SUPPORTING INFORMATION

The synthesis of poly(thiophene-*co*-fluorene) gradient copolymers

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Reagents and Instrumentation. All reagents were purchased and used without further purification. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). 2-bromo-7-iodofluorene[1], 2-bromo-5-iodo-3-((*S*)-3,7-dimethyloctyl) thiophene (**1**)[2]and the initiator (**3**)[3] were synthesized according to literature procedures.

^{1}H-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 10A GPC system. The column is a PLgel 5µm mixed-D type column and the detection system consists of a differential refractometer and a UV-vis spectrophotometer. The SEC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF (c ≈ 1 mg/mL) and filtered over a pore size of 0.2 µm. Mass spectra are recorded using an Aligent HP5989. UV-vis and CD measurements were performed on a Perkin-Elmer Lambda 900 UV-Vis NIR and a JASCO 62 DS apparatus, respectively. DSC samples were put in Tzero Aluminium Hermetic pans and the spectra were recorded in a TA Instruments Q2000 DSC, calibrated towards indium. A heating rate of 10°C/min was used.

Synthesis of 2. A solution of 3-bromo-7-iodofluorene (16.5 mmol, 6.25 g) in DMSO (60 mL) was sealed with a $CaCl_2$-tube. An aqueous solution of NaOH (50%, 6.50 mL) was added slowly, after which (*S*)-3,7-dimethyloctylbromide (41.3 mmol, 7.87g) was also added to the reaction mixture. After 12 hours, the mixture was poured into 100 mL of ethyl acetate. The salts precipitated and were filtered off. The organic layer was washed with an aqueous NaOH-solution, brine and water. Afterwards, the organic phase was dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The remaining alkylbromide was removed by vacuumdestillation and the crude product was further purified using column chromatography (SiO_2; eluens: heptane). Yield: 19.8g (76%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (dd, J=8Hz, J=2Hz, 1H), 7.63 (d, J=2Hz, 1H), 7.52 (d, J=8Hz, 1H), 7.44 (dd, J=8HZ, J=2Hz, 1H), 7.43 (d, J=2Hz, 1H), 7.40 (d, J=8HZ, 1H), 1.91 (m, 4H), 1.45 (m, 2H), 1.20-0.90 (m, 14H), 0.82 (d, 12H), 0.68 (d, 6H), 0.61-0.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 152.6, 152.2, 139.8, 139.2, 136.0, 132.0, 130.1, 126.0, 121.6, 121.4, 121.2, 92.9, 55.4, 39.2, 37.4, 36.5, 32.8, 27.9, 24.5, 22.7, 22.6, 19.5. MS (EI): 650/652 ($M^{\bullet+}$), 524/526 ($M^{\bullet+}$-I), 383/385 ($M^{\bullet+}$-I-C_9H_{19}), 369/371 ($M^{\bullet+}$-2xC_9H_{19}), 279 ($M^{\bullet+}$-I-Br-$C_{12}H_{25}$), 243/245 ($M^{\bullet+}$-I-2xC_9H_{19}).

Random copolymer synthesis via CTP. 1 (250 µmol, 107 mg) and **2** (250 µmol, 163 mg) are put in separate flasks, brought under argon atmosphere and dissolved in dry THF (5mL). A iPrMgCl•LiCl-solution (250 µmol, 210 µL, 1.19 M) is added dropwise to both flasks in order to start the Grignard Metathesis. After 1 hour, the monomers are combined and stirred for 10 minutes, after which the monomer mixture in cannulated to a flask containing Ni(dppp)Cl_2 (10.0 µmol, 5.40 mg) in dry THF (2 mL) under argon atmosphere. After 1 hour, the polymerization is terminated with acidified THF and the polymer is precipitated in methanol. The polymer is then purified using a Soxhlet extraction with methanol and chloroform. The chloroform-soluble fraction is again precipitated in methanol, filtered off and dried *in vacuo*.

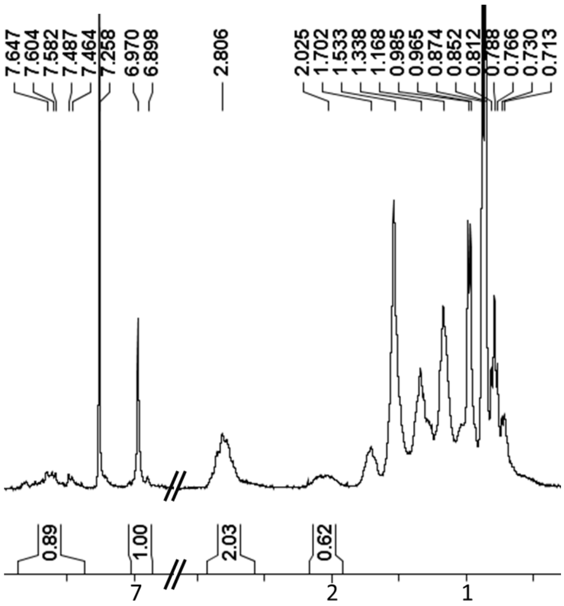


Figure S1. ^{1}H NMR spectrum of the copolymer formed by adding a 50/50 mixture of thiophene and fluorene monomers to a Ni(dppp)Cl_2 catalyst. The amount of thiophene and fluorene in the polymer chain is determined using the α-methylene protons of thiophene (2.80 ppm) and fluorene (2.02 ppm). These protons give clear separate signals in the spectrum, and their integration immediately provides the ratio between both monomers, off course taking into account the amount of protons each peak represents (2 and 4, respectively). It is concluded that almost pure poly(thiophene) is formed, with only a very small amount (13%) of fluorene monomer.

Synthesis of thiophene monomer (1'). The precursor monomer (**1**) (3.05 mmol, 1.31 g) is loaded in a flask and dried overnight using P_2O_5. Afterwards, the flask is purged with argon and dry THF (10 mL) is added. 1 equivalent of *t*BuMgCl (3.05 mmol, 2.03 mL, 1.50 M) is added and this is left to react for 1 hour. Then, a sample (0.05 mmol) is quenched with D_2O and analyzed with ^{1}H NMR spectroscopy to check for full conversion. The reaction mixture is subsequently cannulated to a flask containing pre-dried $ZnBr_2$ under argon atmosphere. The transmetalation takes place for 15 minutes, after which the monomer is ready for use in the polymerization.

Synthesis of fluorene monomer (2'). The precursor monomer (**2**) (3.05 mmol, 1.99 g) is loaded in a flask and dried overnight using P_2O_5. To convert this precursor monomer to the bromozincio analogue, the Turbo Grignard reagent *t*Bu_3MgLi needs to be prepared first. A small flask is purged with argon and 2 mL of dry THF is added. First, *t*BuMgCl (1.50 mmol, 1.00 mL, 1.50 M) and subsequently *t*BuLi (1.50 mmol, 2.00 mL, 1.50 M) are added to the solvent. This is left to stir for 1 hour. Meanwhile, the flask with precursor monomer (**2**) is purged with argon and dry THF (10 mL) is added. Once the Turbo Grignard reagent is ready, it is added to the precursor monomer in exactly 1 equivalent (3.05 mmol, 3.39 mL, 0.900 M). After one hour, a sample (0.05 mmol) is taken and quenched with D_2O. The conversion is checked with ^{1}H NMR spectroscopy. When the reaction has reached full conversion, the reaction mixture is cannulated to a flask containing pre-dried $ZnBr_2$ under argon atmosphere. The transmetalation takes place for 15 minutes, after which the monomer can be used in the polymerization.

General polymerization procedure. The thiophene (**1'**) and fluorene (**2'**) monomers are cannulated to 6 different dry flasks under argon atmosphere for mixing in the desired ratios. After a few minutes of mixing, the monomer solutions are transferred to flasks containing the initiator (**3**) (30.0 µmol, 26.0 mg) dissolved in dry THF. The polymerization proceeds during 1 hour, after which it is stopped by adding a few drops of acidified THF. The polymers are precipitated in methanol and filtrated. Soxhlet extraction with methanol and chloroform is used for purification. The chloroform-soluble fraction is again precipitated in methanol, filtered off and dried *in vacuo*.

Polymer **1**: Fluorene monomer (**2'**) (1.00 mmol, 650 mg) was combined with the initiator. Yield: 255 mg (57%).

Polymer **2**: Thiophene monomer (**1'**) (0.200 mmol, 90.0 mg) was combined with Fluorene monomer (**2'**) (0.800 mmol, 520 mg) and the initiator. Yield: 195 mg (49%).

Polymer **3**: Thiophene monomer (**1'**) (0.400 mmol, 170 mg) was combined with Fluorene monomer (**2'**) (0.600 mmol, 390 mg) and the initiator. Yield: 198 mg (56%).

Polymer **4**: Thiophene monomer (**1'**) (0.600 mmol, 260 mg) was combined with Fluorene monomer (**2'**) (0.400 mmol, 260 mg) and the initiator. Yield: 209 mg (67%).

Polymer **5**: Thiophene monomer (**1'**) (0.800 mmol, 340 mg) was combined with Fluorene monomer (**2'**) (0.200 mmol, 130 mg) and the initiator. Yield: 194 mg (73%).

Polymer **6**: Thiophene monomer (**1'**) (1.00 mmol, 430 mg) was combined with the initiator. Yield: 164 mg (73%).

The data shown in Table 1 for $\overline{M}_\mathrm{n}$ and Đ are recorded after purification by Soxhlet extraction. However, since only methanol was used during this purification, mostly monomer was removed and the dispersity was only affected to a limited extent (as shown for an example in Figure S2). A similar change is to be expected for the polymers **P1-P6**.

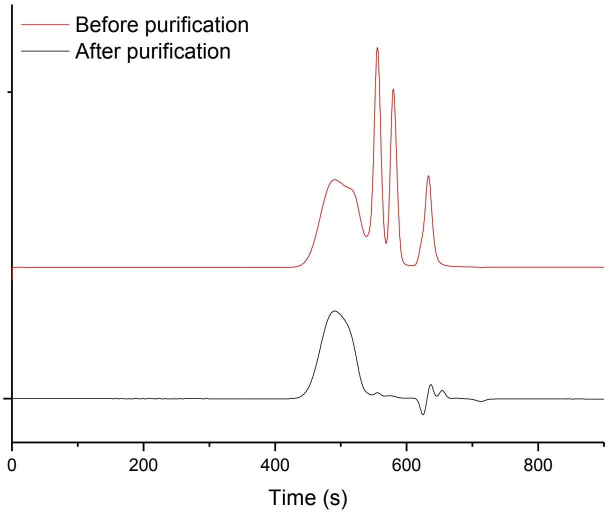


Figure S2. The effect of purification by Soxhlet with methanol for a 50/50 thiophene/fluorene copolymerization, showing that mostly monomer is removed. Nevertheless, the dispersity was changed from 1.58 (before purification) to 1.47 (after purification) and the $\overline{M}_n$ shifted from 3.2 kg/mole to 3.4 kg/mole in this example.

Chain extension experiment. The thiophene monomer (**1'**) (0.370 mmol, 0.159 g) and fluorene monomer (**2'**) (0.120 mmol, 78.1 mg) are synthesized according to the procedures described above. **2'** is subsequently mixed with **1'** (0.120 mmol) and this mixture is transferred to a solution of the initiator (**3**) (25.0 µmol, 20.5 mg) in THF (2.00 mL). The copolymerization continues for 1h, after which a sample is taken for GPC analysis. Subsequently, a fresh batch of **1'** (the remaining 0.25 mmol) is added. After 1 hour, the polymerization is terminated with acidified THF and another GPC spectrum is recorded (Figure S3).

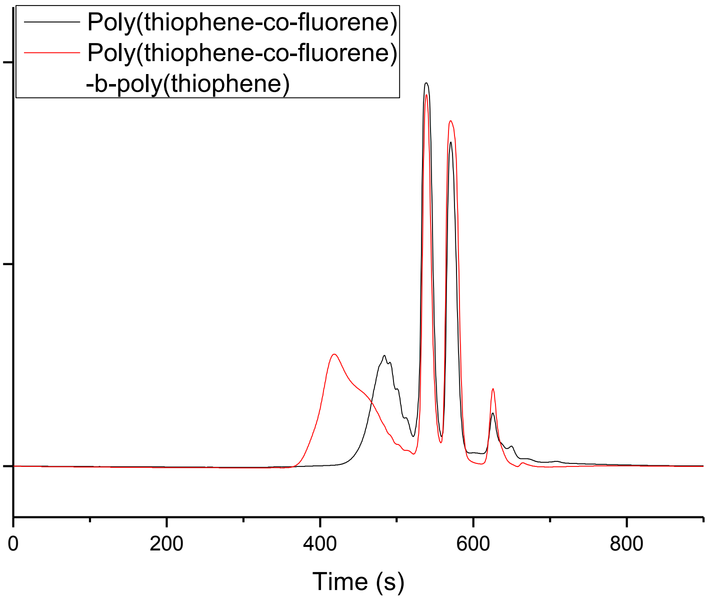


Figure S3. Chain extention experiment to verify the living character of the polymerization. After the copolymerization of thiophene and fluorene (50/50) during 1 hour, a fresh batch of thiophene monomer was added and the polymerization was continued for another hour. The majority of the polymer chains shows further growth and the formation of a copolymer. However, also a lower molar mass shoulder is observed, which is ascribed to the occurrence of transfer reactions. This is inherent to the Pd(RuPhos) protocol, since even the smallest presence of moisture results in the formation of transfer agents.

Lewis-Mayo Plot. In order to obtain the Lewis-Mayo plot, the polymerization procedure was followed as described previously, but the monomers **1’** and **2’** were now mixed during several minutes in dry flasks containing 1,2,3-trimethoxybenzene (0.500 mmol, 83.0 mg). This compound serves as internal reference in the GPC analysis. An aliquot of the monomer mixture is taken, and the remainder is transferred to the initiator. The polymerizations were quenched within 10s after all monomer was added, since a previous experiment has shown that 10% conversion was already reached within that time frame. Each monomer mixture showed 3 different peaks in GPC analysis, which could be ascribed to the fluorene monomer, thiophene monomer and internal reference, respectively. Calibration with the internal reference allowed for comparison of the monomer mixtures with their respective quenched polymerizations, and the determination of the conversion of both monomers separately. The fraction of each monomer in the polymer at low conversion can then easily be calculated. This experiment was performed at room temperature and at 0°C.

Data (25°C)

f_A	*Thiophene Conversion*	*Fluorene conversion*	*total conversion*	F_A
0.2	12%	4%	8%	0.43
	13%	9%	11%	0.26
	14%	6%	10%	0.37
0.4	16%	6%	11%	0.64
	18%	4%	11%	0.75
	17%	5%	11%	0.69
0.6	20%	8%	14%	0.79
	16%	4%	10%	0.85
	18%	4%	11%	0.86
0.8	43%	22%	33%	0.84
	40%	15%	28%	0.81
	36%	21%	29%	0.87

f_A	*Average conversion*	*Average* F_A	*Standard deviation*
0.2	10%	0.35	0.069
0.4	11%	0.69	0.045
0.6	12%	0.83	0.031
0.8	30%	0.84	0.024

Data (0°C)

f_A	Thiophene Conversion	Fluorene conversion	Total conversion	F_A
0.2	10%	6%	8%	0.29
	15%	12%	14%	0.24
	11%	3%	7%	0.36
0.4	8%	2%	5%	0.72
	14%	6%	10%	0.61
	9%	4%	7%	0.60
0.6	14%	3%	9%	0.87
	10%	2%	6%	0.83
	13%	3%	8%	0.83
0.8	14%	9%	12%	0.86
	10%	4%	7%	0.91
	12%	5%	9%	0.91

f_A	Average conversion	Average F_A	Standard deviation
0.2	10%	0.30	0.049
0.4	7%	0.64	0.053
0.6	8%	0.84	0.019
0.8	9%	0.90	0.024

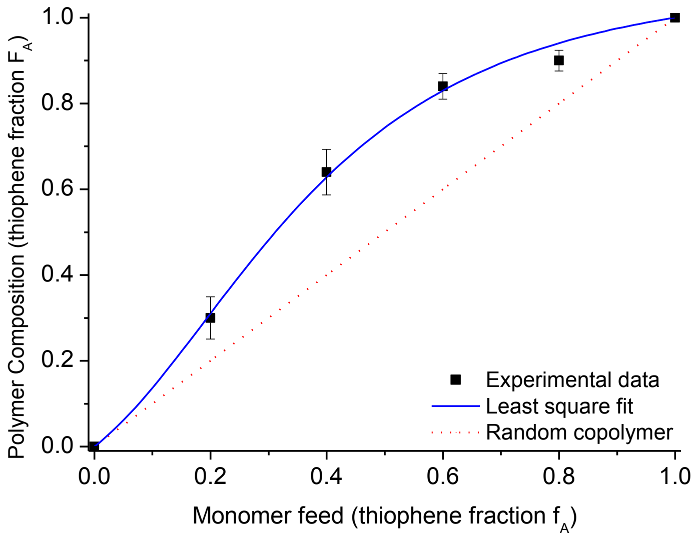


Figure S4. Lewis-Mayo plot for the thiophene/fluorene copolymerization performed at 0°C. In this case, $r_A = 4.6 \pm 1.0$ and $r_B = 0.95 \pm 0.22$.

The concentration during the polymerization is 0.1 M, but the quenches are diluted to a concentration of around 0.02 M for GPC analysis to avoid saturation of the UV-Vis detector. In the concentration region around 0.02 M, the law of Lambert-Beer is still obeyed and the peak surface in a GPC spectrum relates linearly to the concentration (Figure S5).

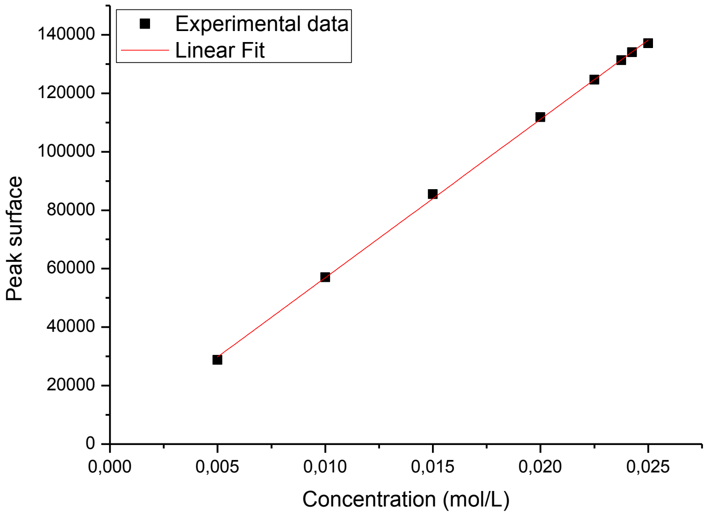
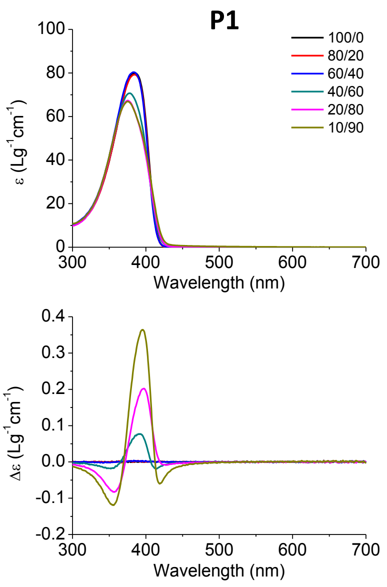
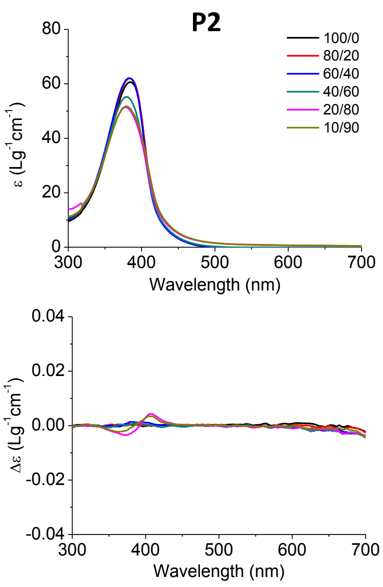
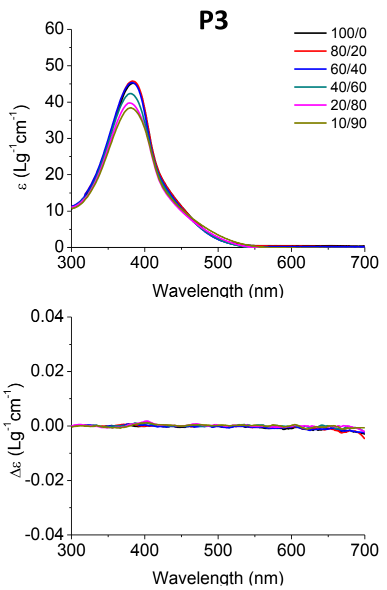
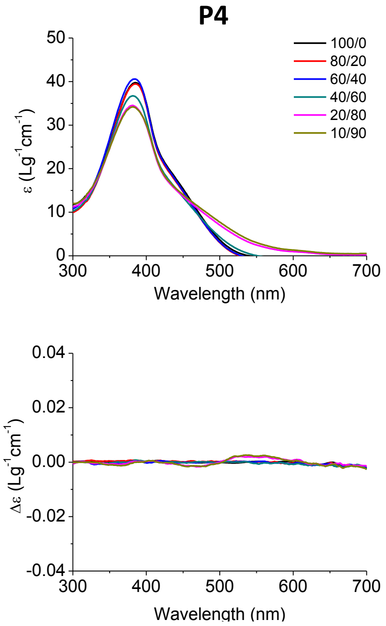


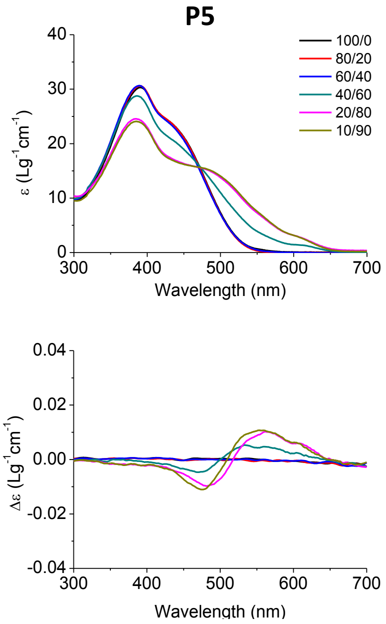
Figure S5. The peak surface of 1,3,5-trimethoxybenzene in function of its concentration. The linear relation shows that the law of Lambert-Beer is followed in the concentration region around 0.02M.


P1
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
20
40
60
80
100
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.2
-0.1
0.0
0.1
0.2
0.3
0.4
300
400
500
600
700
Wavelength (nm)


P2
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
20
40
60
80
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.04
-0.02
0.00
0.02
0.04
300
400
500
600
700
Wavelength (nm)


P3
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
10
20
30
40
50
60
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.04
-0.02
0.00
0.02
0.04
300
400
500
600
700
Wavelength (nm)


P4
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
10
20
30
40
50
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.04
-0.02
0.00
0.02
0.04
300
400
500
600
700
Wavelength (nm)


P5
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
10
20
30
40
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.04
-0.02
0.00
0.02
0.04
300
400
500
600
700
Wavelength (nm)

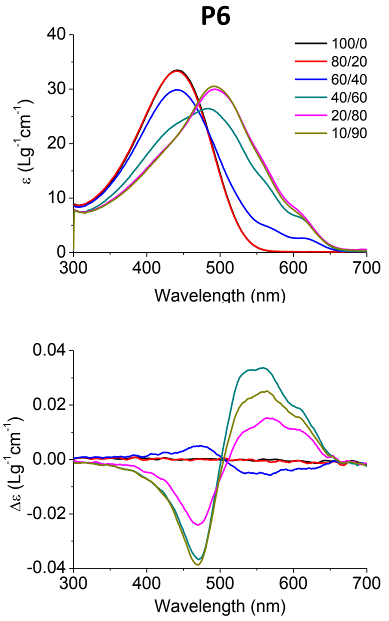
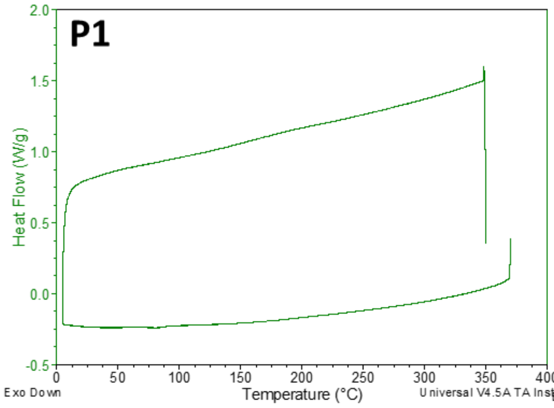
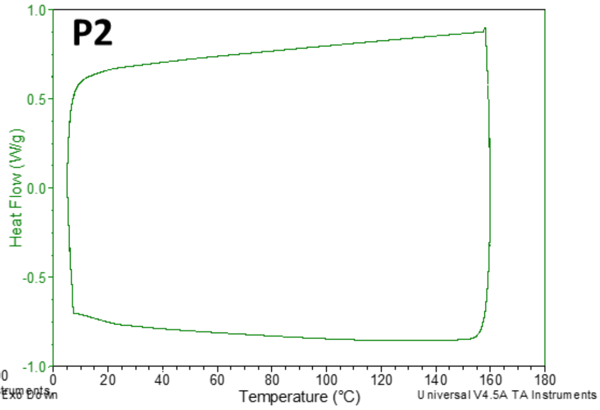
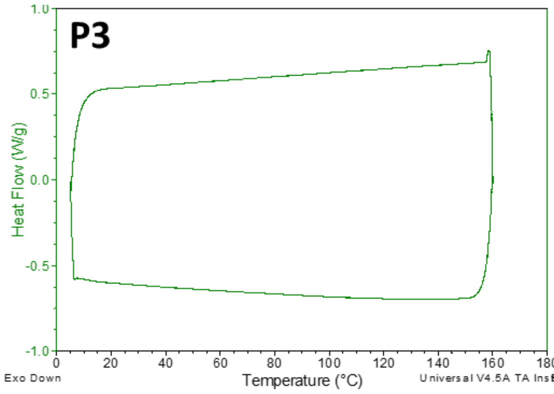
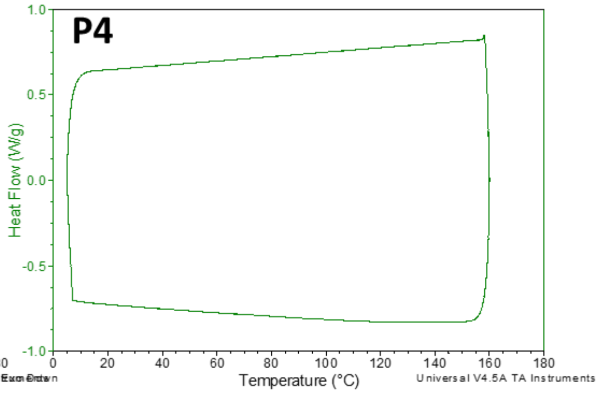

P6
100/0
80/20
60/40
40/60
20/80
10/90
ε (Lg^{-1}cm^{-1})
0
10
20
30
40
300
400
500
600
700
Wavelength (nm)
Δε (Lg^{-1}cm^{-1})
-0.04
-0.02
0.00
0.02
0.04
300
400
500
600
700
Wavelength (nm)

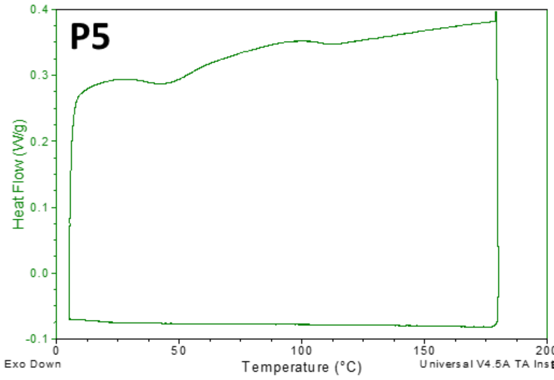
Figure S6. Absorption and CD spectra of all thiophene/fluorene copolymers upon addition of increasing amounts of methanol to the polymer solutions in chloroform (Chloroform/Methanol ratio is indicated in the graphs)


P1
Heat Flow (W/g)
2.0
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
250
300
350
400
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments


P2
Heat Flow (W/g)
1.0
0.5
0.0
-0.5
-1.0
0
20
40
60
80
100
120
140
160
180
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments


P3
Heat Flow (W/g)
1.0
0.5
0.0
-0.5
-1.0
0
20
40
60
80
100
120
140
160
180
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments


P4
Heat Flow (W/g)
1.0
0.5
0.0
-0.5
-1.0
0
20
40
60
80
100
120
140
160
180
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments


P5
Heat Flow (W/g)
0.4
0.3
0.2
0.1
0.0
-0.1
0
50
100
150
200
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments

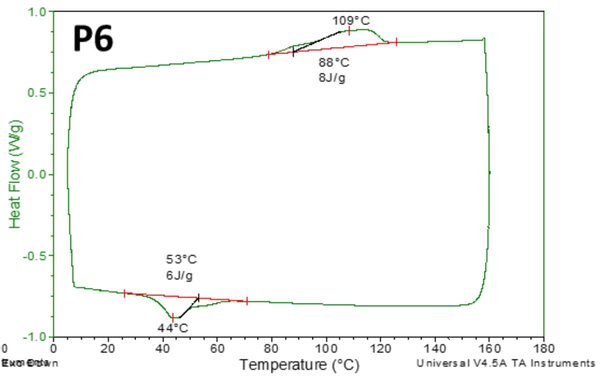

P6
109°C
88°C
8J/g
53°C
6J/g
44°C
Heat Flow (W/g)
1.0
0.5
0.0
-0.5
-1.0
0
20
40
60
80
100
120
140
160
180
Temperature (°C)
Exo Down
Universal V4.5A TA Instruments

Figure S7. DSC results for all copolymers. Only **P6** shows clear crystallization and melting. For **P5** a signal is observed during heating, but it is ill defined. All other polymers show no melting or crystallization.

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(2) Van den Bergh, K.; Cosemans, I.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2010**, *43* (8), 3794–3800.

(3) Verswyvel, M.; Verstappen, P.; De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49* (24), 5339–5349.