Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Effects of flexibility and branching of side chains on the mechanical properties of low-bandgap conjugated polymers

Fumitaka Sugiyama,[1,2] Andrew T. Kleinschmidt,[1] Laure V. Kayser,[1] Daniel Rodriquez,[1] Mickey Finn III,[1] Mohammad A. Alkhadra,[1] Jeremy M.-H. Wan,[1] Julian Ramírez[1], Andrew S.-C. Chiang,[1] Samuel E. Root,[1] Suchol Savagatrup,[1] and Darren J. Lipomi[1,]*

[1]Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive,
Mail Code 0448, La Jolla, CA 92093-0448

[2]JSR Corporation, 1-9-2, Higashi-Shimbashi, Minato-ku, Tokyo 105-8640, Japan

*Author to whom correspondence should be addressed: dlipomi@eng.ucsd.edu

General

All reagents were obtained from commercial suppliers and used without purification. Chloroform, ortho-dichlorobenzene (ODCB), dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. Unless otherwise noted, all reactions were carried out under nitrogen with standard Schlenk techniques. Flash chromatography was performed using Alfa Aesar™ Silica gel 60 (particle size 36-71 μm, 215-400 mesh). All compounds were characterized by ^{1}H NMR (300 MHz, Bruker or 500 MHz, Jeol) using $CDCl_3$ as the solvent. The residual chloroform peak at 7.28 ppm was used to calibrate the chemical shifts for ^{1}H NMR. Gel permeation chromatography (GPC) was performed in chloroform using Agilent 1260 Separation Module equipped with 1260 Refractive Index Detector and 1260 Photodiode Array Detector. Molecular weights were calculated relative to linear PS standards. Ultraviolet-visible (UV-vis) spectra were obtained of the polymers in chloroform and in the solid state, as-cast from chloroform (by volume, 10 mg mL^{-1}) using a Perkin Elmer Lambda 1050 UV-vis-NIR spectrophotometer. We synthesized the three known polymers, PDPP-EH, PDPP-HD, and PDPP-C16, according to previously reported procedures.[1]

Synthesis

EOx-OTs: EO4-OTs and EO5-OTs were synthesized according to previously reported procedures.[2,3] PEO3-OTs was obtained from Sigma-Aldrich and used without purification.

3,6-di(furan-2-yl)-2,5-di(2,5,8,11-tetraoxatridecan-13-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (3-EO4): Compound **2** (4.02 g, 15.0 mmol), EO4-OTs (20.71g, 57.0 mmol), tetra-n-butylammonium bromide (0.483 g, 1.5 mmol) and 150 mL of dry DMF were added to a 250 mL single-neck round–bottom flask, equipped with stir-bar and placed under nitrogen atmosphere. The mixture was heated to 120 °C, stirred for 40 h. The reaction mixture was cooled to room temperature. DMF was removed under vacuum distillation, and distilled water (200 mL) was added. The product was extracted with chloroform, then washed with brine, and dried over $MgSO_4$, and red solid was purified by silica gel chromatography eluting with $CHCl_3$ / acetone (9:1 to 6:4). 3.80 g of **3-EO4** were isolated (39% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, *J* = 3.7 Hz, 2 H), 7.66 (d, *J* = 1.7 Hz, 2 H), 6.69 (dd, *J* = 1.7 Hz, 3.8 Hz, 2 H), 4.37 (t, *J* = 6.3 Hz, 4 H), 3.77 (m, 4 H), 3.70 – 3.40 (m, 24 H), 3.38 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 160.89, 145.48, 144.59, 133.85, 120.30, 113.51, 106.52, 71.99, 70.67, 70.65, 70.58, 70.56, 69.56, 59.11, 41.62. HR-MS: m/z calc'd for $C_{23}H_{45}N_2O_{12}$ $[M+H]^+$ 649.2961 found 649.2967.

3,6-bis(5-bromofuran-2-yl)-2,5-di(2,5,8,11-tetraoxatridecan-13-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4-EO4): Compound **3-EO4** (3.78 g, 5.83 mmol) and 280 mL of $CHCl_3$ was charged in a 500 mL single-neck round–bottom flask, equipped with stir-bar and placed under nitrogen atmosphere. The mixture was cooled to 0 °C and stirred while NBS (2.19 g, 12.23 mmol) was added in small portions. The mixture was allowed to warm to room temperature and stirred for 74 h following complete addition of NBS. The organic phase was extracted with $CHCl_3$ and washed with water. The $CHCl_3$ was evaporated, and the resulting tacky solid (dark red) was purified by silica gel chromatography eluting with $CHCl_3$ / acetone (9:1 to 8:2). 3.44 g of **4-EO4** were isolated (73% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.23 (d, *J* = 3.7 Hz, 2 H), 6.63 (d, *J* = 3.7 Hz, 2 H), 4.31 (t, *J* = 6.0 Hz, 4 H), 3.75 (t, *J* = 6.1 Hz, 4 H), 3.70 – 3.40 (m, 26 H), 3.37 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 160.45, 146.17, 132.63, 126.49, 122.12, 115.56, 106.39, 71.97, 70.66, 70.65, 70.54, 70.51, 69.49, 59.09, 41.65. HR-MS: m/z calc'd for $C_{23}H_{43}Br_2N_2O_{12}$ $[M+H]^+$ 805.1172 found 805.1177.

3,6-di(furan-2-yl)-2,5-di(2,5,8,11,14-pentaoxahexadecan-16-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (3-EO5): Compound **2** (2.47 g, 9.2 mmol), EO5-OTs (14.88 g, 36.6 mmol), tetra-n-butylammonium bromide (0.30 g, 0.92 mmol) and 90 mL of dry DMF were added to a 250 mL single-neck round–bottom flask, equipped with stir-bar and placed under nitorogen atmosphere. The mixture was heated to 120 °C, stirred for 66 h. The reaction mixture was cooled to room temperature. DMF was removed under vacuum distillation, and distilled water (200 mL) was added. The product was extracted with chloroform, then washed with brine, and dried over $MgSO_4$, and red solid was purified by silica gel chromatography eluting with

$CHCl_3$ / acetone (10:0 to 4:6). 0.44 g of **3-EO5** were isolated (7% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, *J* = 3.7 Hz, 2 H), 7.67 (d, *J* = 1.8 Hz, 2 H), 6.69 (dd, *J* = 1.6 Hz, 3.7 Hz, 2 H), 4.37 (t, *J* = 6.3 Hz, 4 H), 3.74 (t, *J* = 6.4 Hz, 4 H), 3.70 – 3.40 (m, 34 H), 3.38 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 160.87, 145.51, 144.57, 133.83, 120.30, 113.51, 106.50, 71.99, 70.66, 70.65, 70.63, 70.60, 70.57, 69.55, 59.11, 41.60. HR-MS: m/z calc'd for $C_{36}H_{52}N_2O_{14}Na$ $[M+Na]^+$ 759.3311 found 759.3300.

3,6-bis(5-bromofuran-2-yl)-2,5-di(2,5,8,11,14-pentaoxahexadecan-16-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4-EO5): Compound **3-EO5** (0.44 g, 0.64 mmol) and 30 mL of $CHCl_3$ was charged in a 100 mL single-neck round–bottom flask, equipped with stir-bar and placed under nitrogen atmosphere. The mixture was cooled to 0 °C and stirred while NBS (0.24 g, 1.33 mmol) was added in small portions. The mixture was allowed to warm to room temperature and stirred for 72 h following complete addition of NBS. The organic phase was extracted with $CHCl_3$ and washed with water. The $CHCl_3$ was evaporated, and the resulting tacky solid (dark red) was purified by silica gel chromatography eluting with $CHCl_3$ / acetone (8:2 to 5:5). 0.28 g of **4-EO5** were isolated (50% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.23 (d, *J* = 3.7 Hz, 2 H), 6.63 (d, *J* = 3.7 Hz, 2 H), 4.32 (t, *J* = 6.1 Hz, 4 H), 3.75 (t, *J* = 6.0 Hz, 4 H), 3.70 – 3.40 (m, 34 H), 3.38 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 160.58, 146.19, 132.74, 126.57, 122.21, 115.60, 106.44, 71.9, 70.66, 70.65, 70.64, 70.61, 70.60, 70.56, 70.52, 69.54, 59.12, 41.69. HR-MS: m/z calc'd for $C_{36}H_{51}Br_2N_2O_{14}$ $[M+H]^+$ 893.1695 found 893.1702.

PDPP2FT-EO4 (6-EO4): 4-EO4 (242 mg, 0.300 mmol), 2,5-bis(trimethylstannyl)-thiophene (**4**) (117 mg, 0.285 mmol), $Pd_2(dba)_3$ (2.7 mol %) and $P(o\text{-}tol)_3$ (10.7 mol %) were charged within a 25 mL 3-necked flask, cycled with nitrogen and subsequently dissolved in 6 mL of degassed chlorobenzene. The mixture was stirred for 20 h at 110 °C. The reaction mixture was allowed to cool to 25 °C, 5 mL of $CHCl_3$ was added, and precipitated into methanol (200 mL). The precipitate was purified via Soxhlet extraction for 3 h with methanol and 3 h with hexanes, followed by collection in chloroform. The polymer **6-EO4 (PDPP2FT-EO4)** was obtained as a dark solid (165 mg). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.36 (bs, 2H), 7.28-6.77 (m, 4H), 4.35-3.36 (m, 38H). GPC analysis: see Table S1.

PDPP2FT-EO5 (6-EO5): 4-EO5 (260 mg, 0.253 mmol), 2,5-bis(trimethylstannyl)-thiophene (**4**) (93.9 mg, 0.240 mmol), Pd2(dba)3 (2.7 mol %) and P(o-tol)3 (10.7 mol %) were charged within a 25 mL 3-necked flask, cycled with nitrogen and subsequently dissolved in 4.5 mL of degassed chlorobenzene. The mixture was stirred for 20 h at 110 °C. The reaction mixture was allowed to cool to 25 °C, 5 mL of $CHCl_3$ was added, and precipitated into methanol (200 mL). The precipitate was purified via Soxhlet extraction for 5 h with methanol and 2 h with hexanes, followed by collection in chloroform. The polymer **6-EO5 (PDPP2FT-EO5)** was obtained as a dark solid (175 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.37 (bs, 2H), 7.28-6.79 (m, 4H), 4.37-3.38 (m, 46H). GPC analysis: see Table S1.

Table S1. SEC analysis of PDPP2FT derivatives. (Values in parentheses are for materials tested for electronic properties.)

Side Chain	M_n	M_w	PDI
EO3	14.6	52.8	3.6
EO4	17.1 (21.8)	44.8 (151.6)	2.6 (7.0)
EO5	23.8	116.8	4.9
EH	19.6 (33.8)	63.7 (138.8)	3.3 (4.1)
HD	29.2	101.4	3.5
C16	57.2	331.6	5.8

Measurement of Optical Band Gap and Dichroic Ratio.

Ultraviolet-visible (UV-vis) spectra were obtained of the polymers in chloroform and in the solid state, as-cast from chloroform (by volume, 10 mg mL^{-1}) using a Perkin Elmer Lambda 1050 UV-vis-NIR spectrophotometer. The UV-vis film spectra were converted into a Tauc plot, and the linear region of the plots were used to fit a line. The intercept of the line and the $h\nu$ axis was taken as the optical bandgap. For the dichroic ratio, the films were laminated to a PDMS slab which was quickly removed. The PDMS slab was then strained the desired amount and laminated onto a glass support. The dichroic ratio was taken by placing a polarizer in front of the UV-vis and measuring the spectra perpendicular and parallel to the direction of strain. The dichroic ratio was calculated using the formula: $R = \frac{A_{\parallel}}{A_{\perp}}$ at $\lambda_{\max}$.

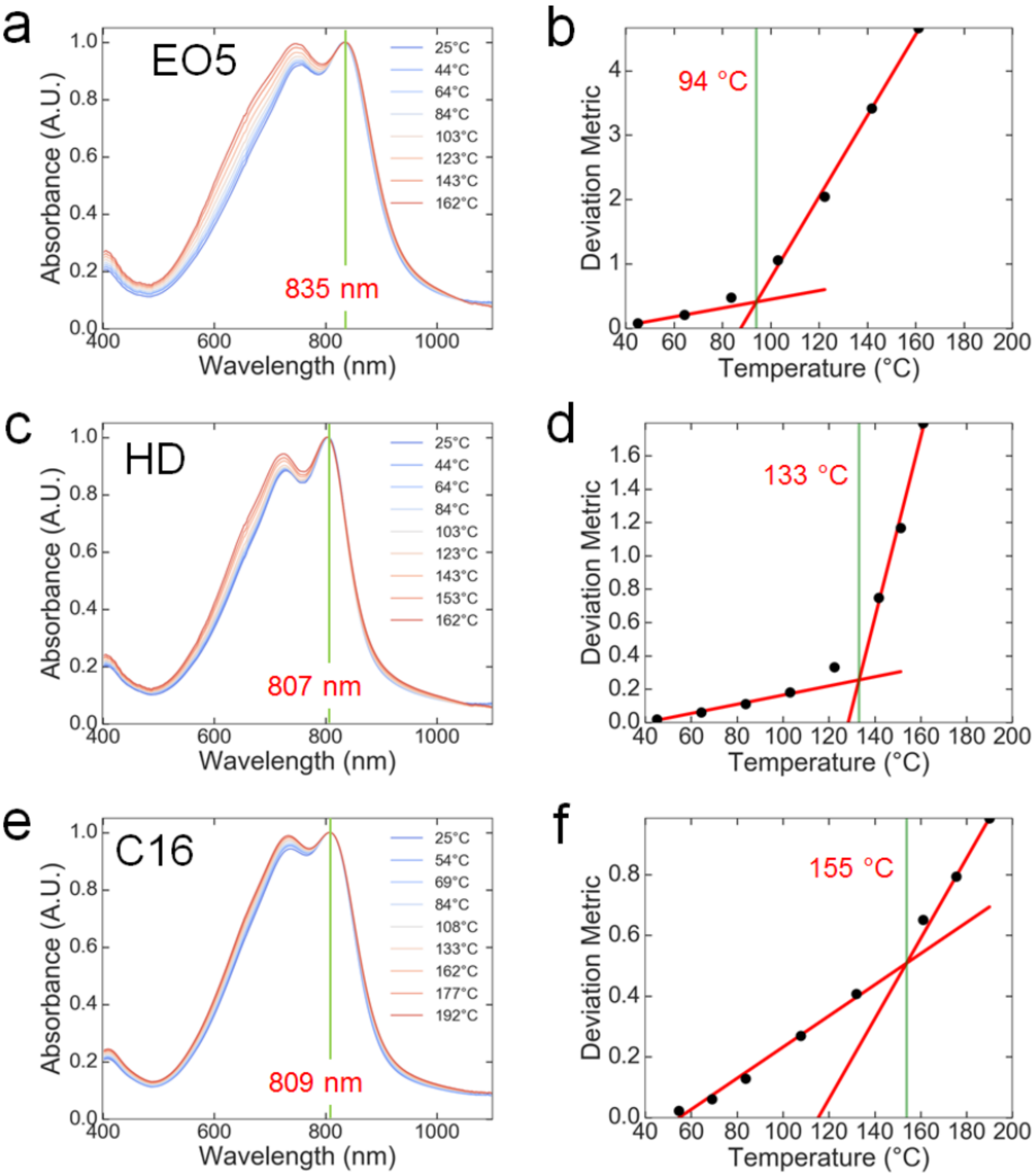

Figure S1. Solid state UV−vis absorption spectra and corresponding deviation metric showing the measurement of the T_g for (a, b) PDPP2FT-EO5, (c, d) PDPP2FT-HD, and (e, f) PDPP2FT-C16.

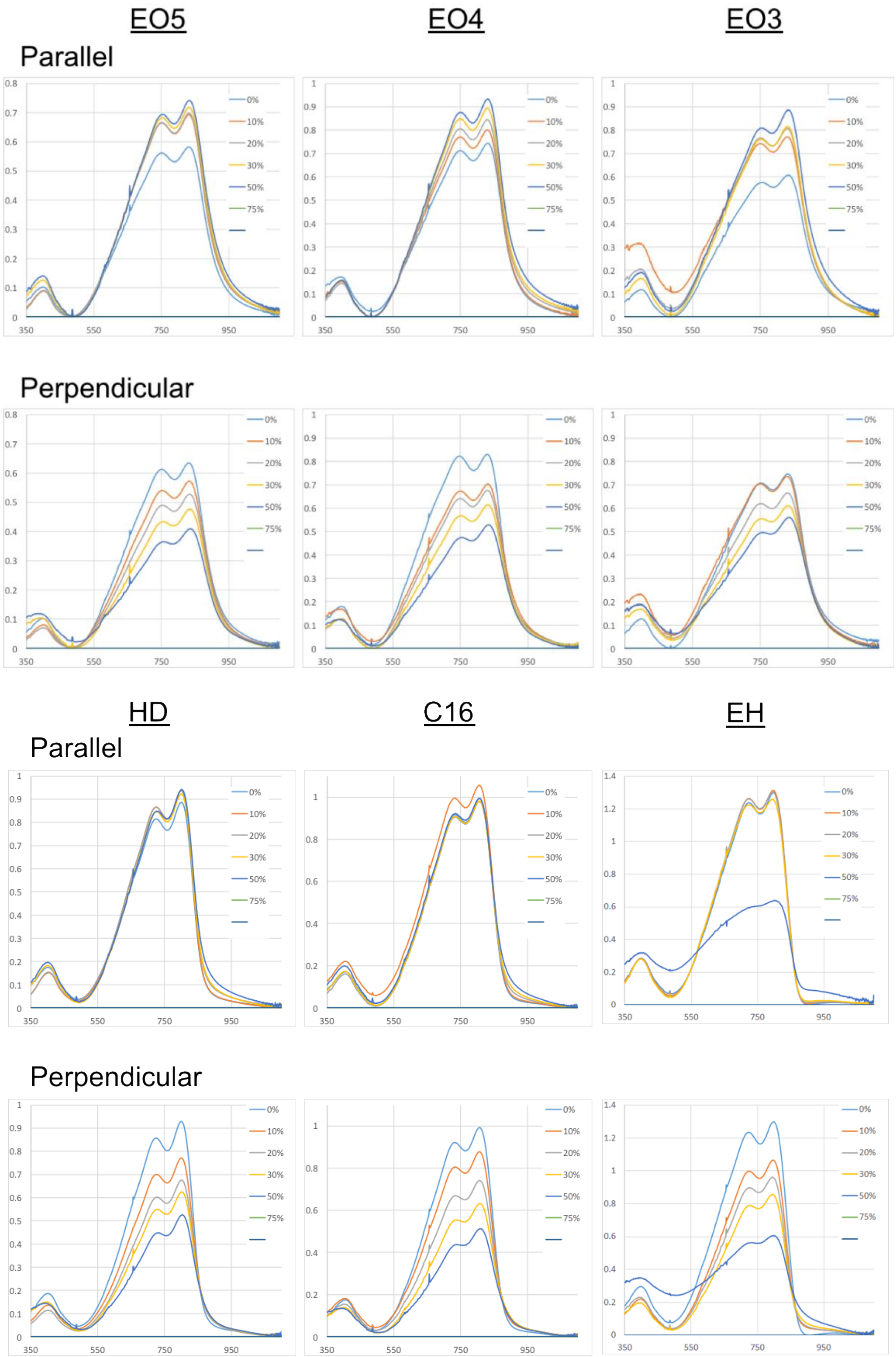

Figure S2. UV-vis spectra of PDPP-HD, PDPP-C16, and PDPP-EH under strain (degrees of strain noted in legend). At top, direction UV-vis taken relative to strain.

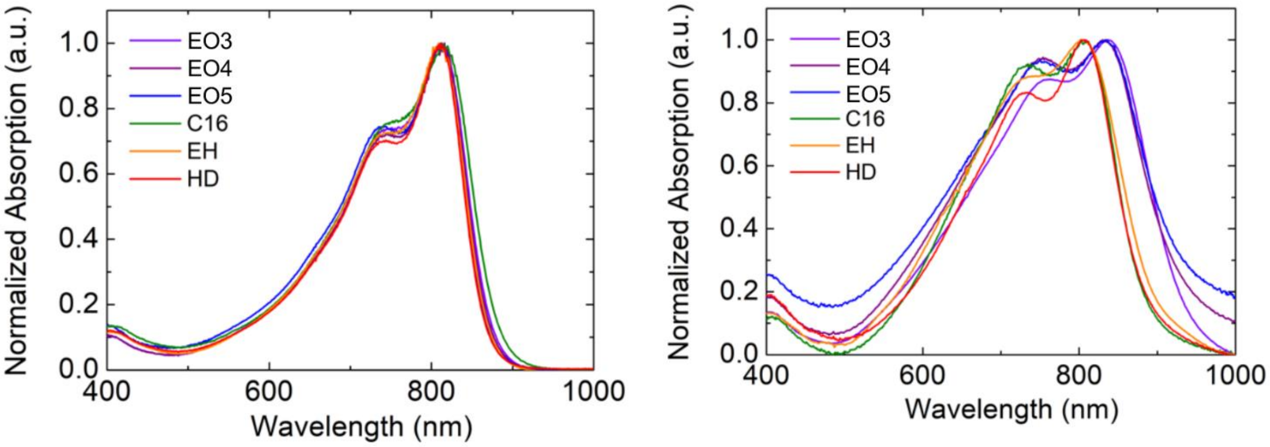

Figure S3. UV-vis spectra of PDPP polymers in chloroform (left) and in spin-coated film (right).

Spectroscopic characterization of the monomers and polymers

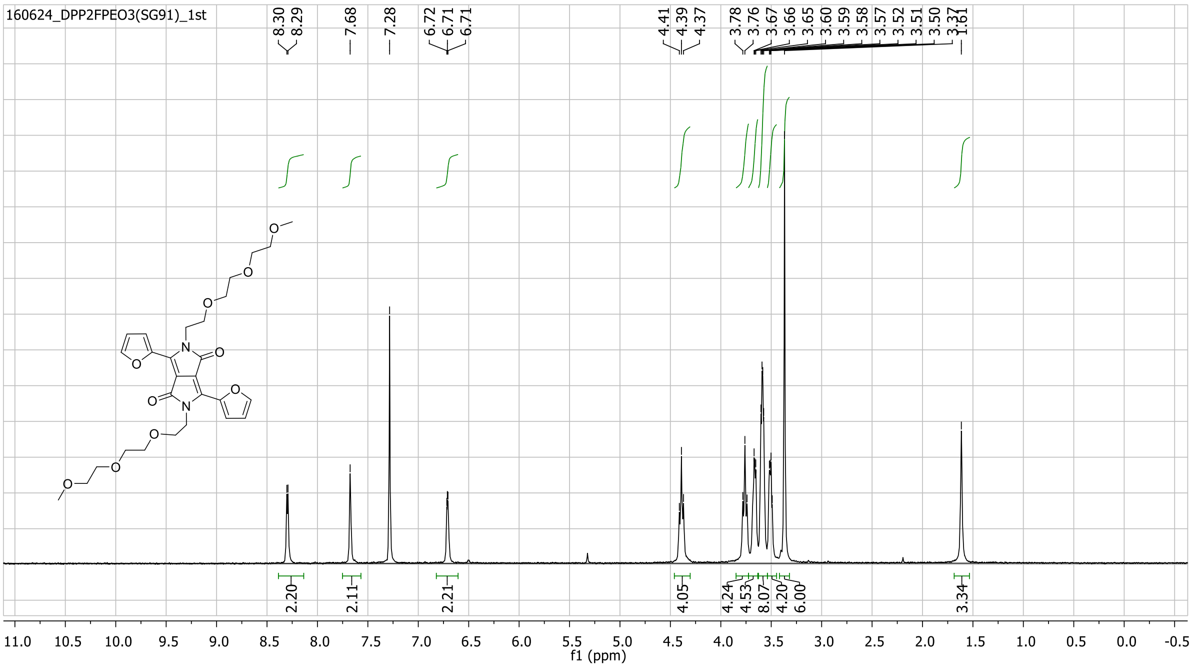

Figure S4. ^{1}H NMR spectrum of compound 3-EO3

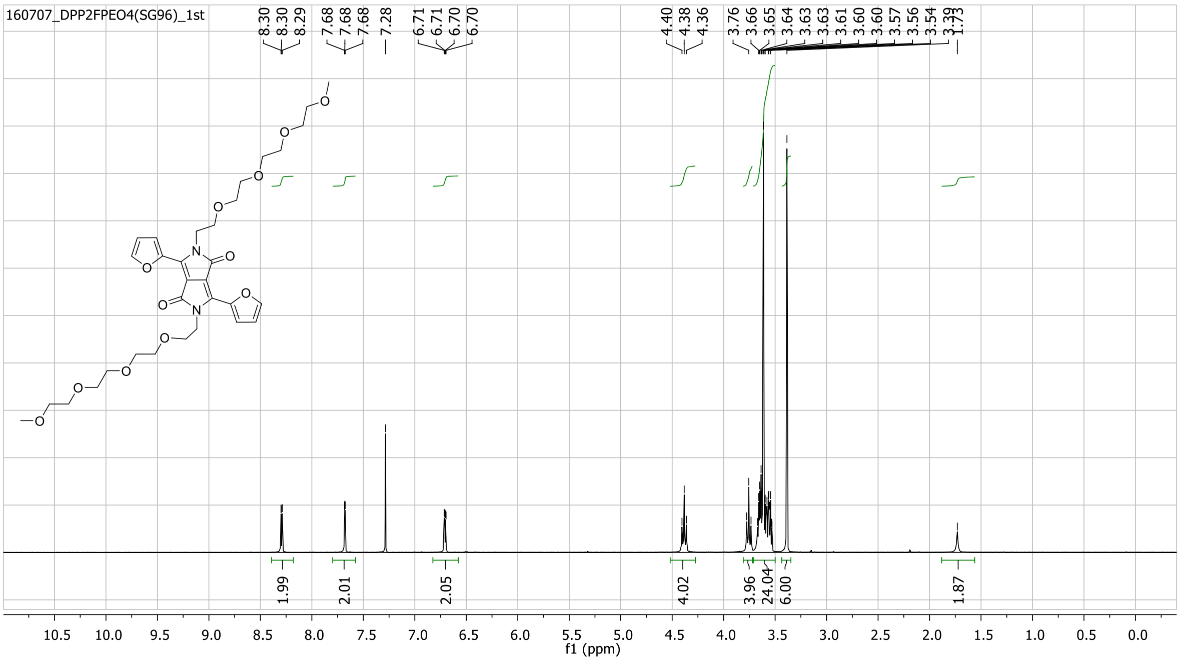

Figure S5. ^{1}H NMR spectrum of compound 3-EO4

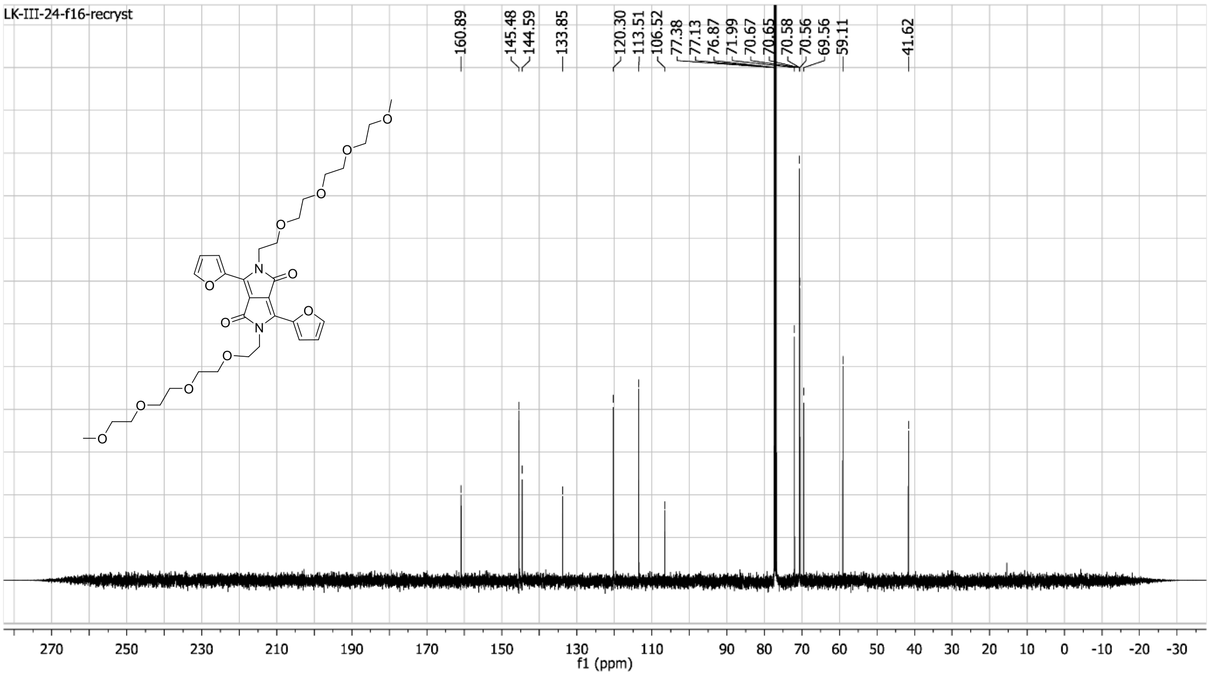

Figure S6. ^{13}C NMR spectrum of compound 3-EO4

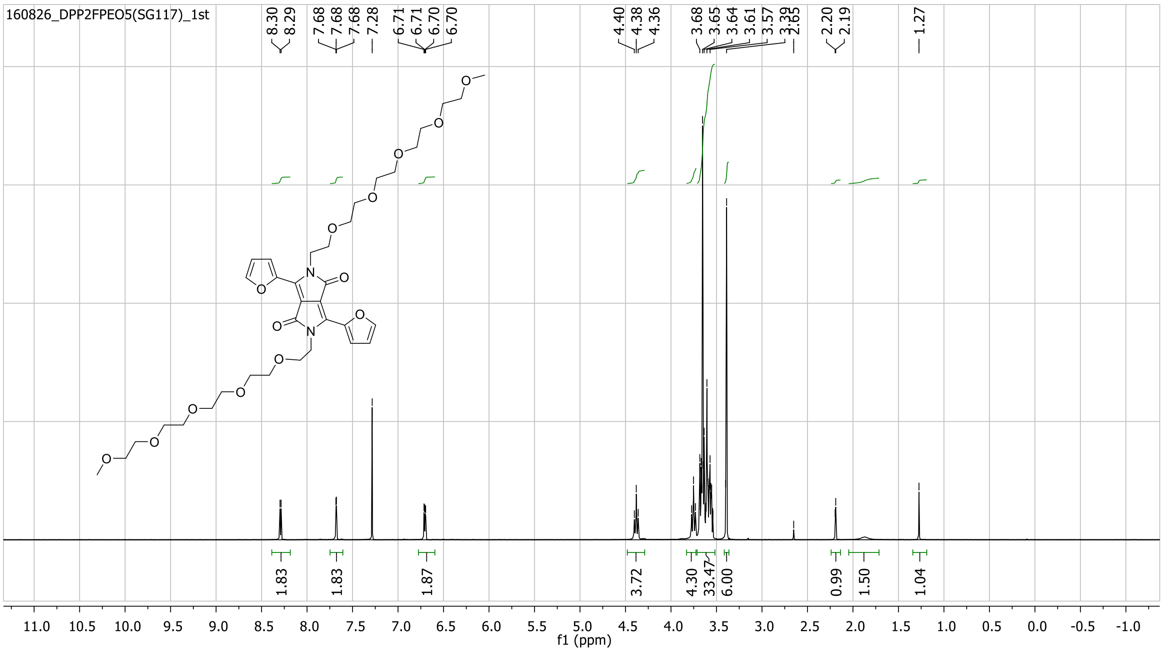

Figure S7. ^{1}H NMR spectrum of compound 3-EO5

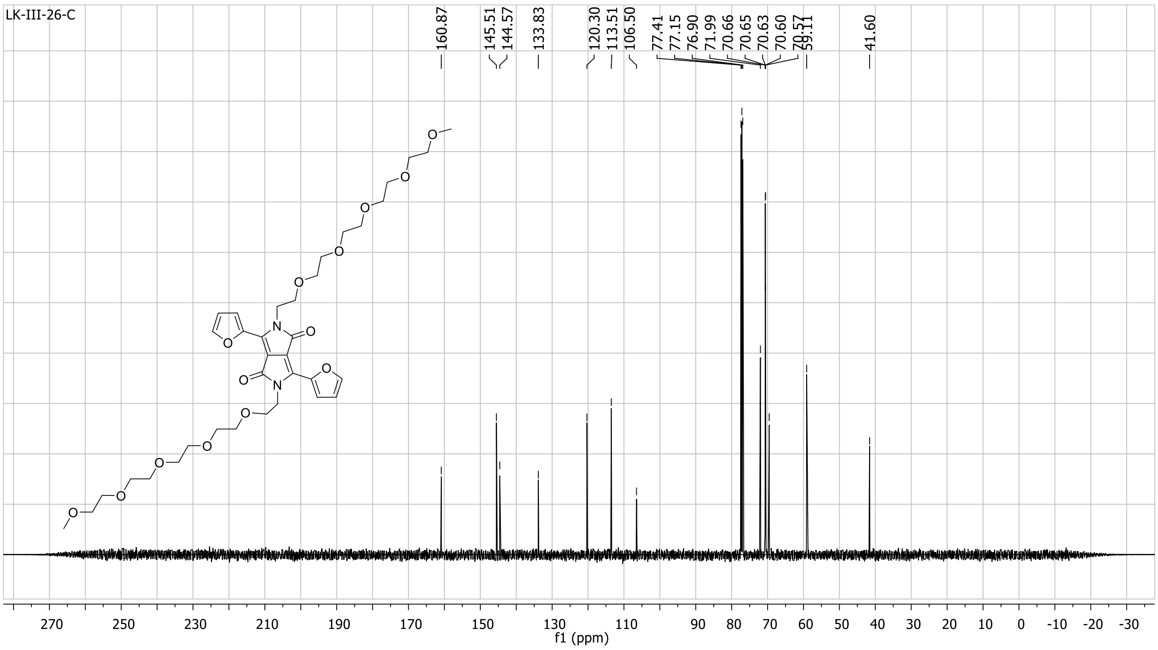

Figure S8. ^{13}C NMR spectrum of compound 3-EO5

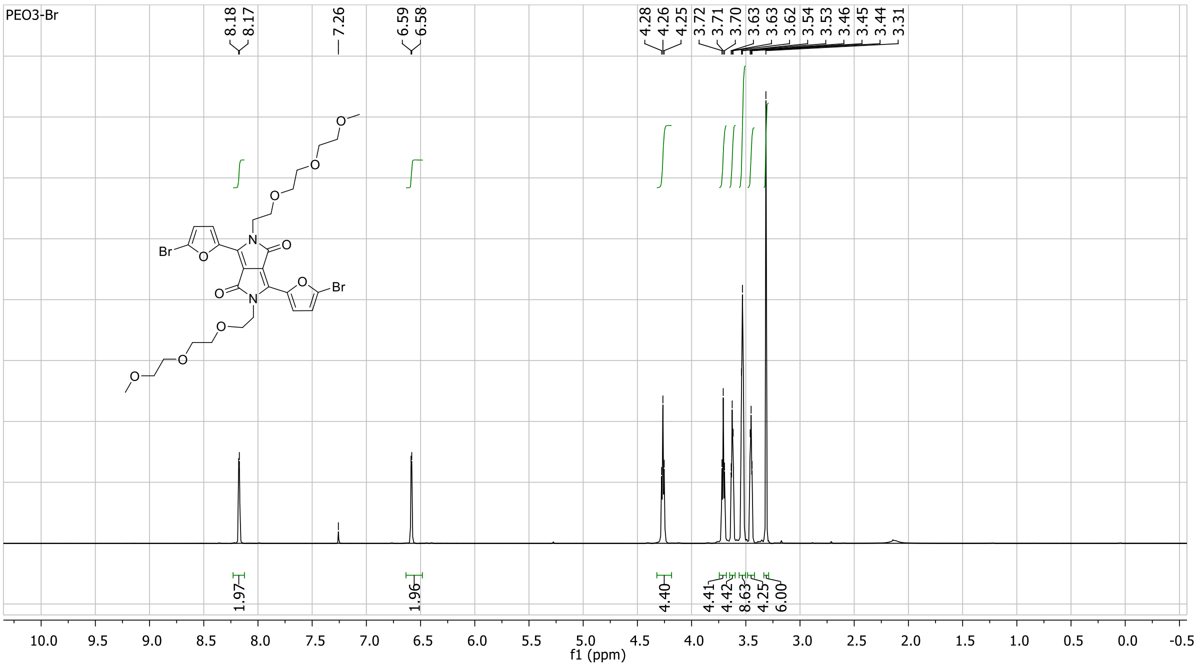

Figure S9. ^{1}H NMR spectrum of compound 4-EO3

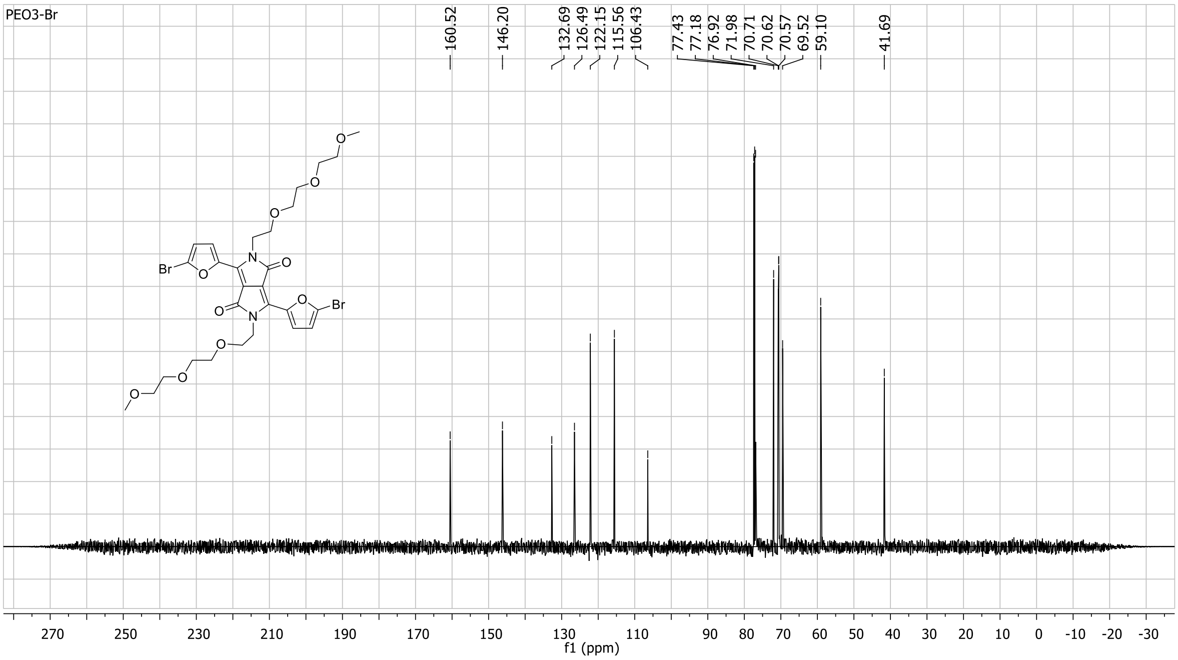

Figure S10. ^{13}C NMR spectrum of compound 4-EO3

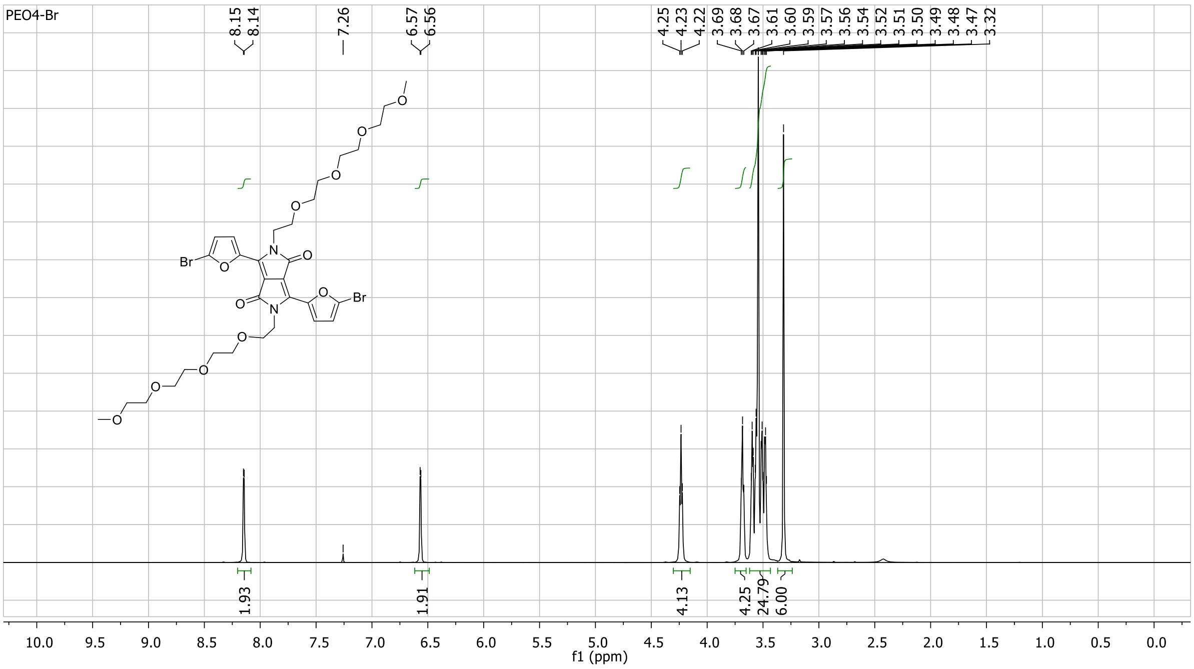

Figure S11. ^{1}H NMR spectrum of compound 4-EO4

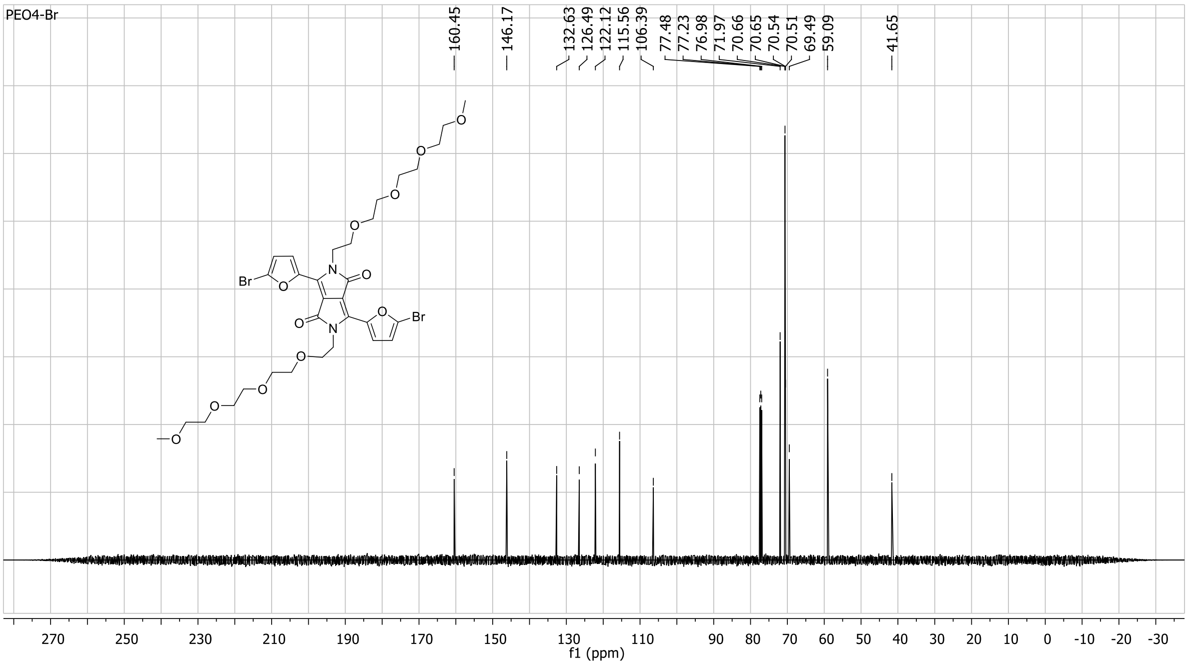

Figure S12. ^{13}C NMR spectrum of compound 4-EO4

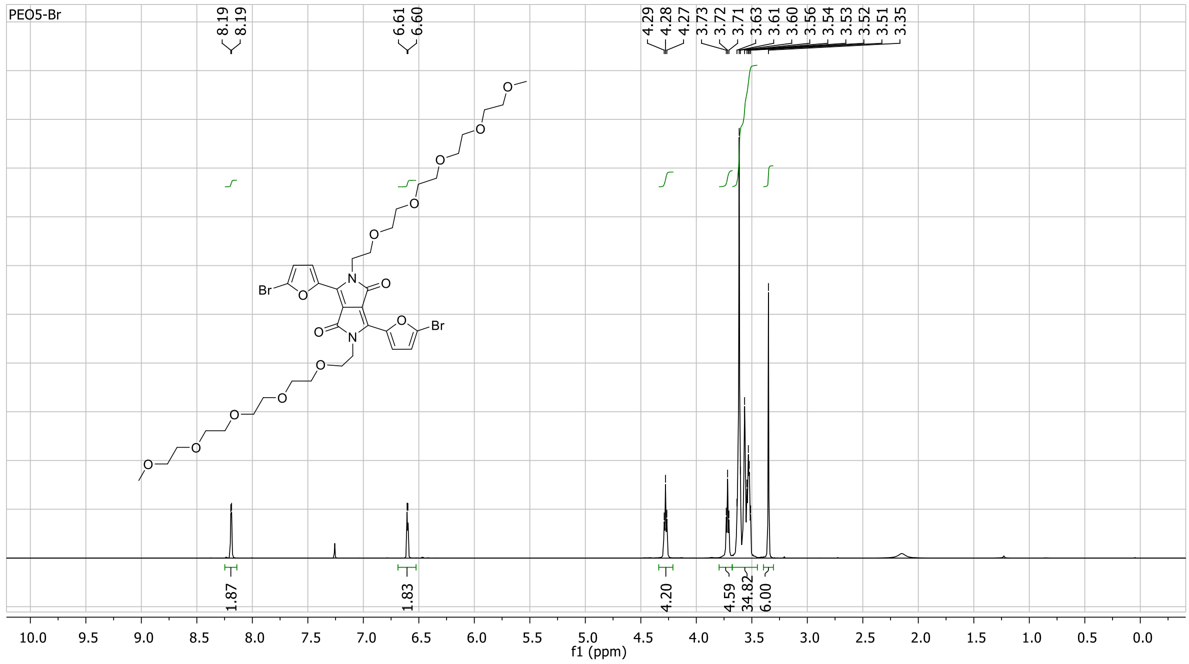

Figure S13. ^{1}H NMR spectrum of compound 4-EO5

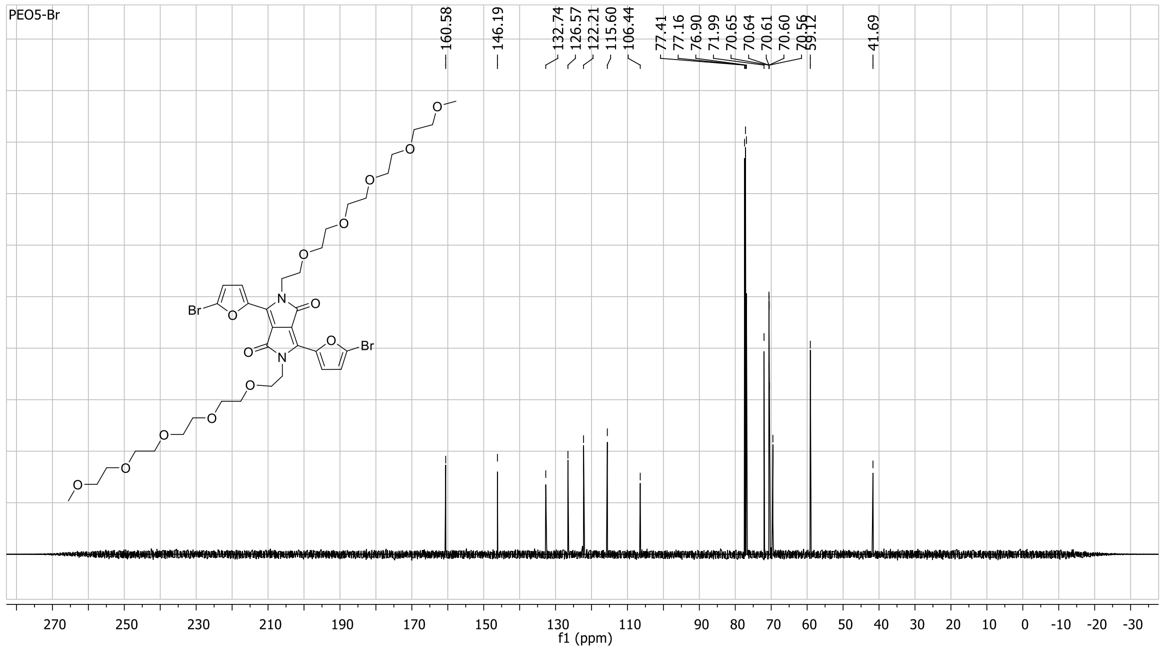

Figure S14. ^{13}C NMR spectrum of compound 4-EO5

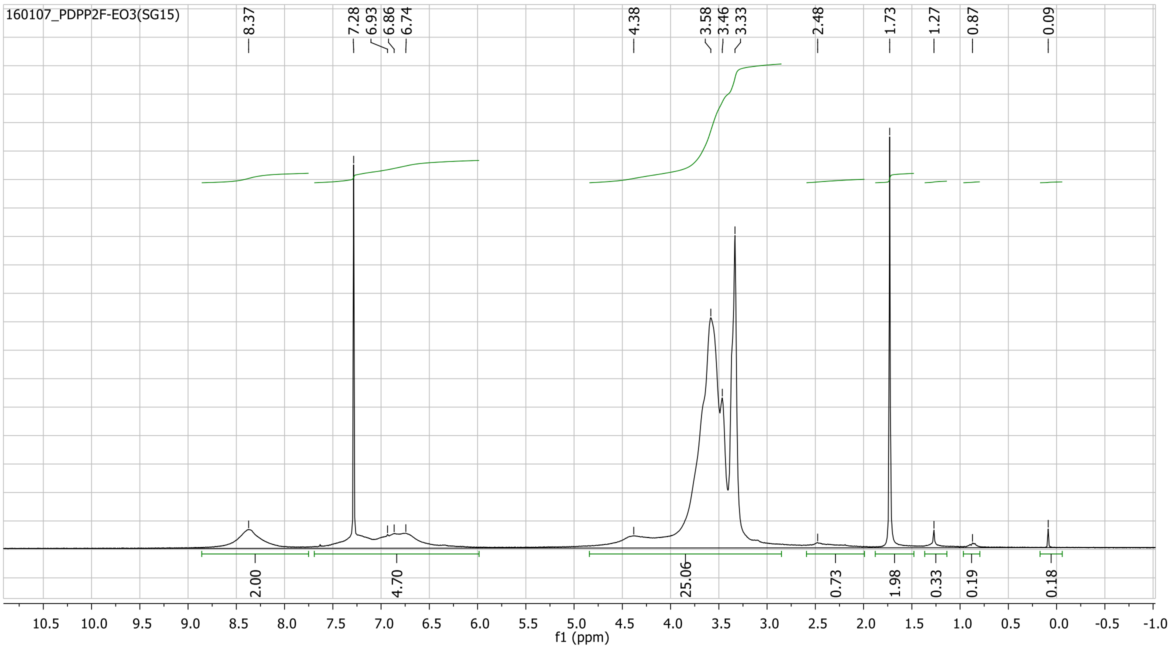

Figure S15. ^{1}H NMR spectrum of polymer PDPP2FT-EO3 (6-EO3)

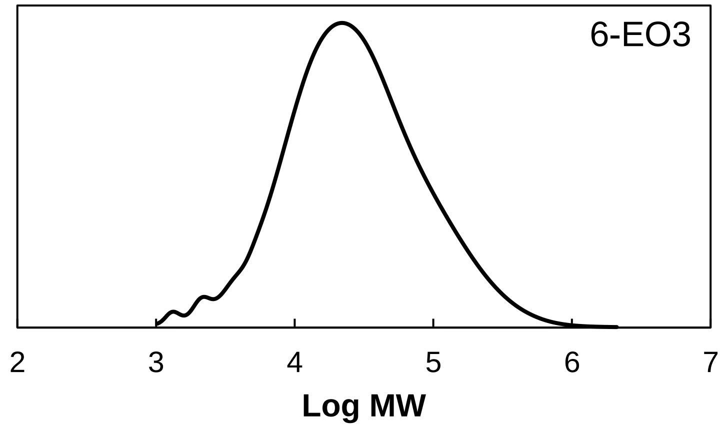

Figure S16. GPC trace of 6-EO3

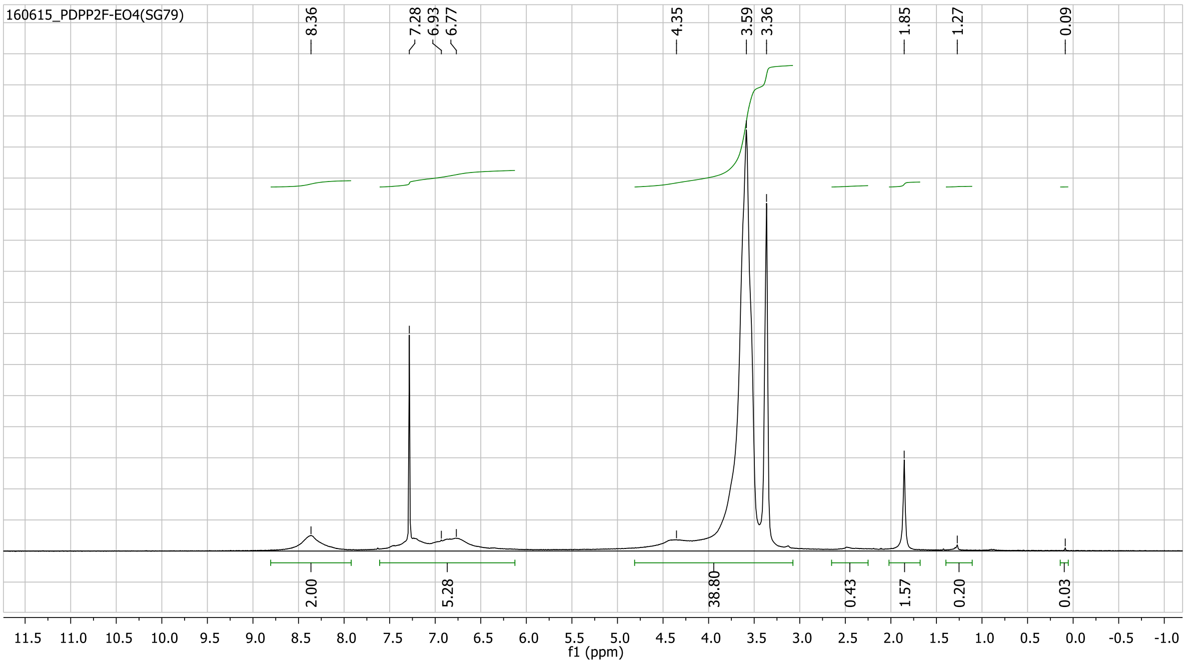

Figure S17. ^{1}**H NMR spectrum of polymer PDPP2FT-EO4 (6-EO4)**

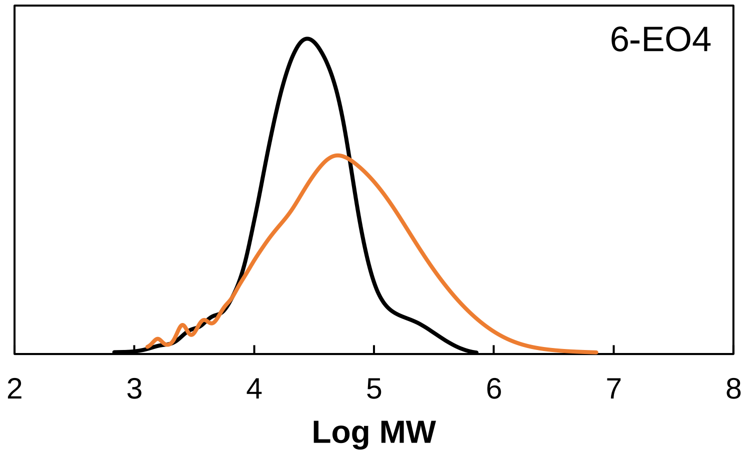

Figure S18. GPC traces of 6-EO4 used for mechanical testing (black) and electronic testing (orange).

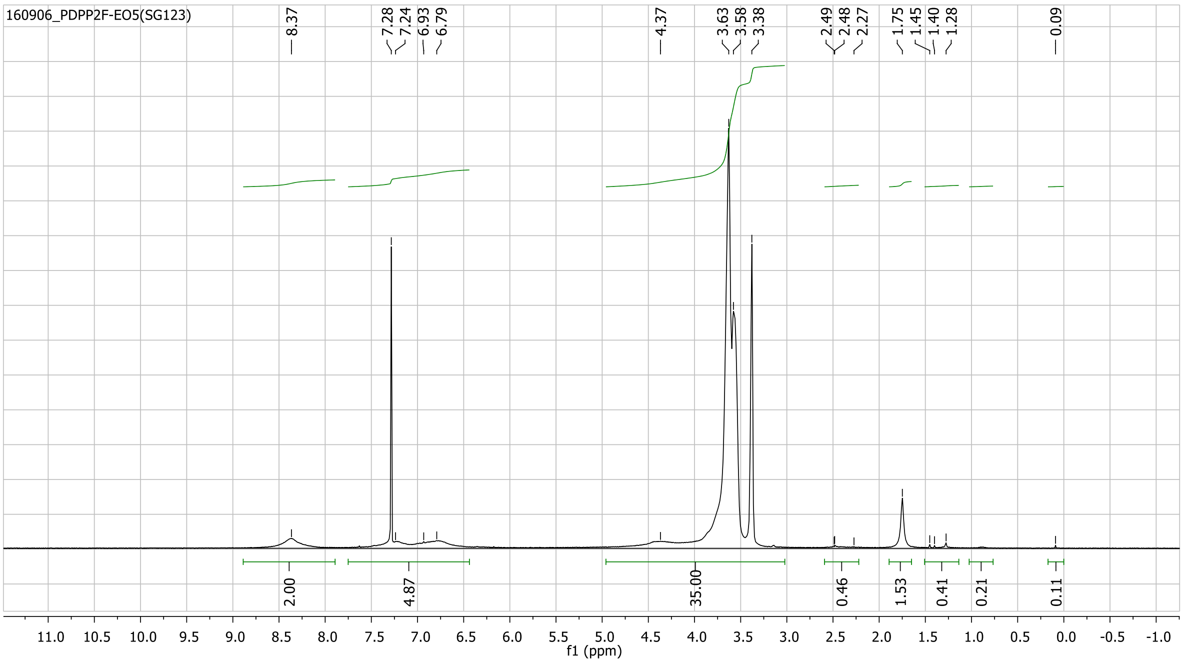

Figure S19. ^{1}**H NMR spectrum of polymer PDPP2FT-EO5 (6-EO5)**

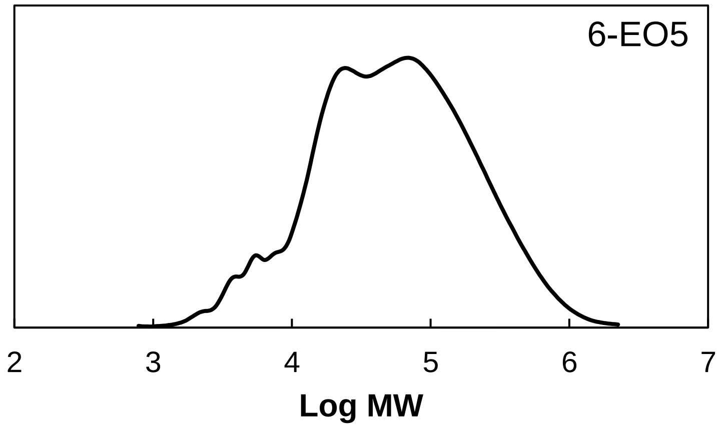

Figure S20. GPC trace of 6-EO5

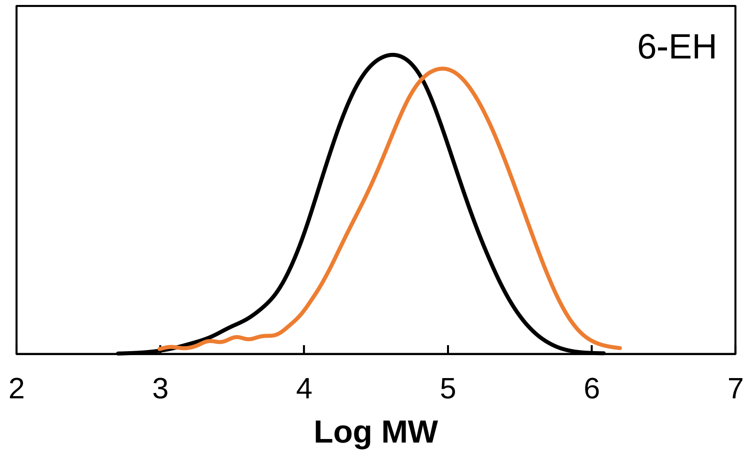

Figure S21. GPC traces of 6-EH polymers used for the mechanical testing (black) and electronic testing (orange)

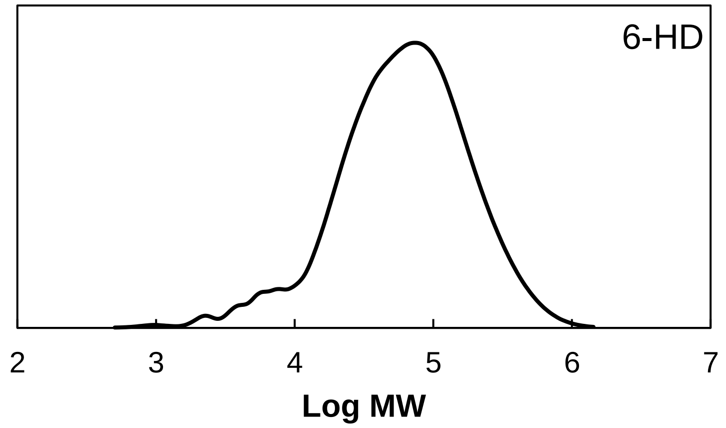

Figure S22. GPC trace of 6-HD

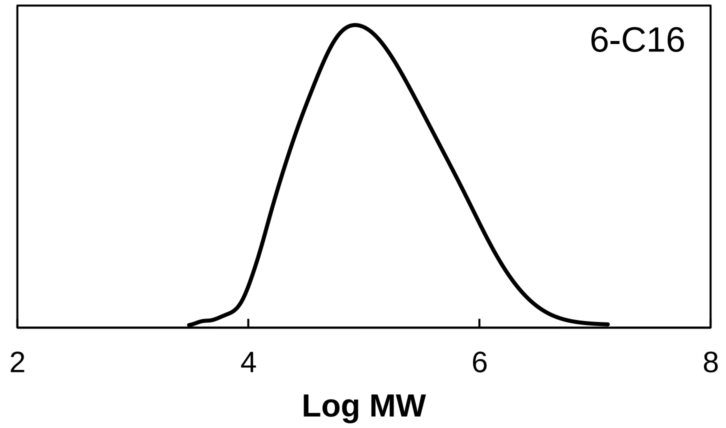

Figure S23. GPC trace of 6-C16

References

1. A. T. Yiu, P. M. Beaujuge, O. P. Lee, C. H. Woo, M. F. Toney, J. M. J. Fréchet *J. Am. Chem. Soc.* **2012**, *134*, 2180-2185.
2. C. Gentilini, M. Boccalon, L. Pasquato, *Eur. J. Org. Chem.* **2008**, *2008*, 3308–3313.
3. C. J. Martin, A. T. L. Lee, R. W. Adams, D. A. Leigh, *J. Am. Chem. Soc.* **2017**, 11998-12002.