

Supplementary Material (ESI) for the Journal of Materials Chemistry

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# Efficient formation, isolation and characterization of poly(3-alkylthiophene) nanofibres: probing order as a function of side-chain length

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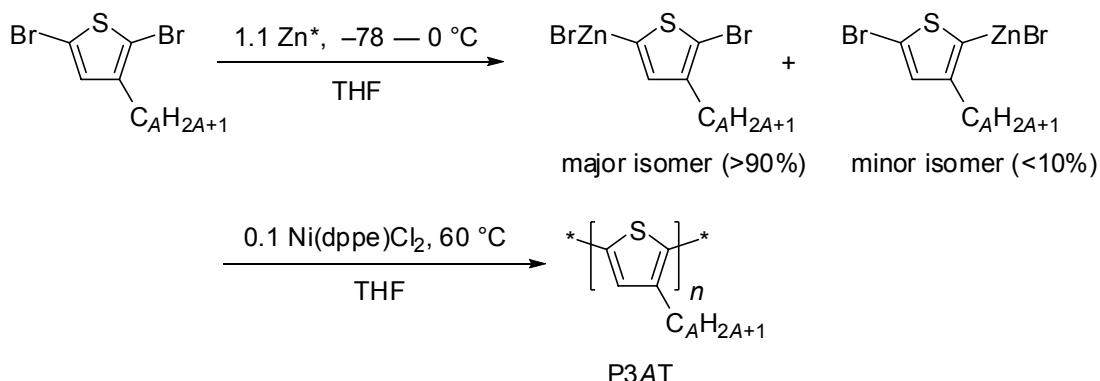
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## Supporting Information

## Poly(3-alkylthiophene) synthesis

A short description of the synthesis of P36T is given. Other polymers were synthesized in an identical way, starting with different alkyl Grignard reagents.

Hexylmagnesium bromide (Aldrich, 2M in diethyl ether) was coupled to 3-bromothiophene (ACROS, 97%) in dry diethyl ether at room temperature using Ni(dppp)Cl<sub>2</sub> as the catalyst following published procedures.<sup>1</sup> The resulting 3-hexylthiophene was purified by vacuum distillation and converted into 2,5-dibromo-3-hexylthiophene in DMF using 2.2 eq. of NBS following Bäuerle *et al.*<sup>2</sup> The resulting product was purified by vacuum distillation.



**Figure S1.** Synthesis of poly(3-alkylthiophene)s (P3AT) via the Rieke method.

Poly(3-hexylthiophene) was prepared by reacting 2,5-dibromo-3-hexylthiophene with Rieke Zn\*, followed by polymerisation with Ni(dppe)Cl<sub>2</sub> (0.1 eq) in THF at 60 °C according to literature procedures.<sup>3,4</sup> The polymers were purified by precipitation in 2 M HCl—MeOH (1 : 2), followed by filtration and Soxhlet extraction with MeOH (24 h) and hexane (24 h). Yields varied from 50 % (P39T) to 66–80% (P33T to P38T). The polymers were characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR, FT-IR and GPC. Analytical data were found to be in agreement with literature.<sup>4</sup> The <sup>1</sup>H- and <sup>13</sup>C-NMR data follow below:

**Poly(3-propylthiophene)** (P33T)  $^1\text{H-NMR}$  (1,4-dichlorobenzene- $d_4$  @ 120 °C):  $\delta$  1.00 (t,  $J = 7.2$  Hz, 3H), 1.75 (tt,  $J \sim 7.4$  Hz, 2H), 2.81 (t,  $J = 7.5$  Hz), 7.04 (s, 1H).  $^{13}\text{C-NMR}$  (1,4-dichlorobenzene- $d_4$  @ 120 °C):  $\delta$  13.9, 23.8, 31.8, 129.0, 131.3, 134.4, 140.0.

**Poly(3-butylthiophene)** (P34T)  $^1\text{H-NMR}$  ( $\text{CS}_2$  with some drops of  $\text{CDCl}_3$  @ 20 °C):  $\delta$  1.00—1.06 (m, 3H), 1.46—1.55 (m, 2H), 1.65—1.75 (m, 2H), 2.53—2.62 (m, 0.07H), 2.76—2.81 (m, 1.93H), 6.89 (s, 1H).  $RR$  96.5%;  $^{13}\text{C-NMR}$  ( $\text{CS}_2$  with some drops of  $\text{CDCl}_3$ )  $\delta$  14.2, 23.0, 29.2, 32.7, 128.3, 130.4, 133.5, 139.2.

**Poly(3-pentylthiophene)** (P35T)  $^1\text{H-NMR}$ :  $\delta$  0.90—0.95 (m, 3H), 1.35—1.45 (m, 4H), 1.66—1.76 (m, 2H), 2.54—2.61 (m, 0.11H), 2.77—2.82 (m, 1.89H), 6.97 (s, 1H).  $^{13}\text{C-NMR}$ :  $\delta$  14.0, 22.5, 29.5, 30.2, 31.8, 128.7, 130.7, 133.9, 140.0.

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**Poly(3-hexylthiophene)** (P36T)  $^1\text{H-NMR}$ :  $\delta$  0.88—0.93 (m, 3H), 1.26—1.46 (m, 6H), 1.65—1.75 (m, 2H), 2.54—2.59 (m, 0.10H), 2.77—2.82 (m, 1.90H), 6.97 (s, 1H).  $^{13}\text{C-NMR}$ :  $\delta$  14.0, 22.6, 29.2, 29.5, 30.5, 31.7, 128.7, 130.7, 133.9, 140.0.

**Poly(3-heptylthiophene)** (P37T)  $^1\text{H-NMR}$ :  $\delta$  0.87—0.91 (m, 3H), (1.31—1.45, 8H), 1.65—1.75 (m, 2H), (2.54—2.59, 0.06H), 2.80 (br m, 1.94H), 6.95 (s, 1H).  $^{13}\text{C-NMR}$ :  $\delta$  14.0, 22.7, 29.2 (2x), 29.6, 30.6, 31.9, 128.7, 130.7, 133.9, 140.0.

**Poly(3-octylthiophene)** (P38T)  $^1\text{H-NMR}$ :  $\delta$  0.86—0.90 (m, 3H), 1.29—1.45 (m, 10H), 1.65—1.75 (m, 2H), 2.54—2.59 (m, 0.07H), 2.80 (br m, 1.93H), 6.95 (s, 1H).  $^{13}\text{C-NMR}$ :  $\delta$  14.0, 22.7, 29.3, 29.5, 29.6, 29.7, 30.6, 31.9, 128.7, 130.7, 133.9, 140.0.

**Poly(3-nonylthiophene)** (P39T)  $^1\text{H-NMR}$ :  $\delta$  0.85—0.92 (m, 3H), 1.28—1.45 (m, 12H), 1.65—1.75 (m, 2H), 2.54—2.59 (m, 0.04H), 2.81 (br m, 1.96H), 6.93 (br s, 1H).  $^{13}\text{C-NMR}$ :  $\delta$  14.0, 22.7, 29.3, 29.5—29.6 (3 overlapping signals), 29.7, 30.6, 31.9, 128.7, 130.7, 133.9, 140.0.

## NMR spectroscopy

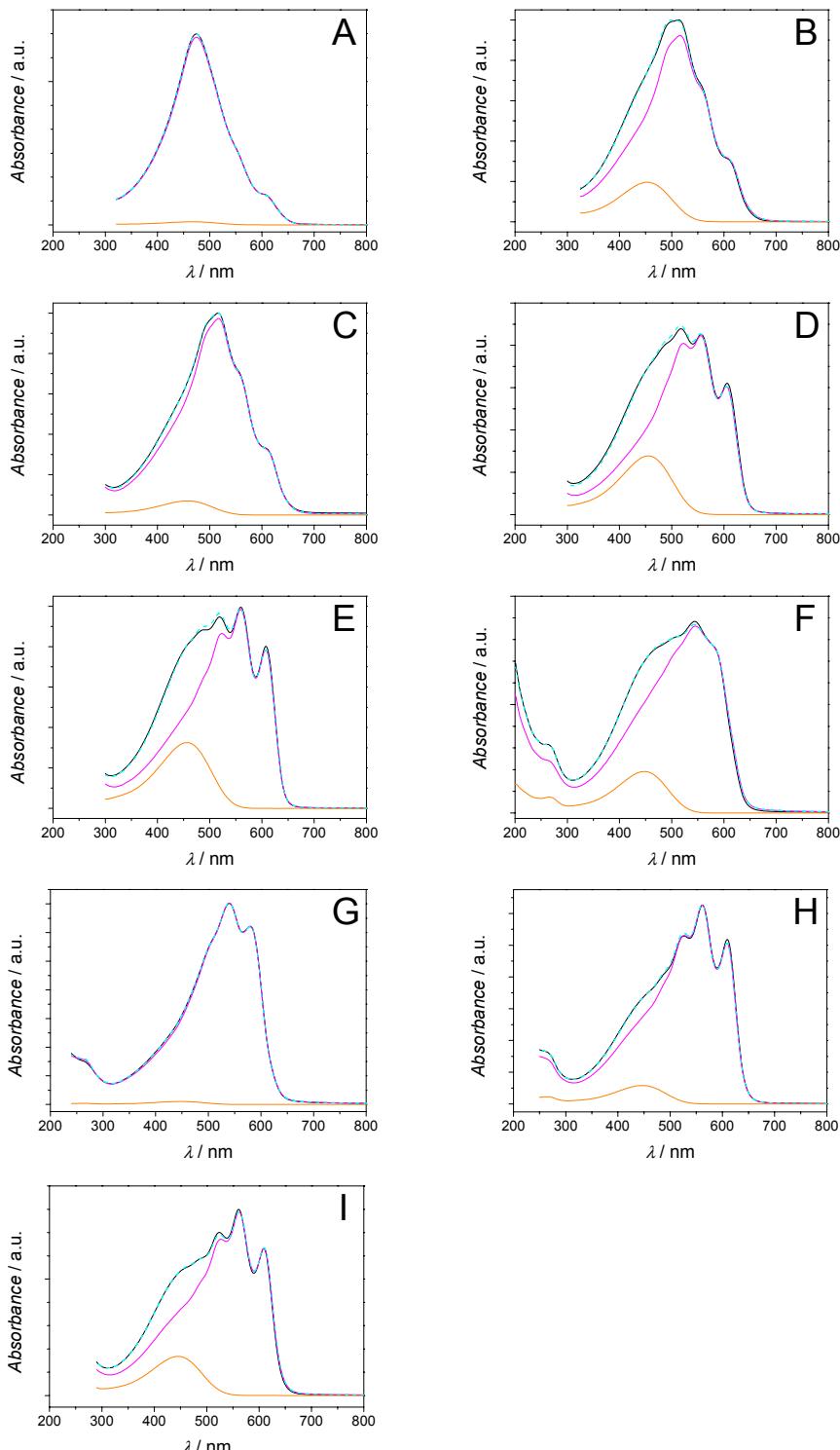
NMR spectra were recorded in  $\text{CDCl}_3$  at 50 °C on a Varian Inova 300 spectrometer at 299.808 MHz for  $^1\text{H}$  and at 75.394 MHz for  $^{13}\text{C}$  using 5 mm probes, unless stated otherwise.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual C-H solvent resonance ( $^1\text{H-NMR}$ ) and the C-D resonance ( $^{13}\text{C-NMR}$ ) as an internal standard. For  $\text{CDCl}_3$  these were set at 7.24 ppm and 77.00 ppm, respectively. For 1,4-dichlorobenzene- $d_4$  at 120 °C they were set at the values that we measure with respect to TMS at 60 °C; 7.03 ppm and 129.4 ppm, respectively. In  $\text{CS}_2$  containing  $\text{CDCl}_3$  (used for P34T), the shifts were referenced to  $\text{CDCl}_3$  with the above-mentioned reference values.

## Literature

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2. P. Bauerle, F. Pfau, H. Schlupp, F. Wurthner, K. U. Gaudl, M. B. Caro and P. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1993, 489-494.
3. T. A. Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1992, **114**, 10087-10088.
4. T. A. Chen, X. M. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233-244.

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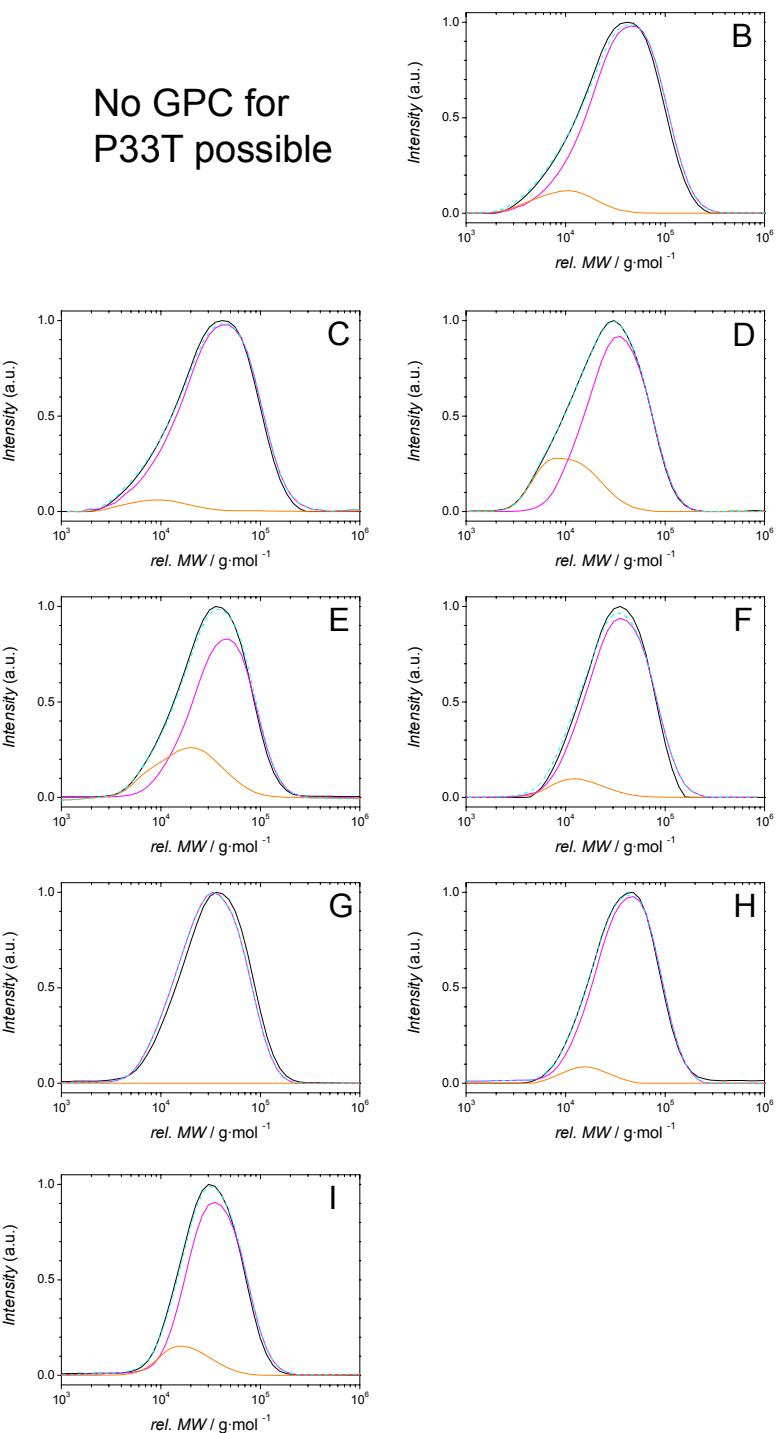
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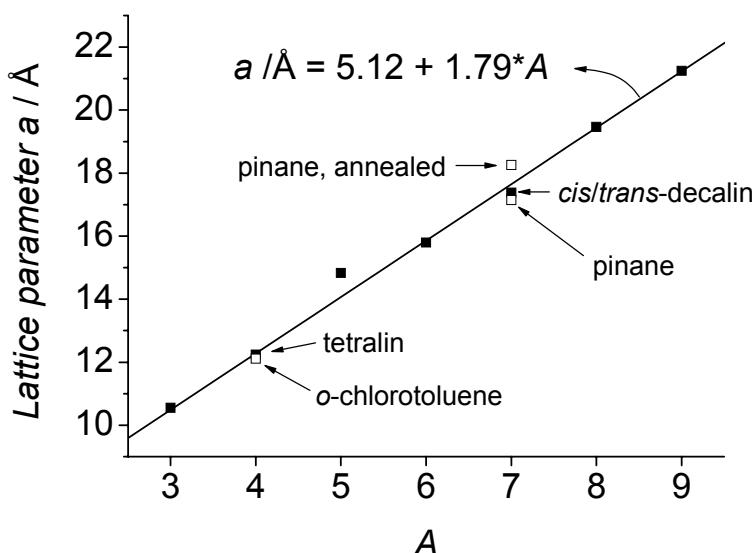
**Figure S2** UV-Vis absorption spectra of pristine fibre solutions of P33T—P39T in various solvents (black line) together with the fit results (blue dash) of fitting them as a sum of the pure fibre (purple line) and 'amorphous' (orange line) spectra. A) P33T in 1,2,4-trichlorobenzene; B) P34T in tetralin; C) P34T in *o*-chlorotoluene; D) P35T in *p*-xylene; E) P36T in *p*-xylene; F) P37T in *cis/trans*-decalin; G) P37T in Pinane; H) P38T in Pinane; I) P39T in Pinane.

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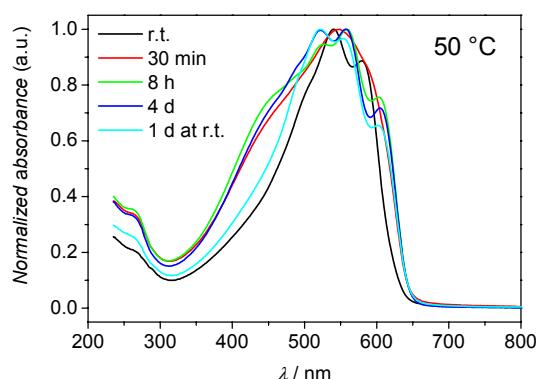
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**Figure S3** GPC curves of P3ATs **P34T**—**P39T** in chlorobenzene at 60 °C versus polystyrene standards (black line) together with the fit results (blue dash) of fitting them as a sum of GPC curves of the isolated fibre (purple line) and 'amorphous' (orange line) fractions. For letter-coding, see **Figure S2** of the Supporting Information.



**Figure S4** Lattice parameter  $a$  for isolated fibres from XRD as a function of alkyl chain length  $A$ , together with a linear fit through the data (except P35T and P37T).



**Figure S5** Time evolution of the UV-Vis spectrum of 0.5 wt. % P37T fibres in pinane at 50 °C. Shown spectra were taken at room temperature, after 30 min, 8 h and after 4 days, when the solution was cooled to r.t. The last spectrum was taken 24 h after cooling to r.t.