Supporting Information to the article:

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

Lukasz Janasz,1 Dorota Chlebosz,2 Marzena Gradzka,2 Wojciech Zajaczkowski,3 Tomasz Marszalek,3 Klaus Müllen,3 Jacek Ulanski,3,* Adam Kiersnowski,2,* Wojciech Pisula,1,3,*

1. Department of Molecular Physics, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland
   Email: jacek.ulanski@p.lodz.pl
2. Polymer Engineering & Technology Division, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
   Email: adam.kiersnowski@pwr.wroc.pl
3. Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
   Email: pisula@mpip-mainz.mpg.de
# Table of contents:

1. Table S1. Summary of solubility parameters of solvents and P3HT................................. 4
2. Figure S1. Deconvolution of diffraction profiles of P3HT$_{34}$........................................ 5
3. Figure S2. Deconvolution of diffraction profiles of P3HT$_{94}$........................................ 6
4. Table S2. Mobilities of thick (~100 nm) P3HT films..................................................... 7
5. Figure S3. Output and transfer characteristics of P3HT$_{94}$ OFETs from fresh and aged
toluene/chloroform solutions...................................................................................................... 7
6. Table S3. Working parameters of P3HT$_{94}$ OFETs from fresh and aged toluene/chloroform
solutions.................................................................................................................................. 8
7. Table S4. Working parameters of P3HT$_{94}$ OFETs from chloroform solutions aged in
different time............................................................................................................................ 8
8. Table S5. Working parameters of P3HT$_{94}$ OFETs from toluene solutions aged in different
time.................................................................................................................................. 8
9. Figure S4. Transfer characteristics of P3HT$_{94}$ OFETs from aged toluene solutions, with
different active film thickness................................................................................................. 9
10. Table S6. Working parameters of P3HT$_{94}$ OFETs from aged toluene solutions, with
different active film thickness............................................................................................... 9
11. Figure S5. Output and transfer characteristics of P3HT$_{34}$ OFETs from aged
toluene/chloroform................................................................................................................ 9
12. Table S7. Working parameters of P3HT$_{94}$ and P3HT$_{34}$ OFETs from aged toluene
solutions.................................................................................................................................. 10
13. Figure S6. Step-high measurements of P3HT$_{94}$ films obtained from fresh and aged chloroform and toluene solutions ................................................................. 10

14. Figure S7. Step-high measurements of P3HT$_{94}$ films with different thicknesses obtained from aged toluene solutions ...................................................................................... 11

15. Figure S8. Step-high measurements of P3HT$_{94}$ and P3HT$_{34}$ films obtained from aged toluene solutions .......................................................................................................................... 11

16. Figure S9. Cross section of fibril obtained from aged P3HT$_{94}$ and toluene solution .......... 11

17. Figure S10. AFM images with marked fibrils for size measurements .................................. 12

18. Table S8. Sizes of P3HT fibril determined from AFM images ............................................. 13
**Table S1.** Physical properties of solvents used in the study and P3HT.

| parameter / unit                        | symbol | chloroform | toluene | P3HT  |
|-----------------------------------------|--------|------------|---------|-------|
| hansen solubility parameter (HSP)       |        |            |         |       |
| components / MPa$^{1/2}$                |        |            |         |       |
| $\delta_d$                              |        | 17.8       | 18      | 17.9  |
| $\delta_p$                              |        | 3.1        | 1.4     | 0.9   |
| $\delta_h$                              |        | 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) / |        | $R_s$      | 3.3     | 1.3   | -     |
| $\delta_d$                              |        |            |         |       |
| dipole moment / D                       |        | 1.10       | 0.31    | -     |
| boiling point / $^\circ$C               |        | 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 $a=15.6\pm0.25$ Å, $b=7.57\pm0.03$, $c=0.7\pm0.9$ Å and $\gamma=87^\circ$.\textsuperscript{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 $a=15.6\pm0.25$ Å, $b=7.57\pm0.03$, $c=0.7\div0.9$ Å and $\gamma=87^\circ$.26
Table S2. Charge carrier mobilities of OFETs with thick (~100 nm) P3HT films

| solvent   | P3HT_{94} mobility / cm^2/Vs | P3HT_{94} mobility / cm^2/Vs |
|-----------|------------------------------|------------------------------|
|           | fresh                        | aged                         |
|           | fresh                        | aged                         |
| toluene   | 7.0 ± 0.2 x 10^{-3}         | 1.8 ± 0.2 x 10^{-2}         |
|           | 4.1 ± 0.4 x 10^{-3}         | 6.0 ± 0.3 x 10^{-3}         |
| chloroform| 6.5 ± 0.6 x 10^{-3}         | 8.8 ± 0.4 x 10^{-2}         |
|           | 4.0 ± 0.5 x 10^{-3}         | 7.8 ± 0.3 x 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 ± 1.0x10^2 |
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 characteristics (b) of OFETs based on ultrathin P3HT$_{34}$/P3HT$_{94}$ films.
Table S7. Working parameters of OFETs based on ultrathin P3HT\textsubscript{94} and P3HT\textsubscript{34} films obtained from aged toluene solution.

| molecular weight / kDa | mobility / cm\textsuperscript{2}/Vs | threshold voltage / V | ON/OFF ratio |
|------------------------|--------------------------------------|-----------------------|--------------|
| 34                     | $2.3 \pm 0.2 \times 10^{-3}$         | $2.9 \pm 1.0$         | $1.1 \pm 0.3 \times 10^{3}$ |
| 94                     | $1.1 \pm 0.1 \times 10^{-2}$         | $-27.3 \pm 2.0$       | $1.5 \pm 0.2 \times 10^{3}$ |

Figure S6. Step-high AFM measurements of P3HT\textsubscript{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\textsubscript{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\textsubscript{94}, b) P3HT\textsubscript{34}.

**Figure S9.** AFM image of single P3HT\textsubscript{94} fibre obtained from aged toluene solution.
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\textsubscript{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\textsubscript{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 \( \mu \)m), 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.

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