

Transition-Metal-Free Synthesis of Alternating Thiophene-Perfluorarene Copolymers

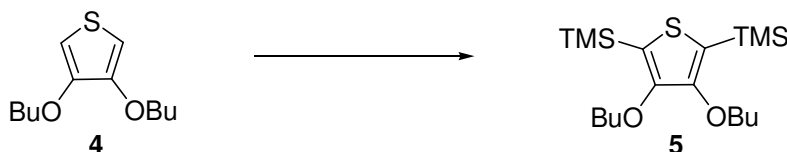
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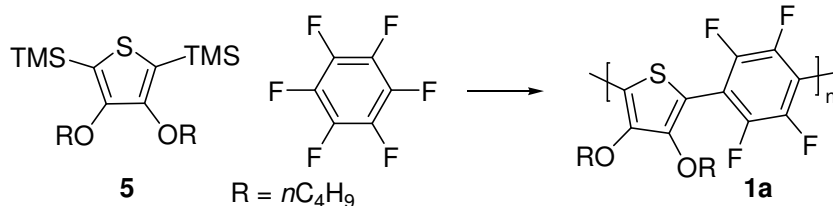
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Materials and Methods. CsF and 18-crown-6 were each dried under reduced pressure ($< 10^{-3}$ mbar) at 180°C and 80°C, respectively and stored in an argon-filled glove box. C_6F_6 and toluene were distilled from CaH_2 and sodium/potassium alloy, respectively, and stored over molecular sieves under argon. 3,4-dialkoxythiophenes were prepared via modified published procedures.¹ All other materials were used as purchased. Unless otherwise stated, all manipulations and reactions were carried out under argon atmosphere using standard Schlenk techniques. 1H , ^{13}C , and ^{19}F NMR spectra were recorded on a Varian INOVA 400MHz spectrometer (purchased under the CRIF Program of the National Science Foundation, grant CHE-9974810). Chemical shifts were referenced to residual protio-solvent signals, except for ^{19}F spectra, where CCl_3F was added as internal standard and set to $\delta = 0$ ppm. Relative molecular weight determinations were made using a Waters 600E HPLC system, driven by Waters Empower Software and equipped with two linear mixed-bed GPC columns (American Polymer Standards Corporation, AM Gel Linear/15) in series. Eluting polymers were detected with both refractive index and photodiode array detectors. The system was calibrated with 11 narrow PDI polystyrene samples in the range 580 - 2×10^6 Da with toluene at a flow rate of 1mL/min. Differential scanning calorimetry was performed using a Mettler 822°. GC-MS data were collected from an Agilent technologies 6890N GC with 5973 MSD.

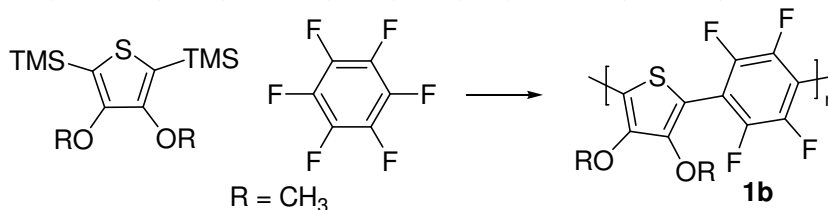
Synthetic procedures.



3,4-dibutyloxy-2,5-bis(trimethylsilyl)thiophene (5). *n*-BuLi (15.51mL, 1.6M in hexanes, 4eq) was added drop-wise to a solution of 3,4-dibutyloxythiophene (1.42g, 6.22mmol) in 30 mL hexanes:DME (2:1) maintained at 0°C. After stirring at room temperature for 30 minutes, then at reflux for 1 hr, TMSCl (3.14mL, 4eq) was added drop-wise into the suspension and the whole was stirred overnight at room temperature. The mixture was extracted with 10% HCl (aq) and deionized water, dried over $MgSO_4$, and concentrated via rotary evaporation. Monomer **5** was isolated after flash chromatography [silica gel, pentane:dichloromethane (3:1)] as a yellow solid (2.10g, 91%). 1H NMR ($CDCl_3$) δ : 4.01 (t, 4H), 1.77 (m, 4H), 1.52 (m, 4H), 1.02 (t, 6H), 0.34 (s, 18H). ^{13}C NMR ($CDCl_3$) δ : 156.85, 126.30, 72.94, 32.41, 19.35, 14.06, -0.39. GC-MS: m/z : 372 ($C_{18}H_{36}O_2SSi_2^+$), 229 (100%).



Polymer 1a. In an argon-filled glove box, monomer **5** (145mg, 0.389mmol), C_6F_6 (53.95 μ L, 1.2 eq), CsF (6.19mg, 0.1 eq), 18-crown-6 (20.56mg, 0.2 eq), and toluene (2 mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at 80°C for 5 days. The solution was extracted with deionized water twice and the polymer precipitated by pouring the solution in 50 mL methanol. The polymer was re-dissolved in chloroform then precipitated again into methanol. After drying under reduced pressure, the polymer was obtained as a colorless solid (123 mg). 1H NMR ($CDCl_3$) δ : 4.12 (m, 4H), 1.65 (m, 4H), 1.39 (m, 4H), 0.90 (m, 6H). ^{13}C NMR ($CDCl_3$) δ : 148.77, 144.32 (d of m), 112.37 (m), 110.75, 73.02, 31.90, 18.92, 13.72. ^{19}F NMR ($CDCl_3$) δ : -137.94 (m, 4 F), -138.81 (m, 147F), -153.41 (m, 2 F), -162.24 (m, 4 F). M_n (GPC) = 28 kDa (PDI = 2.7)



Polymer 1b. Conducted exactly as for **polymer 1a** above, except stoichiometry based upon 145mg monomer **3,4-dimethoxy-2,5-bis(trimethylsilyl)thiophene**, C_6F_6 (69.8 μ L, 1.2 eq), CsF (8.00mg, 0.1 eq), 18-crown-6 (26.59mg, 0.2 eq), and toluene (1.5 mL) and entire reaction conducted at 110°C. Polymer isolated as an insoluble colorless powder. Yield = 124.09mg.

¹ Neeraj Agarwal, Sarada P. Mishra, Anil Kumar, C.-H. Hung and M. Ravikanth, *Chem. Commun.*, **2002**, 2642–2643.

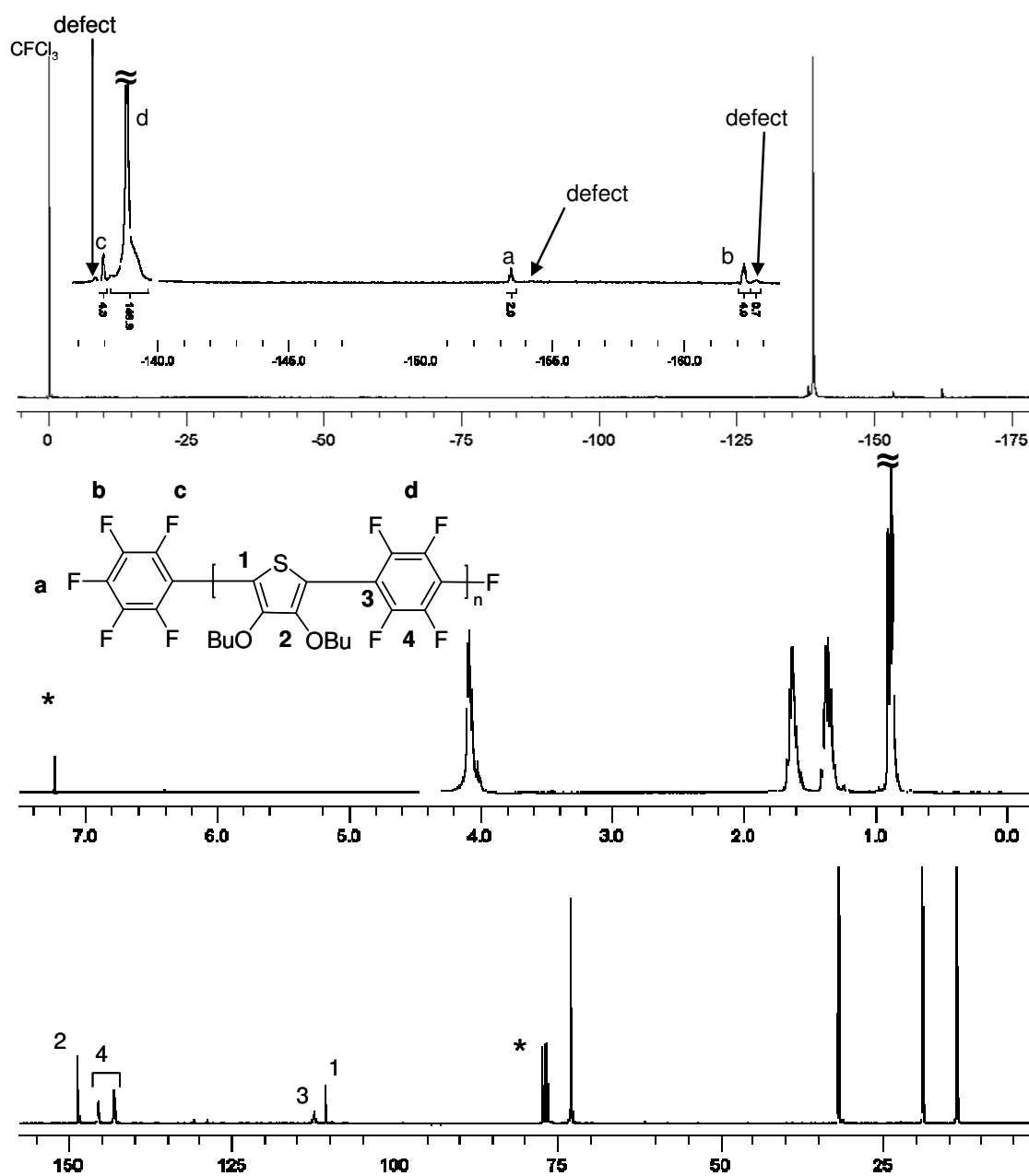
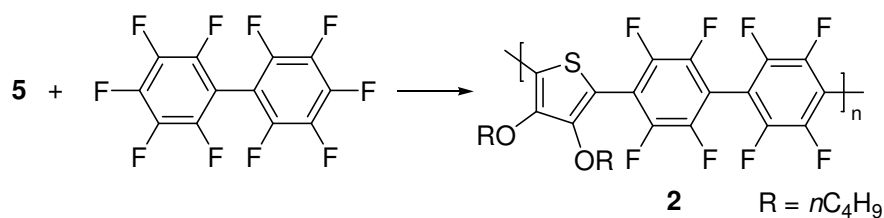


Figure SI 1. ^{19}F , ^1H , and ^{13}C NMR spectra of polymer **1a** in CDCl_3 . Number average degree of polymerization calculated from ^{19}F NMR is $P_n = (146.9\text{F}/4\text{F}) \approx 37$, or 74 aromatic rings ($M_n \approx 14$ kDa), in good agreement with GPC data ($M_n = 28$ kDa, versus polystyrene), which typically overestimates by a factor of 2. * ($\text{H})\text{DCCl}_3$ solvent/reference. The integrals in the ^{19}F spectrum correspond to one polymer chain, terminated by two C_6F_5 groups. The most upfield “defect” signal integrates to 0.7 F. If this should correspond to 1 F, then there are a maximum of 0.7 defects per polymer chain. If the signal corresponds to one type of fluorine, of which there should be 2 for each defect, then there are 0.35 defects per polymer chain.



Polymer 2. In an argon-filled glove box, monomer **5** (106.7mg, 0.286 mmol) decafluorobiphenyl (100.33mg, 1.05 eq), CsF (4.55mg, 0.1 eq), 18-crown-6 (15.12mg, 0.2 eq) and toluene (1 mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at 80°C for 7 days. The polymer was obtained as a colorless powder after purification as described above (148 mg). 1H NMR ($C_2D_2Cl_4$) δ : 4.13 (t, 4H), 1.64 (m, 4H), 1.36 (m, 4H), 0.90 (t, 6H). ^{13}C NMR ($C_2D_2Cl_4$) δ : 148.81, 144.08 (d of m), 113.98 (m), 110.57, 106.79 (m), 73.09, 31.67, 18.81, 13.59. ^{19}F NMR ($C_2D_2Cl_4$) δ : -137.36 (m, 65F), -138.26 (m, 65F), -149.94 (m, 2F), -160.42 (m, 4F). M_n (GPC) = 17 kDa (PDI = 3.9)

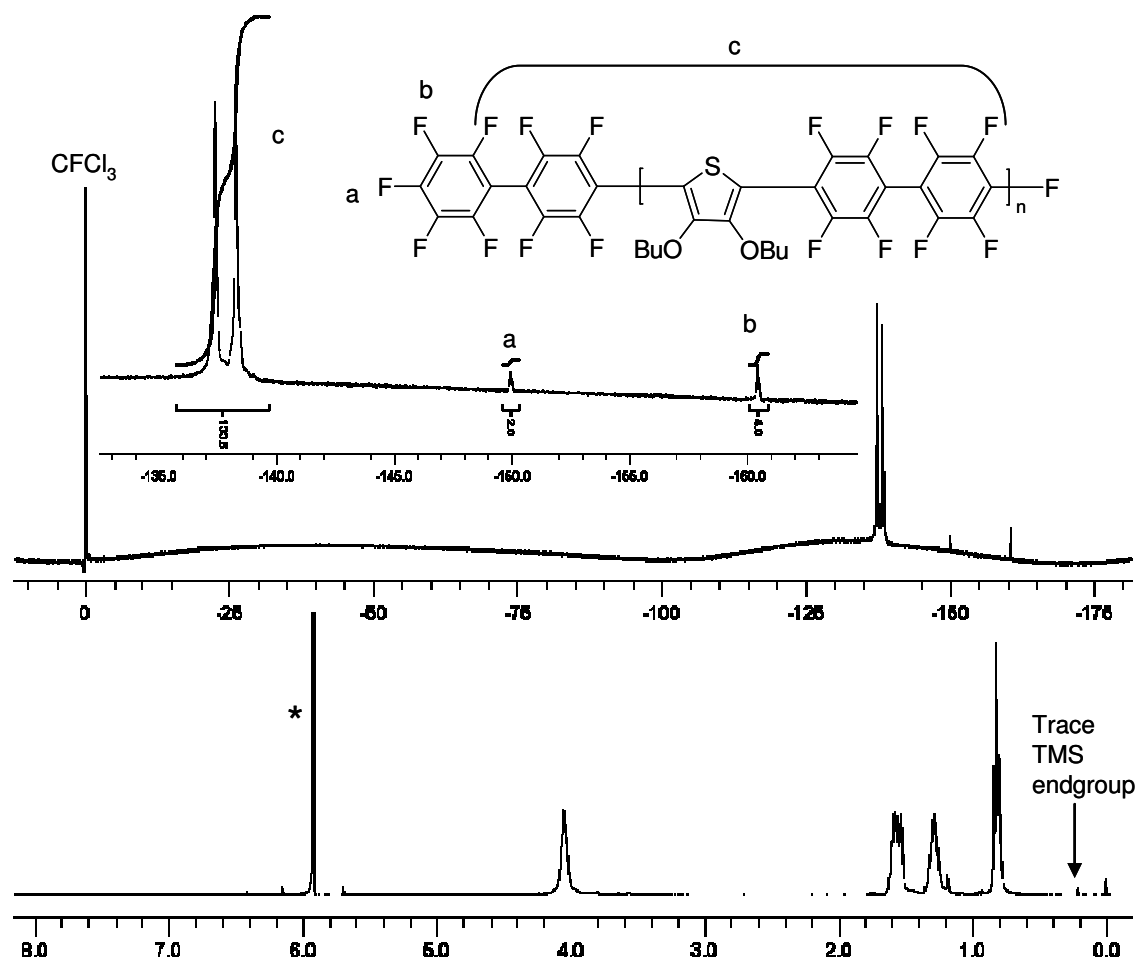
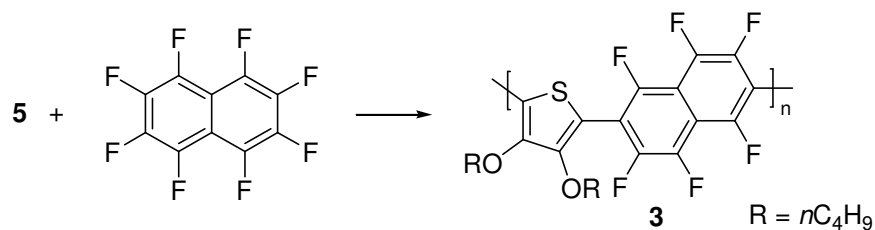
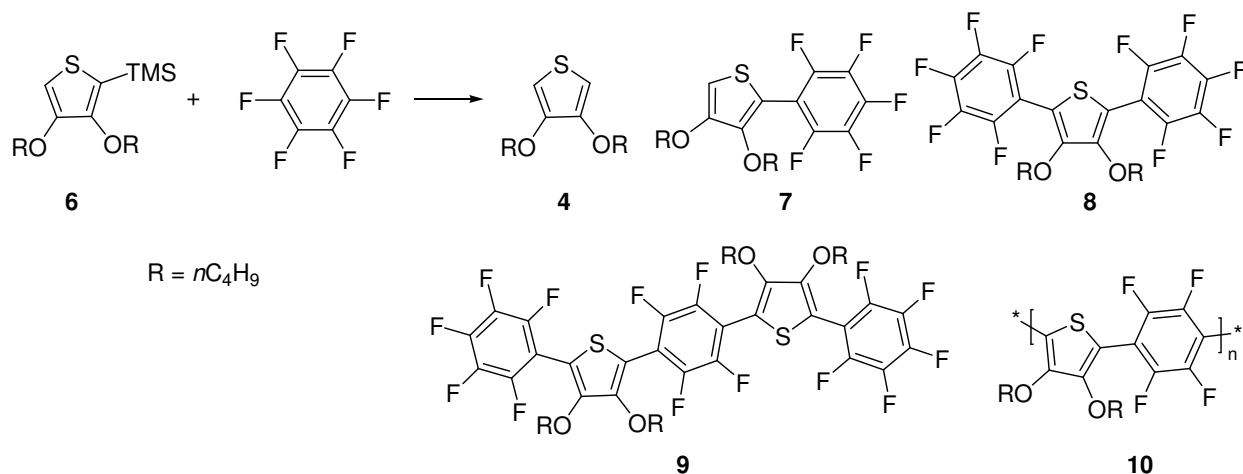


Figure SI 2. ^{19}F and 1H NMR of polymer **2** in $C_2D_2Cl_4$. Number average degree of polymerization calculated from ^{19}F NMR is $P_n = (133.5F/8F) \approx 17$, or 51 aromatic rings ($M_n \approx 8.7$ kDa), in good agreement with GPC data ($M_n = 17$ kDa, versus polystyrene), which typically overestimates by a factor of 2. * (H) $D_2C_2Cl_4$ solvent/reference.



Polymer 3. In an argon-filled glove box, monomer **5** (105.6mg, 0.283mmol), octafluoronaphthalene (80.85mg, 1.05 eq), CsF (4.50mg, 0.1 eq), 18-crown-6 (14.96mg, 0.2 eq) and toluene (1 mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at 80°C for 7 days, during which time it precipitates. The polymer was obtained as a colorless powder after purification as described above (116 mg). 1H NMR ($C_2D_2Cl_4$) δ : 4.12 (broad, 4H), 1.61 (broad, 4H), 1.35 (broad, 4H), 0.86 (broad, 6H). ^{13}C NMR ($C_2D_2Cl_4$) δ : 149.67 (d of m), 148.83, 144.82 (d of m), 140.82 (d of m), 111.45 (m), 110.75, 72.94, 31.73, 18.79, 13.65. ^{19}F NMR ($C_2D_2Cl_4$) δ : *Three signals with equivalent integrals*: -116.46(m, 28F), -134.95(m, 28F), -147.15(m, 28F), *Ten small ^{19}F signals from nonregiospecific addition(3) and OFN end groups (7)*: -113.43(m, 2F), -115.77(m, 2F), -132.11(m, 2F), -133.65(m, 2F), -143.53(m, 2F), -146.09(m, 2F), -148.66(m, 2F), -149.18(m, 2F), -152.53(m, 2F), -155.10(m, 2F). All of these signals coincidentally have approximately the same integral value, so any given one can be used to calculate P_n . M_n (GPC) = 13 kDa (PDI = 3.4). P_n (GPC) = 28. P_n (NMR) = 14.

Small-Molecule Model Studies



In an argon-filled glove box, **6** (518mg, 1.72 mmol), C_6F_6 (199 μ L, 1eq), CsF (26.2 mg, 0.24eq), 18-crown-6 (91.1mg, 0.2eq), and toluene (2mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at 80°C for 7 days. The reaction mixture was concentrated under reduced pressure and subjected to flash chromatography on silica gel with pentane-dichloromethane (5:1, v/v) to give **4** as yellow liquid (172mg, 0.753mmol, 43.7%), **7** as a liquid (14mg, 0.035mmol, 2%), **8** (13mg, 0.023mmol, 1.3%), and **9** as a colorless solid (14mg, 0.015mmol, 1.7%). Purging the column with pure dichloromethane gave a waxy solid which was determined to be higher oligomers **10** (278mg, ~ 43 %). The total isolated yield based on **6** is 92%. **Compound 4:** 1H NMR ($CDCl_3$) δ : 6.18(s, 2H), 3.99(t, 4H), 1.82(m, 4H), 1.49(m, 4H), 0.99(t, 6H). ^{13}C NMR ($CDCl_3$) δ : 147.41, 96.67, 70.08, 30.98, 19.10, 13.75. GC-MS: m/z 228 ($C_{12}H_{20}O_2S^+$), 116 (100%). **Compound 7:** 1H NMR ($CDCl_3$) δ : 6.39(s, 1H), 4.08(t, 2H), 4.01(t, 2H), 1.81(m, 2H), 1.60-1.35(m, 4H), 1.33(m, 2H), 0.998(t, 3H), 0.878(t, 3H). ^{19}F NMR ($CDCl_3$) δ : -138.60(m, 2F), -154.75(m, 1F), -162.96(m, 2F). GC-MS: m/z 394 ($C_{18}H_{19}F_5O_2S^+$), 282 (100%). **Compound 8:** 1H NMR ($CDCl_3$) δ : 4.02(t, 4H), 1.60(m, 4H), 1.34(m, 4H), 0.89(t, 6H). ^{19}F NMR ($CDCl_3$) δ : -137.95(m, 4F), -153.32(m, 2F), -162.18(m, 4F). GC-MS: m/z 560, ($C_{24}H_{18}F_{10}O_2S^+$), 448 (100%). **Compound 9:** 1H NMR ($CDCl_3$) δ : 4.07(t, 4H), 4.05(t, 4H), 1.61(m, 8H), 1.32(m, 8H), 0.89(t, 12H). ^{19}F NMR ($CDCl_3$) δ : -137.96(m, 4F), -138.63(s, 4F), -153.39(m, 2F), -162.22(m, 4F). MALDI: m/z : 934($C_{42}H_{36}F_{14}O_4S_2^+$), 710(100%). **Oligomers 10:** See spectra below. M_n (GPC) = 4.3kDa (PDI=1.89).

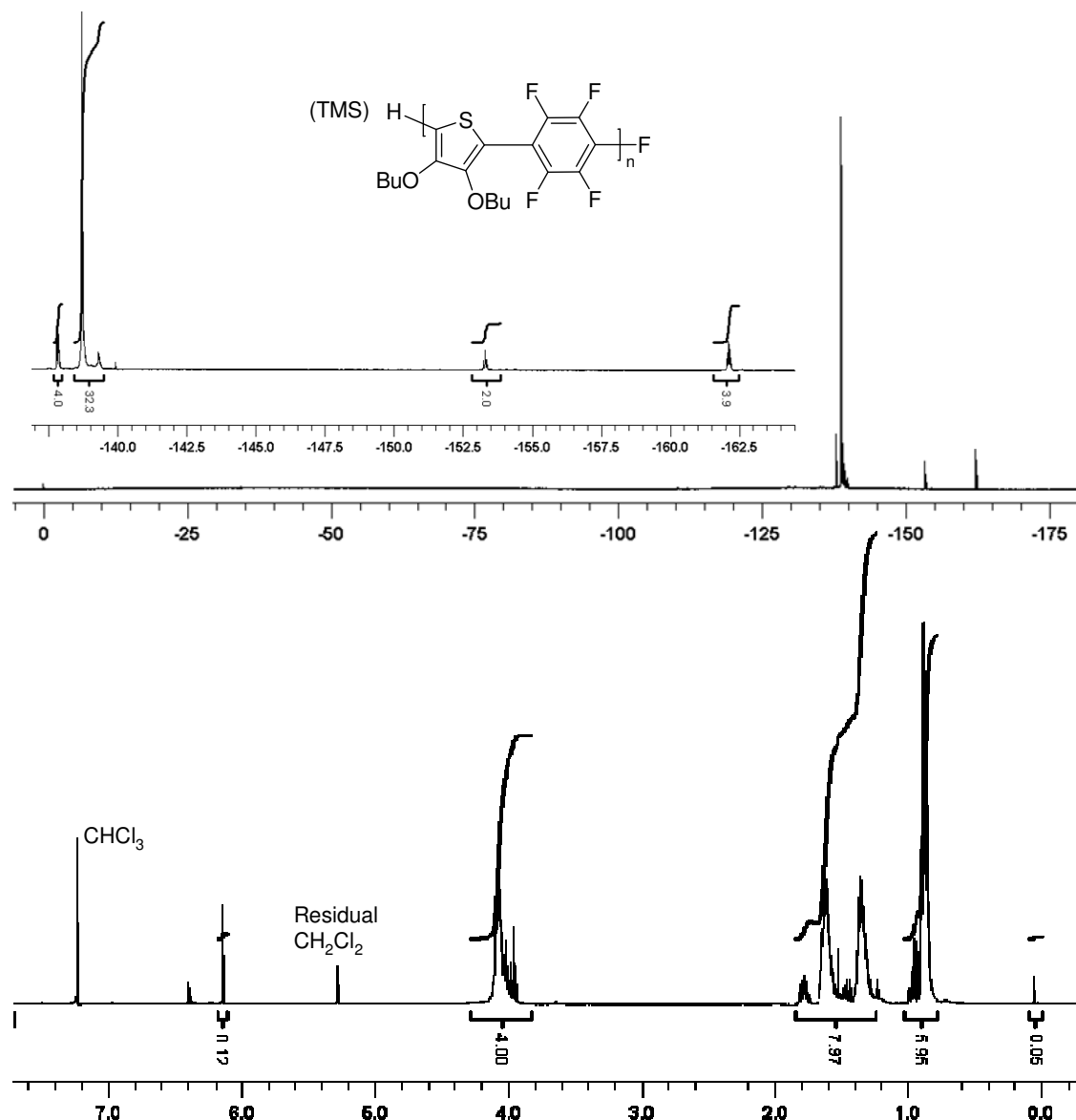
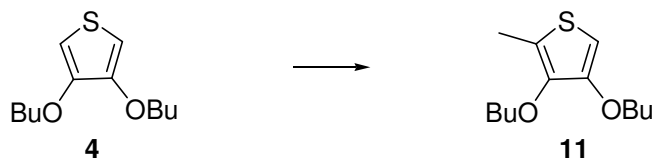
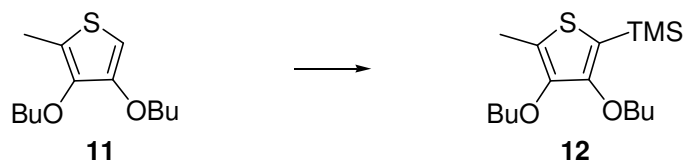


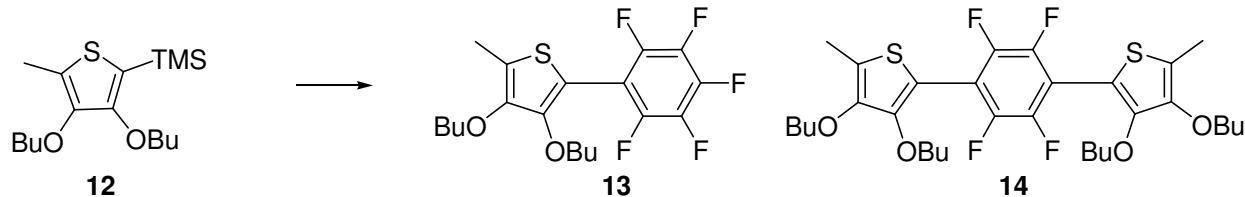
Figure SI 3. ^1H and ^{19}F NMR of oligomers **10** in CDCl_3 . Compare to spectra of analogous higher polymer **1a** in Figure SI-1 above. ^1H spectrum appears complicated due to low molecular weight (signals from endgroups). Number average degree of polymerization, calculated from the ratio of end-groups to repeating units (sums from both ^1H and ^{19}F NMR spectra), for oligomers **10** is $P_n \approx 5.3$. This corresponds to $M_n \approx 2$ kDa, in good agreement with GPC data (4.3 kDa, versus polystyrene), which typically overestimates by a factor of 2.



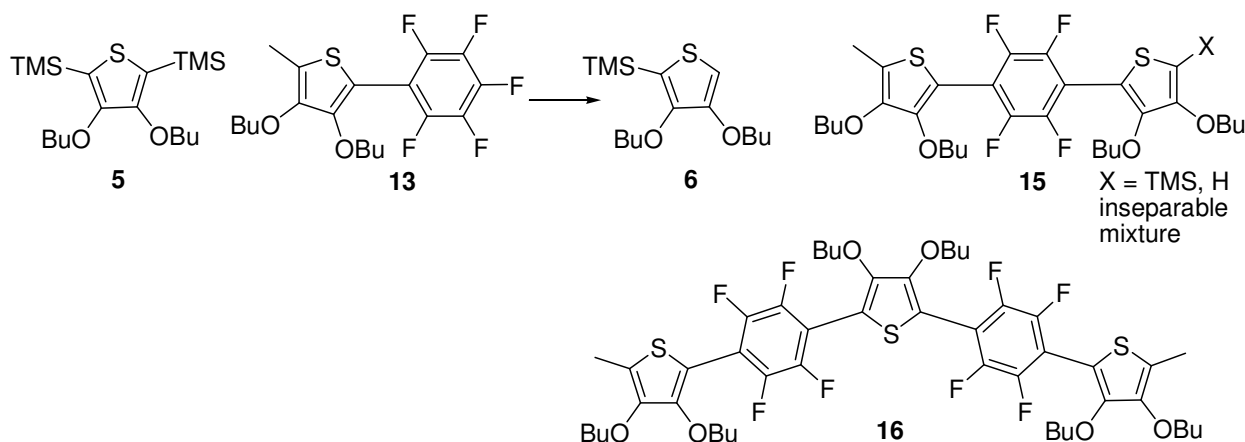
To a solution of **4** (1.12g, 4.90mmol) in THF (10mL) at 0 °C was added a hexane solution of *n*-BuLi (2.5M, 2.06mL, 1.05eq.). The whole was stirred for 30 min, gradually warmed to room temperature, then refluxed for 1 hour. After adding iodomethane (dried over CaH_2) (0.46 mL, 1.5eq.) in one portion at 0°C, the mixture was stirred for 30 min, gradually warmed to room temperature, and left stirring overnight. The reaction mixture was diluted with CH_2Cl_2 , extracted with 10% HCl (aq), dried over MgSO_4 , and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel with pentane-dichloromethane (2:1, v/v) to give **11** as a pale yellow liquid (520mg, 44%). ^1H NMR (CDCl_3) δ : 5.90(s, 1H), 3.98(t, 2H), 3.94(t, 2H), 2.28(s, 3H), 1.77(m, 2H), 1.69(m, 2H), 1.49(m, 4H), 0.98(t, 3H), 0.97(t, 3H). ^{13}C NMR (CDCl_3) δ : 150.11, 142.97, 121.32, 91.69, 72.62, 69.38, 32.12, 31.19, 19.28, 19.11, 13.84, 13.78, 11.75. GC-MS: m/z 242 ($\text{C}_{13}\text{H}_{22}\text{O}_2\text{S}^+$), 130 (100%).



To a solution of **11** (440mg, 1.82 mmol) in THF (5mL) at 0 °C was added a hexane solution of *n*-BuLi (2.5M, 0.80mL, 1.1eq.). The resulting mixture was stirred at the same temperature for 30 min, gradually warmed to room temperature, and then refluxed for 1 hour. After adding chlorotrimethylsilane (0.28 mL, 1.2eq.) in one portion at 0°C, the mixture was stirred for 30 min, gradually warmed to room temperature and left stirring overnight. The reaction mixture was diluted with CH₂Cl₂, extracted with 10% HCl (aq), dried over MgSO₄, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel with pentane-dichloromethane (3:1, v/v) to give **12** as a pale yellow liquid (490mg, 86%). ¹H NMR (CDCl₃) δ: 3.98(t, 2H), 3.95(t, 2H), 2.30(s, 3H), 1.71(m, 4H), 1.49(m, 4H), 0.984(t, 3H), 0.979(t, 3H), 0.29(s, 9H). ¹³C NMR (CDCl₃) δ: 155.63, 147.03, 127.05, 115.12, 72.92, 32.33, 32.26, 19.29, 19.22, 14.00, 13.93, 12.33, -0.27. GC-MS: *m/z* 314 (C₁₆H₃₀O₂SSi⁺), 187 (100%).



In an argon-filled glove box, **12** (380mg, 1.21 mmol), C₆F₆ (140 μL, 1.21 mmol), CsF (18.4mg, 0.1eq), 18-crown-6 (63.9 mg, 0.2eq), and toluene (2mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at RT overnight after which GC-MS revealed essentially no reaction except a trace of **13**. After heating to 80°C overnight, **12** was completely consumed (GC-MS). The reaction mixture was concentrated under reduced pressure to an oily residue, which was subjected to flash chromatography on silica gel with pentane-dichloromethane (3:1, v/v) to give **13** as a pale yellow liquid (217mg, 0.531mmol) and **14** as a colorless solid (183mg, 0.290mmol). The total isolated yield based on **12** was 92%. **Compound 13**: ¹H NMR (CDCl₃) δ: 4.012(t, 2H), 4.009(t, 2H), 2.36(s, 3H), 1.74(m, 2H), 1.57(m, 4H), 1.33(m, 2H), 0.999(t, 3H), 0.879(t, 3H). ¹⁹F NMR (CDCl₃) δ: -138.74(m, 2F), -155.27(m, 1F), -163.09(m, 2F). ¹³C NMR (CDCl₃) δ: 148.92, 145.68, 144.79 (d of m), 140.77 (d of m), 137.64(d of tr), 124.72, 108.46 (m), 102.11, 73.29, 72.36, 32.17, 31.87, 19.19, 18.90, 13.82, 13.62, 11.91. GC-MS: *m/z* 408 (C₁₉H₂₁F₅O₂S⁺), 296 (100%). **Compound 14**: ¹H NMR (CDCl₃) δ: 4.03(m, 8H), 2.37(s, 6H), 1.78(m, 4H), 1.57(m, 8H), 1.35(m, 4H), 1.002(t, 6H), 0.886(t, 6H). ¹⁹F NMR (CDCl₃) δ: -140.24(s, 4F). ¹³C NMR (CDCl₃) δ: 148.80, 145.66, 144.25 (d of m), 124.55, 112.44 (m), 103.46, 73.24, 72.33, 32.15, 31.88, 19.17, 18.89, 13.84, 13.66, 11.93. GC-MS: *m/z* 630 (C₃₂H₄₂F₅O₄S₂⁺), 406(100%).



In an argon-filled glove box, **5** (100.2 mg, 0.269mmol), **13** (109.8mg, 0.269mmol), CsF (4.1mg, 0.1eq), 18-crown-6 (14.2 mg, 0.2eq), and toluene (1mL) were combined in a vacuum flask containing a magnetic stir bar. The vessel was sealed and the contents stirred at 80°C overnight. The reaction mixture was concentrated under reduced pressure to an oily residue, which was subjected to column chromatography on silica gel with pentane-dichloromethane (3:1, v/v) to give **5** (30mg, 30% recovered yield), **6** (11mg, 13% based on **5**) and **16** as a pale yellow liquid (100mg, 74% based on **13**). The remainder of products (**15**) resulting from reaction of **5** and **13** were obtained as an inseparable mixture (43mg). The ¹H NMR spectrum of this mixture contained singlets corresponding to the methyls on the thiophene and TMS groups, as well as protons attached to the thiophene. **Compound 16**: ¹H NMR (CDCl₃) δ: 4.06 (overlapping triplets, 12H), 2.38 (s, 6H), 1.76-1.33 (overlapping multiplets, 24H), 1.00 (t, 6H), 0.90 (t, 6H), 0.89 (t, 6H). ¹⁹F NMR (CDCl₃) δ: -139.59 (m). ¹³C NMR (CDCl₃) δ: 148.98, 148.60, 145.73, 144.26 (d of m), 124.89, 113.45 (m), 111.43 (m), 110.70, 103.31, 73.31, 72.92, 72.40, 32.17, 31.92, 31.90, 19.19, 18.92, 18.90, 13.87, 13.70, 13.68, 12.00. MALDI: *m/z*: 1004(C₅₀H₆₀F₈O₆S₃⁺), 912(100%).

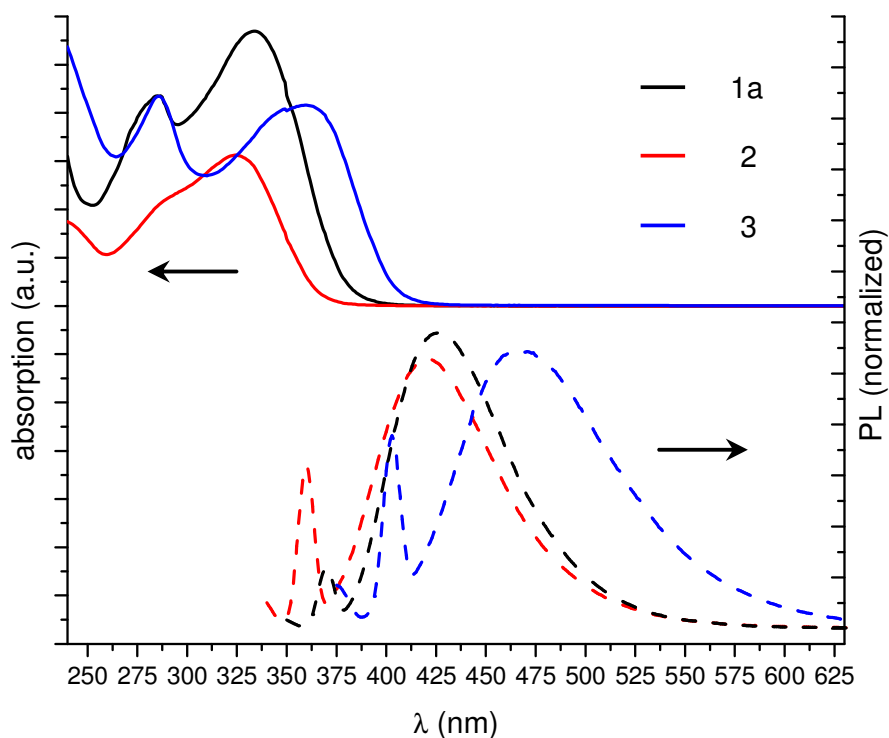


Figure SI 4. Absorption and emission spectra of polymers **1a**, **2**, and **3**. 10^{-5} M in THF (molarity based on formula mass of repeating units).

Complete reference 1i:

Crouch, D.J.; Skabara, P.J.; Lohr, J.E.; McDouall, J.J.W.; Heeney, M.; McCulloch, I.; Sparrowe, D.; Shkunov, M.; Coles, S.J.; Horton, P.N.; Hursthouse, M.B. *Chem. Mater.* **2005**, *17*, 6567-78.