Supporting Information for

Indacenodithiophene Homopolymers via Direct Arylation: Direct Polycondensation versus Polymer Analogous Reaction Pathways

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Experimental section

General measurement and characterization

NMR spectroscopy. NMR spectra were recorded on a Bruker DPX 250 spectrometer (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), on a Bruker AVANCE 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz) and on a Bruker AVANCE III 500 spectrometer (^{1}H: 500 MHz, ^{13}C: 125.8 MHz). $CDCl_3$ (at 30 °C) was used as solvent. The spectra were referenced to the residual solvent peak ($CDCl_3$: $\delta(^{1}H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.0 ppm). Chemical shifts (δ) are reported in ppm.

Size exclusion chromatography. SEC measurements of all samples were carried out on four SDplus 10^4 Å 5 µm columns with pore sizes ranging from 10^3 to 10^6 Å (Polymer Standards), connected in series with a RID20A RI detector and a SPD20AV UV detector (Shimadzu) calibrated with polystyrene standards. THF was used as eluent at 40 °C with a flow rate of 1.0 mL/min.

UV-vis spectroscopy. UV-vis spectra were recorded at 25 °C on a Cary 60 UV-Vis (Agilent Technologies) in chloroform solutions (c = 0.02 mg/mL).

Photoluminescence. PL spectra were recorded at 25 °C with a xenon flash lamp and a Czerny Turner monochromator in chloroform solutions (c = 0.02 mg/mL).

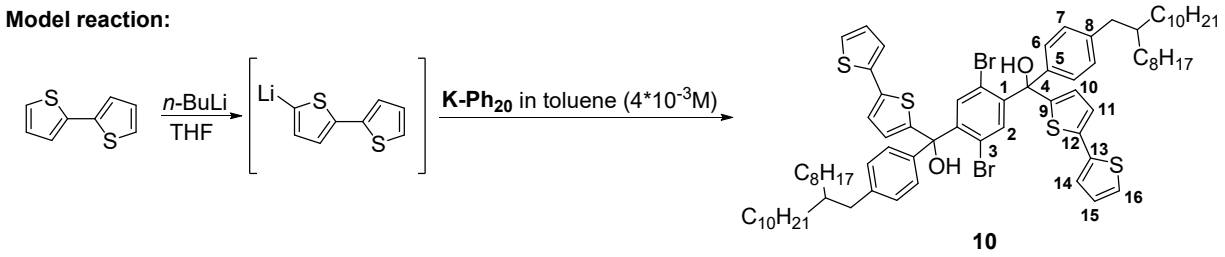
Infrared spectroscopy. IR spectra were obtained at 25 °C on a FTS 165 spectrometer (BIO-RAD) equipped with a Golden Gate single ATR accessory from LOT-Oriel GmbH.

Differential scanning calorimetry. DSC measurements were carried out on a DSC 2500 (TA Instruments) under nitrogen atmosphere. Heating and cooling rates were 20 K/min. The mass of the samples for each measurement was approximately 2-5 mg.

Thermogravimetric analysis. TGA measurements were done on a TGA/DSC3+ from Mettler-Toledo within the temperature range 50 °C to 650 °C at a heating rate of 20 K/min under N_2.

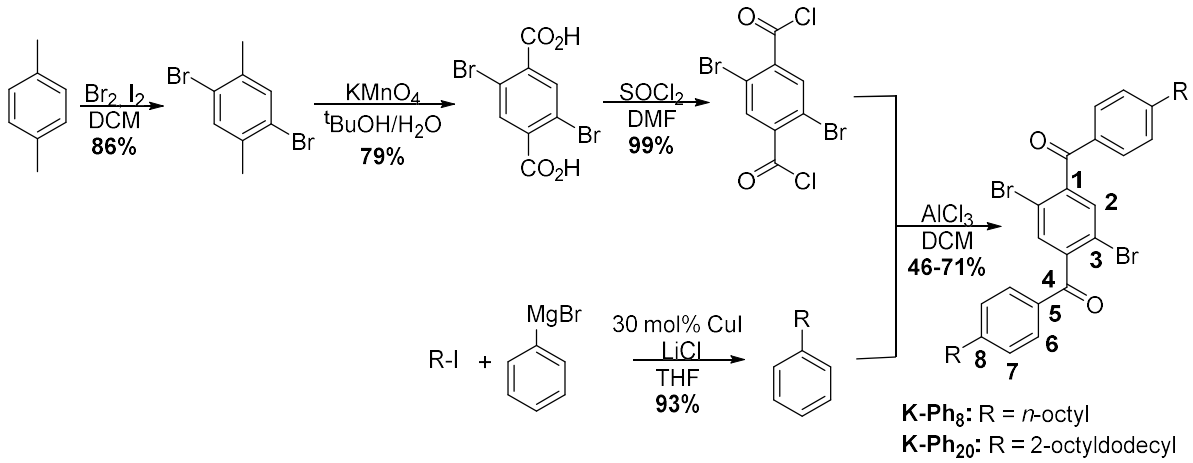
Organic field effect transistors. A top-gate bottom-contact configuration with interdigitated Au source and drain contacts was prepared with a lift-off photolithographic process onto glass substrates and subsequently cleaned in a sonication bath in acetone and isopropanol. Solutions of the IDT copolymers (5 mg/ml in *o*-dichlorobenzene) were spin-coated at ambient conditions at 2000 rpm for 60 seconds. Following semiconductor deposition, CYTOP was spin-coated on top to obtain a ~600 nm thick dielectric layer. 40 nm thick Al gate contacts were finally evaporated with a shadow mask and the devices were measured in a nitrogen-filled glovebox on a Wentworth Laboratories probe station with an Agilent B1500A semiconductor device analyzer.

Scheme S1. Synthesis of model compound **10**.



*Synthesis of model compound **10**.* To a solution of 2, 2'-bithiophene (355.6 mg, 2.14 mmol. 8 eq) in 4 mL tetrahydrofuran was added n-butyl lithium (0.7 mL, 1.71 mmol, 2.5 M, 6.4 eq) at -78 °C. The reaction solution was stirred for 1.5 h at -78 °C and warmed to room temperature. Then compound **K-Ph$_{20}$** (268 mg, 0.27 mmol, 1 eq) in 5 mL toluene was added dropwisely. After stirring for 16 h at room temperature the reaction mixture was quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (PE:DCM, 1:1) to afford **10** as a solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.24 (s, 2H; 2), 7.23 (d, 7.9 Hz, 4H; 6), 7.20 (d, 5.1 Hz, 2H; 16), 7.16 (d, 3.6 Hz, 2H; 14), 7.15 (d, 7.9 Hz, 4H; 7), 7.02 (d, 3.7 Hz, 2H; 11), 7.00 (dd, 5.1 Hz, 3.6 Hz, 2H; 15), 6.53 (d, 3.7 Hz, 2H; 10), 4.46 (s, 2H; OH), 2.55 (d, 6.9 Hz, 4H; Ar-CH_2), 1.62 (m, 2H; CH), 1.4 – 1.1 (64H; 16 x CH_2 of R^1), 0.87 (t, 6.5 Hz, 12H; 2 x CH_3 of R^1). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.3 (9), 145.9 (1), 142.0 (8), 141.2 (5), 138.1 (12), 137.3 (13), 136.9 (2), 129.2 (7), 127.9 (10), 127.8 (15), 127.0 (6), 124.5 (16), 123.8 (14), 122.9 (11), 121.2 (3), 81.0 (4), 40.3 (Ar-CH_2), 39.6 (CH), 33.3, 31.9, 30.0, 29.6, 29.4, 26.6 and 22.7 (CH_2 of R^1), 14.1 (CH_3).

Scheme S2. Synthesis of keto monomer **K (2,5-dibromo-1,4-phenylenebis[(4-alkylphenyl)methanone]).**



*Synthesis of 2,5-dibromo-1,4-phenylenebis[(4-octylphenyl)methanone] (**K-Ph$_8$**)*. To a solution of 2,5-dibromotherephthaloyl dichloride (140 mg, 0.4 mmol, 1 eq) and aluminum chloride (125 mg, 0.9 mmol, 2.4 eq) in 0.5 mL dichloromethane, *n*-octylbenzene (307 mg, 1.6 mmol, 4 eq) was added dropwisely in 1 mL dichloromethane at 0 °C. After stirring overnight at room temperature, the mixture was poured onto ice/1 M HCl, extracted with dichloromethane, washed with sat. $NaHCO_3$ solution and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was recrystallized from *iso*-hexanes to afford **K-Ph$_8$** as colourless crystals (119 mg, 178 µmol, 46 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.76 (d, 8.1 Hz, 4H; 6), 7.58 (s, 2H; 2), 7.32 (d, 8.1 Hz, 4H; 7), 2.70 (t, 7.7 Hz, 4H; α-CH_2), 1.66 (m, 4H; β-CH_2), 1.4-1.2 (20H; 5 x CH_2 of R), 0.89 (t, 6.9 Hz, 6H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 193.4 (4), 150.6 (8), 143.4 (1), 132.9 (5), 132.9 (2), 130.5 (6), 130.0 (7), 118.4 (3), 36.2 (α-CH_2), 31.8, 31.0, 29.4, 29.3, 29.2 and 22.6 (CH_2 of R), 14.1 (CH_3).

Synthesis of 2,5-dibromo-1,4-phenylenebis[(4-(2-octyldodecyl)phenyl)methanone] ***(K-Ph$_{20}$).*** Preparation similar to **K-Ph$_8$**. The crude product was purified by column chromatography (PE:DCM, 1:1) to afford **K-Ph$_{20}$** as colourless oil. Yield: 71 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.77 (d, 4H), 7.6 (s, 2H), 7.29 (d, 4H), 2.63 (d, 4H), 1.68 (m, 2H), 1.26 (64H), 0.89 (t, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 193.6, 150.0, 143.5, 133.1, 133.0, 130.5, 129.9, 118.6, 41.1, 39.7, 33.4, 32.1, 30.1, 29.8, 29.7, 29.5, 26.7, 22.8, 14.3.

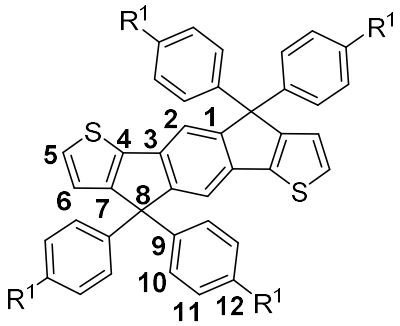
Synthesis of 2,5-di(thiophen-2-yl)-1,4-phenylenebis[(4-octylphenyl)methanone] ***(1)****.*

Compound **K-Ph$_8$** (380 mg, 0.6 mmol, 1 eq), potassium carbonate (236 mg, 1.7 mmol, 3 eq) and pivalic acid (58.1 mg, 0.6 mmol, 1 eq) were weight into a Schlenk tube and dissolved in 6 mL degassed THF. Then degassed thiophene (957 mg, 0.9 mL, 11.4 mmol, 20 eq) and PCy_3 Pd G2 (16.8 mg, 5 mol%) were added. After stirring for 72 h at 100 °C, the reaction mixture was allowed to cool to room temperature, filtered and the solvent was removed under reduced pressure. The crude product was recrystallized from *iso*-hexanes to afford **1** as yellow crystals (148 mg, 0.3 mmol, 48 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.70 (d, 4H), 7.62 (s, 2H), 7.17 (m, 6H), 7.00 (dd, 2H), 6.85 (dd, 2H), 2.61 (t, 4H), 1.60 (m, 4H), 1.27 (20H), 0.88 (t, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 197.5, 149.7, 140.5, 140.1, 134.3, 132.0, 130.3, 129.6, 128.6, 128.1, 127.8, 126.9, 36.2, 31.9, 31.0, 29.5, 29.3, 22.8, 14.2.

Synthesis of 1-bromo-4-(2-octyldodecyl) benzene. To a mixture of 2-octyldodecyliodide (5.77 g, 14.1 mmol, 1 eq), copper(I) iodide (0.81 g, 30 mol%) and lithium chloride (1.20 g, 28.26 mmol, 2 eq) was added dropwisely 45 mL 4-bromophenyl magnesium bromide in dry THF (42.39 mmol, 1 M, 3 eq) at 0 °C. After stirring overnight, the mixture was quenched with 1 M hydrochloride acid, extracted with diethyl ether and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (petroleum

ether) to afford the title compound as colourless oil (3.7 g, 8.6 mmol, 61 %). ^{1}H NMR (250 MHz, $CDCl_3$, *δ*): 7.37 (d, 2H), 7.00 (d, 2H), 2.47 (d, 2H), 1.58 (m, 1H), 1.25 (32H), 0.88 (t, 6H). ^{13}C NMR (63 MHz, $CDCl_3$, δ): 141.2, 131.4, 131.3, 119.5, 39.4, 33.4, 32.3, 30.3, 30.0, 29.7, 27.3, 26.9, 23.0, 14.4.

Synthesis of compound ***IDT-Ph$_8$***. To a solution of 1-bromo-4-octylbenzene (119 mg, 444 µmmol, 3 eq) in 2 mL THF at -78 °C was added *n*-butyl lithium (0.2 mL, 459 µmol, 2.5 M, 3.1 eq). After stirring at -78 °C for 1 h, compound **1** (100 mg, 148 µmol, 1 eq) in 1 mL THF was added slowly. The reaction mixture was stirred overnight and then quenched with sat. sodium chloride solution, extracted with ethyl acetate and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in octane/acetic acid (1:1, v/v). After the addition of sulfuric acid (0.1 mL in 0.5 mL acetic acid) the mixture was stirred under reflux (125 °C) for 30 min. Then the greenish reaction mixture was extracted with dichloromethane, washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (petroleum ether) to afford **IDT-Ph$_8$** as yellow crystals (80 mg, 78.5 µmol, 53 %). ^{1}H NMR (250 MHz, $CDCl_3$, *δ*): 7.45 (s, 2H), 7.25 (d, 2H), 7.17 (d, 8H) 7.06 (d, 8H), 7.01 (d, 2H), 2.57 (d, 8H), 1.60 (m, 8H), 1.29 (40H), 0.89 (m, 12H). ^{13}C NMR (63 MHz, $CDCl_3$, *δ*): 155.9, 153.4, 142.1, 141.4, 135.1, 128.3, 127.9, 127.4, 123.2, 117.5, 62.7, 35.6, 31.9, 31.4, 29.5, 29.3, 22.7, 14.2.



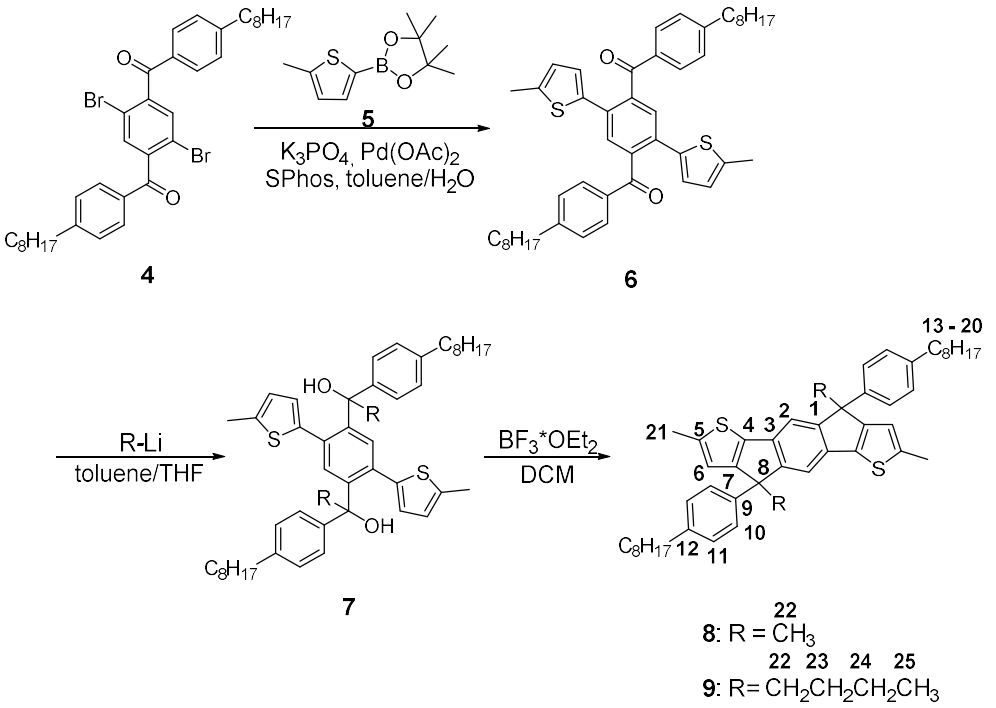
IDT-Ph$_{20}$

13 14

$R^1 = CH_2\text{-}CH(C_8H_{17})C_{10}H_{21}$

*Synthesis of compound **IDT-Ph$_{20}$**.* Preparation similar to **IDT-Ph$_8$** using 1-bromo-4-(2-octyldodecyl) benzene as starting material. Yield: 15 %, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.43 (s, 2H; 2), 7.23 (d, 4.9 Hz, 2H; 6), 7.14 (d, 8.4 Hz, 8H; 10), 7.00 (10H; 5 and 11), 2.47 (d, 6.9 Hz, 8H; 13), 1.57 (m, 4H; 14), 1.4 – 1.1 (128H; 16 x CH_2 of R^1), 0.87 (t, 6.5 Hz, 24H; 2 x CH_3 of R^1). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 155.9 (7), 153.4 (1), 142.0 (9), 141.2 (4), 140.2 (12), 135.1 (3), 129.0 (11), 127.7 (10), 127.2 (5), 123.2 (6), 117.5 (2), 62.7 (8), 40.2 (13), 39.4 (14), 33.2, 31.9, 30.0, 29.6, 29.4, 26.6 and 22.7 (CH_2 of R^1), 14.1 (CH_3).

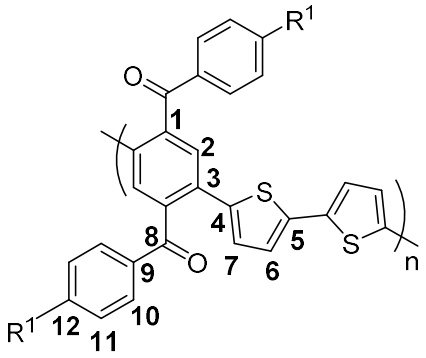
Scheme S3. Synthesis of model compounds **8** and **9**.



*Synthesis of model compound **8***. To a solution of compound **6** (150 mg, 0.21 mmol, 1 eq) in 10 mL toluene at room temperature was added methyl lithium (1.1 mL, 1.71 mmol, 1.6 M, 8 eq) and after 30 minutes 3 mL THF was added. After stirring for 3 h at room temperature the reaction mixture was quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in dichloromethane. After the addition of boron trifluoride diethyl etherate (0.5 mL, 575 mg, 4.05 mmol, 19 eq), the mixture was stirred for 3 h at room temperature and then quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (PE:DCM, 4:1) to afford **8** as yellow solid (69 mg, 0.1 mmol, 46 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.2-7.15 (6H; 2 and 10), 7.06 (d, 8.0 Hz, 4H; 11), 6.56 (m, 2H; 6), 2.55 (t,

7.8 Hz, 4H; 13), 2.49 (d, 2.0 Hz, 6H; 21), 1.83 (s; 22), 1.58 (m, 4H; 14), 1.4 – 1.2 (20H; 15-19), 0.88 (t, 7.0 Hz, 6H; 20). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.5 (7), 155.2 (1), 142.4 (5), 141.2 (9), 141.0 (12), 138.4 (4), 134.6 (3), 128.4 (11), 126.1 (10), 119.9 (6), 114.2 (2), 52.7 (8), 35.5 (13), 31.9 (18), 31.4 (14), 29.5 and 29.2 (15,16,17), 24.5 (22), 22.7 (19), 16.3 (21), 14.1 (20). Two signals appear for several positions due to the presence of two diastereomers.

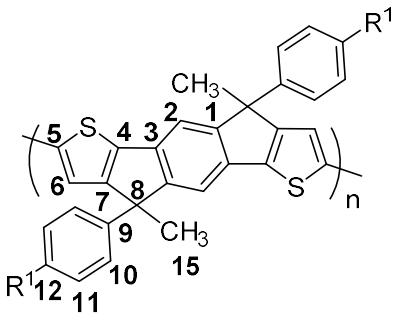
Synthesis of model compound ***9***. To a solution of compound **6** (150 mg, 0.21 mmol, 1 eq) in 10 mL toluene at room temperature was added *n*-butyl lithium (0.7 mL, 1.71 mmol, 2.5 M, 8 eq) and after 30 minutes 3 mL THF was added. After stirring for 3 h at room temperature the reaction mixture was quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in dichloromethane. After the addition of boron trifluoride diethyl etherate (0.5 mL, 575 mg, 4.05 mmol, 19 eq) the mixture was stirred for 3 h at room temperature and then quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (PE:DCM, 4:1) to afford **9** as yellow oil (26 mg, 0.1 mmol, 16 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20 and 7.18 (two d, 8.3 Hz, 4H; 10), 7.15 and 7.14 (two s, 2H; 2), 7.07 and 7.05 (two d, 8.3 Hz, 4H; 11), 6.58 (m, 2H; 6), 2.54 (t, 7.8 Hz, 4H; 13), 2.53 (s, 6H; 21), 2.41 and 2.17 (m, 4H; 22), 1.58 (m, 4H; 14), 1.4 – 1.1 (24H; 15-19,24), 0.95 (m, 4H; 23), 0.88 (t, 7.0 Hz, 6H; 20), 0.78 (t, 7.2 Hz, 6H; 25). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 155.2 (7), 153.5 (1), 141.9 (5), 141.0 (9,12), 139.6 (4), 135.1 (3), 128.4 (11), 126.4 (10), 120.8 (6), 114.1 (2), 57.1 (8), 37.8 (22), 35.5 (13), 31.9 (18), 31.3 (14), 29.5 and 29.2 (15,16,17), 26.8 (23), 23.1 (24), 22.7 (19), 16.4 (21), 14.1 (20), 13.9 (25). Two signals appear for several positions due to the presence of two diastereomers.



$R^1 = CH_2\text{-}CH(C_8H_{17})C_{10}H_{21}$

P(K-*alt*-T2)

NMR data of **P(K-*alt*-T2)** (entry 19): ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.67 (d, 8.2 Hz, 4H; 10), 7.53 (s, 2H; 2), 7.11 (d, 8.2 Hz, 4H; 11), 6.83 (d, 3.6 Hz, 2H; 7), 6.78 (d, 3.6 Hz, 2H; 6), 2.52 (d, 4H; 13), 1.58 (m, 4H; 14), 1.4 – 1.1 (64H; 16 x CH_2 of R^1), 0.86 (12H; 2 x CH_3 of R^1). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 197.0 (8), 148.9 (12), 140.1 (2), 139.1 (4) 138.2 (5), 134.0 (9), 131.3 (3), 130.0 (10), 129.4 (11), 129.2 (3), 128.7 (7), 124.6 (6), 40.6 (13), 39.4 (14), 33.1, 31.9, 29.9, 29.6, 29.4, 26.6 and 22.7 (CH_2 of R^1), 14.1 (CH_3).



13 14

$R^1 = CH_2\text{-}CH(C_8H_{17})C_{10}H_{21}$

$P1^A$-Me/Ph_{20}

NMR data of **$P1^A$-Me/Ph_{20}**. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25-7.1 (2 and 10), 7.04 (11), 6.98 (6), 2.47 (13), 1.87 (15), 1.58 (14), 1.4 – 1.0 (16 x CH_2 of R^1), 0.86 (2 x CH_3 of R^1). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.7 (7), 155.9 (1), 141.5 – 140.0 (5,9,12), 139.5 (4), 134.6 (3), 129.3 (11), 125.9 (10), 117.6 (6), 114.6 (2), 52.9 (8), 40.1 (13), 39.4 (14), 33.1, 31.9, 30.0, 29.6, 29.4, 26.3 and 22.7 (CH_2 of R^1), 24.8 and 24.6 (15), 14.1 (CH_3).

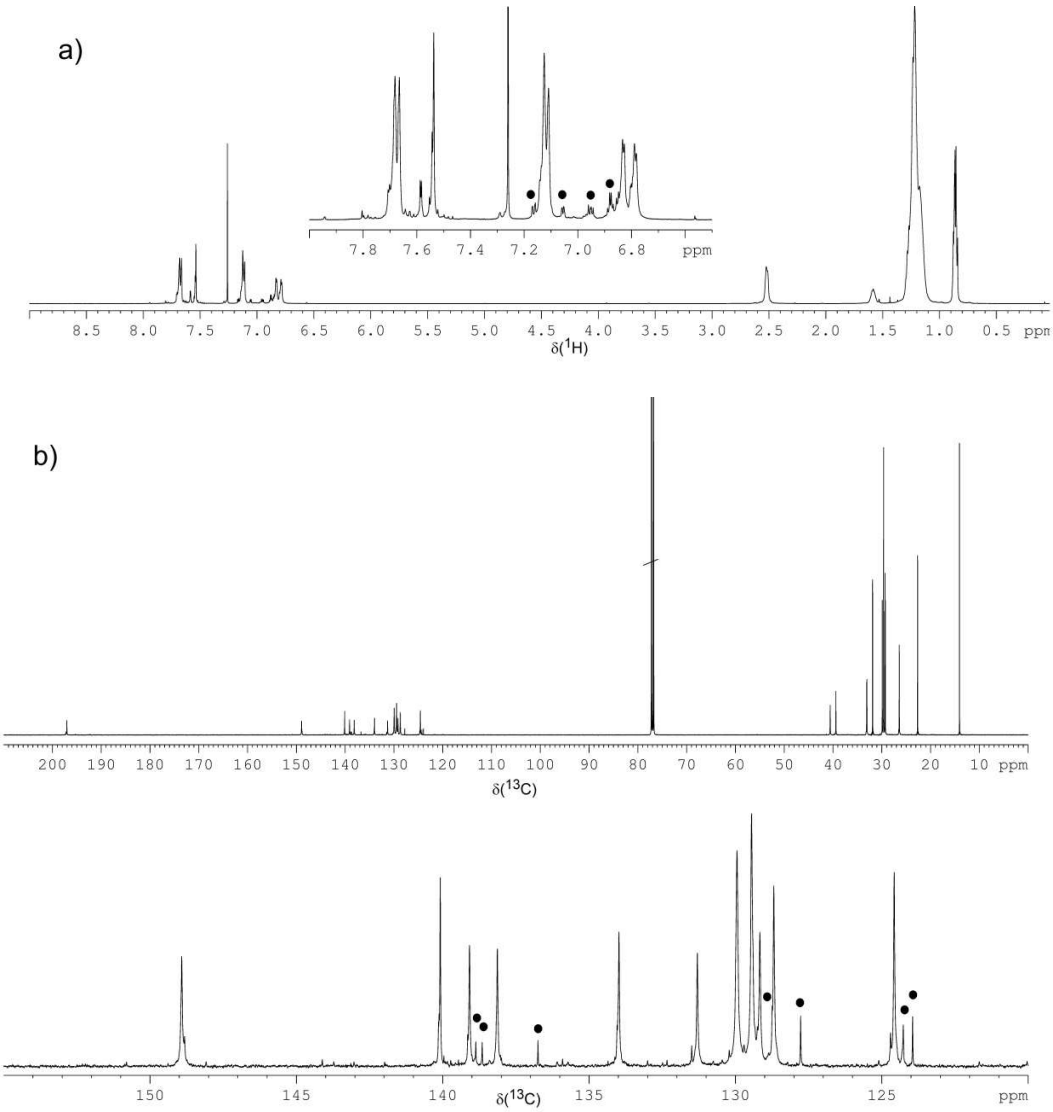


Figure S1. ^{1}H NMR (top) and ^{13}C NMR spectrum (bottom) of **P(K-*alt*-T2)**, entry 19, in $CDCl_3$. The dots mark signals of the –T2H end group.

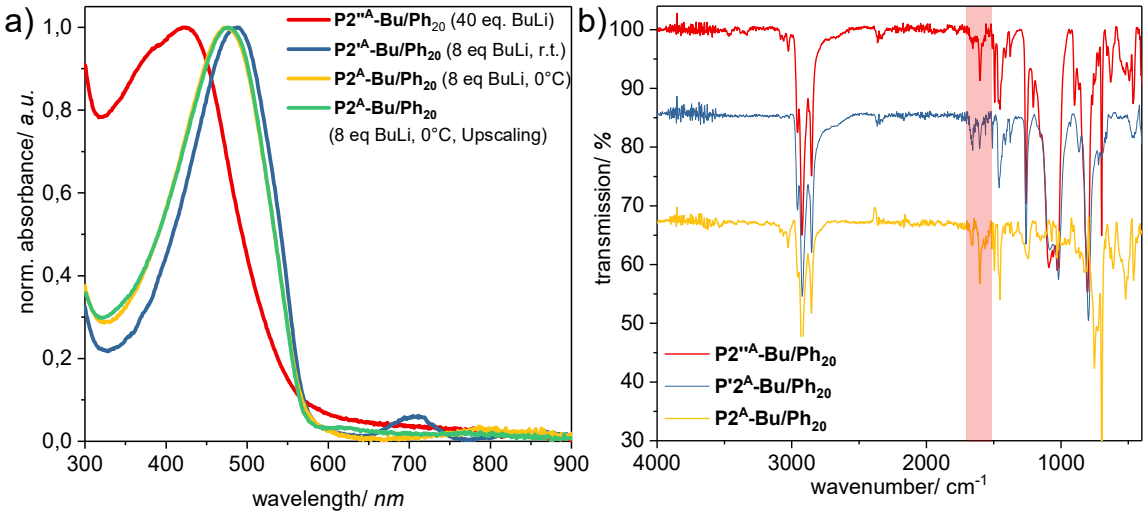


Figure S2. UV-vis (a) and IR spectra (b) of butyl derivatives **P2^{A}-Bu/Ph$_{20}$** synthesized under different reaction conditions.

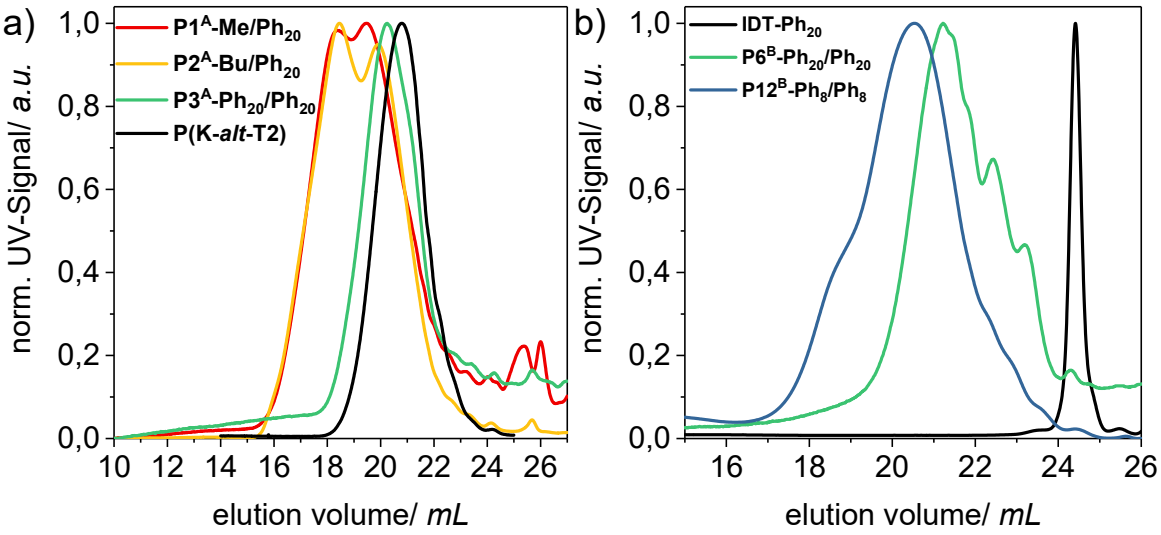


Figure S3. SEC curves of **PIDT**s via route A (**P1^{A}-Me/Ph$_{20}$**, **P2^{A}-Bu/Ph$_{20}$**, **P3^{A}-Ph$_{20}$/Ph$_{20}$**) (a) and via route B (**P6^{B}-Ph$_{20}$/Ph$_{20}$**, **P12^{B}-Ph$_{8}$/Ph$_{8}$**) (b).

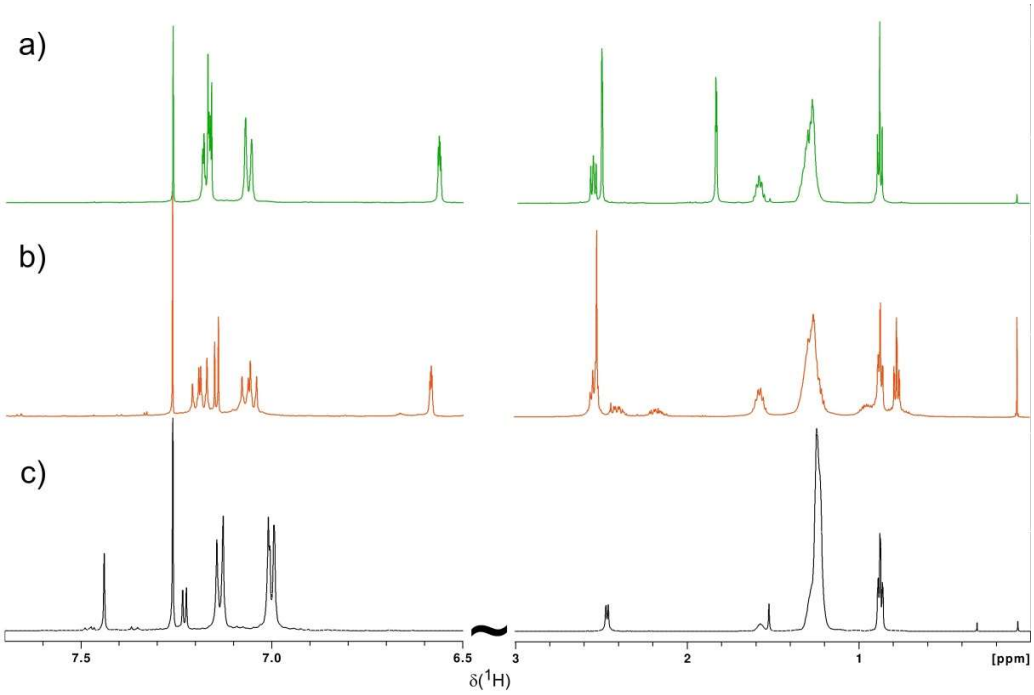


Figure S4. ^{1}H NMR spectra of model compound **8** (a), **9** (b) and monomer **IDT-Ph$_{20}$** (c) in $CDCl_3$.

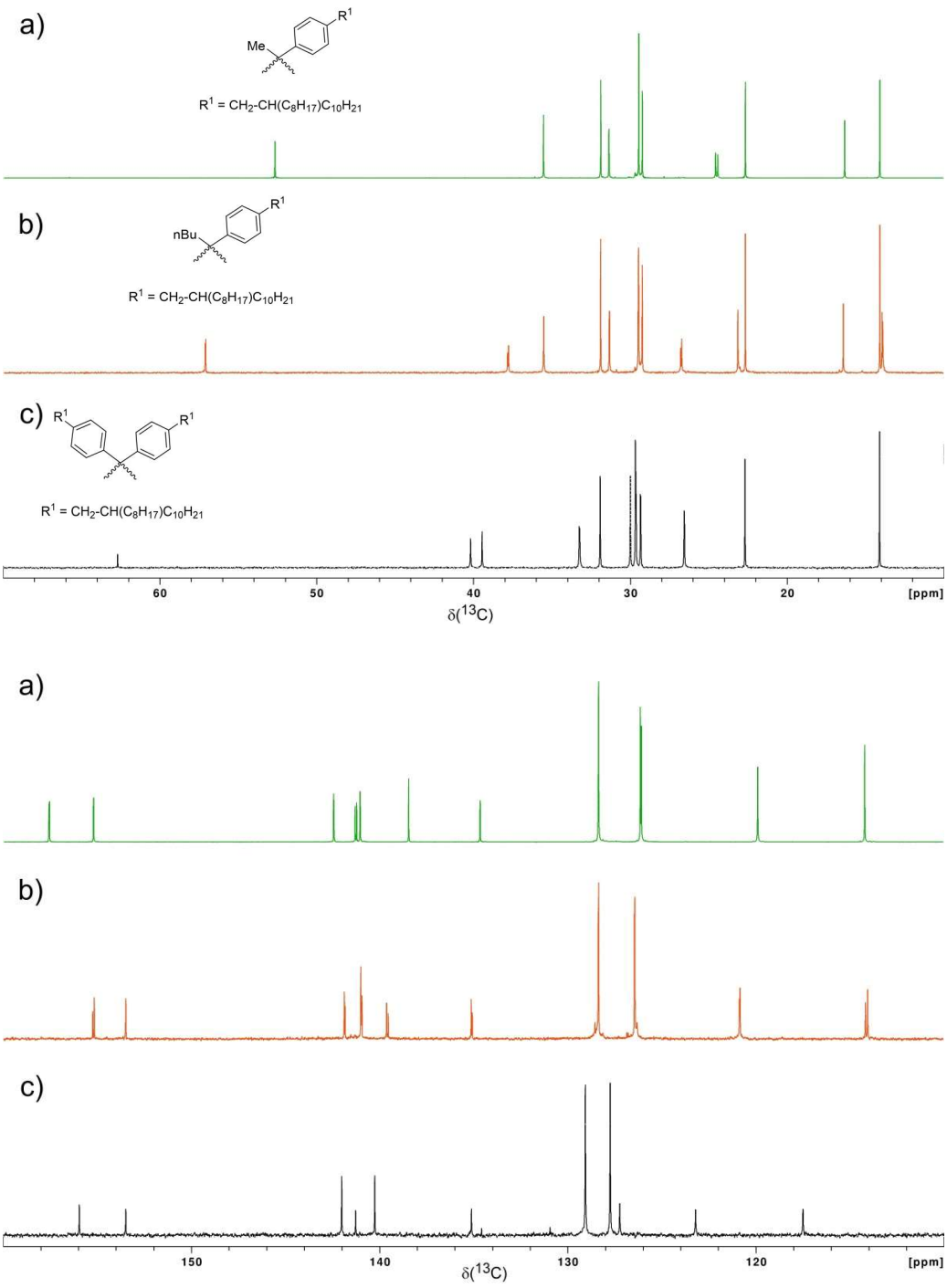


Figure S5. ^{13}C NMR spectra (aliphatic (top) and aromatic carbons' region (bottom)) of model compound **8** (a), **9** (b) and monomer **IDT-Ph$_{20}$** (c) in $CDCl_3$.

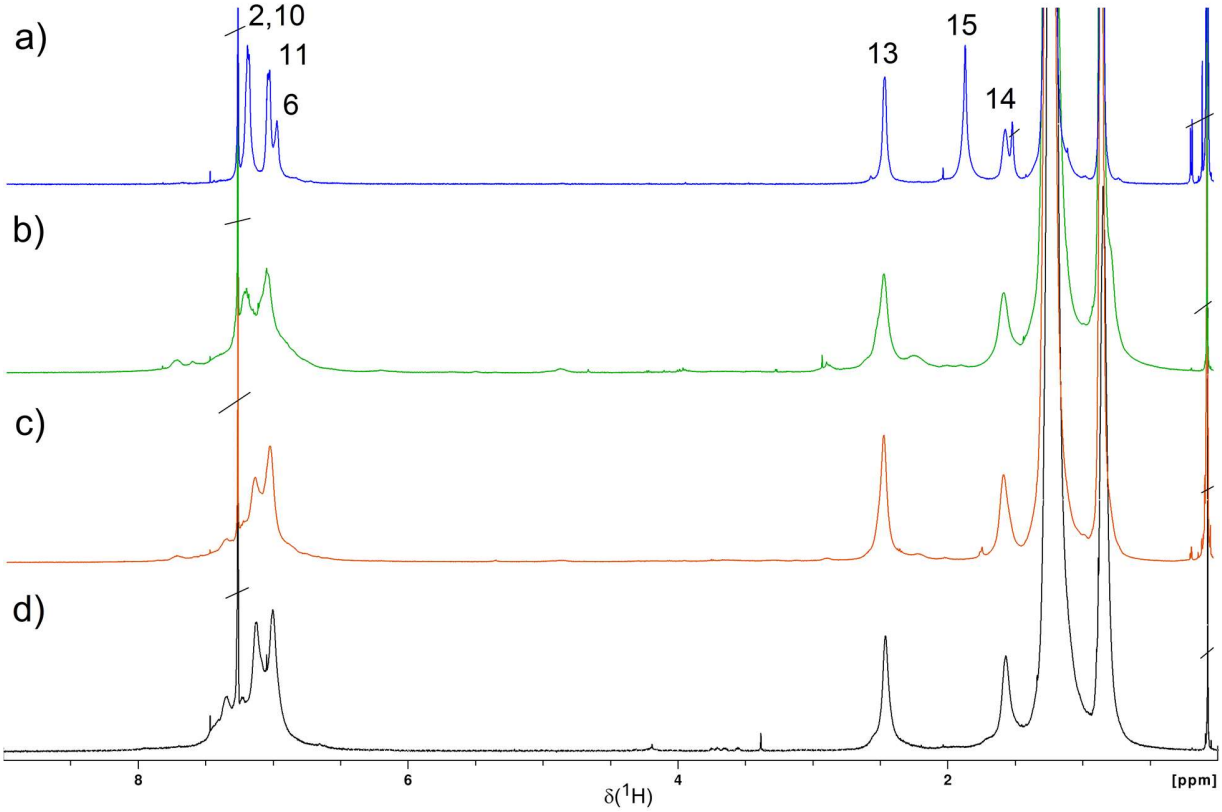


Figure S6. ^{1}H NMR spectra of **PIDT** polymers **P1^{A}-Me/Ph$_{20}$** (a), **P2^{A}-Bu/Ph$_{20}$** (b), **P3^{A}-Ph$_{20}$/Ph$_{20}$** (c) and **P11^{B}-Ph$_{20}$/Ph$_{20}$** (d) in $CDCl_3$.

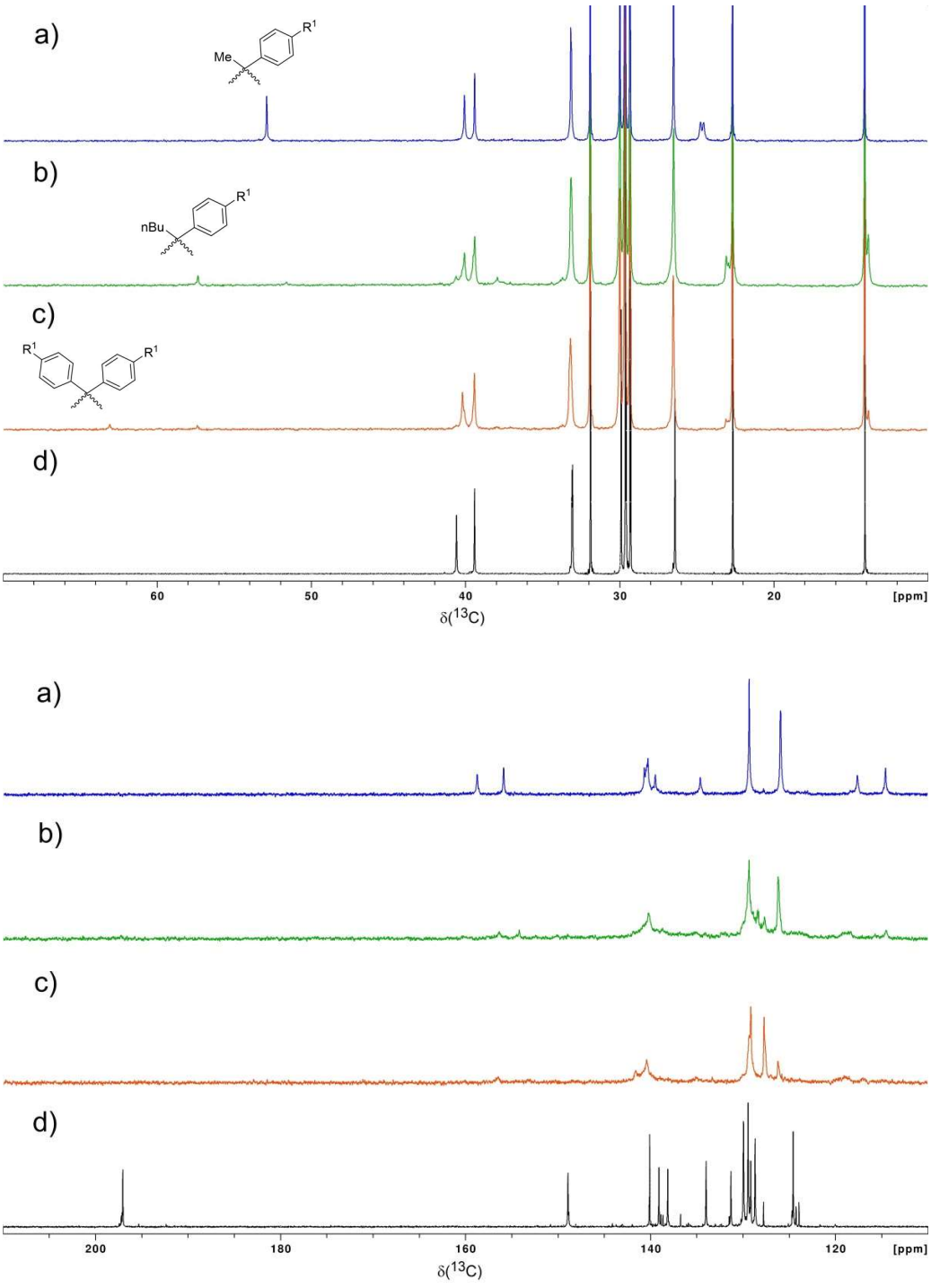


Figure S7. ^{13}C NMR spectra (aliphatic (top) and aromatic carbons' region (bottom)) of **PIDT** polymers **P1^{A}-Me/Ph$_{20}$** (a), **P2^{A}-Bu/Ph$_{20}$** (b), **P3^{A}-Ph$_{20}$/Ph$_{20}$** (c) and **P(K-*alt*-T2)**, entry 19, (d) in $CDCl_3$. R^1 = 2-octyldodecyl.

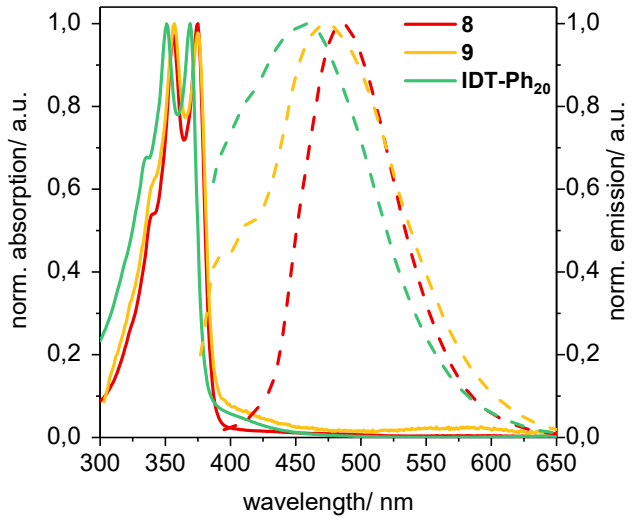


Figure S8. UV-vis and emission spectra of model compounds **8**, **9** and monomer **IDT-Ph$_{20}$**.

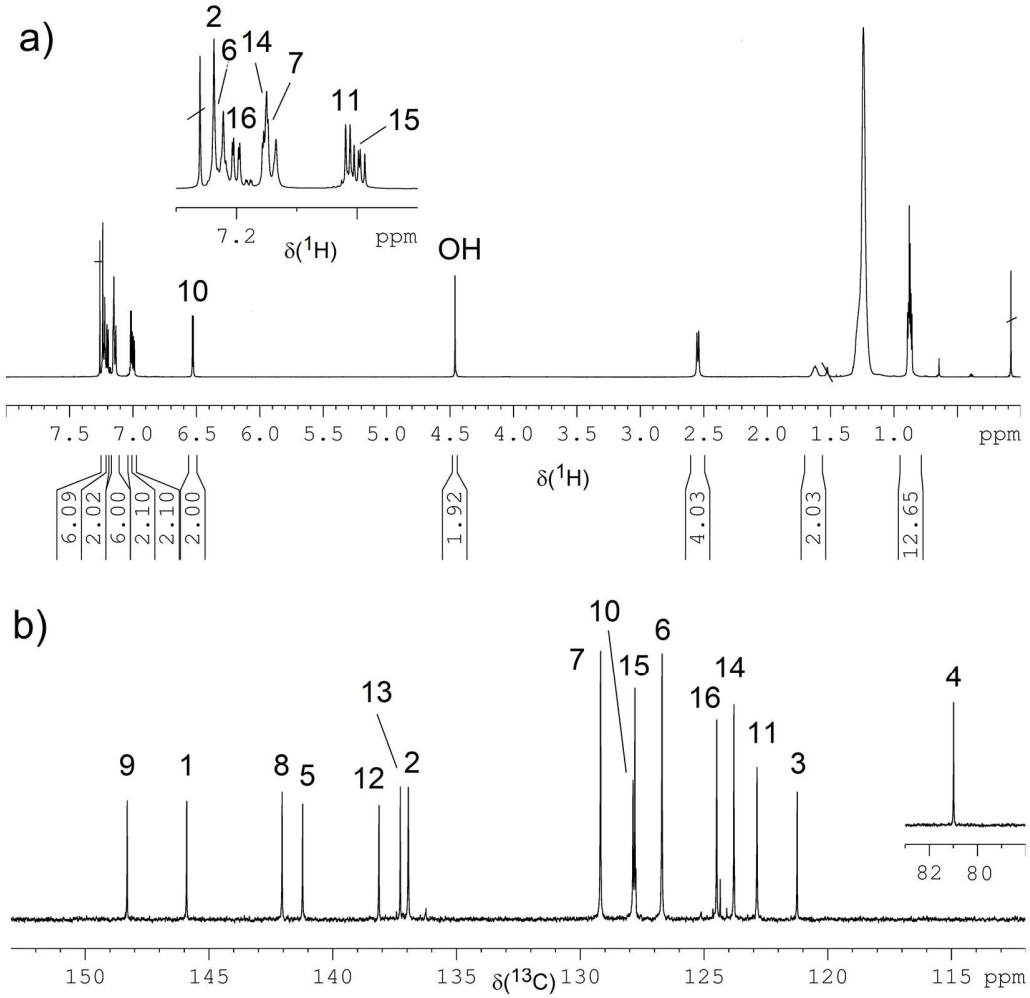


Figure S9. ^{1}H (a) and ^{13}C NMR spectrum (b, regions) of model compound **10** in $CDCl_3$.

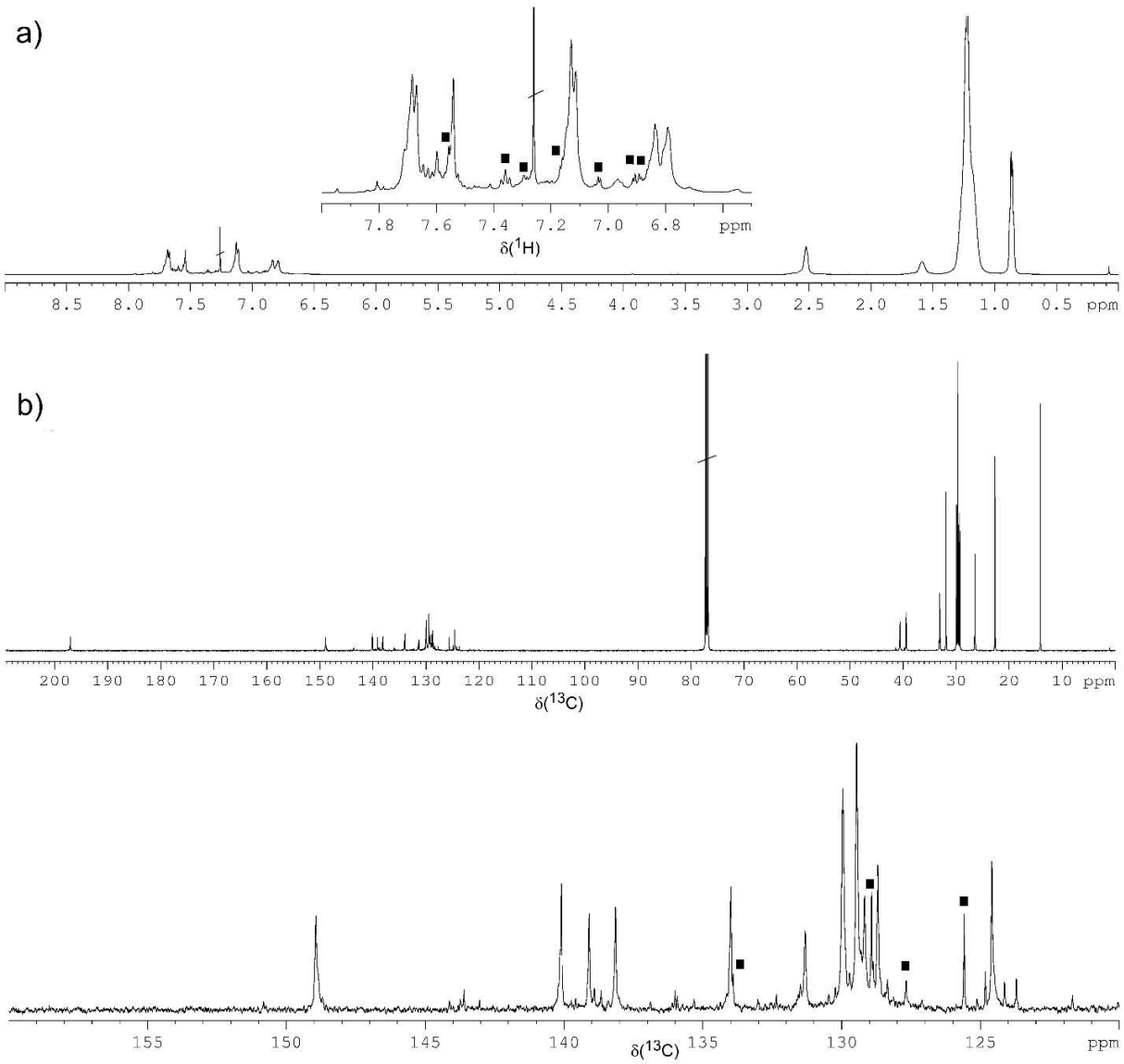


Figure S10. ^{1}H NMR (top) and ^{13}C NMR spectrum (bottom) of **P(K-*alt*-T2)$_{term}$** in $CDCl_3$. The squares mark signals of the seven ^{1}H NMR signals of the –T2Ph end group and the four ^{13}C NMR signals of the Ph group, respectively.

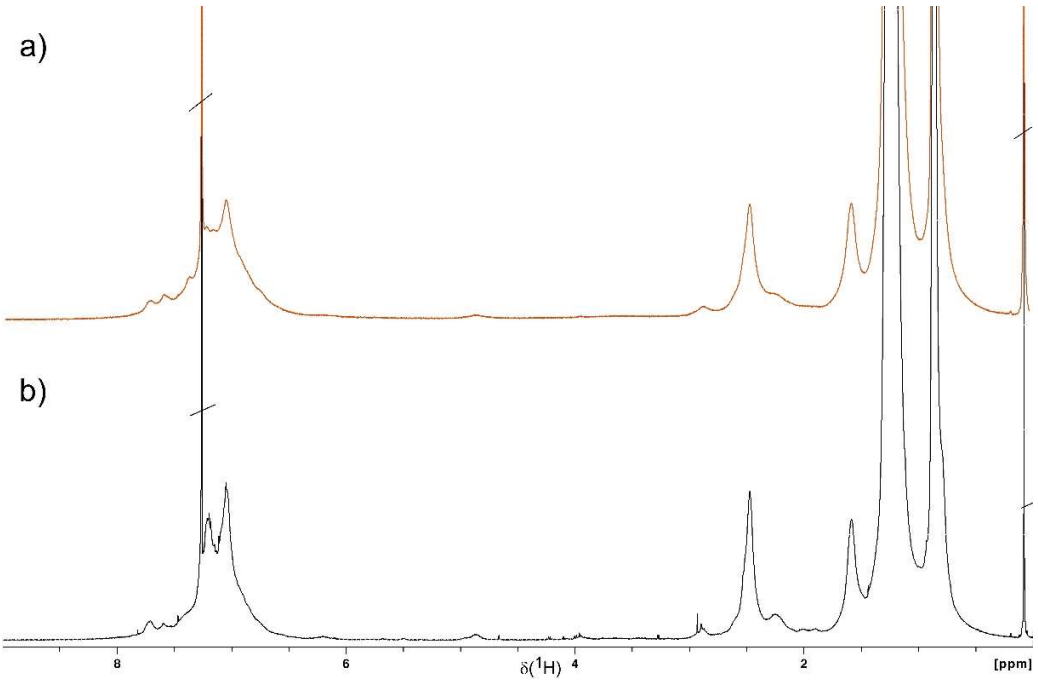


Figure S11. ^{1}H NMR spectra of **P2$^{A}_{term}$-Bu/Ph$_{20}$** (a) and **P2^{A}-Bu/Ph$_{20}$** (b) in $CDCl_3$.

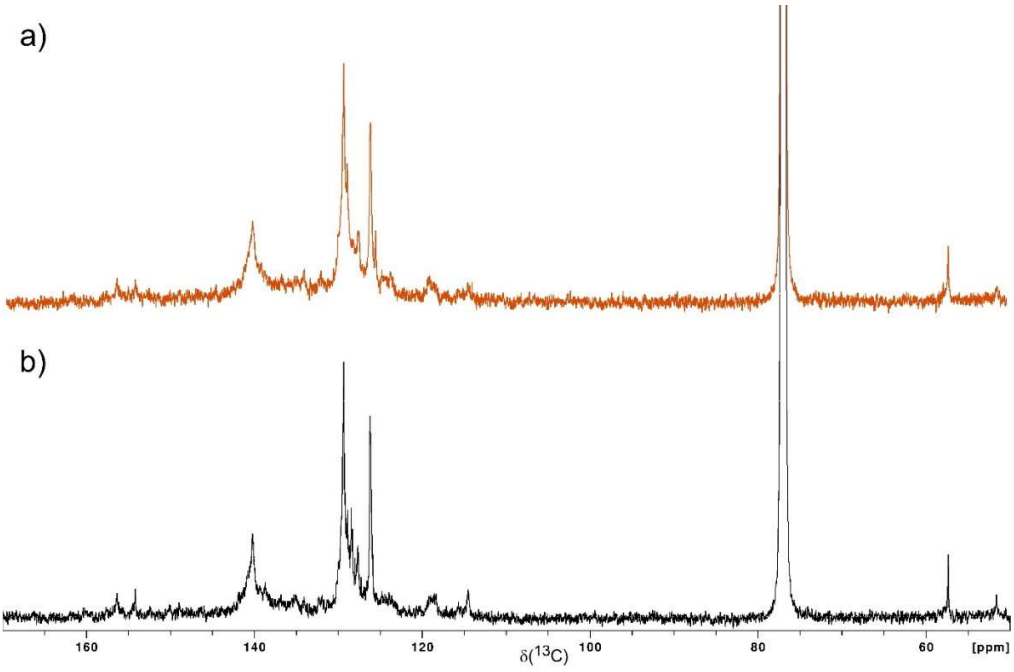


Figure S12. ^{13}C NMR spectra (region) of **P2$^{A}_{term}$-Bu/Ph$_{20}$** (a) and **P2^{A}-Bu/Ph$_{20}$** (b) in $CDCl_3$.

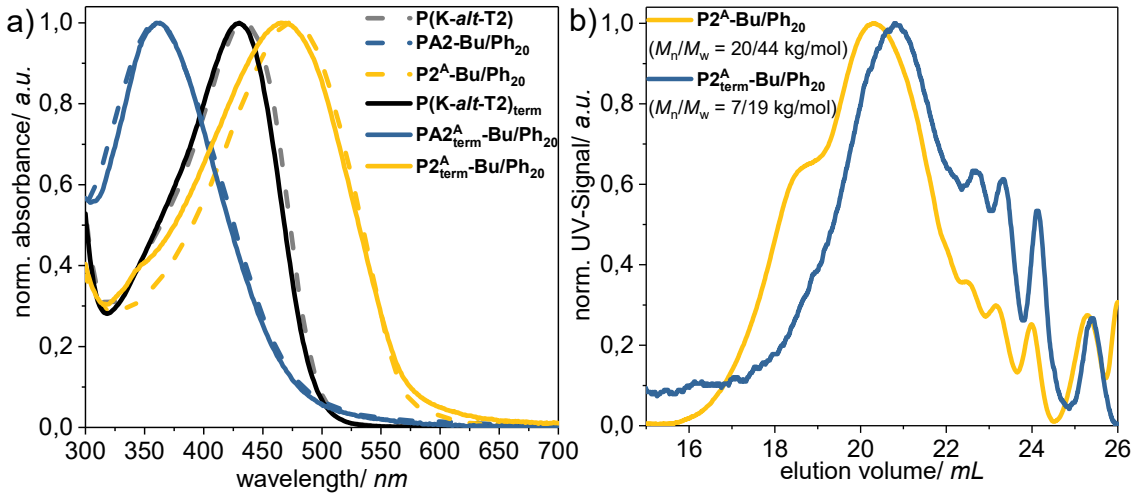


Figure S13. a) Comparison of reaction control by UV-vis spectroscopy of polymer analogous cyclization to of **P2^{A}-Bu/Ph$_{20}$** and **P2$^{A}_{term}$-Bu/Ph$_{20}$** in $CHCl_3$ solution at r.t. b) SEC curves of **P2^{A}-Bu/Ph$_{20}$** and **P2$^{A}_{term}$-Bu/Ph$_{20}$**.

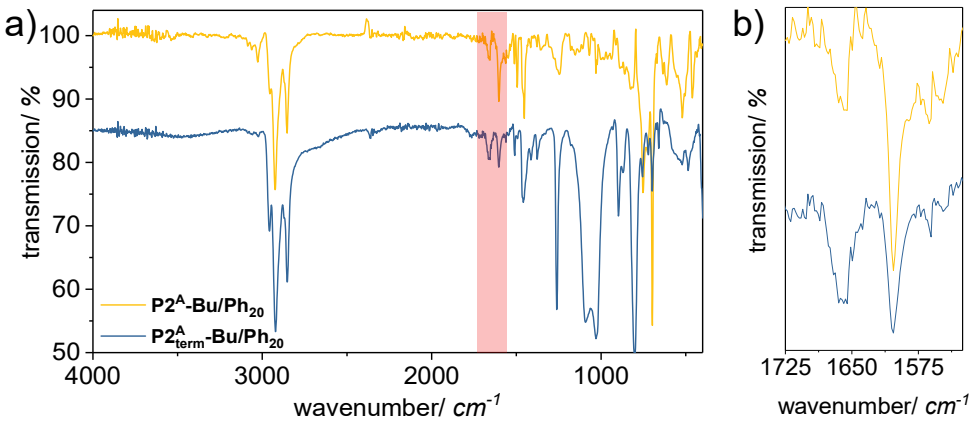


Figure S14. a) Comparison of IR spectra of **P2^{A}-Bu/Ph$_{20}$** and **P2$^{A}_{term}$-Bu/Ph$_{20}$** b) shows the enlarged wavenumber range of the red box.

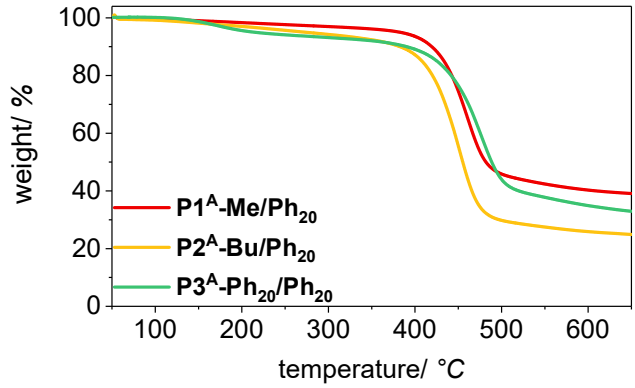


Figure S15. Thermograms of **PIDTs** in N_2.

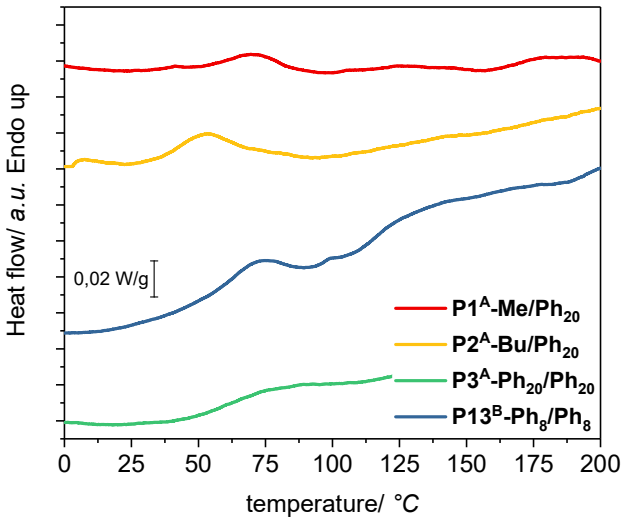


Figure S16. DSC curves of **PIDT**s polymers **P1^{A}-Me/Ph$_{20}$**, **P2^{A}-Bu/Ph$_{20}$**, **P3^{A}-Ph$_{20}$/Ph$_{20}$** and **P13^{B}-Ph$_{8}$/Ph$_{8}$**. First heating measured with 20 K/min.

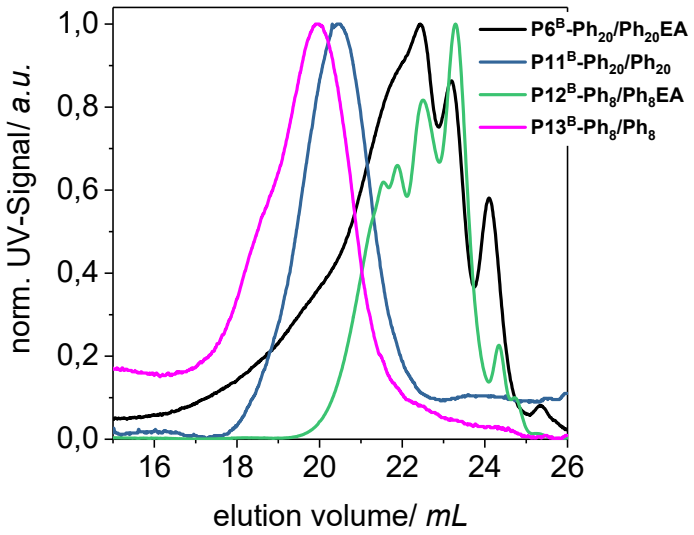


Figure S17. SEC curves of **P11^{B}-Ph$_{20}$/Ph$_{20}$** and **P13^{B}-Ph$_{8}$/Ph$_{8}$** via oxDAP (ethyl acetate (EA) fractions **P6^{B}-Ph$_{20}$/Ph$_{20}$EA** and **P12^{B}-Ph$_{8}$/Ph$_{8}$EA** as starting material).

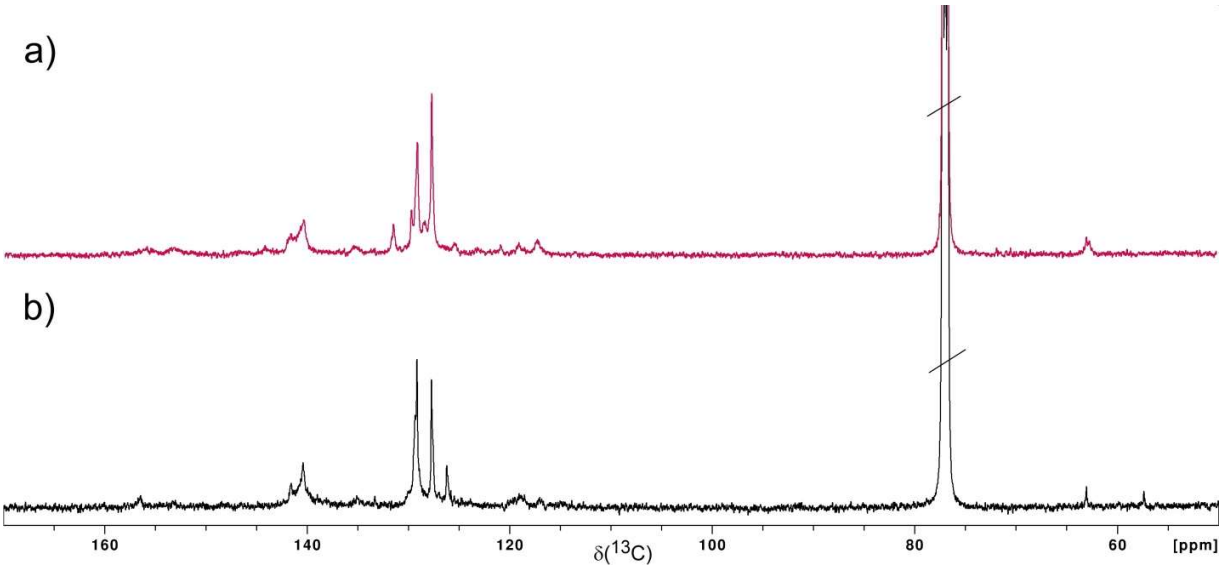


Figure S18. ^{13}C NMR spectra (region) of **P11^{B}-Ph$_{20}$/Ph$_{20}$** (a) and **P3^{A}-Ph$_{20}$/Ph$_{20}$** (b) in $CDCl_3$.