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Design of experiment optimization of aligned polymer thermoelectrics doped by ion-exchange

Yuxuan Huang,1 Dionisius Hardjo Lukito Tjhe,1 Ian E. Jacobs,1 Xuechen Jiao,2 Qiao He,3 Martin Statz,1,4 Xinglong Ren,1 Xinyi Huang,1 Iain McCulloch,6,7 Martin Heeney,3 Christopher McNeill,2 and Henning Sirringhaus1,a)

AFFILIATIONS
1Optoelectronics Group, Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom
2Department of Materials Science and Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
3Department of Chemistry and Centre for Processable Electronics, Imperial College London, London, United Kingdom
4Georg-August-Universität Göttingen, I. Physikalisches Institut, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
5School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
6KAUST Solar Center, Physical Sciences and Engineering Division (PSE), Materials Science and Engineering Program (MSE), King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia
7Department of Chemistry, University of Oxford, Oxford, United Kingdom

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a)Author to whom correspondence should be addressed: hs220@cam.ac.uk

ABSTRACT

Organic thermoelectrics offer the potential to deliver flexible, low-cost devices that can directly convert heat to electricity. Previous studies have reported high conductivity and thermoelectric power factor in the conjugated polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT). Here, we investigate the thermoelectric properties of PBTTT films in which the polymer chains were aligned uniaxially by mechanical rubbing, and the films were doped by a recently developed ion exchange technique that provides a choice over the counterions incorporated into the film, allowing for more optimized morphology and better stability than conventional charge transfer doping. To optimize the polymer alignment process, we took advantage of two Design of Experiment (DOE) techniques: regular two-level factorial design and central composite design. Rubbing temperature $T_{rub}$ and post-alignment annealing temperature $T_{anneal}$ were the two factors that were most strongly correlated with conductivity. We were able to achieve high polymer alignment with a dichroic ratio $>15$ and high electrical conductivities of up to 4345 S/cm for transport parallel to the polymer chains, demonstrating that the ion exchange method can achieve conductivities comparable/higher than conventional charge transfer doping. While the conductivity of aligned films increased by a factor of 4 compared to unaligned films, the Seebeck coefficient ($S$) remained nearly unchanged. The combination of DOE methodology, high-temperature rubbing, and ion exchange doping provides a systematic, controllable strategy to tune structure–thermoelectric property relationships in semiconducting polymers.

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Conjugated polymers are promising candidates for thermoelectrics due to their low thermal conductivity and high Seebeck coefficients. However, in many materials, low electrical conductivity limits the thermoelectric figure of merit (ZT) and, therefore, real-world applications.1–3 Improving electrical conductivity in these materials through improvements in film morphology and doping techniques is critical to the future success of organic thermoelectrics.1,4 Charge transport in conjugated polymers tends to be fastest along the polymer backbone reflecting the intrinsic anisotropy of the electronic structure.5–8 Hence, various methods to induce a uniaxial chain alignment along the direction of charge transport have been found effective to improve the charge transport and maximize the electric conductivity and thermoelectric properties. Some approaches achieved a particularly high degree of orientation, such as mechanical rubbing,9–12 shear coating,13,14 stretch alignment,15,16 or epitaxy.17,18 Among them, mechanical rubbing is one of the most versatile...
methods to facilitate the crystallization and high-level orientation of conjugated polymers.10,11

Of similar importance is the choice of the doping method that is needed to induce a high concentration of mobile charge carriers in the polymer film after it has been aligned. One of the most commonly used methods for p-type doping involves exposing a solid polymer film to a solution of a charge transfer dopant with a high electron affinity19,20 or depositing the charge transfer dopant onto the surface of the polymer by evaporation.21–23 The dopant accepts an electron from the polymer, generating an anion, which is then incorporated into the film to provide the charge stabilizing counterions for the mobile polarons generated on the polymer. By combining polymer chain alignment by mechanical rubbing with charge transfer doping using FeCl₃, very high electrical conductivities of up to $10^5$ S/cm have recently been reported for the conjugated polymer PBTTT.11 However, the charge transfer doping technique has some clear limitations, in particular, the limited chemical stability of the dopant anions, which can lead to rapid degradation of the electrical conductivity of the doped films.

In this work, we use a recently developed ion-exchange (IEX) doping technique, which involves exposing the films to a solution comprising both a molecular dopant and an electrolyte.24 The dopant induces the charge transfer as above, but the reduced dopant anion is not incorporated into the film. Instead, it exchanges with the negative ion of the electrolyte, which is chosen to be a chemically stable, closed shell ion. We have recently demonstrated that this technique is broadly applicable to a broad range of conjugated polymers, including PBTTT, and can achieve higher electrical conductivity than F₄TCNQ or FeCl₃ doping without ion exchange.25 Here, we apply this recent technique to PBTTT films aligned by mechanical rubbing and investigate the thermoelectric properties that can be achieved.

The fabrication process of aligned polymer films [Fig. 1(a)] involves a large number of process parameters that require optimization. The high dimensionality of the problem makes optimization time-consuming; therefore, researchers often focus on the impact of individual parameters like rubbing temperature $T_{rub}$ or the number of rubbing cycles.7 The effect of many of these parameters on the resulting film is not obvious and is generally not included in the literature reports; additionally, they may interact with one another in non-trivial ways, preventing straightforward optimization of each parameter individually. To facilitate the optimization, we have used a Design of Experiment (DOE) approach, which is widely used as a statistical tool in industrial process development, such as pharmaceutical or biotechnology processes.26–29 This allows for a systematic investigation of the key parameters that influence the high-temperature rubbing process. In our previous work, the ion-exchange doping process had been optimized with the combination of FeCl₃ and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP TFSI) for PBTTT, which leads to a complete bleaching of the PBTTT neutral absorption band and a high doping concentration on the order of $8 \times 10^{20}$ cm$^{-3}$ [Figs. 1(b) and 1(c)].25 The same process is used in the optimization process without further modification.

The use of the DOE methodology provides several benefits [Fig. 2(a)]. First, DOE allows us to systematically investigate a large number of potentially key process parameters to maximize electrical conductivity and then combine each optimized parameter for an overall optimized process.26–28 We conducted the optimization by varying all parameters simultaneously due to the potential cross correlation effects between rubbing parameters. At the outset, the key parameters for achieving alignment were not known; therefore, we considered all parameters that could conceivably affect alignment quality in our optimization, including stage speed, roller rotation and height, number of rubbing cycles, the temperature during rubbing $T_{rub}$, and the post-alignment annealing temperature $T_{anneal}$ (Table I). The impact of the rubbing cloth types, side chain length of PBTTT, and film thickness on polymer crystallization and orientation was also considered in the later screening rounds. The DOE methodology allowed us to keep the experiments needed to identify an optimum in such a multi-dimensional design space to a reasonable number.
The first-round screening experiment, screening A, was designed using regular two-level factorial design. The purpose of the first-round screening was to screen the multidimensional factors to rule out insignificant rubbing factors and locate a maximum in conductivity to direct the next-level screening. The lower level of $T_{rub} \leq 125^\circ C$, was extracted from the previous studies, while the higher $T_{rub}$ at 180 $^\circ C$ was selected to be above the first phase transition in the differential scanning calorimetry (DSC) trace of PBTTT. Both stage speed and roller rotation were set at the lowest (100 rpm) and highest (1500 rpm) values supported by our rubbing machine. (Note: stage speed was not varied in this experiment.)

![Graphs showing conductivity results](image)

**FIG. 2.** (a) Conductivity results of aligned and doped C12-PBTTT from screening A to E, the evolution of conductivity as a function of (b) $T_{rub}$, and (c) $T_{anneal}$ measured from screening B.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>Optimum</th>
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<td>Polymer</td>
<td>C14-PBT</td>
<td>C14-PBT</td>
<td>C14-PBT</td>
<td>C12-PBT</td>
<td>C12-PBT</td>
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<tr>
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<td>C14-PBT</td>
<td>C14-PBT</td>
<td>C12-PBT</td>
<td>C12-PBT</td>
<td></td>
</tr>
<tr>
<td>C14-PBT</td>
<td>Rayon</td>
<td>Rayon</td>
<td>Rayon</td>
<td>Microfiber cloth</td>
<td>Microfiber cloth</td>
<td>Microfiber cloth</td>
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<tr>
<td>Solution concentration (mg/ml)</td>
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<td>10</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>10</td>
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<tr>
<td>Spin-coating speed (rpm)</td>
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<td>1500</td>
<td>1500</td>
<td>(500), 750, 1500, (8000)</td>
<td>600, 1000, (1500)</td>
<td>1000</td>
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<td>Rubbing temperature ($^\circ C$)</td>
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<td>(115), 125, 140, (155), (165)</td>
<td>(132), 140, 160, (180), (188)</td>
<td>(115), 125, 140, 155</td>
<td>155</td>
<td>155</td>
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<tr>
<td>Stage speed (rpm)</td>
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<td>(1200), 1300, 1400, 1500</td>
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<td>1500</td>
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<td>1500</td>
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<tr>
<td>Roller rotation speed (rpm)</td>
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<td>(950), 1100, 1300, 1500</td>
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<tr>
<td>Rubbing cycles</td>
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<td>0.5</td>
<td>0.5</td>
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<tr>
<td>Post-alignment annealing (rpm)</td>
<td>RT, 180</td>
<td>(140), 150, 165, 180, (190)</td>
<td>(166), 180, 215, 250, (264)</td>
<td>RT, (163), 170, 180, 190, 197</td>
<td>190</td>
<td>190</td>
</tr>
</tbody>
</table>

Table I. Parameters of film preparation and high-temperature rubbing in screening A-E.
speed is also set in rpm in our rubbing machine; 1500 rpm is approximately 0.8 cm/s. The number of rubbing cycles, which may likely affect the dichroic ratio of oriented polymer films, was set at either half a cycle or three cycles in screening A. Post-alignment annealing was previously reported to play a significant role in increasing the crystallinity and conductivity; however, in previous work on the thermoelectric performance of rubbed PBT, the films did not undergo post-annealing. Therefore, we tested both conditions without post-alignment annealing and with post-alignment annealing at $T_{\text{anneal}}$ = 180°C. The DOE methodology required only 16 samples to characterize this five-dimensional design space in the pilot screening (Table I).

Among the 16 process routes in screening A (coded A-1 through A-16, Table S1 in the supplementary material for detailed parameters), the two top-performing samples, A-5 and A-9, resulted in higher conductivity than other results in this round (supplementary material, Table S1). There were two statistically significant factors, characterized by p-values (that is, the probability that the observed differences are due to random chance) lower than 0.05, from screening A: stage speed ($p = 0.0424$) and post-alignment annealing ($p = 0.0096$), as shown in the supplementary material, Table S2. In addition, the two optimum process routes in this round, A-5 and A-9, share common factors: higher roller rotation (1500 rpm), higher stage speed (1500 rpm), three rubbing cycles, and $T_{\text{anneal}}$ at 180°C; the only difference here is the higher $T_{\text{rub}}$ at 180°C for A-5 compared to $T_{\text{rub}}$ at 125°C for A-9.

The second-generation screening, screening B (coded B-1 to B-21 in the supplementary material, Table S1), was generated using a central composite design with other parameter ranges extracted from model analysis of the first screening (supplementary material Table S1). Based on the first screening, we could rule out the potential effect from rubbing cycles, and then set at half cycle for the rest of optimization experiments. B-3 was the top-performing with an electric conductivity of 2793 S/cm among 21 process routes in screening B. A quadratic model with a p-value of 0.0083 (indicating strong predictive power) was used to fit the data from screening B (supplementary material, Table S3). Here, $T_{\text{rub}}$ and $T_{\text{anneal}}$ turn out to be the statistically significant factors controlling conductivity [Figs. 2(b) and 2(c)]; however, no cross correlation effects were considered to be statistically significant yet. Table S3 in the supplementary material contains an additional description of the statistical model.

The most apparent trend from screening B was that higher $T_{\text{anneal}}$ resulted in higher conductivity, in particular, sample B-3 with the highest conductivity was annealed at the highest temperature of 190°C in this round of screening [Fig. 2(c)]. Because the films are annealed before rubbing, this suggests that the alignment process may disrupt the film morphology, as we will address below. The effect of $T_{\text{rub}}$ is likely more complex. Higher $T_{\text{rub}}$ could promote the disentangling process of polymer backbones by promoting chain mobility, especially of the higher molecular-weight segments in the polydisperse polymer. However, if some of the thermal fluctuations of chain conformation that are present at high temperatures are frozen in when the films are cooled to room temperature, this could lead to enhanced disorder and lower conductivity, suggesting that there could be an optimum rubbing temperature.

The third-round screening, screening C (coded C-1 to C-11), was also generated by central composite design. Both stage speed and roller rotation were fixed in the previous round, 1500 rpm, as they were not found to be statistically significant factors in the previous round. Instead, in this round, we focused on the higher temperature regime for both $T_{\text{rub}}$ (132–188°C) and $T_{\text{anneal}}$ (166–264°C) compared to screening B (Table I). The top-performing sample from this round is C-10 with a conductivity over 2900 S/cm with $T_{\text{rub}}$ at 140°C and $T_{\text{anneal}}$ at 180°C.

To further boost the electric conductivity of rubbed and doped PBT film after the previous three-round screenings, we then explored switching the side chain length of PBT to C12 and changing the rubbing cloth material from Rayon to a microfiber cloth (Table I). In addition, we explored the influence of film thickness that may also affect the degree of crystallinity in conjugated polymer films. Therefore, pristine PBT films of various thickness were prepared by spin-coating 20 mg/ml PBT solution at speeds ranging from 500 to 8000 rpm (Table I). We again varied $T_{\text{rub}}$ from 125 to 155°C, while $T_{\text{anneal}}$ was varied from 163 to 190°C in the screening D (coded D1–D18). Switching to C12-PBT and a microfiber cloth increased the conductivity up to the level of 3800 S/cm, while it appears that increasing the film thickness brings no significant advantage in conductivity enhancement.

Considering that spin coating from a high solution concentration may have produced non-uniform polymer films, we switched back to 10 mg/ml PBT solution and only varied polymer film spin coating speed at 600/1000/1500 rpm as the fifth and final screening. Spin coating of 10 mg/ml C12-PBT at 1000 rpm with $T_{\text{rub}}$ at 155°C and $T_{\text{anneal}}$ at 190°C (E-2, supplementary material, Table S1) was selected as the final conductivity-optimized rubbing process parameters, since no significant enhancement in electrical conductivity was achieved beyond the level of 3800–3900 S/cm.

Grazing incidence wide-angle x-ray scattering (GIWAXS) was performed on the films after the optimized rubbing process. The GIWAXS images in Fig. 3 show the high in-plane polymer chain alignment, inferred from the strong in-plane (010) π–π stacking peak and almost complete absence of the in-plane (003) backbone peak in the measurement parallel to the rubbing direction [Fig. 3(a)]. The inverse is seen in the same film measured perpendicular to the rubbing direction [Fig. 3(b)]. Without post-alignment annealing, we observe a predominantly face-on film texture (supplementary material, Fig. S1), consistent with previous reports. In contrast, the annealed samples demonstrated much stronger out-of-plane (h00) reflections from edge-on crystalline population, with a smaller population of face-on crystallites, giving a broad distribution of in-plane (h00) reflections. Therefore, our findings suggest that while high-temperature rubbing tends to induce some face-on texture, post-alignment annealing largely returns the films to the edge-on texture observed in unaligned films [Fig. 3(c)]. This edge-on texture is generally beneficial for charge transport, consistent with our findings that post-alignment annealing improves conductivity in doped films.

Polarized optical microscopy images [Figs. 4(a) and 4(b)] are also consistent with a very high degree of alignment. Remarkably, strong birefringence was observed when aligning the crossed polarizers at 45° to the rubbing direction, while near complete extinction was observed when the polarizers were aligned parallel/perpendicular to the rubbing direction [Figs. 4(a) and 4(b)]. The images provide clear evidence for a uniform and high level of chain alignment across the film, in good agreement with the GIWAXS data.

Polarized UV-VIS spectroscopy was used to monitor the degree of chain alignment before and after doping and quantify the dichroic...
ratio and to monitor spectroscopically the level of polymer oxidation after doping [Fig. 4(c)]. The highly efficient ion-exchange doping by FeCl₃ and BMP TFSI leads to a near complete bleaching of the neutral polymer absorption band at 558 nm. In the doped films, we observe instead the characteristic charge induced P₂ (854 nm for 1 mM and 834 nm for 5 mM) and P₁ (>1800 nm) absorption bands of oxidized PBTTT. We compare here two different doping concentrations of 1 and 5 mM that will be used below for thermoelectric characterization. With the polarizer parallel to the alignment direction, we find that in the 1 mM FeCl₃, ion-exchange doped sample P₂ band is slightly higher than in the 5 mM sample, while the P₁ band shows the opposite trend. This is likely to reflect slight differences in the electronic state delocalization of the polaronic charge carriers in the film. From the polarized UV-VIS spectra, we can extract the dichroic ratio defined as \( \frac{I_{\text{max}}}{I_{\text{min}}} \) [or alternatively as \( \frac{(I_{\text{max}}-I_{\text{min}})}{(I_{\text{max}}+I_{\text{min}})} \), supplementary material, Fig. S2]. Notably, the dichroic ratio \( \frac{I_{\text{max}}}{I_{\text{min}}} \) reached the maximum value of 16.4 at 584 nm for undoped PBTTT, while in the doped samples, when using the P₂ band at 910–920 nm, we extract slightly lower values of 11.1 (13.3) in the 1 (5) mM samples. This small drop in dichroic ratio of P₂ band upon doping could indicate a loss of orientation upon intercalation of anions into the film. However, the P₁ dichroic ratios of the doped sample are higher and continue increasing as we approach the low-energy limit of our measurements. In the 5 mM sample, the P₁ dichroic ratio is slightly higher than that of the undoped polymer, suggesting that the P₂ dichroic ratios may limited by scattering on the rough film surface generated by rubbing. This scattering gives rise to a background absorption signal in the perpendicular spectra similar in intensity to
the P2 band, which makes it difficult to determine an accurate value of
dichroic ratio at this high-level alignment where the P2 band can no
longer be resolved. In any case, the UV-VIS data indicate clearly that
the degree of alignment remains high after doping and is higher than
the highly conducting PBTTT samples reported in Ref. 11. For both
doped samples, we observe no residual FeCl4− anions, which would
lead to an absorption signature at 367 nm.22 This demonstrates the
effectively complete exchange of dopants by TFSI− anions, consistent
with our previous findings.

To assess the merits of our aligned PBTTT for thermoelectric
applications, we investigated two representative samples with doping
concentrations of 1 and 5 mM that gave high electrical conductivities.
We previously observed that FeCl3 dopant concentrations above
1 mM etched uncovered gold electrodes in a matter of minutes, forcing
us to limit the dopant concentration to 1 mM. Here, we use Pt electro-
des in the transport measurements, allowing us to increase the dopant
solution concentration and achieve slightly higher doping levels. We
measured electrical conductivity and Seebeck coefficient as a function
of temperature using an on-chip microfabricated device architecture
in which the polymer film is patterned into a Hall bar shape as detailed
previously.32–34 This design allows very accurate determination of the
Seebeck coefficient and the electrical conductivity. It uses on-chip cali-
brated temperature sensors for the Seebeck measurements as well as
four-point probe electrical conductivity measurements of the same
film region (supplementary material, Fig. S3). We established that
there was no significant degradation of the electrical conductivity of
the polymer films during the Hall bar patterning. Compared to the
unaligned samples, the electrical conductivity of the aligned samples in
the parallel direction is enhanced by a factor of 3 to 4, and the perpen-
dicular direction is suppressed to only around 0.1 of the value of the
unaligned samples. The conductivity values of our samples reaching a
maximum of 4345 S/cm in the parallel direction compared very favor-
able to recent reports on PBTTT thin films,21,23–25 but they are lower than the very high values reported in Ref. 11. The reasons for this are unclear, particularly given that the dichroic ratio of our aligned
films is comparable/higher than that of the samples in Ref. 11. In our
previous study,27 we also observed ion-exchange doped samples to
exhibit higher conductivities than reference samples doped by tradi-
tional charge transfer doping with FeCl3 as used in Ref. 11. We cannot
exclude that further optimization of our aligned, ion-exchanged doped
samples is possible, but we note that the conductivity measurements in Ref. 11 were performed on unpatterned films, which leads to less
accurate estimates of conductivity than the Hall bar geometry used
here, especially for high-conductivity samples in which the film con-
ductance becomes comparable to that of the electrodes.

To extract some information on the charge transport physics, we
also measured the conductivity and Seebeck coefficient as a function of
temperature. For all samples and alignment conditions, a finite con-
ductivity remains in the 0 K limit. For low temperatures of up to 30 K,
the conductivities scale approximately as Ω−1/2, and some samples show
metallic temperature dependence dσ/dT < 0 in the high-temperature
regime of around 250 K. These features are traditionally taken to sig-
nify the presence of metallic states in the samples, as observed in
doped polycarbonate49 and polyaniline.37 We adopt a model proposed
by Kaiser and Graham38 to extract some of the relevant transport
parameters. Details of the models are discussed in the supplementary
material, and the fits to our experimental data are shown as solid lines
in Fig. 5(a). From the fits, it is evident that the aligned polymers have a
higher value of the Efros–Shklovskii variable-range hopping activation
term T0, which is also reflected by their lower normalized conductivity at
low temperature σ(T)/σ(250 K) (supplementary material, Fig. S4). This
suggests that rubbing though beneficial in terms of inducing poly-
mer alignment also increases somewhat the degree of energetic disor-
der in the films, which is evident also in the less well-defined edge-on
texture in the GIWAXS measurements.

The Seebeck coefficients of all samples vary linearly with tempera-
ture, obeying the Mott formula for metals, in agreement with a previ-
ous study on anion-exchange doped PBTTT.16 Our Seebeck measurements do not show a significant dependence on the alignment
direction amongst the six considered samples, consistent with previous
reports in the doped PBTTT,17 but contrasts with that of stretch aligned
polyacetylene.15 Whereas increasing conductivity through simply
doping generally leads to a decrease in Seebeck coefficient due to the
increase in carrier density,16 alignment may promote the conduc-
tivity by improving the charge mobility.17 This modification leaves the
Seebeck coefficient virtually unchanged, suggesting that alignment is a
promising approach to optimizing the power factor in organic ther-
molectrics. Our results suggest that increasing the dopant concentra-
tion only leads to a moderate increase in the hole density beyond
1 mM FeCl3, as evidenced by the comparable Seebeck coefficients.
The parallel aligned samples doped with 1 and 5 mM FeCl3 showed power
factors of 109 and 137 μW·cm−1·K−2, respectively, at room temperature, a
fivelfold increase from their unaligned counterparts.

Given that figure of merit (ZT) is the crucial factor to evaluate the
thermoelectric properties, it is necessary to consider the effect of align-
ment and doping on the thermal conductivity. We have not yet per-
formed measurements of thermal conductivity, but we expect signifi-
cant anisotropy in thermal transport between the parallel and per-
pendicular directions, arising from the differences in bonding character
(van der Waals vs covalent) and electrical conductivity along each crys-
tal axis. In our case of high electronic conductivity after doping and
alignment, the electronic contribution to the thermal conductivity will
likely be significant. In addition, alignment may also affect the phonon
(lattice) contribution to the thermal conductivity by increasing phonon
mean free path. Previous studies reported a factor of 2–3 enhancement
in thermal conductivity for ultra-high molecular weight polyethylene
(UHMWPE) along the chain axis (high degree of alignment) to the con-
ventional textile materials.50 We may expect a similar increase in the lat-
tice thermal conductivity along the alignment direction, although no
experimental data have been obtained yet. Since the electronic and lat-
tice contributions to thermal conductivity should, therefore, be greater
in aligned films, the increase in ZT will probably be smaller than the sig-
nificant improvement in the power factor observed above.

In conclusion, we have demonstrated a controllable and system-
atic strategy for optimizing the parameters for aligning PBTTT by
mechanical rubbing and identifying process conditions for maximiz-
ing the conductivity of ion-exchange doped samples. Our optimization
approach based on the design of experiment methodology leads to a
high degree of polymer alignment verified by both GIWAXS and
polarized UV-VIS spectroscopy, and a fourfold increase in conductivity
relative to spin-coated PBTTT films under the same condition of ion-
exchange doping. In addition to this increase in conductivity, our careful
temperature-dependent Seebeck measurements indicate that high-
temperature rubbing does not strongly affect the Seebeck coefficient.
The possibility of increasing conductivity uncoupled from the Seebeck coefficient provides a clear route for power factor enhancement. This opens the opportunities for further improving the microstructure of the mechanically rubbed polymer films, reducing their energetic disorder, and enhancing their thermoelectric performance. The DOE method applied here also simplifies performance optimization and should be widely applicable to other organic semiconductor devices.

See the supplementary material for more details on materials and methods, design of experiment optimization, additional characterization, and transport measurements.

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DATA AVAILABILITY

The data that support the findings of this study are openly available at https://www.data.cam.ac.uk/repository.

REFERENCES
