherwise noted all samples were run under nitrogen atmosphere.

DSC prep/procedures: Polymer sample (10–20 mg) were placed in an aluminum pan and cooled to -50 °C and equilibrated for 2 minutes. The samples were then heated to 100 °C at a

rate of 20 °C/min with a 2-minute pause at 100 °C. Samples were then cooled back down to -50 °C at a rate of 15 °C/min with a 2-minute pause at -50 °C. This cycle was then repeated two additional times.

Photochemistry assembly: Our homemade photobox was assembled to the shape of the UV light source (Risk reactor (Output power density >5000 μ W/cm² at 15" (38 cm), voltage range 90-265V ac, output power: 3*325 mW at 365 nm peak)) using cardboard and black tape. The interior was then coated with aluminum foil and holes were cut on the top sample placement.



Small molecule procedures:

9,9,10,10,11,11,12,12,13,13,14,14-dodecafluoro-7,16-diiododocosa-7,15-diene, s1 (E,E) and s2 (E,Z):

Diiodoperfluorohexane (1.1 g, 2.0 mmol, 1.0 eq) was dissolved in acetonitrile (8 mL) and water (6 mL). 1-Octyne (0.451 g, 4.09 mmol, 2.1 eq) was added, followed by sodium bicarbonate (0.39 g, 4.6 mmol, 2.3 eq). Sodium dithionite (0.80 g, 4.6 mmol, 2.3 eq) was then added and the solution was placed in a sonication bath for 2 hours. The reaction mixture was diluted with brine (10 mL) and extracted with EtOAc (3 x 15 mL). The organic layer was dried with MgSO₄, decanted, and concentrated to give crude oil. Purification through silica plug with hexanes as the eluent yielded the product as a clear oil and mix of isomers (0.83 g, 1.3 mmol, 65%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.31 (t, *J* = 12 Hz, 1.6H), 6.23 (t, *J* = 12 Hz, 0.4H), 2.62 (m, 4H), 1.57 (m, 4H), 1.30 (m, 12H), 0.9 (t, *J* = 8 Hz, 6H). ¹³C NMR (CDCl₃, 126 MHz), δ ppm: 126.7 (t, *J* = 25.2 Hz), 122.8 (t, *J* = 6.3 Hz), 121.8 (t, *J* = 25.2 Hz), 117.0-107.0, (m, 7C), 41.1, 31.5, 30.0, 29.0, 28.1, 27.6, 22.5, 14.0. ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -105.35 (s, 4F), -108.46 (s, 0.8F), -121.51 (s, 4.8F), -123.00 (s, 0.8F), -123.29 (s, 4F). HRMS (EI) Calculated for C₂₂H₂₈F₁₂I₂ [M-I]: 774.0089, found: 774.0069.

1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotetradec-7-ene, s3:

lodoperfluorohexane (1.5 g, 3.3 mmol, 1.1 eq) was dissolved in acetonitrile (6 mL) and water (4.5 mL). 1-Octyne (0.33 g, 3.0 mmol, 1.0 eq) was added followed by sodium bicarbonate (0.32 g, 3.8 mmol, 1.2 eq). Sodium dithionite (0.66 g, 3.8 mmol, 1.2 eq) was then added and the solution was placed in a sonication bath for 2 hours. The reaction mixture diluted with brine (10 mL) and extracted with EtOAc (3 x 15 mL). The organic layer was dried with MgSO₄, decanted, and concentrated to give crude oil. Purification through a silica plug with hexanes as the eluent gave pure product as a clear oil (1.38 g, 2.71 mmol, 82%). NMR data matched known compound.²

((9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradec-7-en-7-yl)oxy)benzene, s4:

Compound **s3** (0.52 g, 0.93 mmol, 1.0 eq) was dissolved in dioxane (6.5 mL). Phenol (0.350 g, 3.92 mmol, 4.0 eq) and dimethyl glycine (0.028 g, 0.28 mmol, 0.30 eq) were then added. The solution was degassed via freeze-pump-thaw (x3). Cesium carbonate (0.636 g, 1.81 mmol, 2.0 eq) and copper iodide (0.017 g, 0.093 mmol, 0.10 eq) were then added and the reaction was set to 90 °C for 16 hours. The reaction was cooled to room temperature, concentrated and run through a silica column with hexanes as the eluent to give a mixture of compounds **s4** and **s5** in a 4:1 ratio as a clear oil (0.210 g, 0.402 mmol, 43%). This mixture was further separated by preparatory TLC. ¹H NMR (CDCl₃, 500 MHz), δ ppm: 7.40 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 4.41 (t, *J* = 14.9 Hz, 1H), 2.52 (t, *J* = 7.7 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.49 – 1.28 (m, 6H), 0.91 (t, *J* = 8.3, 7.5 Hz, 3H). ¹³C NMR (CDCl₃, 126 MHz), δ ppm: 170.1, 153.5, 130.1, 125.6, 121.4, 119.4 – 107.2 (m, 6C), 92.1 (t, *J* = 25.2 Hz), 31.5, 31.4 (t, *J* = 2.5 Hz), 28.9, 27.4, 22.5, 14.0.¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: δ -80.81 (t, *J* = 9.9 Hz, 3F), -102.56 (q, *J* = 13.6 Hz, 2F), -121.67 (m, 2F), -122.86 (m, 2F), -123.38 (m, 2F), -126.14 (m, 2F). HRMS (EI) Calculated for C₂₀H₁₉F₁₃O [M-HOC₆H₅]: 428.0810, found: 428.0633.

1,1,1,2,2,3,3,4,4,5,5,6-dodecafluorotetradec-6-en-8-yne, s5:

Compound s3 (0.42 g, 0.75 mmol, 1.0 eg) was dissolved in dioxane (4.2 mL). Phenol (0.28 g, 3.0 mmol, 4.0 eq) and 3,4,7,8-tetramethyl phenanthroline (0.053 g, 0.23 mmol, 0.30 eq) were then added. The solution was sparged under nitrogen gas for 20 minutes. Cesium carbonate (0.53 g, 1.5 mmol, 2.0 eq) and copper iodide (0.014 g, 0.075 mmol, 0.10 eq) were then added and the reaction was set to 90 °C for 16 hours. The reaction was cooled to room temperature. concentrated and run through a long silica column with hexanes as the eluent to give a mixture of compounds with predominately the en-yne rearrangement product s5 as a 3:1 ratio of E/Z isomers, but with a small fraction of starting material and phenol coupled product which couldn't be removed (0.080 g, 0.20 mmol, 26%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: δ 6.09 – 5.99 (m, 0.25H), 5.71 (dt, J = 29.3, 2.1 Hz, 0.75H), 2.39 (t, J = 6.7 Hz, 1.5H), 2.33 (t, J = 6.9 Hz, 0.5H), 1.61 – 1.54 (m, 2H), 1.43 – 1.22 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 126 MHz), δ ppm: 152.2 (dt, J = 272.3, 28.3 Hz), 119.6 - 107.3 (m, 6C), 103.4 (d, J = 6.7 Hz), 98.2 (q, J = 6.4 Hz), 69.3, 31.0, 27.9, 22.1, 19.7, 13.9. ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -80.83 (s, 3F), -115.91 - -116.87 (m, 0.5F), -118.02 (q, J = 13.8 Hz, 1.5F), -118.42 - -119.16 (m, 0.75F), -120.12 - -120.91 (m, 0. 25F), -122.47 - -123.73 (m, 4F), -126.23 (2F). Calculated for C₁₄H₁₂F₁₂ [M]: 408.0747, found: 408.0577.

Polymerization procedures:

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3:

Diiodoperfluorohexane (2.0 g, 3.6 mmol, 1.0 eq) was dissolved in acetonitrile (14.4 mL) and water (11.0 mL). 1,9-Decadiyne (0.48 g, 3.6 mmol, 1.0 eq) was added, followed by sodium bicarbonate (0.70 g, 8.3 mmol, 2.3 eq). Sodium dithionite (1.44 g, 8.27 mmol, 2.3 eq) was added and the solution was placed in a sonication bath for 2 hours. The reaction mixture was then precipitated from water (100 mL) and washed with methanol (2 x 100 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum at 60 °C to yield a white solid (2.33 g, 3.38 mmol, 94%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.33 (t, *J* = 14.4 Hz, 1.5H), 6.24 (t, *J* = 13.0 Hz, 0.5H), 2.65 (m, 4H), 1.59 (m, 4H), 1.45 – 1.27 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -105.35 (s, 3F), -108.53 (s, 1F), -121.52 (s, 4F), -122.91 (s, 1F), -123.27(s, 3F). FT-IR: 2932 (C-H str) (w), 1635 (C=C) Vinyl iodide (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 330 °C. *T_q* (DSC): -24.0 °C

Fractionation between THF soluble and insoluble polymer 3:

Polymer **3** (0.176 g, 0.254 mmol, repeat unit eq) was placed in a Soxhlet extraction apparatus lined with a cellulose thimble connected to a round bottom flask charged with THF without inhibitor (100 mL). THF was then brought to reflux for 16 hours. The THF layer was concentrated and dried under high vacuum to give THF soluble polymer **3** (0.105 g, 0.152 mmol, 60%). Polymer **3** remaining in the cellulose thimble was removed and dried under high vacuum for 16 hours to give THF insoluble polymer **3** (0.071g, 0.102 mmol, 40%).

Post-Polymerization Modification Procedures:

Thiol capping of polymer 3, 4:

Polymer **3** (0.80 g, 1.2 mmol, repeat unit eq) was swollen in dioxane (8 mL). Butanethiol (1.05 g, 11.2 mmol, 10 eq) was added, followed by AIBN (0.095 g, 0.58 mmol, 0.50 eq). The reaction mixture was then heated to 90 °C for fourteen hours. The following morning the mixture was precipitated from ice water (100 mL). The precipitate was then washed with cold methanol (2 x 100 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried with high vacuum at 60 °C to yield an orange solid (0.712 g, 1.03 mmol, 89%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.33 (t, *J* = 14.4 Hz, 1.5H), 6.24 (t, *J* = 13.0 Hz, 0.5H), 2.65 (m, 4H), 1.59 (m, 4H), 1.45 – 1.27 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -105.35 (s, 3F), -108.53 (s, 1F), -121.52 (s, 4F), -122.91 (s, 1F), -123.27(s, 3F). FT-IR: 2932 (C-H str) (w), 1635 (C=C str) (s), 1100-1200 (C-F bend) (vs).

Sonogashira coupling of polymer 4, 5:

Polymer **4** (0.100 g, 0.145 mmol, repeat unit eq) was swollen in diisopropylamine (1 mL). 1-Octyne (0.095 g, 0.87 mmol, 6.0 eq) was added. The solution was degassed via freeze-pumpthaw (x3). Copper iodide (0.0015 g, 0.0070 mmol, 0.05 eq) and tetrakis(triphenylphosphine) palladium (0.008 g, 0.007 mmol, 0.05 eq) were added. The reaction mixture was then heated to 50 °C for fourteen hours. The following morning the mixture was precipitated from saturated ammonium chloride (50 mL), followed by washing with water (50 mL) and methanol (50 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum to yield a light brown solid (0.048 g, 0.074 mmol, 74%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 5.71 (t, *J* = 16.2 Hz, 1.4H), 5.57 (t, *J* = 11.3 Hz, 0.7H), 2.40 – 2.27 (m, 5.4H), 2.27 – 2.18 (m, 1.3H), 1.64 – 1.47 (m, 10H), 1.47 – 1.18 (m, 16H), 0.89 (t, *J* = 6.7 Hz, 6H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -105.47 (m, 3F), -108.31 (m, 1F), -121.93 (m, 4F), -123.81 (m, 4F). FT-IR: 2932 (C-H str) (w), 2222 (C=C str) (w), 1630 (C=C str) (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 245 °C. *T_g* (DSC): -25.0 °C

Stille coupling of polymer 4, 6:

Polymer **4** (0.100 g, 0.145 mmol, repeat unit eq) was swollen in toluene (1 mL). 2-(tributytin) furan (0.30 g, 0.87 mmol, 6.0 eq) was added. The solution was degassed via freeze-pump-thaw (x3). Tetrakis(triphenylphosphine) palladium (0.008 g, 0.007 mmol, 0.05 eq) was then added and capped. The reaction mixture was heated to 60 °C for fourteen hours. The following morning the mixture was precipitated from cold methanol (50 mL), followed by washing with methanol two times (50 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried with high vacuum to yield a light orange solid (0.046 g, 0.082 mmol, 57%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 7.45 (s, 0.6H), 7.41 (s, 1.4H), 6.66 (s, 0.6H), 6.53 (s, 1.4H), 6.42 (s, 2H), 6.04 (t, *J* = 16.2 Hz, 1.4H), 5.46 (t, *J* = 16.2 Hz, 0.6H), 2.61 – 2.44 (m, 4H), 1.66 – 1.52 (m, 2H), 1.49 – 1.27 (m, 6H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -104.52 (s, 3F), -104.87 (s, 1F), -121.39 (s, 4F), -122.54 – -124.29 (m, 4F). FT-IR: 2932 (C-H str) (w), 1707 (C=C str) furan (s), 1635 (C=C str) alkene (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 266 °C. *T_g* (DSC): 17.0 °C

Suzuki coupling of polymer 4, 7:

Polymer **4** (0.100 g, 0.145 mmol, repeat unit eq) was swollen in dimethylformamide (2 mL). 7-heptenyl boronic acid (0.082 g, 0.58 mmol, 4.0 eq) was added. The solution was degassed via freeze-pump-thaw (x3). Potassium carbonate (0.12 g, 0.87 mmol, 6.0 eq) and tetrakis(triphenylphosphine) palladium (0.008 g, 0.007 mmol, 0.05 eq) were then added. The reaction mixture was heated to 85 °C for fourteen hours. The following morning the mixture was precipitated from saturated sodium bicarbonate (50 mL), followed by washing with water (50 mL) and methanol (2 x 50 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum to yield a light brown solid (0.066 g, 0.11 mmol, 74%) that included 93% alkene addition and 7% iodide elimination. ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.50 (d, *J* = 16.2 Hz, 1H), 5.96 (s, 3H), 5.41 – 5.30 (m, 1H), 5.29 – 5.20 (m, 1H), 2.52 – 2.03 (m, 8H), 1.65 – 1.15 (m, 20H), 0.89 (s, 6H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -102.92 (s, 1F), -104.38 (s, 3F), -121.44 (s, 4F), -123.01 – -123.80 (m, 4F). FT-IR: 2932 (C-H str) (w), 1646 (C=C str) diene (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 333 °C. *T_g* (DSC): -37 °C

Phenol coupling of polymer 4, 8:

Polymer **4** (0.100 g, 0.145 mmol, repeat unit eq) was swollen in dioxane (1 mL). Phenol (0.110 g, 1.16 mmol, 8.00 eq) and dimethyl glycine (0.009 g, 0.09 mmol, 0.6 eq) were added. The solution was degassed via freeze-pump-thaw (x3). Cesium carbonate (0.204 g, 0.580 mmol, 4.00 eq) and copper iodide (0.005 g, 0.03 mmol, 0.2 eq) were then added and the reaction was set to 90 °C for 16 hours. The following morning the mixture was precipitated from saturated sodium bicarbonate (50 mL), followed by washing with water (50 mL) and methanol (2 x 50 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum to yield a light yellow solid (0.069 g, 0.10 mmol, 88%) that included 65% phenol addition and 35% en-yne rearrangement. ¹H NMR (CDCl₃, 500 MHz), δ ppm: 7.37 (s, 2.6H), 7.20 (s, 1.3H), 6.98 (s, 2.6H), 5.67 (d, *J* = 38.6 Hz, 0.7H), 4.43 (t, *J* = 15.2 Hz, 1.3H), 2.52 (s, 2.6H), 2.42 (s, 1.3), 1.74 (s, 2.6H), 1.62 (s, 1.3), 1.57 (s, 1.3H), 1.47 (s, 2.6H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -102.62 (s, 2.75F), -117.95 (1.85F), -121.55 (s, 2.75F), -122.99 (s, 1.25F), -123.51 (4F). FT-IR: 2932 (C-H str) (w), 2230 (C=C str) (w), 1660 (C=C str) alkene (s), 1590 (C=C str) aromatic (s), 1490 (C=C bend) aromatic (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 329 °C. *T_g* (DSC): -10 ° C.

Thiophenol coupling of polymer 4, 9:

Polymer **4** (0.100 g, 0.145 mmol, repeat unit eq) was swollen in toluene (2 mL). Thiophenol (0.127 g, 1.16 mmol, 8.00 eq), 1,10-phenanthroline (0.010 g, 0.056 mmol, 0.40 eq), and triphenylphosphine (0.030 g, 0.11 mmol, 0.80 eq) were added. The solution was degassed via freeze-pump-thaw (x3). Potassium phosphate (0.121 g, 0.560 mmol, 4.00 eq) and copper iodide (0.010 g, 0.058 mmol, 0.4 eq) were then added and the reaction was set to 90 °C for 16 hours. The following morning the mixture was precipitated from saturated sodium bicarbonate (50 mL), followed by washing with water (50 mL) and methanol (2 x 50 mL). The precipitate was centrifuged at 2500 X g for 5 minutes, and the resulting pellet was dried under high vacuum to yield a light orange solid (0.065 g, 0.10 mmol, 79%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 7.53 – 7.31 (m, 10H), 5.73 – 5.47 (m, 0.5H), 4.95 – 4.72 (m, 1.5H), 2.56 – 2.36 (m, 3H), 2.07 (m, 1H), 1.78 – 1.26 (m, 8H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -103.75 (s, 3F), -104.44 (s, 1F), -121.57 (s, 4F), -123.02 (s, 1F), -123.55 (s, 3F). FT-IR: 2932 (C-H str) (w), 1626 (C=C str) alkene

(s), 1583 (C=C str) aromatic (s), 1477 (C=C bend) aromatic (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 370 °C. T_g (DSC): -6 °C.

Kumada coupling of polymer 3, 10:

Polymer **3** (0.200 g, 0.290 mmol, repeat unit eq) was swollen in THF (4 mL). Iron (III) acetylacetonate (0.050 g, 0.15 mmol, 0.50 eq) was added under nitrogen. Methyl magnesium bromide (1M) (1.8 mL, 1.8 mmol, 6.0 eq) was then added dropwise over an hour at room temperature. After complete addition of methyl magnesium bromide, methanol (1 mL) was slowly added to quench the remaining reagents. The solution was precipitated from water (50 mL), followed by washing with methanol (2 x 50 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum to yield a brown solid (0.115 g, 0.220 mmol, 87%) as 70% methyl addition and 30% iodide reduction by proton NMR. ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.44 – 6.30 (m, 0.25H), 6.12 – 6.00 (m, 0.25H), 5.68 – 5.54 (m, 0.25H), 5.54 – 5.45 (m, 0.25H), 5.31 (t, *J* = 16.7 Hz, 1.5H), 2.24 (s, 3H), 2.19 – 2.03 (m, 1H), 1.87 (s, 4.5H), 1.55 (s, 1H), 1.45 (s, 3H), 1.38 – 1.11 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -104.76 (s, 3F), -105.37(s, 0.35F), -106.65 (s, 0.17F), -111.27 (s, 0.37F), -121.58 (s, 4F), -123.23 – -124.66 (m, 4F). FT-IR: 2932 (C-H str) (w), 1667 (C=C str) (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 373 °C. *T_q* (DSC): -39 °C

Elimination of iodide from polymer 3, 11:

Polymer **4** (0.200 g, 0.290 mmol, repeat unit eq) was swollen in toluene (4 mL). Tetramethylguanidine (0.33 g, 2.9 mmol, 10 eq) was added dropwise and the solution was allowed to stir for 16 hours. The following morning the reaction mixture was precipitated from cold methanol (50 mL) and additionally washed with saturated ammonium chloride (50 mL), followed by an additional wash of methanol (50 mL). The precipitate was centrifuged at 2500 X g for 5 minutes, and the resulting pellet was dried under high vacuum to yield a brown solid (0.090 g, 0.14 mmol, 49%) as polymer with all Z-Isomer iodide eliminated. ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.33 (t, *J* = 14.6 Hz, 1.5H), 2.69 – 2.53 (m, 3H), 2.36 (t, *J* = 5.5 Hz, 1H), 1.60 (s, 4H), 1.47 – 1.31 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -96.31 (s, 1F), -105.37 (s, 3F), -121.19 (s, 1F), -121.53 (s, 3F), -122.61 (s, 1F), -123.36 (s, 3F). FT-IR: 2932 (C-H str) (w), 2260 (C=C str) (w), 1635 (C=C str) (s), 1100-1200 (C-F bend) (vs). TGA: 10% mass loss at 347 °C. *T_g* (DSC): -27 °C

Alkyne-azide coupling of polymer 11, 13:

Polymer **11** (0.010 g, 0.018 mmol, repeat unit eq) was dissolved in xylenes (0.25 mL). 2azidoethyl perfluorooctane (0.030 g, 0.073 mmol, 4.0 eq) was then added and refluxed for 18 hours. The following morning the reaction mixture was precipitated from methanol (10 mL) and washed with methanol (2 x 10 mL). The precipitate was centrifuged at 2500 X *g* for 5 minutes, and the resulting pellet was dried under high vacuum to yield a brown solid (0.013 g, 0.014 mmol, 80%). ¹H NMR (CDCl₃, 500 MHz), δ ppm: 6.32 (t, *J* = 15.0 Hz, 1H), 4.68 (s, 0.5H), 4.53 (s, 0.5H), 3.05 – 2.72 (m, 2H), 2.63 (s, 3H), 1.88 – 1.30 (m, 8H). ¹⁹F NMR (CDCl₃, 376 MHz), δ ppm: -80.89 (s, 1.5F), -105.37 (s, 3F), -107.42 (s, 0.6F), -109.17 (s, 0.4F), -114.35 (s, 1F), -121.07 – -122.62 (m, 7F), -122.88 (s, 1F), -123.46 (s, 5F), -126.25 (s, 1F). FT-IR: 2932 (C-H str) (w), 1632 (C=C str) alkene + aromatic (s), 1458 (C=C bend) aromatic 1100-1200 (C-F bend) (vs). ¹H NMR Spectra:

9,9,10,10,11,11,12,12,13,13,14,14-dodecafluoro-7,16-diiododocosa-7,15-diene, S1, S2:



((9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradec-7-en-7-yl)oxy)benzene, S4:









1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3:

Thiol capping of polymer 3, 4:







Stille coupling of polymer 4, 6:





Suzuki coupling of polymer 4, 7:

Phenol coupling of polymer 4, 8:



Thiophenol coupling of polymer 4, 9:



Kumada coupling of polymer 3, 10:





Elimination of iodide from polymer 3, 11:


Alkyne-azide coupling of polymer 11, 12:

¹³C NMR Spectra:

9,9,10,10,11,11,12,12,13,13,14,14-dodecafluoro-7,16-diiododocosa-7,15-diene, S1, S2:



140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 f1(ppm) ((9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradec-7-en-7-yl)oxy)benzene, S4:





1,1,1,2,2,3,3,4,4,5,5,6-dodecafluorotetradec-6-en-8-yne, S5:

¹⁹F NMR Spectra:

9,9,10,10,11,11,12,12,13,13,14,14-dodecafluoro-7,16-diiododocosa-7,15-diene, S1, S2:



((9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradec-7-en-7-yl)oxy)benzene, S4:





1,1,1,2,2,3,3,4,4,5,5,6-dodecafluorotetradec-6-en-8-yne, S5:





1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3:

Thiol capping of polymer 3, 4:



Sonogashira coupling of polymer 4, 5:



Stille coupling of polymer 4, 6:







Phenol coupling of polymer 4, 8:



Thiophenol coupling of polymer 4, 9:



Kumada coupling of polymer 3, 10:



Elimination of iodide from polymer 3, 11:





Alkyne-azide coupling of polymer 11, 12:

IR Traces:



1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3:

Thiol capping of polymer 3, 4:



Sonogashira coupling of polymer 4, 5:



Stille coupling of polymer 4, 6:



Suzuki coupling of polymer 4, 7:



Phenol coupling of polymer 4, 8:



Thiophenol coupling of polymer 4, 9:



Kumada coupling of polymer 3, 10:









Alkyne-azide coupling of polymer 11, 12:

GPC Traces:



1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, HPLC SEC:

*We hypothesize that the low molecular shoulder is due to a small amount of oligomer or cyclic product that couldn't be removed by precipitation.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 1:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 2



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 3:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 4:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 5:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 6:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 7:



*Peak following 3.1 minutes belongs to solvent delay.

1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 8:



*Peak following 3.1 minutes belongs to solvent delay.
1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3, UHPLC SEC, Table 1, Entry 1:



*Peak following 3.1 minutes belongs to solvent delay.

Thiol capping of polymer 3, 4:



Sonogashira coupling of polymer 4, 5:



Stille coupling of polymer 4, 6:



Suzuki coupling of polymer 4, 7:



Phenol coupling of polymer 4, 8:



Thiophenol coupling of polymer 4, 9:



Kumada coupling of polymer 3, 10:



TGA Traces:



1-perfluorohexyl-2,9-diiodo-1,9-decadiene block polymer, 3:

Sonogashira coupling of polymer 4, 5:



Stille coupling of polymer 4, 6:



Suzuki coupling of polymer 4, 7:



Phenol coupling of polymer 4, 8:













Elimination of iodide from polymer 3, 11:

DSC Traces:

Sonogashira coupling of polymer 4, 5:



Stille coupling of polymer 4, 6:



Suzuki coupling of polymer 4, 7:



Phenol coupling of polymer 4, 8:



Thiophenol coupling of polymer 4, 9:



Kumada coupling of polymer 3, 10:



Supporting References:

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15* (5), 1518–1520.
- (2) Xu, T.; Cheung, C. W.; Hu, X. Iron-Catalyzed 1,2-Addition of Perfluoroalkyl lodides to Alkynes and Alkenes. *Angew. Chemie Int. Ed.* **2014**, 53 (19), 4910–4914.