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Influence of crystallinity on the thermoelectric power factor of P3HT vapour-doped with F4TCNQ

Jonna Hynynen, David Kiefer and Christian Müller*

Doping of the conjugated polymer poly(3-hexylthiophene) (P3HT) with the p-dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) is a widely used model system for organic thermoelectrics. We here study how the crystalline order influences the Seebeck coefficient of P3HT films doped with F4TCNQ from the vapour phase, which leads to a similar number of F4TCNQ anions and hence (bound + mobile) charge carriers of about $2 \times 10^{-4}$ mol cm$^{-2}$. We find that the Seebeck coefficient first slightly increases with the degree of order, but then again decreases for the most crystalline P3HT films. We assign this behaviour to the introduction of new states in the bandgap due to planarisation of polymer chains, and an increase in the number of mobile charge carriers, respectively. Overall, the Seebeck coefficient varies between about 40 to 60 $\mu$V K$^{-1}$. In contrast, the electrical conductivity steadily increases with the degree of order, reaching a value of more than 10 S cm$^{-1}$, which we explain with the pronounced influence of the semi-crystalline nanostructure on the charge-carrier mobility. Overall, the thermoelectric power factor of F4TCNQ vapour-doped P3HT increases by one order of magnitude, and adopts a value of about 3 $\mu$W m$^{-1}$ K$^{-1}$ in the case of the highest degree of crystalline order.

**Introduction**

The interest in organic thermoelectrics is rapidly increasing because it may meet the demand for cheap autonomous power sources that will be needed to run countless electronic devices such as sensors, actuators and identification tags, which are envisaged to make up tomorrow’s Internet of Things. The ability of different materials to turn heat into electricity can be compared based on their thermoelectric figure of merit:

$$ZT = \alpha^2 \sigma / k_T$$

(1)

where $\alpha$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, $k_T$ the thermal conductivity, and $T$ the absolute temperature. For most organic materials, the thermal conductivity is low even at the highest achievable doping levels, i.e. $k_T < 1$ W m$^{-1}$ K$^{-1}$. Hence, to a good approximation the thermoelectric figure of merit can be compared based on the power factor $\alpha^2 \sigma$. The Seebeck coefficient and the electrical conductivity are interrelated, and the highest power factor is typically obtained for the most conducting material. Increasing the number of charge carriers usually leads to an increase in electrical conductivity but a decrease in Seebeck coefficient, which scale according to:

$$\alpha = k_B / e \left( \sigma / \sigma_0 \right)^{-1/4}$$

(2)

where $k_B$ is the Boltzmann constant divided by unit charge, or the natural unit of thermopower 86.17 $\mu$V K$^{-1}$, and $\sigma_0$ is a free parameter set to 1 S cm$^{-1}$. Conjugated polymers are of particular interest because a wide range of rheological and mechanical properties can be selected through careful choice of the molecular weight. Further, many conjugated polymers now offer a high charge-carrier mobility $\mu$, which is needed to reach a high electrical conductivity according to:

$$\sigma = n q \mu$$

(3)

where $n$ is the number of charge carriers and $q$ is their charge, i.e. $\pm 1.6 \times 10^{-19}$ C for electrons and holes. The charge carrier density can be increased through doping, either by acid doping or redox doping. The latter can be conveniently carried out by adding a so-called molecular dopant to the conjugated polymer. The dopant molecule then either accepts or donates an electron from/to the conjugated polymer, which gives rise to p- or n-doping, and leads to the formation of a charge transfer complex (partial charge transfer) or ion pair (integer charge transfer). p-type doping of poly(3-hexylthiophene) (P3HT) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) is a widely used model system (Fig. 1), where an electron is donated from the highest occupied molecular orbital (HOMO) of P3HT to the lowest unoccupied molecular orbital (LUMO) of F4TCNQ, leading to integer charge transfer.

The dopant can be introduced by two means, either through co-processing together with the polymer from the same
solution, which leads to aggregation that disrupts the solid-state order of P3HT, or through sequential doping.
Sequential doping can be carried out by either deposing the dopant onto the polymer from the vapour phase (vapour doping), or by bringing the polymer in contact with an orthogonal solvent that dissolves the dopant. Sequential doping is of interest since it allows to circumvent the aggregation of P3HT that occurs during co-processing. Instead, the nanostructure of the polymer can develop under controlled conditions. Subsequently, P3HT can be doped in a precise manner, which allows to study the interplay of charge-carrier density, nanostructure and electrical properties. Moreover, sequential doping can lead to a significantly higher electrical conductivity above 10 S cm$^{-1}$. We explain the correlation between conductivity and crystallinity with the well-established impact of the former on the charge-carrier mobility. We can use eqn (3) to estimate the mobility if we can determine the number of charge carriers. Since doping of P3HT with F4TCNQ occurs through integer charge transfer, we assume that each F4TCNQ anion corresponds to one charge on the polymer. We here do not distinguish between bound and free charge carriers and instead consider the average mobility. Therefore, we equate the F4TCNQ anion concentration with the number of charge carriers. We estimate the anion concentration by considering the average mobility. Therefore, we equate the F4TCNQ anion concentration with the number of charge carriers. We estimate the anion concentration by

ting the regioregularity and processing solvent the nanostructure of P3HT could be altered leading to a much higher electrical conductivity. For example, by changing the polymer processing solvent we were able to increase the electrical conductivity from 0.01 to 13 S cm$^{-1}$, which we attributed to the higher charge-carrier mobility that resulted from a higher degree of polymer crystallinity. Similar findings were made by Scholes et al. and Chew et al. who concluded that the ordered regions of P3HT give rise to a higher charge-carrier mobility and therefore lead to an increase in the electrical conductivity. Here, we explore how the crystallinity influences the power factor of P3HT vapour-doped with F4TCNQ. We find that an increase in the crystalline order enhances the power factor by one order of magnitude from 0.2 to 2.7 $\mu$W m$^{-1}$ K$^{-2}$.

Results and discussion
To vary the crystalline order of P3HT we spincoated films with a thickness of $\sim$70 nm at 60 °C from six different solvents (chloroform, chlorobenzene, chlorobenzene/o-dichlorobenzene, toluene, 1,2,4-trichlorobenzene and p-xylene). We chose to work with a highly regioregular P3HT that featured a number-average molecular weight of $M_n \sim 29$ kg mol$^{-1}$.

To compare the degree of solid-state order of neat P3HT films, we recorded UV-vis absorbance spectra. We fitted the spectra according to the model developed by Spano et al., assuming a Huang–Rhys factor of 1:

$$A_{0-0}/A_{0-1} = \left(1 - \frac{0.24W}{E_p} \right)^2 \left(1 + \frac{0.072W}{E_p} \right)^2$$

where $E_p$ is the intramolecular vibration (0.18 eV) and the ratio is taken from the absorption spectra. We used eqn (4) to extract the free exciton bandwidth $W$, which we used as a measure for the degree of crystallinity. The free exciton bandwidth varied from 155 meV to 30 meV for chloroform and p-xylene, respectively, indicating the highest degree of order in case of the latter (Fig. 2).

We then doped the neat P3HT films by exposing them to vapour of F4TCNQ at ambient conditions as previously described (for vapour doping setup see Fig. 1). The degree of doping correlates with the period of time that the samples are exposed to F4TCNQ vapour. For the vapour-doped samples, we find that the conductivity sharply increases during the first two minutes of doping but then levels off for longer doping times (Table 1). We therefore selected a doping time of 3 min to compare samples spincoated from different solvents. For the least ordered samples spincoated from chloroform we find an electrical conductivity of only 0.7 S cm$^{-1}$, whereas more highly ordered p-xylene films yielded a value of 12.7 S cm$^{-1}$ after 3 min of doping. We have demonstrated previously that the electrical conductivity increases with the degree of crystalline order of P3HT, as evidenced by the inverse correlation of $\sigma$ and $W$ (Fig. 3).

We explain the correlation between conductivity and crystallinity with the well-established impact of the former on the charge-carrier mobility. We can use eqn (3) to estimate the mobility if we can determine the number of charge carriers. Since doping of P3HT with F4TCNQ occurs through integer charge transfer, we assume that each F4TCNQ anion corresponds to one charge on the polymer. We here do not distinguish between bound and free charge carriers and instead consider the average mobility. Therefore, we equate the F4TCNQ anion concentration with the number of charge carriers. We estimate the anion concentration by fitting UV-vis spectra of doped films according to a procedure first proposed by Wang et al. For all six processing solvents we extract a similar value of about $2 \times 10^{-4}$ mol cm$^{-3}$, which corresponds to 0.03 anions per P3HT repeat unit (or 4.7 wt% anions assuming a density of 1 g cm$^{-3}$). Based on this value we find that for the here studied samples the mobility increases from 0.05 to 0.5 cm$^2$ V$^{-1}$ s$^{-1}$ (Fig. 3). Pingel et al. have shown for F4TCNQ-doped P3HT that only a fraction of anions gives rise to free charge carriers, which implies that our mobility estimate represents a lower bound.

The Seebeck coefficient, instead, shows a markedly different, non-monotonic behaviour. For the most disordered samples, spincoated from chloroform, we measure a low Seebeck coefficient.
coefficient of 51 μV K\(^{-1}\) (Table 2). For more ordered samples we find a slightly higher value of 60 μV K\(^{-1}\), whereas the most ordered samples, spincoated from \(p\)-xylene, display the lowest Seebeck coefficient of 43 μV K\(^{-1}\). In case of poly(3,4-ethylenedioxythiophene):tosylate (PEDOT:Tos) with a constant dopant concentration the Seebeck coefficient has been shown to slightly increase with the degree of crystalline order.\(^{26}\) Fabiano et al. argue that the slight increase in Seebeck coefficient from 32 to 44 μV K\(^{-1}\) arises because of a steeper density of states at the Fermi level, caused by the presence of states in the bandgap as a result of delocalisation in ordered domains. Since the charge-carrier mobility likewise improves through the presence of ordered domains, a correlation between the Seebeck coefficient and mobility is observed for PEDOT:Tos. We argue that a similar behaviour results in the slight increase in Seebeck coefficient that we observe for more
disordered samples, e.g. when changing the spincoating solvent from chloroform to chlorobenzene (Table 2).

The slight decrease in Seebeck coefficient that we observe for more ordered samples may arise because of an increase in the number of mobile charge carriers. The Seebeck coefficient predominately probes mobile charge carriers and therefore a change in their concentration will influence the measured

![Image](14x290 to 26x354)

**Fig. 3** (a) Electrical conductivity $\sigma$ as a function of free exciton bandwidth $W$, calculated by fitting UV-vis spectra according to ref. 21–23: (b) charge-carrier mobility $\mu$ as a function of free exciton bandwidth $W$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$t_{\text{vapour}}$ (min)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$\alpha$ (µV K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene/</td>
<td>0.5–2</td>
<td>0.6 ± 1.3</td>
<td>62 ± 17</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>2.5–5</td>
<td>5.5 ± 2.0</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>10</td>
<td>2.9 ± 2.3</td>
<td>57 ± 4</td>
</tr>
<tr>
<td></td>
<td>0.5–2</td>
<td>5.0 ± 5.4</td>
<td>54 ± 11</td>
</tr>
<tr>
<td></td>
<td>2.5–5</td>
<td>12.7 ± 2.8</td>
<td>43 ± 3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>14.5 ± 0.5</td>
<td>48 ± 2</td>
</tr>
</tbody>
</table>

The variation in Seebeck coefficient with electrical conductivity follows the empirical trend described by eqn (2) (Fig. 4, top). Data points that lie to the left of this empirical line are thought to be mobility limited: a given degree of doping results in a certain Seebeck coefficient, but many charges cannot traverse the material sufficiently quickly because their motion is impeded by structural defects. One illustrative example are ternary blends of P3HT:F4TCNQ with poly(ethylene oxide) (PEO). We have found that in case of a sufficiently high concentration of P3HT:F4TCNQ the Seebeck coefficient and electrical conductivity follow the empirical trend of eqn (2). In contrast, in case of more dilute blends the connectivity between P3HT:F4TCNQ domains is poor, leading to a lower mobility and hence electrical conductivity (cf. red filled circles in Fig. 4). We note that the conductivity that we have measured for samples spincoated from chloroform diverges from the empirical trend of eqn (2). We assign this behaviour to the low charge-carrier mobility that we deduce for these samples, caused by poor connectivity of crystalline domains.

The opposite case are samples that are mobility enhanced, where charges are able to traverse the material more quickly than predicted by the empirical trend of eqn (2), leading to a higher conductivity for a given Seebeck coefficient. An
example is the recent work by Brinkmann et al., who studied sequentially-doped P3HT films that had been uniaxially aligned through rubbing.17 Upon F4TCNQ doping a concomitant increase in electrical conductivity and Seebeck coefficient was observed, with maximum values of $\sigma = 22 \text{ S cm}^{-1}$ for $\alpha = 60 \text{ mV K}^{-1}$, which we rationalise with improved connectivity along the direction of orientation.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$W$ (meV)</th>
<th>Aggregates (%)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$\alpha$ (mV K$^{-1}$)</th>
<th>F4TCNQ anion conc. (10$^{-4}$ mol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>155</td>
<td>33</td>
<td>0.7 ± 0.4</td>
<td>51 ± 2</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>110</td>
<td>38</td>
<td>2.0 ± 0.7</td>
<td>63 ± 1</td>
<td>2.9 ± 0.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>58</td>
<td>42</td>
<td>5.3 ± 2.1</td>
<td>55 ± 4</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>Chlorobenzene/o-dichlorobenzene</td>
<td>64</td>
<td>42</td>
<td>6.1 ± 0.8</td>
<td>59 ± 3</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>54</td>
<td>43</td>
<td>5.6 ± 0.6</td>
<td>56 ± 2</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>30</td>
<td>46</td>
<td>12.7 ± 2.8</td>
<td>46 ± 2</td>
<td>3.0 ± 0.6</td>
</tr>
</tbody>
</table>

Table 2  Calculated values of the free exciton bandwidth $W$, estimated values of aggregate percentage according to ref. 21–23, and measured electrical conductivities and Seebeck coefficients for samples tested in this study.
Conclusions

Overall, for the here studied F4TCNQ vapour-doped P3HT thin films we find that the thermoelectric power factor $\alpha^2\sigma$ increases with the degree of crystalline order from 0.2 to 2.7 according to ref. 21–23. Absorption spectra of F4TCNQ-doped P3HT were fitted according to ref. 11 and 24 using a superposition of two Gaussian peaks (centred at 1.33 and 1.67 eV; FWHM of 0.29 and 0.42 eV, respectively), a P3HT aggregate model ref. 21–23, and the F4TCNQ anion spectrum from ref. 11 and 24.

Electrical characterisation

The electrical resistivity was measured with a four-point probe setup from Jandel Engineering (cylindrical probe head, RM3000) using collinear tungsten carbide electrodes with equidistant spacing of 1 mm that were held down with a constant weight of 60 g. Seebeck coefficients were measured at 300 K with an SB1000 instrument equipped with a K2000 temperature controller from MMR Technologies using a thermal load of 1–2 K and a constantan wire as an internal reference. Samples of about 1 mm times 4 mm were mounted on the sample stage using silver paint (Agar Silver Paint, G302).

Conflicts of interest

There are no conflicts to declare.

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