Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Molecular Strategy Towards ROMP-Derived Hyperbranched Poly(Olefin)s Featuring Various π-Bridged Perylene Diimides

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Experimental Section

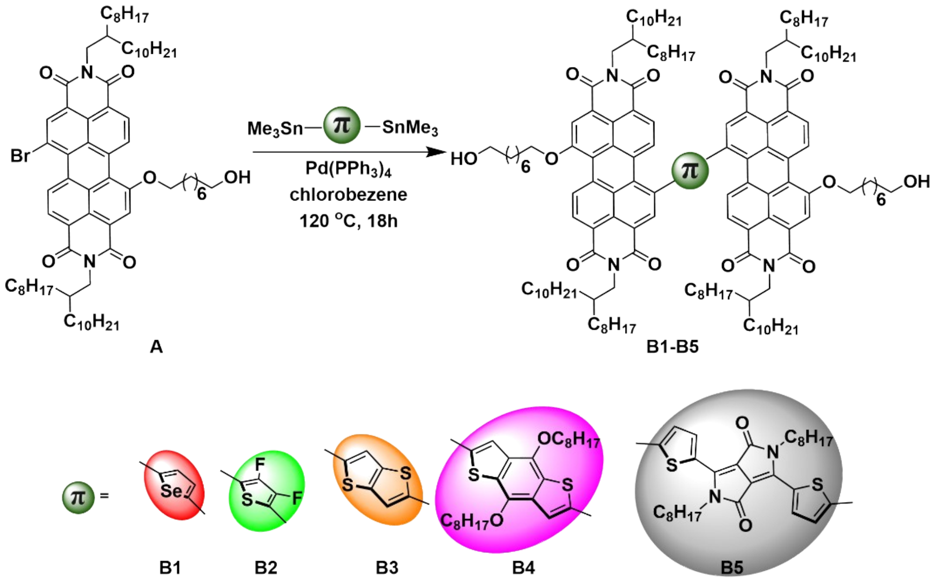
General Remarks

All manipulations were performed in oven- or flame-dried glassware and teflon coated stir bars under an argon atmosphere using standard Schlenk techniques or in a glovebox unless specified otherwise. Solvents were dried according to the reported methods,[1] particularly deuterated solvent was distilled from appropriate drying agents and stored over molecular sieves (4Å) under argon. All starting materials were purchased from Sigma-Aldrich or Alfa Assar and were used without further purification. Synthesized products were purified using flash chromatography on silica gel (pore size 60Å, particle size 230-400 mesh) received from Sigma Aldrich. Celite (Supleco R566) was used for filtration. Reactions were controlled with TLC on Merck Silica Gel 60Å F-254 precoated plates (0.25 mm thickness), and components were visualized under ultraviolet light (254 and 365 nm).

NMR spectra were recorded on a Bruker Avance II 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{19}F: 376 MHz) and Bruker Avance II 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometers using $CDCl_3$ as indicated solvent and are listed in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard for ^{1}H and ^{13}C NMR. Number-average molecular weight (M_n) and polydispersity index ($Đ$) values of the polymer samples were determined by size-exclusion chromatography (SEC). Analyses were performed on an Agilent Technologies 1200 series system composed of GPC equipped with a set of PL mixed B columns in series using chlorobenzene as an eluent at a flow rate of 1.0 mL min^{-1} at 85 °C. The column system was calibrated with polystyrene standards. Prior to injection, samples were diluted to a concentration of 5 mg mL^{-1} and filtered through 0.22 μm PTFE syringe filters. Thermal properties of the polymers were analyzed using PerkinElmer Jade DSC Differential Scanning Calorimeter at a heating rate of 5 °C/min.

UV-Vis spectra were recorded on a PerkinElmer Lambda 1050 UV-Vis spectrometer. The spectral baseline was corrected using Cary Win UV software. Fluorescence emission spectra were recorded on a SCINCO FS-2 spectrofluorometer. IR spectra were recorded on PerkinElmer Spectrum One FT-IR spectrometer using ATR technology and the mass spectra were recorded on Triple Quad LC/MS 6420 (Agilent Technologies) spectrometer. A Bruker Dimension Icon Atomic Force Microscopy (AFM) with Nanoscope V controller was used to collect height and phase images of the samples. The images were collected at 2×2 μm area using the tapping method and a Bruker Tespa V2 probe. The scan rate was 0.8 Hz, and the amplitude setpoint was 11.8 nm. Cyclic voltammetry (CV) measurements of polymer films were performed under argon atmosphere using a CHI760E Voltammetry analyzer with 0.1 M *t*-butylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium (Fc/Fc^+) was used as the internal reference for all measurements. The scanning rate was 100 mV/s. Polymer films were drop-casted from chloroform solutions on a platinum (Pt) working electrode (2 mm in diameter). The estimation of metal contamination in the polymers were analyzed using Thermo Fisher Apreo S Field Emission Scanning Electron Microscope (SEM) with UltraDry Energy-Dispersive X-ray Spectroscopy (EDS) detector and Pathfinder microanalysis software.

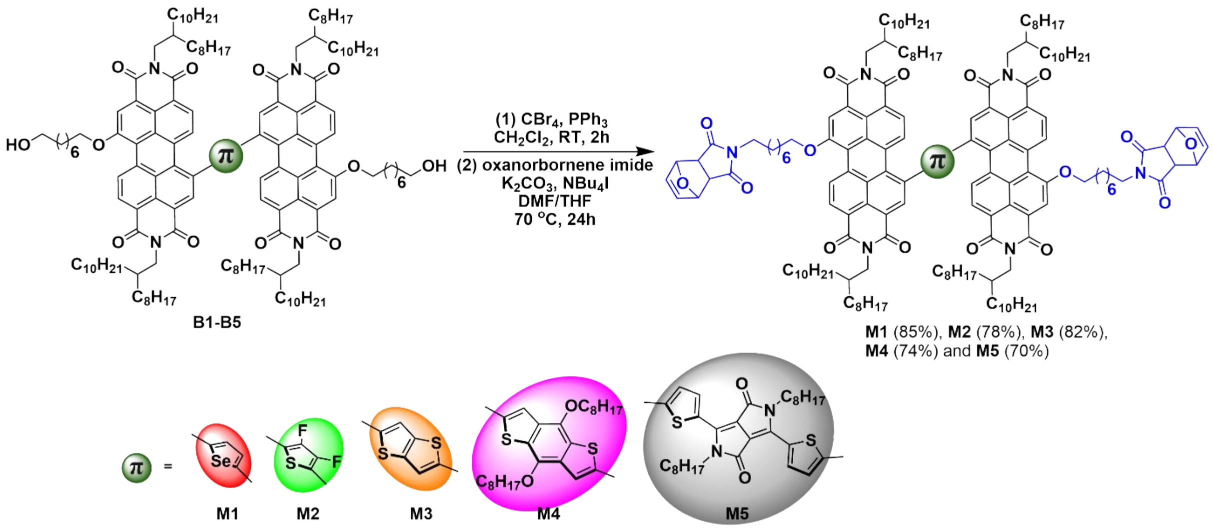
General Procedure A: Stille Coupling Reaction



Scheme S1. Synthesis of PDI-diol **B1-B5.**

An oven dried microwave vial was charged with the desired bis-stannylated monomer (0.1 mmol), $Pd(PPh_3)_4$ (0.01 mmol) and perylene diimide bromo octanol (PDI(Br)octanol) **A** (0.25 mmol). PDI(Br)octanol was prepared according to our previously reported procedure.[2] The vail containing reaction mixture was purged with argon and added dry chlorobenzene (2 mL) followed by additional 3 cycles of argon purging. Reaction solution was heated at 120 ^{o}C for 18 hours. The deep violet solution was transferred to a silica column and purified with a gradient of *n*-hexane/DCM (1:1) to remove unreacted PDI(Br)octanol, and 0-5% of EtOAc/DCM eluents was used to isolate the desired products as dark violet waxy solids.

General Procedure B: Synthesis of Oxanorbornene Imide Monomers (M1-M5)



Scheme S2. Synthesis of PDI-based oxanorbornene imide monomers **M1**-**M5**.

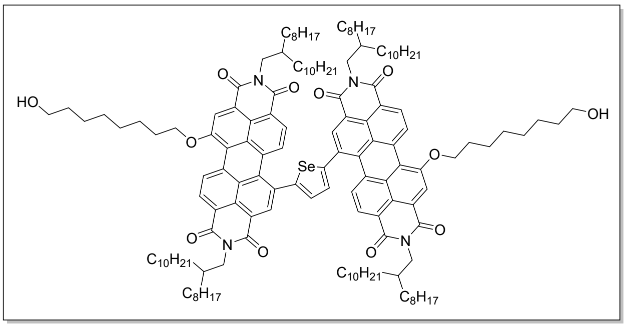
Stage 1

As presented in **Scheme S2**, PDI-diols **B1-B5** (0.1 mmol) were dissolved in dry DCM (3 mL), degassed and slowly argon was bubbled through the solution. PPh_3 (0.25 mmol) was added in one portion followed by addition of CBr_4 (0.25 mmol) portion wise over 10 minutes. After 2 h completion of the reactions was confirmed using TLC. The solvent was removed in vacuo under reduced pressure and the dark residue was washed thoroughly with EtOH and acetone, then dried in high vacuum. ^1H NMR analysis confirmed the formation of the precursor and the obtained material was used for the next step without further purification.

Stage 2

Oven-dried round-bottom flask was charged with material obtained from **Stage 1**, K_2CO_3 (2 mmol), NBu_4I (0.01 mmol), and oxanorbornene imide (1 mmol) under argon atmosphere. A mixture of dry THF (6 mL) and DMF (2 mL) was added to the reaction mixture and was heated at 70 °C up to 24-36 hours depending on the completion of the reaction. After cooling, the crude reaction mixture was quenched with water (100 mL), and precipitates were washed with EtOH and dried in vacuum under reduced pressure. The obtained material was purified using column chromatography with 0-10% of EtOAc/DCM as eluent, and the desired products **M1**-**M5** were isolated as waxy dark violet solids in 70-85% yields.

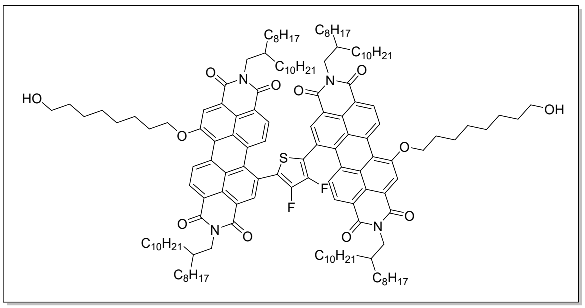
Synthesis of PDI-Diol (B1)



Compound **B1** was synthesized according to the general procedure described above and this compound was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.42 (br. d, J = 8.8 Hz, 2H), 8.37-8.81 (m, 10H), 7.47-7.70 (m, 2H), 4.51 (br. s, 4H), 4.07 (br. s, 8H), 3.69 (t, J = 6.5 Hz, 4H), 2.06-2.13 (m, 4H), 1.95 (br. s, 4H). 1.61-1.69 (m, 16H), 1.16-1.54 (m, 134H), 0.79-0.85 (m, 24H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 163.9, 163.5, 157.5, 153.6, 135.1, 134.4, 133.7, 133.4, 132.9, 132.1, 131.3, 131.1, 129.4, 128.7, 128.3, 127.8, 127.2, 124.0, 123.5, 122.5, 121.4, 121.2, 120.3, 118.0, 70.6, 62.9, 44.8, 44.7, 36.6, 22.6-32.7 (multiple aliphatic carbons), 14.08, 14.06.

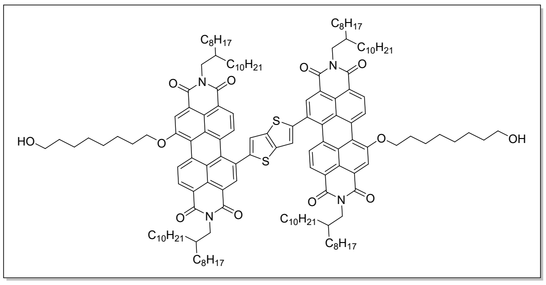
Synthesis of PDI-Diol (B2)



Compound **B2** was synthesized according to the general procedure described above and this compound was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.47 (d, J = 8.4 Hz, 2H), 8.22-8.81 (m, 10H), 4.53 (br. s, 4H), 4.08 (br. s, 8H), 3.69 (t, J = 6.5 Hz, 4H), 2.16 – 2.04 (m, 4H), 1.97 (br. s, 4H), 1.08-1.83 (m, 150H), 0.79-0.85 (m 24H); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): δ 163.7, 163.48, 163.4, 163.3, 157.9, 135.0, 134.6, 133.1, 132.0, 129.1, 128.7, 128.4, 128.2, 127.8, 125.1, 124.3, 123.6, 123.0, 122.1, 121.3, 120.1, 118.3, 70.7, 62.9, 44.8, 44.7, 36.65, 36.61, 22.6-32.7 (multiple aliphatic carbons) 14.1, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ -131.21.

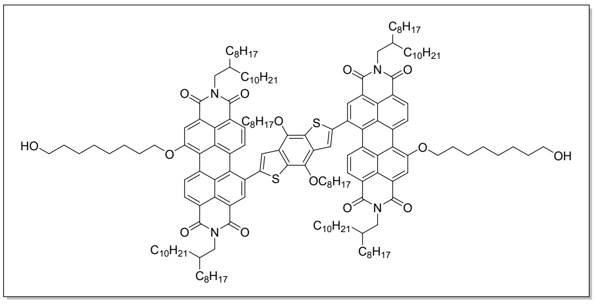
Synthesis of PDI-Diol (B3)



Compound **B3** was synthesized according to the general procedure described above and this compound was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): *δ* 9.38 (d, *J* = 8.2 Hz, 2H), 8,53-8.68 (m, 4H), 8.30, (br. s, 4H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 2H), 4,45 (br. s, 4H), 3.96-4.17 (m, 8H), 2.03-2.13 (m, 4H), 1.88-2.02 (m, 4H), 1.84 (br. s, 2H), 1.59-170 (m, 8H), 1.09-1.58 (m, 144H), 0.74-0.88 (m, 24H); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): *δ* 163.8, 163.4, 163.3, 157.4, 147.3, 141.1, 135.6, 134.4, 133.6, 132.8, 131.7, 131.2, 130.4, 129.3, 128.6, 128.1, 127.9, 127.6, 123.9, 123.3, 122.2, 121.6, 121.3, 120.1, 119.7, 117.7, 70.6, 62.9, 44.7, 36.64, 36.57, 22.6-32.7 (multiple aliphatic carbons), 14.08, 14.06.

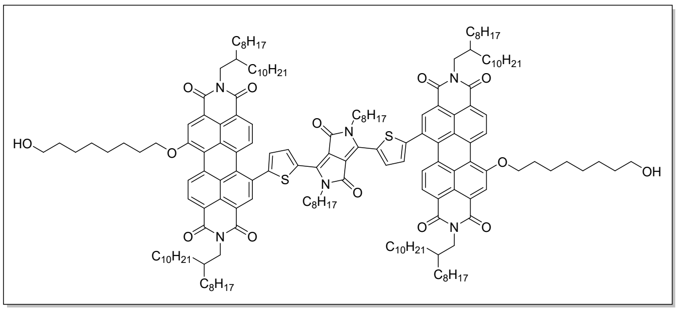
Synthesis of PDI-Diol (B4)



Compound **B4** was synthesized according to the general procedure described above and this compound was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): *δ* 9.50 (br. d, *J* = 8.3 Hz, 2H), 8.04-8.84 (m, 10H), 7.76 (s, 2H), 7.76 (s, 2H), 4.51 (br. s, 4H), 4.27 (t, *J* = 6.4 Hz, 4H), 4.18 (d, *J* = 7.3 Hz, 4H), 4.08 (d, *J* = 7.2 Hz, 4H), 3.69 (q, *J* = 6.2 Hz, 4H), 1.87-2.17 (m, 8H), 0.93-1.86 (m, 172H), 0.76-0.91 (m, 24H), 0.68-0.76 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): *δ* 164.0, 163.8, 163.6, 163.4, 157.6, 145.1, 135.6, 134.6, 134.0, 132.8, 131.9, 130.9, 130.7, 129.3, 128.7, 128.2, 127.6, 124.1, 123.4, 122.4, 121.7, 121.3, 120.4, 117.8, 116.8, 74.3, 70.7, 62.9, 44.8, 36.7, 36.6, 22.58-32.7 (multiple aliphatic carbons), 14.1, 14.0.

Synthesis of PDI-Diol (B5)

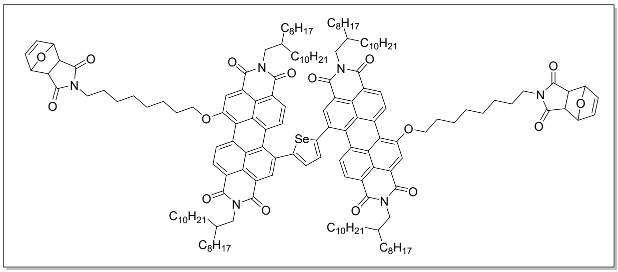


Compound **B5** was synthesized according to the general procedure described above and this compound was used for the next step without further purification.

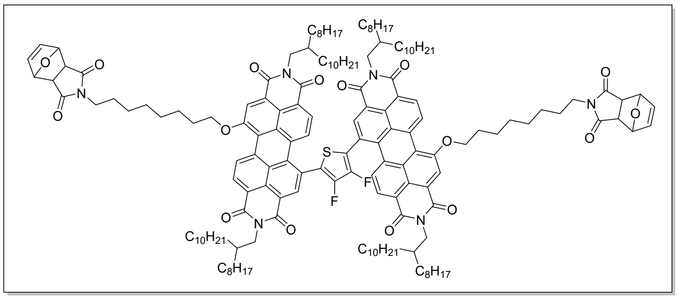
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.43 (br. d, $J = 8.4$ Hz, 2H), 9.11 (br. s, 2H), 8.64 (br. s, 2H), 8.55 (br. s, 2H), 8.35 (br. s, 2H), 8.17 (br. s, 4H), 7.45 (br. s, 2H), 4.49 (br. s, 4H), 4.09 (br. s, 8H), 4.00 (br. s, 4H), 3.70 (t, $J = 6.5$ Hz, 4H), 2.11 (br. s, 4H), 1.96 (br. s, 4H), 159-1.80 (m, 18H), 1.9-1.58 (m, 154H), 0.75-0.90 (m, 32H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 163.7, 163.4, 161.1, 157.6, 149.7, 139.2, 137.3, 135.0, 134.4, 134.0, 132.6, 131.6, 130.4, 129.3, 128.6, 128.2, 128.0, 127.5, 124.1, 123.4, 122.4, 121.6, 121.2, 120.1, 117.8, 108.7, 70.7, 62.9, 44.8, 42.3, 36.7, 36.6, 32.7-22.5 (multiple aliphatic carbons), 14.07, 14.03.

Synthesis of M1

This compound was synthesized according to the general procedure described above and the pure compound as isolated as waxy violet solid in 85% yield.



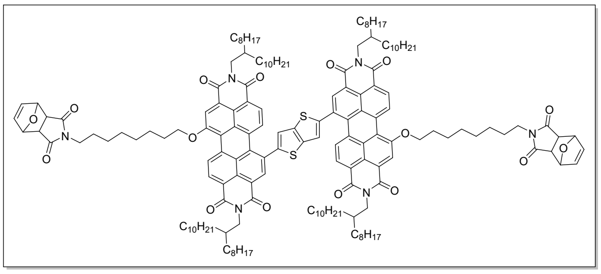
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.38 (br. s, 2H), 8.33-8.79 (m, 10H), 6.50 (s, 4H), 5.26 (s, 4H), 4.48 (br. s, 4H), 4.02 (br. s, 8H), 3.49 (t, $J = 7.3$ Hz, 4H), 2.84 (s, 4H), 2.10 (br. s, 4H), 1.92 (br. s, 4H), 1.58-1.66 (m, 8H), 0.91-1.49 (m, 142H), 0.78-0.83 (m, 24H); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): δ 176.2, 163.6, 163.3, 157.4, 153.6, 136.5, 134.9, 134.2, 133.6, 133.3, 131.10, 129.3, 128.5, 128.2, 127.7, 127.1, 123.9, 123.3, 122.4, 121.2, 120.1, 117.8, 80.9, 70.6, 47.4, 44.6, 38.8, 36.6, 22.6-31.9 (multiple aliphatic carbons), 14.05, 14.03; UV-Vis (chloroform): 398, 503 (sh), and 562 nm; Emission (chloroform): 640, 5534 (sh) nm; IR (ATR mode): 2924 (s), 2853 (m), 1701 (s), 1659 (s) cm^{-1}.



Synthesis of M2

This compound was synthesized according to the general procedure described above and the pure compound as isolated as waxy violet solid in 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.48 (d, J = 8.5 Hz, 2H), 8.70 (br. s, 4H), 8.38-8.53 (m, 6H), 6.50 (s, 4H), 5.26 (s, 4H), 4.52 (br. s , 4H), 4.09 (br. s, 8H), 3.49 (t, J = 7.2 Hz, 4H), 2.84 (s, 4H), 1.95-2.13 (m, 10H), 1.54-1.72 (m, 14H), 1.14-1.57 (m, 132H), 0.79-0.85 (m, 24H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 176.3, 163.7, 163.6, 163.5, 157.9, 136.5, 135.1, 134.7, 133.3, 132.1, 129.3, 128.8, 128.5, 128.3, 127.8, 125.2, 124.4, 123.7, 123.1, 122.3, 121.4, 120.3, 118.4, 80.9, 70.7, 47.4, 44.9, 38.9, 36.7, 22.6-31.9 (multiple aliphatic carbons) 14.07, 14.06; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ -131.28; UV-Vis (chloroform): 398, 571, and 543 nm; Emission (chloroform): 625, 563 (sh) nm; IR (ATR mode): 2924 (s), 2853 (m), 1702 (s), 1659 (s) cm^{-1}.

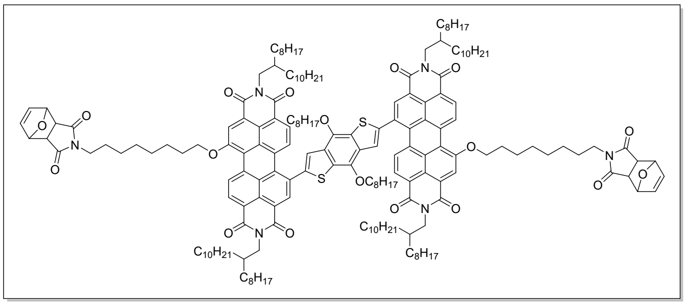


Synthesis of M3

This compound was synthesized according to the general procedure described above and the pure compound as isolated as waxy violet solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.48 (d, J = 8.4 Hz, 2H), 8.76 (s, 2H), 8.67 (d, J = 8.4 Hz, 2H), 8.23-8.45 (m, 6H), 7.51 (s, 2H), 6.51 (s, 4H), 5.27 (s, 4H), 4.50 (t, J = 6.6 Hz, 4H), 4.15 (d, J = 7.0 Hz, 4H), 4.09 (d, J = 7.1 Hz, 4H), 3.49 (t, J = 7.3 Hz, 4H), 2.84 (s, 4H), 1.91-2.14 (m, 8H), 1.14-1.55 (m, 148H), 0.80-0.86 (m, 24H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 176.3, 163.9, 163.7, 157.6, 147.4, 141.1, 136.5, 135.7, 134.7, 133.9, 133.2, 131.9, 131.5, 130.6, 129.6, 128.9, 128.1, 128.3, 127.8, 124.1, 123.6, 122.3, 121.9, 121.5, 120.6, 119.7, 118.2, 80.9, 70.6, 47.4, 44.8, 44.7, 38.9, 36.7, 36.6, 22.6-31.9 (multiple aliphatic carbons), 14.09, 14.08; UV-Vis (chloroform): 384, 573 and 489 nm; Emission (chloroform): 694, 535 (sh) nm; IR (ATR mode): 2923 (s), 2853 (m), 1702 (s), 1659 (s) cm^{-1}.

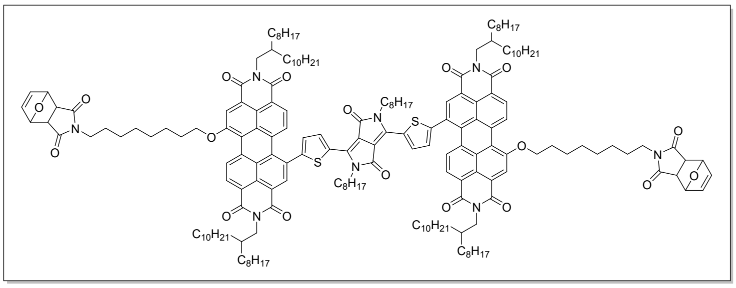
Synthesis of M4



This compound was synthesized according to the general procedure described above and the pure compound as isolated as waxy violet solid in 74% yield.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): *δ* 9.49 (d, *J* = 8.4 Hz, 2H), 8.05-8.87 (m, 10H), 7.76 (s, 2H), 6.51 (s, 4H), 5.27 (s, 4H), 4.50 (br. s, 4H), 4.26 (t, *J* = 6.5 Hz, 4H), 4.18 (d, *J* = 7.1 Hz, 4H), 4.08 (d, *J* = 7.1 Hz, 4H), 3.49 (t, *J* = 7.3 Hz, 4H), 2.85 (s, 4H), 1.90-2.15 (m, 8H), 1.70-1.83 (m, 4H), 1.54-1.67 (m, 8H), 0.99-1.53 (m, 160H), 0.77-0.89 (m, 24H), 0.68-0.76 (m, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K) *δ* 176.3, 163.8, 163.7, 163.5, 163.3, 157.5, 145.1, 145.0, 136.5, 135.5, 134.5, 133.9, 133.5, 132.7, 131.8, 131.4, 130.9, 130.6, 129.3, 128.6, 128.1, 127.7, 124.0, 123.4, 122.4, 121.7, 121.3, 120.4, 120.3, 117.8, 80.9, 74.3, 70.6, 47.4, 44.7, 38.8, 36.6, 22.53-31.9 (multiple aliphatic carbons), 14.1, 14.0; UV-Vis (chloroform): 370, 357 nm; Emission (chloroform): 696, 617 (sh) nm; IR (ATR mode): 2924 (s), 2854 (m), 1702 (s), 1659 (s) cm^{-1}

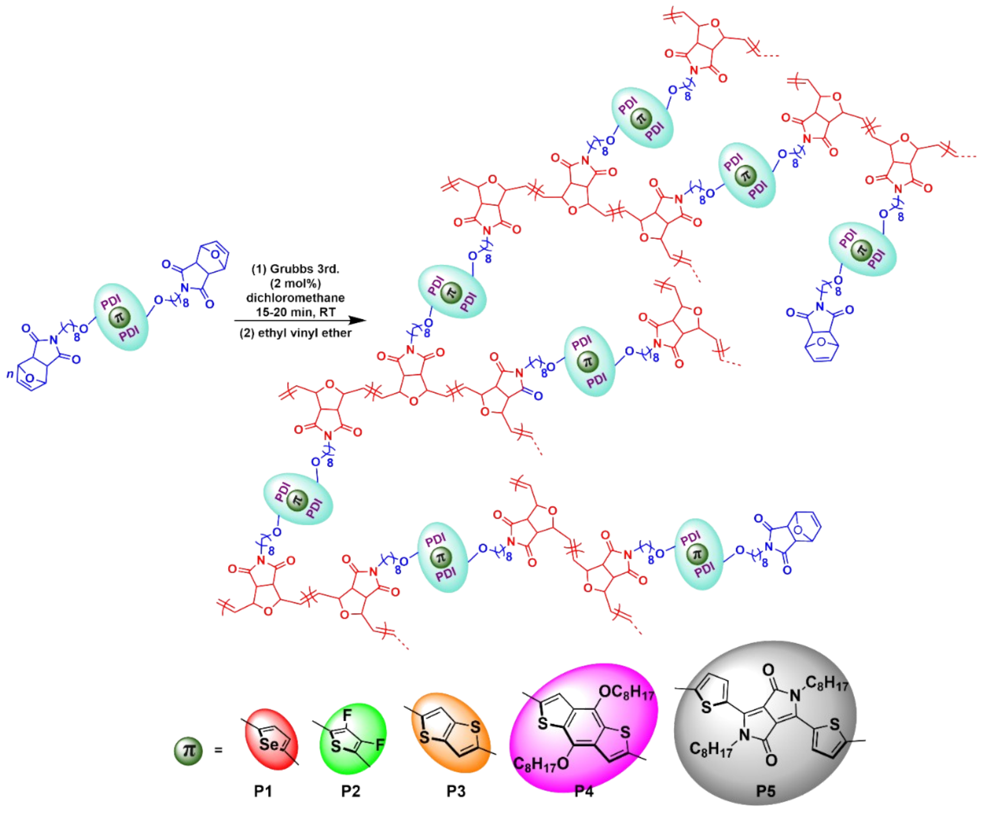
Synthesis of M5



This compound was synthesized according to the general procedure described above and the pure compound as isolated as waxy violet solid in 70% yield.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): *δ* 9.45 (d, *J* = 8.4 Hz, 2H), 9.10 (br. s, 2H), 8.61-8.67 (m, 4H), 8.40, (br. s, 2H), 8.20 (br. s, 4H), 7.45 (br. s, 2H), 6.51 (s, 4H), 5.27 (s, 4H), 4.49 (br. s, 4H), 4.10 (br. s, 8H), 4.00 (br. s, 4H), 3.49 (t, *J* = 7.3 Hz, 4H), 2.84 (s, 4H), 2.09 (br. s, 4H), 1.98 (br. s, 4H), 1.55-1.75 (m, 18H), 1.05-1.50 (m, 152H), 0.75-0.86 m, 32H); **^{13}C NMR** (151 MHz, CDCl$_3$): *δ* 176.3, 163.6, 163.45, 163.36, 161.1, 157.6, 149.8, 139.2, 136.5, 135.0, 134.5, 134.0, 132.7, 131.6, 130.5, 129.4, 128.7, 128.2, 128.1, 127.5, 124.1, 123.5, 122.4, 121.8, 121.4, 120.2, 118.0, 108.7, 80.9, 70.6, 47.4, 44.8, 44.7, 42.3, 38.8, 36.65, 36.60, 22.5 - 31.9 (multiple aliphatic carbons) 14.07, 14.03; UV-Vis (chloroform): 681, 548, and 398 nm; Emission (chloroform): 549, 592 (sh) nm; IR (ATR mode): 2923 (s), 2858 (m), 1698 (s), 1657 (s) cm^{-1}.

General Polymerization Procedure: All polymerizations were carried out in a Glovebox under an argon atmosphere. A solution of Grubbs‘ 3rd generation catalyst (**G3**) (1.2×10^{-3} mmol, 2 mol%) in CH_2Cl_2 (2 mL) was added to monomer **M** (0.020 mmol) in the same solvent (5 mL) and the reaction solution was stirred at RT for 15-20 min depends on the complete consumption of monomer to polymers. Then, ethyl vinyl ether (2 mL) was added to the reaction mixture and stirred for another 20 min. Solvent was removed in vacuum under reduced pressure, then to the concentrated polymer solution, 10 mL of methanol was added dropwise to precipitate the polymer. Solvent was filtered off dissolved the rsesultant material again in the minimum amount of CH_2Cl_2 and polymer reprecipitated methanol. This process was repeated multiple times to remove any traces of residual ruthenium contamination in the polymeric material. After removing the solvents by filtration, resultant material was dried in vacuo yielded dark violet solids. EDS analysis were performed to determine the presence of metal traces in the polymers and no ruthenium contamination was detected except major elemental compositions of the polymeric materials (**Figure S50-S54**).



Scheme S3. Synthesis of PDI-derived hyperbranched-type poymers **P1-P5**.

P1. (mixture of *cis/trans* hyperbranched polymeric structure): Isolated as dark violet solid in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.52-9.54 (brm, 1.3H, ArH), 9.11 (brm, 0.9H, ArH), 8.20-8.72 (brm, 7H, ArH), 7.30-7.42 (brm, 2.79, ArH), 6.51 (brs, 0.11H, =CH of nonpolymerized oxaNB), 5.12-6.79 (brm, 3.75, =CH (mixture of *cis* and *trans* protons)), 4.23 (brm, 4.4H, CH_2), 3.69 (brm, 7.01H, CH_2), 3.40-3.68 (brm, 5.92H, CH_2), 1.20-1.68 (brm, 160H, CH_2), 0.83 (brm, 24H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 177.4 (CO of nonpolymerized oxaNB), 174.6, 162.3 (br), 159.7, 156.4, 148.7, 121.5-133.05 (brm), 107.55, 79.80-81.23 (brm), 72.63, 69.6-70.0 (brm), 51.8-52.3 (brm), 43.7, 37.9, 35.6, 30.8, 30.7, 28.6-29.05 (brs), 28.3 (br), 21.64, 13.08; UV-Vis (chloroform): 545 nm; Emission (chloroform): 701 nm; IR (ATR mode): 2924 (s), 2853 (s), 1695 (s), 1653 (s), 1595, 1329, 905 (s), 727 (s) cm^{-1}; SEC analysis in chlorobenzene as an eluent: M_n = 62.0 kDa, $Đ$ = 1.5.

P2. (mixture of *cis/trans* hyperbranched polymeric structure): Isolated as dark violet solid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.40-9.51 (brm, 1.1H, ArH), 8.41-8.76 (brm, 6.76H, ArH), 7.30-7.42 (brm, 0.68, ArH), 6.51 (brs, 0.12H, =CH of nonpolymerized oxaNB), 5.18-6.78 (brm, 2.1, =CH (mixture of *cis* and *trans* protons)), 4.53 (brm, 4.76H, CH_2), 4.15 (brm, 5.29H, CH_2), 3.42-3.59 (brm, 6.20H, CH_2), 1.19-2.02 (brm, 166H, CH_2), 0.82 (brm, 24H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 177.2 (xx), 174.6, 162.1 (br), 159.7, 156.4, 148.7, 121.5-133.05 (brm), 107.55, 79.80-81.23 (brm), 72.63, 69.6-70.0 (brm), 51.8-52.3 (brm), 43.7, 37.9, 35.6, 30.8, 30.7, 28.6-29.05 (brs), 28.3 (br), 21.64, 13.08; UV-Vis (chloroform): 540, and 577 (sh) nm; Emission (chloroform): 673 nm; IR (ATR mode): 2922 (s), 2853 (s), 1699 (s), 1657 (s), 1597 (m), 1329 (s), 1261 (s), 1024 (vs), 721 (m) cm^{-1}; SEC analysis in chlorobenzene as an eluent: M_n = 88.3 kDa, $Đ$ = 2.4.

P3. (mixture of *cis/trans* hyperbranched polymeric structure): Isolated as dark violet solid in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.92-9.33 (brm, 2.4H, ArH), 8.15-8.49 (brm, 5.5H, ArH), 7.32-7.42 (brm, 2.4, ArH), 6.52 (brs, 0.08H, =CH of nonpolymerized oxaNB), 5.17-6.80 (brm, 6.50H, =CH (mixture of *cis* and *trans* protons)), 4.45-4.66 (brm, 30H, CH_2), 3.97 (brm, 4H, CH_2), 3.42-3.59 (brm, 11H, CH_2), 1.19-2.12 (brm, 170H, CH_2), 0.83 (brm, 24H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 177.2 (CO of nonpolymerized oxaNB), 175.5 (br), 163.5 (br), 126.79-133.03 (brm), 120.95-122.63 (brm),116.20, 116.08, 80.92, 73.68, 70.31, 64.24 52.56-53.38 (brm), 44.76, 38.78, 31.92, 30.10, 29.70, 29.36, 27.69, 26.61, 22.67, 14.10; UV-Vis (chloroform): 502, and 555 (sh) nm; Emission (chloroform): 717 nm; IR (ATR mode): 2921 (s), 2852 (s), 1701 (s), 1657 (s), 1596, 1325 (s), 808 cm^{-1}; SEC analysis in chlorobenzene as an eluent: M_n = 74.3 kDa, $Đ$ = 1.9.

P4. (mixture of *cis/trans* hyperbranched polymeric structure): Isolated as dark violet solid in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.56 (brm, 1.35H, ArH), 7.52-8.88 (brm, 6.84H, ArH), 7.30-7.42 (brm, 1.88H, ArH), 6.51 (brs, 0.11H, =CH of nonpolymerized oxaNB), 5.36-6.96 (brm, 3.92, =CH (mixture of *cis* and *trans* protons)), 4.12-4.48 (brm, 7.1H, CH_2), 3.45-3.59 (brm, 6.1H, CH_2), 1.25-2.18 (brm, 150H, CH_2), 0.83 (brs, 24H, CH_3), 0.64 (brm, 6.11H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 177.2 (CO of nonpolymerized oxaNB), 175.7 (br), 163.5 (br), 156.1, 128.61-133.9 (brm), 120.95-122.63 (brm), 80.91, 73.60, 70.32, 64.24, 52.51-53.40 (brm), 44.75, 38.71, 31.90, 30.10, 29.75, 29.37, 27.68, 26.69, 22.50, 14.0; UV-Vis (chloroform): 546 nm; Emission (chloroform): 550, 605 and 696 nm; IR (ATR mode): 3027, 2926 (m), 2851, 1698 (s), 1655 (s), 1214, 746 (vs), 667 cm^{-1}; SEC analysis was not performed due to the insolubility of the polymer in chlorobenzene.

P5. (mixture of *cis/trans* hyperbranched polymeric structure): Isolated as dark violet solid in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.12-9.44 (brm, 2.1H, ArH), 8.17-8.69 (brm, 6.02H, ArH), 7.27-7.42 (brm, 2.91, ArH), 6.51 (brs, 0.10H, =CH of nonpolymerized oxaNB), 5.16-6.79 (brm, 3.25H, =CH (mixture of *cis* and *trans* protons)), 4.53-4.66 (brm, 3.30H, CH_2), 4.07 (brm, 4.6H, CH_2), 3.43-3.61 (brm, 5.60H, CH_2), 1.42-2.23 (brm, 130H, CH_2), 0.84 (br, 24H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 177.4 (CO of nonpolymerized oxaNB), 174.6, 162.8 (br), 161.5, 159.6, 156.4, 148.5 (br), 121.5-133.05 (brm), 122.6, 121.4, 119.8, 107.55, 81.1, 80.5, 79.8, 72.6, 69.2, 69.5, 51.8-52.4 (brm), 43.7, 37.9, 35.7, 30.8 (br), 30.6, 28.6-29.05 (br), 28.3 (br), 25.4, 21.64, 13.08; UV-Vis (chloroform): 539 nm; Emission (chloroform): 544, 588 and 700 nm; IR (ATR mode): 2922 (s), 2852 (s), 1698 (s), 1658 (s), 1596, 1330, 1245, 729 cm^{-1}; SEC analysis in chlorobenzene as an eluent: M_n = 79.0 kDa, $Đ$ = 2.1.

^{1}H- and ^{13}C-NMR Spectra of Monomers and Polymers

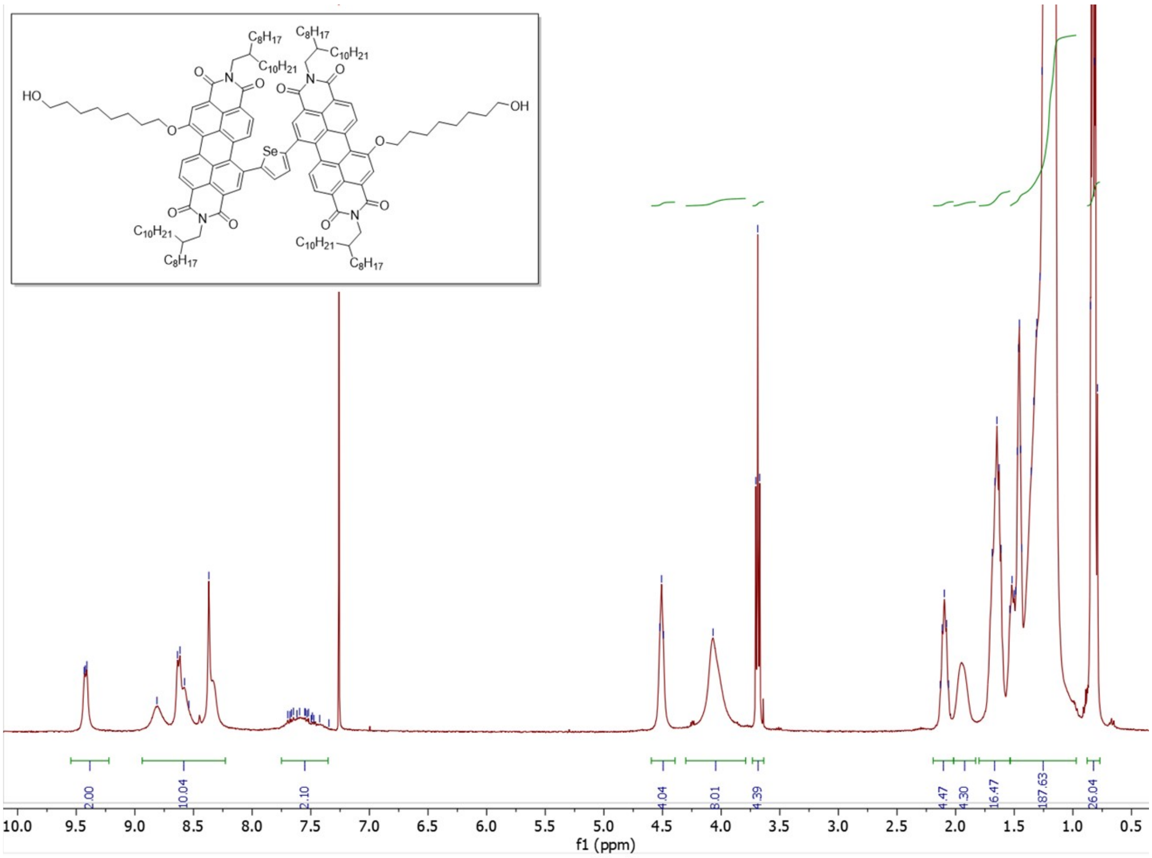


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **B1** (**PDI-diol)**

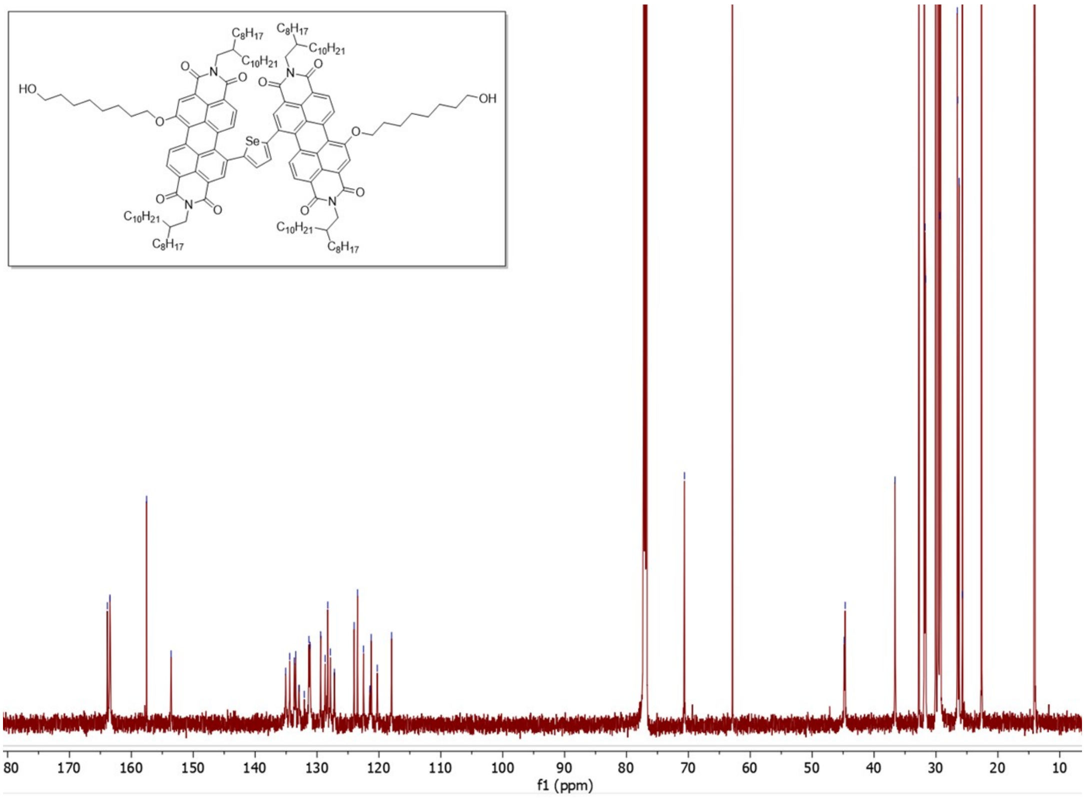


Figure S2. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **B1** (**PDI-diol)**

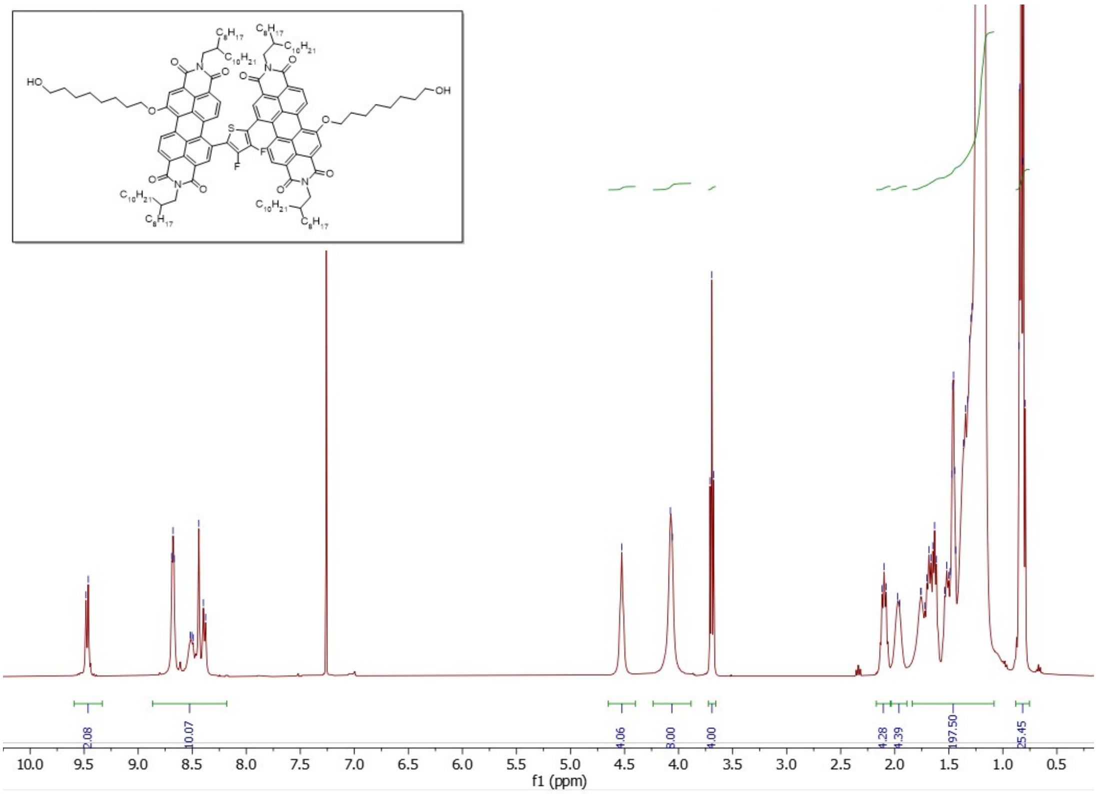


Figure S3. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B2** (**PDI-diol)**

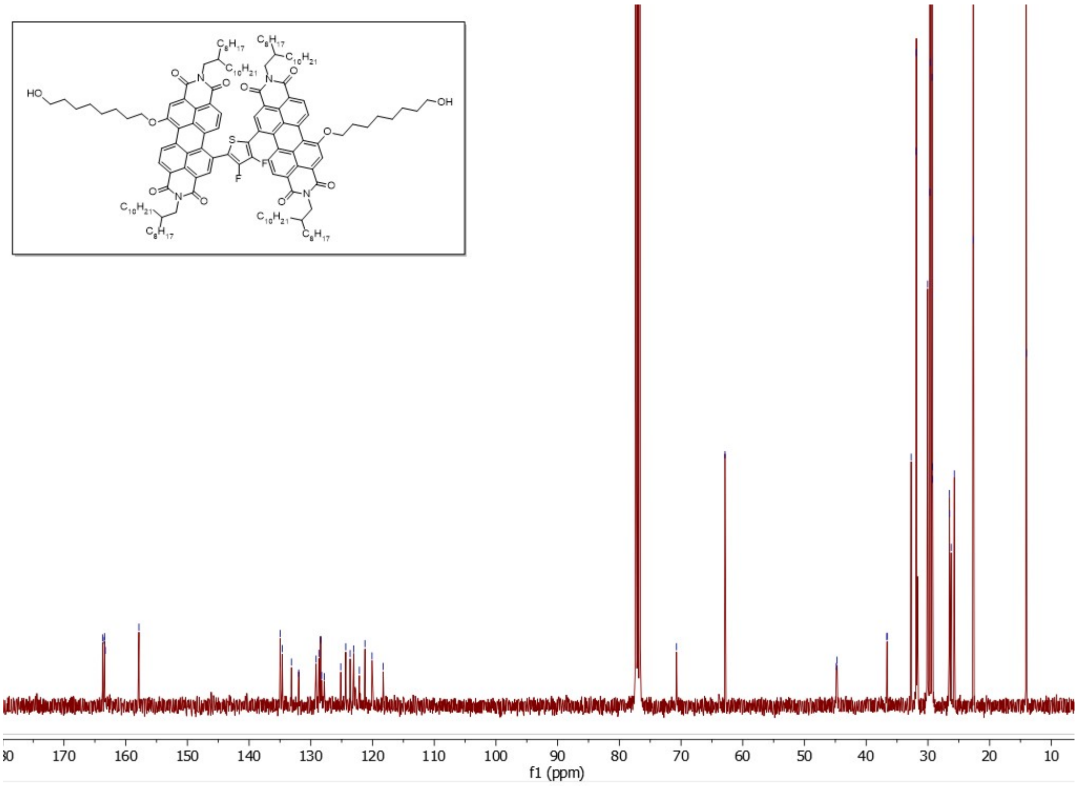


Figure S4. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B2** (**PDI-diol)**

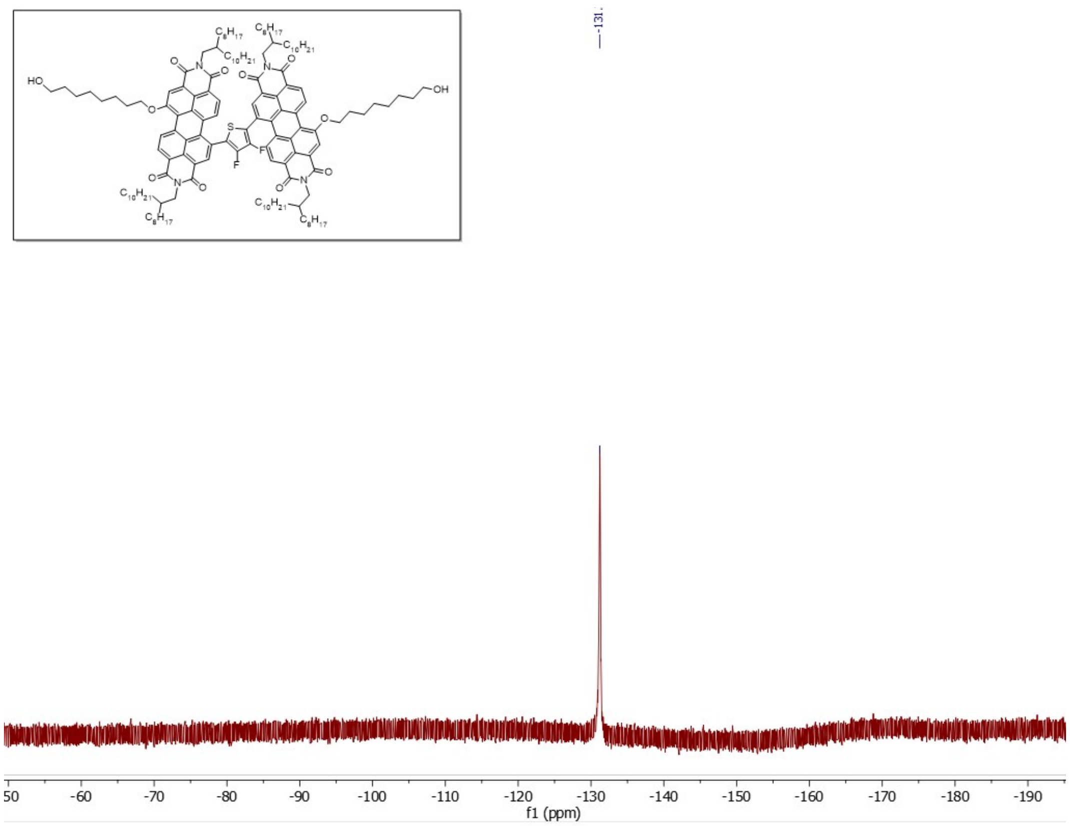


Figure S5. ^{19}F NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B2** (**PDI-diol**)

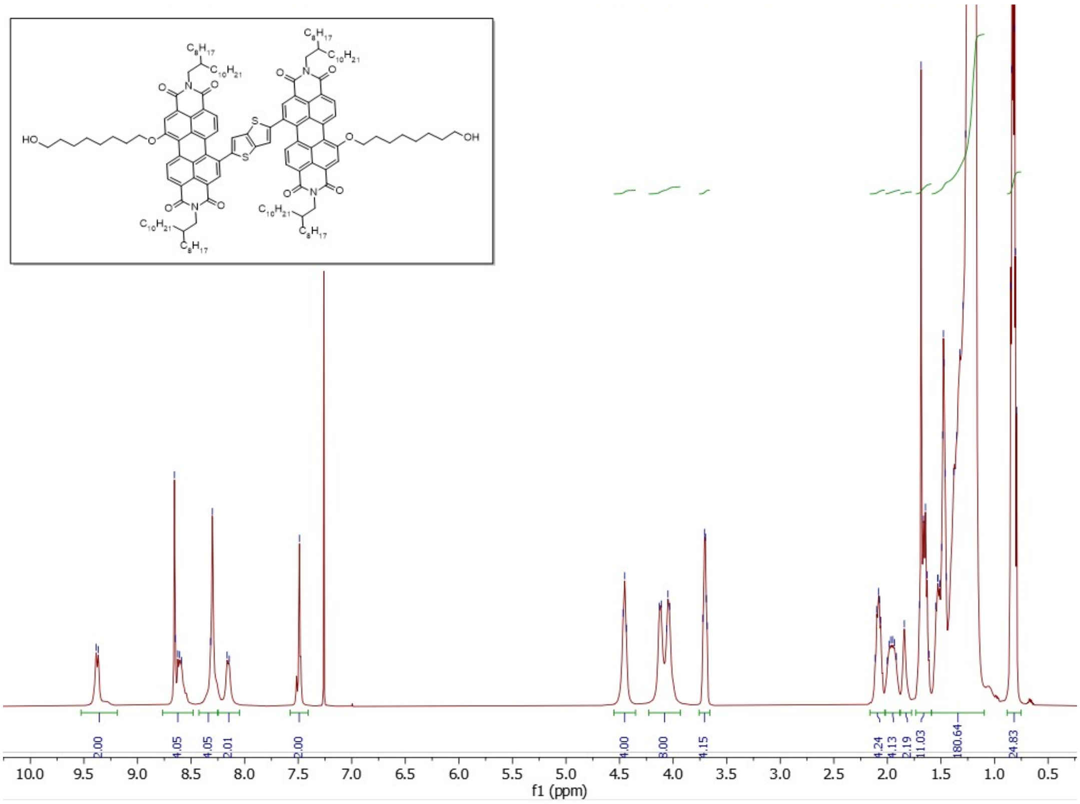


Figure S6. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B3** (**PDI-diol**)

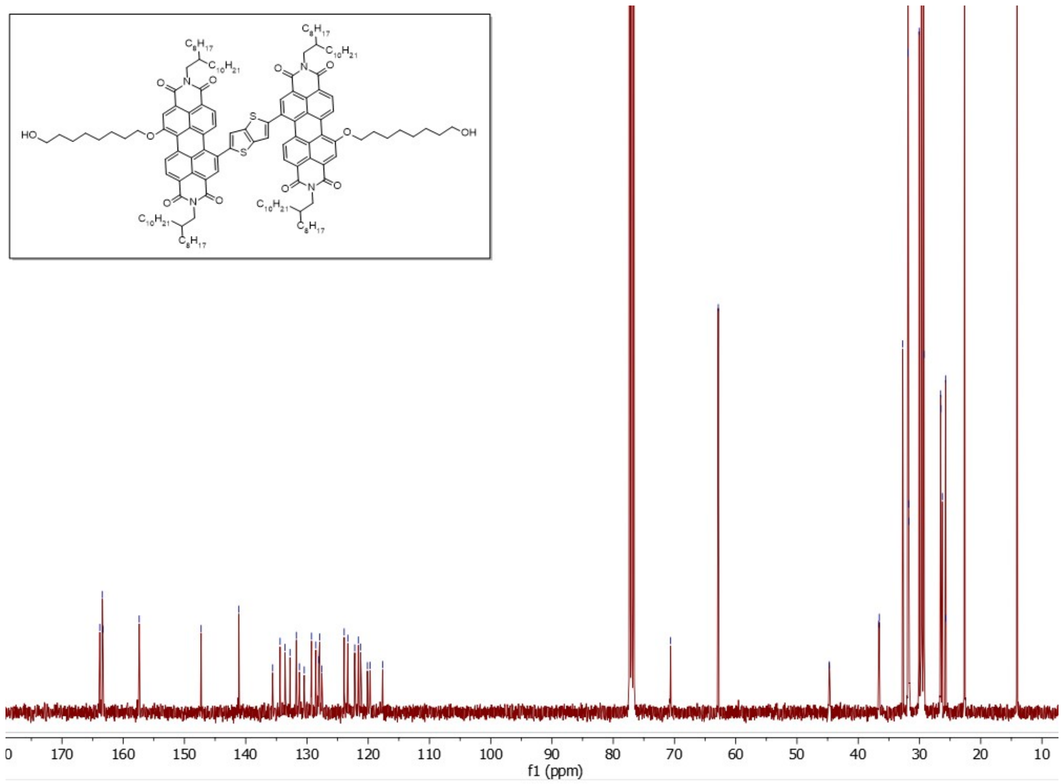


Figure S7. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **B3** (**PDI-diol)**

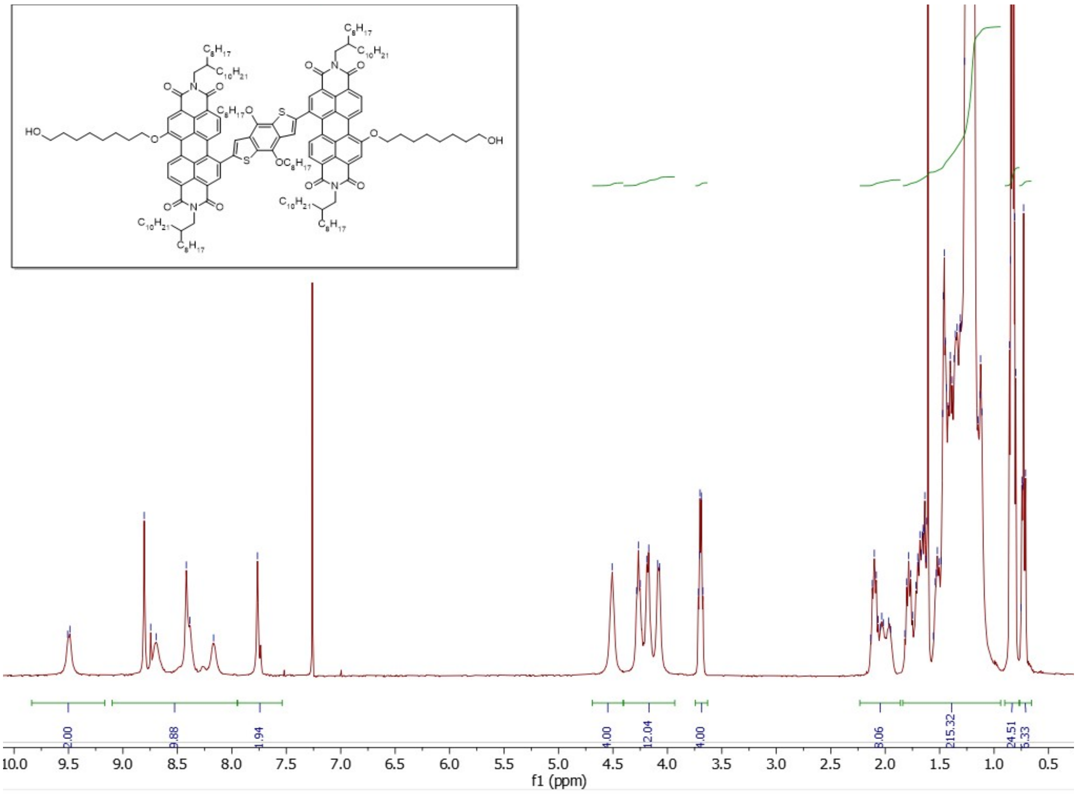


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **B4** (**PDI-diol)**

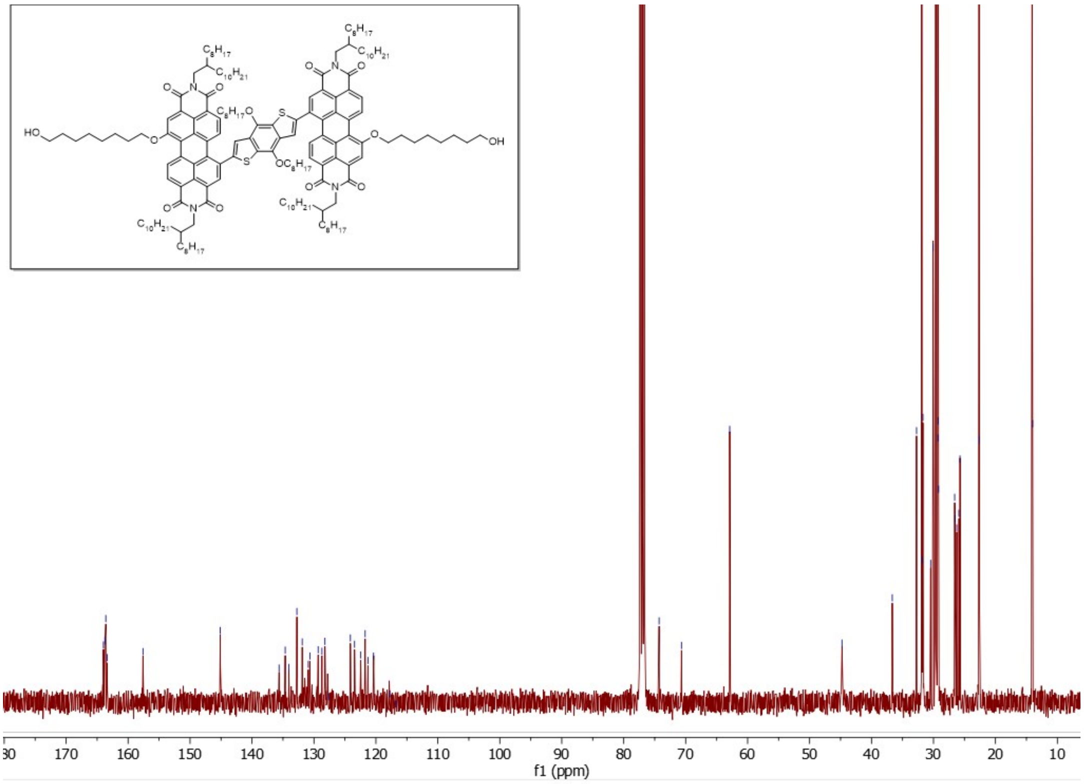


Figure S9. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B4** (**PDI-diol)**

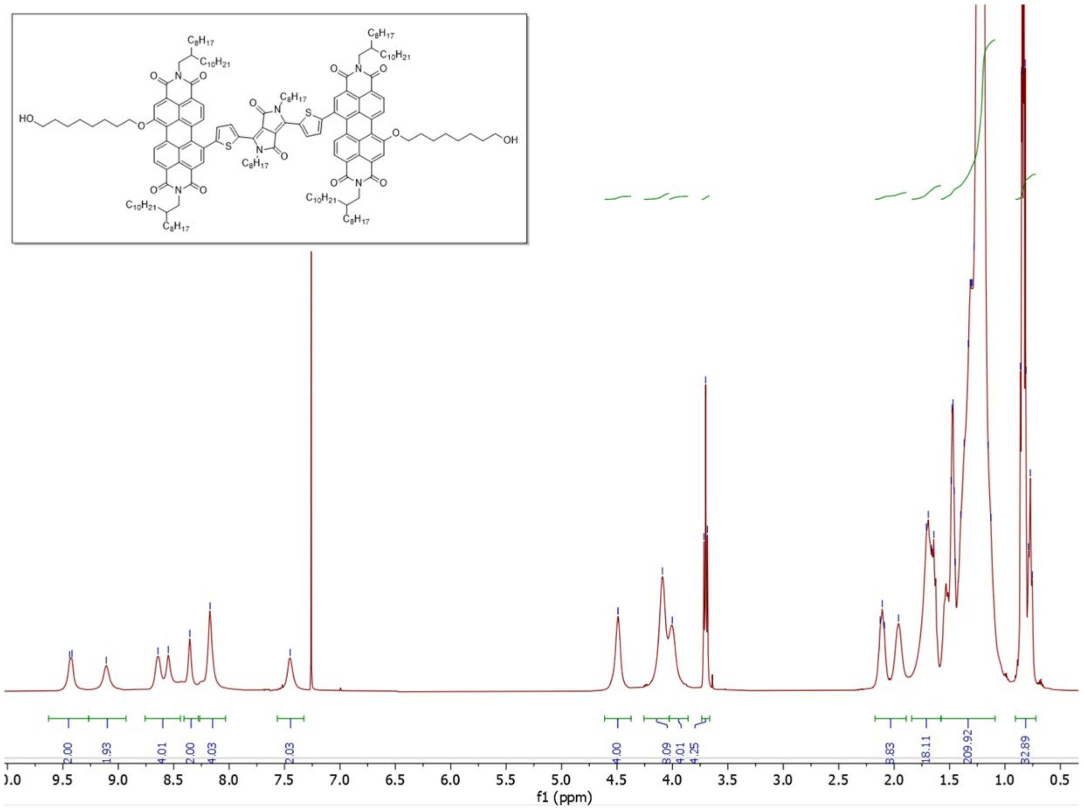


Figure S10. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **B5** (**PDI-diol)**

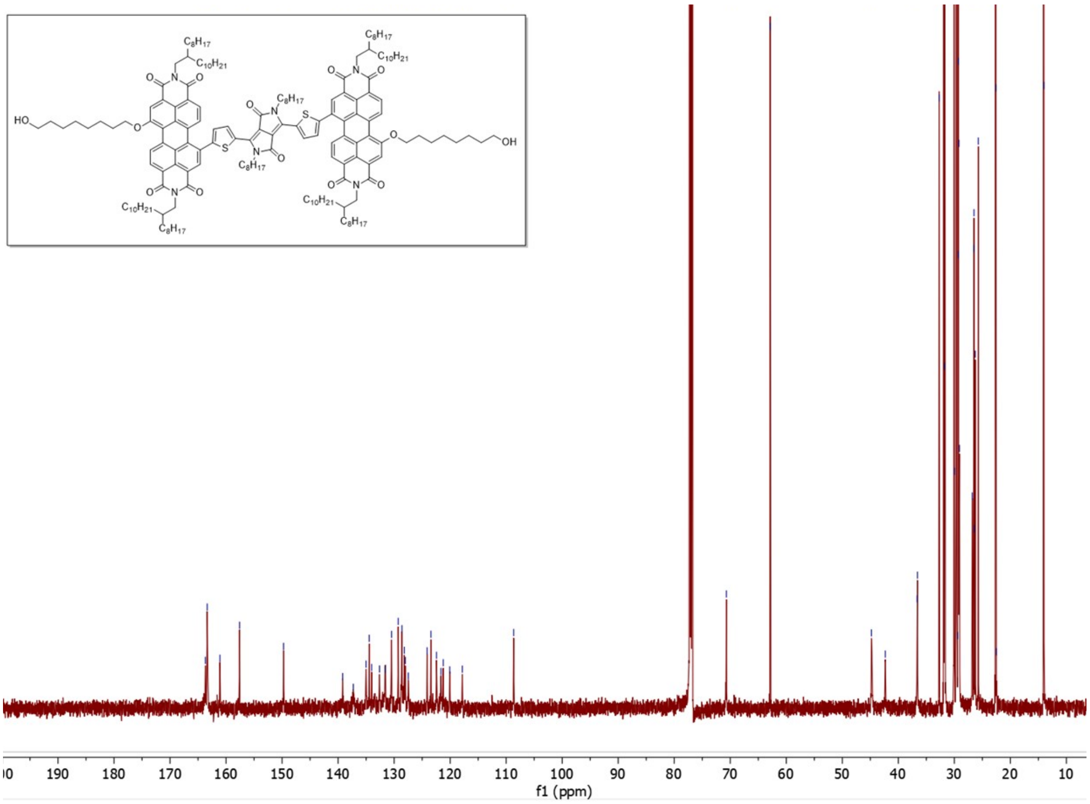


Figure S11. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **B5** (**PDI-diol)**

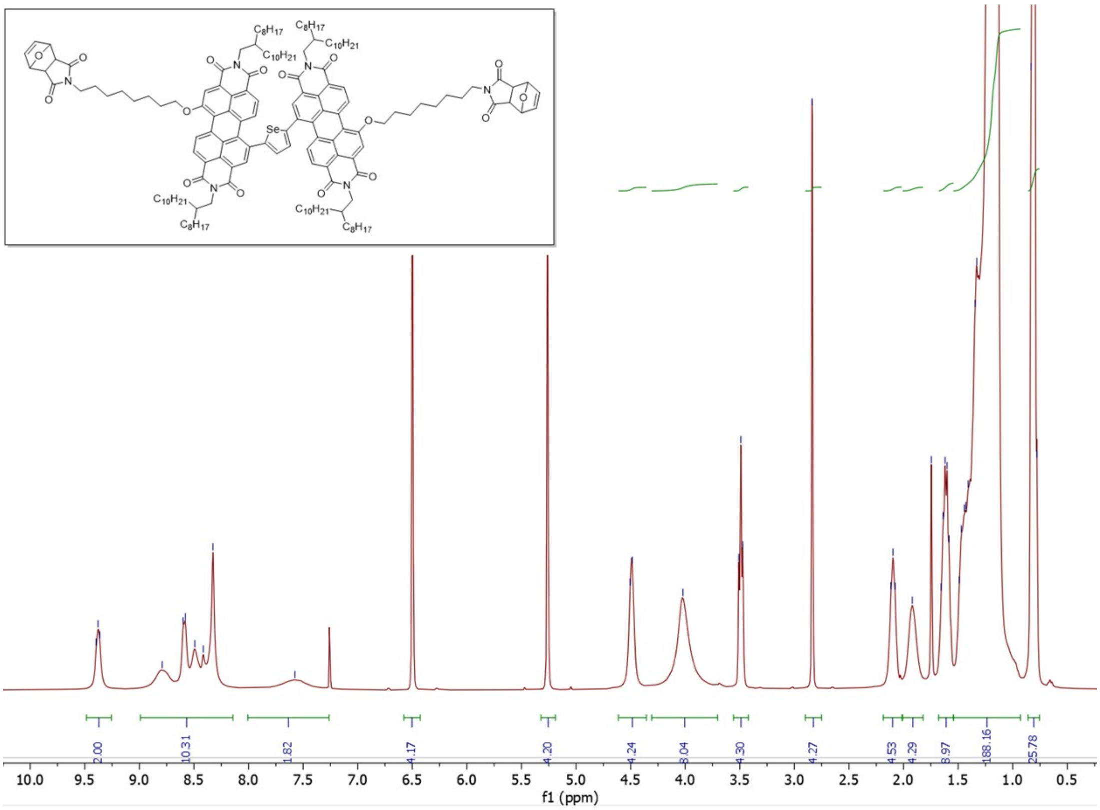


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **M1**

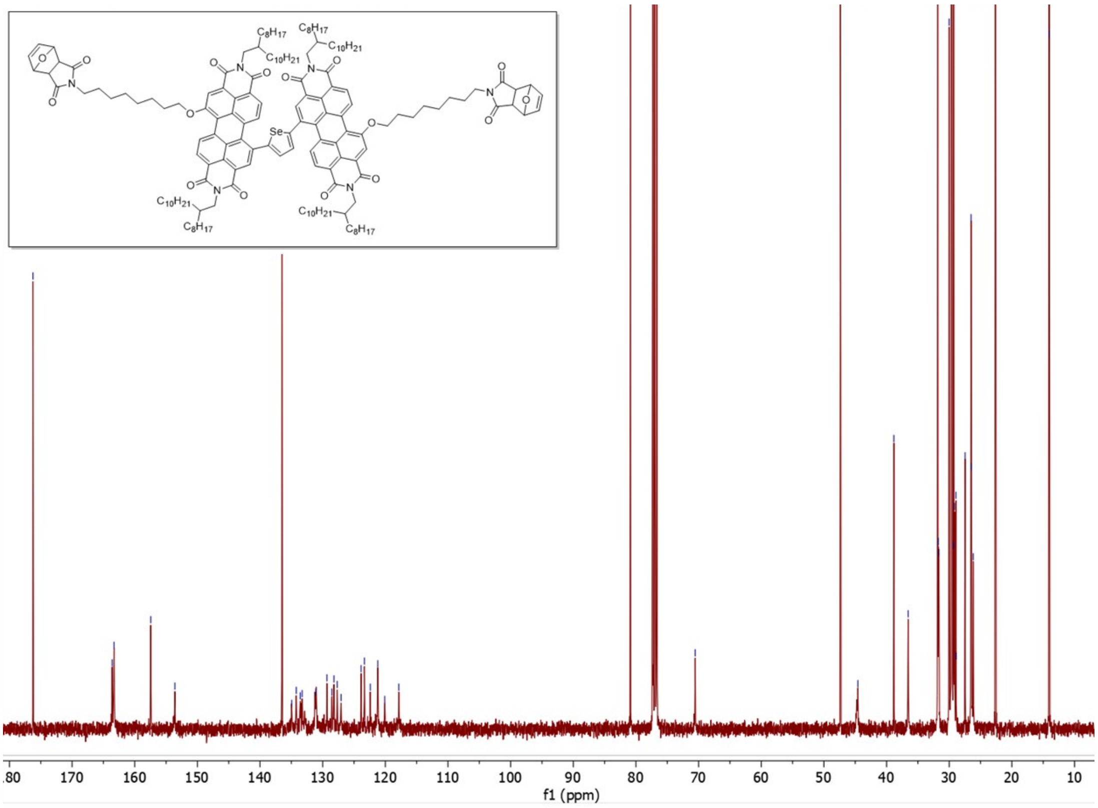


Figure S13. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M1**

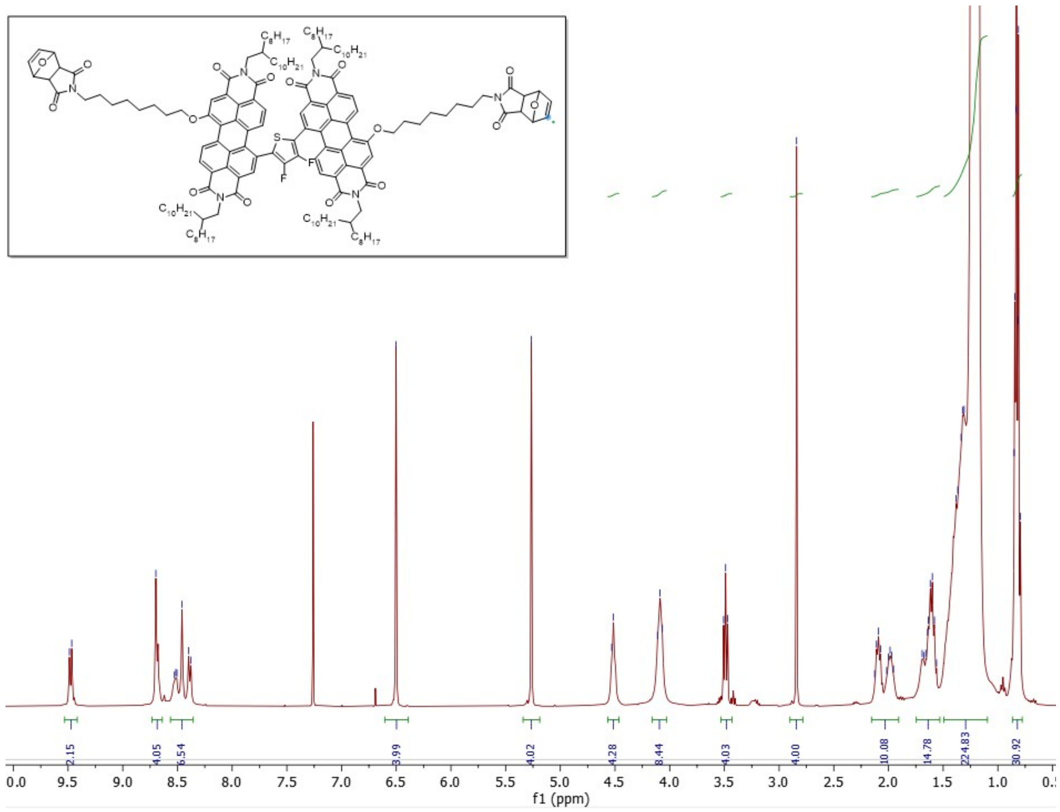


Figure S14. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M2**

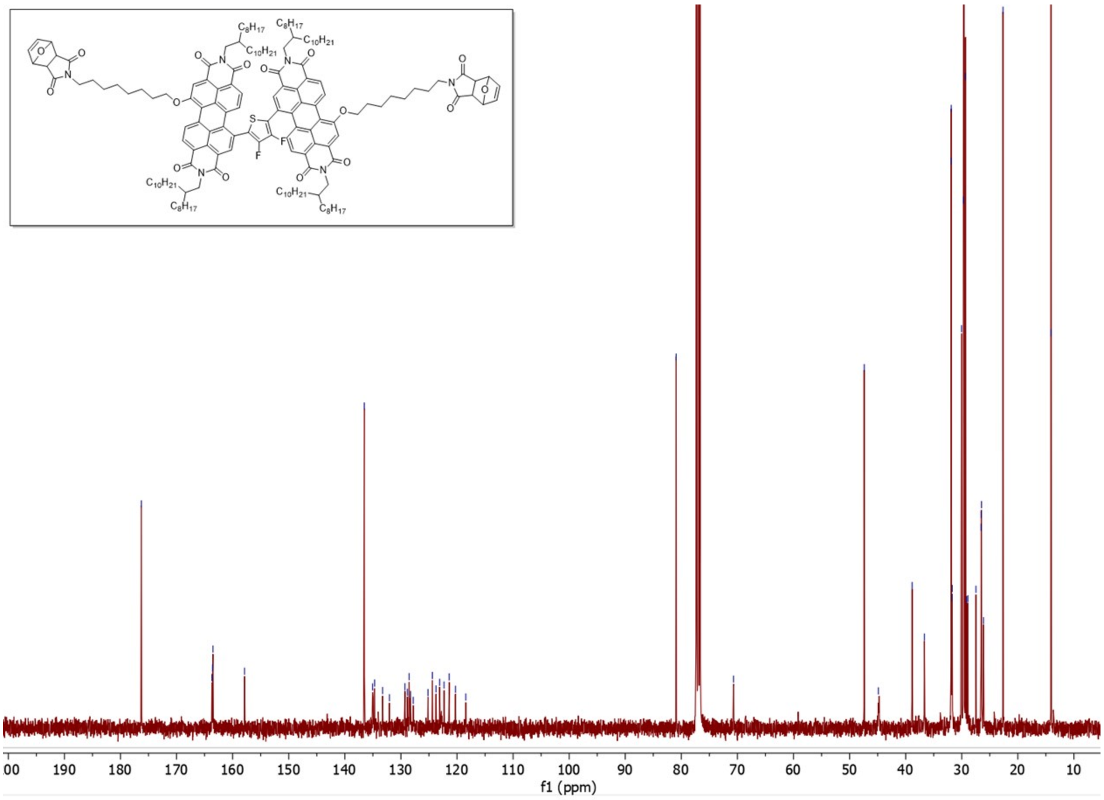


Figure S15. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **M2**

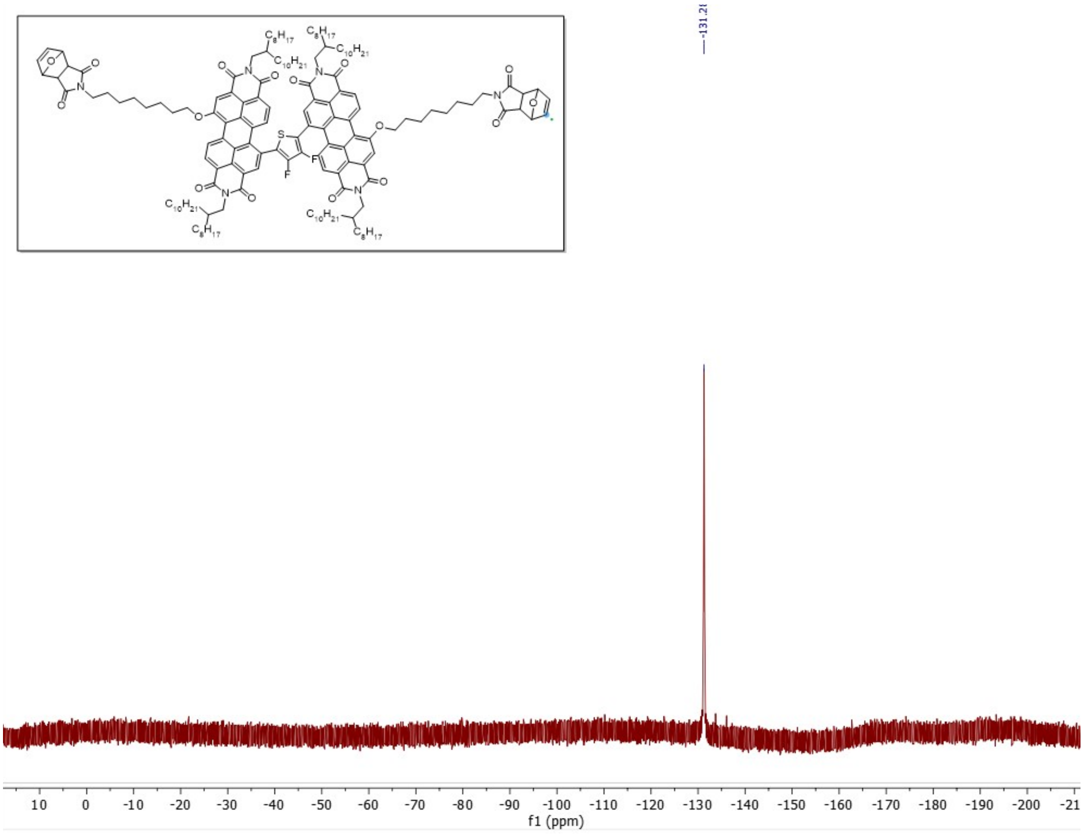


Figure S16. ^{19}F NMR (400 MHz, $CDCl_3$, 298K) spectrum of **M2**

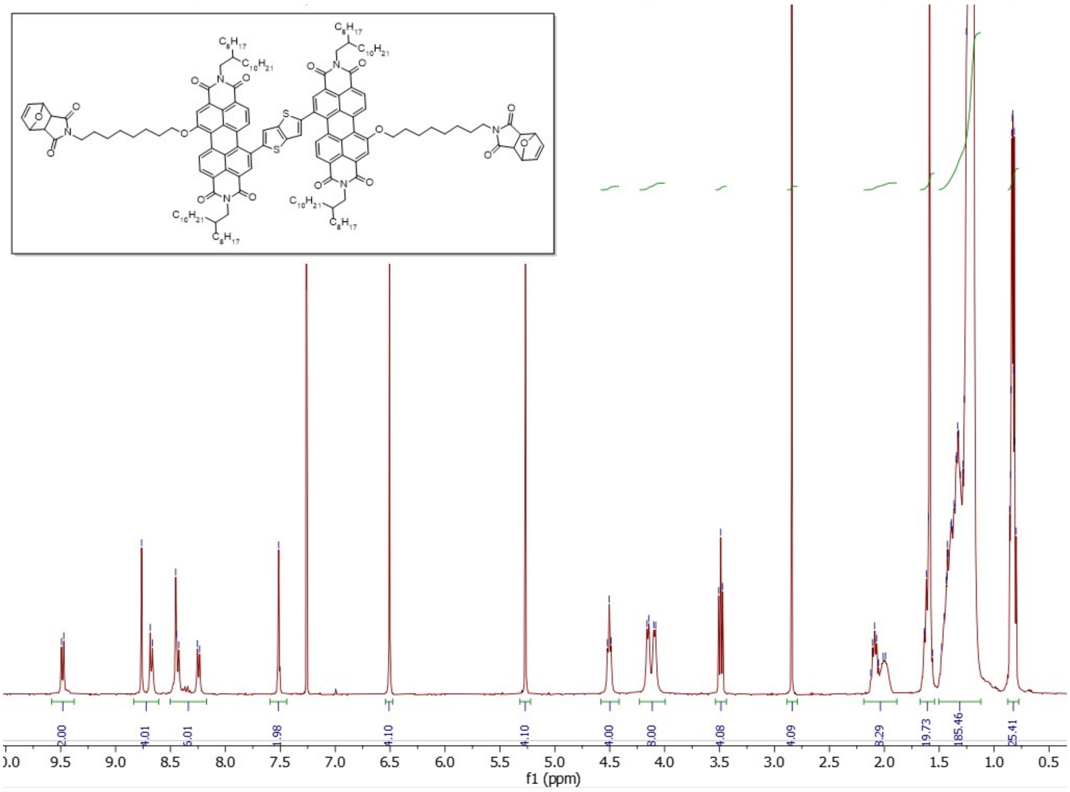


Figure S17. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M3**

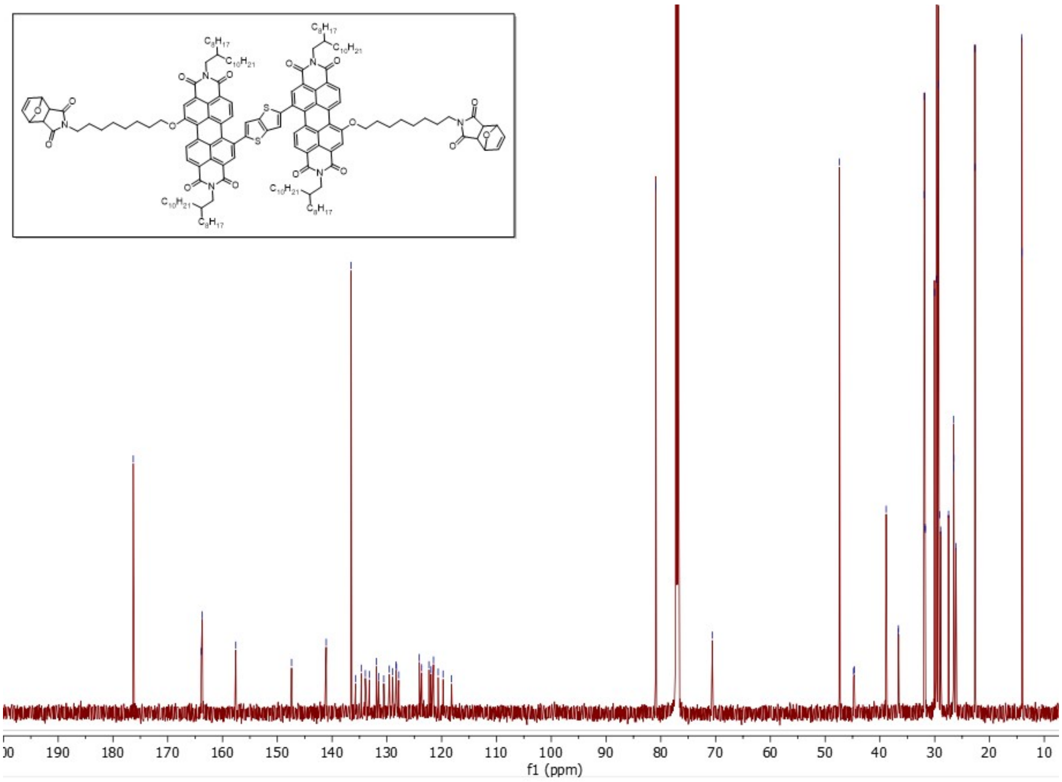


Figure S18. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M3**

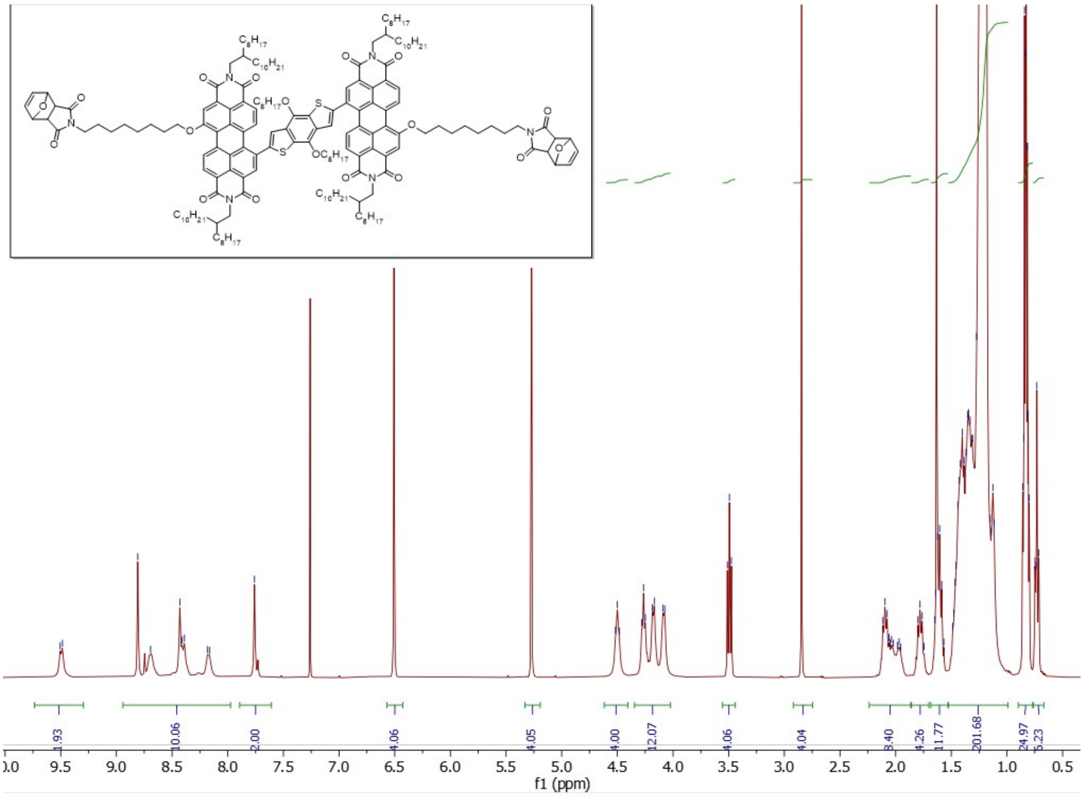


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **M4**

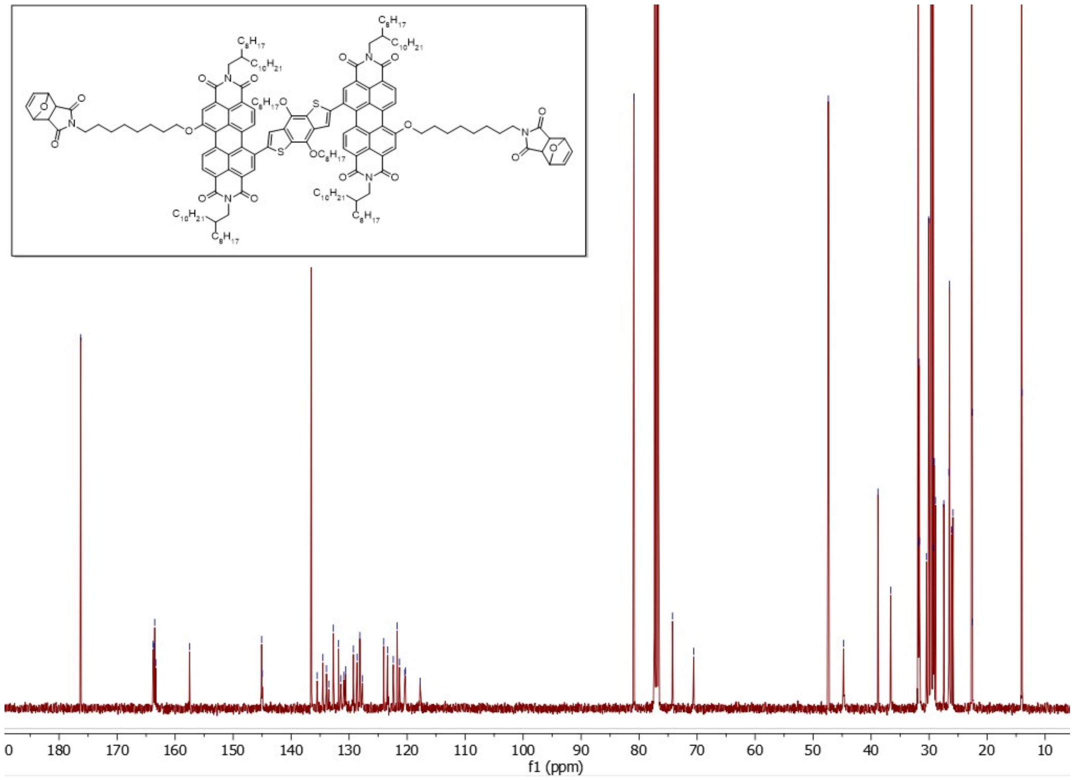


Figure S20. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **M4**

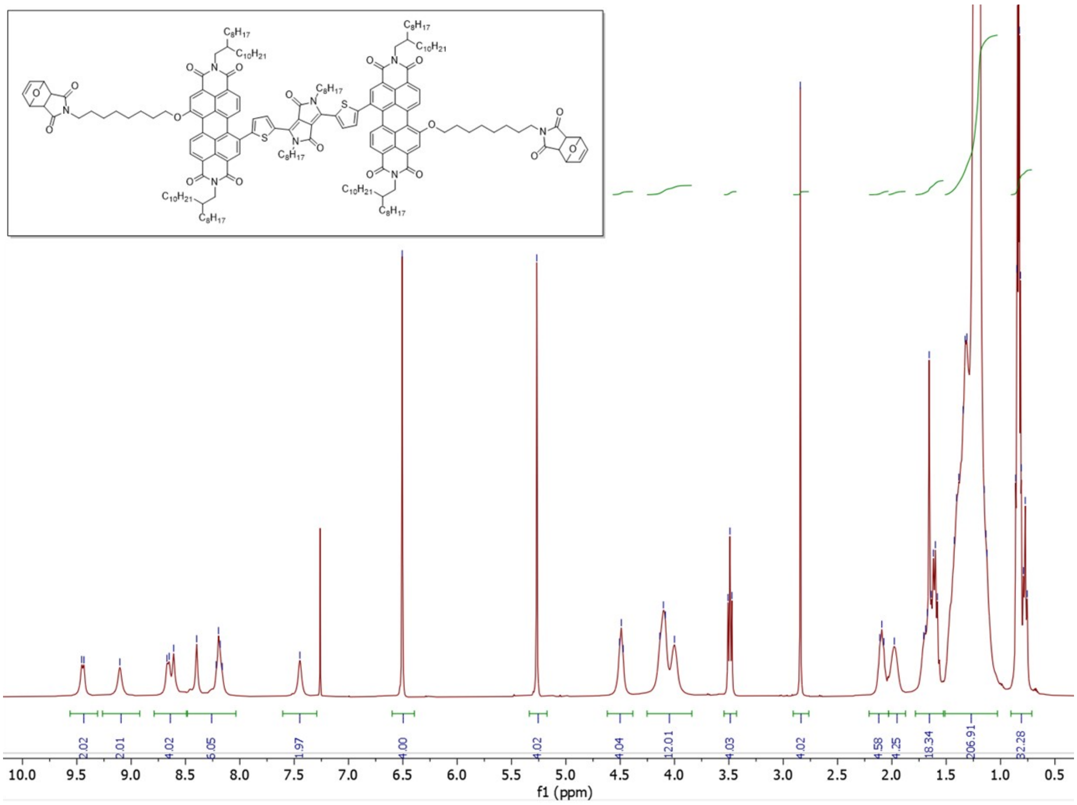


Figure S21. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M5**

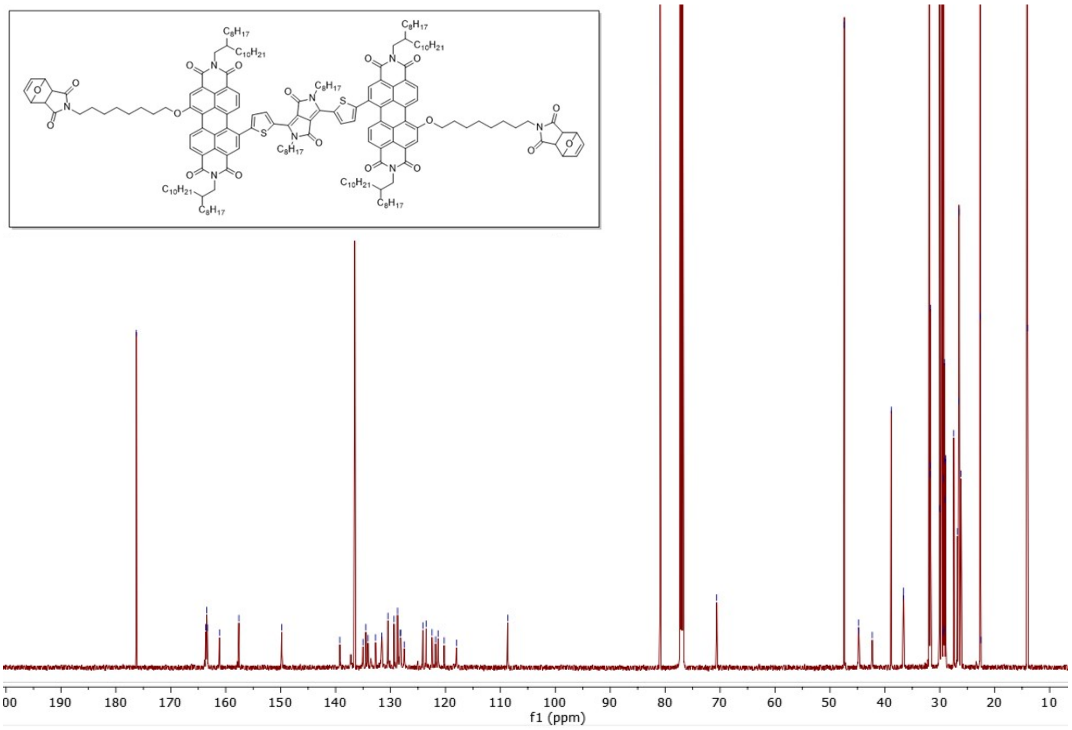


Figure S22. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **M5**

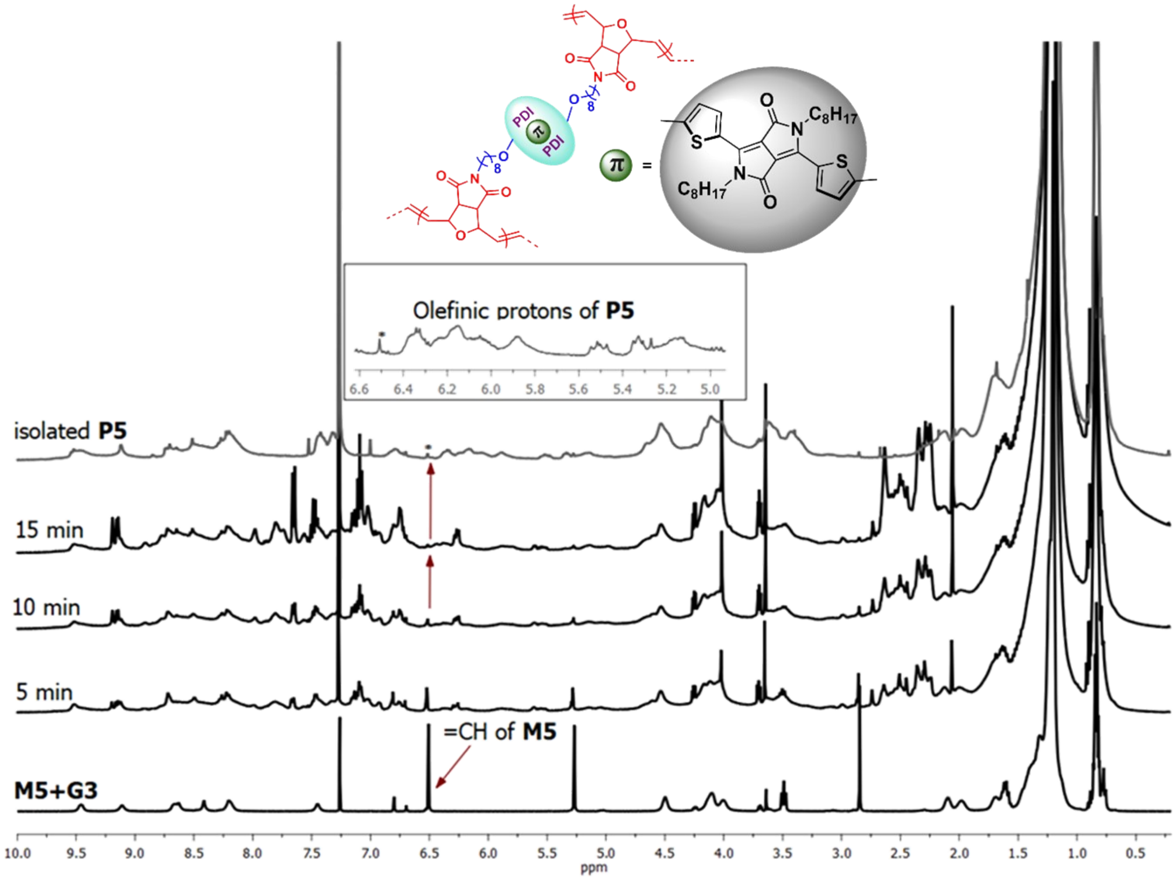


Figure S23. Time-dependent ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectra of polymerization of **M5** using **G3**. Dark gray line spectrum represents isolated **P5** and *denotes the olefinic protons of nonpolymerized oxanorbornene imide functional groups in the hyperbranched polymer chain after termination using ethyl vinyl ether and further purification.

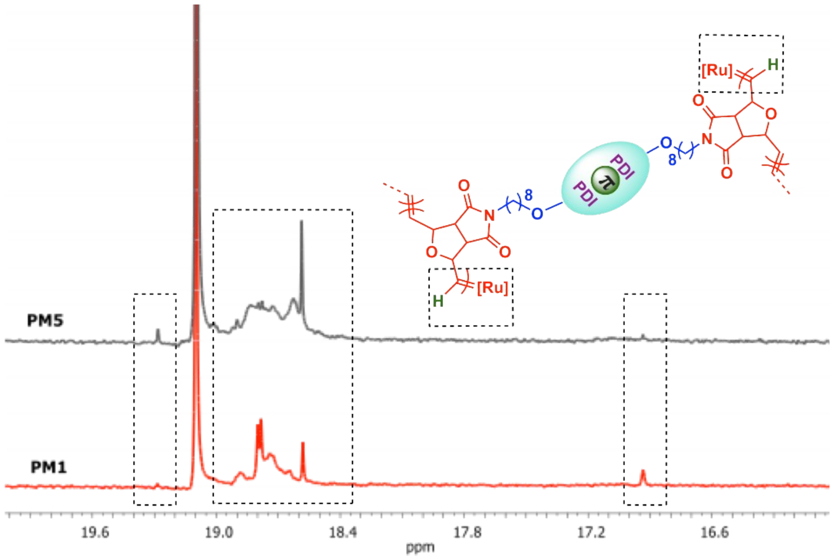


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectra of the of [Ru]=CH protons of growing propagating units of **P1** (red) and **P5** (gray).

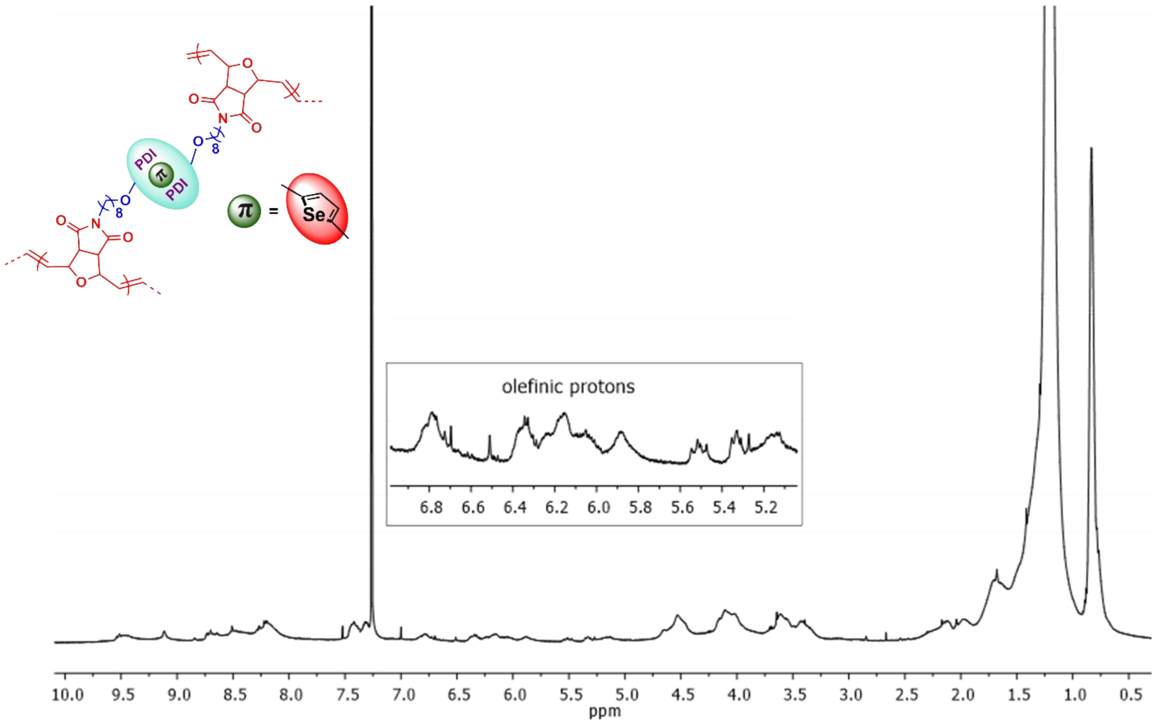


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P1**

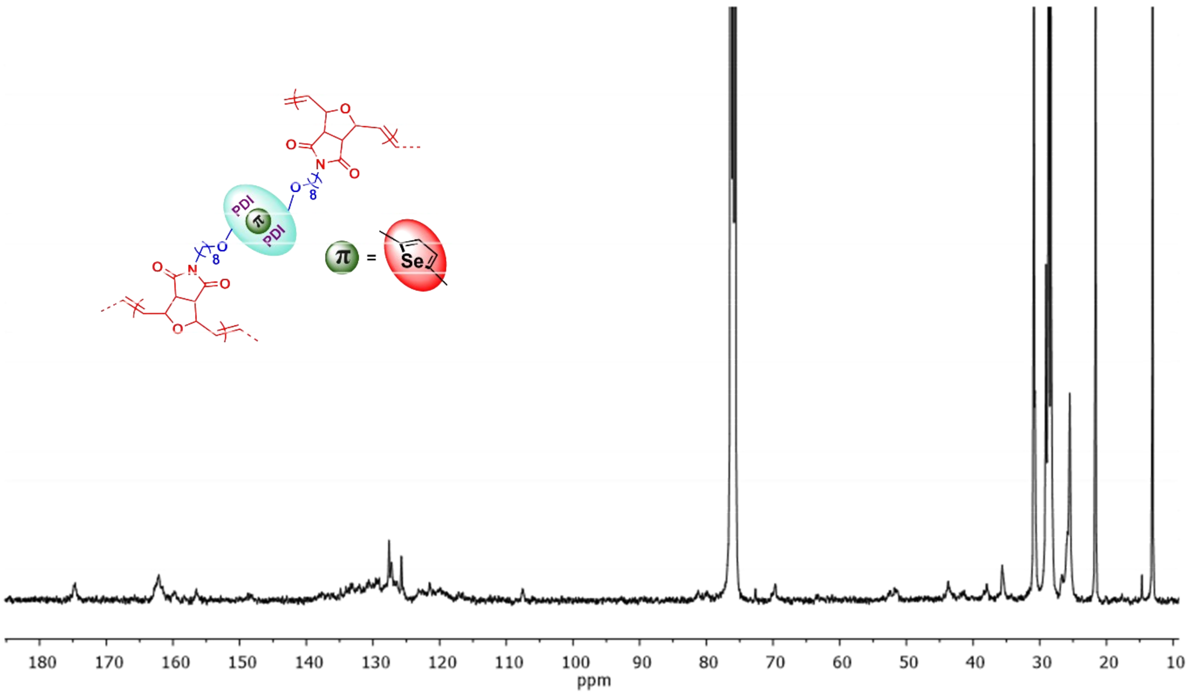


Figure S26. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P1**

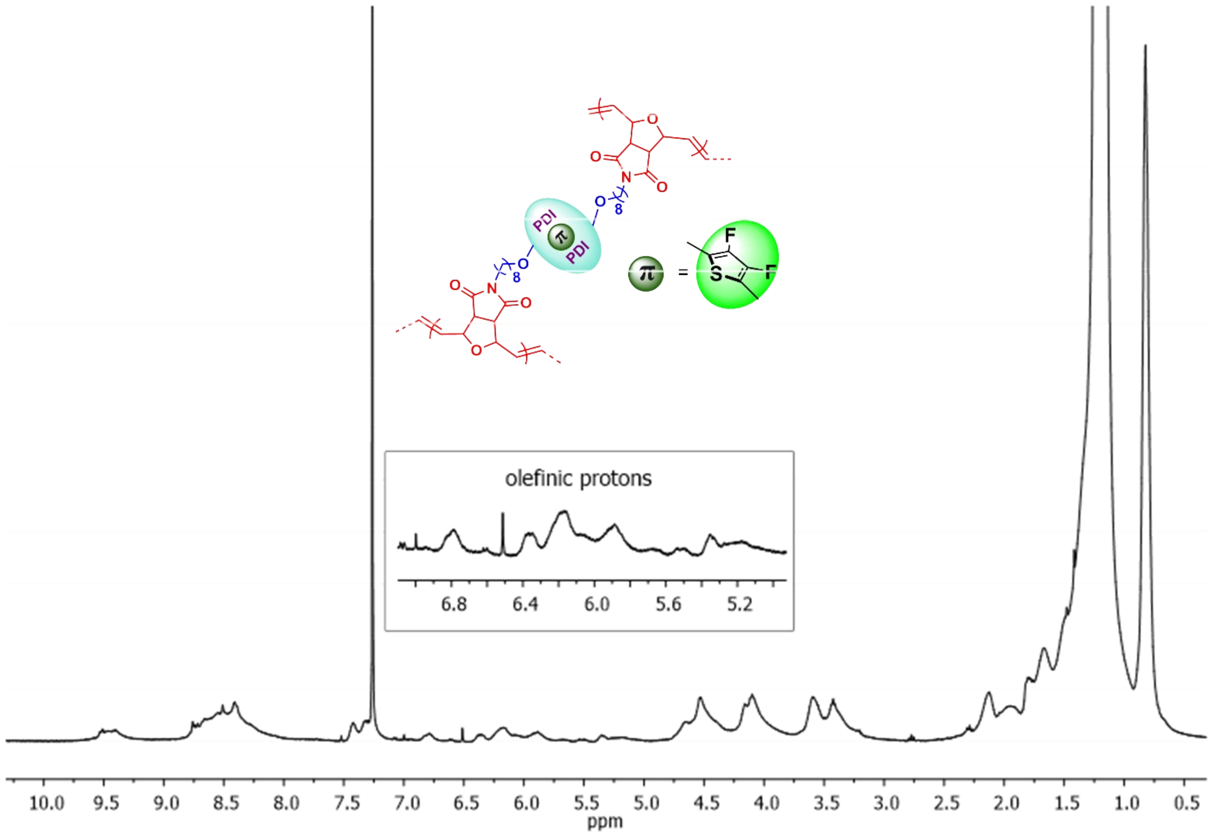


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P2**

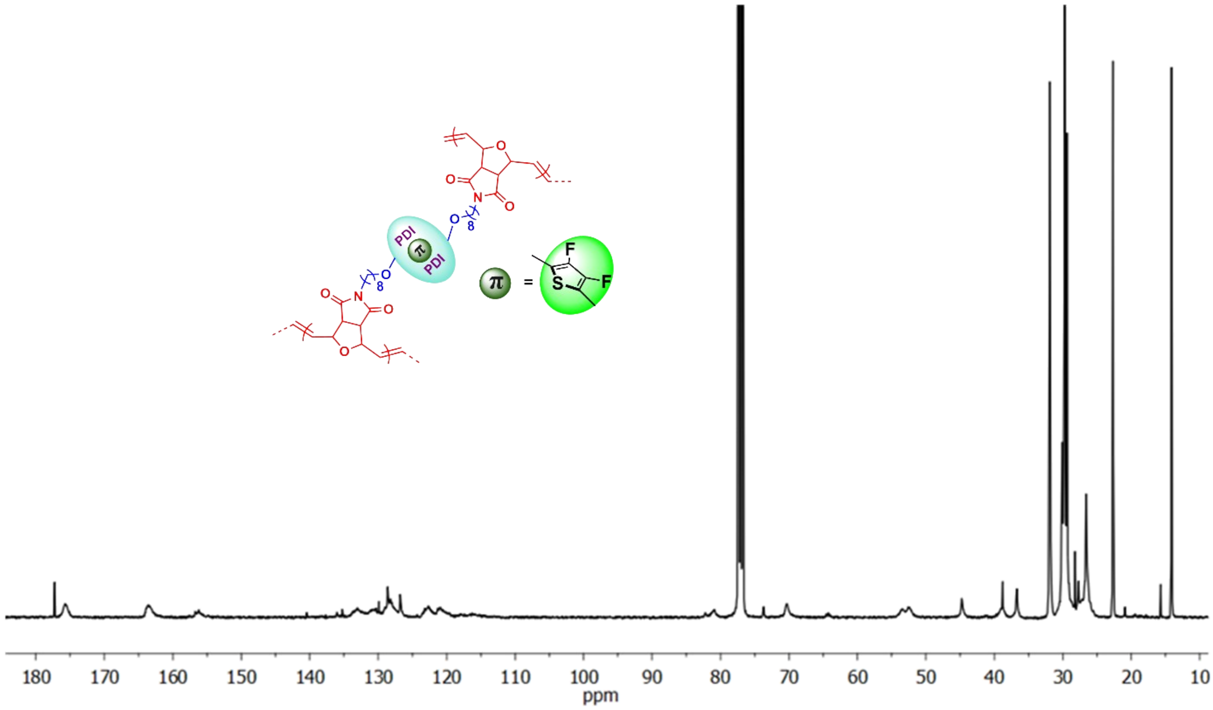


Figure S28. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P2**

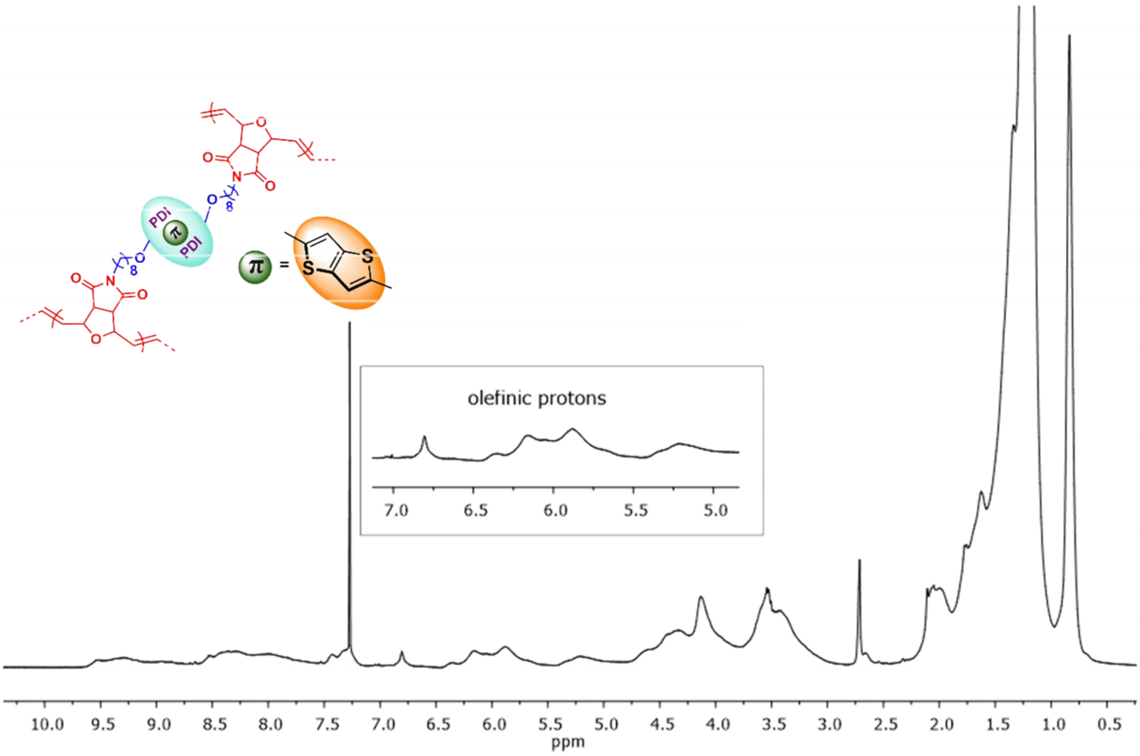


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P3**

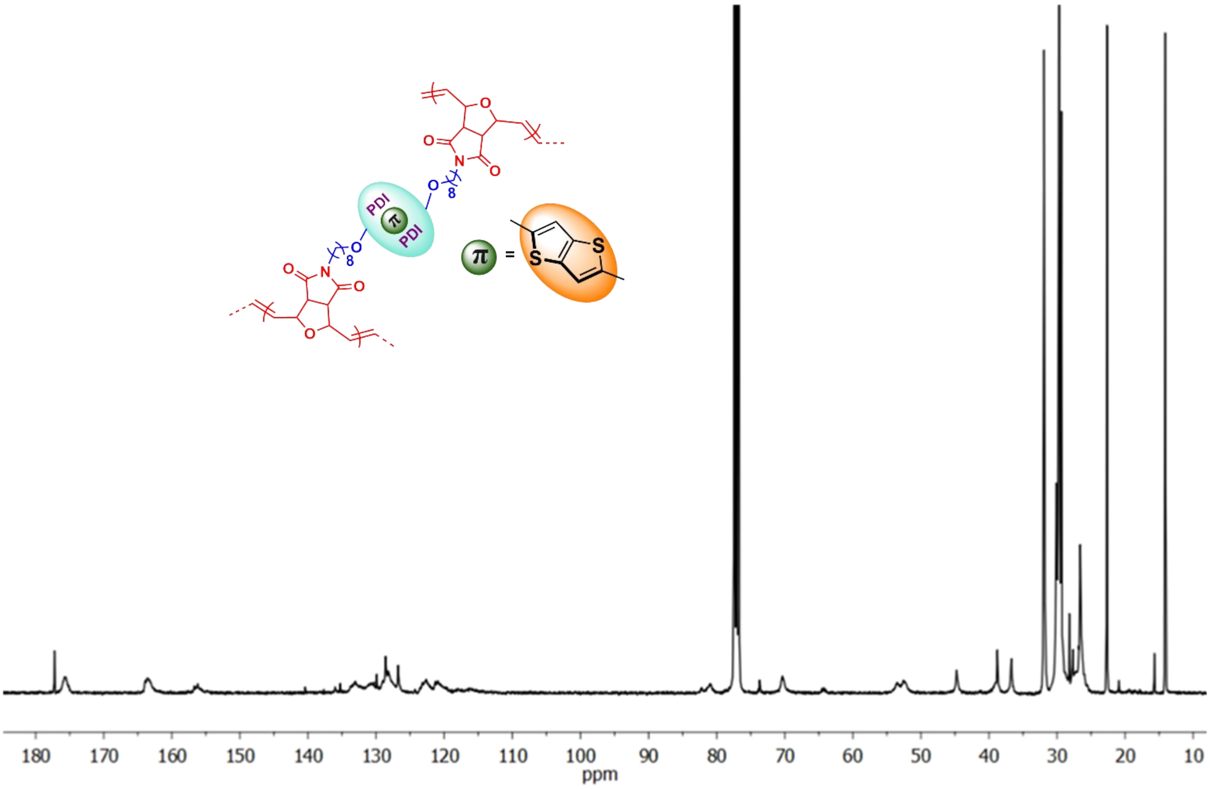


Figure S30. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P3**

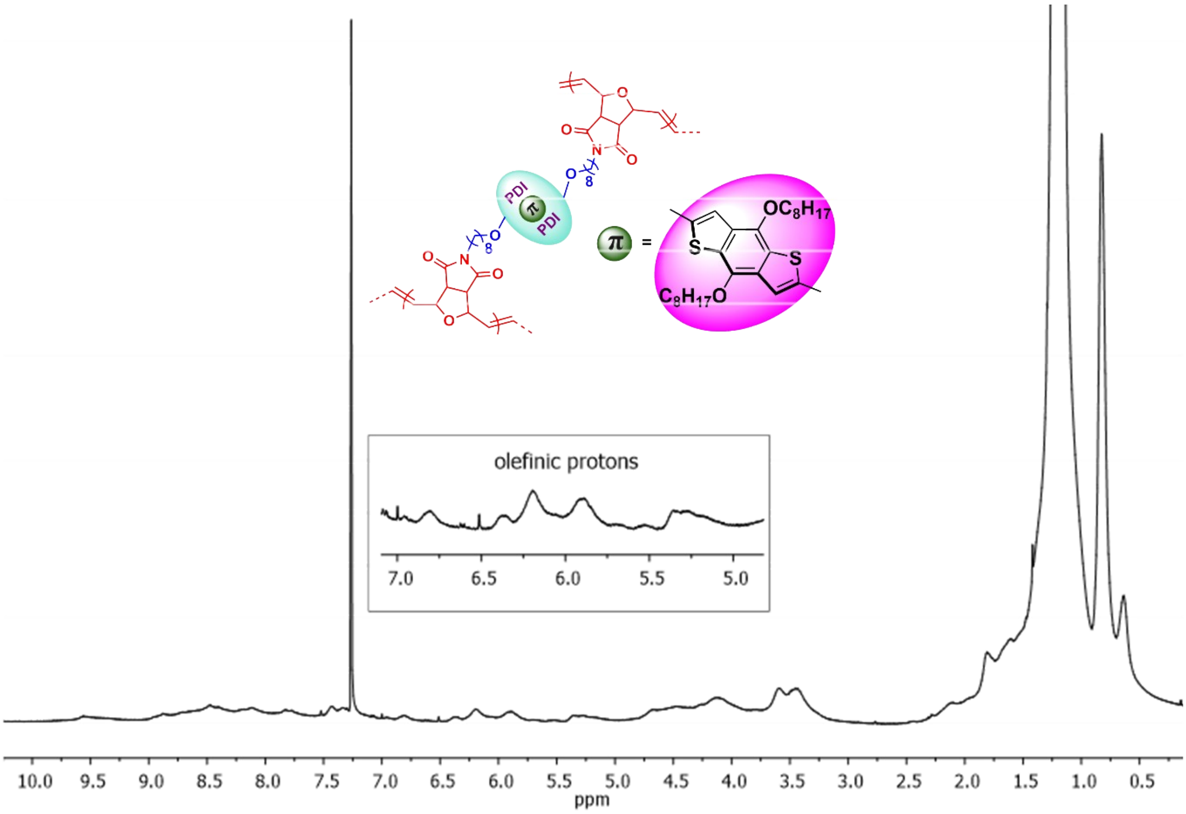


Figure S31. ^{1}H NMR (400 MHz, CDCl$_3$, 298K) spectrum of **P4**

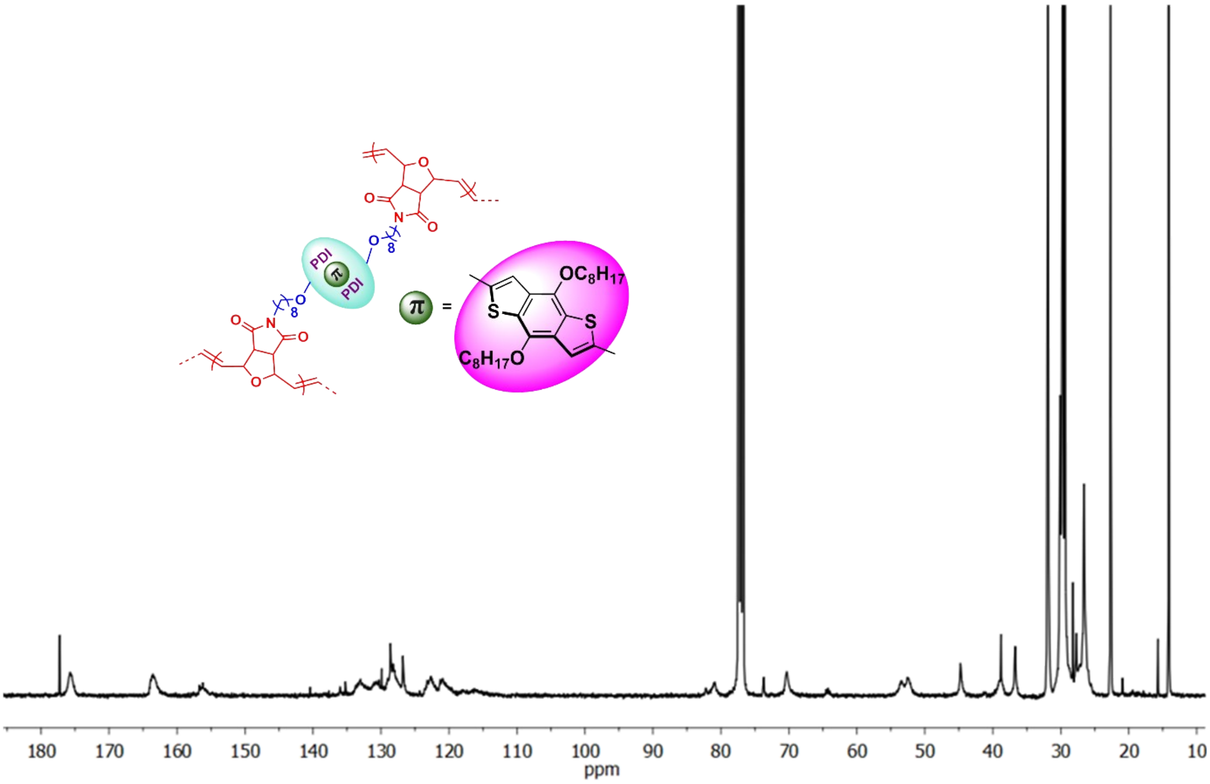


Figure S32. ^{13}C NMR (400 MHz, CDCl$_3$, 298K) spectrum of **P4**

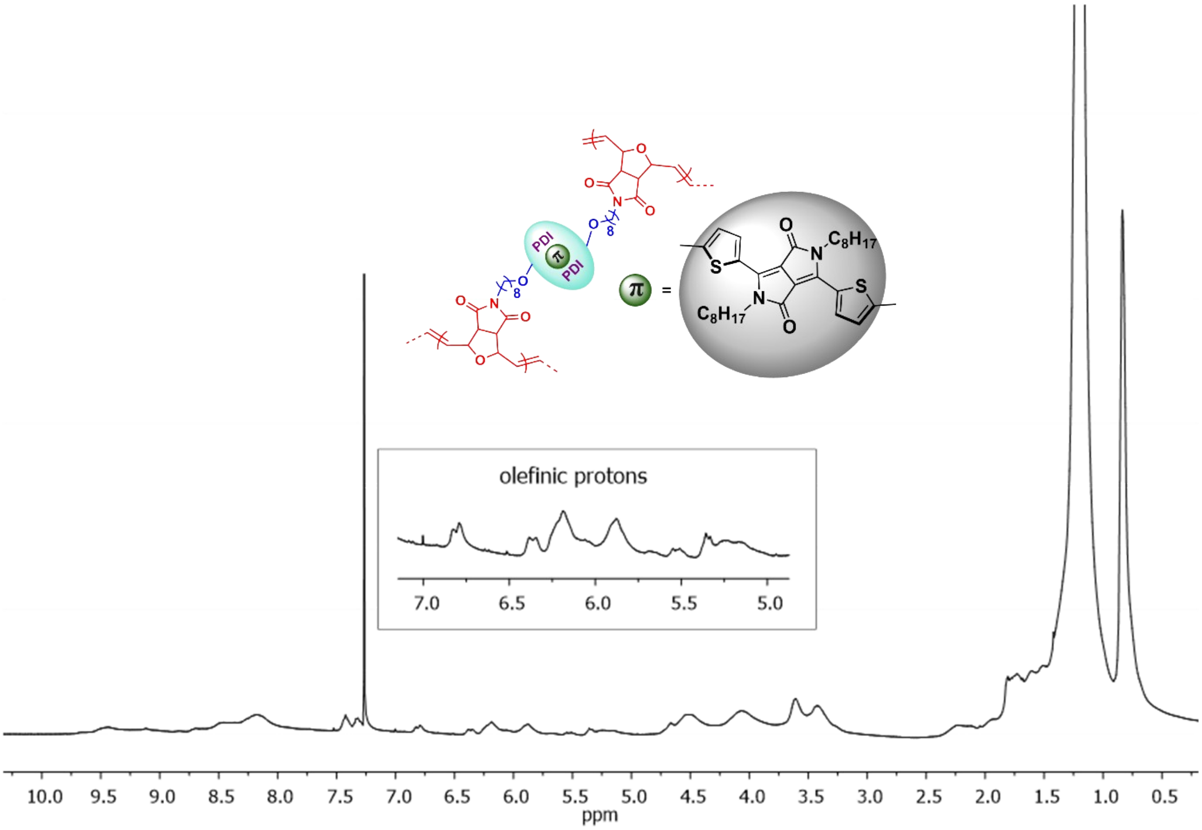


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P5**

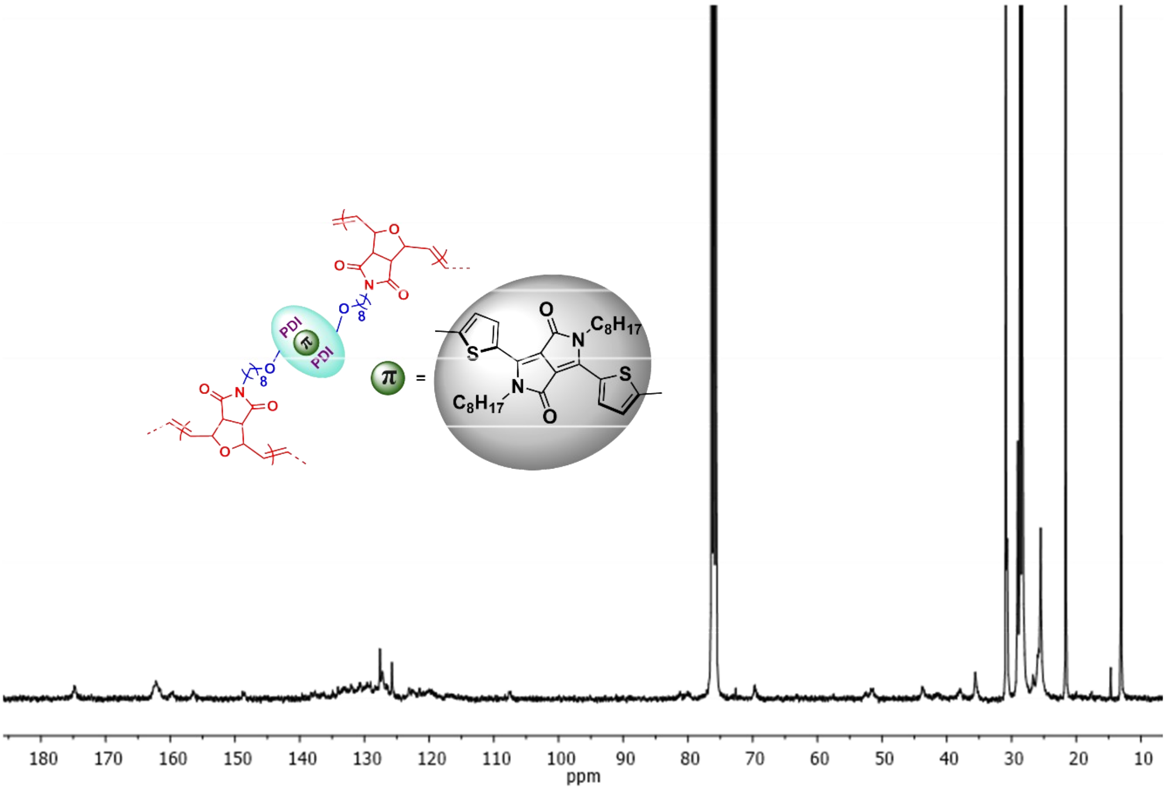


Figure S34. ^{13}C NMR (400 MHz, $CDCl_3$, 298K) spectrum of **P5**

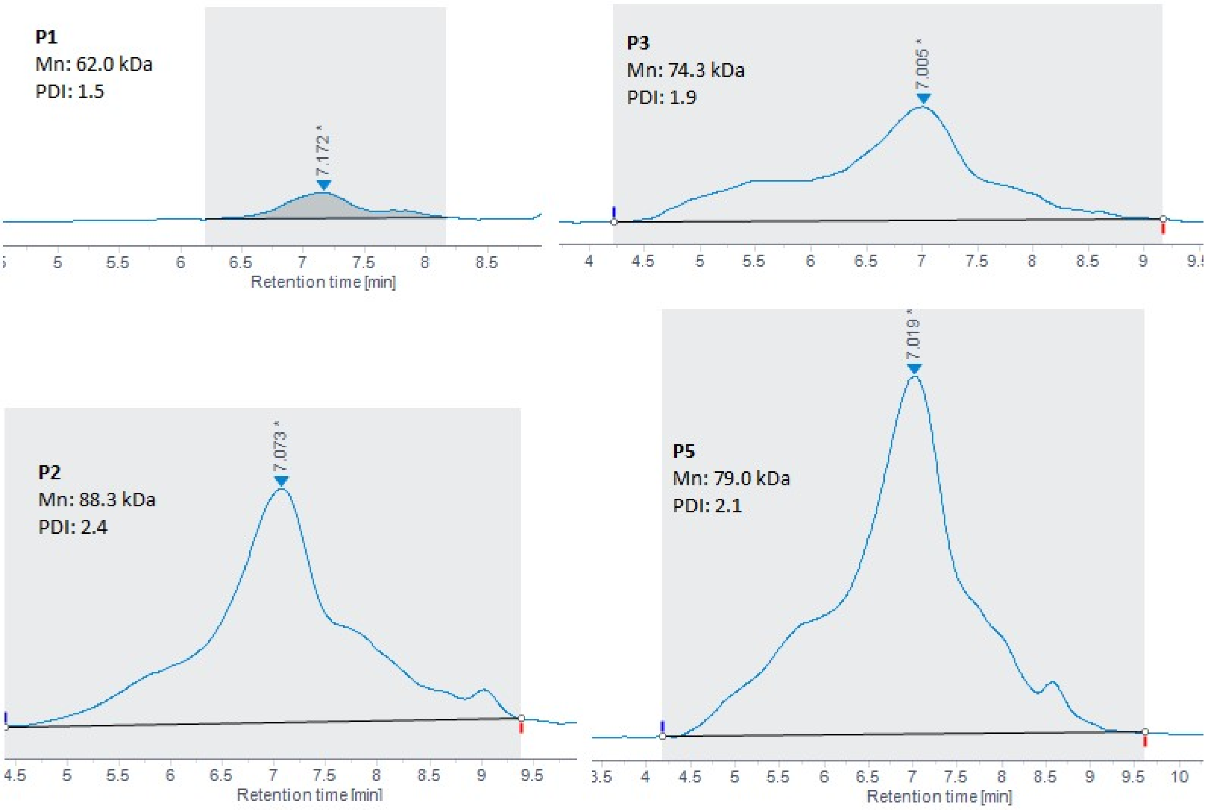


Figure S35. SEC traces of **P1-P5** using refractive index (RI) detector. SEC analysis of **P4** was not performed due to insolubility of the polymer in chlorobenzene.

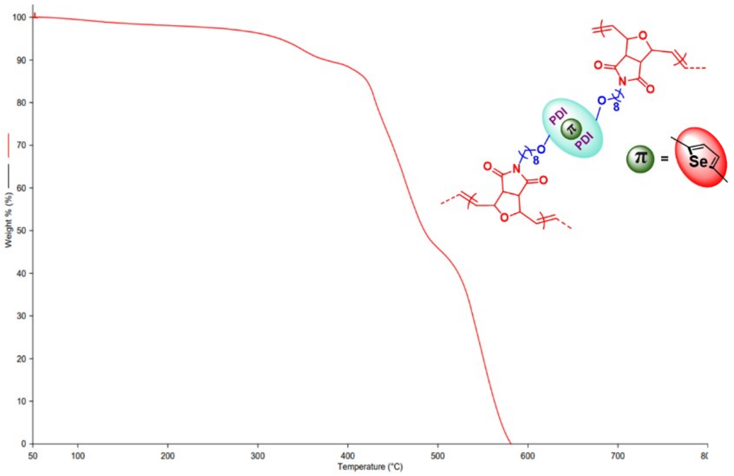


Figure S36. TGA curve of polymer **P1** (heating rate = 10 °C min^{-1})

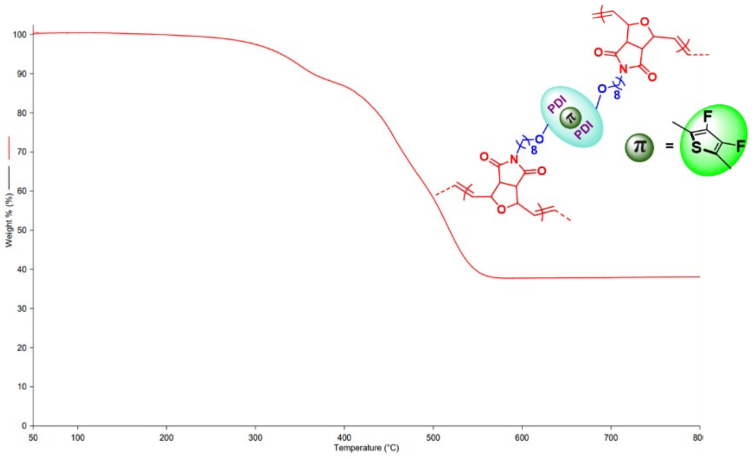


Figure S37. TGA curve of polymer **P2** (heating rate = 10 °C min^{-1})

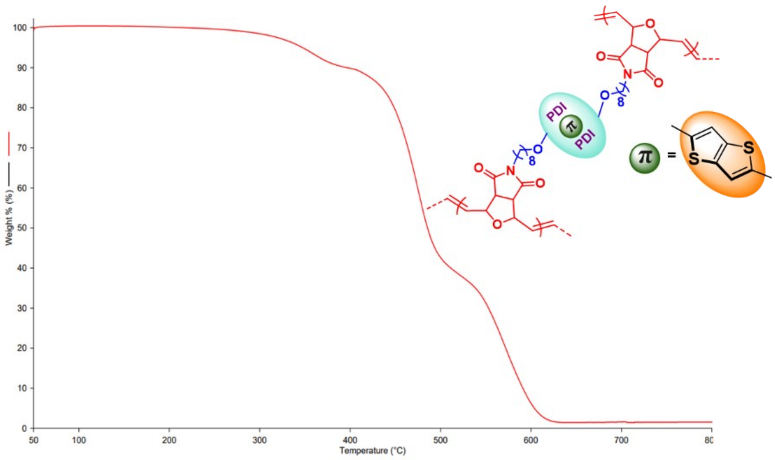


Figure S38. TGA curve of polymer **P3** (heating rate = 10 °C min^{-1})

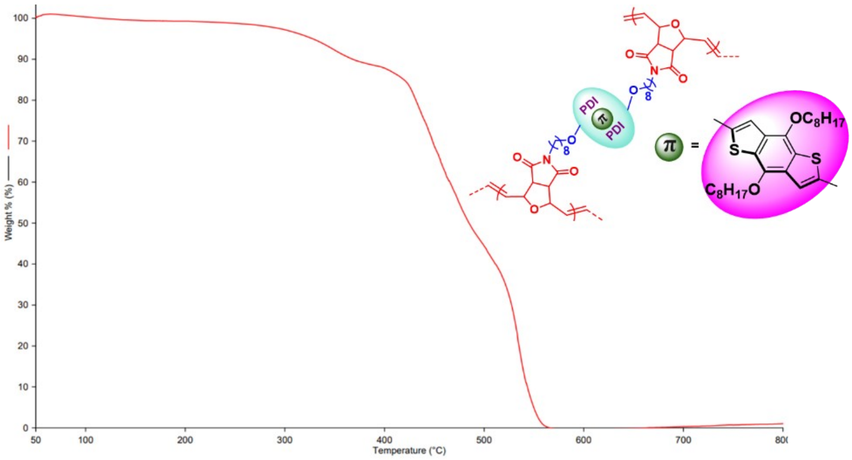


Figure S39. TGA curve of polymer **P4** (heating rate = 10 °C min^{-1})

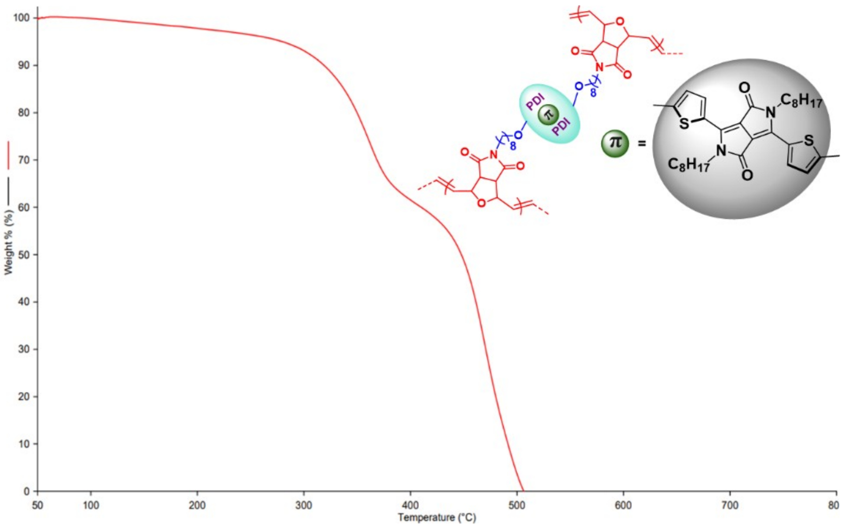


Figure S40. TGA curve of polymer **P5** (heating rate = 10 °C min^{-1})

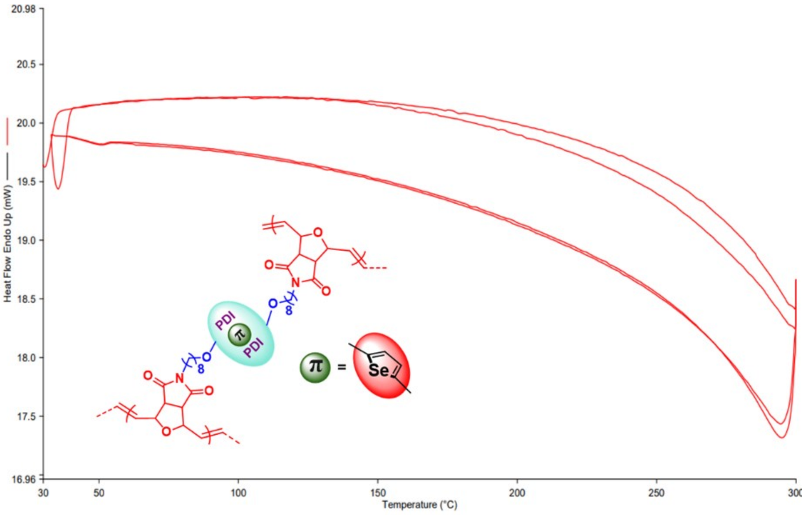


Figure S41. DSC curves of polymer **P1** (heating/cooling rate = 10 °C min^{-1})

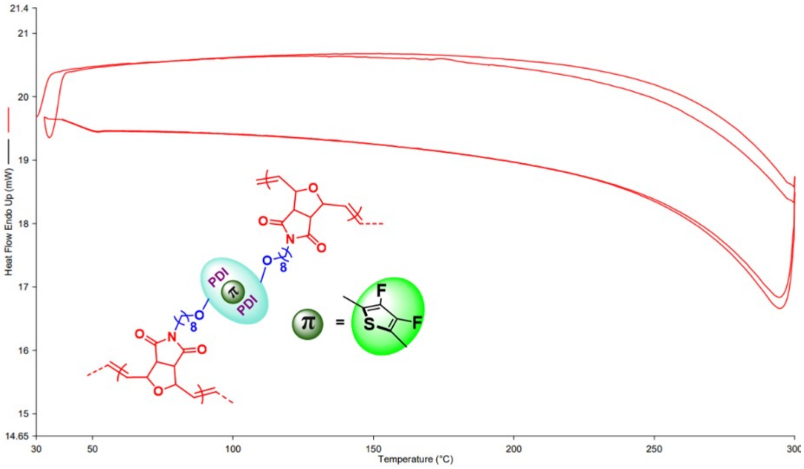


Figure S42. DSC curves of polymer **P2** (heating/cooling rate = 10 °C min^{-1})

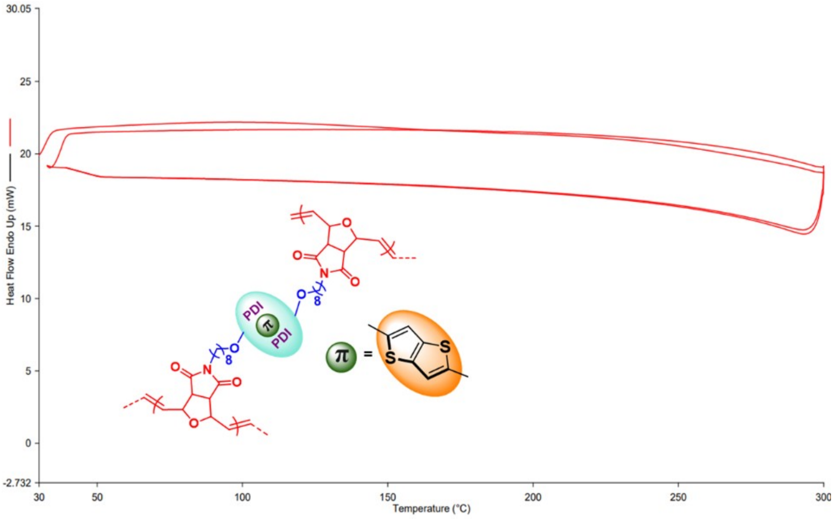


Figure S43. DSC curves of polymer **P3** (heating/cooling rate = 10 ˚C min^{-1})

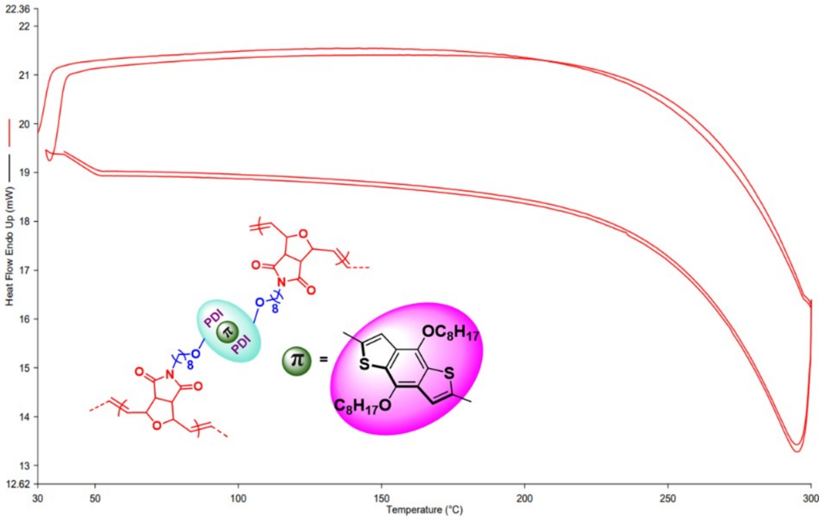


Figure S44. DSC curves of polymer **P4** (heating/cooling rate = 10 ˚C min^{-1})

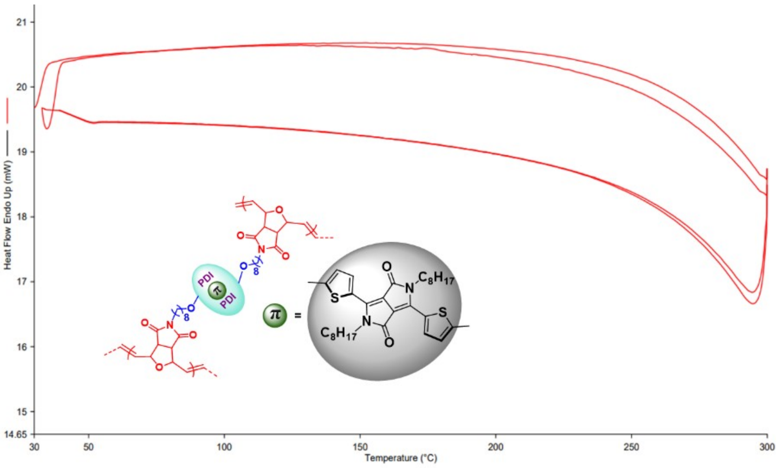


Figure S45. DSC curves of polymer **P5** (heating/cooling rate = 10 ˚C min^{-1})

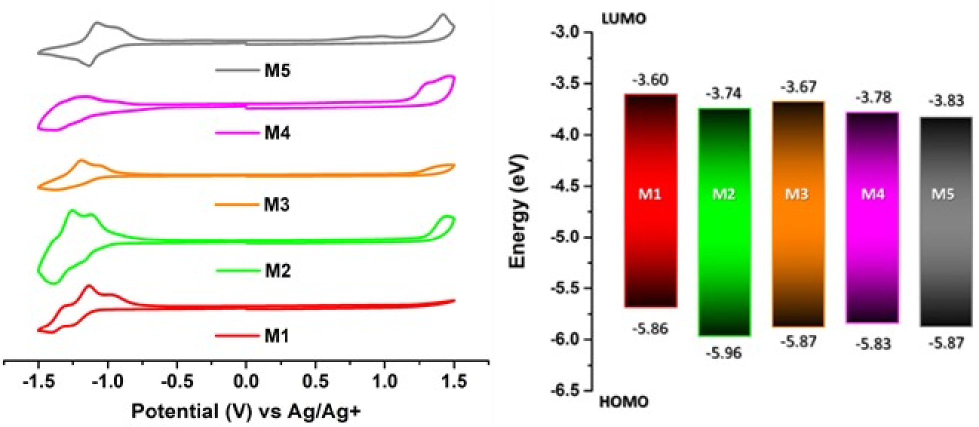


Figure S46. CV traces of monomers **M1** (red), **M2** (green), **M3** (orrange), **M4** (pink), and **M5** (gray); scan rate = 100 mV s.

DFT Calculations

Table S1. Vertical transition energies (E_{vert}/λ_{max} [eV/nm]), oscillator strengths (f), and electronic configurations of the three most pronounced excitations, as calculated by TD-DFT at CAM-B3LYP/6-31+G(d,p)/SMD(C_6H_5Cl) level.[2]

Monomer	Excitation	E_{vert}/χ_{max}	f	Electronic configuration
M1	$S_0 \rightarrow S_2$	2.00 eV/619 nm	0.32	H-1 → L (0.54) (58%); H-2 → L (0.42) (35%)
	$S_0 \rightarrow S_3$	2.26 eV/549 nm	0.65	H → L+3 (0.61) (74%)
	$S_0 \rightarrow S_4$	2.33 eV/533 nm	0.45	H-2 → L (0.44) (39%); H → L+1 (0.42) (35%)
M2	$S_0 \rightarrow S_2$	2.05 eV/605 nm	0.37	H-1 → L (0.50) (50%); H-2 → L (0.44) (39%)
	$S_0 \rightarrow S_3$	2.25 eV/551 nm	0.83	H → L+3 (0.55) (61%); H → L+2 (0.33) (22%)
	$S_0 \rightarrow S_4$	2.44 eV/507 nm	0.35	H → L+1 (0.46) (42%);
M3	$S_0 \rightarrow S_2$	1.99 eV/622 nm	0.34	H → L+2 (0.54) (58%); H → L+1 (0.41) (34%)
	$S_0 \rightarrow S_3$	2.10 eV/590 nm	1.10	H-2 → L (0.44) (39%); H → L+1 (0.37) (27%)
	$S_0 \rightarrow S_4$	2.59 eV/478 nm	0.28	H → L+3 (0.50) (50%)
M4	$S_0 \rightarrow S_2$	2.06 eV/602 nm	0.80	H → L+4 (0.56) (63%)
	$S_0 \rightarrow S_3$	2.10 eV/591 nm	0.62	H-4 → L (0.55) (61%)
	$S_0 \rightarrow S_4$	2.58 eV/480 nm	0.22	H → L+1 (0.45) (41%); H → L+6 (0.41) (34%)
M5	$S_0 \rightarrow S_2$	2.05 eV/605 nm	0.52	H → L+4 (0.45) (41%)
	$S_0 \rightarrow S_3$	2.11 eV/587 nm	0.36	H-4 → L (0.43) (37%); H-2 → L (0.46) (42%)
	$S_0 \rightarrow S_4$	2.44 eV/507 nm	1.23	H-1 → L+2 (0.40) (32%)

H and L represent HOMO and LUMO, respectively. Data in parentheses denote the contributions of the electronic configuration.

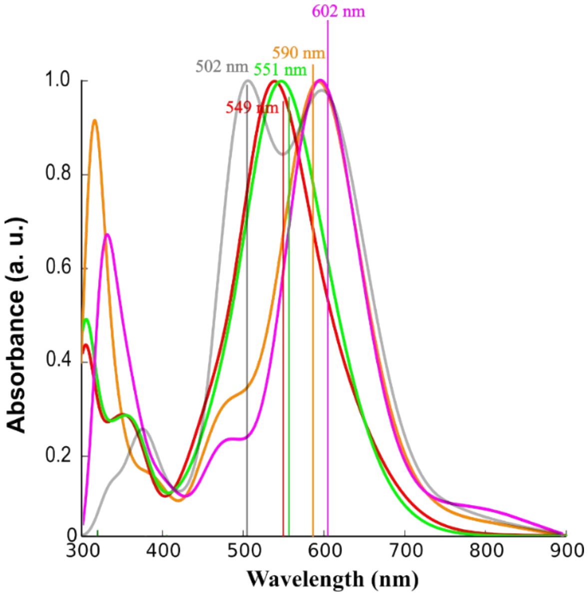


Figure S47. The electronic excitation spectra of **M1-M5** monomers calculated by convolution with full width at a half maximum of 3000 cm^{-1}. The most pronounced excitation for every spectrum is presented. **M1** -red, **M2** - green, **M3** - orange, **M4** - magenta and **M5** - gray.

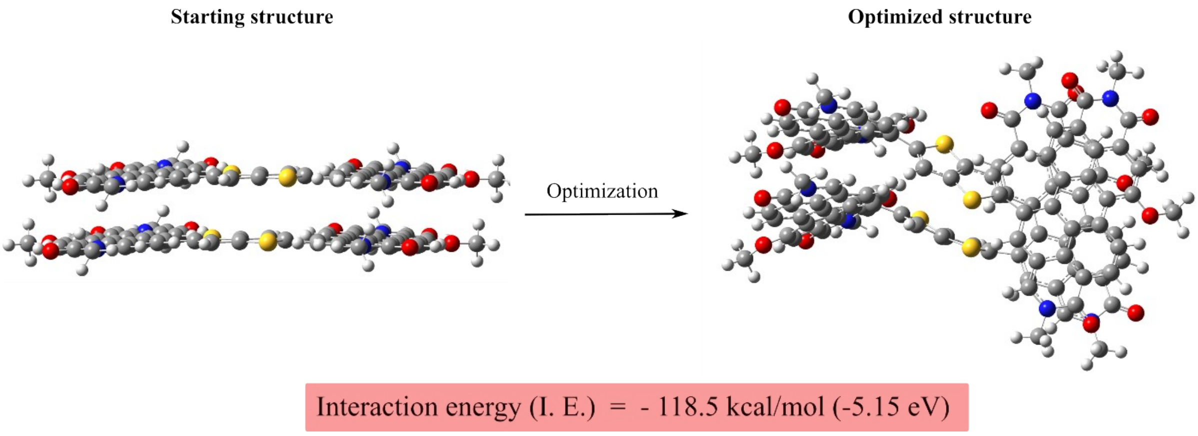
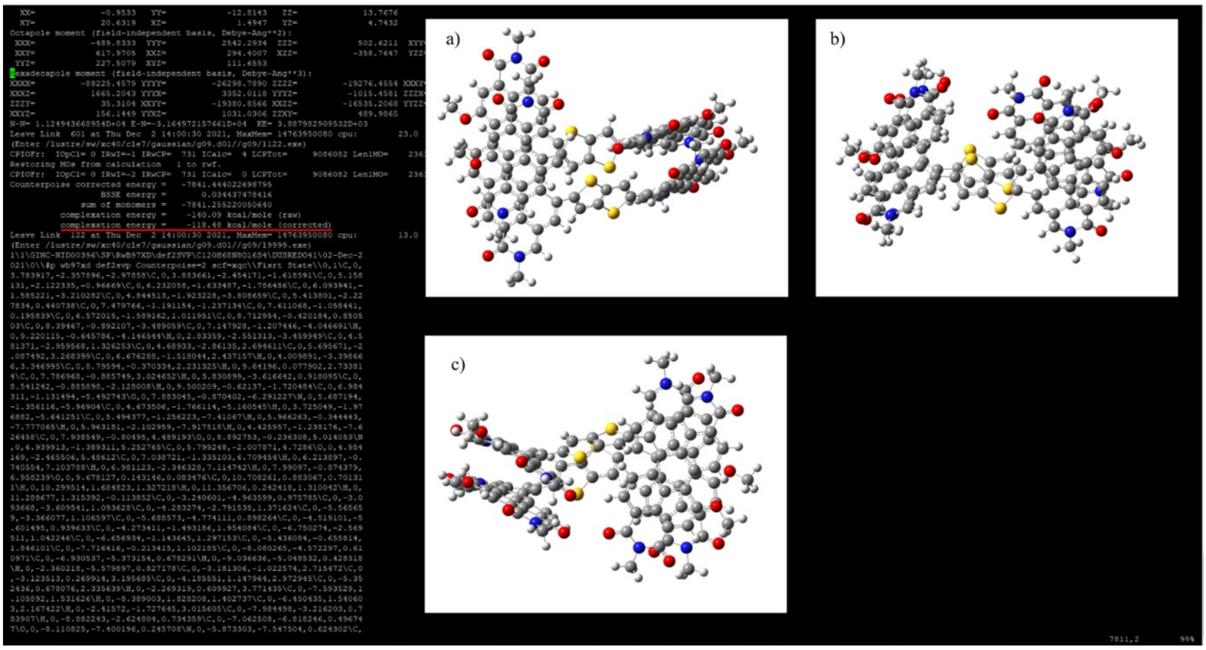


Figure S48. The optimized dimer structure of two **M3** monomers in π-π stacking conformation at wB97xD/6-31G** level of theory.



```
  XX=            -0.9533   YY=            -12.8143   ZZ=             13.7676
  XY=            20.6319   XZ=              1.4947   YZ=              4.7432
 Octapole moment (field-independent basis, Debye-Ang**2):
 XXX=          -489.8333  YYY=           2542.2934  ZZZ=            502.6211  XYY
 XXY=           617.9705  XXZ=            294.4007  XZZ=           -358.7647  YZZ
 YYZ=           227.5079  XYZ=            111.6553
 Hexadecapole moment (field-independent basis, Debye-Ang**3):
 XXXX=        -88225.4579 YYYY=         -26298.7890 ZZZZ=         -19276.4554 XXXY
 XXXZ=          1665.2043 YYYX=           3352.0118 YYYZ=          -1015.4581 ZZZX
 ZZZY=            35.3104 XXYY=         -19380.8566 XXZZ=         -16535.2068 YYZZ
 XXYZ=           156.1449 YYXZ=           1031.0306 ZZXY=            489.9865
 N-N= 1.124943668954D+04 E-N=-3.164972157661D+04  KE= 3.887982909532D+03
 Leave Link  601 at Thu Dec  2 14:00:30 2021, MaxMem= 14763950080 cpu:        23.0
 (Enter /lustre/sw/xc40/cle7/gaussian/g09.d01//g09/l122.exe)
 CPIOFr:  IOpCl= 0 IRwI=-1 IRwCP=  731 ICalc=  4 LCPTot=     9086082 Len1MO=    236
 Restoring MOs from calculation   1 to rwf.
 CPIOFr:  IOpCl= 0 IRwI=-2 IRwCP=  731 ICalc=  0 LCPTot=     9086082 Len1MO=    236
 Counterpoise corrected energy =   -7841.444022698795
                   BSSE energy =       0.034437478416
               sum of monomers =   -7841.255220050640
           complexation energy =    -140.09 kcal/mole (raw)
           complexation energy =    -118.48 kcal/mole (corrected)
 Leave Link  122 at Thu Dec  2 14:00:30 2021, MaxMem= 14763950080 cpu:        13.0
 (Enter /lustre/sw/xc40/cle7/gaussian/g09.d01//g09/l9999.exe)
 1\1\GINC-NID00396\SP\RwB97XD\def2SVP\C120H68N8O16S4\DUSREDO41\02-Dec-2
 021\0\\#p wb97xd def2svp Counterpoise=2 scf=xqc\\Fisrt State\\0,1\C,0,
 3.783917,-2.357896,-2.97858\C,0,3.883661,-2.454171,-1.618591\C,0,5.158
 131,-2.122335,-0.96669\C,0,6.232058,-1.633487,-1.786486\C,0,6.093941,-
 1.585221,-3.210282\C,0,4.844513,-1.923228,-3.808659\C,0,5.413801,-2.22
 7834,0.440738\C,0,7.479766,-1.191154,-1.237134\C,0,7.611068,-1.058441,
 0.195839\C,0,6.572015,-1.589162,1.011951\C,0,8.712954,-0.420184,0.8505
 03\C,0,8.39467,-0.892107,-3.489059\C,0,7.147928,-1.207446,-4.046691\H,
 0,9.220115,-0.645786,-4.146544\H,0,2.83359,-2.551313,-3.459949\C,0,4.5
 81371,-2.959568,1.326253\C,0,4.68933,-2.86135,2.694611\C,0,5.695671,-2
 .087492,3.268399\C,0,6.676288,-1.518044,2.437157\H,0,4.009891,-3.39866
 6,3.346995\C,0,8.79594,-0.370334,2.231325\H,0,9.64196,0.077902,2.73381
 4\C,0,7.786968,-0.885749,3.024652\H,0,3.830899,-3.616642,0.918095\C,0,
 8.541242,-0.885898,-2.128008\H,0,9.500209,-0.62137,-1.720484\C,0,6.984
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 -7.777065\H,0,5.963181,-2.102959,-7.917518\H,0,4.425957,-1.238176,-7.6
 26458\C,0,7.938549,-0.80495,4.489193\O,0,8.892753,-0.236308,5.014053\N
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 740554,7.103788\H,0,6.981123,-2.346328,7.114742\H,0,7.99097,-0.874379,
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 93668,-3.609541,1.093628\C,0,-4.283274,-2.791538,1.371624\C,0,-5.56565
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 0971\C,0,-6.930537,-5.373154,0.678291\H,0,-9.036636,-5.048532,0.428318
 \H,0,-2.360218,-5.579897,0.827178\C,0,-3.181306,-1.022574,2.715472\C,0
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 83907\H,0,-8.882243,-2.624804,0.734359\C,0,-7.062508,-6.818246,0.49674
 7\O,0,-8.110825,-7.400196,0.245708\N,0,-5.873303,-7.547504,0.624302\C,
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Figure S49. The output file with indicated complexation energy value (underlined in red), corrected for BSSE. Three views of two interacting **M3** monomer.

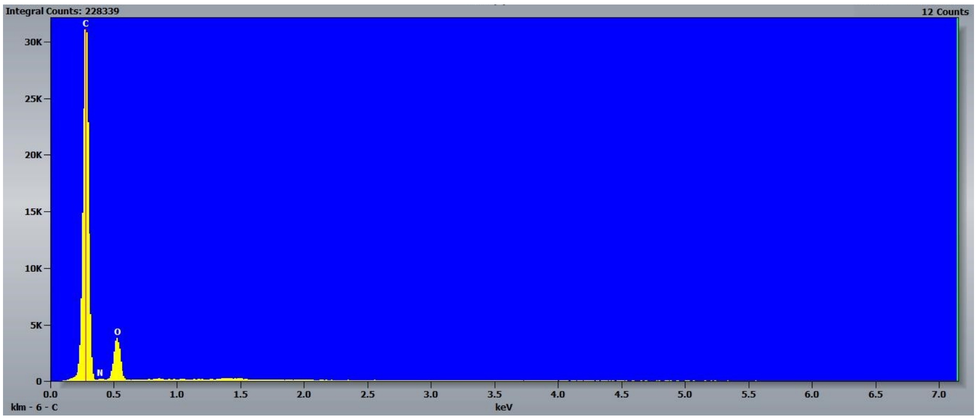

Figure S50. EDS analysis of **P1**, no residual catalyst contamination was detected except major elemental composition in the polymer.

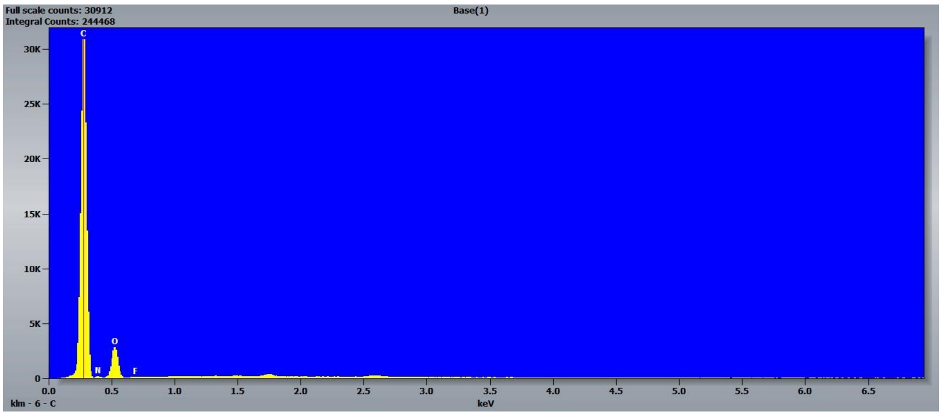

Figure S51. EDS analysis of **P2**, no residual catalyst contamination was detected except major elemental composition in the polymer.

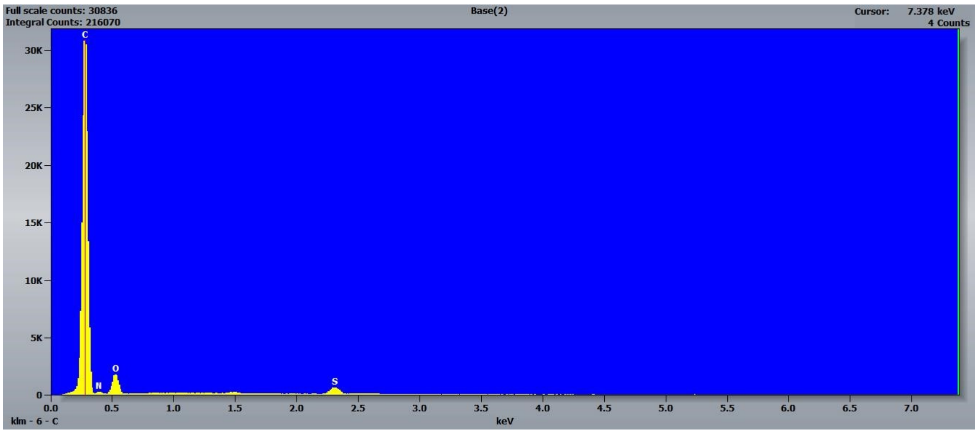

Figure S52. EDS analysis of **P3**, no residual catalyst contamination was detected except major elemental composition in the polymer.

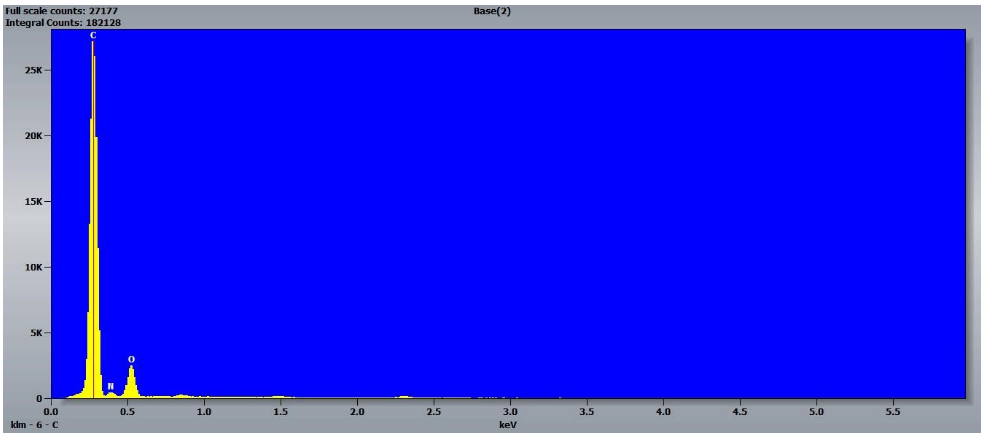

Figure S53. EDS analysis of **P4**, no residual catalyst contamination was detected except major elemental composition in the polymer.

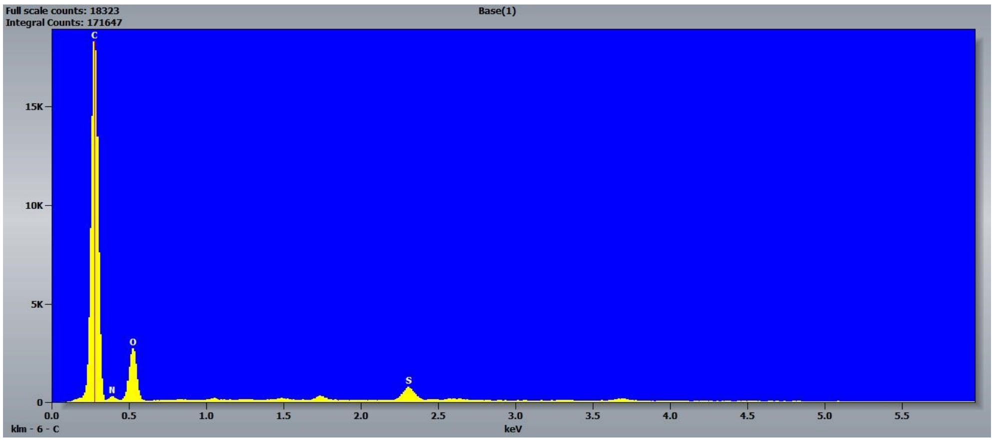

Figure S54. EDS analysis of **P5**, no residual catalyst contamination was detected except major elemental composition in the polymer.

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