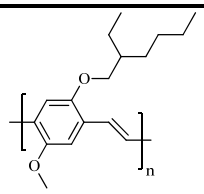
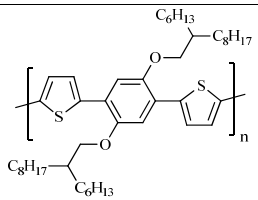
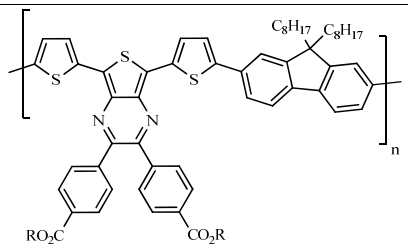
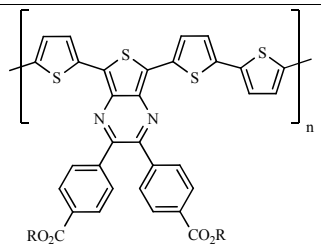
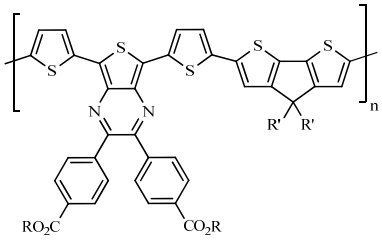
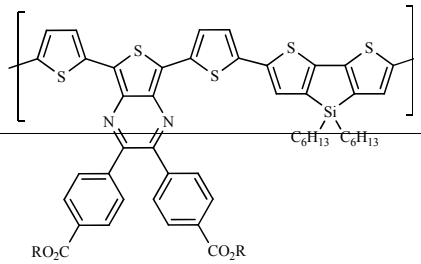
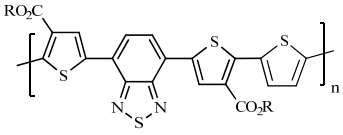
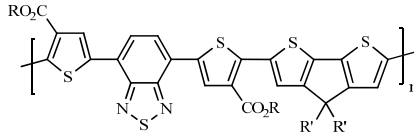
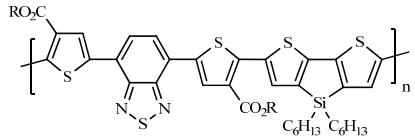
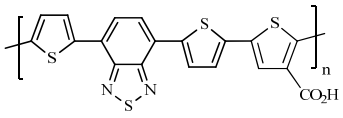
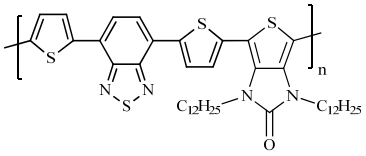
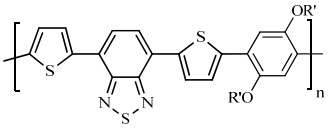
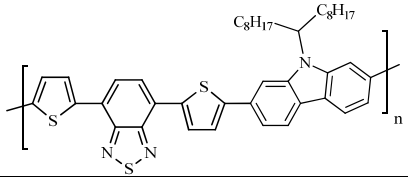
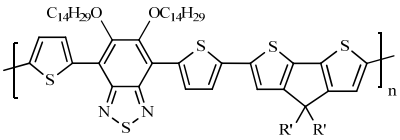
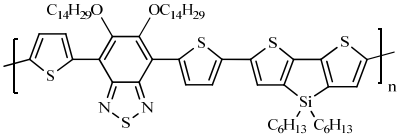
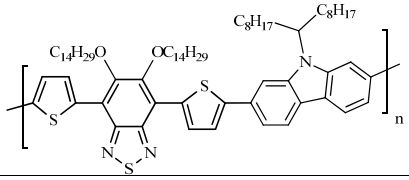
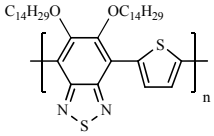
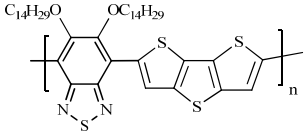
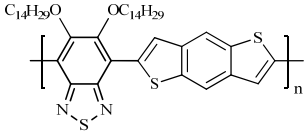
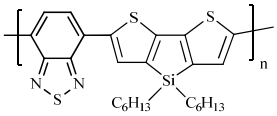
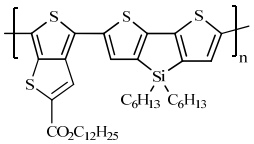
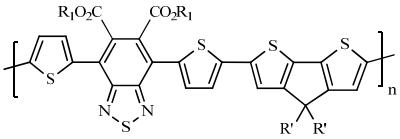
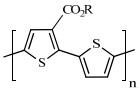
Table S1: Band-gaps, molecular weights and best reported efficiencies.

	Sample Chemical Structure	M_w (kg mol^{-1})	PDI	E_g^{opt} (eV)	PCE (%)	Integration Range λ_1 (nm) – λ_2 (nm)	Ref.
P1		305.2	7.9	2.15	3.2	300 – 650	[1]
P2		11.7	2.4	2.2	0.4	300 – 650	[2]
P3		42.3	3.0	1.4	0.54 0.33 [a]	300 – 1100 300 – 1100[a]	[3]
P4		39.4	1.9	1.3	0.57 0.35 [a]	300 – 1100 300 – 1100 [a]	[3]
P5		363	4.8	1.25	1.21 0.64 [a]	300 – 1100 300 – 1100 [a]	[3]
P6		157.3	9.2	1.25	-	300 – 1100 300 – 1100 [a]	

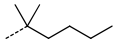
P7		173	2.6	1.69	0.21 0.42 [a]	300 – 800 300 – 800 [a]	[4]
P8		41.6	2.7	1.69	1.92 1.47 [a] 1.49 [b]	300 – 800 300 – 900 [a] 300 – 900 [b]	[5]
P9		99.8	4.6	1.70	-	300 – 800 300 – 900 [a]	
P10		-	-	1.65	-	300 – 850	
P11		15.5	1.9	1.70	-	300 – 800	
P12		16.2	2.2	1.70	2.2	300 – 800	[2]
P13		190.9	32.9	1.88	6.1	300 – 700	[6]
P14		67.5	2.25	1.75	-	300 – 800	
P15		88.0	2.6	1.74	-	300 – 800	

P16		30.0	2.1	1.85	-	300 – 700	
P17		16.6	1.7	1.74	2.22	300 – 800	[4]
P18		73	6.0	1.6	2.2	300 – 900	[7]
P19		101.6	4.9	1.90	-	300 – 750	
P20		8.2	2.4	1.48	-	300 – 900	
P21		16.5	7.0	1.24	-	300 – 1100	
P22		79.1	2.4	1.75	-	300 – 800	
P23		28.3	2.6	1.97	0.9 0.1 [a] 1.4 [b]	300 – 700 300 – 800[a] 300 – 800[b]	[8]

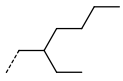
a: cleavage to the carboxylic acid

b: full cleavage

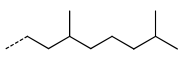
R =



R' =



R_1 =



[1] S. Alem, R. de Bettignies and J.-M. Nunzi, *Appl. Phys. Lett.*, 2004, **84**, 2178-2180.

[2] J.E. Carlé, J.W. Andreasen, M. Jørgensen and F.C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 774-780.

[3] M. Helgesen and F.C. Krebs, *Macromolecules*, 2010, **43**, 1253-1260.

[4] M. Helgesen, S.A. Gevorgyan, F.C. Krebs and R.A.J. Janssen, *Chem. Mater.*, 2009, **21**, 4669-4675.

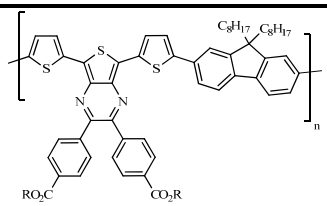
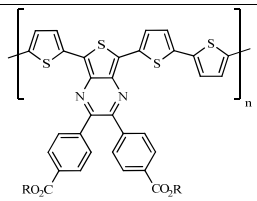
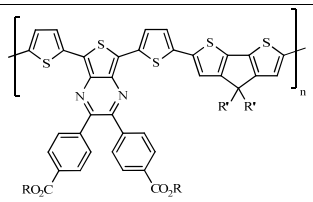
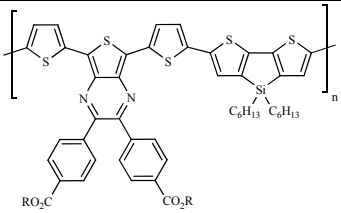
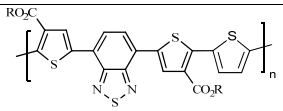
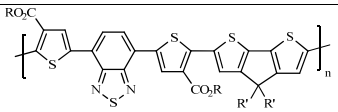
[5] M. Helgesen, M. Bjerring, N.C. Nielsen and F.C. Krebs, *Chem. Mater.*, 2010, DOI:10.1021/cm1019537.

[6] S.H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee and A.J. Heeger, *Nat. Photon.*, 2009, **3**, 297-303.

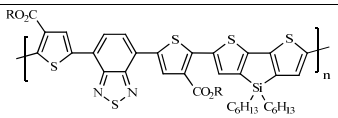
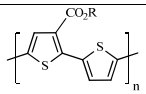
[7] E. Bundgaard, O. Hagemann, M. Manceau, M. Jørgensen and F.C. Krebs, *Macromolecules*, accepted.

[8] S.A Gevorgyan and F.C. Krebs, *Chem. Mater.*, 2008, **20**, 4386-4390.

Table S2: Thermal cleavage conditions.

Sample Chemical Structure	T (°C)	t (min)	Stability Increase Factor (X) *
	250 [a]	5 [a]	4.8 [a]
	240 [a]	2 [a]	12.1 [a]
	245 [a]	5 [a]	3.7 [a]
	250 [a]	5 [a]	5.8 [a]
	250 [a]	5 [a]	20 [a]
	225 [a] 300 [b]	5 [a] 7 [b]	1.5 [a] 2.5 [b]

* Practically, this means that the thermocleaved sample is "X" times more stable than the corresponding pristine polymer
[a] cleavage to the carboxylic acid ; [b] full cleavage

	245 [a]	5 [a]	3.4 [a]
	250 [a] 305 [b]	5 [a] 15 [b]	4.6 [a] 6.8 [b]

Abbreviations List

Fluorene: 9,9-dioctly-9H-fluorene

Carbon-bridged cyclopentadithiophene (CPDT): 4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene

Silicon-bridged cyclopentadithiophene (Si-CPDT): 4,4-bis(hexyl)-4H-silolo[3,2-b:4,5-b']dithiophene

Thienoimidazolone: 1,3-didodecyl-1H-thieno[3,4-d]imidazol-2(3H)-one

Carbazole: 9-(heptadecan-9-yl)-9H-carbazole

Dialkoxybenzene: 1,4-bis((2-ethylhexyl)oxy)benzene

Benzodithiophene: benzo[1,2-b:4,5-b']dithiophene

Dithienothiophene: dithieno[3,2-b:2',3'-d]thiophene

Benzodiathiazole (BTD): benzo[c][1,2,5]thiadiazole

Thienopyrazine (TPz): 5,7-dimethyl-2,3-diphenylthieno[3,4-b]pyrazine

Thienothiophene: dodecyl thieno[3,4-b]thiophene-2-carboxylate

Supplementary Material (ESI) for Journal of Materials Chemistry

Figure S1: Evolution of the IR spectrum under ageing of the materials from the Dithienylthienopyrazine series

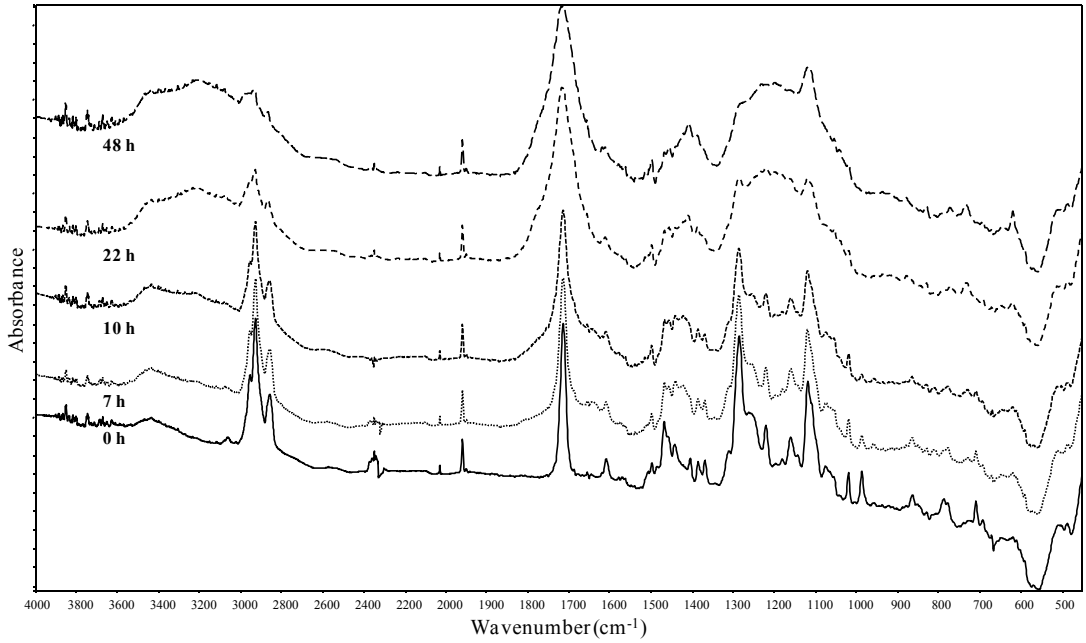


Fig. S1a Fluorene derivative

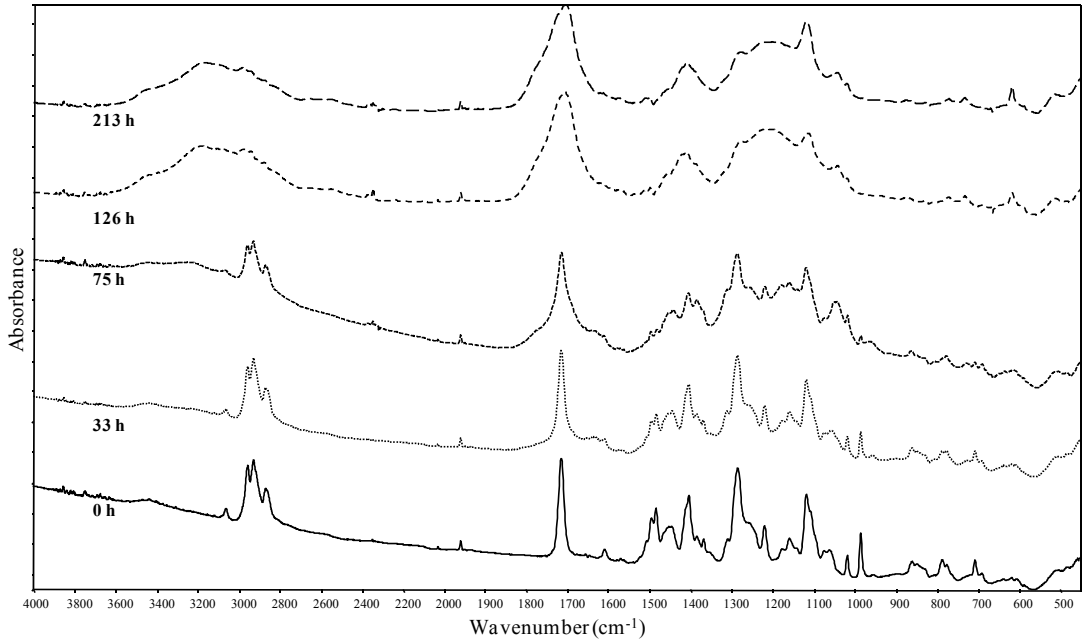


Fig. S1b CPDT derivative

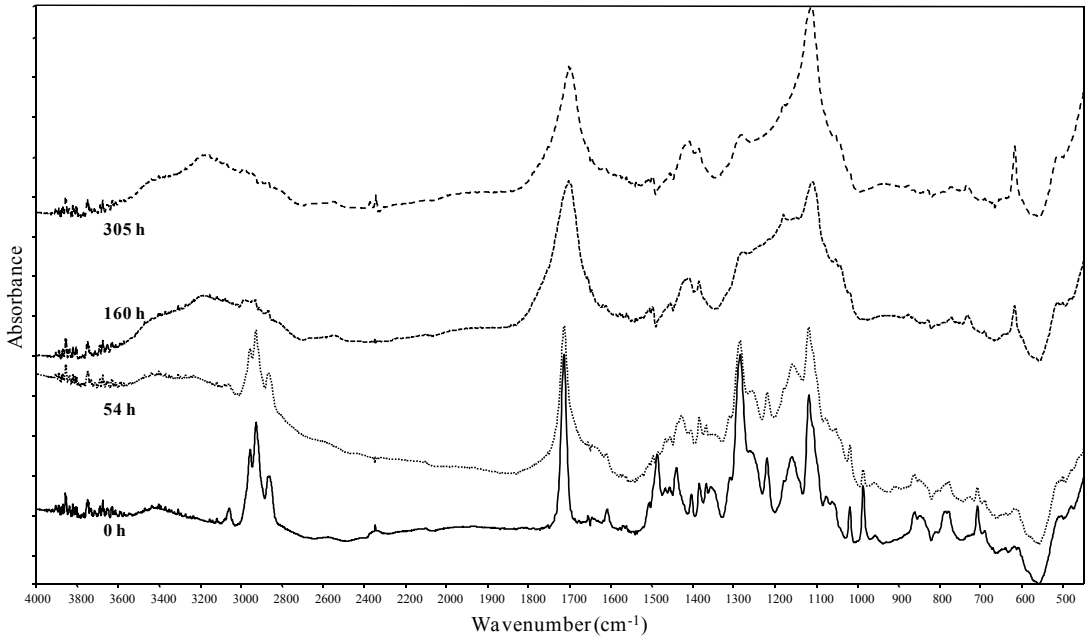


Fig. S1c Si-CPDT derivative

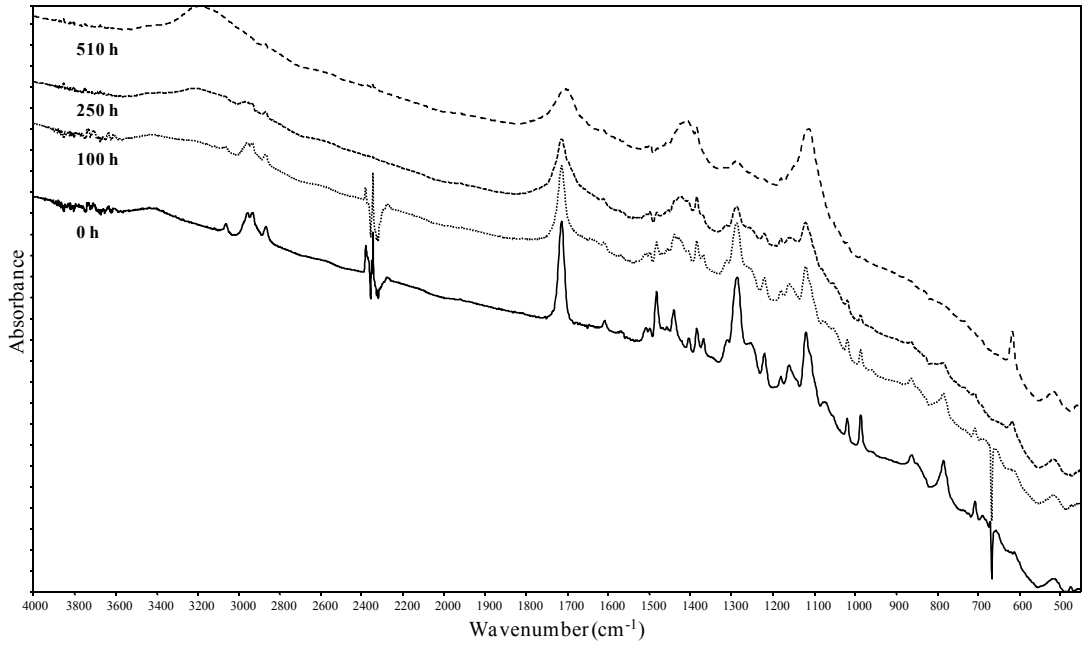


Fig. S1d Thiophene derivative

Figure S2: Evolution of the IR spectrum under ageing of the materials from the Dithienylbenzothiadiazole series 2

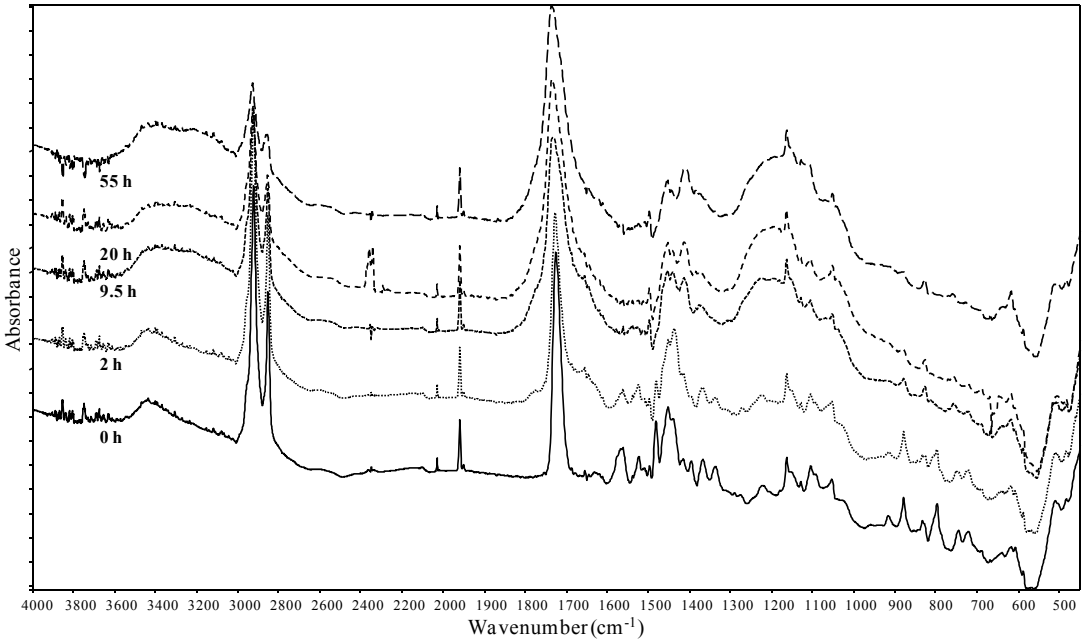


Fig. S2a Thienoimidazolone derivative

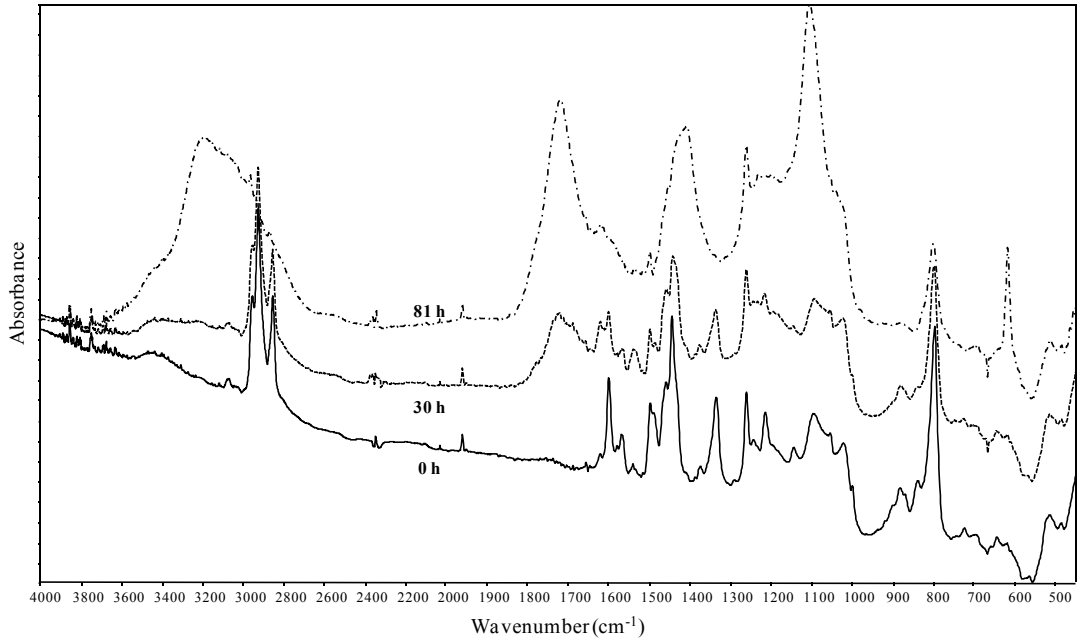


Fig. S2b Carbazole derivative

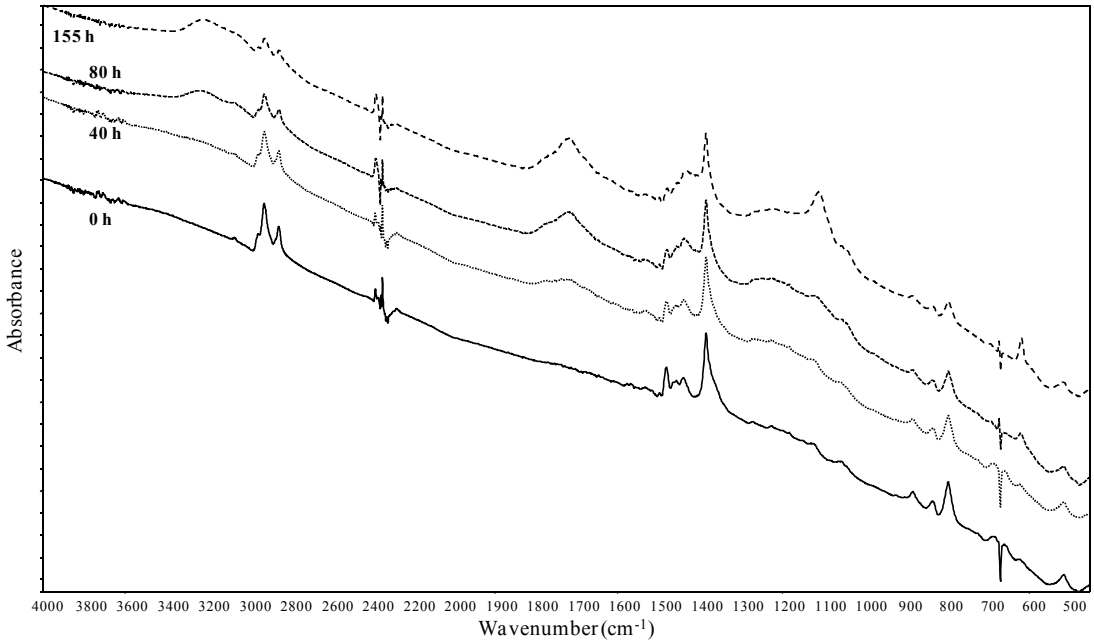


Fig. S2c Dialkoxybenzene derivative

Figure S3: Evolution of the IR spectrum under ageing of the materials from the Si-bridged cyclopentadithiophene series

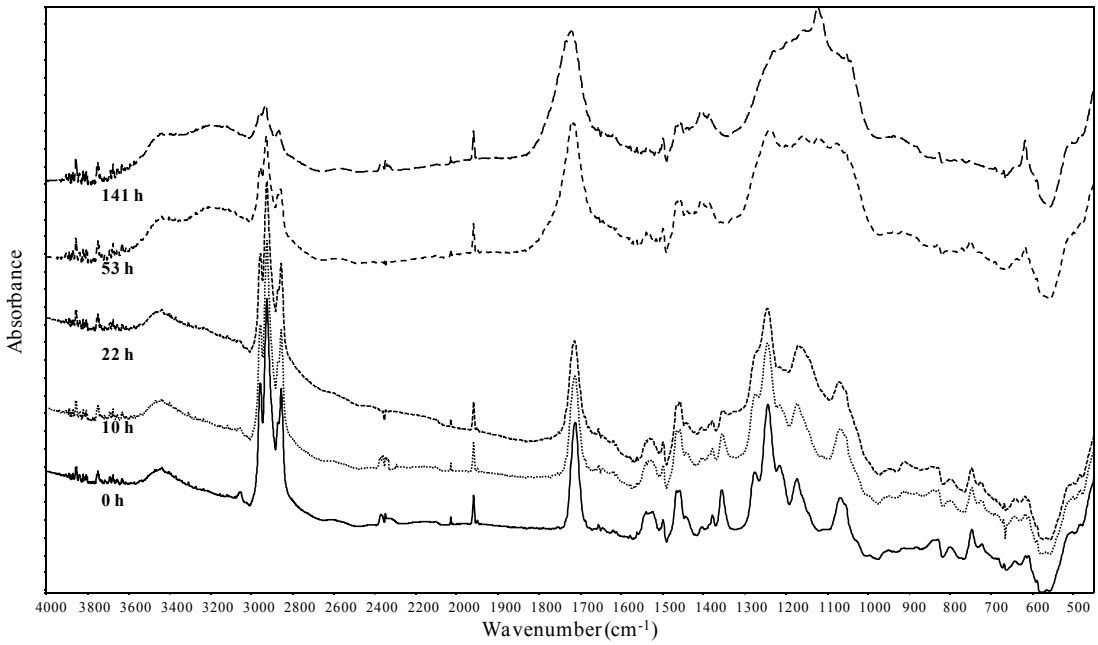


Fig. S3a Thienothiophene derivative

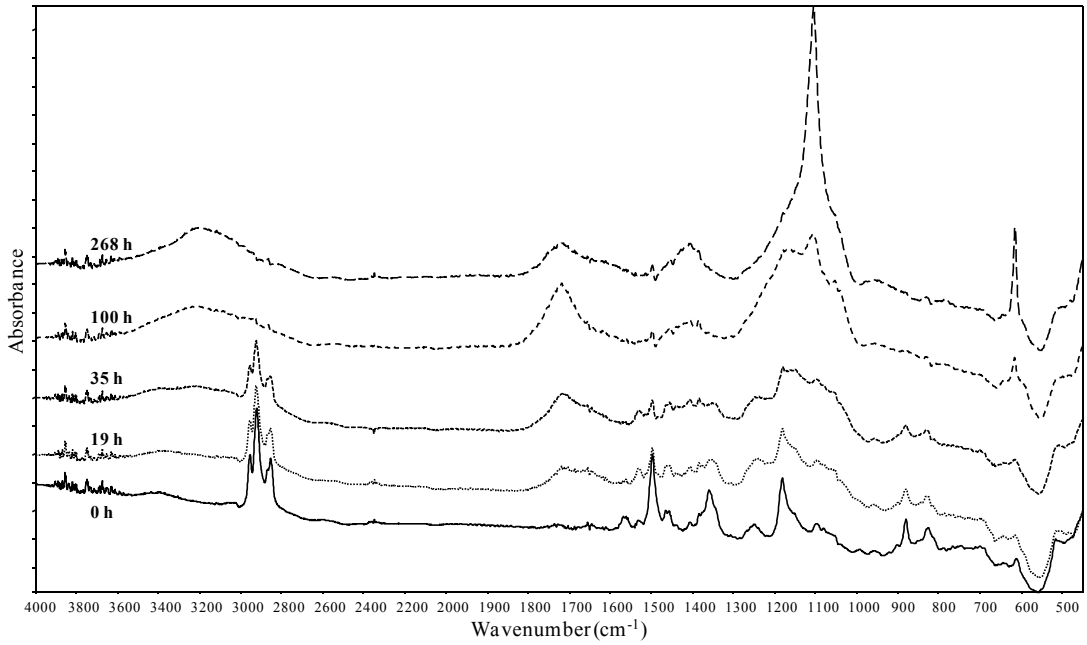


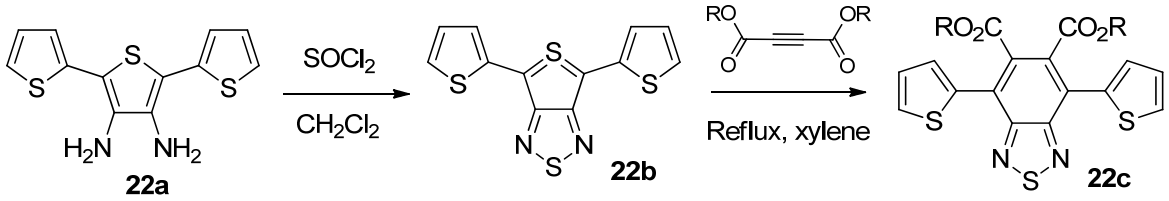
Fig. S3b Benzothiadiazole derivative

Synthetic details

22a,[†] **6a** and **22e**,[‡] **9a**,[§] **14a** and **20a**[**] were prepared according to literature procedures or slight modifications thereof.

21a and **P13** were bought from Lumtec.

Synthesis of **P15** and **P16** will be described in a forthcoming paper[††]



Scheme S1. Synthesis of the monomer **22c**. R = 3,7-dimethyloctyl

4,6-Dithienyl[3,4-*c*][1,2,5]thiadiazole (22b).

To a mixture of **22a** (200 mg, 0.72 mmol) and triethylamine (5.75 mmol, 0.8 ml) in 5 ml dichloromethane was slowly added a solution of thionyl chloride (1.44 mmol, 105 µL) in 1 ml dichloromethane. After addition the mixture was heated to reflux for 16 hours. After cooling to room temperature the reaction mixture was concentrated on celite in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with toluene) afforded **22b**. Yield: 155 mg (70 %), blue solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.58 – 7.54 (m, 2H), 7.34 –

[†] M. Helgesen, S.A. Gevorgyan and F.C. Krebs, *Macromolecules,* 2008, **41**, 8986-8994.
[‡] M. Helgesen and F.C. Krebs, *Macromolecules*, 2010, **43**, 1253-1260.
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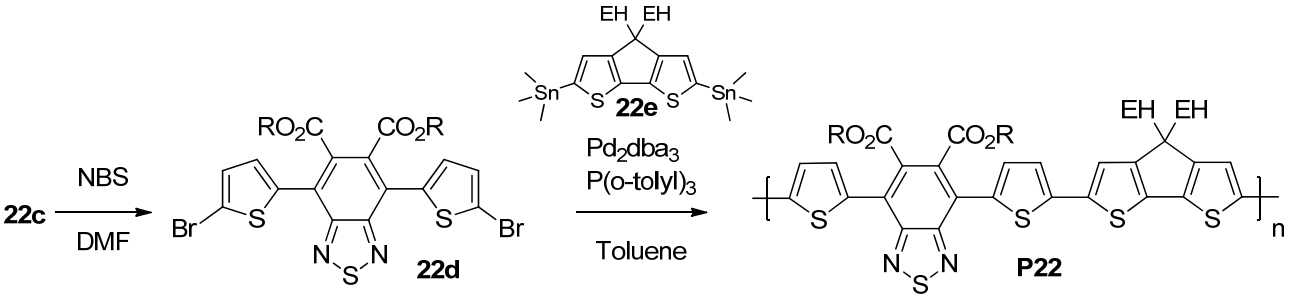
[**] M. Helgesen, S.A. Gevorgyan, F.C. Krebs and R. A.J. Janssen, *Chem. Mater.*, 2009, **21**, 4669-4675.
[††] E. Bundgaard and F.C. Krebs, *In preparation*.

7.30 (m, 2H), 7.13 – 7.07 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ = 156.17, 134.88, 128.08, 125.30, 124.23, 112.33.

Bis(3,7-dimethyloctyl)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-dicarboxylate (22c).

A solution of **22b** (1.5 g, 4.9 mmol) and acetylenedicarboxylic acid di-(3,7-dimethyloctyl) ester (2.9 g, 7.4 mmol) in xylene (20 mL) was refluxed, under argon for 6 hours. After cooling to room temperature the reaction mixture was concentrated directly on celite in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with Heptane/EtOAc, gradient 0-2.5% EtOAc) afforded **22c**. Yield: 3 g (92 %), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.59 (dd, J = 5.1 Hz, 1.2 Hz, 2H), 7.41 (dd, J = 3.6 Hz, 1.2 Hz, 2H), 7.18 (dd, J = 5.1 Hz, 3.6 Hz, 2H), 4.22 – 4.14 (m, 4H), 1.55 – 1.43 (m, 4H), 1.34 – 1.05 (m, 16H), 0.89 – 0.79 (m, 18H). ^{13}C NMR (250 MHz, $CDCl_3$) δ = 167.55, 153.61, 135.09, 132.67, 129.55, 128.49, 127.08, 126.08, 64.87, 39.06, 37.04, 35.00, 29.49, 27.91, 24.49, 22.64, 22.55, 19.30.

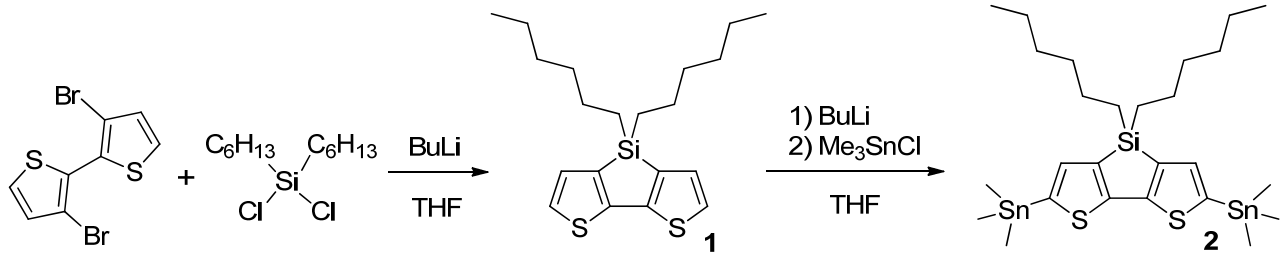


Scheme S2. Synthesis of the polymer **P22**. R = 3,7-dimethyloctyl, EH = Ethylhexyl

Bis(3,7-dimethyloctyl)-4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-dicarboxylate (22d).

To a solution of **22c** (545 mg, 0.82 mmol) in DMF (20 mL) was added NBS (294 mg, 1.65 mmol). The resulting mixture was then stirred at room temperature for 24 hours. The resulting mixture was poured into water and extracted several times with dichloromethane. The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuum. The crude product was purified by dry column chromatography (silica gel 15-40 µm, eluted with Heptane/Toluene, gradient 0-100% Toluene) to afford **22d**. Yield: 500 mg (74 %), orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.16 (d, J = 3.9 Hz, 2H), 7.15 (d, J = 3.9 Hz, 2H), 4.28 – 4.18 (m, 4H), 1.59 – 1.49

(m, 4H), 1.38 – 1.08 (m, 16H), 0.89 – 0.84 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.32, 153.23, 136.63, 132.60, 130.08, 129.92, 125.30, 116.34, 65.11, 39.25, 37.17, 35.10, 29.56, 27.95, 24.55, 22.70, 22.61, 19.25.



Scheme S3. Synthesis of the monomer **2**.

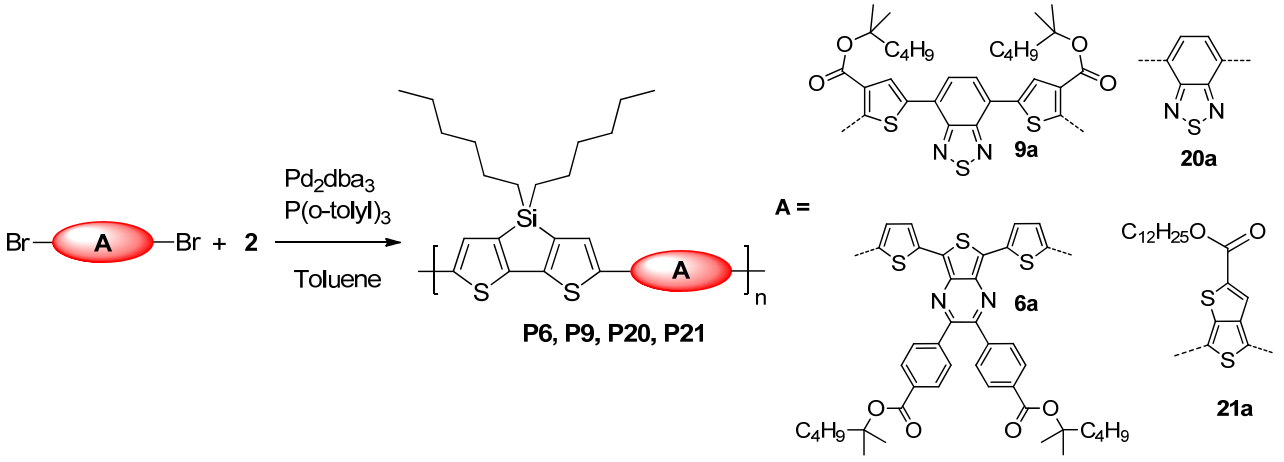
4,4-dihexyl-4*H*-silolo[3,2-b:4,5-b']dithiophene (1).

To a solution of 24 ml *n*-BuLi (1.6M in hexane) in anhydrous THF (300 mL) at -78 °C was added dropwise a solution of 3,3'-dibromo-2,2'-bithiophene (5.73 g, 18 mmol) in anhydrous THF (60 mL) over the course of 30 min. The mixture was then stirred at -78 °C for 1 hour. A solution of dichlorodihexylsilane (5.24 g, 19 mmol) in anhydrous THF (60 mL) was subsequently added dropwise over the course of 30 min. The reaction mixture was stirred at -78 °C for an additional 2 hours and then allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with ether (3 × 100 ml). The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuum. The crude product was purified by dry column chromatography (silica gel 15-40 μm, eluted with Heptane) to afford **1**. Yield: 2 g (31 %), light yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.20 (d, J = 4.7 Hz, 2H), 7.05 (d, J = 4.7 Hz, 2H), 1.44 – 1.17 (m, 16H), 0.95 – 0.80 (m, 10H). ^{13}C NMR (250 MHz, $CDCl_3$) δ = 149.22, 141.63, 129.50, 124.85, 32.67, 31.35, 24.08, 22.42, 13.87, 11.94.

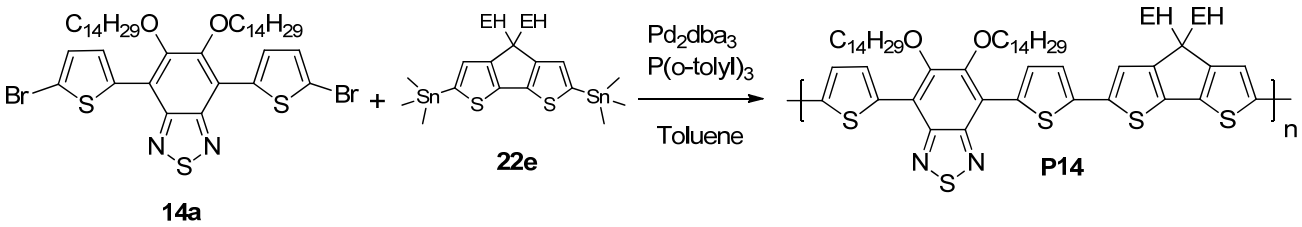
4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene (2).

1 (1.76 g, 4.85 mmol) was dissolved in dry THF (35 ml). The solution was cooled to -78 °C and 1.6 M *n*-butyllithium in hexane (9 ml, 14.4 mmol) was added dropwise under argon. The reaction mixture was stirred at -78 °C for 1 hour and allowed to warm to room temperature over the course of 1 hour resulting in a light brown suspension. The reaction mixture was then cooled back to -78 °C and trimethyltin chloride (3.9 g, 19.6 mmol) dissolved in 10 ml dry THF was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 17 hours. Water was added to the reaction mixture followed by extraction with ether. The combined organic phase was washed with water, dried over magnesium sulphate, filtered and concentrated in vacuum. The residue was dissolved in toluene and quickly passed through a plug of aluminium oxide pretreated with triethylamine. Solvent was removed and the residue was dried under vacuum at 50 °C. Yield: 3 g (90 %),

light brown oil. ^{1}H NMR (250 MHz, CDCl3) δ 7.15 – 7.04 (m, 2H), 1.48 – 1.18 (m, 16H), 0.94 – 0.82 (m, 10H), 0.51 – 0.25 (m, 18H). ^{13}C NMR (250 MHz, $CDCl_3$) δ = 155.03, 143.12, 137.64, 137.56, 32.70, 31.35, 24.16, 22.46, 13.89, 12.09, -8.27.



Scheme S4. Synthesis of polymers **P6**, **P9**, **P20** and **P21**.



Scheme S5. Synthesis of the polymer **P14**.

General procedure for the Stille polymerization.

Dibromo monomer (0.27 mmol), distannyl monomer (0.27 mmol), Pd_2dba_3 (0.013 mmol) and tri-(o-tolyl)phosphine (0.11 mmol) was mixed in dry degassed toluene (13 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 130 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform phase was concentrated in vacuum and the

residue was re-dissolved in chlorobenzene or toluene and precipitated in methanol (1:10). Finally the polymer was filtered and dried in vacuum at 50 °C for 24 hours.

Figure S4. ^{1}H-NMR Spectrum of **22b** in $CDCl_3$

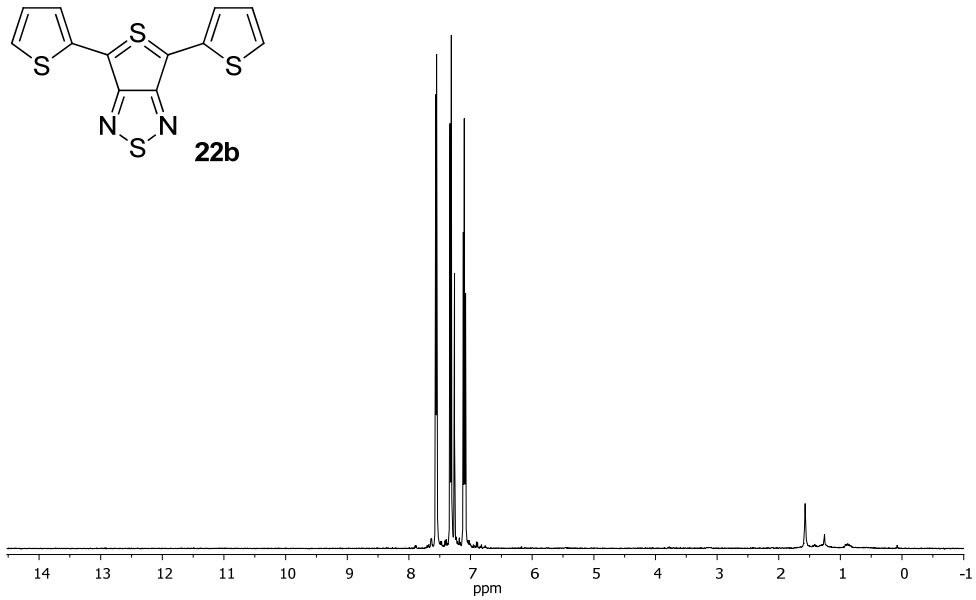


Figure S5. ^{13}C-NMR Spectrum of **22b** in $CDCl_3$

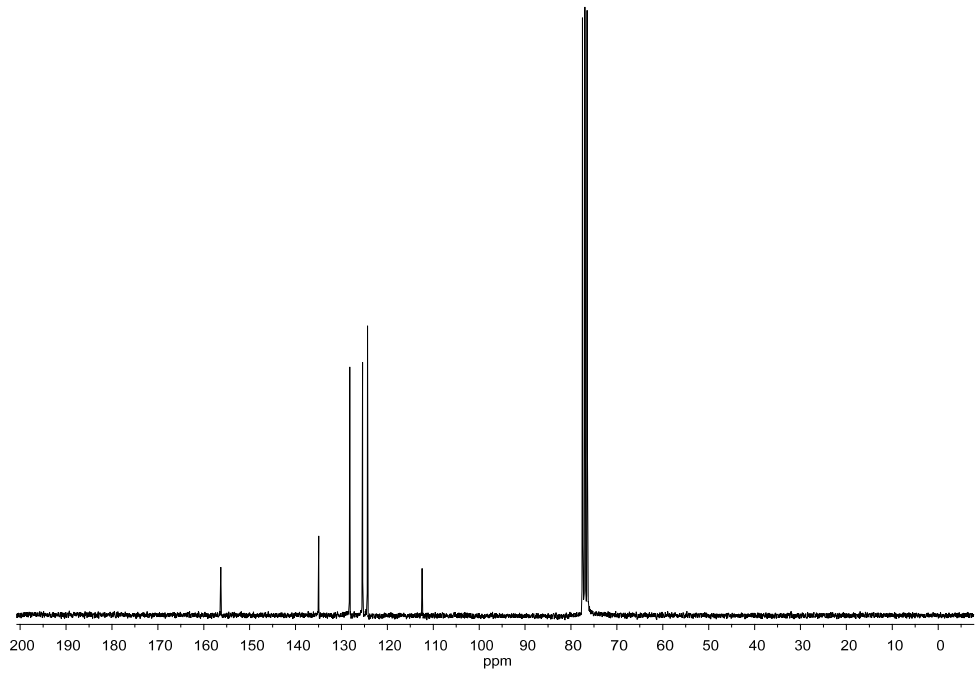


Figure S6. ^{1}H-NMR Spectrum of **22c** in $CDCl_3$

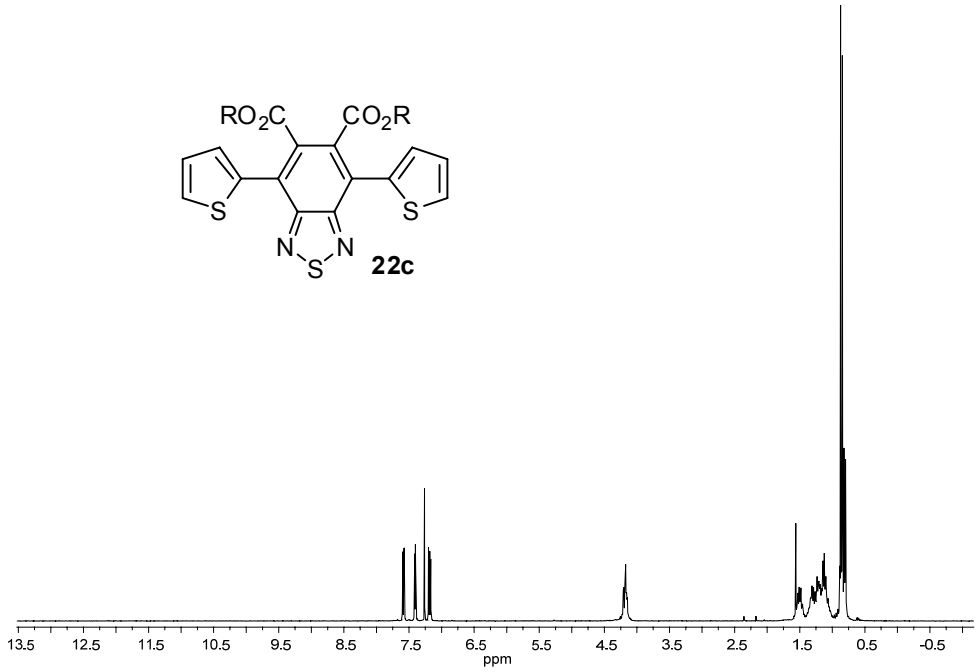


Figure S7. ^{13}C-NMR Spectrum of **22c** in $CDCl_3$

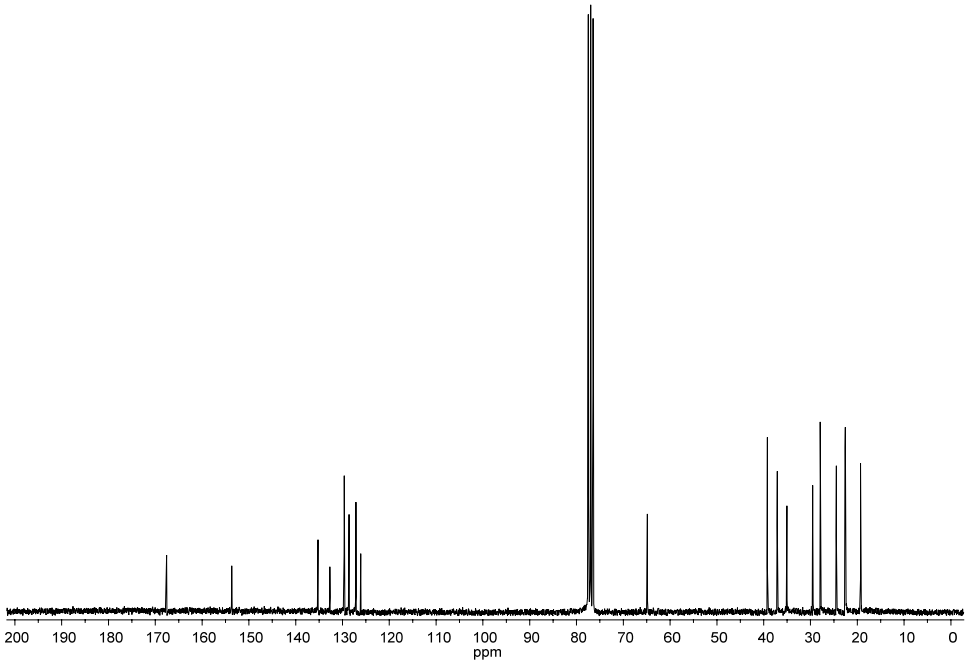


Figure S8. ^{1}H-NMR Spectrum of **22d** in $CDCl_3$

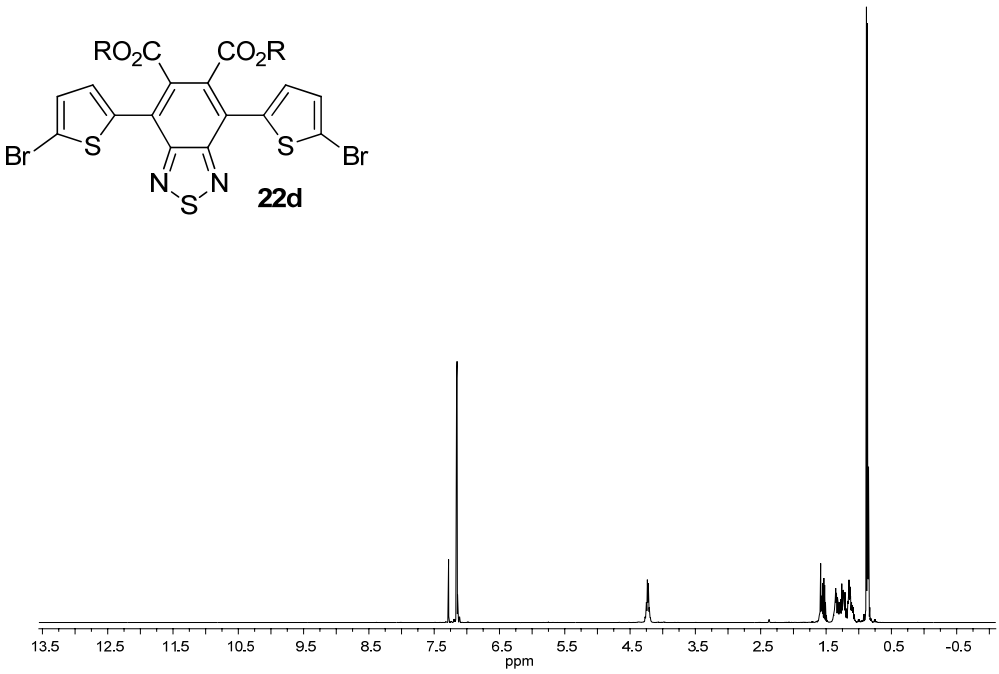


Figure S9. ^{13}C-NMR Spectrum of **22d** in $CDCl_3$

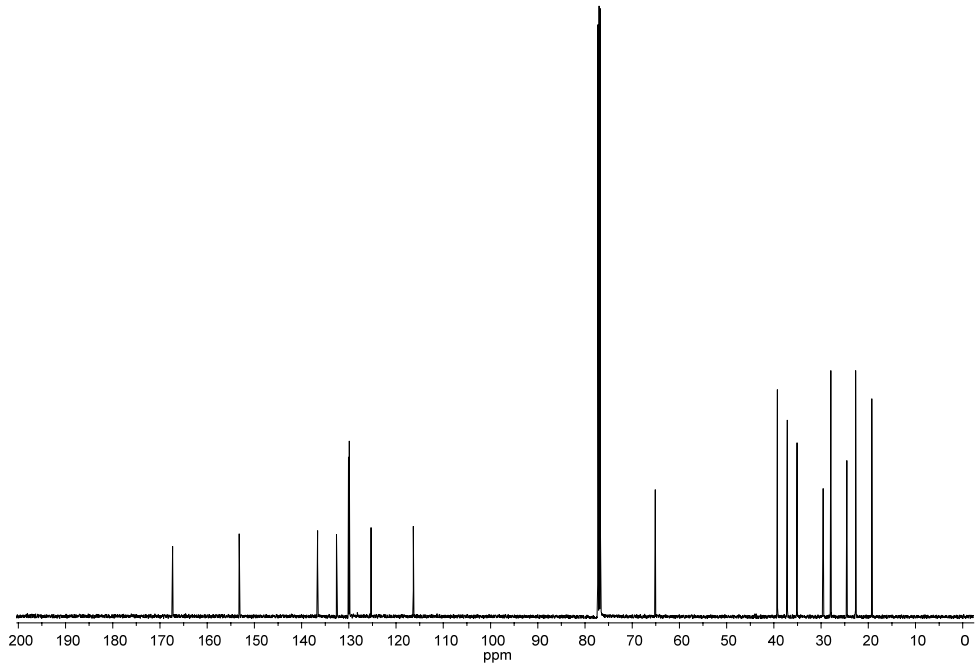


Figure S10. ^{1}H-NMR Spectrum of **1** in $CDCl_3$

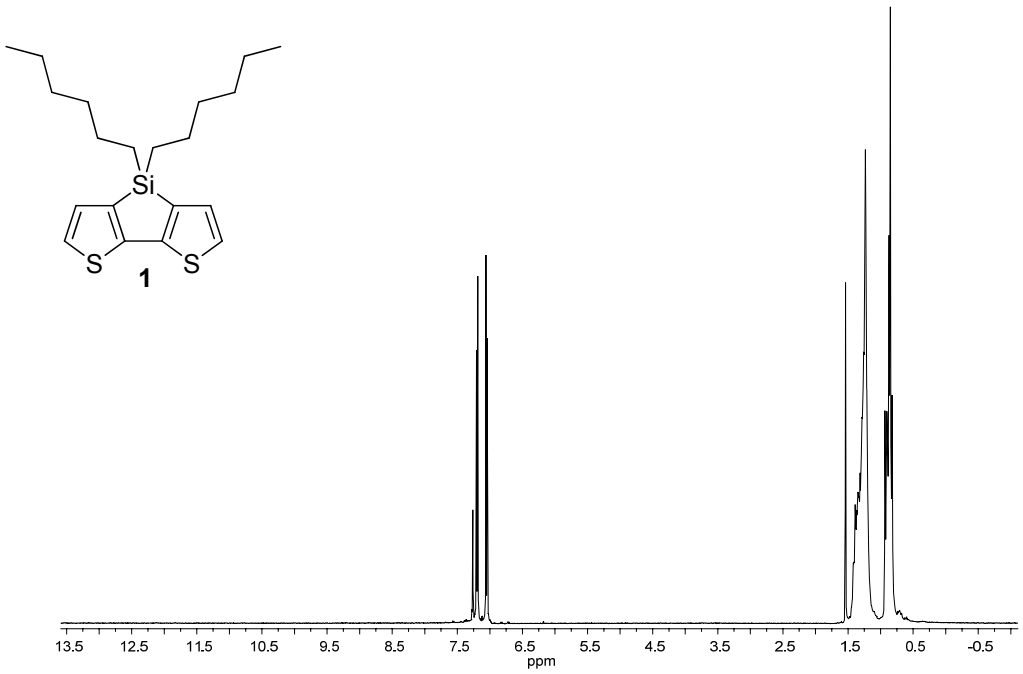


Figure S11. ^{13}C-NMR Spectrum of **1** in $CDCl_3$

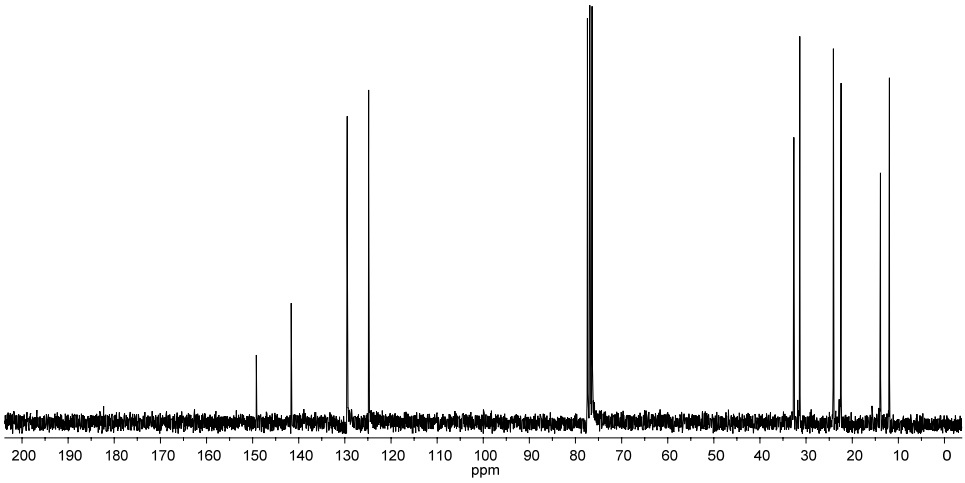


Figure S12. ^{1}H-NMR Spectrum of **2** in $CDCl_3$

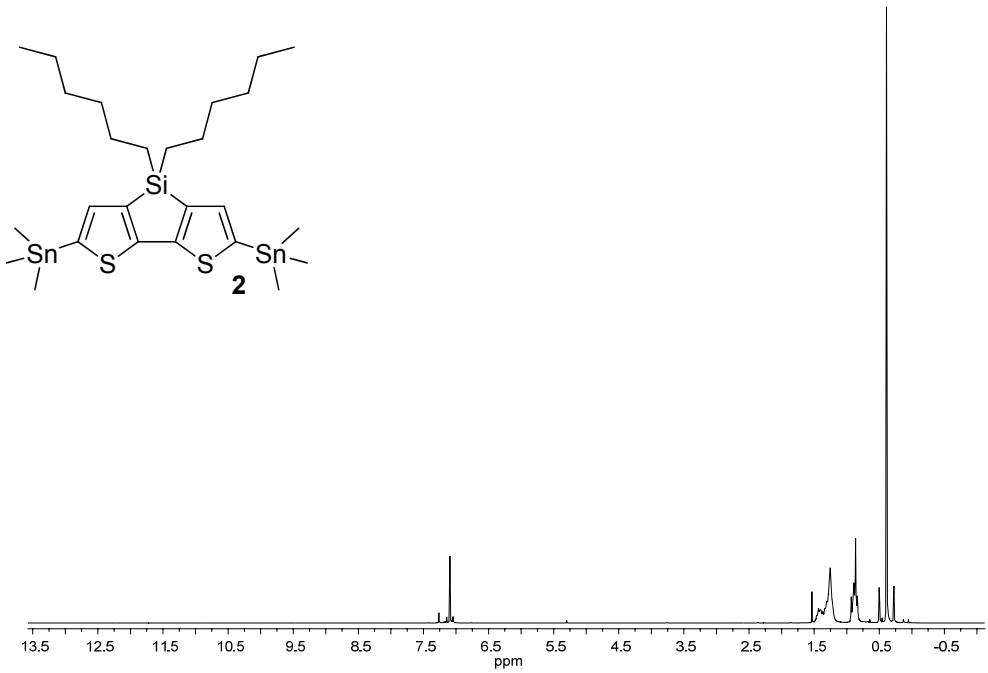


Figure S13. ^{13}C-NMR Spectrum of **2** in $CDCl_3$

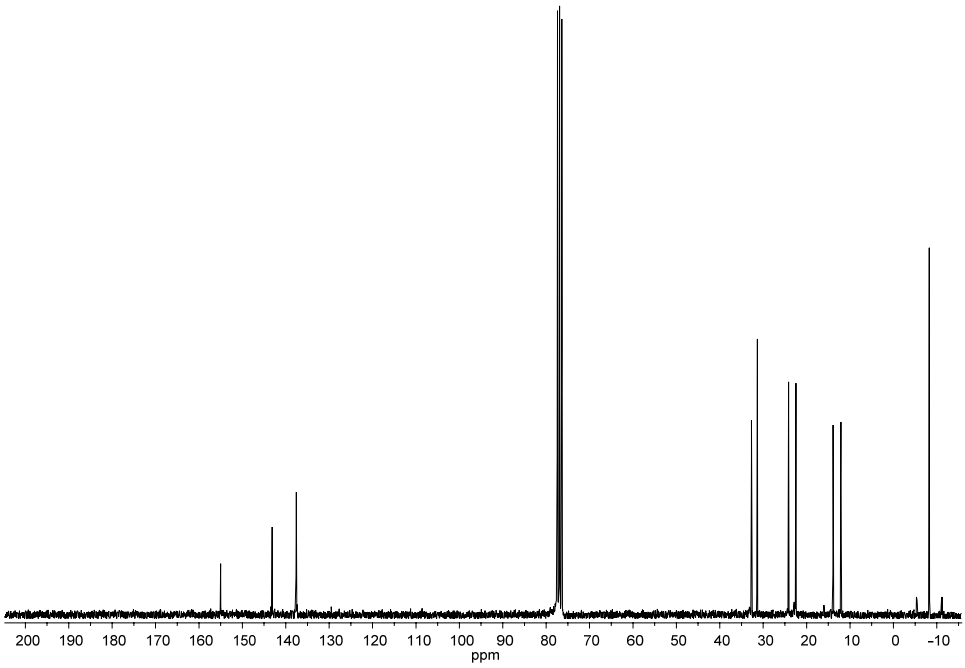


Figure S14. ^{1}H-NMR Spectrum of **P22** in $CDCl_3$

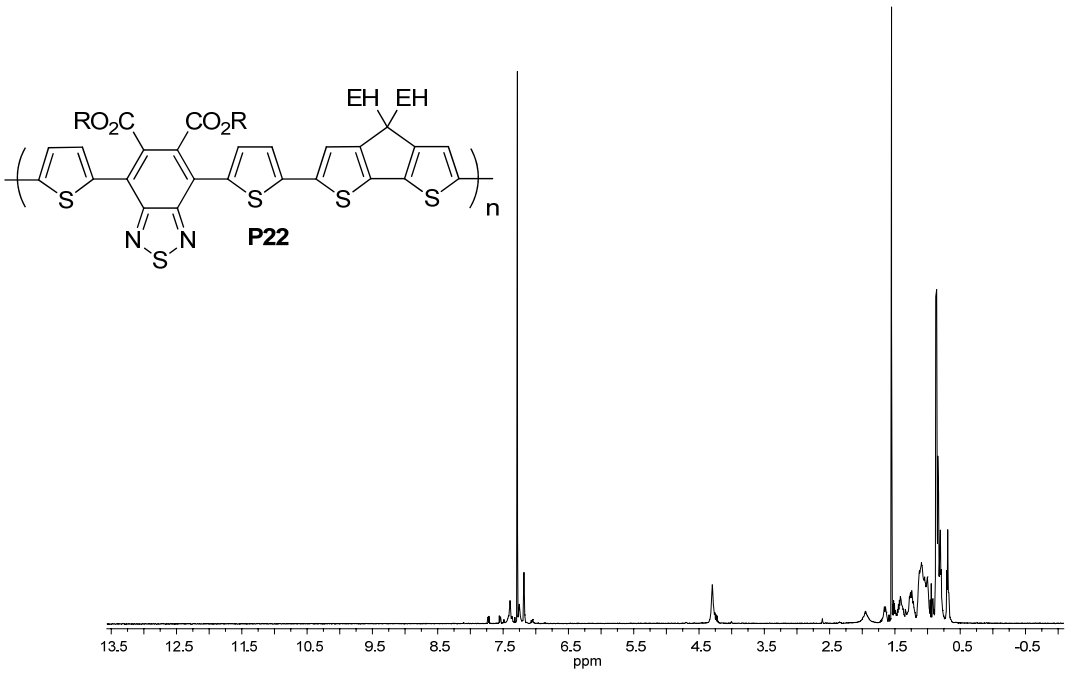


Figure S15. ^{1}H-NMR Spectrum of **P9** in $CDCl_3$

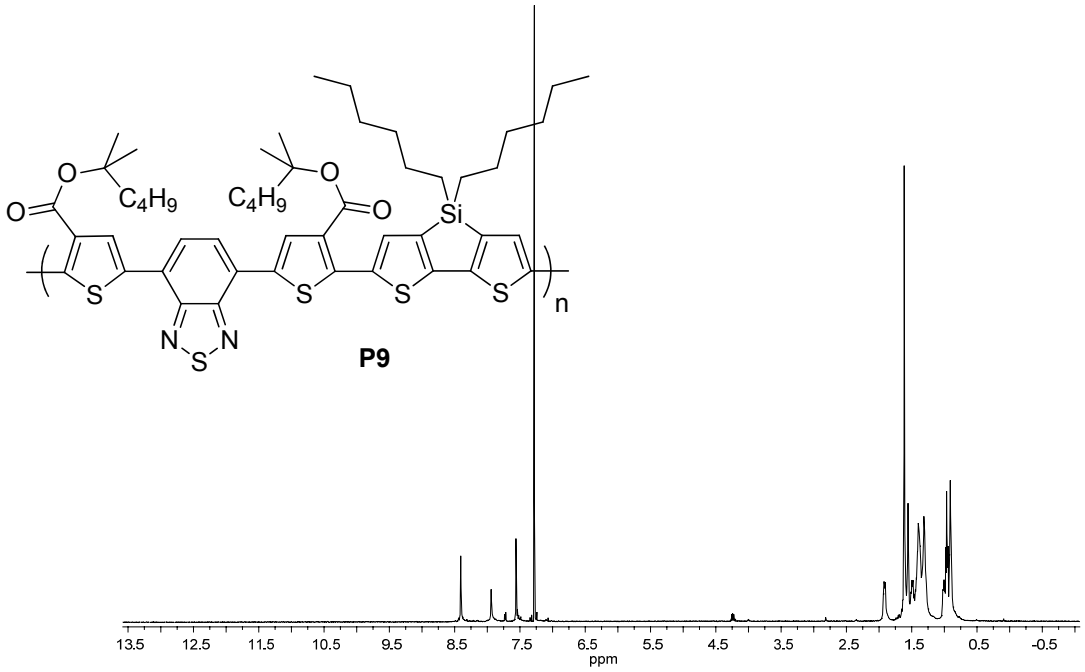


Figure S16. ^{1}H-NMR Spectrum of **P6** in $CDCl_3$

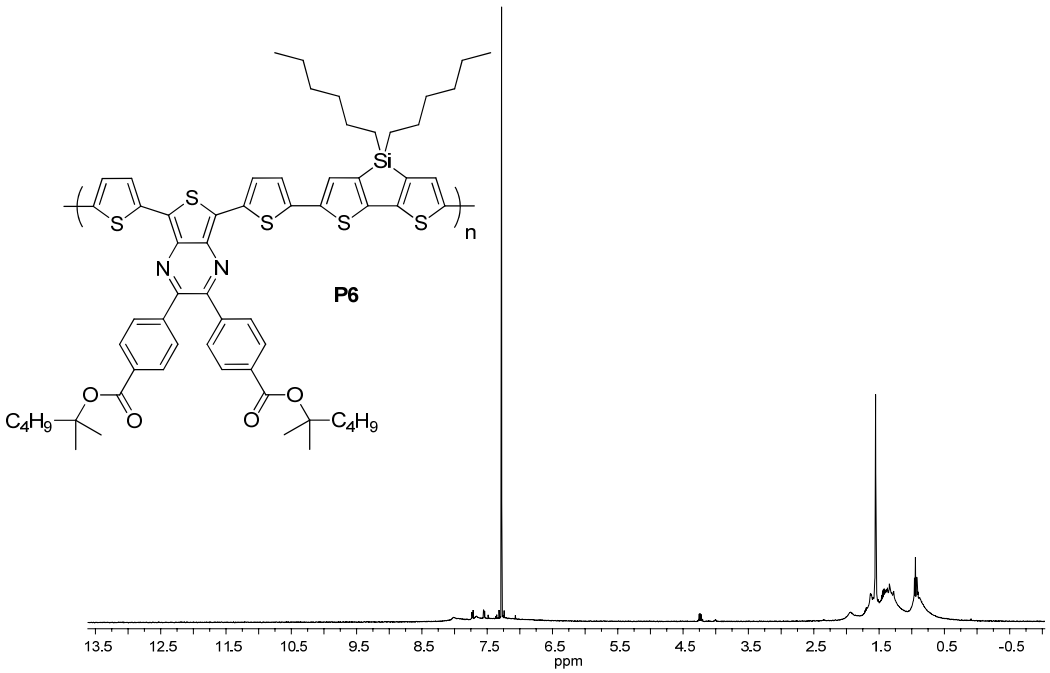
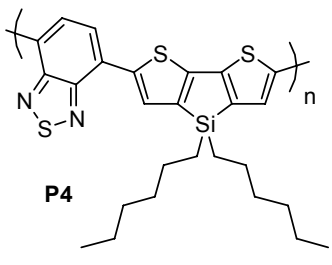


Figure S17. ^{1}H-NMR Spectrum of **P20** in $CDCl_3$



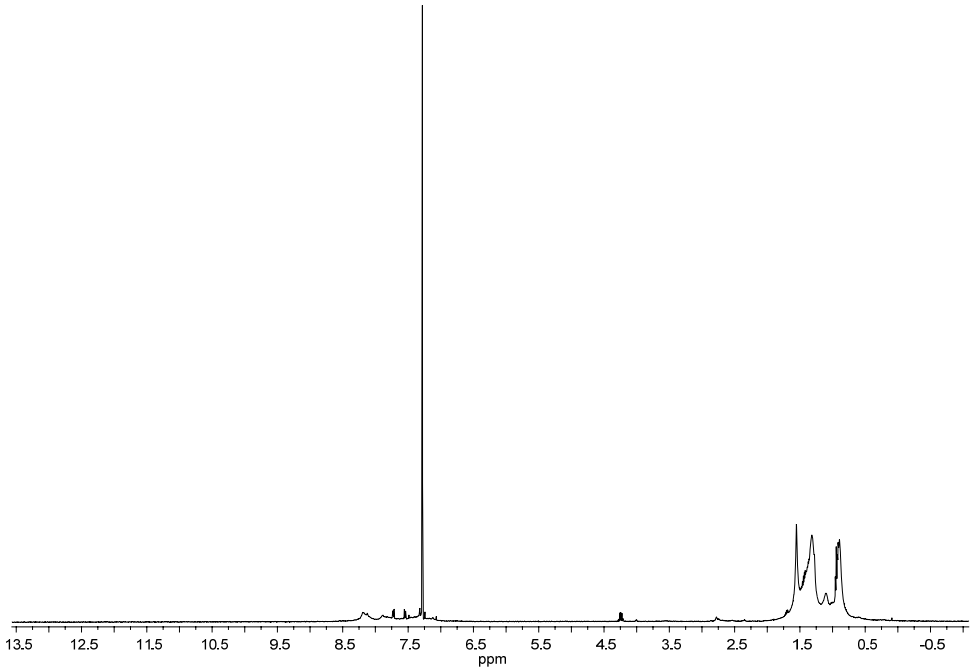


Figure S18. ^{1}H-NMR Spectrum of **P14** in $CDCl_3$

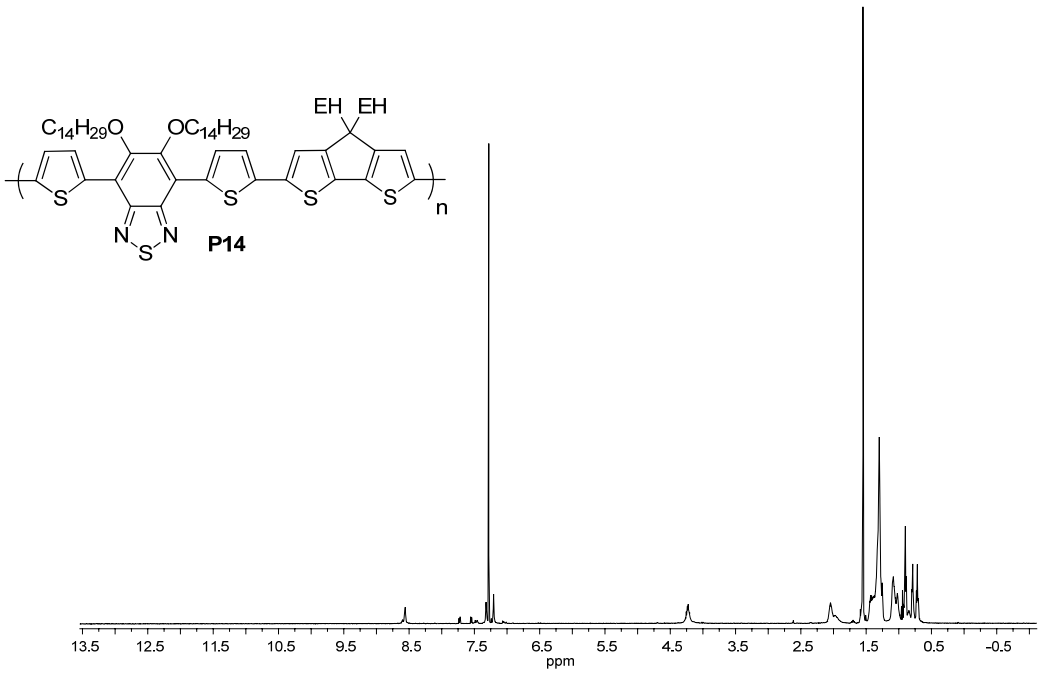
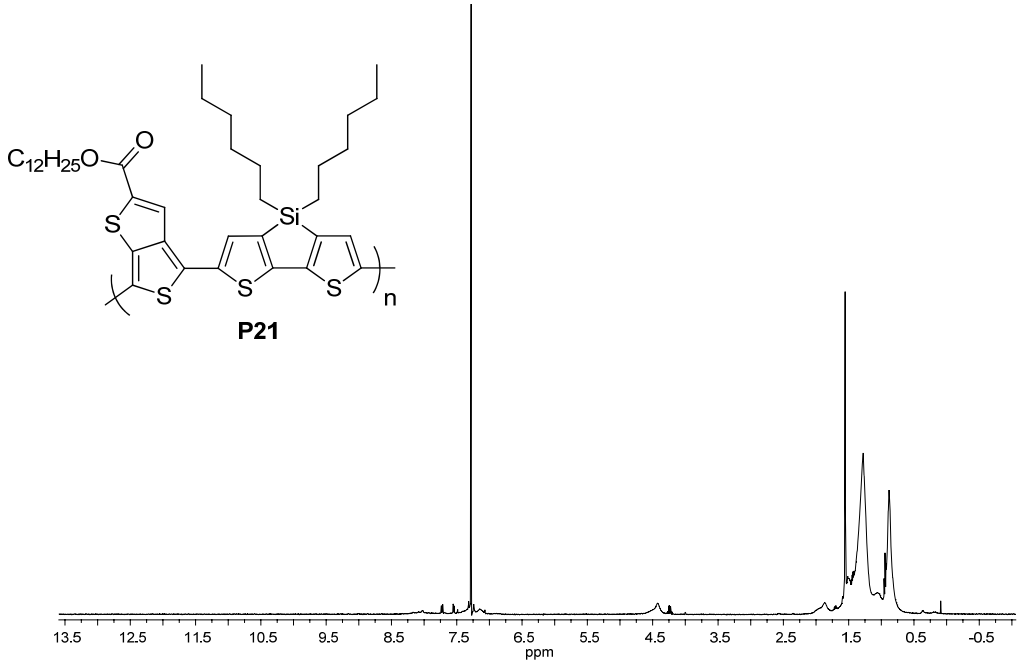
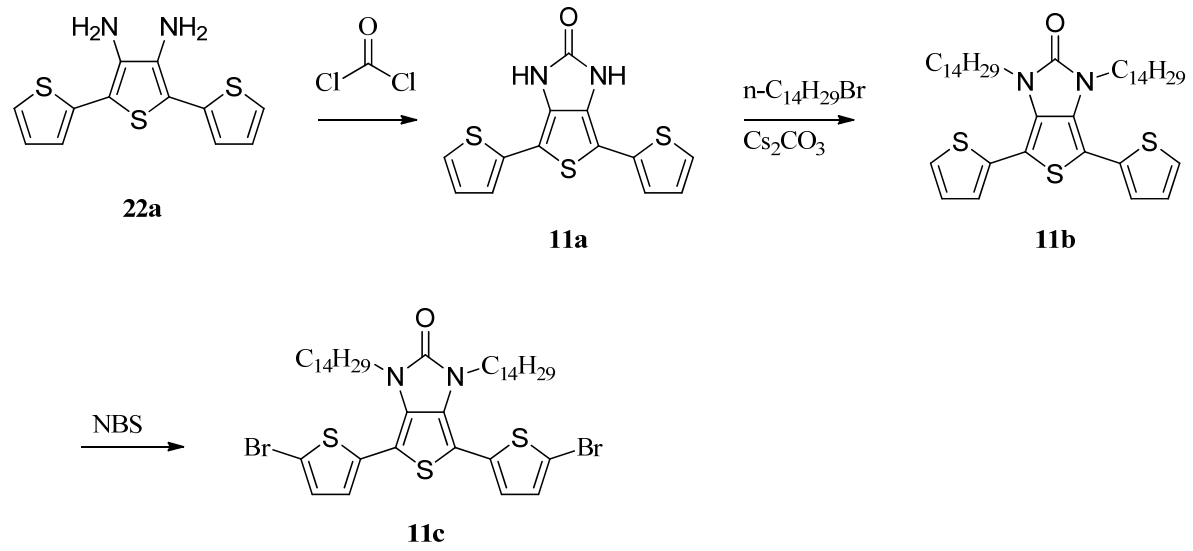


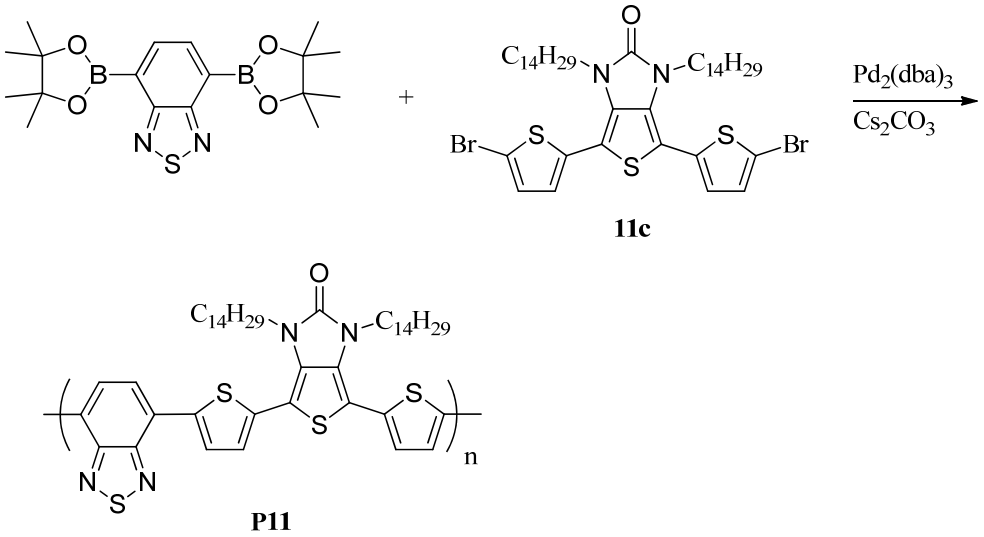
Figure S19. ^{1}H-NMR Spectrum of **P21** in $CDCl_3$

Supplementary Material (ESI) for Journal of Materials Chemistry



P21





Scheme S6. Synthesis of the polymer **P11**.

4,6-di(thiophen-2-yl)-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one (11a).

3',4'-diamino-[2,2';5',2"]terthiophene (3.0 g, 10.78 mmol) and triethylamine (4.7 ml, 33.4 mmol) was dissolved in toluene (60 ml) and cooled on an ice bath. Phosgene (20% in toluene) (6.3 ml, 12.10 mmol) in additional toluene (30.0 ml) was then added drop wise over 20 min while stirring (immediate precipitation - green). The reaction was then stirred at RT for 1 hour after which MeOH was added (400 ml) and the precipitate was isolated by filtration followed by washing with water and drying in a vacuum oven (2.12 g). Evaporation of the solvents from the toluene/MeOH filtrate and treatment of the resulting solid with water (200 ml) and drying in vacuum yielded a crude (1.13 g) which after purification by gradient column chromatography (heptanes/Ethyl acetate, 5% steps) resulted in additional pure compound (0.57 g), thus giving a total yield of 2.69 g (82%). ^{1}H NMR (500 MHz, DMSO) d 11.09 (s, 2H), 7.48 (d, J = 5.0, 2H), 7.39 (d, J = 3.7, 2H), 7.12 (dd, J = 3.7, 5.0, 2H). ^{13}C NMR (126 MHz, DMSO) d 160.21, 133.91, 128.51, 127.79, 124.44, 123.98, 103.32.

1,3-ditetradecyl-4,6-di(thiophen-2-yl)-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one (11b).

11a (1.0 g, 3.29 mmol), 1-bromotetradecane (2.37 g, 8,54 mmol) and cesium carbonate (3.2 g, 9,9 mmol) in N-Methyl-2-pyrrolidinone (11 ml) was heated to 120 °C for 3 hours. Water was added and the mixture extracted with ether. The collected organic phases were washed extensively with water followed by wash with brine and drying over $MgSO_4$. Evaporation of the solvent yielded a crude (2.84 g) which was purified by gradient column chromatography (heptanes/DCM, 6% steps) yielding the pure product.(1.71 g, 75%). ^{1}H NMR (500 MHz, CDCl3) δ 7.37 (dd, J = 5.2, 1.2, 2H), 7.13 (dd, J = 3.5, 1.2, 2H), 7.08 (dd, J = 5.2, 3.5, 2H), 3.78 (t, J = 7.5, 4H), 1.38 - 1.03 (m, 48H), 0.87 (t, J = 7.0, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 158.65, 132.47, 128.77, 128.68, 127.49, 127.11, 104.95, 42.25, 32.08, 29.86, 29.83, 29.82, 29.78, 29.67, 29.52, 29.21, 29.09, 26.46, 22.85, 14.28.

4,6-bis(5-bromothiophen-2-yl)-1,3-ditetradecyl-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one (11c).

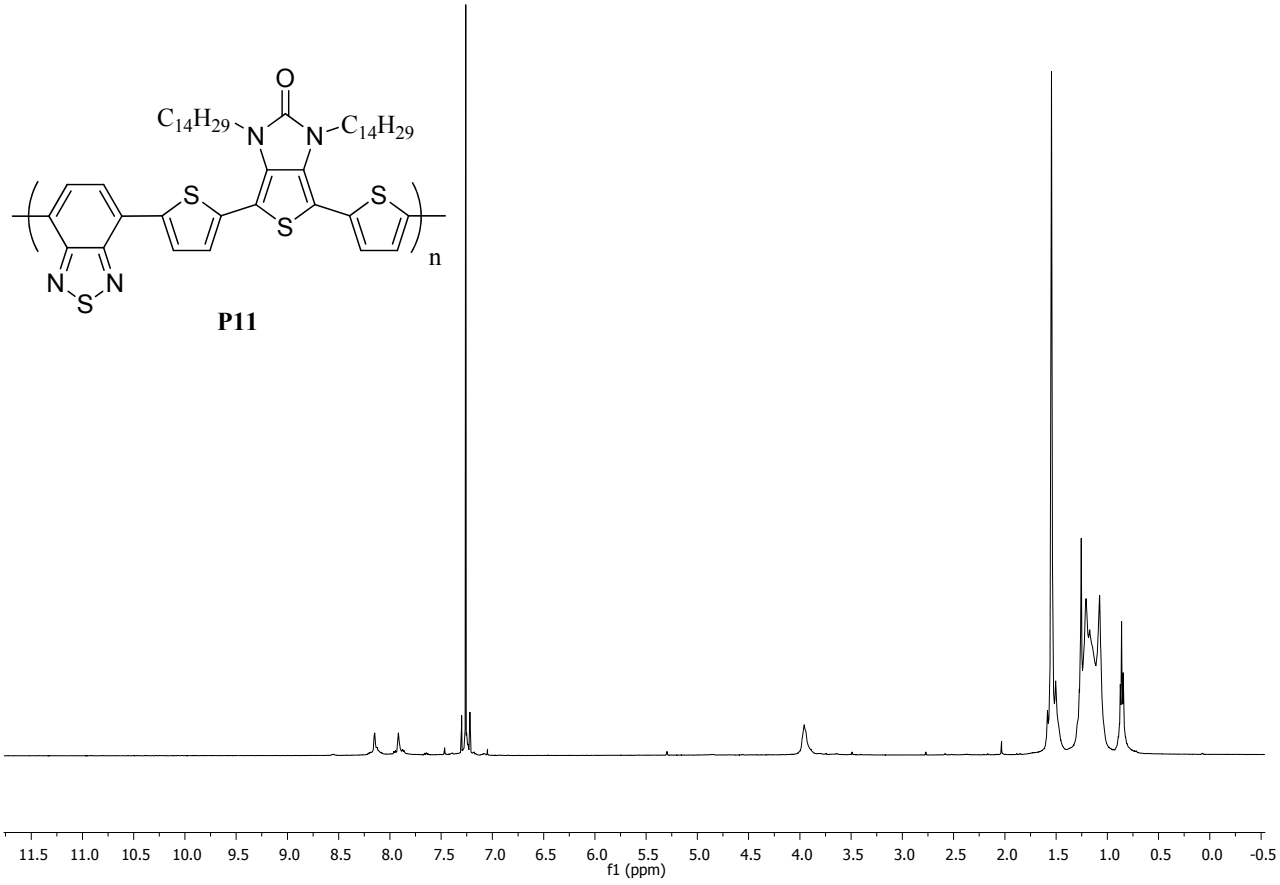
To a solution of **11b** (1.42 g, 2.04 mmol) in $CHCl_3$ (50 ml) was added NBS (1.80 g, 10.11 mmol) in small portions (200 mg at a time) over a period of 18 hours while simultaneously monitoring the reaction by TLC. The reaction mixture was then washed with water and brine and then dried over $MgSO_4$. Removal of the solvent in vacuo yielded a crude (1.9 g) which upon purification by gradient

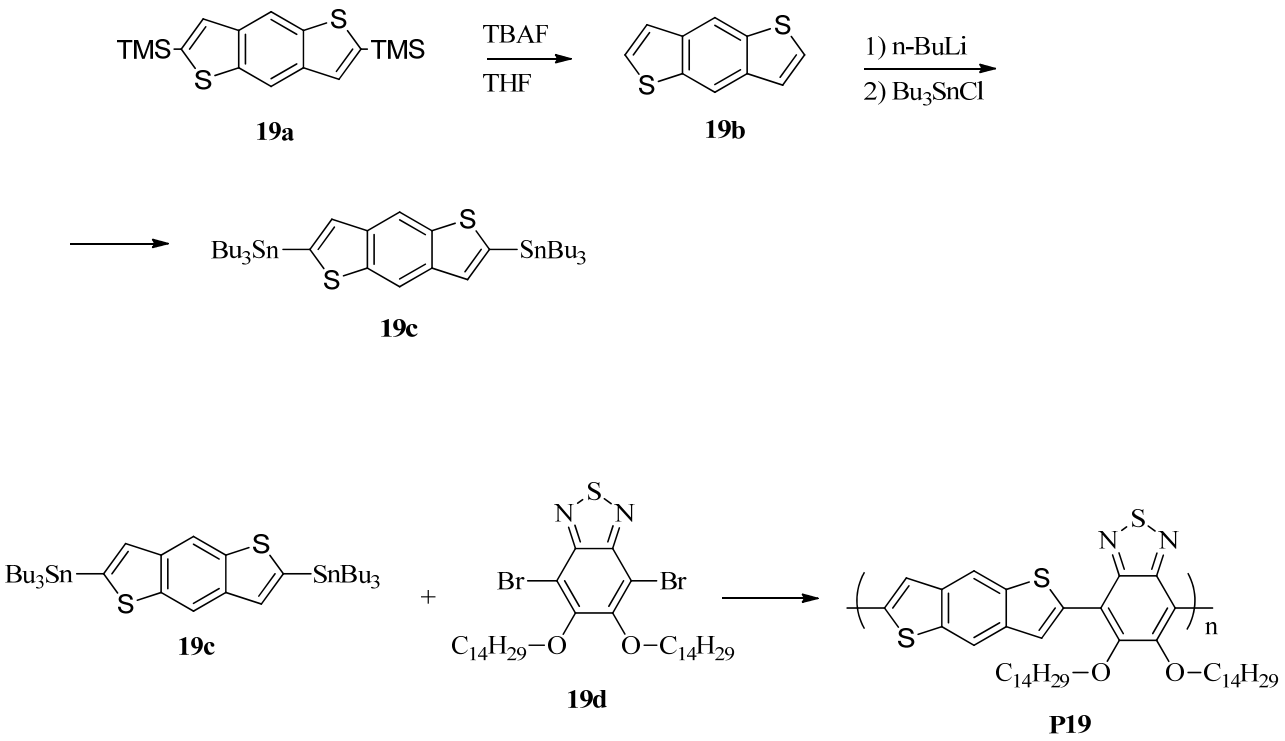
column chromatography (heptanes/DCM) yielding the pure product (1.46 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 3.8 Hz, 2H), 6.88 (d, *J* = 3.8 Hz, 2H), 3.80 – 3.72 (m, 4H), 1.41 – 1.32 (m, 4H), 1.33 – 1.06 (m, 44H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.42, 133.82, 130.42, 129.19, 129.03, 113.53, 104.23, 42.30, 32.08, 29.86, 29.84, 29.82, 29.80, 29.69, 29.55, 29.52, 29.22, 29.11, 26.48, 22.85, 14.27.

Poly(4-(5-(benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-1,3-ditetradecyl-6-(thiophen-2-yl)-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one) (P11).

11c (171.7 mg, 0.201 mmol), 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (82.2 mg, 0.201 mmol), Cs_2CO_3 (654 mg, 2.01 mmol), $Pd_2(dba)_3$ (11.5 mg, 0.013 mmol), tri-*o*-tolylphosphine (25 mg, 0.082 mmol) and a drop of Aliquat 336 is mixed in dry, degassed toluene (8 ml) and degassed Water (0.75 ml). The temperature was then raised to 90 °C and the mixture was stirred for 24 hours. Precipitation of the polymer was performed by drop wise addition of the mixture to methanol (120 ml), and the polymer was subsequently purified by soxhlet extraction with MeOH (24 h) and hexane (24 h) followed by extraction with chloroform, evaporation of the solvent and reprecipitation from toluene solution to methanol.

Figure S20. ^{1}H-NMR Spectrum of **P11** in $CDCl_3$





19a **19b** **19c** **19c** **19d** **P19**

Scheme S6. Synthesis of the polymer **P19**.

19a[‡‡] and **19d**[§§] were prepared as previously reported.

Benzo[1,2-*b*:4,5-*b'*]dithiophene (19b).

To a solution of **19a** (0.800 g, 2.39 mmol) in THF (30 ml) was added a solution of 1 M TBAF (5.26 ml, 5.26 mmol). The mixture was allowed to stir at RT for 3 hours, after which the solution was poured into water (100 ml). The formed precipitate was filtered of and washed with excess water and water/methanol (1:1). The crude (431 mg) was the purified by gradient column chromatography (hep/AcOEt, 2% steps) to yield the pure compound as colorless crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ

‡‡ K. Takimiya, Y. Konda, H. Ebata, N. Niihara, and T. Otsubo, *J. Org. Chem.*, 2005, **70**, 10569-10571.
§§ §§ M. Helgesen, S.A. Gevorgyan, F.C. Krebs and R. A.J. Janssen, *Chem. Mater.*, 2009, **21**, 4669-4675.

8.32 (s, 2H), 7.47 (d, *J* = 5.5 Hz, 2H), 7.37 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.66, 137.29, 127.18, 123.07, 116.99.

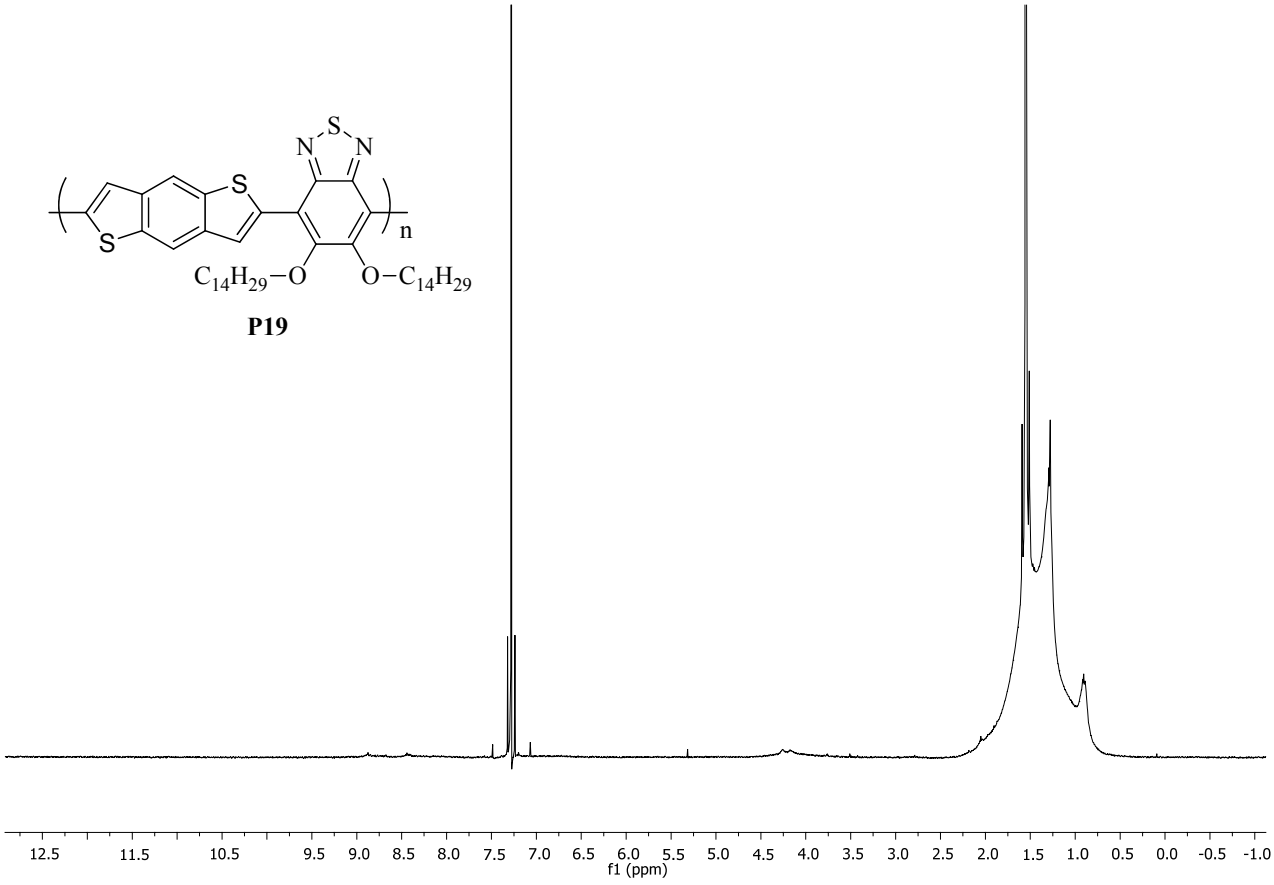
2,7-bis(tributylstannyl)benzo[1,2-*b*:6,5-*b'*]dithiophene (19c).

19b (0.5 g, 2.63 mmol) was dissolved in THF (60 ml) and cooled to -78 °C. Butyllithium (7 ml, 1.6 M, 11.2 mmol) was added drop wise while monitoring the reaction by NMR. Tributylchlorostannane (3.89 g, 11,95 mmol) in THF (5 ml) was then added after which the temperature was allowed to reach RT. The Reaction mixture was concentrated in vacuo, followed by purification by column chromatography using basic Al_2O_3 and 3% Et_3N in hexane as eluent. The (by TLC) pure product (1.21 g, 60%) was used without further purification or analysis.

Poly(4-(benzo[1,2-b:4,5-b']dithiophen-2-yl)-5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole) (P19).

19c (200 mg, 0.260 mmol), **19d** (187 mg, 0.260 mmol)), $Pd_2(dba)_3$ (17 mg, 0.019 mmol) and Tri-o-tolyl phosphine (43 mg, 0.141 mmol) were mixed in dry, degassed Toluene (10 ml) first at 80 °C and then 110 °C overnight. After precipitation in methanol the polymer was purified by soxhlet extraction with methanol (24 h) and hexane (24 h) followed by extraction of the polymer with chloroform. After removal of the solvent the polymer was redissolved in toluene and precipitated in methanol. The yield after filtration and drying was 190 mg.

Figure S21. ^{1}H-NMR Spectrum of **P19** in $CDCl_3$



P19