Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information to the article:

Improved charge carrier transport in ultrathin poly(3-hexylthiophene) films via solution aggregation

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Table S1. Physical properties of solvents used in the study and P3HT.

parameter / unit	symbol	chloroform	toluene	P3HT
hansen solubility parameter (HSP) components / **$MPa^{1/2}$**	δ_d	17.8	18	17.9
	δ_p	3.1	1.4	0.9
	δ_h	5.7	2	3.2
HSP (total) / **$MPa^{1/2}$**	HSP_{tot}	26.6	21.4	22.0
hansen interaction radius / **$MPa^{1/2}$**	R_h	-	-	4.20
solubility distance (relative to P3HT)*/ **$MPa^{1/2}$**	R_a	3.3	1.3	-
dipole moment / **D**		1.10	0.31	-
boiling point / **ºC**	b.p.	61	111	-

* The Hansen solubility distances (R_a) were calculated in the conventional manner:

$R_a = (4\Delta\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$, where $\Delta\delta_x^2 \equiv (\delta_{x,P3HT} - \delta_{x,solvent})^2$, and x=d (dispersion), p (polar) or h (h-bond) interactions.

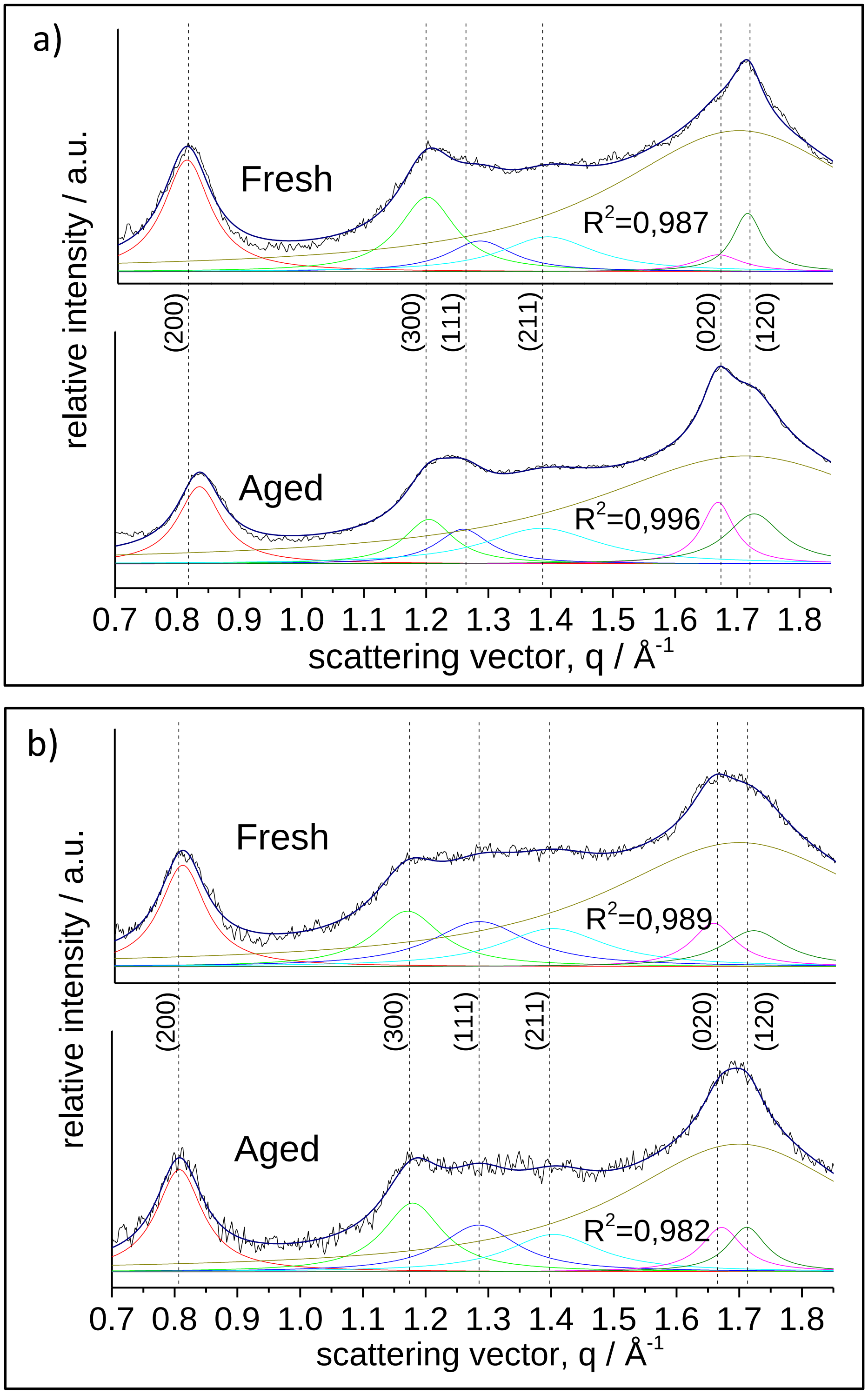

Figure S1. Diffraction profiles of a) $P3HT_{94}$ and b) $P3HT_{34}$ crystallized from fresh and aged chloroform solutions. R^2 is coefficient of determination for the monoclinic unit cell model assumed to fit the experimental data. Dashed lines indicate ideal positions of diffraction maxima for the monoclinic cell with the following parameters a=15.6±0.25 Å, b=7.57±0.03, c=0.7÷0.9 Å and γ=87°.[26]

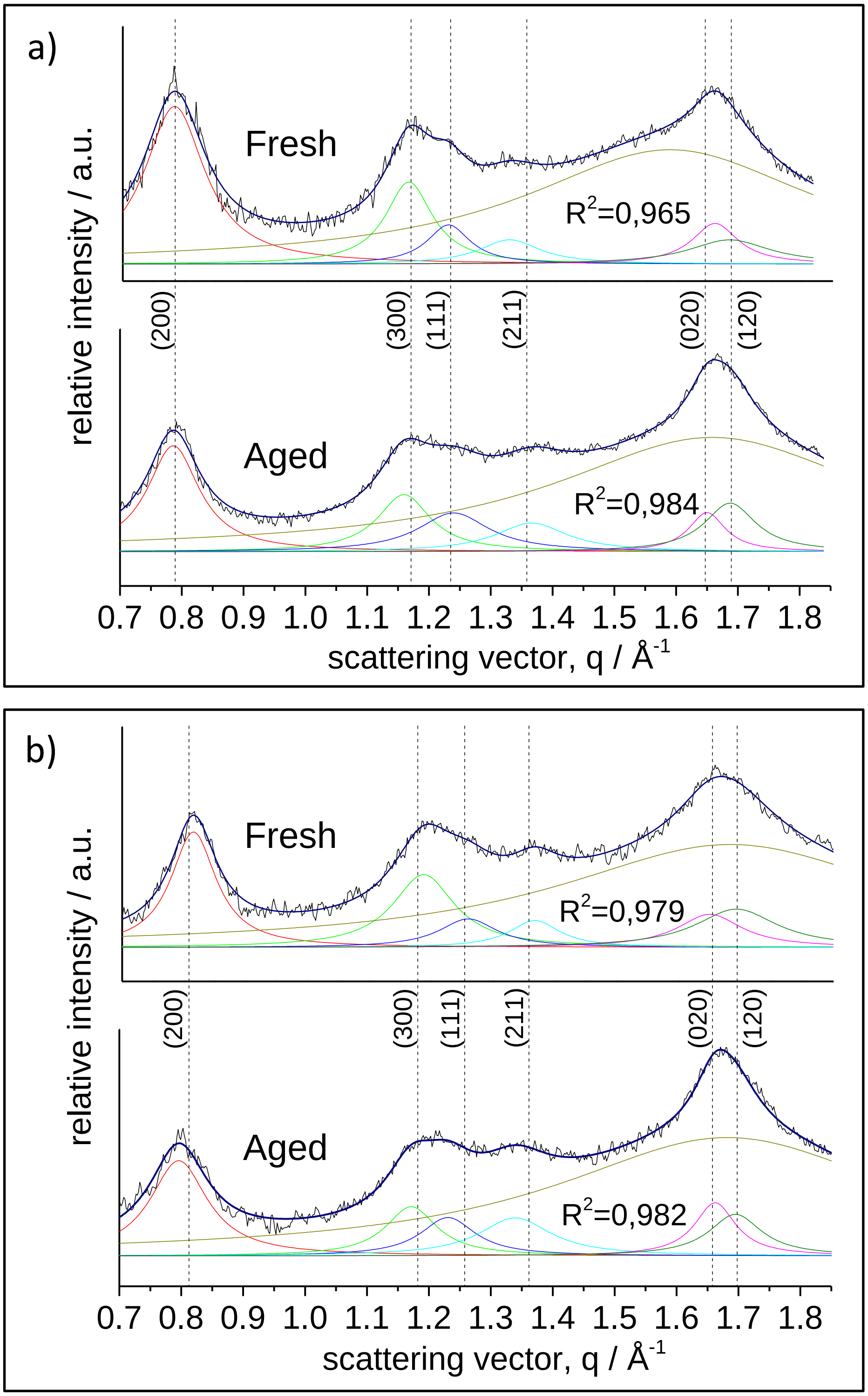

Figure S2. Diffraction profiles of a) $P3HT_{94}$ and b) $P3HT_{34}$ crystallized from fresh and aged toluene solutions. R^2 is coefficient of determination for the monoclinic unit cell model assumed to fit the experimental data. Dashed lines indicate ideal positions of diffraction maxima for the monoclinic cell with the following parameters a=15.6±0.25 Å, b=7.57±0.03, c=0.7÷0.9 Å and γ=87°.[26]

Table S2. Charge carrier mobilities of OFETs with thick (~100 nm) P3HT films

solvent	$P3HT_{94}$ moblity / cm^2/Vs		$P3HT_{34}$ moblity / cm^2/Vs	
	fresh	aged	fresh	aged
toluene	$7.0 \pm 0.2 \times 10^{-3}$	$1.8 \pm 0.2 \times 10^{-2}$	$4.1 \pm 0.4 \times 10^{-3}$	$6.0 \pm 0.3 \times 10^{-3}$
chloroform	$6.5 \pm 0.6 \times 10^{-3}$	$8.8 \pm 0.4 \times 10^{-2}$	$4.0 \pm 0.5 \times 10^{-3}$	$7.8 \pm 0.3 \times 10^{-3}$

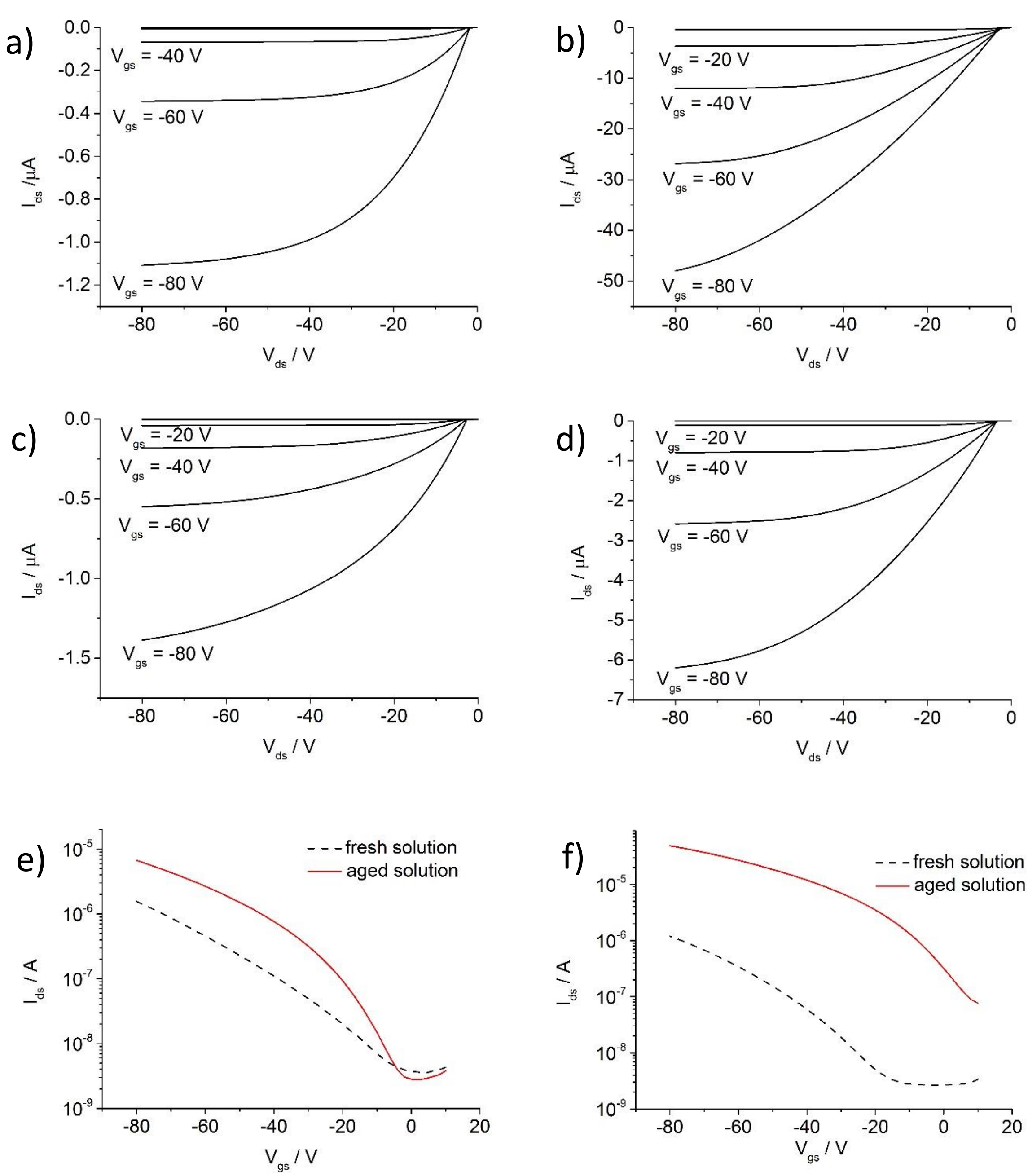

Figure S3. Output characteristics of OFETs with ultrathin $P3HT_{94}$ films obtained from: a) fresh chloroform, b) aged chloroform, c) fresh toluene and d) aged toluene solutions. Transfer characteristics of the same OFETs obtained from: a) fresh / aged toluene, b) fresh / aged chloroform.

Table S3. Working parameters of OFETs with ultrathin P3HT$_{94}$ films obtained from fresh and aged toluene / chloroform solutions.

solvent	mobility / cm^2/Vs		threshold voltage / V		ON/OFF ratio	
	fresh	aged	fresh	aged	fresh	aged
toluene	5.1 ± 0.4 x 10^{-3}	1.1 ±0.1 x 10^{-2}	-31.0 ± 2.0	-27.3 ± 2.0	4.0 ± 0.2x10^2	1.5 ± 0.2x10^3
chloroform	3.7 ± 0.1 x 10^{-3}	5.8 ± 0.3 x 10^{-2}	-37.0 ± 0.5	-2.7 ± 1.4	7.0 ± 1.0x10^2	3.0 ± 0.3x10^2

Table S4. Working parameters of OFETs with ultrathin P3HT$_{94}$ films obtained from chloroform solutions aged over different times.

time	mobility / cm^2/Vs	threshold voltage / V	ON/OFF ratio
10 min.	3.7 ± 0.1 x 10^{-3}	-37.0 ± 0.5	7.0 ± 1.0x10^2
1 day	3.2 ± 0.2 x 10^{-3}	-34.0 ± 2.0	6.5 ± 1.3x10^2
7 days	5.8 ± 0.3 x 10^{-2}	-2.7 ± 1.4	3.0 ± 0.3x10^2
30 days	5.9 ± 0.5 x 10^{-2}	-4.4 ± 2.0	2.0 ± 0.5x10^2
120 days	1.1 ± 0.2 x 10^{-1}	-2.0 ± 1.6	1.7 ± 0.4x10^2

Table S5. Working parameters of OFETs with ultrathin P3HT$_{94}$ films obtained from toluene solutions aged over different times.

time	mobility / cm^2/Vs	threshold voltage / V	ON/OFF ratio
10 min.	5.1 ± 0.4 x 10^{-3}	-31.0 ± 2.0	4.0 ± 0.2x10^2
5 h.	1.0 ± 0.1 x 10^{-2}	-32.5 ± 2.7	1.2 ± 0.1x10^2
7 days	1.1 ±0.1 x 10^{-2}	-27.3 ± 2.0	1.5 ± 0.2x10^3
120 days	1.7 ±0.5 x 10^{-2}	-15.0 ± 3.5	8.0 ± 1.0 x10^2

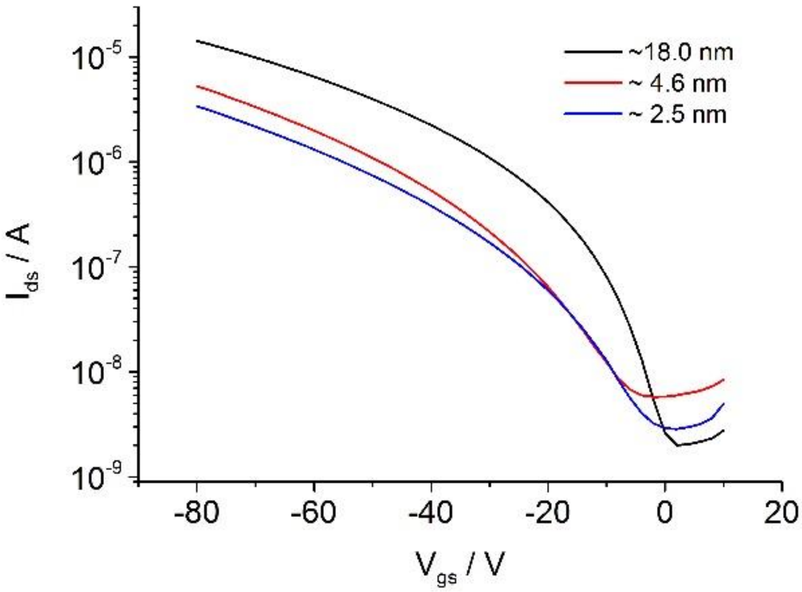

Figure S4. Output characteristics of OFETs based on ultrathin $P3HT_{94}$ films with different thicknesses obtained from aged toluene solution.

Table S6. Working parameters of OFETs based on $P3HT_{94}$ films with different thicknesses, obtained from aged toluene solution.

thickness / nm	mobility / cm^2/Vs	threshold voltage / V	ON/OFF ratio
2.5 ± 0.7	6.5 ± 0.2x10^{-3}	-28.2 ± 1.4	1.2 ± 0.2x10^{3}
4.6 ± 1.0	1.1 ± 0.1x10^{-2}	-27.3 ± 2.0	1.5 ± 0.2x10^{3}
18.0 ± 1.0	2.0 ± 0.1x10^{-2}	-15.6 ± 1.2	6.5 ± 0.3x10^{3}

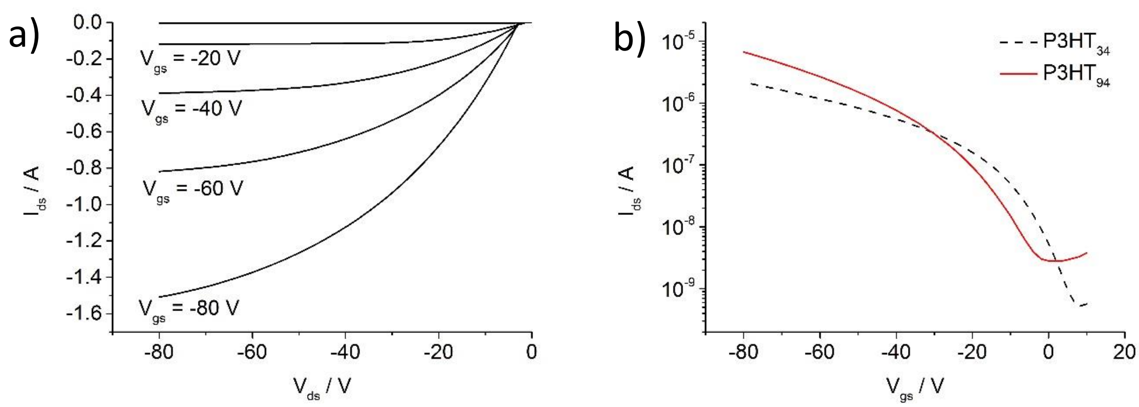

Figure S5. Output (a) characteristics of OFETs based on ultrathin $P3HT_{34}$ films, and comparision of transfer charasteristics (b) of OFETs based on ultrathin $P3HT_{34}$ / $P3HT_{94}$ films.

Table S7. Working parameters of OFETs based on ultrathin $P3HT_{94}$ and $P3HT_{34}$ films obtained from aged toluene solution.

molecular weight / kDa	mobility / cm^2/Vs	threshold voltage / V	ON/OFF ratio
34	$2.3 \pm 0.2x10^{-3}$	2.9 ± 1.0	$1.1\pm 0.3x10^{3}$
94	$1.1 \pm 0.1x10^{-2}$	-27.3 ± 2.0	$1.5 \pm 0.2x10^{3}$

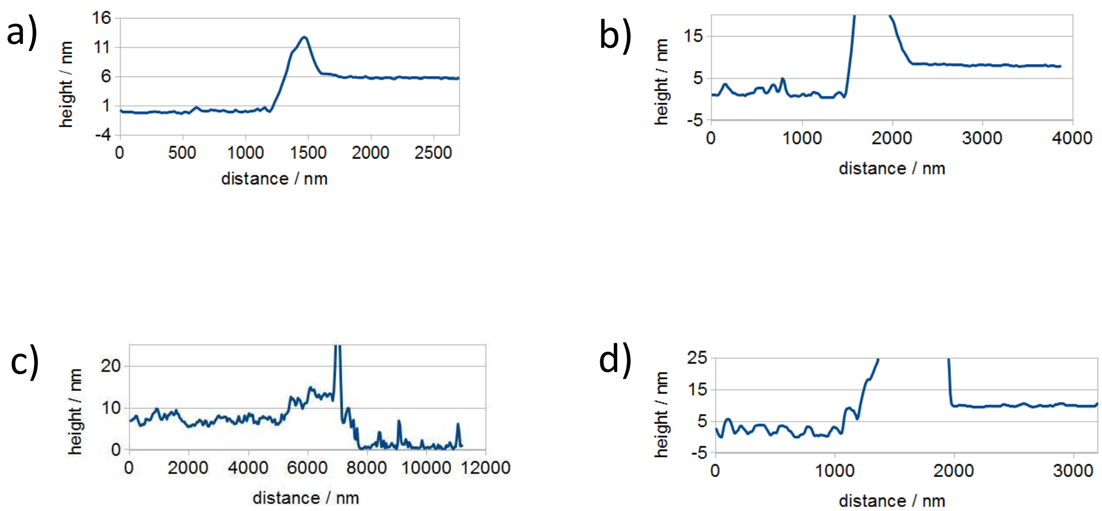

Figure S6. Step-high AFM measurements of $P3HT_{94}$ layers deposited from: a) fresh toluene, b) fresh chloroform, c) aged toluene, d) aged chloroform solutions.

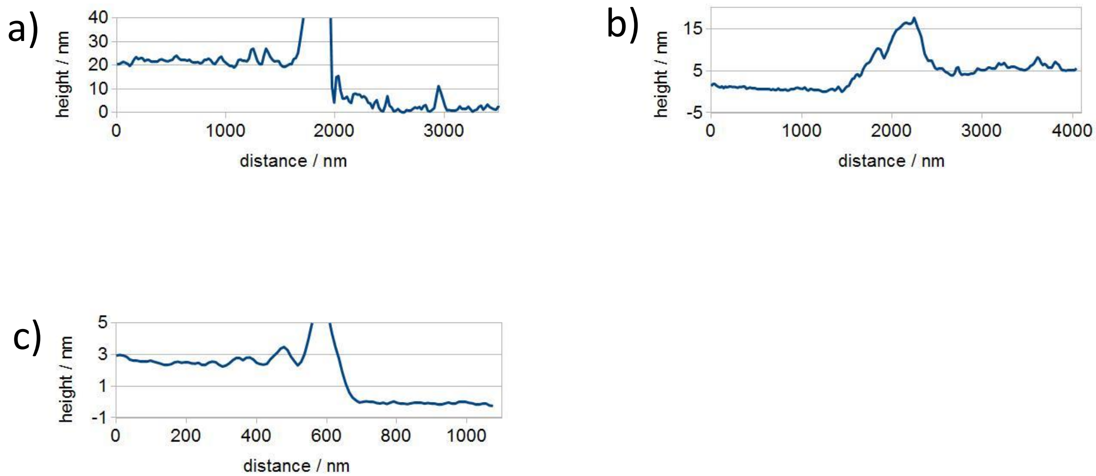

Figure S7. Step-high AFM measurements of $P3HT_{94}$ layers deposited from aged toluene solutions: a) 18.0 nm, b) 4.6 nm, c) 2.5 nm

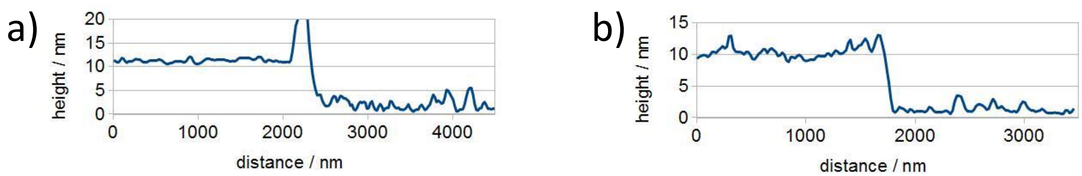

Figure S8. Step-high AFM measurements of P3HT layers deposited from aged toluene solutions: a) $P3HT_{94}$, b) $P3HT_{34}$.

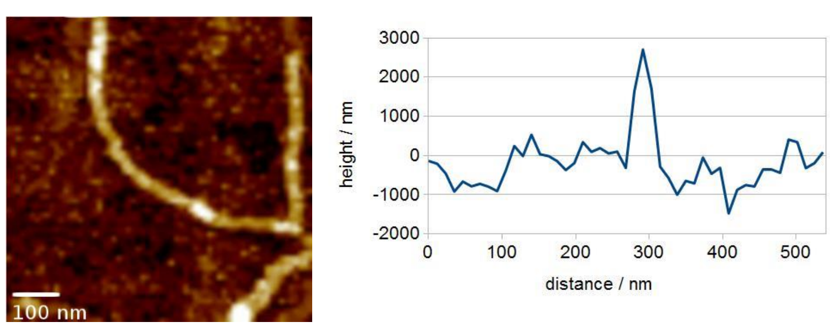

Figure S9. AFM image of single $P3HT_{94}$ fibre obtained from aged toluene solution.

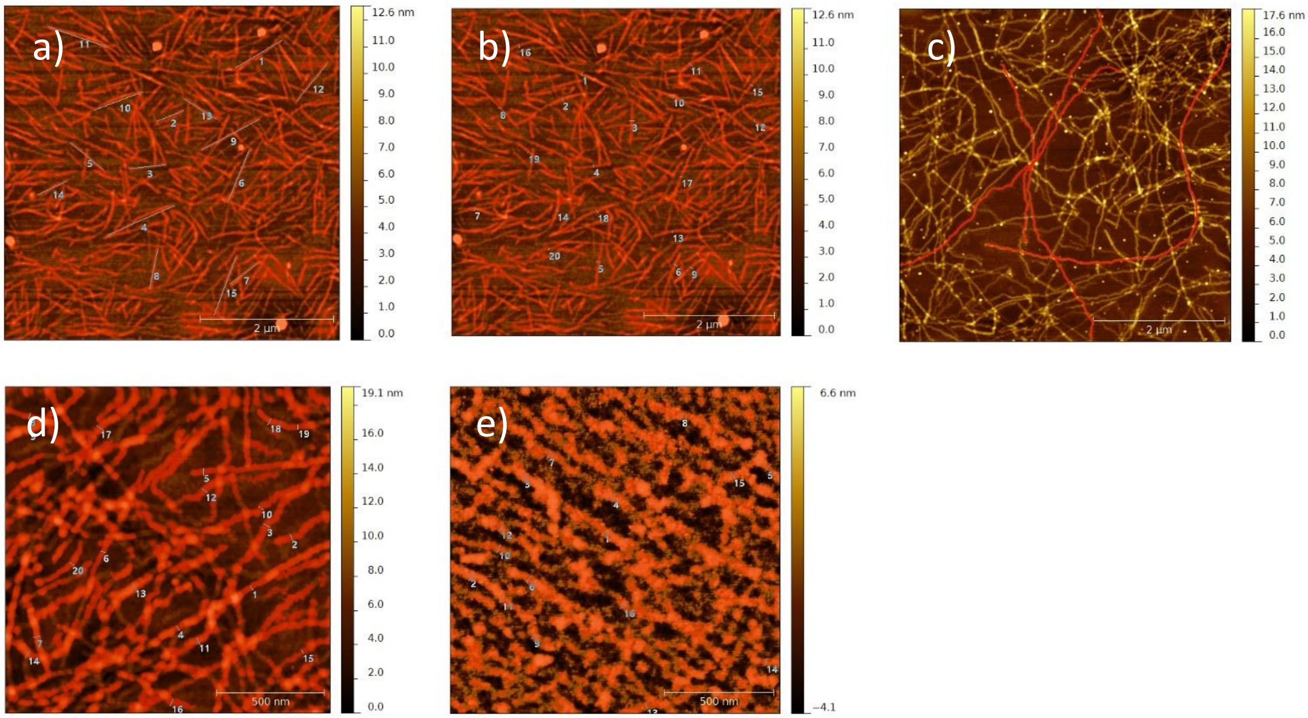

Figure S10. AFM images of P3HT films cast from aged solutions: a) $P3HT_{34}$ / toluene, fibril length measurements, b) $P3HT_{34}$ / toluene, fibril width measurements, c) $P3HT_{94}$ / toluene, several fibrils highlighted, d) $P3HT_{94}$ / toluene, fibril width measurements, e) $P3HT_{94}$ / chloroform, fibril width measurements.

In order to estimate the sizes of obtained fibrils length and width were evaluated using the Gwyddion software and its grain marking functions. For the films obtained from $P3HT_{34}$ dissolved and aged in toluene, several representative fibrils were measured in the terms of length (Figure. S10a) and width (Figure S10b). In this case such estimation was relatively easy to perform due to the low degree of fibrils overlapping and small sizes. However in the case of $P3HT_{94}$ dissolved and aged in toluene fibril thickness could been estimated (Figure S10c), but due to the entanglement of long fibrils, measurement of their length was extremely difficult. Although it can be clearly seen that the fibrils extend the length of few microns (even more than 5 µm), as was highlighted in Figure S10c. Similar situation occurred for the films cast from aged chloroform solution; thickness of fibrils could been estimated (Figure S10d), but due to high level of density and overlapping no precise length measurements could been performed.

Table S8. Sizes of P3HT fibrils determined from AFM images.

P3HT molar weight / kDa	solvent	average fibril width / nm	average fibril length / nm
34	chloroform	-	-
	toluen	46 ± 10	860 ± 20
94	chloroform	34 ± 4	-
	toluen	30 ± 5	~ several microns