Electronic Supplementary Information

Poly(3-alkylthiophene) with tuneable regioregularity: synthesis and self-assembling properties.

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Experimental details

Reagents and Instrumentation

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, TCI and Alfa Aesar. Reagent grade solvents were dried by distillation over a suitable drying agent. Tetrahydrofuran (THF), diethylether (Et_2O) and toluene were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). ^{1}H NMR and ^{13}C NMR measurements were carried out with a Bruker Avance 300 MHz. ^{31}P NMR measurements were performed on a Bruker Avance 400 MHz. Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with an absorbance detector and a differential refractometer in THF toward polystyrene standards. Mass spectra were recorded using an Agilent HP5989, using chemical ionisation (CIMS). UV-vis spectra were recorded with a Perkin Elmer Lambda 900UV-vis NIR spectrometer. Circular Dichroism measurements were performed on a JASCO 62 DS apparatus. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q 2000 apparatus. The morphological AFM characterisation was carried out in ambient conditions, with a Bruker Multimode microscope equipped with a Nanoscope V controller. Measurements operated in intermittent-contact mode, using commercially available silicon probe-tips (PPP-NCHR, Nanosensors GmbH) with a spring constant of 42 N/m, a resonance frequency of about 330 kHz and a typical radius of curvature of the tipa apex below 7 nm. The C-AFM measurements were carried out in the same conditions as the standard AFM measurements with an additional external module (Ref. TUNA) for detection of low current (<1 pA). The measurements were operated in contact mode, using commercially available silicon probe-tips metal coated with $PtIr_5$. The spring constant of the cantilever lies around 0.1 N/m corresponding to contact forces below 1 nN. These low forces guarantee no scan induced topographical damage of the

fibrillar structure. $[\alpha]_D$ values are given in deg dm^{-1} g^{-1} mL. Compounds **1**, **4** and **6** were synthesized according to literature procedure.[1,2]

Synthesis of 5-bromo-3-((*S*)-3',7'-dimethyloctyl)thiophene (2)

n-BuLi (3.37 ml; 2.5 M in hexane) is added dropwise to an argon purged solution of tetramethylpiperidine (8.84 mmol; 1.25 g) in dry THF (10 mL) at -78°C. After 1 h reaction at room temperature, a solution of 3-((*S*)-3',7'-dimethyloctyl)thiophene (**1**) (8.90 mmol; 0.200 g) in dry THF (5 mL) is added through cannulae at -78°C. After a reaction time of 3 h at -78°C, an argon purged solution of CBr_4 (12.0 mmol; 3.98 g) in dry THF (10 mL) is cannulated to the reaction mixture. After stirring for 1 h at -78°C, the mixture is allowed to reach room temperature, after which the reaction is terminated by dropwise addition of H_2O. Afterwards, the product is extracted with heptane, washed with an aqueous $NaHCO_3$-solution and subsequently dried with $MgSO_4$. The crude product is obtained after solvent evaporation and is further purified by means of column chromatography (silica; eluent= heptane) and isolated as a colorless oil (1.96 g, 92%).

$[\alpha]_D^{20}$ +0.64 (*c* 17.8 g/ 100 mL in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 6.89 (1H, s), 6.81 (1H, s), 2.57 (2H, m), 1.52 (3H, m), 1.1-1.4 (7H, m), 0.92 (3H, d), 0.86 (6H, d); δ_C (75 MHz, $CDCl_3$, Me_4Si) 144.1, 131.0, 121.2, 111.6, 39.3, 37.5, 37.1, 32.3, 28.2, 28.0, 24.7, 22.7, 22.6, 19.5; CIMS *m*/*z*: 303 (M^+), 223 (M^+-Br).

Synthesis of 5-bromo-2-iodo-3-((*S*)-3',7'-dimethyloctyl)thiophene (3)

A solution of **2** (5.00 mmol; 1.50 g) in CH_2Cl_2 (30 mL) is brought under an argon atmosphere, cooled down to 0°C and shielded from light. Afterwards, I_2 (2.75 mmol, 0.700 g) and $PhI(OAc)_2$ (3.00 mmol; 0.960 g) are added. The reaction is monitored using TLC (silica; eluent= heptane) and after completion, an aqueous $Na_2S_2O_3$-solution is added to the reaction mixture. The mixture is subsequently extracted with heptane and the combined organic layers are dried with $MgSO_4$, after which the solvent is evaporated under reduced pressure. The crude product is further purified by means of column chromatography (silica; eluent= heptane) and obtained as a colorless oil (1.81 g, 85%).

$[\alpha]_D^{20}$ +0.45 (*c* 15.9 g/ 100 mL in $CHCl_3$); δ_H (300 MHz, $CDCl_3$, Me_4Si) 6.72 (1H, s), 2.48 (2H, m), 1.42-1.55 (3H, m), 1.08-1.37 (7H, m), 0.93 (3H, d), 0.87 (6H, d); δ_C (75 MHz, $CDCl_3$, Me_4Si) 148.3, 130.8, 115.1, 73.3, 39.5, 37.2, 37.2, 32.6, 30.3, 28.2, 28.0, 24.9, 23.1, 23.0, 20.0; CIMS *m*/*z*: 429 (M^+), 347 (M^+-Br), 303 (M^+-I).

Synthesis of the initiator (5)

A solution of $Pd_2(dba)_3$ (0.500 mmol, 0.458 g), RuPhos (1.02 mmol, 0.416 g) and 2-bromo-3-((*S*)-3',7'-dimethyloctyl)thiophene (**4**) (2.00 mmol, 0.605 g) are dissolved in dry toluene (10 mL), brought under an argon atmosphere and shielded from light. The reaction mixture is allowed to react overnight at 60°C. Subsequently, the total volume is reduced to 2 mL under reduced pressure, after which diethylether is added to the mixture. The solution is filtrated over Celite 545 and the filtrate volume is reduced again to 2 mL. Afterwards, 10 mL of pentane is added and the solution is stirred at 4°C overnight. Subsequently, the precipitate is filtered off, and the filtrate is further purified by means of column chromatography (alumina, eluent= 9/1 CH_2Cl_2/EtOAc). The pure product is obtained as a yellow powder (0.440 g, 25%).

δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.70 (1H, t), 7.57 (1H, m), 7.40 (2H, m), 7.28 (1H, d), 6.84 (2H, m), 6.68 (1H, d), 6.58 (1H, d), 4.61 (2H, m), 2.90 (1H, m), 2.68 (1H, m), 2.56 (1H, m), 2.38 (1H, m), 2.18 (1H, m), 1.58-1.82 (10H, m), 1.00-1.50 (27H, m), 0.70-0.95 (14H, m); δ_C (75 MHz, $CDCl_3$, Me_4Si)

160.3, 159.2, 144.9, 143.5, 135.9, 134.1, 133.7, 132.4, 130.6, 128.0, 126.9, 126.3, 117.5, 109.9, 107.63, 106.9, 71.7, 70.3, 39.5, 37.8, 37.5, 37.3, 35.1, 34.7, 33.8, 33.5, 32.9, 32.7, 29.8, 28.7, 28.0, 27.6, 26.9, 26.0, 25.8, 25.4, 24.9, 22.8, 22.6, 22.5, 21.6, 21.4, 19.7; δ_P (162 MHz, $CDCl_3$, H_3PO_4) -12.3 ppm

Synthesis of the polymers

t-BuMgCl (4.24 ml, 1.50 M in hexane) is added to an argon purged solution of 2-bromo-5-iodo-3-((*S*)-3',7'-dimethyloctyl)thiophene **(6)** (6.36 mmol; 2.73 g) in dry THF (63.6 ml). After 15 min reaction at 40°C, followed by 30 min reaction at room temperature, a part of this solution (0.28 mL) is quenched with D_2O to check the conversion, the remainder is cannulated to a flask containing dried $ZnBr_2$ (12.7 mmol, 2.86 g). After 30 min reaction at room temperature, a part of the solution (0.27 mL) is quenched with D_2O. Simultaneously, the same procedure is performed for a solution of **3** (0.75 mmol, 0.553 g) using dry THF (7.10 ml), *t*-BuMgCl (0.50 ml, 1.50 M in hexane) and $ZnBr_2$ (1.50 mmol, 0.338 g). Afterwards, these two monomer solutions are combined in the predefined quantities (see Table S1). The resulting mixtures of the two isomers are subsequently cannulated to an argon purged solution of **5** (4 mol%, 0.352 g) in dry THF (1 mL). The polymerisation occurs overnight at room temperature, after which the reactions are quenched by addition of a droplet of acidified THF. Subsequently, the polymers are precipitated in MeOH at 0°C. They are then filtered off and further purified using Soxhlet extraction with MeOH and $CHCl_3$. The $CHCl_3$-fraction is, again, precipitated in MeOH at 0°C, filtered off and dried in vacuum.

Table S1: Monomer quantities and resulting mass and yield of the polymers

Polymerisation	Monomer 10 (mL)	Monomer 8 (mL)	Mass (g)	Yield (%)
P1	10.7	-	0.184	82
P2	10.7	-	0.181	81
P3	10.59	0.107	0.203	90
P4	10.38	0.321	0.204	91
P5	10.17	0.535	0.201	90
P6	9.63	1.07	0.203	90
P7	5.35	5.35	0.142	63

1. G. Bidan, S. Guillerez, and V. Sorokin, *Adv. Mater.*, 1996, **8**, 157-160.

2. K. Van den Bergh, I. Cosemans, T. Verbiest, and G. Koeckelberghs, *Macromolecules*, 2010, **43**, 3794-3800.

NMR spectra

5-bromo-3-((S)-3,7-dimethyloctyl)thiophene (2)

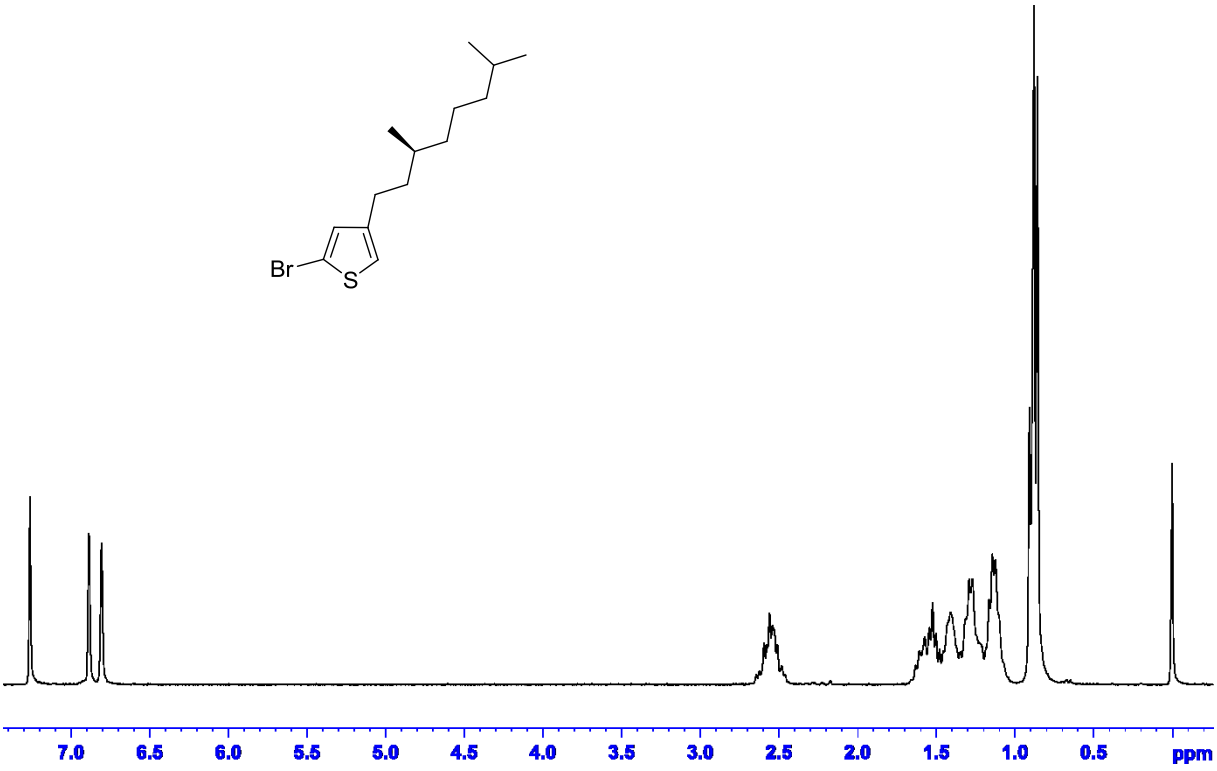


Figure S1: ^{1}H NMR spectrum of molecule 2 in $CDCl_3$.

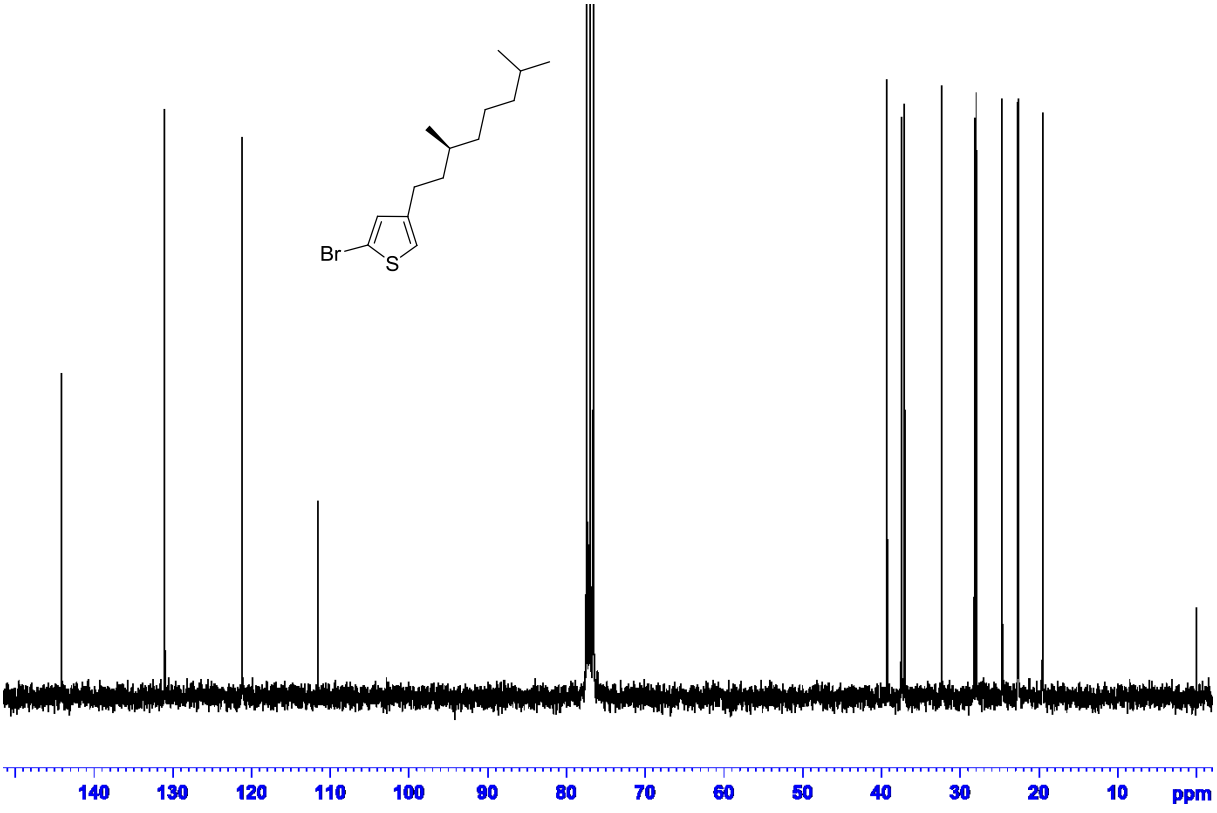


Figure S2: ^{13}C NMR spectrum of molecule 2 in $CDCl_3$.

5-bromo-2-iodo-3-((S)-3,7-dimethyloctyl)thiophene (3)

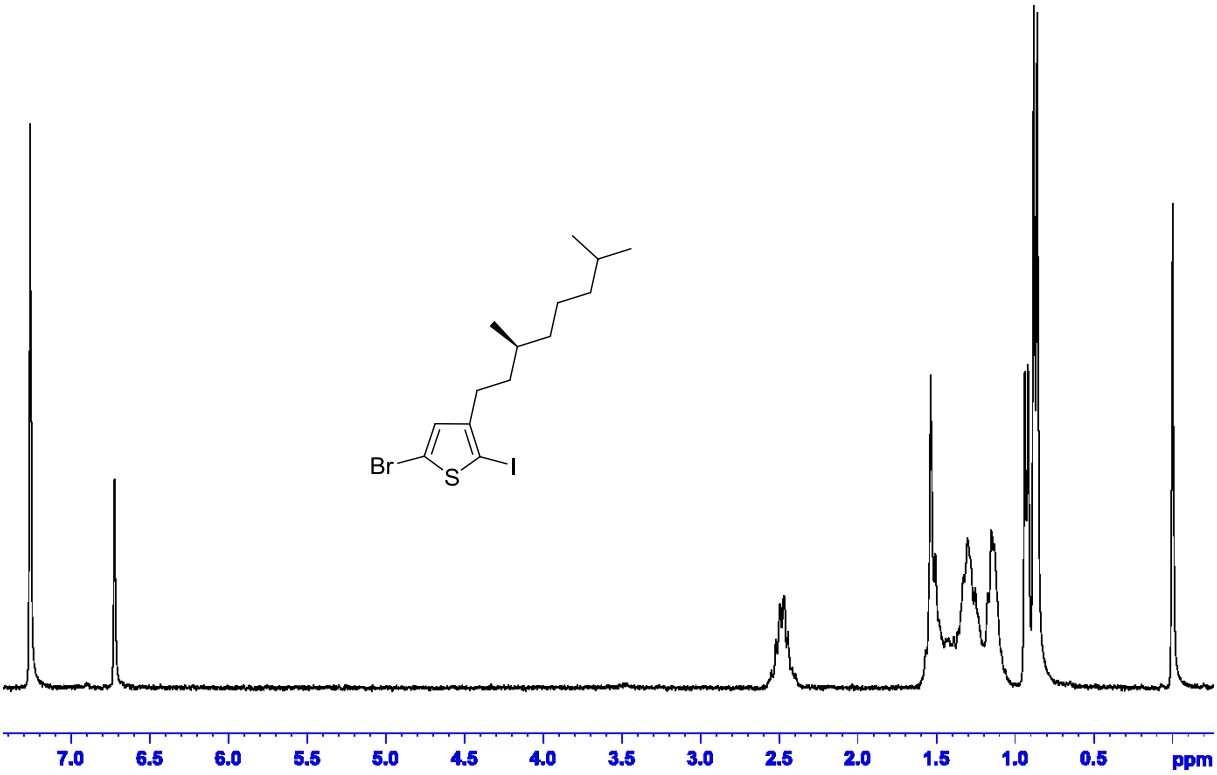


Figure S3: ^{1}H NMR spectrum of molecule 3 in $CDCl_3$.

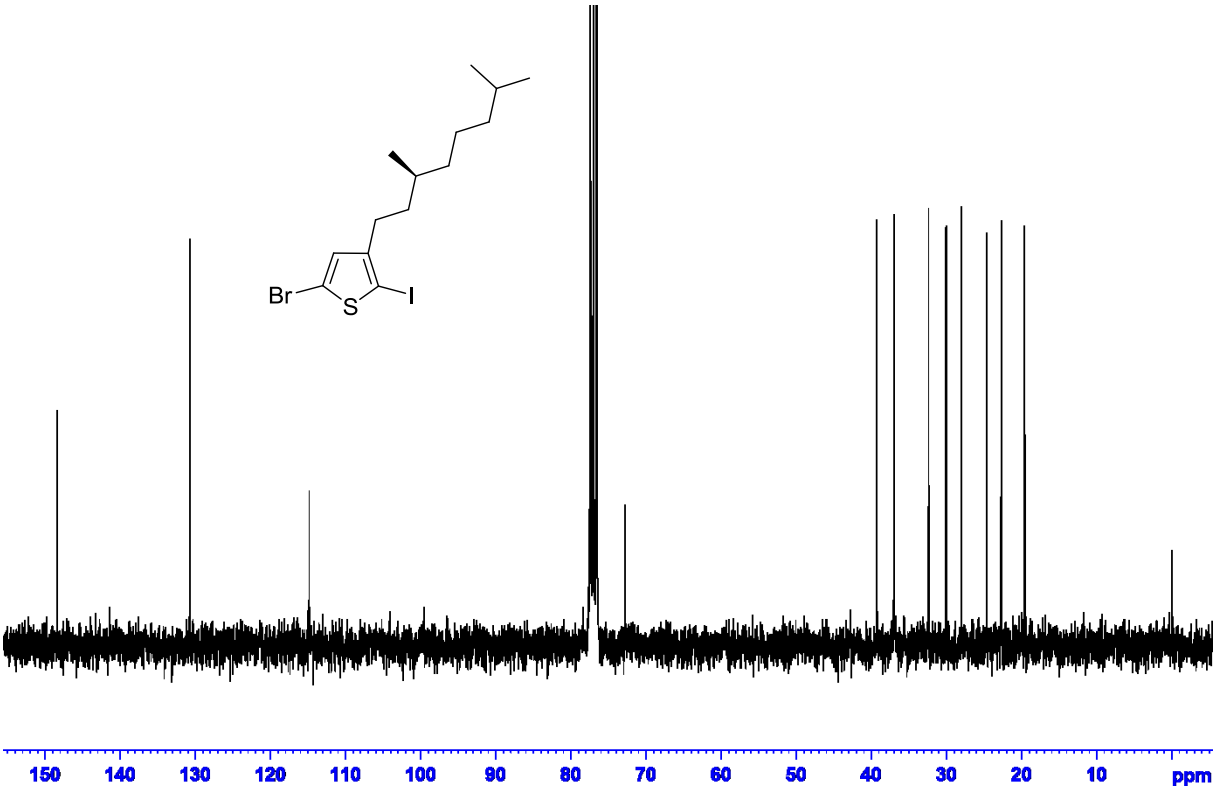


Figure S4: ^{13}C NMR spectrum of molecule 3 in $CDCl_3$.

Initiator (5)

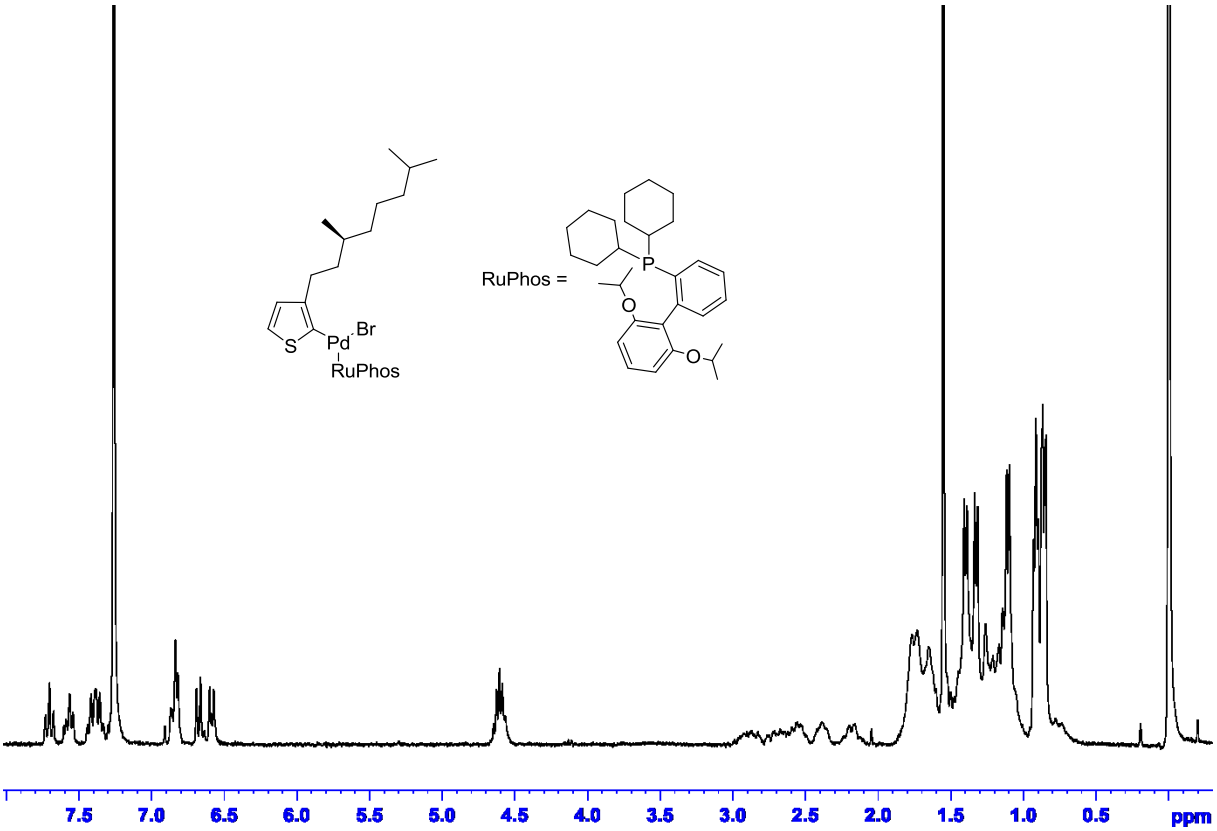


Figure S5: ^{1}H NMR spectrum of the initiator (5) in $CDCl_3$.

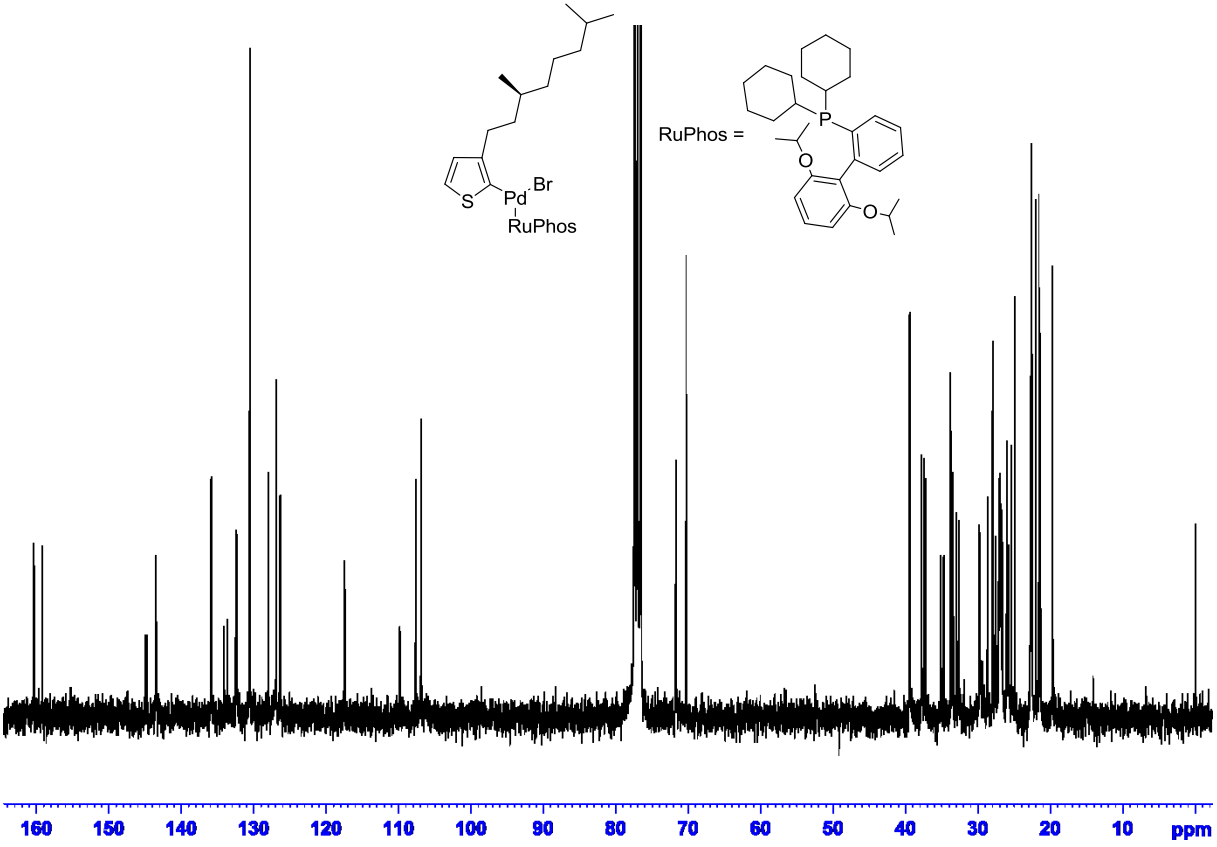


Figure S6: ^{13}C NMR spectrum of the initiator (5) in $CDCl_3$.

P1

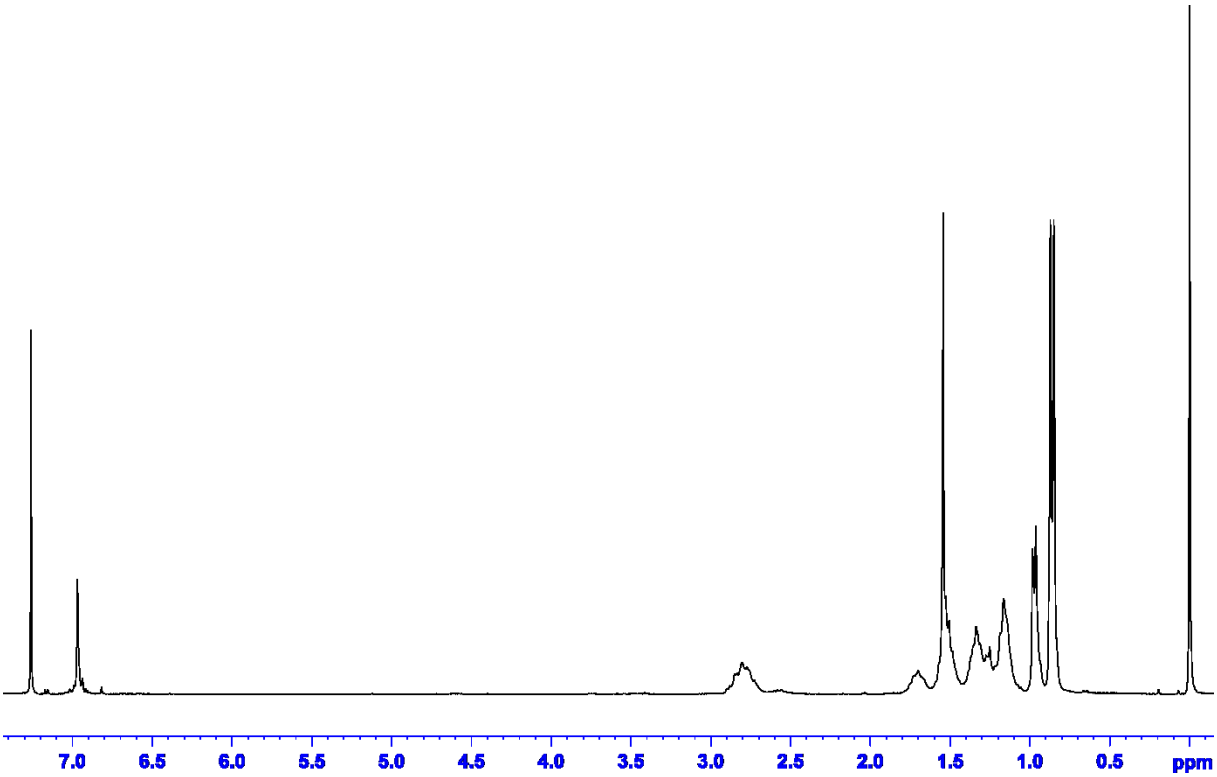


Figure S7: ^{1}H NMR spectrum of polymer P1 in $CDCl_3$.

P2

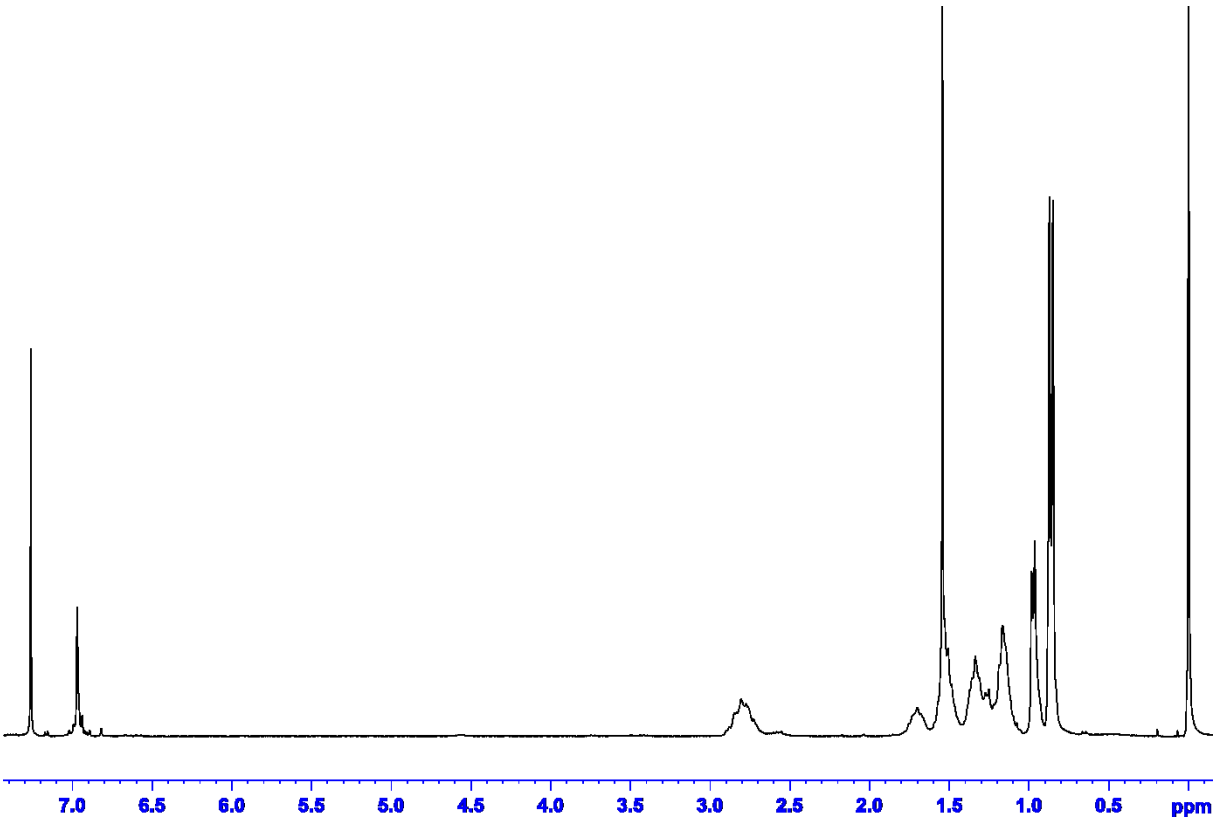


Figure S8: ^{1}H NMR spectrum of polymer P2 in $CDCl_3$.

P3

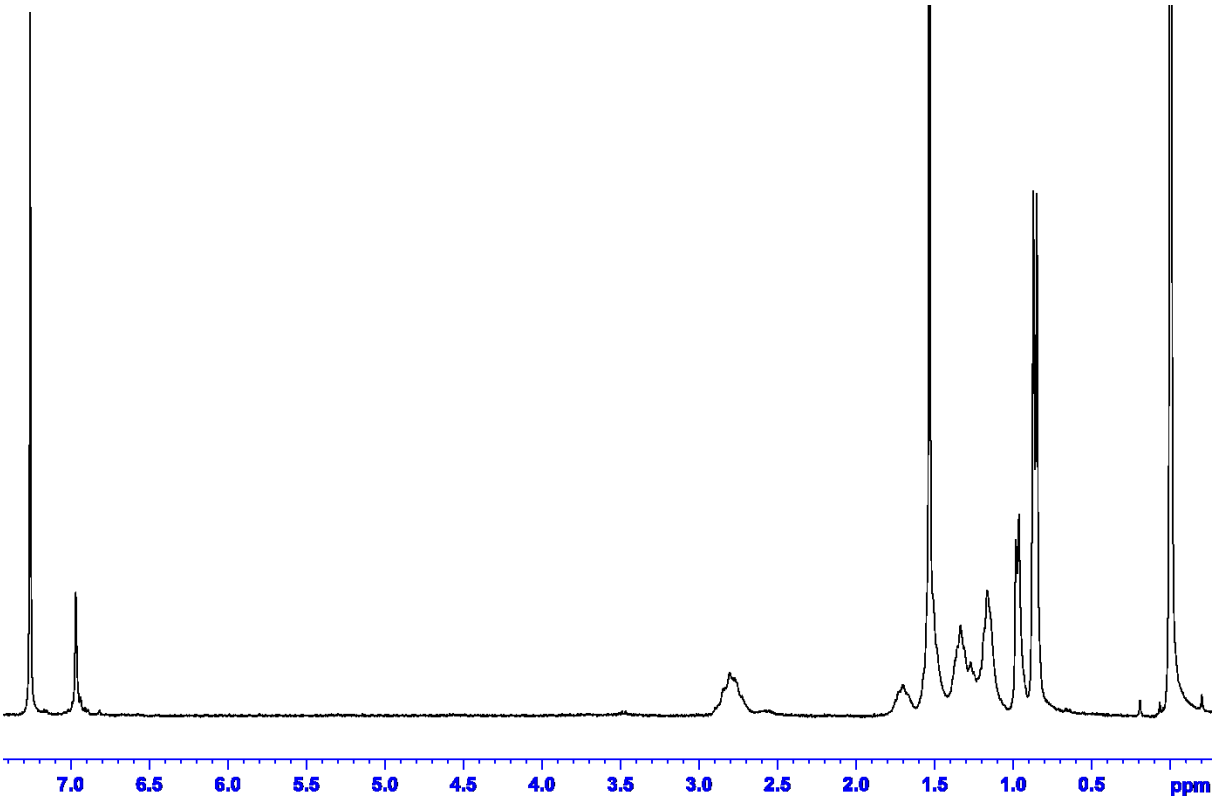


Figure S9: ^{1}H NMR spectrum of polymer P3 in $CDCl_3$.

P4

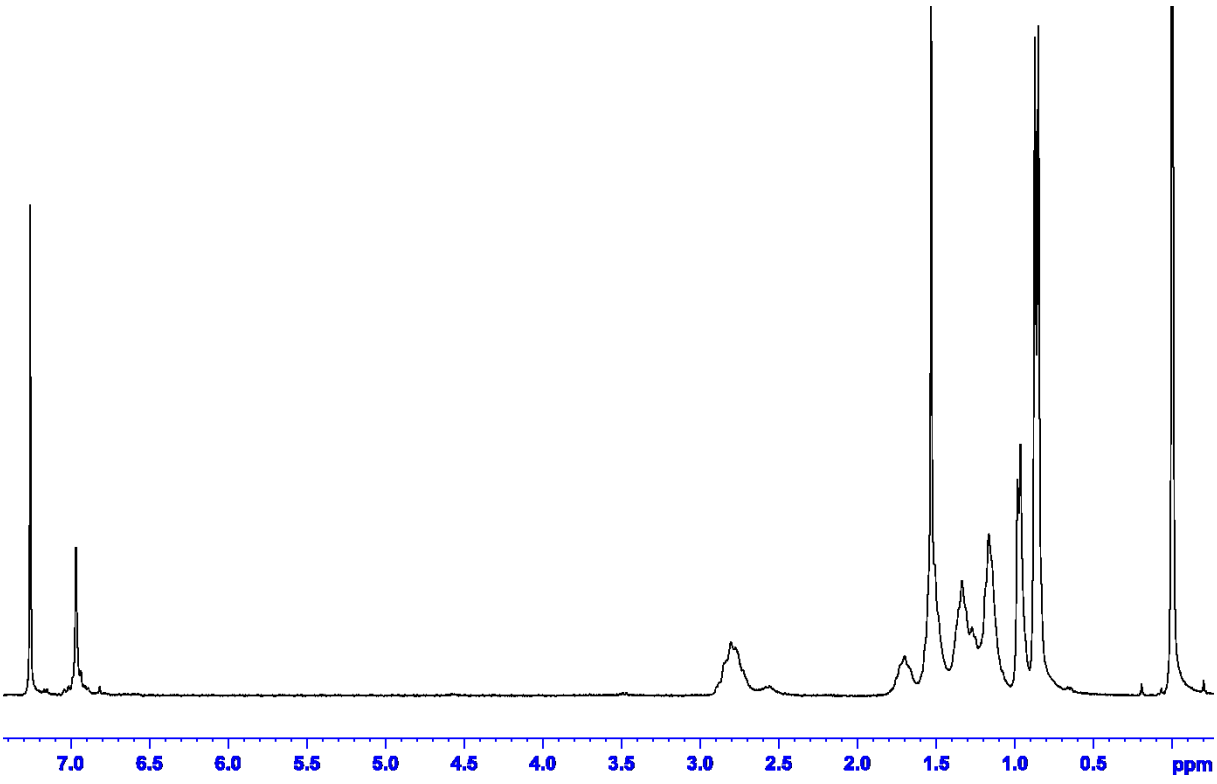


Figure S10: ^{1}H NMR spectrum of polymer P4 in $CDCl_3$.

P5

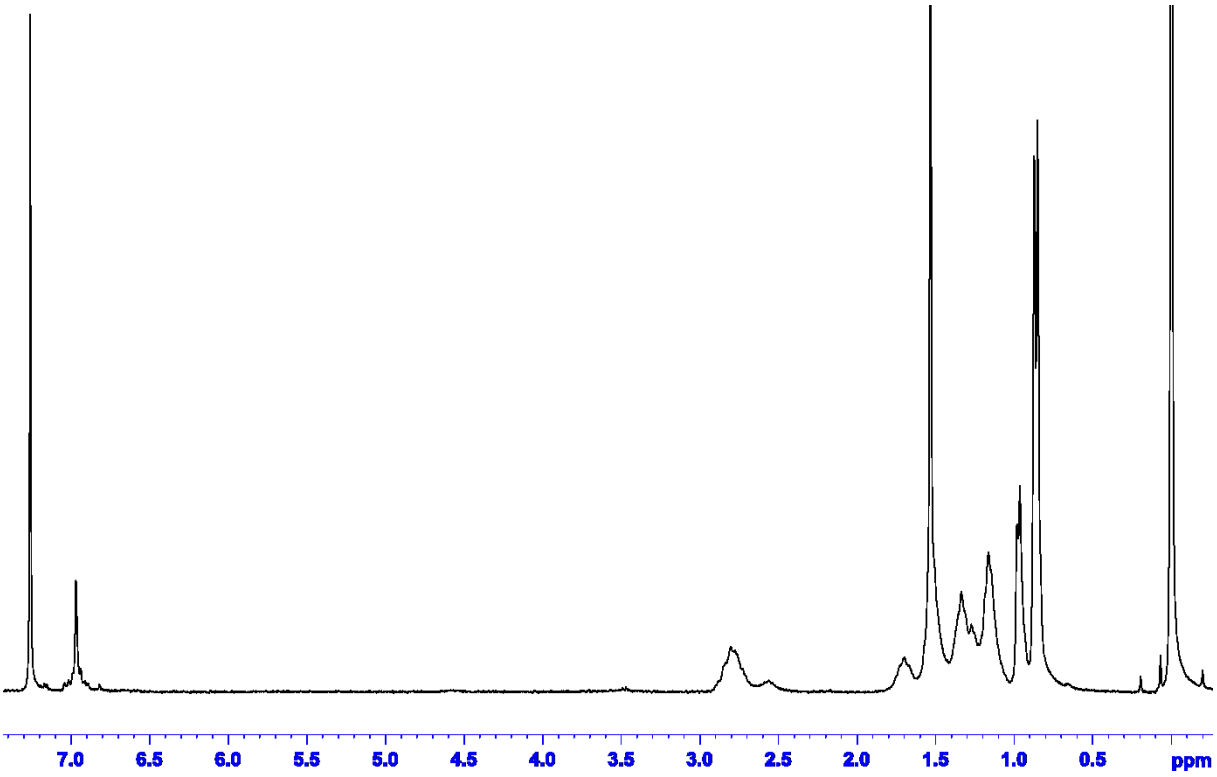


Figure S11: ^{1}H NMR spectrum of polymer P5 in $CDCl_3$.

P6

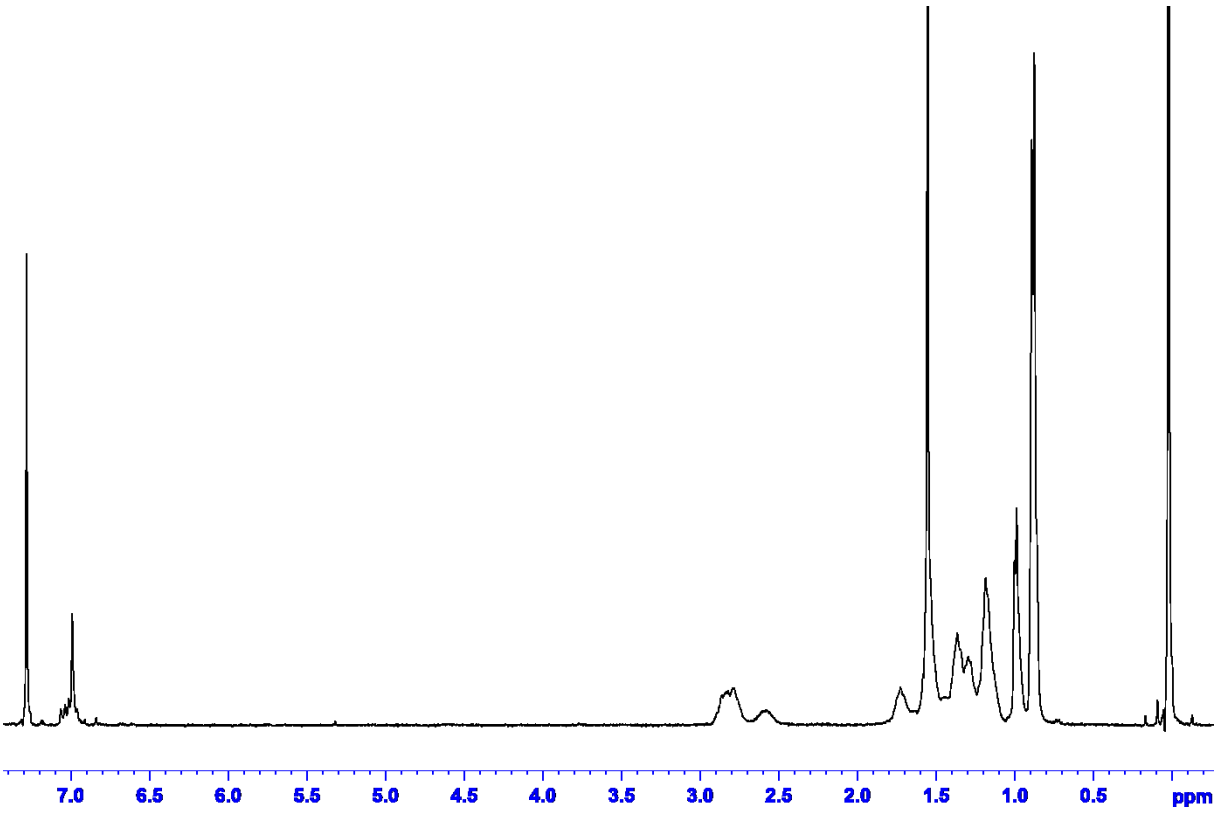


Figure S12: ^{1}H NMR spectrum of polymer P6 in $CDCl_3$.

P7

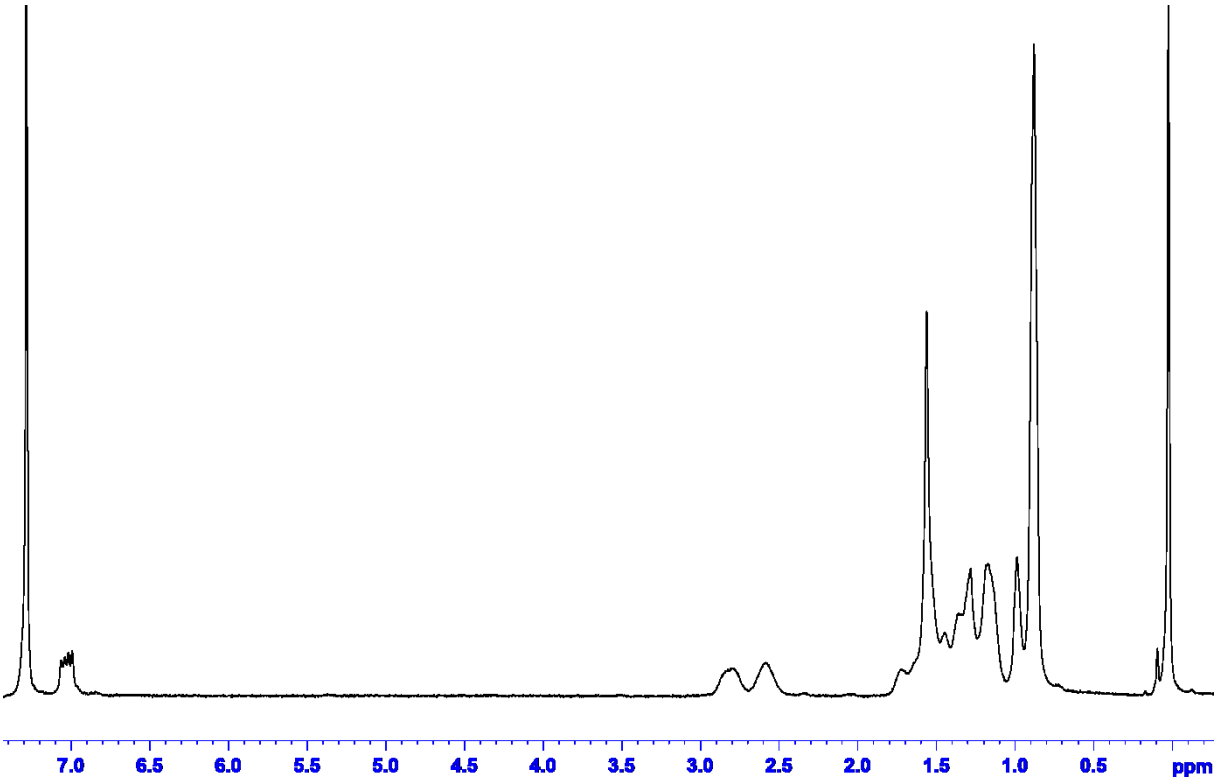


Figure S13: ^{1}H NMR spectrum of polymer P7 in $CDCl_3$.

UV-vis & CD solvatochromism spectra

In solution

P1

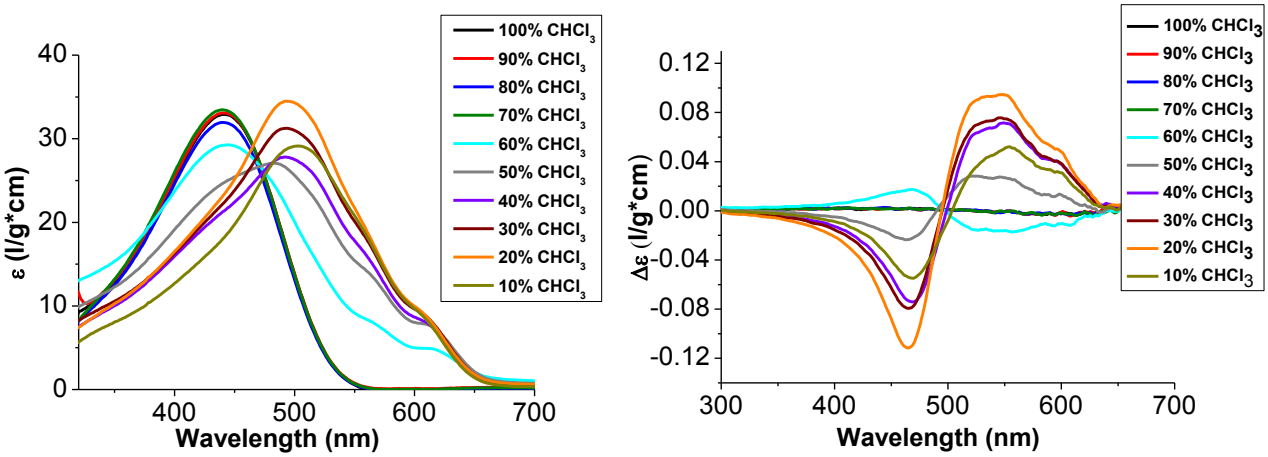


Figure S14: UV-vis and CD spectra of P1 in different $CHCl_3/CH_3OH$ mixtures.

P2

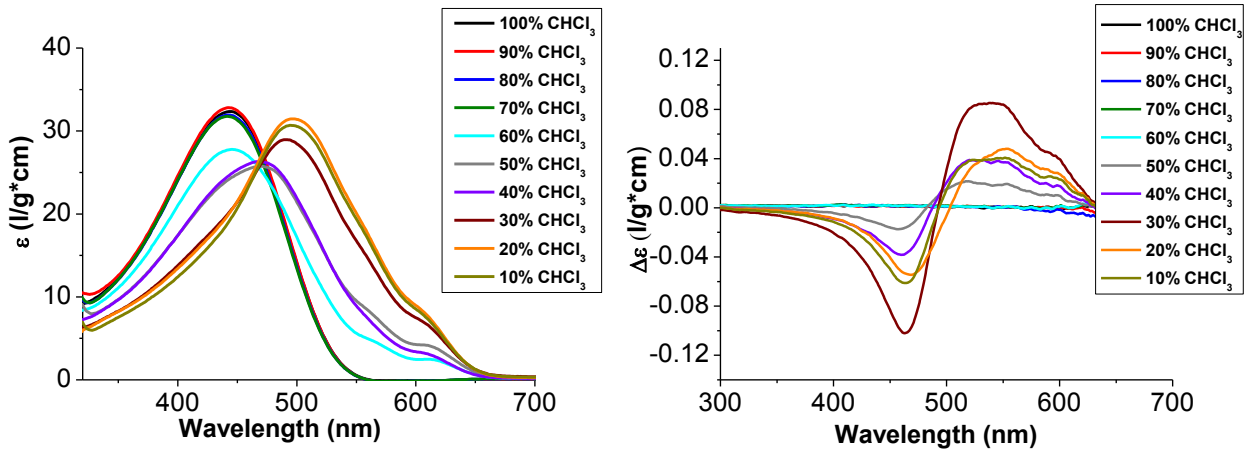


Figure S15: UV-vis and CD spectra of P2 in different $CHCl_3/CH_3OH$ mixtures.

P3

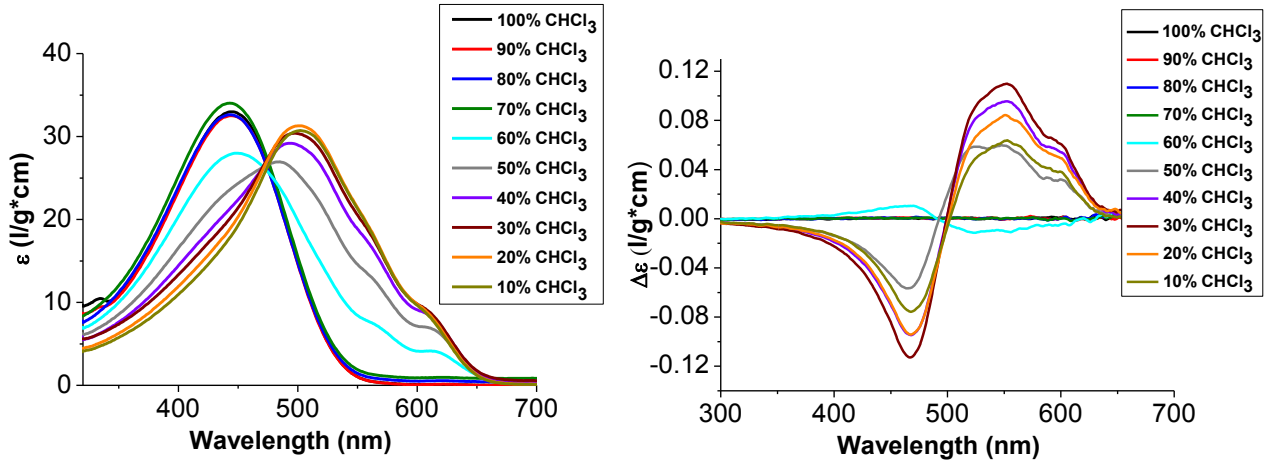


Figure S16: UV-vis and CD spectra of P3 in different $CHCl_3/CH_3OH$ mixtures.

P4

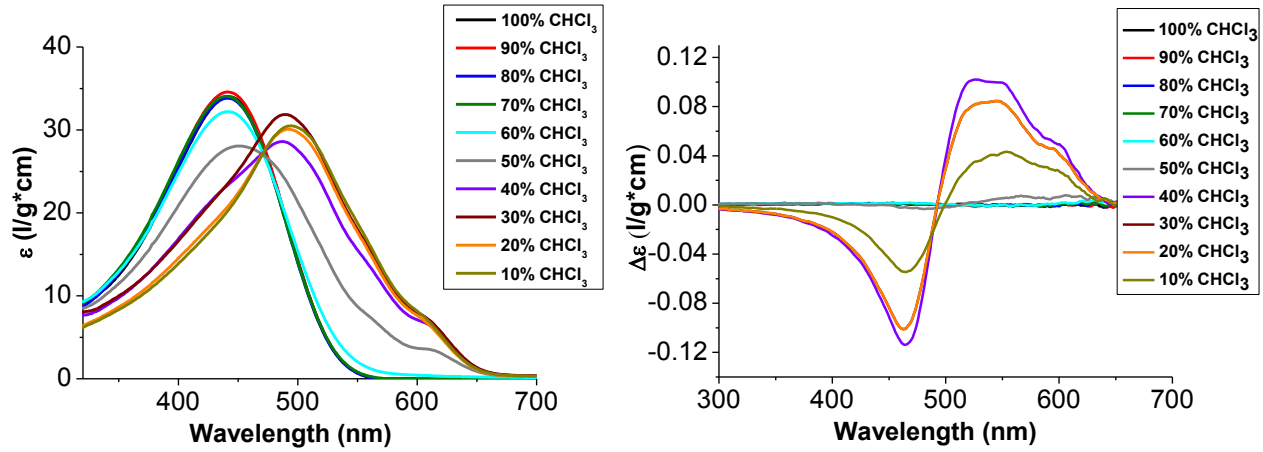


Figure S17: UV-vis and CD spectra of P4 in different $CHCl_3/CH_3OH$ mixtures.

P5

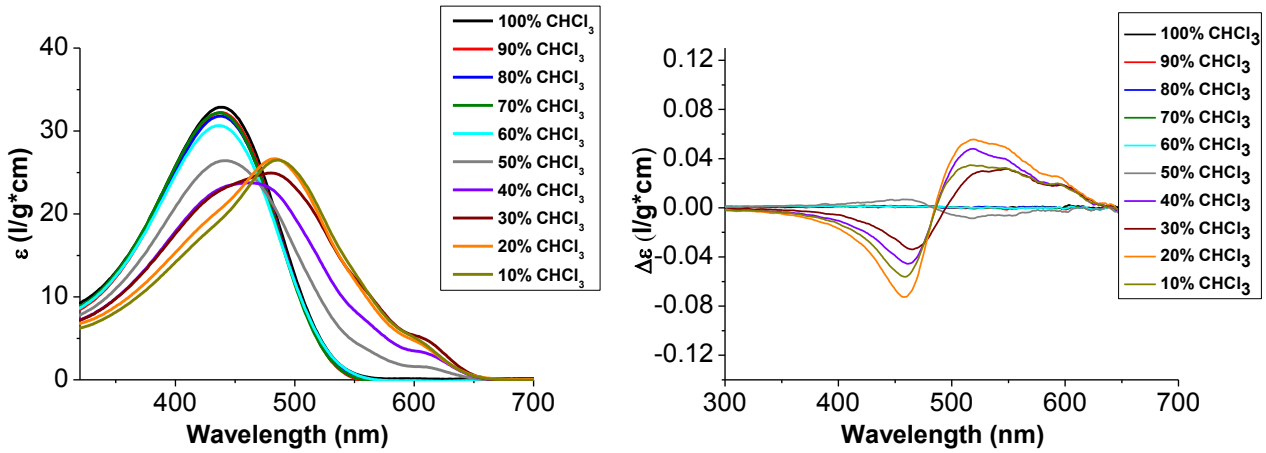


Figure S18: UV-vis and CD spectra of P5 in different $CHCl_3/CH_3OH$ mixtures.

P6

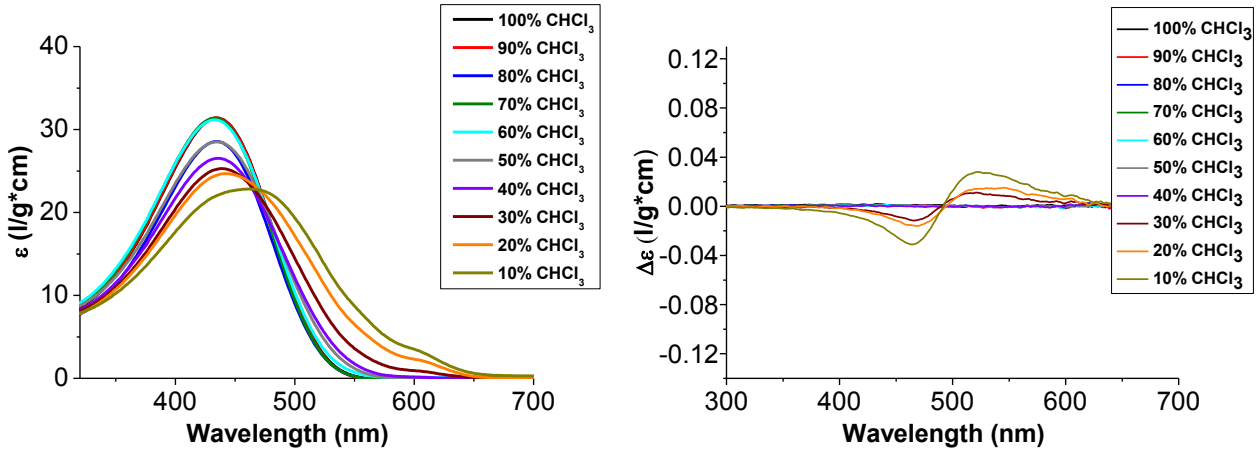


Figure S19: UV-vis and CD spectra of P6 in different $CHCl_3/CH_3OH$ mixtures.

P7

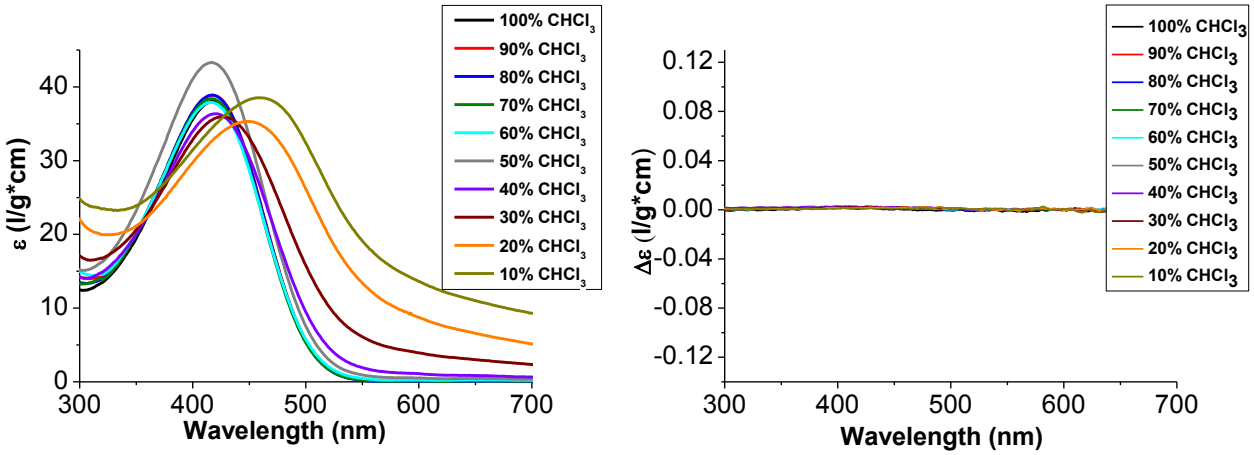
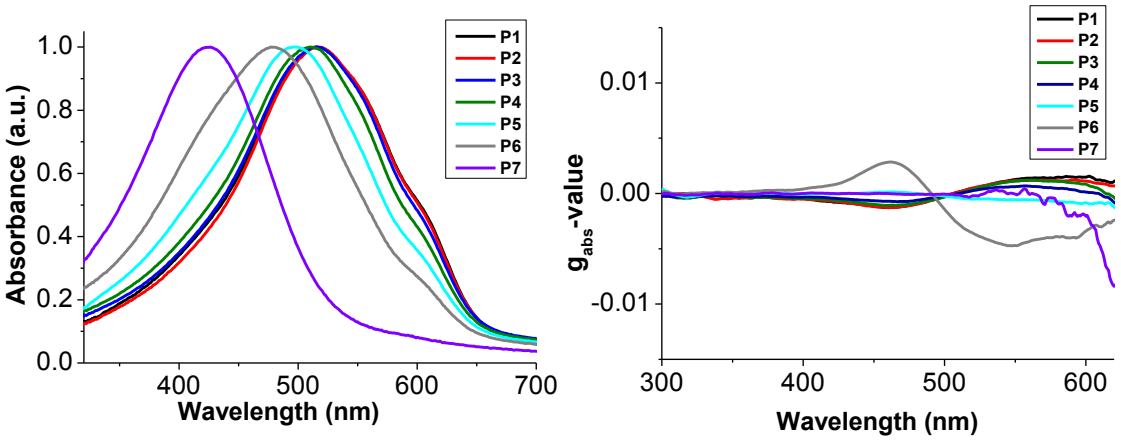


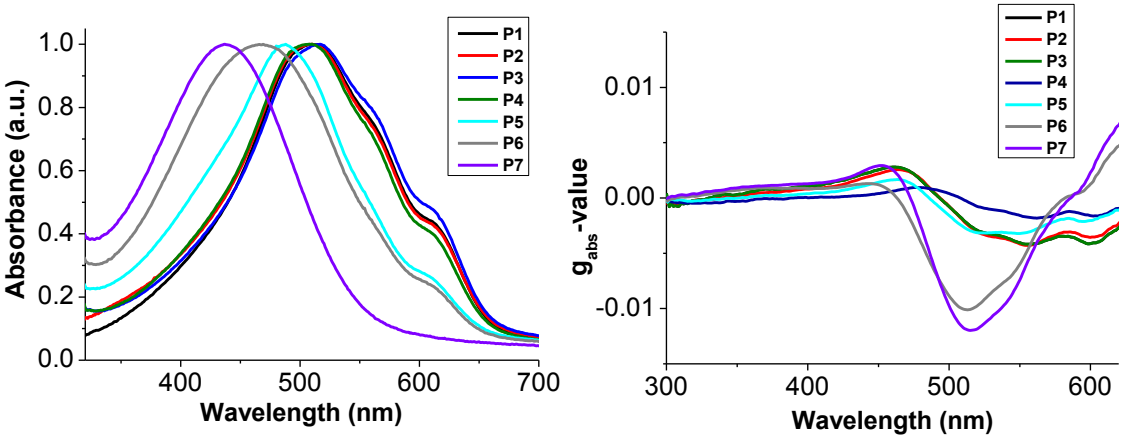
Figure S20: UV-vis and CD spectra of P7 in different $CHCl_3/CH_3OH$ mixtures.

In thin film

Before Annealing



After Annealing



Deconvoluted UV-vis spectra

In solution (20% $CHCl_3$)

P1

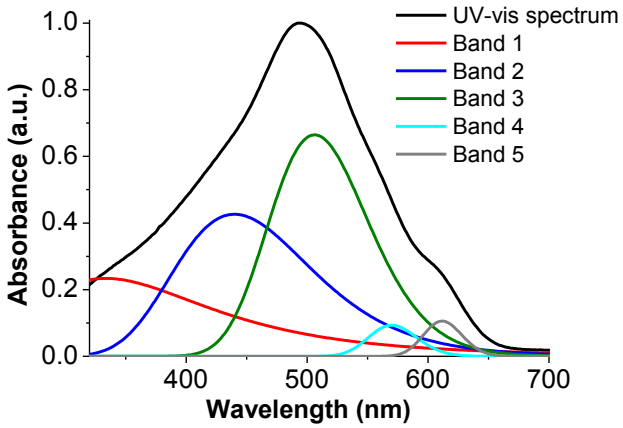


Figure S23: Deconvoluted UV-vis spectrum of P1.

P2

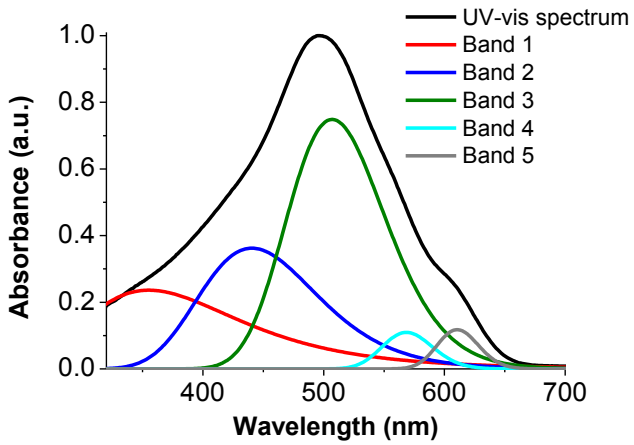


Figure S24: Deconvoluted UV-vis spectrum of P2.

P3

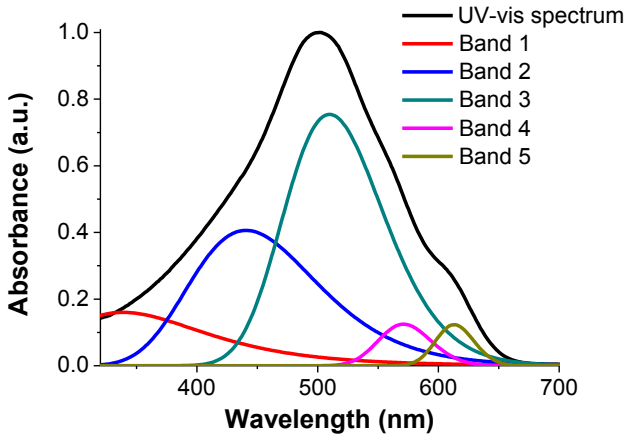


Figure S25: Deconvoluted UV-vis spectrum of P3.

P4

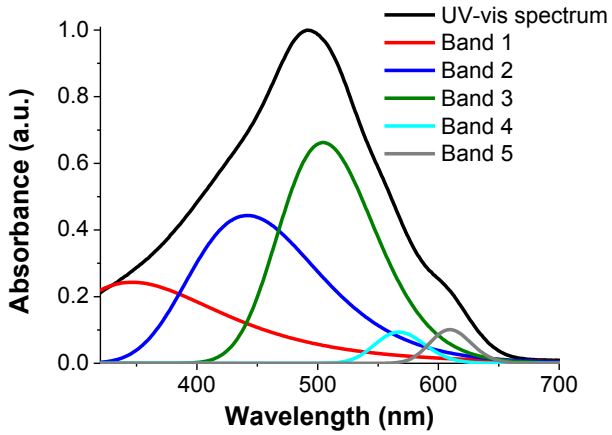


Figure S26: Deconvoluted UV-vis spectrum of P4.

P5

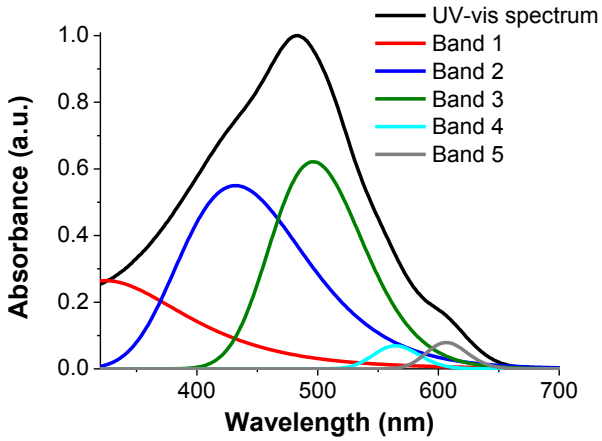


Figure S27: Deconvoluted UV-vis spectrum of P5.

P6

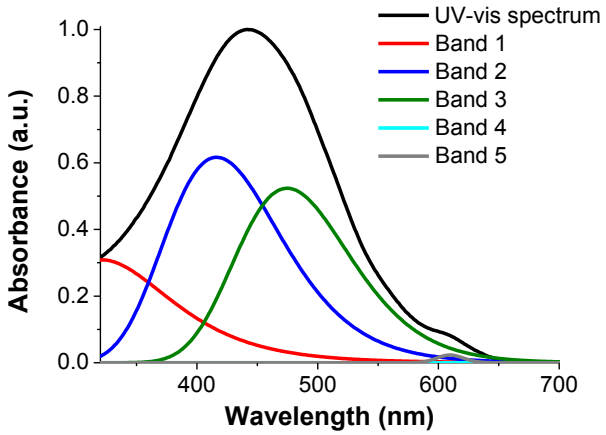


Figure S28: Deconvoluted UV-vis spectrum of P6.

In thin film before annealing

P1

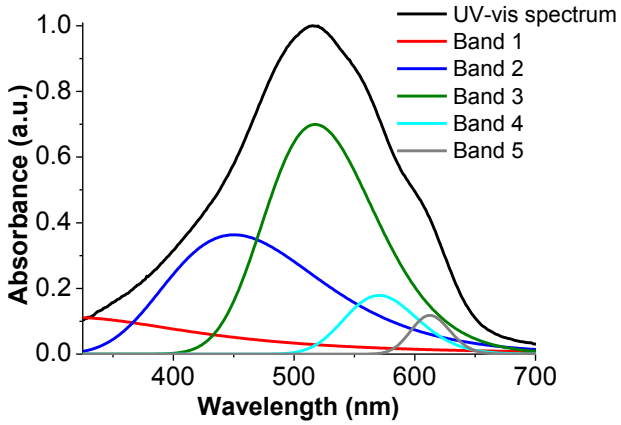


Figure S29: Deconvoluted UV-vis spectrum of P1 in thin film before annealing.

P2

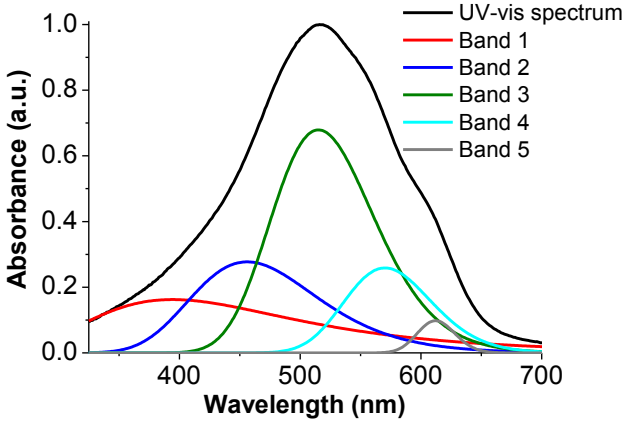


Figure S30: Deconvoluted UV-vis spectrum of P2 in thin film before annealing.

P3

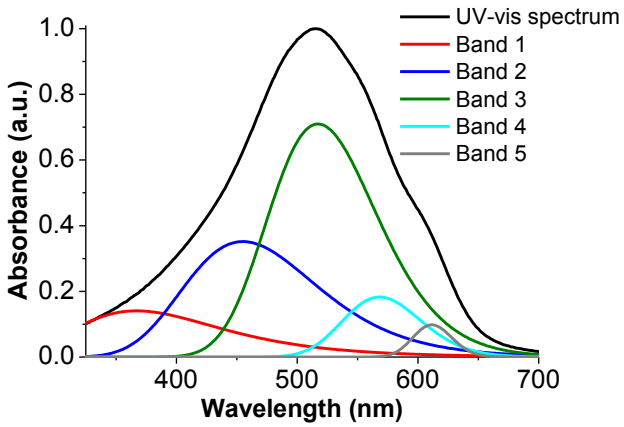


Figure S31: Deconvoluted UV-vis spectrum of P3 in thin film before annealing.

P4

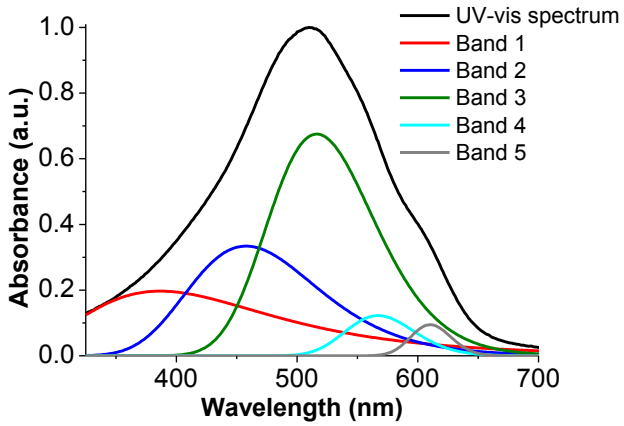


Figure S32: Deconvoluted UV-vis spectrum of P4 in thin film before annealing.

P5

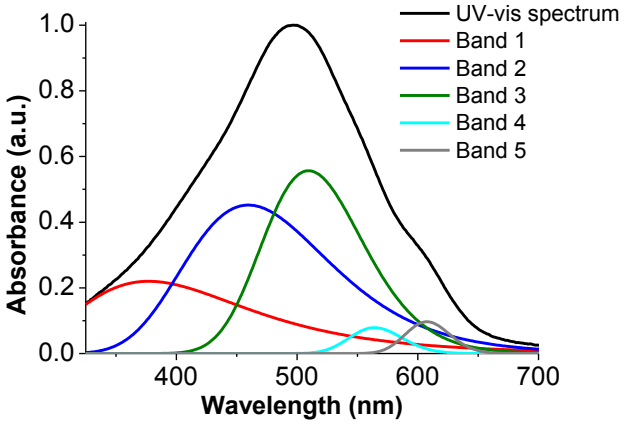


Figure S33: Deconvoluted UV-vis spectrum of P5 in thin film before annealing.

P6

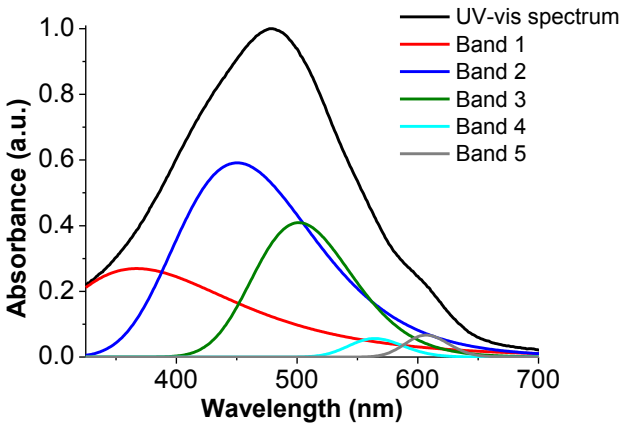


Figure S34: Deconvoluted UV-vis spectrum of P6 in thin film before annealing.

In thin film after annealing

P1

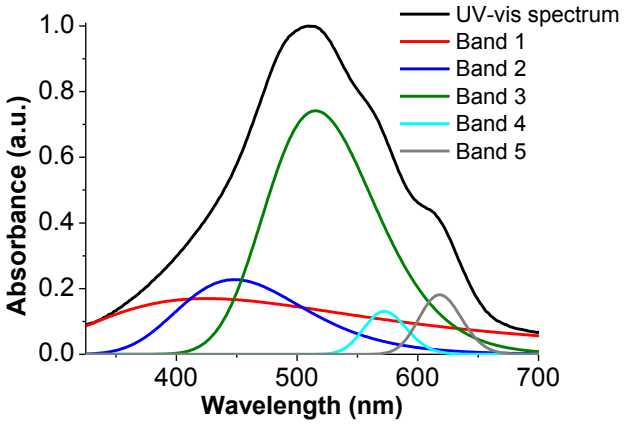


Figure S35: Deconvoluted UV-vis spectrum of P1 in thin film after annealing.

P2

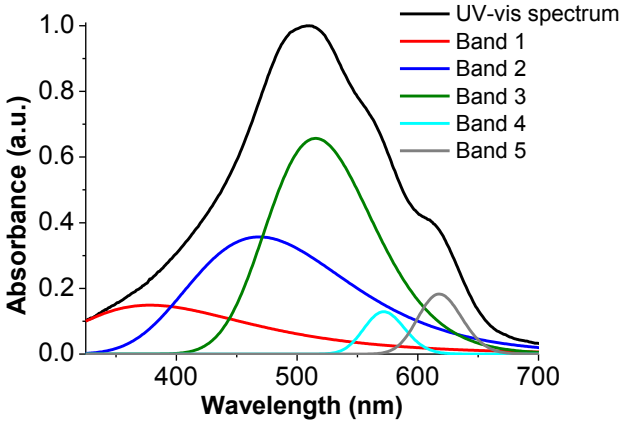


Figure S36: Deconvoluted UV-vis spectrum of P2 in thin film after annealing.

P3

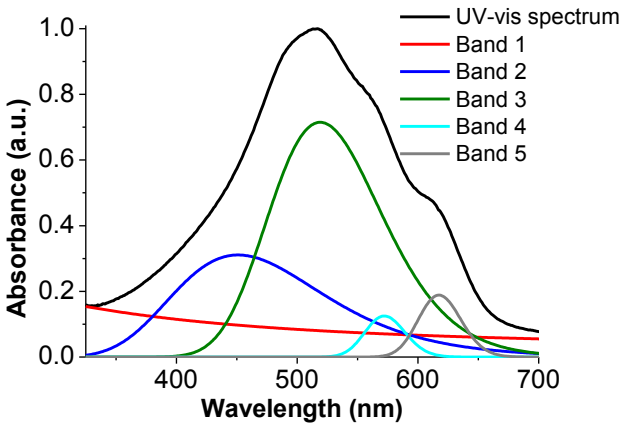


Figure S37: Deconvoluted UV-vis spectrum of P3 in thin film after annealing.

P4

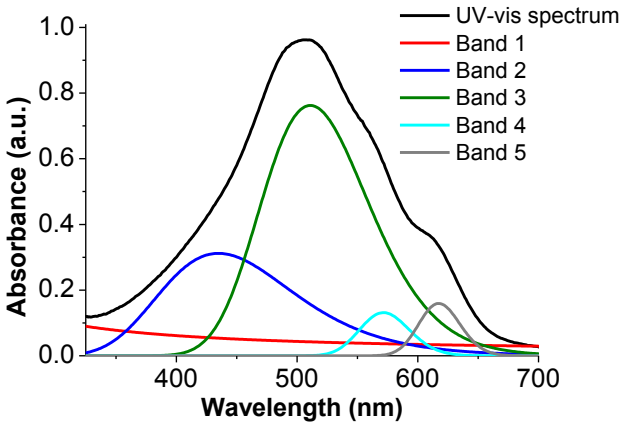


Figure S38: Deconvoluted UV-vis spectrum of P4 in thin film after annealing.

P5

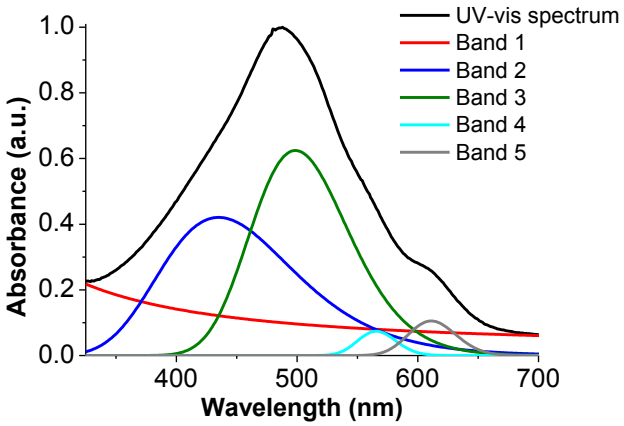


Figure S39: Deconvoluted UV-vis spectrum of P5 in thin film after annealing.

P6

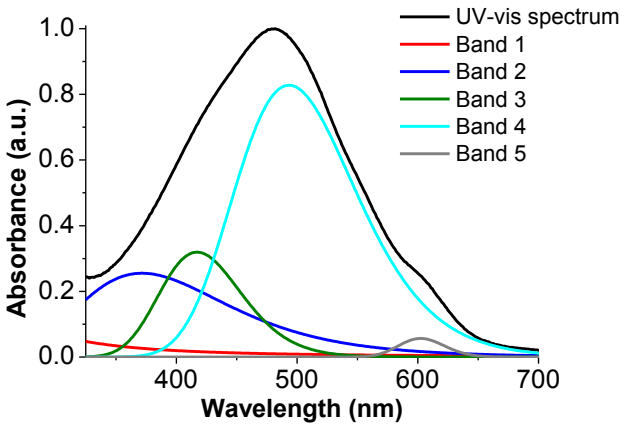


Figure S40: Deconvoluted UV-vis spectrum of P6 in thin film after annealing.