Electronic Supplementary Information

Chloroform Outperforms Chlorobenzene for Enhanced Mobility in Amphiphilic Polymer OFETs

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TABLE OF CONTENTS

1. Materials and Methods

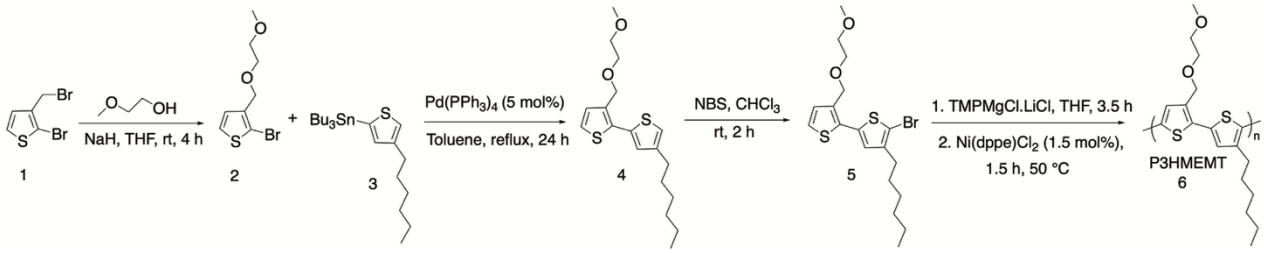
1.1 Materials

N-bromosuccinimide (NBS), 2-bromo-3-(bromomethyl)thiophene, 3-hexylthiophene**,** ethylene glycol monomethyl ether, sodium hydride, lithium diisopropylamide (LDA), and 2,2,6,6-tetramethylpiperidinylmagenisum chloride lithium chloride complex solution (TMPMgCl.LiCl), 1,2-[bis(diphenylphosphino)ethane]dichloronickel(II) Ni(dppe)Cl_2, were purchased from Sigma Aldrich and used as received. Tetrakis(triphenylphosphine)palladium and tributyltin chloride were purchased from Tokyo Chemical Industries. Anhydrous tetrahydrofuran, and toluene were dried and deoxygenated on a glass contour solvent purification system. NBS was recrystallized using hot water. All the other commercially available reagents were used as received without any further purifications. 5-Tributylstannyl-3-hexylthiophene was synthesized by following the literature procedure.[1]

1.2 Experimental Methods and Characterizations

All the chemical reactions were carried out using standard Schlenk techniques. All the reaction glassware were dried overnight in an oven at 120 °C before their use. ^{1}H NMR was recorded on either Bruker 500 MHz or JEOL 400 MHz spectrometer using $CDCl_3$ as solvent. Molecular weights of the polymers relative to polystyrene standards were determined using a MALVERN Viscotek TDA 305 GPC equipped with a UV detector using THF as eluent at a temperature of 40 °C and a flow rate of 1 mL/min.

Synthesis procedure Scheme S1: Synthesis route to polymer P3HMEMT.



Synthesis of 2-bromo-3-methoxyethoxythiophene (2): To a three-neck round-bottom flask containing sodium hydride (0.96 g, 40 mmol) and THF, ethylene glycol monomethyl ether (0.76 g, 10 mmol) was added dropwise over a period of 20 minutes under a nitrogen atmosphere. The reaction was allowed to stir for another 30 minutes. To this, a solution of 2-bromo-3-(bromomethyl)thiophene (5.63 g, 10 mmol), in anhydrous THF was added dropwise through a dropping funnel over a period of 15 minutes. The reaction was stirred at room temperature for 4 hours. The reaction mixture was passed through a celite pad, and the solvent was concentrated. The product was purified by column chromatography using hexane and ethyl acetate (60:40) giving a colorless oil in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) 7.23(d, 1H), 7.00 (d, 1H), 4.52(s, 2H), 3.62 (m, 2H), 3.57 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 138.23, 128.42, 126.11, 111.39, 71.99, 69.44, 67.25, 59.21.

Synthesis of 3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene (4): To a two-neck flask containing 2-bromo-3-methoxyethoxythiophene (768.9 mg, 3.0 mmol) and 5-tributylstannyl-3-hexylthiophene (2) (2.80 g, 6.1 mmol), anhydrous toluene (60 mL) and $Pd(PPh_3)_4$ (5 mol%) were added. The reaction mixture was refluxed for 24 h and extracted with ethyl acetate. The organic layer was washed with brine and dried over $MgSO_4$ and concentrated and purified by column chromatography using hexane and ethyl acetate (90:10) affording a light yellow color product in 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) 7.17 (d, 1H), 7.13(d, 1H), 7.02 (s, 1H), 6.91(s, 1H), 4.62 (s, 2H), 3.65 (m, 2H), 3.57(s, 2H), 3.39(s, 3H), 2.60(t, 2H), 1.63(m, 2H), 1.32(m, 6H), 0.89(t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 144.11, 135.01, 134.93, 134.90, 130.12, 128.23, 123.93, 120.81, 72.06, 69.35, 67.01, 59.21, 31.83, 30.67, 30.53, 29.16, 22.76, 14.25.

Synthesis of 2-bromo-3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene (5): To a two-neck round bottom flask compound (3) (703 mg, 2.0 mmol) and chloroform (30 mL) were added and the solution was degassed by bubbling nitrogen for 15 minutes. Then NBS (0.38 g, 2.1 mmol) was added slowly in 4 equal portions and the reaction was allowed to stir for two hours. After completion of the reaction, the product was extracted with chloroform, washed with brine, and dried over $MgSO_4$. Column chromatography using hexane and ethyl acetate (90:10) gave the product in a 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) 7.19(d, 1H), 7.11(d, 1H), 6.89(s, 1H), 4.56(s, 2H), 3.64(m, 2H), 3.57(m, 2H), 3.39(s, 2H), 2.55(t, 2H), 1.60(m, 2H), 1.32(m, 6H), 0.89(t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 142.95, 135.33, 134.78, 134.18, 130.34, 127.76, 124.36, 109.53, 72.04, 69.44, 66.87, 59.22, 31.77, 29.80, 29.74, 29.07, 22.75, 14.25.

Synthesis of polymer P3HMEMT: To a 30 mL Schlenk flask compound (**5**) (146.3 mg, 0.35 mmol) was added and then degassed under a high vacuum for 30 minutes. The flask was kept under nitrogen and then 2.5 mL of THF was added. Then TMPMgCl.LiCl (0.35 mL, 1.0 M in THF) was added dropwise over a period of 10 minutes at 0 °C. The reaction flask was allowed to warm to room temperature and stirred for 3.5 h. Then Ni(dppe)Cl_2 (2.80 mg, 1.5 mol%) was added to the flask, and polymerization was stirred at 50 °C for 1.5 h and then quenched using dil. HCl (5 M) and polymeric products were precipitated into 400 mL of methanol. Finally, the precipitates were filtered and purified with successive Soxhlet extraction using methanol, acetone, and hexane and then collected using chloroform. The polymer was again precipitated into methanol, filtered, and dried overnight under a vacuum at 60°C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.19(s, 1H), 7.08(s, 1H), 4.66 (s, 2H), 3.72(m, 2H), 3.64(m, 2H) 3.42(s, 3H), 2.80 (t, 2H), 1.68 (m, 2H),1.43(m, 2H), 1.35(m, 4H), 0.91(s, 3H). The molecular weight distribution estimated by GPC is as follows M_n = 29.6 kg/mol, M_w = 66.0 kg/mol, PDI = 2.2.

2. Thin film preparation and characterization

Film Preparation: The polymer samples were dissolved in chloroform (CF) or chlorobenzene (CB) at a concentration of 15 mg/mL, and they were sitting on a hotplate overnight at 40 °C. The final solution was spin-coated at 400 rpm (for 2 s), then 1000 rpm (for 60 s) onto substrates. Each substrate was cleaned in an ultrasonic bath with acetone, isopropyl alcohol (IPA), deionized (DI) water, and treated with UV–ozone for 30 min before use. The obtained films were annealed at 130 °C under vacuum.

IR-pMAIRS analysis: p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) measurements were performed using a spectrometer (iS-50; Thermo Fisher Scientific) equipped with a sample rotation stage in dry air. The samples for pMAIRS measurements were prepared on FZ Si substrates (Pier Optics Co, ltd.).

UV-vis measurements: For UV-vis absorption spectra polymer films were coated on ITO-coated glass substrate and their absorption spectra was recorded using Shimadzu 3600i plus UV-Vis-NIR spectrophotometer. For solution UV-Vis studies, dilute solutions of 0.015 mg/mL of P3HMEMT and P3HT were prepared in both CF and CB.

GIWAXS measurements: GIWAXS measurements were performed with a HUBER multi-axis diffractometer installed in the beamline BL13XU at SPring-8. The X-ray beam from the undulator was monochromatized by a double-crystal Si(111) monochromator. The X-ray energy was 12.39 keV (λ = 1 Å), and the X-ray beam size was 40 μm (height) × 300 μm (width) at the sample position. The diffraction from the samples was detected by a two-dimensional (2D) X-ray photon counting pixel detector (PILATUS 300 K). The X-ray beam incidence angle was set to 0.12°, and the camera length (sample-to-detector distance) was set to 174 mm. The polymer neat films were prepared by spin-coating the polymer solution in CF or CB on the Si substrate, where the substrate size was 2 cm × 2 cm. The measurements were performed in air at rt. The exposure time was 1 s, and no irradiation damage was observed on the samples. The coherence length (L) was estimated from the simplified

Scherrer's equation, $L = 2\pi/\text{fwhm}$, where fwhm is the full-width at half-maximum of the lamellar and π–π stacking diffraction peaks. Note that fwhm was not corrected for the resolution function typically caused by the sample size.

OFET Fabrication and Measurement: OFET devices were fabricated in top-contact bottom-gate geometry, using a doped p-type silicon wafer with a 50 nm thick SiO_2 surface layer. Polymer P3HMEMT was deposited using spin coating as described above and annealed at 130°C for 30 minutes under vacuum. Source and drain electrodes of gold (100 nm) were deposited using the electron beam deposition method. Transistor devices were characterized using a Keithley semiconducting analyzer.

Peak assignments of IR spectra

For the assignments of oligo ethylene side chains of homo- and copolymers, **Figure S1** summarizes DFT calculation and measurements of reference compounds. The calculation was done for an optimized structure with an all-trans conformation, and it has a strong peak at 1157 cm^{-1}, ascribed to antisymmetric stretching vibrations ν(C–O). Other minor peaks were assigned and annotated in the figure. Noteworthy, twisting $\tau(CH_2)$ and rocking $\rho(CH_2)$ modes have zero intensity due to the symmetry of the all-trans conformer. These two modes are very weak in a liquid state of PEG oligomer and a vapor phase of monoglyme. Still, they are observed in measured samples, especially solid-state polyethylene glycol samples where gauche conformers are present. This means that these two peaks are a good indicator of the presence of gauche conformers.

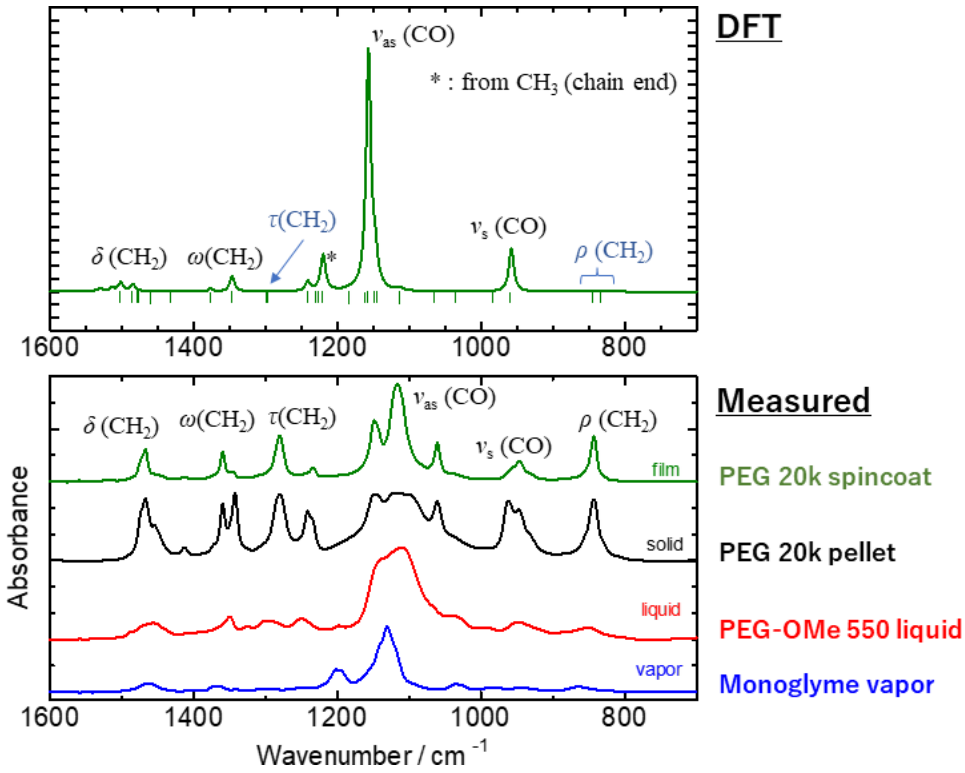


Figure S1. DFT calculated (top) and measured (bottom) IR spectra of oligo and polyethylene glycols. The top DFT spectra were for diglyme (diethylene glycol dimethyl ether) at B3LYP/6-311G++(d)(p) level.

Figure S2 shows DFT calculated IR spectra of monomer model molecules. To reduce the effect of chain ends, two different end groups (R = H and Me) were examined, and the peaks that remained the same in the two cases were considered for discussion. Note that the ethylene glycol side chains take all-trans conformation in these optimized structures. The antisymmetric stretching vibrations ν(C–O) peak of side chains clearly split into two peaks in all cases, and they are ascribed to two different C-O bonds on the near and far side from the thiophene ring, respectively. Notably, even in all-trans

conformation, as shown in **Figure S3** for comparison, gives a bimodal peak in this region. Therefore, this peak is powerful for discussing chain orientation and conformation in the polymer film state.

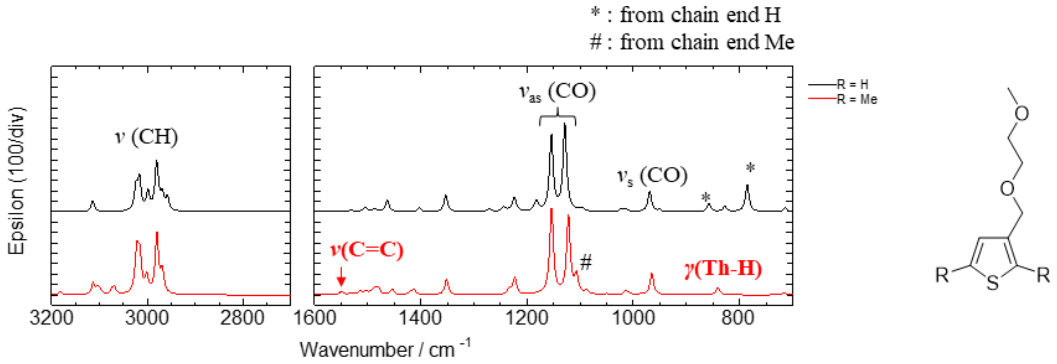


Figure S2. DFT calculated IR spectra of thiophene monomer models with oligo ethylene glycol chains. The top DFT calculation was done at the B3LYP/6-311G++(d)(p) level.

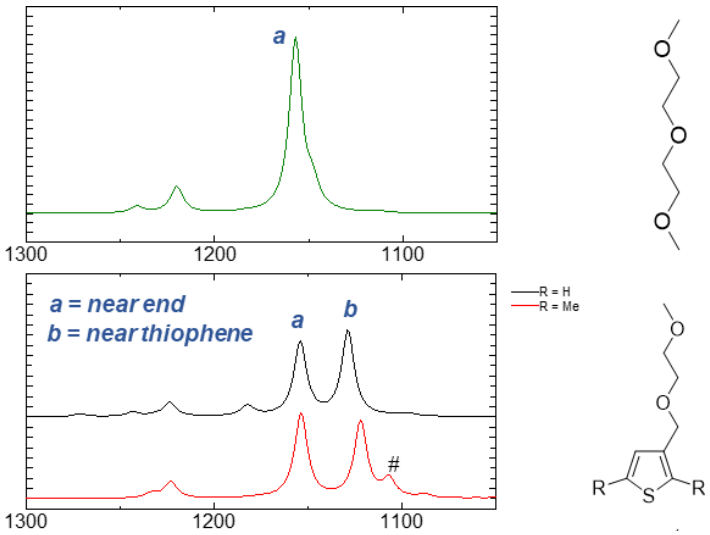


Figure S3. Enlarged DFT calculated IR spectra of diglyme and thiophene monomer models with oligo ethylene glycol chains.

Table S1 Summary of OFET charge mobilities of polymer films prepared from CF and CB at different channel width/length (W/L) ratios.

(W/L)	Charge Mobility (cm^2/Vs)[a]	
	CF	CB
24.5	4.2×10^{-3}	9.8×10^{-4}
12.1	3.9×10^{-3}	9.8×10^{-3}
8.2	$4.9 (\pm 1.2) \times 10^{-3}$	$4.1(\pm 5.1) \times 10^{-3}$

6.0	6.0(±2.4) x 10^{-3}	8.4(±0.4) x 10^{-4}
4.8	4.5(±0.4) x 10^{-3}	1.1(±0.3) x 10^{-3}
4.0	8.8 x 10^{-3}	1.3 x 10^{-3}
3.3	3.5 x 10^{-3}	8.0 x 10^{-4}

[a]Field-effect mobilities were extracted by fitting the linear part of the plot sqrt(Drain current) versus Gate voltage once the device is turned on. A total of 13 devices were fabricated for each sample: 1 each for W/L = 24.5, 12.1, 4.0, and 3.3; 3 each for W/L 8.2, 6.0, and 4.8 (average mobility indicated).

For CF, Average charge mobility = 5.1 x 10^{-3} cm^2/Vs, standard deviation = 1.7 x 10^{-3} cm^2/Vs and standard error = 4.8 x 10^{-4} cm^2/Vs. For CB, average charge mobility = 2.7 x 10^{-3} cm^2/Vs, standard deviation = 3.6 x 10^{-3} cm^2/Vs and standard error = 1.0 x 10^{-3} cm^2/Vs.

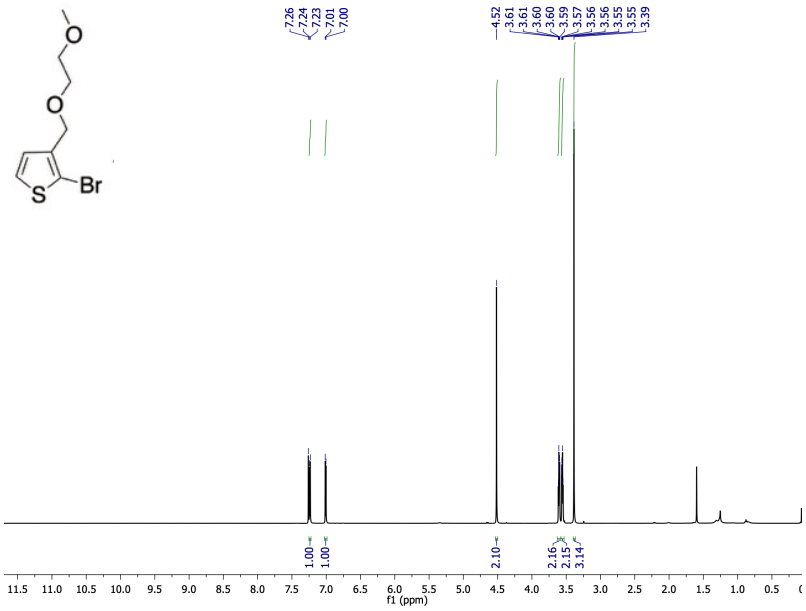


Figure S4. ^{1}H NMR spectrum of 2-bromo-3-methoxyethoxythiophene.

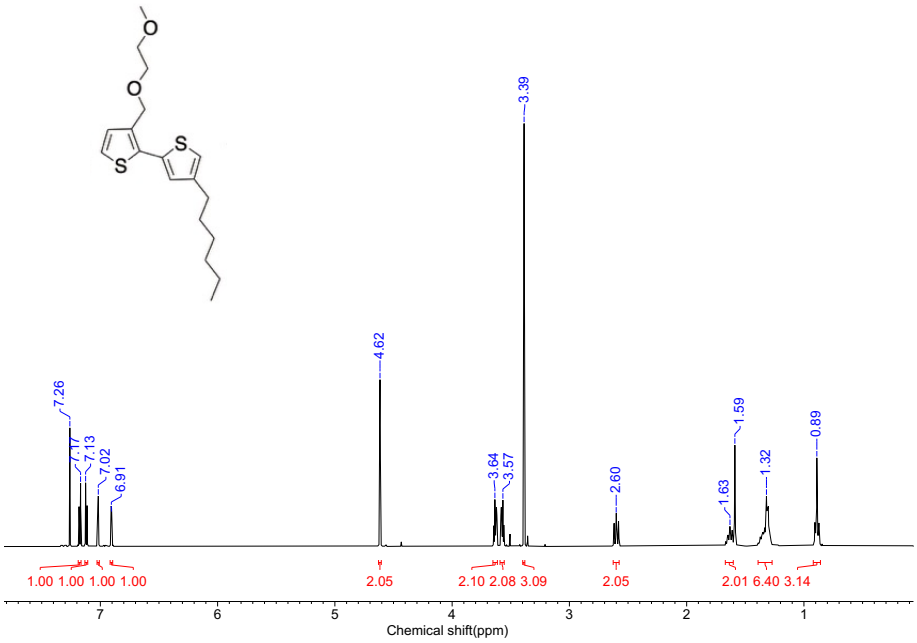


Figure S5. ^{1}H NMR spectrum of 3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene.

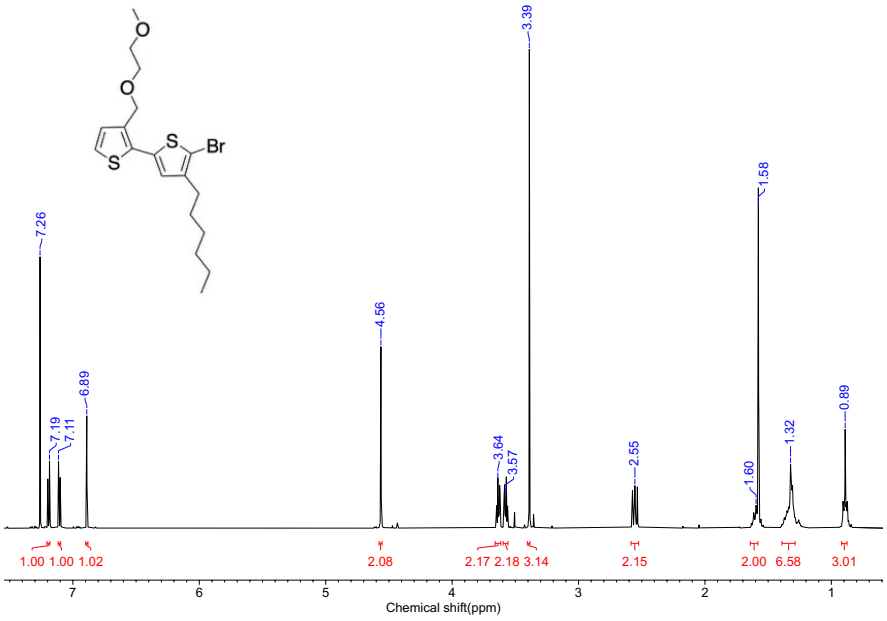


Figure S6. ^{1}H NMR spectrum of 2-bromo-3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene.

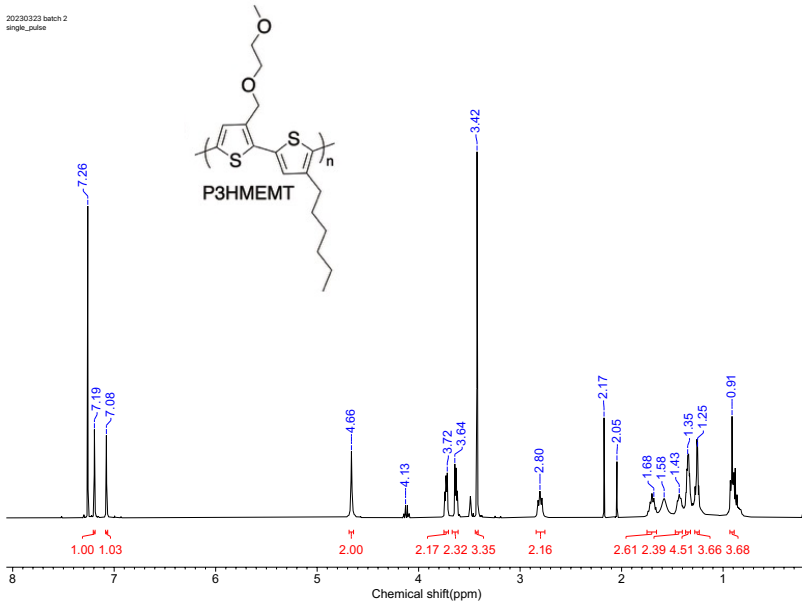


Figure S7. ^{1}H NMR spectrum of Polymer P3HMEMT.

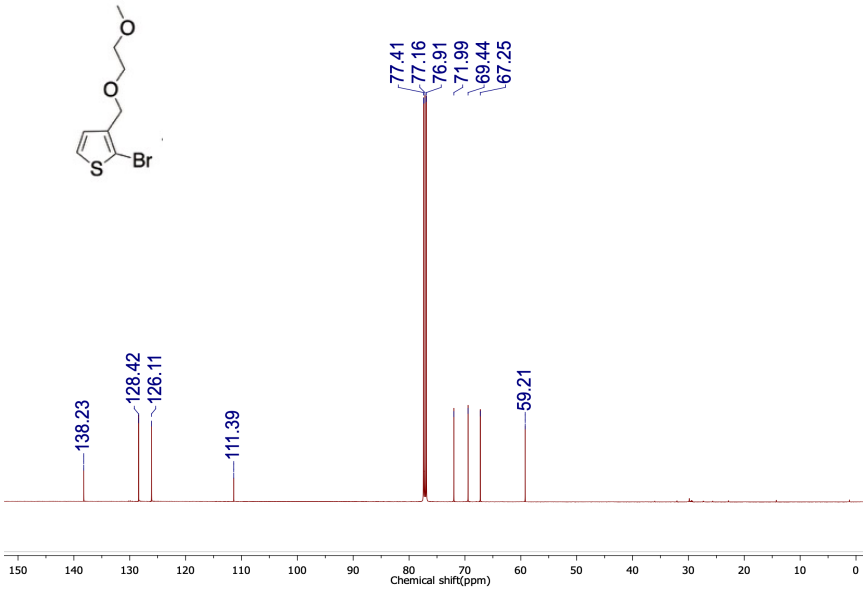


Figure S8. ^{13}C NMR spectrum of 2-bromo-3-methoxyethoxythiophene.

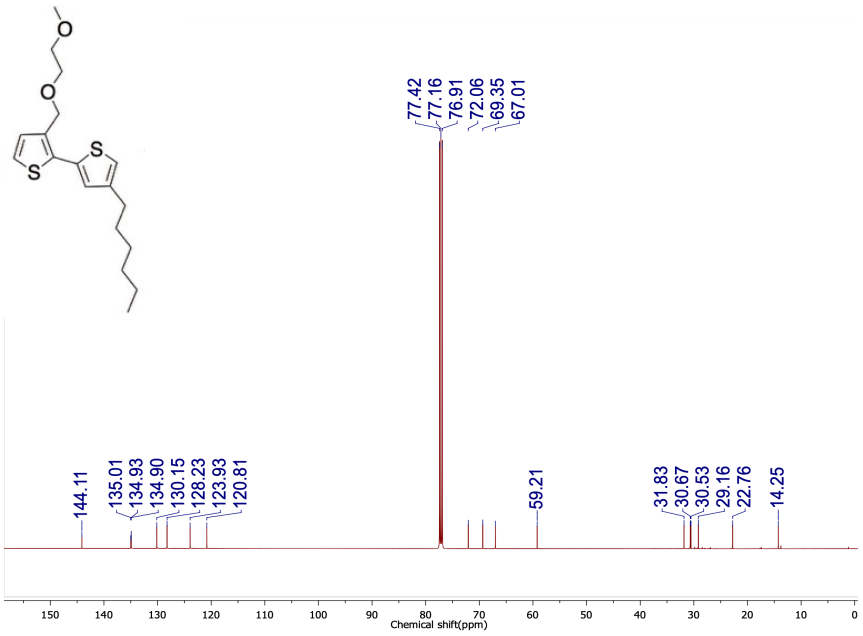


Figure S9. ^{13}C NMR spectrum of 3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene.

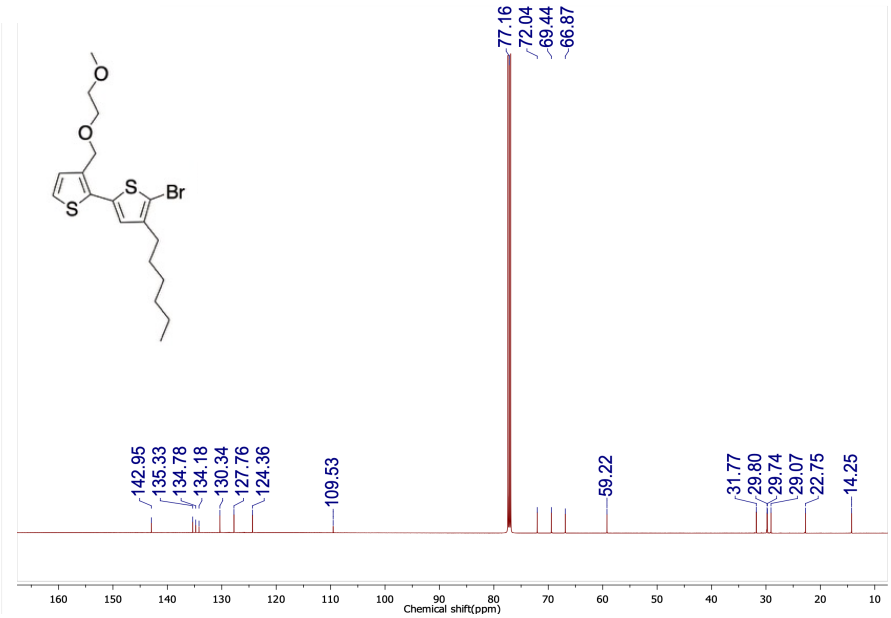


Figure S10. ^{13}C NMR spectrum of 2-bromo-3-hexyl-4'-((2-methoxyethoxy)methyl)-2,2'-bithiophene.

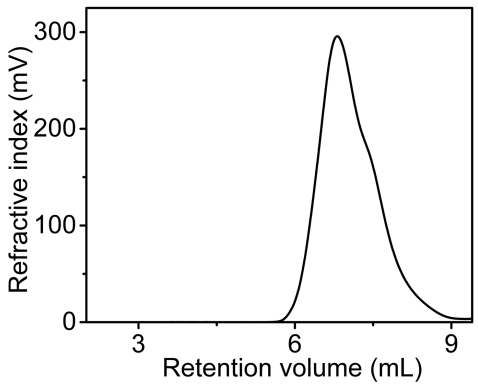


Figure S11. GPC profile of P3HMEMT.

References

1. F. P. V. Koch, P. Smith and M. Heeney, “Fibonacci’s Route” to Regioregular Oligo(3-hexylthiophene)s, *J. Am. Chem. Soc.*, 2013, **135**, 13695–13698.